

## Statistical mechanics with topological constraints: II

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## Statistical mechanics with topological constraints: II

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**Abstract.** It is shown that the full specification of an assembly of long flexible molecules, needed for a statistical-mechanical study, requires an infinite set of topological invariants, and the first two of these are derived in detail. It is argued that these invariants provide a better description of the topology of the system than a more intuitively obvious one, for example, to state the condition that a molecule contains a single knot is very complicated requiring an infinite number of invariants, just as the specification of a function at a point requires an infinite number of Fourier coefficients. It is shown that the probability of molecules taking up configurations with given values for the invariants is a problem in quantum field theory, and that for example the first invariant leads to a formalism isomorphic with the electrodynamics of scalar bosons, and the governing differential equations for one and two molecules are derived. The transition from a real polymer to its representation by a continuous curve leads to divergences, but these can be absorbed by renormalizing the step length and entropy per monomer; within these two changes the topological properties are independent of monomer structure.

### 1. Introduction

In the previous paper (Edwards 1967 a, to be referred to as I) a discussion was given of the effect of topological constraints on the statistical mechanics of long chain molecules and the discussion was illustrated by examples where the constraint was caused by the configuration of the molecule relative to some given curve in space. This is an incomplete discussion since a path in space can have an invariant topology relative to itself, and also to obtain topological invariance of one curve relative to two or more others requires a knowledge of the ordering of the entanglements. This also leads to a more complicated set of differential equations when the curves in question are Brownian motion paths.

In this paper we shall try to produce a set of invariants in terms of the intrinsic equations of the curves which serve to define topological characters. Then the probabilities of these characters being taken up will be shown to satisfy certain differential equations. The situation is much more complicated than that of I, but, nevertheless, it appears that it must be resolved before any really complete theory of polymers can be attempted.

### 2. The specification of knots

To have knots at all, that is configurations of a curve falling into a certain class which cannot be transformed into other classes (i.e. different knots, including no knot), one must have infinite or closed curves. To start the discussion consider two unknotted closed curves. Two possible configurations are

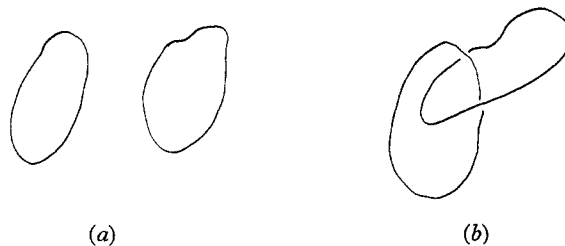


Figure 1.

Let the curves be  $\mathbf{r}_1(s)$  and  $\mathbf{r}_2(s)$  where  $\mathbf{r}_1(L_1) = \mathbf{r}_1(0)$  and  $\mathbf{r}(L_2) = \mathbf{r}_2(0)$ , and let  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ . Let us consider

$$\oint \oint \frac{(\mathbf{dr}_1 \times \mathbf{dr}_2) \cdot \mathbf{r}_{12}}{|\mathbf{r}_{12}|^3} = \oint \mathbf{dr}_1 \cdot \oint \frac{\mathbf{dr}_2 \times \mathbf{r}_{12}}{|\mathbf{r}_{12}|^3} \quad (2.1)$$

$$= \oint \mathbf{dr}_1 \cdot \text{curl}_1 \oint \frac{\mathbf{dr}_2}{|\mathbf{r}_{12}|} \quad (2.2)$$

which, using Stokes' theorem,

$$= \int d\mathbf{S}_1 \cdot \text{curl curl} \oint \frac{\mathbf{dr}_2}{|\mathbf{r}_{12}|}. \quad (2.3)$$

But  $\text{curl curl} = \text{grad div} - \nabla^2$ , and from Green's lemma

$$\int \text{div}_1 \frac{\mathbf{dr}_2}{|\mathbf{r}_{12}|} = - \int \frac{\mathbf{dr}_2 \cdot \mathbf{r}_{12}}{|\mathbf{r}_{12}|^3} = - \int d\mathbf{S}_2 \cdot \text{curl grad} \frac{1}{|\mathbf{r}_{12}|} \quad (2.4)$$

$$= 0$$

whereas

$$\nabla^2 \left( \frac{1}{|\mathbf{r}_{12}|} \right) = -4\pi\delta(\mathbf{r}_1 - \mathbf{r}_2).$$

Now

$$\int d\mathbf{S}_1 \cdot \oint \mathbf{dr}_2 \delta(\mathbf{r}_1 - \mathbf{r}_2) = \begin{array}{l} \text{algebraic number of times the curve } \mathbf{r}_2 \text{ passes through} \\ \text{the surface } S_1 \text{ with } \mathbf{r}_1 \text{ as perimeter, } n, \text{ say.} \end{array} \quad (2.5)$$

Therefore

$$\oint \oint \frac{(\mathbf{dr}_1 \times \mathbf{dr}_2) \cdot \mathbf{r}_{12}}{|\mathbf{r}_{12}|^3} = 4\pi n. \quad (2.6)$$

For example, figure 1(a) has  $n = 0$ , figure 1(b) has  $n = \pm 1$ , according to the sign ascribed to  $\mathbf{r}_1, \mathbf{r}_2$ , i.e.



Figure 2.

have opposite signs of  $n$ . When one has an explicit integral constraint one can start asking for the probability, total entropy, etc., with the constraint integral having a particular  $n$ . Now, say one had a closed curve in the configurations

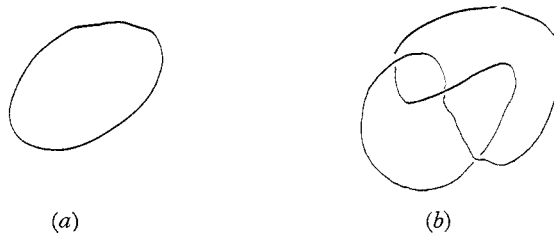


Figure 3.

If one evaluates

$$\oint \oint \frac{\{\dot{\mathbf{r}}(s_1) \times \dot{\mathbf{r}}(s_2)\} \cdot \{\mathbf{r}(s_1) - \mathbf{r}(s_2)\}}{|\mathbf{r}(s_1) - \mathbf{r}(s_2)|^3} ds_1 ds_2 \quad (2.7)$$

essentially a self-integral version of the previous form, one obtains different values for (a) and (b). For 3(a) one can deform it into a circle when  $\mathbf{r}(s_1) \times \mathbf{r}(s_2)$  is at right angles to  $\mathbf{r}(s_1) - \mathbf{r}(s_2)$ , so the value is zero. 3(b) can be deformed into figure 4, and the two strips 13, 24 can

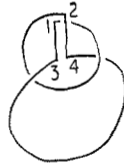


Figure 4.

be brought together to cancel, giving the final value  $4\pi$ . But it is also possible to have the value  $-4\pi$ , since if we consider the two curves



Figure 5.

these give equal and opposite values. If both these knots are on one curve

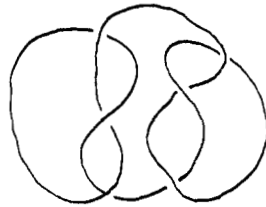


Figure 6.

the integral gives zero, although it is not possible to unknot the curve back to 3(a). A double knot can then give the values  $8\pi$ ,  $0$ ,  $-8\pi$  to the integral, so it is clear that, whilst figure 3(a) implies zero for the integral (2.6), the converse is not the case. To understand this, let us return to the case of separate closed curves which have no self-knots. For three such, consider the equivalent configurations

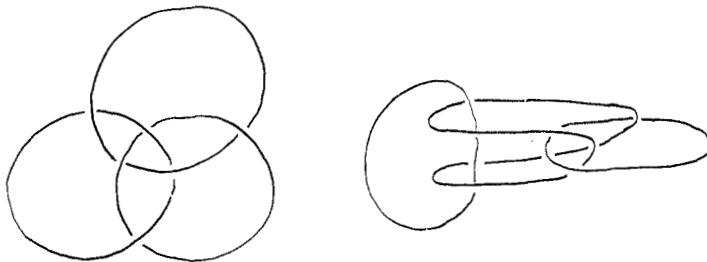


Figure 7.

These are known as Borromean rings. The integral (2.6) vanishes for each pair, and if any one of the curves is removed the remaining pair are indeed free. But the three together are clearly locked together, so some new integral has to be found to express this in addition

to the previous pair integral. The situation here is clarified by considering an equivalent two-dimensional problem. Let us consider two of the rings expanded infinitely to be straight lines which are twisted until parallel. The third ring (which is now topologically a square lashing) can now be shown in projection on the plane perpendicular to the lines thus:

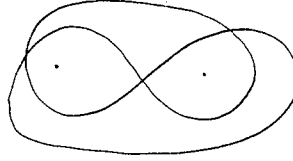


Figure 8.

The angle swept out by the whole curve around either point is zero, but the curve is clearly entangled with the points, i.e. cannot be removed without one of the points passing through the curve. Clearly the order in which the points are circumnavigated is giving rise to a new topological invariant. A similar situation can arise in which a non-zero angle is swept about the one point, whilst zero about the other, with entanglement:

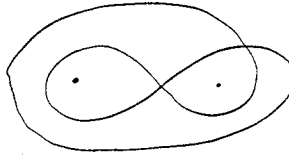


Figure 9.

To pursue this study further in two dimensions it is evident that the appropriate tool is the study of functions defined over Riemann surfaces joined along cuts linking the various points about which the topology is defined. For example, figure 8 leads to the study of elliptic functions (see Ito and McKean 1965). This approach does not appear useful for three-dimensional problems such as are encountered in physics, so the rest of the present discussion will aim to develop invariants in forms analogous to (2.6) and (2.7).

Let us consider then a version of figure 7 in which surfaces  $S_1$  and  $S_2$  containing points  $\mathbf{R}_1$  and  $\mathbf{R}_2$  have boundaries  $\mathbf{r}_1, \mathbf{r}_2$

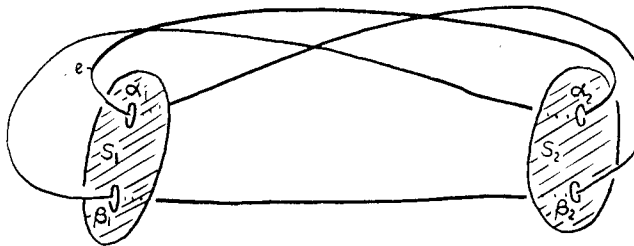


Figure 10.

Let  $\mathbf{r}_3$  meet  $S_1$  at  $\alpha_1, \beta_1$  and  $S_2$  at  $\alpha_2, \beta_2$ , and also draw on  $S_2$  a curve from  $\alpha_2$  to  $\beta_2$ . Roughly speaking, one wants to be able to get the sense of  $\mathbf{r}_3(s)$  to change as it passes through  $S_2$ , so that if one starts, say, at  $e$ , denoting by  $\mathbf{B}_1$  the integral

$$\oint \frac{d\mathbf{r}_1 \times (\mathbf{r}_3 - \mathbf{r}_1)}{|\mathbf{r}_3 - \mathbf{r}_1|^3} \tag{2.8}$$

the value

$$\int_e^{\beta_1} \mathbf{B}_1 \cdot d\mathbf{r}_3 - \int_{\beta_2}^{\alpha_2} \mathbf{B}_1 \cdot d\mathbf{r}_3 + \int_{\alpha_2}^e \mathbf{B}_1 \cdot d\mathbf{r}_3$$

is roughly equal to  $8\pi$ . So one wants an operator placing the minus sign in front of  $\int_{\beta_2}^{\alpha_2} \mathbf{B}_1 \cdot d\mathbf{r}_3$ , and also to add  $2 \int_{\alpha_2}^{\beta_2} d\mathbf{R}_2 \cdot \mathbf{B}_1$ , which will exactly produce the  $8\pi$ . So one is led to consider

$$I_{12,3} = \oint \mathbf{B}_1 \cdot d\mathbf{r}_3(\tau) \left\{ 1 - 2 \int_0^\tau \int d\mathbf{S}_2 \cdot d\mathbf{r}_3' \delta(\mathbf{r}_3' - \mathbf{R}_2) \right\} + 2 \int_{\alpha_2}^{\beta_2} d\mathbf{R}_2 \cdot \mathbf{B}_1 \quad (2.9)$$

where 0 denotes an arbitrary origin, say the point e. It is readily checked that this is indeed an invariant for the change in its value on choosing a different surface  $S_2$ , or a non-topological change in  $\mathbf{r}_3(s)$ , can be evaluated by Stokes' theorem and is zero. The expression

$$\left\{ 1 - 2 \int_0^\tau \int d\mathbf{S}_2 \cdot d\mathbf{r}_3' \delta(\mathbf{r}_3' - \mathbf{R}_2) \right\} \quad (2.10)$$

has the value unity from e to  $\beta_2$ , but changes to  $-1$  as one passes through the surface, staying  $-1$  until  $\alpha_2$ , when it returns to unity. But to be precise one has to add the second term, which clearly leads to two circuits. It is also true that for figure 10 the value of  $\oint \mathbf{B}_1 \cdot d\mathbf{r}_3$  is zero, so only the surface integrals remain. The problem is now to transform (2.9) into an integral solely containing  $\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2, d\mathbf{r}_3, d\mathbf{r}_1, d\mathbf{r}_2$ . It is shown in the appendix that the final form is

$$I_{12,3} = \oint \oint \frac{(d\mathbf{r}_1 \times d\mathbf{r}_3) \cdot \mathbf{r}_{13}}{|\mathbf{r}_{13}|^3} \oint \int \frac{(d\mathbf{r}_2 \times d\mathbf{r}_3) \cdot \mathbf{r}_{23}}{|\mathbf{r}_{23}|^3} + \oint \oint \oint \frac{(d\mathbf{r}_1 \times \mathbf{r}_{13}) \cdot (d\mathbf{r}_3 \times d\mathbf{r}_2)}{|\mathbf{r}_{13}|^3 |\mathbf{r}_{23}|^3}. \quad (2.11)$$

There are, of course, many ways of transforming this expression: in particular, integration by parts will interchange the roles of 1 and 2, and in the particular case under consideration of figure 10, i.e. figure 7,  $I_{12,3}$  can be recast in a form with symmetry.

The invariant  $I_{12,3}$  having a non-vanishing value, whilst  $I_{13}, I_{23}$  vanish, tells one that the curve  $\mathbf{r}_3$ , whilst sweeping out a net angle zero around curve 1, is still entangled around curve 1 by virtue of its topological relation with curve 2. We shall not attempt to evaluate higher terms, since we are assured that a systematic classification of entanglements and knots does not exist, but it is clear, given any configurations, an invariant characterizing it can be found. It is also clear that such an invariant will not specify the particular situation; it needs an infinite number of these invariants to do this. The situation is like defining a function in terms of its Fourier series: one needs all the Fourier coefficients to specify it. Knots are similarly described. By considering the formula for  $I_{12,3}$  with  $r_1 \equiv r_2 \equiv r_3$ , a new invariant for a single closed curve is obtained which will distinguish between the configurations of figure 6 and figure 3(a), both of which have the simple invariant (2.7) equal to zero. But the vanishing of the first invariant and the non-vanishing of the second does not imply the configuration of figure 6. These circumstances are necessary but not sufficient.

### 3. The application to statistical problems

For the thermodynamic properties of a system defined to be created in a completely random fashion, the specification of the topology of the system in terms which are common to one's experience is quite unnecessary. For example, suppose one is told that an ensemble of strings exists, these strings taking up random flight configurations, and are all closed. One can ask for the probability that a string contains a knot. But one could equally ask for the probability that a string has a first invariant equal to  $4\pi$ . As has been noted in the previous paper (I), the entropy change of the system under distortion is

$$\Delta S = \kappa \sum_{\mathbf{T}} p_{\mathbf{T}} \log \left( \frac{\tilde{G}_{\mathbf{T}}}{G_{\mathbf{T}}} \right) \quad (3.1)$$

where  $p_{\mathbf{T}}$  is the probability of a string having a topological specification  $\mathbf{T}$ ,  $G_{\mathbf{T}}$  the total number of configurations,  $\tilde{G}_{\mathbf{T}}$  the total number in the new circumstances (usually  $\tilde{G}_{\mathbf{T}}/G_{\mathbf{T}} = \tilde{p}_{\mathbf{T}}/p_{\mathbf{T}}$  since the total number of configurations is often not altered in distortions). Now, one clearly can never specify all the properties labelled  $\mathbf{T}$ , so rather than attempt the impossible, which is to label knots and entanglements in the simple intuitive way, one should do so by using the set of invariants developed here. Thus if the first invariant is used it will forbid a pair of infinite molecules going from

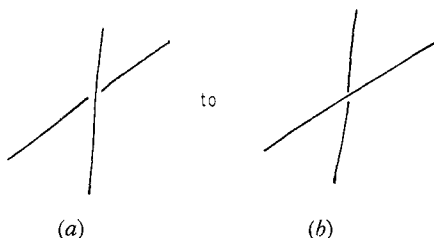


Figure 11.

but will not forbid the change to



Figure 12.

The former ought to be the most important effect, but should the latter also matter, then the second invariant can be used, and so on.

Another reason for preferring the system of classification by invariants is that treating a polymer, for example, as a random path clearly must fail at small distances when the precise molecular structure dominates. It appears from the calculations of I and those below that the invariants permit one to separate the short-range behaviour from the long, just as the renormalization programme in quantum field theory separates self-energy effects from the dynamic behaviour of the electron in an electromagnetic field. It is not clear, however, whether the question of whether a random path contains a knot is at all meaningful in the mathematical idealization of infinitesimal steps. One would guess that such questions are not meaningful, getting into unresolved, perhaps unresolvable, questions of measure, i.e. the probability of a single knot is always zero since a random path permitting infinitesimal steps will be 'unfinitely knotted'. The invariants, however, appear to be meaningful by explicit calculation. Presumably very high-order invariants will depend more and more on effects over very small path lengths, and these of course will be blotted out by physical requirements. We have no proof, however, of these statements. The following explicit calculations will discuss how equations can be deduced to give, for example, the probability that two random paths become entangled in the sense that the invariants take on specified values. The problem of one random path with topology relative to fixed given curves was discussed in I for the first invariant and was found to reduce to the solution of a differential equation. The problem of the topology of a single chain relative to itself amounts to the constraint

$$\mathcal{J} \equiv \oint \oint \frac{\{d\mathbf{r}(s) \times d\mathbf{r}(s')\} \cdot \{\mathbf{r}(s) - \mathbf{r}(s')\}}{|\mathbf{r}(s) - \mathbf{r}(s')|^3} = \mathfrak{D} \quad (3.2)$$

being added to the probability of the configuration. Thus

$$G_{\vartheta}(\mathbf{r}, \mathbf{r}'; s, s') = \mathcal{N} \int_{\mathbf{r}(s')=\mathbf{r}'}^{\mathbf{r}(s)=\mathbf{r}} \exp\left(-\frac{3}{2l} \int_{s'}^s \dot{\mathbf{r}}^2 ds'\right) \delta(\vartheta - \mathcal{J}) \delta\mathbf{r}(\tau) \quad (3.3)$$

$$= \frac{\mathcal{N}}{2\pi} \int_{-\infty}^{\infty} d\lambda \int_{\mathbf{r}(s')=\mathbf{r}'}^{\mathbf{r}(s)=\mathbf{r}} \exp\left(-\frac{3}{2l} \int_{s'}^s \dot{\mathbf{r}}^2 ds' - i\lambda\vartheta + i\lambda\mathcal{J}\right) \delta\mathbf{r}(\tau) \quad (3.4)$$

where  $\mathcal{N}$  is the normalization of the Wiener integral. The values taken by  $\vartheta/4\pi$  will be integral for closed curves and differ by integers for paths going off to infinity. One can bring (3.4) into the form of a single  $s$  integral by a parametric representation. Let us consider a vector field variable  $\zeta_{\mathbf{k}}$  such that  $\mathbf{k} \cdot \zeta_{\mathbf{k}} = 0$ , then it is an identity that

$$\begin{aligned} \int \delta\zeta \exp\left\{-i\lambda \int d^3k (\zeta_{\mathbf{k}} \times \zeta_{-\mathbf{k}}) \cdot \mathbf{k} - i\lambda \int \zeta_{\mathbf{k}} \cdot \phi_{\mathbf{k}} d^3k\right\} &= \exp\left\{-i\lambda \int (\phi_{\mathbf{k}} \times \phi_{-\mathbf{k}}) \cdot \mathbf{k} k^{-2} d^3k\right\} \\ &\times \int \delta\zeta \left\{-i\lambda \int d^3k (\zeta_{\mathbf{k}} \times \zeta_{-\mathbf{k}}) \cdot \mathbf{k}\right\} \end{aligned} \quad (3.5)$$

where  $\int \delta\zeta = \int \Pi d\zeta_{\mathbf{k}}$  represents the integral over all the functions  $\zeta_{\mathbf{k}}$ . The identity is proved by writing  $\zeta_{\mathbf{k}} = \zeta_{\mathbf{k}'} - \phi_{-\mathbf{k}} \times \mathbf{k} k^{-2}$ , and invoking  $\mathbf{k} \cdot \zeta_{\mathbf{k}} = 0$ . In terms of the Fourier transforms of  $\zeta_{\mathbf{k}}$  and  $\phi_{\mathbf{k}}$ ,  $\text{div } \zeta = 0$  and

$$\begin{aligned} &\int \delta\zeta \exp\left\{-i\lambda \int \zeta \cdot \text{curl } \zeta d^3r - i\lambda \int \zeta(\mathbf{r}) \phi(\mathbf{r}) d^3r\right\} \\ &= \int \delta\zeta \exp\left\{-i\lambda \int \zeta \cdot \text{curl } \zeta d^3r\right\} \\ &\times \left[ \exp \int \int \frac{\{\phi(\mathbf{r}) \times \phi(\mathbf{r}')\} \cdot (\mathbf{r}' - \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|^3} d^3r' d^3r \right]. \end{aligned} \quad (3.6)$$

If one takes

$$\phi(r') = \int \dot{\mathbf{r}}(s) \delta\{\mathbf{r}' - \mathbf{r}(s)\} ds \quad (3.7)$$

one has

$$\begin{aligned} \exp(i\lambda\mathcal{J}) &= \int \delta\zeta \exp\left(-i\lambda \int \zeta \text{curl } \zeta d^3r - i\lambda \int \zeta \cdot \dot{\mathbf{r}} ds\right) \\ &\times \left\{ \int \delta\zeta \exp\left(-i\lambda \int \zeta \text{curl } \zeta d^3r\right) \right\}^{-1}. \end{aligned} \quad (3.8)$$

Under the  $\delta\zeta$  integral one has a Markov process, one integral in  $ds$ , so the path integral becomes a differential equation as in I. Thus

$$G_{\vartheta} = \frac{1}{\alpha\pi} \int d\lambda \int \delta\zeta G_{\lambda}(\mathbf{r}, \mathbf{r}'; s, s'; [\zeta]) W(\zeta) \exp(-i\lambda\vartheta) \quad (3.9)$$

where

$$G_{\lambda}([\zeta])$$

satisfies

$$\left\{ \frac{\partial}{\partial s} + \frac{l}{6} (\nabla - i\lambda\zeta)^2 \right\} G_{\lambda}([\zeta]) = \delta(\mathbf{r} - \mathbf{r}') \delta(s - s') \quad (3.10)$$

and  $W(\zeta)$  is the weight factor  $\exp(-i\lambda\zeta \cdot \text{curl } \zeta d^3r)$ , normalized as in (3.8).

At this point it is convenient to look at the series for  $G_{\lambda}$  in terms of  $\zeta$ . This appears linearly and quadratically in the differential equation, so a convenient graphical repre-



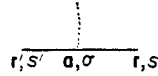
sentation is to represent by a full line the solution  $G_0$  of

$$\left(\frac{\partial}{\partial s} - \frac{l}{6} \nabla^2\right) G_0 = \delta(\mathbf{r} - \mathbf{r}')\delta(s - s')$$

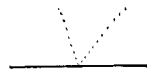
to represent  $i\lambda [\nabla, \zeta]$  by a dotted line emerging from a full line, i.e.

$$i\lambda G_0(\mathbf{r}, \mathbf{a}; s, \sigma) [\nabla_a, \zeta(a)] G_0(\mathbf{a}, \mathbf{r}'; \sigma, s')$$

is represented by



and to represent  $\lambda^2 \zeta^2$  by two dotted lines emerging from a full line:  $\lambda^2 G_0 \zeta^2 G_0$  is represented as



The effect of integrating over  $\zeta$  is to link up the dotted lines into closed dotted lines starting and ending in full lines

$$\begin{aligned} D_{\mathbf{k}}^{\alpha\beta} &= \int \zeta_k^{\alpha} \zeta_l^{\beta} \exp\left(-i\lambda \int \zeta \cdot \text{curl} \zeta\right) \delta\zeta \\ &= \frac{i}{2\lambda} \delta(\mathbf{k} + \mathbf{j}) \frac{\epsilon^{\alpha\beta\gamma k\gamma}}{k^2} \int \exp\left(-i\lambda \int \zeta \cdot \text{curl} \zeta\right) \delta\zeta \end{aligned} \quad (3.11)$$

$$\begin{aligned} &\int \zeta_{\mathbf{k}_1}^{\alpha_1} \zeta_{\mathbf{k}_2}^{\alpha_2} \dots \exp\left(-i\lambda \int \zeta \cdot \text{curl} \zeta\right) \delta\zeta \\ &= \prod_{\text{all perm}} \left(\frac{i}{2\lambda}\right) \delta(k_a + k_b) \frac{\epsilon^{abc k^c}}{k^2} \int \exp\left(-i\lambda \int \zeta \cdot \text{curl} \zeta\right) \delta\zeta \end{aligned} \quad (3.12)$$

$$= \prod_{\text{all perm } k_a \dots k_b \text{ amongst } k_1, k_2, \dots} D(k_a) \delta(k_a + k_b). \quad (3.13)$$

The series for  $G_2([\zeta])$  is then represented by

$$\text{---} + \text{---} + \left[ \text{---} + \text{---} \right] + \left[ \text{---} + \text{---} + \text{---} \right] + \dots \quad (3.14)$$

and upon integration over  $\zeta$  by

$$\text{---} + \circ \left[ \text{---} + \text{---} \right] + \circ \left[ \text{---} + \text{---} + \text{---} \right] + \dots \quad (3.15)$$

Written out explicitly one has

$$\begin{aligned}
 G_\lambda &= G_0(\mathbf{r}, \mathbf{r}'; s, s') + \lambda^2 \iiint G_0(\mathbf{r}, \mathbf{x}; s, \sigma) \nabla^\alpha G_0(\mathbf{x}, \mathbf{y}; \sigma, \tau) \nabla^\beta \\
 &\quad \times G_0(\mathbf{y}, \mathbf{r}'; \tau, s') \epsilon^{\alpha\beta\gamma} \nabla^\gamma |\mathbf{x} - \mathbf{y}|^{-1} d^3x d^3y d\sigma d\tau \\
 &\quad + \lambda^2 \iiint G_0(\mathbf{r}, \mathbf{x}; s, \sigma) \delta(\mathbf{x} - \mathbf{y}) \delta(\sigma - \tau) |\mathbf{x} - \mathbf{y}|^{-4} \\
 &\quad \times G_0(\mathbf{y}, \mathbf{r}'; \tau, s') d^3x d^3y d\sigma d\tau + \dots
 \end{aligned} \tag{3.16}$$

Readers familiar with quantum field theory will recognize the graphical series as that encountered in the quantum field theory of charged scalar mesons. They will also not be surprised to find that the first diagrams are divergent. In electrodynamics the dotted line represents

$$D^{\mu\nu} = k^{-2}(\delta^{\mu\nu} - k^\mu k^\nu k^{-2})$$

as against our

$$\overline{D^{\alpha\beta}} = k^{-2} k^\alpha k^\beta$$

and the full lines stem from the Klein-Gordon operator

$$G_0 = (k^2 - m^2)^{-1}$$

where  $m$  is the mass of the meson. Since the length here represented by  $s$  may be replaced by Fourier transform, i.e. let

$$G(\mathbf{k}; \alpha) = \int \exp(-\alpha^2 s) G(\mathbf{r}; s) \exp(i\mathbf{k} \cdot \mathbf{r}) d^3r ds.$$

This propagator is very close to that of the meson. However, quantum electrodynamics works in four dimensions, space and time, whilst here there are three dimensions. Now, in electrodynamics the divergences are not understood, but their influence has been circumscribed by the renormalization theorems. The idea of these theorems lies in the fact that the basic quantities appearing in  $G_0$  will not be those observed in physical situations. Thus the pole of  $G_0$  comes at  $k^2 = m^2$ . The physical mass is defined from the pole of the complete  $G$ , the equivalent of the present  $G_\lambda$ . Thus if one formally writes the solution in meson theory as

$$\{k^2 - m^2 + \Sigma(k, m)\}G = 1 \tag{3.17}$$


and defines

$$m^2 + \Sigma(m', m) = m'^2$$

$$\begin{aligned}
 \Sigma' &= \left\{ \Sigma(k, m) - (k^2 - m'^2) \frac{\partial \Sigma}{\partial k^2} \Big|_{k^2 = m'^2} \right\} \left( 1 + \frac{\partial \Sigma}{\partial k^2} \Big|_{k^2 = m'^2} \right) \\
 G' &= \left( 1 + \frac{\partial \Sigma}{\partial k^2} \Big|_{k^2 = m'^2} \right) G
 \end{aligned} \tag{3.18}$$

then

$$\{k^2 - m'^2 + \Sigma'(k, m')\}G' = 1 \tag{3.19}$$

and the pole of  $G'$  comes now at  $m'$  and there is no contribution to the residue from  $\Sigma'$ . The change  $m$  to  $m'$  renormalizes the mass, from  $G$  to  $G'$  the wave functions, and there is also in meson theory the need to renormalize the charge, here  $\lambda$ . The apparent non-linearity of transformation (3.18) is rather deceptive; in practice, one just has to throw away all divergences and this proves an easy matter in the perturbation expansion of  $\Sigma$ . In the present problem it all goes through. The renormalization of  $m$  is mainly a change in effective step length, and of  $G$  amounts to a change of the entropy per unit length of the chain. One does not have to renormalize  $\lambda$  since graphs of the type .....

which do appear in electrodynamics, do not here. (Something like them appears in polymerized material, but it is hoped to consider that in a later paper.) This is as well since  $\lambda$  is intimately associated with integers as can be explicitly shown (see I), but not here. The proof of these statements in electrodynamics was first given by Salam, the key point being to order the diagrams and study the order of divergence of the diagrams. Now, for every Fourier integration in a diagram there will be a dotted line and thus a  $d^3k k^{\alpha} k^{-2}$  times factors from the  $G$ 's. In electrodynamics there is  $d^4k k^{-2}$  times the same factors from  $G$ 's. Thus, although the present  $D$  is different and the dimensionality is different, the contribution from each dotted line is still  $k dk$  and, since the diagrams are the same, Salam's proof will hold.

There are, of course, no divergences in the study of a real polymer system's topology. The divergences found here are a consequence of assuming the monomers being infinitesimal, and by cutting off the offending integrals at a distance of the order of a monomer size one can hope to make it all physically sensible. But the theorem goes much further than this. It states that the effect of finite monomer size appears in an effective step length and an effective entropy per link. There are no further effects on the asymptotic behaviour of the topological properties of the polymer. Although one is now in a position to go on to calculate the probability of a closed Brownian path to have a certain value for its invariant, the problem of two paths interlocking seems of more interest, and so will be considered in a little more detail in the next section.

#### 4. The entanglement of a pair of molecules

The diagrammatic analysis of the previous section can be used also to discuss two or more molecules. The simplest diagrams are (excluding those already given above)

$$(a) \quad (b) \quad (c) \quad (d) \quad (e) \quad (f) \tag{4.1}$$

and interferences

$$(g) \quad (h) \tag{4.2}$$

The order of the diagrams is shown by  $\lambda$ , but these now must carry indices. Diagrams (a) ... (f) refer to simple entanglements where the second molecule does not get involved in knots in the first and vice versa; this arises in diagrams (g), (h) and higher order diagrams, whilst knots not involving the other molecules are given in the series in the previous section. For simplicity it will be assumed that the knottedness of the separate molecules has been absorbed as before, and the 'Lamb shift' diagrams (e), (f), etc., will be ignored. So one is now discussing the probability of the entanglement of molecules which are not self-entangled. The literature of electrodynamics carries an extensive discussion of these diagrams since they occur in a study of the relativistic theory of energy levels of, say, an electron-positron bound state, positronium. Following the work of Schwinger, and Bethe and Salpeter (1956), one can rearrange the diagrams so that there are no repetitions in the sense that (b) is an iterate of (a). So, let us introduce  $\mathcal{G}$  satisfying

$$\begin{aligned} G_{01}^{-1} G_{02}^{-1} \mathcal{G} + \int \int \mathcal{I}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1'' \mathbf{r}_2'') \mathcal{G}(\mathbf{r}_1'', \mathbf{r}_2''; \mathbf{r}_1' \mathbf{r}_2') d^3r_1'' d^3r_2'' \\ = \delta(r_1 - r_1') \delta(r_2 - r_2') \delta(s_1 - s_1') \delta(s_2 - s_2') \end{aligned} \tag{4.3}$$

where

$$G_{01}^{-1} = \frac{\partial}{\partial s_1} + \frac{l}{6} \nabla_1^2$$

$$G_{02}^{-1} = \frac{\partial}{\partial s_2} + \frac{l}{6} \nabla_2^2$$
(4.4)

and  $\mathcal{I}(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2'')$  is chosen to give the diagrams

$$\mathcal{I} = \text{(alpha)} + \text{(beta)} + \text{(gamma)} + \text{(delta)} + \text{(epsilon)}$$
(4.5)

taking it to order  $\lambda^2$ . The first two diagrams will contain  $\delta(\mathbf{r}_1 - \mathbf{r}_1'')\delta(\mathbf{r}_2 - \mathbf{r}_2'')$ , etc. This rearrangement is such that, should one of the molecules be turned into a definite rather than Brownian path, for example, if  $G_0$  is replaced by the function appropriate to a straight line, the exact differential equation of  $I$  is obtained. But because both paths are Brownian the present infinite series is needed. In electrodynamics  $\lambda$  plays the role of charge, and it is shown in the references cited that the problem is resolved in weak coupling by basing the calculation on  $\mathcal{G}$  derived from the simplest approximation to  $\mathcal{I}$ . In the present problem one has to integrate over  $\lambda$ , so that there appears no very good reason why the series for  $\mathcal{I}$  should converge. Nevertheless, if one asks for the probability of high entanglement, i.e. large  $\vartheta$ , small  $\lambda$ , and imposes boundary conditions on  $\mathcal{G}(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2')$  that  $\mathbf{r}_1, \mathbf{r}_1'$  are far from  $\mathbf{r}_2, \mathbf{r}_2'$ , for that is compared with the natural size  $(Ll)^{1/2}$ , then all the higher terms are small compared with  $(\alpha)$  and  $(\beta)$ , since they all have dimension  $r^{-4}$ , but the higher terms all contain  $G_0$ 's which yield exponential factors at large separation. Outside this condition we have not made much progress. Assuming then that the series for  $\mathcal{I}$  is good, one can further simplify by working at a particular problem. Writing  $\mathcal{G}$  in terms of

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \quad \text{and} \quad \mathbf{S} = \frac{1}{2}(\mathbf{r}_1 - \mathbf{r}_2)$$

one can introduce

$$\Gamma(\mathbf{S}, \mathbf{S}') = \int \mathcal{G}(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2') d^3R d^3R'. \quad (4.6)$$

Further, one can take an average over lengths equivalent to studying the Laplace transform

$$\Gamma(\mathbf{S}, \mathbf{S}'; \alpha) = \int \exp(-\alpha L_1 - \alpha L_2) \mathcal{G} dL_1 dL_2 d^3R d^3R'. \quad (4.7)$$

Under these circumstances diagrams  $(\alpha)$ ,  $(\gamma)$ ,  $(\delta)$  and  $(\epsilon)$  all vanish, for example  $(\alpha)$  is

$$\frac{\lambda \mathbf{S}}{S^3} \cdot \left( \frac{\partial}{\partial \mathbf{R}} \times \frac{\partial}{\partial \mathbf{S}} \right)$$

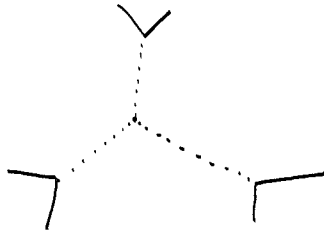
whereas  $(\beta)$  is  $\lambda^2 S^{-4}$ , so that (absorbing constants like  $l/6$ , etc.)

$$\{(\nabla^2 + \alpha)^2 + \lambda^2 S^{-4}\} \Gamma(\mathbf{S}, \mathbf{S}') = \delta(\mathbf{S} - \mathbf{S}'). \quad (4.8)$$

This equation describes the mean behaviour of the simple entanglement of two chains, provided that their separation is not small. This is the simplest situation we have found, and from now on the treatment of  $\Gamma$  follows as in I, except that being a fourth-order differential equation it cannot be expressed in explicit terms, though there is no singularity in the equation and approximate solutions are readily obtained at small and large  $S$ . It is hoped to return to quantitative solutions in a later publication.

It is perhaps worth noting finally that, if the higher invariants were required, as would be noticeably the case when three or more molecules were highly entangled, the corresponding interactions would lie outside electrodynamics and enter a class which have only

been speculated upon in meson theory. For example, one would have things like



## 5. Conclusion

This paper has done little more than set up the problem of the entanglement of random walks. But, given a technique for constructing invariants, and given the probabilities expressed in perturbation theory and in the various summations explored already in quantum theory, one is in a position to assess the difficulties involved in accurate solutions to entanglement problems.

Problems of real polymers have other questions as well as these, and cruder methods will probably be needed to handle them (e.g. Edwards 1967 b); nevertheless, it is important to have an exact background against which to judge the accuracy of any approach.

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## Appendix

The invariant was obtained in (2.9) in the form

$$\oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \left\{ 1 - 2 \int d\mathbf{S}_2 \cdot \int^\tau d\mathbf{r} \delta(\mathbf{r}_3 - \mathbf{R}_2) \right\} + 2 \int_{\alpha_2}^{\beta_2} (\mathbf{B}_1 \cdot d\mathbf{R}_2) \quad (\text{A1})$$

where

$$\mathbf{B}_1(\mathbf{r}_3) = \text{curl} \oint \frac{d\mathbf{r}_1}{|\mathbf{r}_3 - \mathbf{r}_1|} \quad (\text{A2})$$

and the curve  $\mathbf{r}_3$  intersects the surface  $S_2$ , whose perimeter is  $\mathbf{r}_2$  at the points  $\alpha_2, \beta_2$ . Points in  $S_2$  are denoted  $\mathbf{R}_2$ . To write this in a manifestly invariant way, it should not refer to  $S_2$  at all. To do this we note that

$$\begin{aligned} d\mathbf{r}_3 \delta(\mathbf{r}_3 - \mathbf{R}_2) &= -(4\pi)^{-1} \nabla_2^2 d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \\ &= (4\pi)^{-1} (\text{curl}_2 \text{curl}_2 - \text{grad}_2 \text{div}_2) d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1}. \end{aligned} \quad (\text{A3})$$

Then

$$\begin{aligned} &2 \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int d\mathbf{S}_2 \cdot \int^\tau d\mathbf{r}_3 \delta(\mathbf{r}_3 - \mathbf{R}_2) \\ &= \frac{1}{2\pi} \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \left\{ \int d\mathbf{S}_2 \cdot \text{curl}_2 \left( \text{curl}_2 \int^\tau d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \right) \right. \\ &\quad \left. - \int d\mathbf{S}_2 \cdot \nabla_2 \left( \text{div}_2 \int^\tau d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \right) \right\}. \end{aligned} \quad (\text{A4})$$

Now, by Stokes' theorem

$$\int d\mathbf{S}_2 \cdot \text{curl } \mathbf{F} = \oint \mathbf{F} \cdot d\mathbf{r}_2 \quad (\text{A5})$$

and if

$$\text{curl} \oint d\mathbf{r}_2 |\mathbf{r}_3 - \mathbf{r}_2|^{-1} = \mathbf{B}_2(\mathbf{r}_3) \quad (\text{A6})$$

$$\begin{aligned} & \frac{1}{2\pi} \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int d\mathbf{S}_2 \cdot \text{curl}_2 \left( \text{curl}_1 \int^\tau d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \right) \\ &= \frac{1}{2\pi} \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int^\tau \mathbf{B}_2 d\mathbf{r}_3 \end{aligned} \quad (\text{A7})$$

whilst

$$\begin{aligned} & \left( \frac{1}{2\pi} \right) \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int d\mathbf{S}_2 \cdot \nabla_2 \left( \text{div}_2 \int^\tau d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \right) \\ &= \frac{1}{2\pi} \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int d\mathbf{S}_2 \cdot \nabla_2 \int^\tau d\tau \frac{d}{d\tau} |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \\ &= \frac{1}{2\pi} \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int d\mathbf{S}_2 \cdot \nabla_2 (|\mathbf{r}_3 - \mathbf{R}_2|^{-1} - |\mathbf{r}_{30} - \mathbf{R}_2|^{-1}) \\ &= \frac{1}{2\pi} \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int d\mathbf{S}_2 \cdot \nabla_2 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \end{aligned} \quad (\text{A8})$$

$$\quad (\text{A9})$$

where  $\mathbf{r}_{30}$  is the origin of the  $d\mathbf{r}_3$  integral and, being a constant, is removed since  $\oint \mathbf{B}_1 \cdot d\mathbf{r}_3 = 0$ . This can now be rearranged to

$$\frac{1}{2\pi} \int d\mathbf{S}_2 \cdot \nabla_2 \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 |\mathbf{r}_3 - \mathbf{R}_2|^{-1}. \quad (\text{A10})$$

Returning now to  $\int_{\alpha_2}^\beta d\mathbf{R}_2 \cdot \mathbf{B}_1$  one can always arrange that the surface  $S_2$  does not intersect some surface  $S_1$ , which can be taken as making single valued a scalar potential representation for  $\mathbf{B}_1$ . Thus, if one writes

$$\mathbf{B}_1 = \nabla \phi_1 \quad (\text{A11})$$

$$\begin{aligned} 2 \int d\mathbf{R}_2 \cdot \mathbf{B}_1 &= -2\phi_1(\alpha_2) + 2\phi_1(\beta_2) \\ &= 2 \int d\mathbf{S}_2 \cdot \oint d\mathbf{r}_3 \delta(\mathbf{r}_3 - \mathbf{R}_2) \phi_1(\mathbf{r}_3) \\ &= -\frac{1}{2\pi} \int d\mathbf{S}_2 \cdot \oint d\mathbf{r}_3 \nabla_2^2 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \phi_1(\mathbf{r}_3). \end{aligned} \quad (\text{A12})$$

Using this representation also in (A10), and also changing the coordinate system of  $\mathbf{r}_3$  to  $\mathbf{r}_3 + \mathbf{R}_2$ , the two integrals become

$$\frac{1}{2\pi} \int d\mathbf{S}_2 \cdot \nabla_2 \int (d\mathbf{r} \cdot \nabla_2) \phi_1(\mathbf{r}_3 + \mathbf{R}_2) |\mathbf{r}_3|^{-1} - \frac{1}{2\pi} \int d\mathbf{S}_2 d\mathbf{r}_3 \nabla_2^2 \phi_1(\mathbf{r}_3 + \mathbf{R}_2) |\mathbf{r}_3|^{-1}. \quad (\text{A13})$$

If we now invoke the vector identity

$$(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) = (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) - (\mathbf{a} \cdot \mathbf{d})(\mathbf{b} \cdot \mathbf{c})$$

we may rewrite this expression as

$$\frac{1}{2\pi} \int d\mathbf{S}_2 \times \nabla_2 \int (d\mathbf{r}_3 \times \nabla_2) \phi_1(\mathbf{r}_3 + \mathbf{R}_2) |\mathbf{r}_3|^{-1}. \quad (\text{A14})$$

But  $\mathbf{B}_1 = \nabla\phi_1$ , so, returning to the original coordinate system, one has

$$\frac{1}{2\pi} \int d\mathbf{S}_2 \times \nabla_2 \int d\mathbf{r}_3 \times \mathbf{B}_1 |\mathbf{r}_3 - \mathbf{R}_2|^{-1} \quad (\text{A15})$$

which by Stokes' theorem yields

$$\frac{1}{2\pi} \oint d\mathbf{r}_2 \cdot \int d\mathbf{r}_3 \times \mathbf{B}_1 |\mathbf{r}_3 - \mathbf{r}_2|^{-1}. \quad (\text{A16})$$

Finally, one obtains

$$\begin{aligned} 2\pi I_{12,3} &= 2\pi \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 - \oint \mathbf{B}_1 \cdot d\mathbf{r}_3 \int^{\tau} \mathbf{B}_2 \cdot d\mathbf{r}_3 \\ &\quad - \oint d\mathbf{r}_2 \cdot \oint d\mathbf{r}_3 \times \mathbf{B}_1 |\mathbf{r}_3 - \mathbf{r}_2|^{-1} \end{aligned} \quad (\text{A17})$$

$$\begin{aligned} &= - \oint \oint \frac{(d\mathbf{r}_1 \times d\mathbf{r}_3) \cdot (\mathbf{r}_3 - \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_3|^3} \int^{\tau} \oint \frac{(d\mathbf{r}_2 \times d\mathbf{r}_3) \cdot (\mathbf{r}_3 - \mathbf{r}_2)}{|\mathbf{r}_3 - \mathbf{r}_2|^3} \\ &\quad + \oint d\mathbf{r}_2 \cdot \oint \oint \frac{d\mathbf{r}_3 \times \{d\mathbf{r}_1 \times (\mathbf{r}_3 - \mathbf{r}_1)\}}{|\mathbf{r}_3 - \mathbf{r}_2| |\mathbf{r}_3 - \mathbf{r}_1|^3} \end{aligned} \quad (\text{A18})$$

since in our example  $\oint \mathbf{B}_1 \cdot d\mathbf{r}_3 = 0$ . This form can be put in a more symmetrical form by integration by parts, and also by constructing the other invariants by permuting 12, 3 and taking the various combinations of them.

Clearly the same method can be used to construct invariants of an arbitrarily high order, corresponding to more complicated topological situations.

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