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A topological study of the dynamical effects of entanglements

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Abstract. The constraint that extended molecules such as polymers cannot pass through each other is formulated in terms of a topological invariant. A simple model of the motion of a labelled loop entangled in a uniform background of amorphous loops is studied. A dynamical weighting factor is found which effectively removes configurational changes that would lead to the labelled loop passing through the strands of the background material. A perturbation treatment of this weighting factor is presented which describes the effects of the entanglements in terms of random environmental forces possessing considerable space and time correlations. A detailed analytic calculation is presented for the case of a labelled molecule with a rigid-ring configuration. This calculation illustrates the limited validity of perturbation theory in dealing with entanglements and suggests the existence of a transition in time to a random 'tube'-like behaviour, where the centre-of-mass motion of the ring depends on the time as $t^{1/4}$ instead of the usual diffusive $t^{1/2}$. The origin of this behaviour can be located in the long-time persistence of the bond vector correlation function of the labelled ring.

1. Introduction

The simple intuitive observation that extended molecules such as polymers cannot pass directly through each other has long been recognised as the dominant feature determining the dynamical behaviour of these systems in the concentrated or liquid state. For polymer molecules either in the form of rigid rods (Odell *et al* 1984) or as flexible chains (Graessley 1974), the most immediate observation is the dramatic increase in the viscosity as a function of concentration and molecular weight. In addition the polymeric fluid will show considerable elasticity and be able to support a stress over many decades of time. These effects and the general lack of mobility in dense systems are commonly referred to in the literature as being due to entanglements. This notion is at best phenomenological and has been freely adapted from the theory of cross-linked rubbers in which entanglements are considered as temporary crosslinks.

In order to understand the viscoelasticity of extended molecular structures one needs a well defined model of entanglements. Edwards, in a series of papers (Edwards 1967a, b, 1968, Edwards and Deam 1976) chiefly concerned with the equilibrium (static) properties of rubber networks, has introduced a topological description of entanglements in terms of winding numbers. The application of these ideas to dynamical properties has been very difficult to implement (Edwards and Miller 1976) and has necessitated a great deal of approximation. The consequence of this has been that the original topological content of the theory has given way to the expediency of a 'tube' in which the entangled polymer molecules are trapped. This model was combined by Edwards and Doi (1978a, b, c, 1979) with the reptation idea of de Gennes (1971) to

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produce one of the most popular and successful theories to account for the dynamical effects of entanglements.

The basic tube-reptation model has been well described in the literature and does not require any further elaboration here. The review by Graessely (1982) gives a full account of this model. We would simply emphasise here that despite the many illustrations in the literature of the tube as an actual tube formed by strands of surrounding material, it is in fact only meant to represent the topological rather than mechanical aspects of entanglements. This is emphasised by values for the tube radius which are considerably in excess of the interchain distances (Graessley 1982). Furthermore, in order to account for experimental observations (Graessley 1982) the tube radius must scale as $(\text{concentration})^{-1/2}$ instead of the geometrical factor $(\text{concentration})^{1/3}$. The mechanistic picture of a writhing polymer trapped in a tube is conceptually easy to grasp and has come to dominate the field of entanglement dynamics; however, in order to accommodate the tube model to detailed experimental observations, modifications have had to be made. These build on and reinforce the mechanistic picture at the further expense of the original topological description. For example, Graessley in his recent review has described an additional process which he calls 'tube leakage' which pictures the tube as a mesh through which local loops of polymer can bulge out and withdraw in a dynamic manner.

In this paper we wish to return to and analyse the intrinsically topological character of entanglements without the aid of any tube model. To illustrate our approach consider the two entangled situations shown in figures 1(*a*) and (*b*). Whilst they are similar in a configurational sense, they are nevertheless topologically distinct in that the configuration depicted in figure 1(*a*) could never evolve into that shown in 1(*b*) and vice versa without one strand cutting through the other. In other words, the configurational phase space is partitioned up into mutually inaccessible trajectories, each labelled by an appropriate set of topological invariants. For a given initial state, formed at the fabrication of the system, configurational changes can only occur along trajectories labelled by the initial conditions. The restricted phase space available to configurational changes will inevitably slow down the rate of any dynamical process and the existence of topological invariants will impart a memory to such changes.

In this paper we want to present in detail the dynamical effects specifically arising from the conservation of the topology. Our approach does not locate the entanglements at any point on the molecule, like crosslinks, or in any region of space, like the tube;

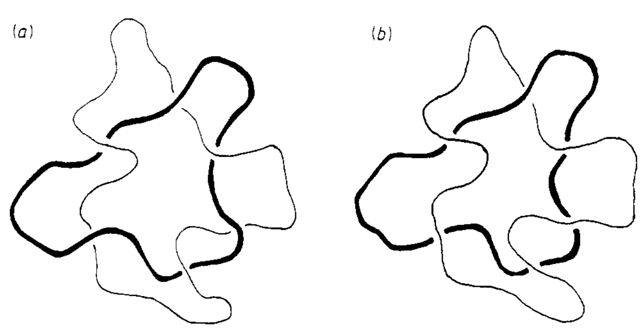

Figure 1. Entangled loops which are configurationally similar but topologically distinct. The configuration in (*a*) could never evolve into that shown in (*b*) without one strand cutting through the other.

instead they are treated as global properties of the total configuration. In § 7 we will briefly present evidence that this topological approach is able to reproduce in an oblique manner some features of the tube model. However, the main thrust of this paper is to establish a formalism for dealing with entanglements in arbitrary dynamical situations. It is an extension of earlier work (Brereton and Shah 1980) on the static properties of entanglements, where again we endeavoured to keep the topological aspects of the problem intact.

2. A model of entanglements

In order to model the essential features of an entangled situation we consider a macroscopic box filled to a uniform density with long continuous loops of material. Into this spaghetti-like medium we introduce and entangle a labelled closed-loop configuration whose dynamical properties in the presence of the entangling background will be our main concern. The model is shown schematically in figure 2. Our object in this paper is to develop a formalism whereby we can constrain the dynamical development of the labelled loop so that it does not pass through any of the strands of the background material. The background is simply to provide the entanglement constraints after which it will be averaged over and play no further role in our considerations. Formulae describing the entanglement-restricted configurational motion of the labelled loop are obtained by a perturbation calculation in § 5. By choosing a simple geometrical shape for the labelled loop such as a rigid ring we can illustrate the physical content of our formalism by explicit analytic calculation. This is done in § 6 where we consider the influence of entanglements on the centre-of-mass and orientational motion of the ring. This calculation makes clear what the controlling features associated with entanglements are and illustrates the limited applicability of perturbation theory.

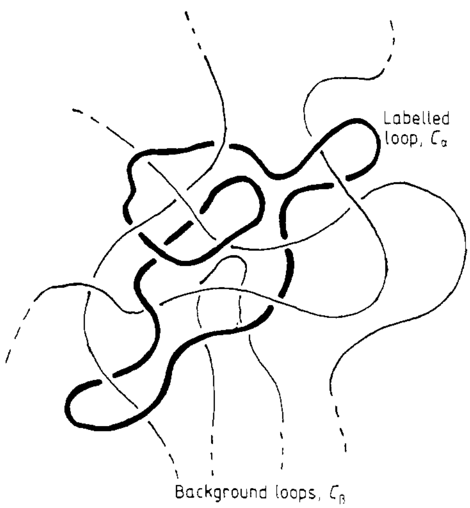

Figure 2. The labelled loop C_α of finite length is entangled in a uniform background of very long amorphous loops C_β. Each entanglement is described in terms of a winding number m_β which is to be conserved in any dynamical configurational changes. The paper deals with the resulting restricted motion of the labelled loop in this background.

To describe the number of times one configuration is wrapped round another we use the Gauss winding number formula. This has the form of a double line integral taken round the two configurations and can be written as

$$I\{C_\alpha(t), C_\beta(t)\} = \frac{1}{4\pi}\oint_{C_\alpha(t)} \mathrm{d}\boldsymbol{r}_\alpha \times \oint_{C_\beta(t)} \mathrm{d}\boldsymbol{r}_\beta \cdot \nabla \frac{1}{|\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta|}. \tag{2.1}$$

$\boldsymbol{r}_\alpha$ and $\boldsymbol{r}_\beta$ are the position vectors to the two curves which at a time t are in configurations described by $C_\alpha(t)$ and $C_\beta(t)$. One of these configurations, say the C_β, will be used to describe the spaghetti background, whilst the other, C_α, will represent the labelled configuration of interest. It is more convenient to describe the background material in terms of a continuous vector field $\boldsymbol{A}(\boldsymbol{R})$ defined at every space point $\boldsymbol{R}$ in the macroscopic box. This vector field is defined from (2.1) as

$$\boldsymbol{A}(\boldsymbol{R}, t) = \frac{1}{4\pi}\oint_{C_\beta(t)} \mathrm{d}\boldsymbol{r}_\beta \times \nabla \frac{1}{|\boldsymbol{r}_\beta - \boldsymbol{R}|} \tag{2.2}$$

so that the winding number formula can then be written as a line integral taken round the labelled configuration C_α:

$$I\{C_\alpha(t), C_\beta(t)\} = \oint_{C_\alpha(t)} \mathrm{d}\boldsymbol{r}_\alpha \cdot \boldsymbol{A}(\boldsymbol{r}_\alpha). \tag{2.3}$$

The background configuration C_β acts as a vector source $\boldsymbol{u}(\boldsymbol{R}, t)$ for this $\boldsymbol{A}$ field through the relation

$$\begin{aligned} \boldsymbol{u}(\boldsymbol{R}, t) &= \operatorname{curl} \boldsymbol{A}(\boldsymbol{R}, t) \\ &= \oint_{C_\beta(t)} \mathrm{d}\boldsymbol{r}_\beta\, \delta(\boldsymbol{r}_\beta - \boldsymbol{R}). \end{aligned} \tag{2.4}$$

Thus $\boldsymbol{u}(\boldsymbol{R}, t)$ is zero everywhere except at the actual location of the matrix material where it has the direction of the tangent vector of the thread of material at that point.

The integral (2.3) takes integer values (the winding numbers m) which, while being topological invariants, are not very good discriminators between different topological situations. However, in dynamical situations the absolute value of m is not so important; what really matters is that m should remain constant during configurational changes, since if one curve crosses through the other the value of the integral $I(C_\alpha, C_\beta)$ changes by ± 1. Consequently if we impose the constraint that

$$I\{C_\alpha(t), C_\beta(t)\} = m \qquad \text{(a constant)} \tag{2.5}$$

at all times t, then we can achieve the desired constraint that prevents one curve from passing through the other. Edwards and Miller (1976) has already shown that the equation $\mathrm{d}I/\mathrm{d}t = 0$ expresses the fact that the relative velocities of the two curves perpendicular to the plane formed by the tangent vectors to the curves where they touch, vanish. This forces the curves to slide past each other when they come into contact.

In the next section we will show how this constraint leads to a dynamical statistical weighting factor for entanglements. This will be used to appropriately bias the sequences of configurational changes of the labelled loop that conserve the winding number.

3. A dynamical weighting factor for entanglements

We will formulate the constraint that the winding number should be conserved and hence ensure the inability of loops to pass through each other in terms more general than are strictly necessary for our problem. This will enable us to develop a more physical interpretation of the formalism. In particular we will constrain the winding number integral at each time t to take on a definite value $m(t)$. Only at a later stage do we insist that $m(t)=m$ (a constant). We explicitly accomplish this by incorporating into all our statistical calculations the following product of topology-conserving delta functions:

$$\prod_t \delta(I\{C_\alpha(t), C_\beta(t)\}-m(t)). \tag{3.1}$$

We will treat the time as a discrete variable so that our theoretical manipulations are well defined; later there is no difficulty in taking the continuum limit.

The behaviour of the background material is not our concern in this paper and it was only introduced so that entanglements could be defined. We will now average over the configurations of this material and convert the product of topology-conserving delta functions into a single statistical weighting factor:

$$p(\{C_\alpha\};\{m\})=\left\langle\prod_t \delta(I\{C_\alpha(t), C_\beta(t)\}-m(t))\right\rangle_{\{C_\beta\}}. \tag{3.2}$$

This represents the probability that a sequence of configurations $\{C_\alpha\}=C(t_1), C(t_2), \ldots$ of the labelled molecule will be constrained to the sequence of topologies described by the sequence of winding numbers $\{m\}=m(t_1),\ m(t_2), \ldots$ respectively.

To see how this averaging can be done we return to the description (2.4) of the background configurations by the source vector $\boldsymbol{u}(\boldsymbol{R}, t)=\operatorname{curl}\boldsymbol{A}(\boldsymbol{R}, t)$ and treat $\boldsymbol{u}(\boldsymbol{R}, t)$ and hence the field $\boldsymbol{A}(\boldsymbol{R}, t)$ as a field of Gaussian random variables. That is, the statistical properties of the background are to be completely described by the correlation function

$$\boldsymbol{\Gamma}(\boldsymbol{R}-\boldsymbol{R}', t-t')=\langle \boldsymbol{A}(\boldsymbol{R}, t)\boldsymbol{A}(\boldsymbol{R}', t)\rangle_{\{C_\beta\}} \tag{3.3}$$

in which case it is relatively easy to show (the appendix) that

$$\begin{aligned} p(\{C_\alpha\};\{m\})&=\left\langle\prod_t \delta\left(\oint_{C_\alpha}\boldsymbol{A}\cdot\mathrm{d}\boldsymbol{r}_\alpha-m(t)\right)\right\rangle_{\{A\}}\\ &=(2\pi\det\mathbf{M}^{-1})^{-1/2}\exp\left(-\tfrac{1}{2}\sum_{tt'} m(t)\mathbf{M}^{-1}_{tt'}\{C_\alpha\}m(t')\right) \end{aligned} \tag{3.4}$$

where $\mathbf{M}^{-1}_{tt'}\{C_\alpha\}$ is the inverse 'matrix' of $\mathbf{M}\{C\}$, given by

$$\mathbf{M}_{tt'}\{C_\alpha\}=\oint_{C_\alpha(t)}\oint_{C_\alpha(t')}\mathrm{d}\boldsymbol{r}\cdot\boldsymbol{\Gamma}(\boldsymbol{r}-\boldsymbol{r}', t-t')\cdot\mathrm{d}\boldsymbol{r}'. \tag{3.5}$$

We can interpret the matrix $\mathbf{M}_{tt'}\{C_\alpha\}$ in the following way. Imagine that we allow the labelled loop to behave like a phantom coil so that it can freely wander and cut through the strands of the background material. At any moment of time it will have a winding number $m(t)$ which will fluctuate as the coil passes through the background strands. The distribution of these phantom coil winding numbers taken over all background configurations will be given by (3.4) and so we can identify the matrix

$\mathbf{M}_{tt'}\{C\}$ with the correlation function of winding numbers appropriate to a phantom coil

$$\langle m(t)m(t')\rangle_{\text{phantom coil}} = \mathbf{M}_{tt'}\{C_\alpha\}. \tag{3.6}$$

We have already shown in our work on the static properties of entanglements (Brereton and Shah 1982) that for a frozen, randomly oriented loop of background material the correlation function (3.3) is given by

$$\Gamma(\boldsymbol{R}, t) = \frac{\rho l^2}{24\pi}\frac{1}{R}\left(\mathbf{1} + \frac{\boldsymbol{RR}}{R^2}\right) \tag{3.7}$$

where ρ is the density and l is the step length. In this case the function $\mathbf{M}_{tt'}\{C_\alpha\}$ is given by

$$\mathbf{M}_{tt'}\{C_\alpha\} = \oint_{C_\alpha(t)}\oint_{C_\alpha(t')}\frac{\mathrm{d}\boldsymbol{r}\cdot\mathrm{d}\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} + \oint_{C_\alpha(t)}\oint_{C_\alpha(t')}\frac{\mathrm{d}\boldsymbol{r}\cdot(\boldsymbol{r}-\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'\cdot(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}. \tag{3.8}$$

The first term of this expression describes a geometrical relationship between the two configurations of the same loop at different times t and t' which is essentially the mutual inductance. Thus for a phantom coil wandering in a frozen configuration of randomly oriented strands the loss of winding number correlation is directly measured by the geometrical property described by the mutual inductance formula (3.8). To transform our phantom coil into a real impenetrable loop we finally impose the condition

$$m(t) = m \qquad \text{for all } t$$

so that the statistical weighting factor describing the effect of entanglements on an impenetrable loop becomes

$$p(\{C_\alpha\};\{m_\beta\}) = \prod_{\beta=1}^{N_c}(2\pi\det\mathbf{M}^{-1})^{-1/2}\exp\left(-\frac{m_\beta^2}{2}\sum_{tt'}\mathbf{M}_{tt'}^{-1}\{C_\alpha\}\right). \tag{3.9}$$

In this formula we have also allowed for the additional possibility that the labelled loop C_α can entangle independently with N_C other background strands. Each set of entanglements is described by the winding number m_β and the number of background loops N_C will remain a parameter of our model.

The actual distribution of winding number $\{m_\beta\}$ found in any physical situation will depend on the details of fabrication. Loops formed outside of the box containing the background material and then introduced will have $m = 0$, whereas for loops formed from open linear chains already integrated in the matrix we can expect the ensemble average $\overline{m^2}$ to be the same as the phantom coil result:

$$\overline{m^2} = \langle m^2(t)\rangle = \langle \mathbf{M}_{tt}\{C_\alpha\}\rangle_{\{C_\alpha\}}. \tag{3.10}$$

The case $t = t'$ governs the influence of entanglements on the static properties of configurations (Brereton and Shah 1982). In particular we have shown (Brereton and Filbrandt 1984) that the form (3.8) for $\mathbf{M}_{tt}\{C\}$ can account for the deviations in rubber elasticity theory that are normally described by the phenomenological theory of Mooney and Rivlin. The dramatic and specifically dynamic effects of entanglements occur at long time differences between t and t'. We can see that in our formalism they are due to the increasing difference between the functional form of m (a constant) and $\mathbf{M}_{tt'}^{-1}$. Since a phantom coil retains no memory of its initial configuration or topological state we have $\mathbf{M}_{tt'} \to 0$ as $|t-t'| \to \infty$ and so the exponential factor of the distribution function (3.9) behaves like

$$\exp\left(-\frac{m^2}{2}\sum_{tt'} \mathbf{M}_{tt'}^{-1}\right) \to 0 \qquad |t-t'| \to \infty. \tag{3.11}$$

This then effectively suppresses such sequences of phantom coil configurations and the average $\bar{x}$ of any dynamic configuration property $X\{C_\alpha\}$ of the labelled loop in the presence of entanglements is calculated according to

$$\bar{X} = \langle X\{C_\alpha\} p(\{C_\alpha\}; m)\rangle_{\{C_\alpha\}} \tag{3.12}$$

where the averaging $\langle \cdots \rangle$ is performed over all dynamical configurations possible in the absence of entanglements.

We now have the central problem of implementing this calculation for a variety of dynamical systems. In the next section we outline a general approach which develops the idea of entanglements as introducing, both spatially and temporally, correlations into the random environmental forces invariably present in such systems.

4. Entanglements and random forces

We will assume that in the absence of entanglements the motion of the labelled loop is generated by the linear action of random environmental forces $\{\xi_j\}$ acting at all points on the loop. Consequently the coordinate $\boldsymbol{r}_i(t)$ of any point i on the loop at a time t can be expressed as a linear history of all the random force events that the whole loop has been subjected to. This takes the form

$$r_i(t) = \sum_j \int_{-\infty}^{t} \mathrm{d}t'\, G_{ij}(t-t')\boldsymbol{\xi}_j(t'). \tag{4.1}$$

The function $G_{ij}(t-t')$ depends only on the specific model chosen to describe the dynamics of the labelled loop. The dynamical average of any configurational property is then obtained by averaging over all random force histories $\{\xi_j\}$. As a particular example we can consider the correlation function $\langle \boldsymbol{r}_k(t) \cdot \boldsymbol{r}_l(t')\rangle$ which in the presence of entanglements is given using (4.1) and (3.12) by

$$\langle \boldsymbol{r}_k(t) \cdot \boldsymbol{r}_l(t')\rangle = \sum_{ij} \iint_{-\infty}^{t} \mathrm{d}t_1\, \mathrm{d}t_2\, G_{ki}(t-t_1) G_{lj}(t-t_2) \langle \boldsymbol{\xi}_i(t_1) \cdot \boldsymbol{\xi}_j(t_2) p(\{C_\alpha\}; m)\rangle_{\{\xi\}}. \tag{4.2}$$

Since there is a linear relation (4.1) between the configuration variables $\{\boldsymbol{r}\}$ and the random force variables $\{\boldsymbol{\xi}\}$, we can replace one set by the other according to

$$\{\boldsymbol{r}\} \to \{\xi\}$$

and

$$p(\{C_\alpha\}; m) \to P(\{\xi\}; m) \tag{4.3}$$

in which case we can regard $P(\boldsymbol{\xi}\}; m)$ as the probability distribution function that a certain history $\{\boldsymbol{\xi}\}$ of random force events does not lead to a violation of the topology. That is, they do not cause the labelled loop C_α to cross a strand of background material.

The dynamical effects of entanglements are then completely determined by the correlation function of the random forces in the presence of the entanglement constraint:

$$D_{ij}(t_1-t_2)=\langle \boldsymbol{\xi}_i(t_1)\cdot\boldsymbol{\xi}_j(t_2)P(\{\xi\};m)\rangle_{\{\xi\}}. \tag{4.4}$$

The averaging represented by $\langle\cdots\rangle$ is done on the assumption that in the absence of entanglements the random forces are both fast and short ranged so that

$$\langle \boldsymbol{\xi}_i(t_1)\cdot\boldsymbol{\xi}_j(t_2)\rangle_{\{\xi\}}=6D_0\delta_{ij}\delta(t_1-t_2). \tag{4.5}$$

We will show in the following sections that the introduction of the probability distribution function $P(\{\boldsymbol{\xi}\};m)$ in (4.4) leads to large arc lengths and extended time correlations in the fluctuation function $D_{ij}(t-t')$. In this manner our formalism can begin to mimic a tube constraint. The additional correlations introduced by the entanglements are reflected in the configurational properties of the labelled loop C_α by being convoluted with the reponse functions $G_{ij}(t-t')$. Thus for example we have from (4.2) that

$$\langle \boldsymbol{r}_k(t_1)\cdot\boldsymbol{r}_l(t_2)\rangle=\sum_{ij}\int_{-\infty}^{t_1}\int_{-\infty}^{t_2}\mathrm{d}t_1\,\mathrm{d}t_2\,G_{ki}(t-t_1)G_{lj}(t'-t_2)D_{ij}(t_1-t_2). \tag{4.6}$$

The random force correlation function $D_{ij}(t-t')$ is the single most important quantity through which the dynamical effects of entanglements can be calculated. However, there are substantial difficulties in dealing with the precise form of $P(\{\xi\};m)$ and in the next section we approach this problem in a perturbative manner.

5. Perturbation calculation

If we formally couple an external field $\boldsymbol{J}_i(t)$ to the random forces and define a generating function $Z\{J\}$ as

$$Z\{J\}=\left\langle \exp\left(\sum_{i,t}\boldsymbol{J}_i(t)\cdot\boldsymbol{\xi}_i(t)\right)P(\{\xi\};m)\right\rangle_{\{\xi\}} \tag{5.1}$$

then the random force correlation function in the presence of entanglements is given by

$$\begin{aligned}\langle \boldsymbol{\xi}_i(t_1)\cdot\boldsymbol{\xi}_j(t_2)\rangle&=D_{ij}(t_1-t_2)\\&=\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{J}_i(t_1)}\cdot\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{J}_i(t_2)}\ln Z\{J\}\bigg|_{\{J\}=0}.\end{aligned} \tag{5.2}$$

To do the averaging over the random forces (ξ) we note that the statistics given by (4.5) are equivalent to treating the $\{\xi\}$ as Gaussian random variables, so that

$$\langle\cdots\rangle_{\{\xi\}}=\int p\{\xi\}\,\mathrm{d}\{\xi\}\ldots$$

where

$$p\{\xi\}\,\mathrm{d}\{\xi\}=\mathcal{N}\exp\left(\frac{-3}{2D_0}\sum_{i,t}\boldsymbol{\xi}_i^2(t)\right)\prod_{i,t}\mathrm{d}\boldsymbol{\xi}_i(t) \tag{5.3}$$

and $\mathcal{N}$ is a normalisation factor. By a change of variable

$$\boldsymbol{\xi} \rightarrow \boldsymbol{\eta}$$

where

$$\boldsymbol{\eta}_i(t) = \boldsymbol{\xi}_i(t) + \tfrac{1}{3}D_0\boldsymbol{J}_i(t) \tag{5.4}$$

and using (3.9) for the entanglement weighting factor, the generating function $Z\{J\}$ can be expressed as

$$Z\{J\} = \exp\left(\sum_{i,t} J_i^2(t)\frac{D_0}{6}\right) \int \mathrm{d}\{\eta\}p\{\eta\}\frac{\exp[(-\frac{1}{2}m^2\,\Sigma_{tt'}\,\mathbf{M}_{tt'}^{-1}(\boldsymbol{\eta} - \frac{1}{3}D_0\boldsymbol{J})]}{[2\pi\det\mathbf{M}^{-1}(\boldsymbol{\eta} - \frac{1}{3}D_0\boldsymbol{J})]^{1/2}}. \tag{5.5}$$

The functional integrals over the $\{\boldsymbol{\xi}\}$ cannot be done in any analytic manner and in this preliminary study we use a perturbative approach. This consists of replacing the phantom coil winding number correlation function $\mathbf{M}_{tt'}\{C_\alpha\}$ by an unperturbed average value. In particular we set

$$\mathbf{W}_{tt'}\{J\} = \langle \mathbf{M}_{tt'}\{\boldsymbol{\eta} - \tfrac{1}{3}D_0\boldsymbol{J}\}\rangle_{\{\boldsymbol{\eta}\}} \tag{5.6}$$

and formally find the inverse matrix $\mathbf{W}_{tt'}^{-1}$, so that with this approximation $Z\{J\}$ can be written as

$$Z\{J\} = \exp\left(\sum_{it} J_i^2(t)\frac{D_0}{6}\right)\frac{\exp(-\frac{1}{2}m^2\,\Sigma_{tt'}\,\mathbf{W}_{tt'}^{-1}\{J\})}{(2\pi\det\mathbf{W}^{-1})^{1/2}}. \tag{5.7}$$

The differentiations with respect to the $\boldsymbol{J}_i(t_1)$ and $\boldsymbol{J}_j(t_2)$ can now be done and the result written as

$$D_{ij}(t_1, t_2) = D_0\delta_{ij}\delta(t_1 - t_2) - \sum_{tt'}\left(\mathbf{W}_{tt'}^{-1}\frac{\mathrm{d}^2\mathbf{W}_{tt'}}{\mathrm{d}\boldsymbol{J}_i(t_1)\cdot\mathrm{d}\boldsymbol{J}_j(t_2)} - m^2\sum_{t''t'''}\mathbf{W}_{tt''}^{-1}\frac{\mathrm{d}^2\boldsymbol{W}_{t't''}}{\mathrm{d}\boldsymbol{J}_i(t_1)\,\mathrm{d}\boldsymbol{J}_j(t_2)}\mathbf{W}_{t''t'''}^{-1}\right) \tag{5.8}$$

where $\mathbf{W}$ and $\mathrm{d}^2\mathbf{W}/\mathrm{d}\boldsymbol{J}\cdot\mathrm{d}\boldsymbol{J}$ are evaluated at $\{\boldsymbol{J}\} = 0$. The result is still formal in that we have not specified the inverse matrix $\mathbf{W}_{tt'}^{-1}$. This can be done using a Fourier transform, since in the limit $\{\boldsymbol{J}\} = 0$ we have time translational invariance and we can write

$$\mathbf{W}_{tt'}^{-1} \equiv \mathbf{W}^{-1}(t - t') \tag{5.9}$$

and

$$\frac{\mathrm{d}^2\mathbf{W}_{tt'}}{\mathrm{d}\boldsymbol{J}_i(t_1)\cdot\mathrm{d}\boldsymbol{J}_j(t_2)} = \chi_{ij}(t - t', t - t_1, t' - t_2) \tag{5.10}$$

Under these circumstances a Fourier transform will 'diagonalise' the matrix $\mathbf{W}_{tt'}$. We define

$$\mathbf{W}(\omega) = \int_{-\infty}^{\infty}\mathrm{d}\tau\,\mathbf{W}(\tau)\exp(\mathrm{i}\omega\tau) \tag{5.11}$$

so that

$$\mathbf{W}^{-1}(\omega) = 1/\mathbf{W}(\omega). \tag{5.12}$$

Finally the result (5.8) for the random force correlation function in the presence of entanglements can be written in terms of Fourier transform variables as

$$D_{ij}(\omega)=D_0\delta_{ij}-\sum_{\beta=1}^{N_\xi}\int \mathrm{d}\omega'\left(\frac{\chi_{ij}(\omega-\omega',\omega,-\omega)}{\mathbf{W}(\omega)}-\frac{m_\beta^2\chi_{ij}(\omega-\omega',\omega,-\omega)\,\delta(\omega')}{\mathbf{W}^2(\omega')}\right). \qquad (5.13)$$

This is an explicit expression which can be evaluated once the phantom coil winding number correlation function $\mathbf{M}_{tt'}(\xi\}$ has been specified and its average over the $\{\boldsymbol{\xi}\}$ evaluated in the presence of an external field $\{\boldsymbol{J}\}$.

We emphasise that this result has been obtained in a perturbative manner and it is necessary to obtain some indication of its range of applicability. We do this in the next section by presenting an explicit calculation based on the result (5.13) for the case where the labelled coil is described by a particularly simple geometry.

6. Model example: an entangled rigid ring

The physical content of the formalism developed in previous sections can be readily illustrated by considering the situation where the labelled loop entangled with the background material has the configuration of a rigid ring. We consider the centre of mass and orientation of the ring as the dynamical variables whose time dependence will reflect the influence of the entanglements. This choice of a simple geometry enables us to explicitly calculate the functions appearing in (5.13) and in particular the 'mutual inductance' $\mathbf{M}(t, t')$ Without loss of generality we can set $t'=0$ and write

$$\mathbf{M}_{tt'}\{C\}\equiv\mathbf{M}(t;C)=\oint_{C(0)}\mathrm{d}s'\oint_{C(t)}\mathrm{d}s\,\dot{\boldsymbol{r}}(s,t)\cdot\boldsymbol{\Gamma}(\boldsymbol{r}-\boldsymbol{r}')\cdot\dot{\boldsymbol{r}}(s'0). \qquad (6.1)$$

The term $\boldsymbol{\Gamma}(\boldsymbol{r}-\boldsymbol{r}')$ is determined by the nature of the background material and is expressed by (3.3) in terms of a vector field correlation function. For the case where the background loops are static with tangent vectors that are randomly orientated $\boldsymbol{\Gamma}$ is explicitly given by (3.7); however, in anticipation of the averaging we will be doing we take the simpler form

$$\boldsymbol{\Gamma}(\boldsymbol{r}-\boldsymbol{r}')=\left(\frac{3}{2\pi}\right)^{1/2}\frac{\rho l^2}{9\pi}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathbf{1} \qquad (6.2)$$

where ρ and l are the number density and step length of the segments forming the background strand. Thus we have to evaluate

$$\mathbf{M}(t;C)=\left(\frac{3}{2\pi}\right)^{1/2}\frac{\rho l^2}{9\pi}\oint_{C(0)}\mathrm{d}s'\oint_{C(t)}\mathrm{d}s\frac{\dot{\boldsymbol{r}}(st)\cdot\dot{\boldsymbol{r}}(s'0)}{|\boldsymbol{r}-\boldsymbol{r}'|}. \qquad (6.3)$$

In figure 3 we show the rigid ring in two arbitrary configurations at the times t and $t'=0$. The mutual inductance between these rings can be written down exactly as

$$\iint\frac{\mathrm{d}\boldsymbol{r}\cdot\mathrm{d}\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}=\iint_0^{2\pi a}\mathrm{d}s\,\mathrm{d}s'\frac{[f^+(t)\cos(s/a)+f^-(t)\cos(s'/a)]}{\{R^2(t)+a^2[2-f^+(t)\cos(s/a)-f(\bar{t})\cos(s'/a)]\}^{1/2}} \qquad (6.4)$$

where

$$f^{\pm}(t)=1\pm\cos\theta(t)$$

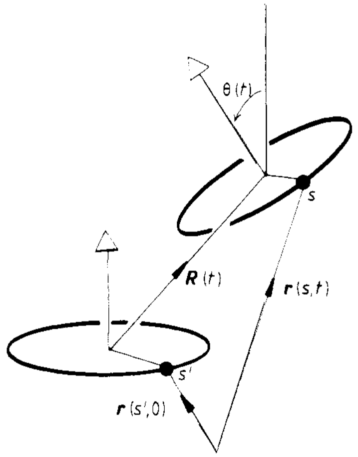

Figure 3. The geometry used to describe the configuration of a rigid ring at two arbitrary times.

and a is the radius of the ring, s and s' are points on the circumferences and $R(t)$ is the distance between the centres of mass of the rings. $\theta(t)$ is the angle between the two normals to the planes of the rings. The integrals in (6.4) can be evaluated in terms of hypergeometric functions; however, for long times when the distance between the rings is much larger than the size a of the ring we find the approximate result

$$a^4 \frac{1-\cos^2\theta(t)}{(R^2(t)+2a^2)^{3/2}}. \tag{6.5}$$

In this result both $\theta(t)$ and $R(t)$ are dynamic variables which we will assume in the absence of entanglements to undergo Brownian motion. The time evolution can be described by the following Langevin equations

$$\frac{\mathrm{d}\boldsymbol{R}(t)}{\mathrm{d}t} = \boldsymbol{\xi}_R(t) \qquad \frac{\mathrm{d}\theta(t)}{\mathrm{d}t} = \xi_\theta(t). \tag{6.6}$$

$\boldsymbol{\xi}_R$ and ξ_θ are treated as Gaussian random variables with correlation in the absence of entanglements given by

$$\langle \boldsymbol{\xi}_R(t) \cdot \boldsymbol{\xi}_R(t') \rangle = 6D_R^0 \delta(t-t')$$
$$\langle \xi_\theta(t) \xi_\theta(t') \rangle = 2D_\theta^0 \delta(t-t'). \tag{6.7}$$

For a rigid ring D_R^0 and D_θ^0 are not independent but related by

$$D \equiv D_\theta^0 = (2/3a^2) D_R^0. \tag{6.8}$$

To apply the perturbative approach developed in the last section we need to average over the whole history of random forces acting on the loop in the presence of generator terms. Thus we evaluate

$$\mathbf{W}(t; J) = \langle \mathbf{M}(t; C) \rangle_J \tag{6.9}$$

where the averaging $\langle\cdots\rangle$ in the presence of the generating terms is done by replacing

$$\xi_R(t)\to\xi_R(t)+\tfrac{1}{3}D_R^0 J_R(t)$$
$$\xi_\theta(t)\to\xi_\theta(t)+D_\theta^0 J_\theta(t)$$

Using the expression (6.5) and some factorisation of Gaussian random variables, we have

$$\mathbf{W}(t;J)=\left(\frac{3}{2\pi}\right)^{1/2}\frac{\rho l^2}{9\pi}a^4\frac{1-\langle\cos\theta\rangle_{J_\theta}^2}{(\langle R^2(t)\rangle_{J_R}+2a^2)^{3/2}}. \tag{6.10}$$

From the Langevin equations the average values of $R^2(t)$ and $\cos\theta(t)$ can be found as

$$\langle R^2(t)\rangle_{J_R}=6D_R t+\tfrac{1}{9}D_R^2\sum_{t_1t_2}J_R(t_1)\cdot J_R(t_2)$$
$$\langle\cos\theta(t)\rangle_{J_\theta}=\mathrm{e}^{-Dt}\left(1+D^2\sum_{t_1t_2}J_\theta(t_1)J_\theta(t_2)\cdots\right). \tag{6.11}$$

Hence we find

$$\mathbf{W}(t;J=0)\equiv\mathbf{W}(t)=\rho l^2 L\frac{1+\mathrm{e}^{-2Dt}}{(\frac{9}{2}Dt+1)^{3/2}} \tag{6.12}$$

$$\chi_R(t;t_1t_2)=\left.\frac{\mathrm{d}^2\mathbf{W}(t)}{\mathrm{d}J_R(t_1)\cdot\mathrm{d}J_R(t_2)}\right|_{J_R=0}$$
$$=\rho l^2 L\frac{9D}{2}\frac{1+\mathrm{e}^{-2Dt}}{(\frac{9}{2}Dt+1)^{5/2}}H(t;t_1t_2) \tag{6.13}$$

$$\chi_\theta(t;t_1t_2)=\left.\frac{\mathrm{d}\mathbf{W}(t)}{\mathrm{d}J_\theta(t_1)\,\mathrm{d}J_\theta(t_2)}\right|_{J_\theta=0}$$
$$=\rho l^2 L8D\frac{\mathrm{e}^{-2Dt}}{(\frac{1}{2}Dt+1)^{5/2}}H(t;t_1t_2) \tag{6.14}$$

where

$$H(t;t_1t_2)\begin{cases}=1 & 0\leqslant t_1,\quad t_2\leqslant t\\ =0 & \text{otherwise}\end{cases}$$

and L is directly proportional to the ring radius a, but where we have incorporated a series of numerical factors and set

$$L=\tfrac{1}{18}a(6\pi)^{1/2}.$$

The Fourier transforms over the variables t, t_1 and t_2 are readily done in terms of known integrals. When these are substituted in (5.13) they will give the fluctuation of the random forces ξ_R and ξ_θ in the presence of the entanglement constraint. The final results can be written as

$$\langle\xi_R(\omega)\cdot\xi_R(-\omega)\rangle_{\text{entangled}}\equiv 6D_R(\omega)$$
$$=6D_R^0\left(1-\frac{N_c m^2}{\rho l^2 L}\frac{9(3\pi)^{1/2}}{8}\frac{1}{(\omega/2D)^{1/2}}\frac{1}{(1+2\omega/9D)^{3/2}}-\frac{9N_c}{22}\right) \tag{6.15}$$

$$\langle \xi_\theta(\omega)\xi_\theta(-\omega)\rangle_{\text{entangled}} \equiv 2D_\theta(\omega)$$
$$= 2D_\theta^0\left(1 - \frac{N_c m^2}{\rho l^2 L}\cdot\frac{9(3\pi)^{1/2}}{1+(\omega/2D)^{1/2}}\,\frac{1}{(1+2\omega/9D)^{3/2}} - \frac{8N_c}{11}\right). \tag{6.16}$$

We will discuss the meaning of these results in the next section. However, to conclude this section we note that the random force fluctuation functions (6.15) and (6.16) still depend explicitly on the actual winding numbers m, which we noted in § 2 depend on the details of fabrication. For an ensemble of loops formed *in situ* we expect the ensemble average $\overline{m^2}$ of m^2 to be the same as that calculated for a single phantom coil at any time t, i.e.

$$\overline{m^2} = \langle m^2(t)\rangle_{\{C\}} = \langle \mathbf{M}_{tt}\{C\}\rangle_{\{C\}}$$
$$= \mathbf{W}(t=0). \tag{6.17}$$

The expression (6.12) that we have been using for $\mathbf{W}(t)$ is only strictly correct for long times. However, it turns out that we do not make any qualitative error when we use it at $t=0$, in which case we have from (6.17) that

$$\overline{m^2} = \rho l^2 L. \tag{6.18}$$

This result will be used in the subsequent discussion.

7. Discussion

In the absence of entanglements the random force fluctuation functions governing the centre of mass and orientational motion are apart from a geometrical factor, the same for each mode and independent of the frequency:

$$D_R^0 = \tfrac{3}{2}a^2 D_\theta^0 = \tfrac{3}{2}a^2 D. \tag{7.1}$$

We have found that in the presence of entanglements the fluctuation functions are effected in radically different ways. In particular the long time behaviour of the loop which is governed by the $\omega \to 0$ is quite different for the two cases. We have from (6.15) and (6.16) together with the ensembled averaged value for m (6.18), that

$$D_R(\omega)\Big|_{\omega\to 0} = D_R^0\left[1 - \frac{9(3\pi)^{1/2}}{8}N_c\left(\frac{2D}{\omega}\right)^{1/2}\right] \tag{7.2}$$

whereas

$$D_\theta(\omega)\Big|_{\omega\to 0} \simeq D_\theta^0\{1 - [9(3\pi)^{1/2} - \tfrac{8}{11}]N_c\}. \tag{7.3}$$

For rotational motion our result suggests that the diffusion constant is greatly reduced. Unfortunately the perturbation calculation has virtually no range of applicability as the diffusion coefficient cannot be negative. In the case of the motion of the centre of mass the situation is even more critical because of the presence of the $\omega^{-1/2}$ term in the limit $\omega \to 0$. This implies that the usual Fickian diffusion ($\langle R^2\rangle \sim t$) will break down completely in the long time limit. In fact only in the case when the loop is formed outside of the background matrix and subsequently introduced do we obtain centre-of-mass diffusion with a reduced diffusion coefficient

$$D_R(\omega)\Big|_{m^2=0} = D_R^0(1-\tfrac{9}{22}N_c). \tag{7.4}$$

The reason for this is that the coefficient of the $\omega^{-1/2}$ term involves the winding number m and in this particular case $m=0$. Again the validity of this result is very limited. In fact the only broad conclusions that we can draw at this stage are that the use of perturbation theory to deal with the statistical weight factor (3.9) for entanglements is limited and can only be used as a qualitative guide. The reorientational motion, though greatly reduced is still diffusional at long times, whereas the centre-of-mass motion is radically altered. Whether the loop is eventually localised in our model or continues to move in some non-diffusional manner will depend on finding a non-perturbative treatment of the statistical weighting factor. It is of some interest to locate the origin of the $\omega^{-1/2}$ term in $D_R(\omega)$. For the specific geometry of a rigid ring the tangent vector correlation function is given by

$$\langle \dot{r}(st)\cdot\dot{r}(s't')\rangle = \cos(s/a)\cos(s'/a)\exp(-2D|t-t'|] + \sin(s/a)\sin(s'/a) \tag{7.5}$$

from which we can see that there will always be some part of the ring (s, t) in its current position which is parallel to another part (s', t') in its previous location, even as $|t-t'|\to\infty$. When this result is used in the expression (6.3) for the mutual inductance formula between the two configurations it is precisely this persistence of the bond vector correlation that accounts for the $\omega^{-1/2}$ term.

It is not our intention to pursue this much further except to comment briefly that if the result (7.2) represents the first term of a perturbation expansion that could be resummed to give

$$D_R(\omega) = \frac{D_R^0}{1+\frac{9}{8}(3\pi)^{1/2}N_c(2D/\omega)^{1/2}}. \tag{7.6}$$

Then the motion of the centre of mass, which is given by

$$\langle R^2(t)\rangle = 6\int_0^t\!\!\int \mathrm{d}t_1\,\mathrm{d}t_2\,D_R(t_1-t_2) \tag{7.7}$$

would behave as

$$\langle R^2(t)\rangle \sim (a/N_c)(D_R^0 t)^{1/2} \tag{7.8}$$

due to the $\omega^{-1/2}$ term in the denominator of (7.7). The dependence $\langle R^2(t)\rangle \sim t^{1/2}$ is very reminescent of a normal diffusion process confined to a random walk path in space. This in turn forms the basis of the Doi–Edwards–de Gennes tube model of entanglements. It is encouraging that we can tentatively identify this kind of behaviour with the persistence of bond vector correlations in our model. In a further publication we hope to present a non-perturbation calculation that will lead to the kind of resummation that we have speculated on here. We also hope to pursue in detail the application of these results to polymer and rigid rod molecules in not only the static background we have considered here but also in a dynamic background.

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Appendix. Derivation of the statistical weighting factor $p(\{C\}; m)$

We start with the product of topology conserving delta functions

$$p(\{C_\alpha\}; m) = \left\langle \prod_t \delta\left(\oint_{C_\alpha} \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{r}_\alpha - m(t)\right)\right\rangle_{\{A\}}. \tag{A1}$$

The delta functions can be parametrised at each time t by the form

$$\delta\left(\oint_{C_\alpha} \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{r}_\alpha - m(t)\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}g(t) \exp(\mathrm{i}g(t))\left(\oint \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{r} - m(t)\right). \tag{A2}$$

Since we are treating the $\boldsymbol{A}(\boldsymbol{r})$ as Gaussian random variables then

$$\left\langle \exp\left(\mathrm{i} \sum_t g(t) \oint_{C_\alpha(t)} \mathbf{A} \cdot \mathrm{d}\boldsymbol{r}_\alpha\right)\right\rangle_{\{A\}}$$

$$= \exp\left(-\tfrac{1}{2} \sum_{tt'} \oint_{C_\alpha(t)} \oint_{C_\alpha(t')} \mathrm{d}\boldsymbol{r}_\alpha(t) \cdot \langle \boldsymbol{A}(\boldsymbol{r}(t)) \boldsymbol{A}(\boldsymbol{r}(t')) \rangle \cdot \mathrm{d}\boldsymbol{r}_\alpha(t')\right) \tag{A3}$$

and we set

$$\mathbf{M}_{tt'} = \oint_{C_\alpha(t)} \oint_{C_\alpha(t')} \mathrm{d}\boldsymbol{r}_\alpha(t) \cdot \langle \boldsymbol{A}(\boldsymbol{r}(t)) \boldsymbol{A}(\boldsymbol{r}(t')) \rangle \cdot \mathrm{d}\boldsymbol{r}_\alpha(t').$$

The integrals over each of the $g(t)$ can be done as they have the form of a generalised Gauss integral. The result is the one used in the paper, i.e.

$$p(\{C_\alpha\}; m) = (2\pi \det \mathbf{M}^{-1}) \exp\left(-\frac{1}{2} \sum_{tt'} m(t) \mathbf{M}_{tt'}^{-1} m(t')\right). \tag{A4}$$

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