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1995 J. Phys. A: Math. Gen. 28 1149

(http://iopscience.iop.org/0305-4470/28/5/007)

J. Phys. A: Math. Gen. 28 (1995) 1149–1167. Printed in the UK

The statistical mechanics of a melt of polymer rings

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Received 13 October 1994

Abstract. Topological restrictions are introduced into a melt of flexible polymer rings by specifying the linking number between each pair of rings. Attention is focused on the configurational properties of a single ring in the melt, where the winding number between each pair of rings is zero. The configurations of all the other chains are averaged out in the partition sum. The effect of the topological constraint on the remaining chain is expressed as a product of two configurational weighting factors which involve unusual geometrical properties of the configuration. One is a phase factor depending on the *torsion* of the configuration and the other is a Boltzmann-like factor with the *self-inductance* of the configuration in the role of the interaction energy. The term based on the *torsion* has the remarkable property of transforming random walk-like configurations into those of stiff rods, while the *inductance* term promotes a transition to a completely collapsed state. Our preliminary results suggest that the actual configuration of the loop is a non-trivial balance between these opposing tendencies with the size R of the loop scaling with the length as $R^2 \sim L^{1-1/(3\nu)} \sim L^{0.89}$.

1. Introduction

Long chain polymer rings are ideal for studying the role that topology can play in the statistical mechanics of condensed matter systems. In a melt of polymer rings a large diversity of topological structures can be created by controlling the linking number of each ring with every other ring in the melt. The topology is conserved since the chains cannot pass through each other by virtue of the excluded volume interactions present between the chain segments. In contrast, a melt of polymer chains with free ends and excluded volume interactions is an amorphous state that cannot support any further topological structure other than that represented by the chains themselves. The essential topological features of a polymer melt to be accounted for in this paper are shown schematically in figure 1. The configuration shown in figures 1(a) and (b) are topologically distinguished by their winding numbers.

It has long been known from the work of both Flory and Edwards that the configuration of a single chain in a melt of interacting chains can be described as a random walk. This (remarkable) fact can be explained in terms of an attractive self-interaction induced by the density fluctuations in the melt. This acts so as to screen the original repulsive excluded volume interactions. The calculation of Edwards [1] can be trivially extended to polymer rings by replacing the structure factor of a chain by that of a ring. When this is done there are no substantial changes and it is predicted that the configuration of a ring in a melt will also be a random walk. However, a simple Flory-type argument by Deutsch and Cates [2] suggests that the size R of an unlinked ring in a melt of unlinked rings in d dimensions should depend on the length L as $R \approx L^{d/(d+2)} \approx L^{0.4}$ in three dimensions. Computer

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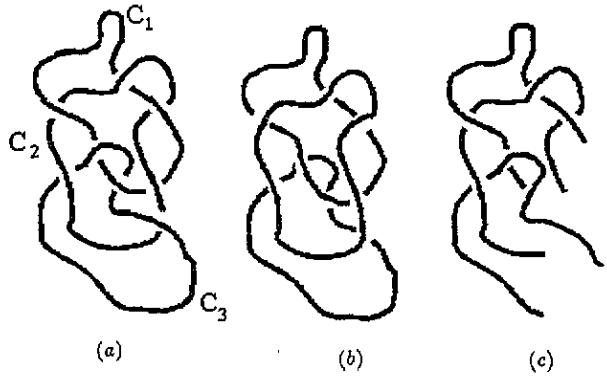

Figure 1. (*a*),(*b*) Loops which are configurationally similar but topologically distinct; (*c*) entangled linear chains cannot sustain the topological properties of loops.

simulation experiments by Pakula and Geyer [3] and Weyersberg and Vilgis [4] also find a non-Gaussian exponent of 0.45 for a melt of unlinked rings.

In this paper we will consider the general problem of the configurational properties of a single ring in a melt of rings where the topological structure can be described in terms of linking numbers. As a special case, particular attention will be given to the situation where all the linking numbers are set to zero, as schematically illustrated in figure 1(*b*). This would be the case for loops formed in dilute solution and then concentrated. It must be added that the linking number does not, however, provide a complete discrimination between topologically different configurations. Consequently our calculation will refer to a somewhat larger ensemble than that of truly unlinked rings. The method we adopt follows in spirit that described in Edwards' paper. The configurations of all the chains, apart from the chosen one, are averaged out in the partition sum. This is done by identifying the relevant collective variables for the problem and treating them as Gaussianly distributed. The justification being that, as they consist of a sum over a macroscopic number of individual random variables, then the ubiquitous law of large numbers states that they should be Gaussian. The effect of the topological constraint on the remaining chain, as a result of this process, is expressed as a product of two weighting factors which involve unusual geometrical, as opposed to topological, properties of the configuration. One is a phase factor depending on the *torsion* of the configuration and the other is a Boltzmann-like factor with the *self-inductance* of the configuration in the role of the interaction energy. The term based on the torsion has the remarkable property of transforming random walk-like configurations into those of stiff rods, while the inductance term promotes a transition to a completely collapsed state. Our preliminary results suggest that the actual configuration of the loop is a non-trivial balance between these opposing tendencies with the size R of the loop scaling with the length as $R^2 \sim L^{1-1/(3\pi)} \sim L^{0.89}$.

2. Formulation of the topological problem

A melt of N_c closed random walk loops is considered where the topological relation of each loop C_α with every other loop C_β ($\beta = 1, \ldots, N_c$) in the system is specified by a winding number $m_{\alpha\beta}$. For any pair of loops (α, β) the winding number is given by the Gauss result

$$G(C_\alpha, C_\beta) = \frac{1}{4\pi} \oint_{C_\alpha} \oint_{C_\beta} \mathrm{d}r^\alpha \times \mathrm{d}r^\beta \cdot \frac{(r^\alpha - r^\beta)}{|r^\alpha - r^\beta|^3} \tag{2.1}$$

and is a topological invariant. The interest in the role of winding numbers in polymer physics stems from the work of Edwards [5], Brereton and Shah [6] and has greatly increased in recent years [7–12].

Since the winding numbers are integers, the constraint that the winding number should take a specific value $m_{\alpha\beta}$ is imposed using a Kronecker delta function

$$\delta\{G(C_\alpha, C_\beta), m_{\alpha\beta}\} = \begin{cases} 1 & G(C_\alpha, C_\beta) = m_{\alpha\beta} \\ 0 & G(C_\alpha, C_\beta) \neq m_{\alpha\beta}. \end{cases}$$

In this paper we study the configuration C_α of a single (labelled) polymer loop α in a melt of polymer loops $\{C_\beta\}$. The topological relation of the labelled loop α with the other loops (β) in the melt is separated out by the product of factors

$$\prod_{\beta\neq\alpha}^{N_c} \delta\{G(C_\alpha, C_\beta), m_{\alpha\beta}\}.$$

The topology of the rest of the melt is specified by the product

$$\prod_{\beta>\beta'\neq\alpha}^{N_c} \delta\{G(C_\beta, C_{\beta'}), m_{\beta\beta'}\}.$$

N_c is the total number of chains in the system. Therefore the partition sum Z for the single chain is given by

$$Z(\{C_\alpha\}, \{m_{\beta\beta'}\}) = \left\langle \prod_{\beta\neq\alpha}^{N_c} \delta(G_{\alpha\beta}, m_{\alpha\beta}) \prod_{\beta>\beta'\neq\alpha}^{N_c} \delta(G_{\beta\beta'}, m_{\beta\beta'}) \right\rangle_{\substack{\text{all chains} \\ \text{except } \alpha}} \tag{2.2}$$

where $G_{\alpha\beta} \equiv G(C_\alpha, C_\beta)$ and the averaging is performed over the configurations of the unperturbed chains. Later in this paper the Gaussian chain model, based on the Wiener measure, will be used.

The restriction $\beta' > \beta$ prevents double counting of the rings, however, it will prove more convenient to work with the complete index range for both β' and β.

The Kronecker delta function can be parameterized as

$$\delta(G_{\beta\beta'}, m_{\beta\beta'}) = \int_0^{2\pi} \frac{\mathrm{d}g_{\beta\beta'}}{2\pi} \exp \mathrm{i} g_{\beta\beta'}(G_{\beta\beta'} - m_{\beta\beta'}) \tag{2.3}$$

then the partition function (2.2) for the single chain can be written as the Fourier transform:

$$Z(\{C_\alpha\}, \{m_{\beta\beta'}\}) = \prod_{\beta\beta'=1}^{N_c} \int_0^{2\pi} \frac{\mathrm{d}g_{\beta\beta'}}{2\pi} Z(\{C_\alpha\}; \{g_{\beta\beta'}\}) \exp -\mathrm{i} g_{\beta\beta'} m_{\beta\beta'} \tag{2.4}$$

where

$$Z(\{C_\alpha\}; \{g_{\beta\beta'}\}) = \left\langle \exp \mathrm{i} \sum_{\beta\beta'} g_{\beta\beta'} G(C_\beta, C_{\beta'}) \right\rangle_{\substack{\text{all chains} \\ \text{except } \alpha}}. \tag{2.5}$$

There are two problems: one is the statistical mechanical problem to evaluate $Z(\{C_\alpha\}; \{g_{\beta\beta'}\})$ given by (2.5) and the second is to perform the Fourier transform (2.4). The statistical mechanical problem is considered in the next section.

3. The statistical mechanical problem and collective variables

The statistical mechanical problem is to evaluate $Z(\{C_\alpha\};\{g_{\beta\beta'}\})$ given by (2.5). The labelled chain α is separated out to give

$$Z(\{r^\alpha\};\{g_{\beta\beta'}\}) = \left\langle \exp \mathrm{i}\left\{ \sum_\beta (g_{\alpha\beta}+g_{\beta\alpha}) G(\{r^\alpha, r^\beta\}) + \sum_{\beta\beta'} g_{\beta\beta'} G(\{r^\beta, r^{\beta'}\}) \right\} \right\rangle_{\substack{\text{all chains} \\ \text{except } \alpha}} \tag{3.1}$$

where we have reverted to a notation $G(\{r^\alpha, r^\beta\})$ for the Gauss winding number that acts as a reminder that the position vectors $r^\beta, r^{\beta'}$ describing the loop configurations are the primary statistical variables. The explicit form for the winding number is given by (2.1), which can be written in an alternative form by using the result

$$\frac{r_k}{|r|^3} = \frac{1}{2\pi^2 \mathrm{i}} \int \mathrm{d}^3 q \, \frac{q_k}{q^2} \exp \mathrm{i} q \cdot r. \tag{3.2}$$

A tangent vector collective variable $u^\alpha(q)$ is defined by

$$u^\alpha(q) = \oint_{C_\alpha} \mathrm{d}r^\alpha \exp \mathrm{i} q \cdot r^\alpha \tag{3.3}$$

which is the Fourier component of the tangent vector density for a single chain

$$u^\alpha(R) = \oint_{C_\alpha} \mathrm{d}r^\alpha \, \delta(r^\alpha - R). \tag{3.4}$$

In terms of these collective variables the winding number becomes

$$\begin{aligned} G(\{r^\alpha, r^\beta\}) \equiv G_{\alpha\beta} &= \frac{1}{(2\pi)^3 \mathrm{i}} \int \mathrm{d}^3 q \, \frac{u^\alpha(q) \times u^\beta(-q) \cdot q}{q^2} \\ &= \frac{1}{\mathrm{i}\Omega} \sum_q \frac{u^\alpha(q) \times u^\beta(-q) \cdot q}{q^2} \end{aligned} \tag{3.5}$$

and the partition sum (3.1) becomes

$$\begin{aligned} Z(C_\alpha;\{g_{\beta\beta'}\}) = \Bigg\langle \exp \frac{1}{\Omega} \sum_{\substack{\beta \neq \alpha \\ q}} (g_{\alpha\beta}+g_{\beta\alpha}) \frac{u^\alpha(q) \times u^\beta(-q) \cdot q}{q^2} \\ + \sum_{\substack{\beta\beta' \neq \alpha \\ q}} g_{\beta\beta'} \frac{u^\beta(q) \times u^{\beta'}(-q) \cdot q}{q^2} \Bigg\rangle_{\{r^\beta\},\{r^{\beta'}\}} \end{aligned} \tag{3.6}$$

where Ω is the volume of the system.

Averaging over the polymer variables $\{r^\beta\}$ in (3.6) is too complicated to be practical. The way forward is to identify collective variables which involve the sum over all chains in the system. By virtue of the law of large numbers the statistical properties of these variables can be well approximated by Gaussian statistics. In the present problem a definition of the collective variables is not so clear and requires careful attention.

For polymer chains in a melt, interacting with each other through an excluded volume interaction, the collective variable is the density fluctuation

$$\rho_q = \Omega^{-1} \sum_{\beta=1,j=1}^{N_c,N} \exp \mathrm{i} q \cdot r_j^\beta.$$

A similar variable can be defined for the bond vector density fluctuation

$$u(q) = \Omega^{-1} \sum_{\beta=1,j=1}^{N_c,N} b_j^\beta \exp \mathrm{i} q \cdot r_j^\beta = \sum_\beta u^\beta(q)$$

and has been found to be very useful in problems involving polymer blends and di-block copolymers [13].

The present problem is complicated by the integration variables $g_{\beta\beta'}$, which are conjugate to the winding numbers $m_{\beta\beta'}$ and which act like coupling constants between chains. They can be regarded as the elements of a $N_c \times N_c$ matrix. The essential step in finding an appropriate collective variable is to 'factorize' the chain indices in the term $g_{\beta\beta'}$. To do this it is convenient to introduce the symmetric and antisymmetric variables $s_{\alpha\beta}$ and $a_{\alpha\beta}$ where

$$s_{\alpha\beta} = \left(\frac{g_{\alpha\beta} + g_{\beta\alpha}}{2}\right) \qquad \text{and} \qquad a_{\alpha\beta} = \left(\frac{g_{\alpha\beta} - g_{\beta\alpha}}{2}\right)$$

and change variables

$$\int_0^{2\pi} \frac{\mathrm{d}g_{\alpha\beta}}{2\pi} \int_0^{2\pi} \frac{\mathrm{d}g_{\beta\alpha}}{2\pi} \exp \mathrm{i}(g_{\alpha\beta} + g_{\beta\alpha}) m_{\alpha\beta} = \frac{1}{\pi^2} \int_0^{\pi} \mathrm{d}a_{\alpha\beta} \int_{a_{\alpha\beta}}^{2\pi - a_{\alpha\beta}} \mathrm{d}s_{\alpha\beta} \exp \mathrm{i} 2 s_{\alpha\beta} m_{\alpha\beta}. \tag{3.7}$$

If the symmetric integration variables $s_{\beta\beta'}$ are considered as the elements of a matrix s, then this may be factorized in terms of another symmetric matrix η so that

$$s = \eta \cdot \eta$$

or

$$s_{\beta\beta'} = \sum_\gamma \eta_{\beta\gamma} \eta_{\gamma\beta'}. \tag{3.8}$$

A collective variable $\Psi_\sigma(q)$ can now be defined as

$$\Psi_\sigma(q) = \sum_{\beta=1}^{N_c} \eta_{\sigma\beta} u_\beta(q) \tag{3.9}$$

so that terms like

$$\sum_{\beta\beta'=1}^{N_c} g_{\beta\beta'} u^\beta(q) \times u^{\beta'}(-q) \cdot q$$

which occur in the partition sum (3.5) can be written entirely in terms of these variables as

$$\sum_{\sigma=1}^{N_c} \Psi_\sigma(q) \times \Psi_\sigma(-q) \cdot q. \tag{3.10}$$

In terms of the $\{\Psi_\sigma(q)\}$ the full statistical factor (3.6) can be written as

$$Z(\{C_\alpha\}; \{s_{\beta\beta'}\}) = \left\langle \exp \frac{2}{\Omega} \sum_{\sigma,q} \eta_{\alpha\sigma} \frac{u^\alpha(q) \times \Psi_\sigma(-q) \cdot q}{q^2} \right\rangle_{\{C_\beta\}} + \left\langle \exp \frac{1}{\Omega} \sum_{\sigma} \frac{\Psi_\sigma(q) \times \Psi_\sigma(-q) \cdot q}{q^2} \right\rangle_{\{C_\beta\}}. \tag{3.11}$$

Since the $\Psi_\sigma(q)$ are the sum over a macroscopic number N_c of random variables they can be considered to be Gaussianly distributed, with the distribution function

$$P\{\Psi\} = \sqrt{\det(\Gamma^{-1})} \exp -\frac{1}{\Omega} \sum_{q,\sigma\sigma',ij'} \Psi_\sigma(-q) \cdot [\Gamma(q)]^{-1}_{\sigma\sigma'} \Psi_{\sigma'}(q) \tag{3.12}$$

where $[\Gamma(q)]_{\sigma\sigma'}$ is the correlation function matrix

$$[\Gamma(q)]_{\sigma\sigma'} = \frac{2}{\Omega} \langle \Psi_\sigma(q) \cdot \Psi_{\sigma'}(-q) \rangle_0.$$

The average is taken with respect to the unconstrained loops. Using the definition (3.9) for $\Psi_\beta(q)$

$$[\Gamma(q)]_{\sigma\sigma'} = \frac{1}{N_c} s_{\sigma\sigma'} \gamma(q) \tag{3.13}$$

where $\gamma(q)$ is

$$\gamma(q) = \frac{N N_c}{\Omega} \oint (\mathrm{d}r \cdot \mathrm{d}r' \exp \mathrm{i}q \cdot (r - r'))_0. \tag{3.14}$$

The complication in using the distribution function (3.12) is that the matrix Γ must be inverted in the $N_c \times N_c$ matrix space of chain labels. The details of this manipulation and the Gaussian integration using the distribution function $P\{\Psi\}$ for the collective variables $\{\Psi_\beta(q)\}$ are given in appendix 1.

The result for the partition function (3.11) can be written as

$$Z(\{C_\alpha\}; \{s_{\beta\beta'}\}) = \exp -\frac{1}{\Omega} \sum_q [A_{\alpha\alpha}(q; \{s_{\beta\beta'}\}) l(q; \{C_\alpha\}) - B_{\alpha\alpha}(q; \{s_{\beta\beta'}\}) \phi(q; \{C_\alpha\})] \tag{3.15}$$

where the terms $A_{\alpha\alpha}(q; \{s_{\beta\beta'}\})$, $B_{\alpha\alpha}(q; \{s_{\beta\beta'}\})$ can be considered as the matrix elements

$$A_{\alpha\alpha}(q; \{s_{\beta\beta'}\}) = \frac{N_c}{\gamma(q)} \left\{ \Gamma^2 \left[1 + \frac{\Gamma^2}{q^2} \right]^{-1} \right\}_{\alpha\alpha}$$

$$B_{\alpha\alpha}(q; \{s_{\beta\beta'}\}) = \frac{N_c}{\gamma(q)} \left\{ \frac{\Gamma^3}{q^2} \left[1 + \frac{\Gamma^2}{q^2} \right]^{-1} \right\}_{\alpha\alpha} \tag{3.16}$$

and Γ is the matrix given by (3.13). The terms $l(q;\{C_\alpha\})$, $\phi(q;\{C_\alpha\})$ depend on geometrical rather than topological features of the configuration C_α of the single chain α and are given by

$$l(q;\{C_\alpha\}) = \frac{u(q)\cdot u(-q)}{q^2} = \oint_{C_\alpha} \mathrm{d}r(s)\cdot \mathrm{d}r(s')\,\frac{\exp \mathrm{i}q\cdot(r(s)-r(s'))}{q^2} \tag{3.17}$$

and

$$\phi(q;\{C_\alpha\}) = \frac{u(q)\times u(-q)\cdot q}{q^2} = \oint_{C_\alpha} \mathrm{d}r(s)\times \mathrm{d}r(s')\cdot q\frac{\exp \mathrm{i}q\cdot(r(s)-r(s'))}{q^2}. \tag{3.18}$$

The final partition sum $Z(\{C_\alpha\};\{m_{\beta\beta'}\})$ is obtained from $Z(\{C_\alpha\};\{s_{\beta\beta'}\})$ by integrating over the variables $s_{\beta\beta'}$. This is considered in the next section.

4. The partition sum $Z(\{C_\alpha\};\{m_{\beta\beta'}\})$

Using the form (3.15) together with (2.4) and (3.7) gives

$$\begin{aligned} Z(\{C_\alpha\};\{m_{\beta\beta'}\}) &= \prod_{\beta\beta'}\frac{1}{\pi^2}\int_0^\pi \mathrm{d}a_{\beta\beta'}\int_{a_{\beta\beta'}}^{2\pi-a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'}\,\exp(\mathrm{i}2s_{\beta\beta'}m_{\beta\beta'})Z(\{C_\alpha\};s_{\beta\beta'}) \\ &= \prod_{\beta\beta'}\frac{1}{\pi^2}\int_0^\pi \mathrm{d}a_{\beta\beta'}\int_{a_{\beta\beta'}}^{2\pi-a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'}\,\exp(\mathrm{i}2s_{\beta\beta'}m_{\beta\beta'}) \\ &\quad\times\exp-\frac{1}{\Omega}\sum_q[A_{\alpha\alpha}(\{s_{\beta\beta'}\})l - B_{\alpha\alpha}(\{s_{\beta\beta'}\})\phi] \end{aligned} \tag{4.1}$$

where only the dependence on the variables $s_{\beta\beta'}$ has been shown.

In the remainder of this paper we will consider the simple case of a melt of unlinked rings where $m_{\beta\beta'}=0$ for all pairs of chains. Even with this simplification the integrals are multi-dimensional and the evaluation is further complicated by the fact that the expressions involving the variables $s_{\beta\beta'}$ are in an infinite series of matrix forms, e.g.

$$A_{\alpha\alpha}(q) \approx \left\{\Gamma^2\left[1+\frac{\Gamma^2}{q^2}\right]^{-1}\right\}_{\alpha\alpha} \approx \sum_\beta \Gamma_{\alpha\beta}\Gamma_{\beta\alpha} - \frac{1}{q^2}\sum_{\beta\gamma\delta}\Gamma_{\alpha\beta}\Gamma_{\beta\gamma}\Gamma_{\gamma\delta}\Gamma_{\delta\alpha}+\cdots.$$

Despite the apparent complexity of this final operation the required integrations can be performed term by term. The fact that we are dealing with a melt turns out to be crucial for the re-summation of these series. The details are given in appendix 2 and the result, which we report here, is that the partition function $Z(\{C_\alpha\};\{m_{\beta\beta'}=0\})$ has the same form as $Z(\{C_\alpha\};\{s_{\beta\beta'}\})$ but where the matrix factors $A_{\alpha\alpha}(q)$, $B_{\alpha\alpha}(q)$ are replaced by

$$A(\{g\};q^2) \to \frac{\rho b^3\pi^2}{6b} = \frac{1}{l} \tag{4.2}$$

and

$$B(\{g\};q^2)\to\pi.$$

l is a length determined by the number density $\rho = NN_c/\Omega$ of chain segments each of statistical length b so that

$$l = b\frac{6}{\rho b^3 \pi^2}. \tag{4.3}$$

For a melt $\rho b^3 \sim 1$ and hence $l \sim b$.

The configurational weighting factor $Z(C_\alpha)$ for a single unlinked ring in a melt of unlinked rings can, therefore, be expressed as the product of two distinct terms

$$Z(\{C_\alpha\}) = Z_\Phi(\{C_\alpha\})Z_L(\{C_\alpha\}) = \exp[i\pi\Phi(\{C_\alpha\})]\exp\left[-\frac{1}{l}L(\{C_\alpha\})\right] \tag{4.4}$$

where

$$\Phi(\{C_\alpha\}) = \frac{-i}{\Omega}\sum_q \phi(q;\{C_\alpha\}) = \frac{1}{4\pi}\oint\!\!\oint_{C_\alpha} \frac{dr \times dr' \cdot (r-r')}{|r-r'|^3} \tag{4.5}$$

and

$$L(\{C_\alpha\}) = \frac{1}{\Omega}\sum_q l(q;\{C_\alpha\}) = \frac{1}{4\pi}\oint\!\!\oint_{C_\alpha} \frac{dr \cdot dr'}{|r-r'|}. \tag{4.6}$$

$\Phi(\{C_\alpha\})$ is known as the *writhe* of the configuration; it has the form of the Gauss winding-number formula but applied to a single configuration. It is not a topological invariant and will be discussed in detail in the next section. $L(\{C_\alpha\})$ is essentially the self-inductance of the C_α configuration.

Equations (4.4)–(4.6) are the major results of this paper. It is noteworthy that the coefficient of the self-linking, or writhe term, is independent of any of the physical parameters in this problem and is the pure number π. It is present as a phase factor, whereas the self-inductance is present as a traditional Boltzmann factor. The influence of these terms separately is discussed in the next two sections.

5. Writhe and the configuration of a single loop

The statistical factor containing the writhe term is

$$Z_\Phi = \exp i\pi\Phi(C) = \exp\frac{i}{4}\oint_C dr(s) \times dr(s') \cdot \frac{(r-r')}{|r-r'|^3}. \tag{5.1}$$

In the integration, which is around the same loop C, it would appear that singularities appear when point $r = r'$. This problem had been considered long ago by Calugareanu [14] and more recently by [7, 15–17]. The integral is well defined if two curves are created:

$$C_1: \{r(s)\} \qquad \text{and} \qquad C_2: \{r(s) + \varepsilon n(s)\}$$

where ε is a small parameter which will ultimately be set equal to zero and n is the principal normal to the curve C_1, where

$$n = \frac{\dot{e}}{|\dot{e}|} = \frac{\ddot{r}}{|\ddot{r}|}.$$

The Gauss winding-number formula applied to the two curves C_1 and C_2 gives the linking number m_{12} between the two curves. This is the integer

$$m_{12} = G(C_1, C_2) = \frac{1}{4\pi} \oint_{C_1} \oint_{C_2} \mathrm{d}r^1 \times \mathrm{d}r^2 \cdot \frac{(r^1 - r^2)}{|r^1 - r^2|^3}. \tag{5.2}$$

If the curve C_2 is allowed to approach C_1 smoothly, i.e. as $\varepsilon \to 0$, $C_2 \to C_1 = C$ then the integer valued left-hand side of the above equation will remain as an integer, whereas on the right-hand side there are two contributions:

$$m_{12} = \frac{1}{4\pi} \oint_C \oint_C \mathrm{d}r^1 \times \mathrm{d}r^2 \cdot \frac{(r^1 - r^2)}{|r^1 - r^2|^3} + \frac{1}{2\pi} \oint_C \frac{\dot{r}(s) \cdot \ddot{r}(s) \times \dddot{r}(s)}{|\ddot{r}(s)|^2} \mathrm{d}s. \tag{5.3}$$

The first term on the right-hand side is by definition the *writhe* $\Phi(C)$ of the curve C, whereas the second term is the integral of the torsion $\tau(s)$ of the curve at a point s along the curve (see for example [18]), where

$$\tau(s) = \frac{\dot{r}(s) \cdot \ddot{r}(s) \times \dddot{r}(s)}{|\ddot{r}(s)|^2}.$$

Hence the writhe of a curve is given by

$$\Phi(\{C_\alpha\}) = \text{integer} - \frac{1}{2\pi} \oint_C \tau(s)\, \mathrm{d}s \tag{5.4}$$

and the statistical weighting factor can be written as

$$Z_{\mathrm{Wr}} = \exp \mathrm{i}\pi \mathrm{Wr}(C) = (-1)^{\text{integer}} \exp \frac{\mathrm{i}}{2} \oint_C \mathrm{d}s\, \tau(s). \tag{5.5}$$

The presence of the factor π multiplying the *writhe* is quite vital in eliminating any contribution from the unspecified integer terms. The sign ambiguity needs further consideration but for the moment will be ignored; in which case the weighting factor can be directly related to the total torsion of the curve.

The polymer configuration can now be described as a closed random walk made up of unit tangent (or bond) vectors $\{e(s)\}$. The configuration is weighted by a phase-factor dependent on the total torsion of the polymer configuration C. The configurational properties can be obtained from the partition sum

$$Z(\boldsymbol{R}, s) = \left\langle \delta\left(\int_0^s \mathrm{d}s'\, e(s') - \boldsymbol{R} \right) \delta\left(\int_0^L \mathrm{d}s'\, e(s') \right) \exp\left(\frac{-\mathrm{i}}{2} \int_0^L \mathrm{d}s' \frac{e \cdot \dot{e} \times \ddot{e}}{|\dot{e}|^2} \right) \right\rangle. \tag{5.6}$$

The first delta function ensures that the curve at an arc length s is at the spatial position $\boldsymbol{R}$, while the second delta function ensures that the curve forms a closed loop of arc length L.

The evaluation of this partition sum $Z(\boldsymbol{R}, s)$ was first given by Polyakov [19, 20] and created a great deal of excitement (see for example [21–23]). In Polyakov's work the configuration C represented a particle moving in time in two spatial dimensions. He showed that the phase factor based on the total torsion is able to transform a boson into a fermion. In the present problem in polymer physics the transformation is equally spectacular. If the original configuration is regarded as a random walk then the phase factor converts the

large scale configuration into that of a rigid rod. Kholodenko [24] has also considered this possibility in the context of the reptation dynamics of polymer chains.

In detail, the propagator or probability distribution function $G(R, s)$ for the configuration is given by

$$G(R, s) = \frac{Z(R, s)}{\int d^3R\, Z(R, s)}. \tag{5.7}$$

This is evaluated in appendix 3 to give

$$G(R, s) = \frac{1}{4\pi Rs}\delta(R - s). \tag{5.8}$$

This is essentially the propagator for a rigid rod.

6. Inductance and the configuration of a single loop

It would be a strange phenomenon if topological entanglements in a melt of flexible polymers could transform them into rigid rods, as discussed in [24] and, in fact, there is no experimental evidence for this. This extreme situation is partly neutralized if we recall that the conservation of the winding numbers gave two weighting factors: one dependent on the writhe or torsion of the curve and the other on the self-inductance. In this section the effect of the self-inductance is briefly examined, i.e. the effect that the statistical factor

$$Z_L = \exp -L(C_\alpha) = \exp -\left[\frac{1}{l}\oint_{C_\alpha} \frac{dr(s) \cdot dr(s')}{|r(s) - r(s')|}\right] \tag{6.1}$$

has on the configuration of a single loop. This looks more like a conventional Boltzmann factor which strongly favours globular configurations; that is, this factor is large for configurations where the directions of the tangent vectors are continually in antiparallel ($dr(s) \cdot dr(s') < 0$) arrangements and spatially close together ($|r(s) - r(s')| \approx 0$). This factor was found in previous work [6, 25] and in appendix 4 a crude argument is given which suggests that, under the influence of the self-inductance term, the size of the loop collapses to the size of a single monomer $R \sim b$. A more reliable argument to substantiate this claim can be made if the problem is converted into a field theoretic one. This will be reported elsewhere.

The actual configuration of the loops in the melt is determined by the competition between the torsion factor and the self-inductance term. The first factor will extend the configuration into a rigid rod, while the second would collapse it. This problem has not been solved but in the next section we briefly report on a perturbation approach which is indicative of the form that the solution may take.

7. A perturbation calculation

Separately, the effect of the writhe and inductance on the configuration of a single loop are clearly beyond perturbation theory. A perturbation calculation of these effects would appear to have little validity; however, the two effects act on the configuration in an opposite manner and perhaps the combined effect can be treated perturbatively. The computer simulations

[3, 4] and the scaling argument of Cates and Deutsch [2] suggest that the size R of rings in a melt of unlinked rings is almost Gaussian with $R \sim L^{0.4}$ instead of $R \sim L^{0.5}$ for true Gaussian chains. We present here the results of a perturbation calculation without presenting any of the calculational details. (A fuller discussion, including a field theoretic approach, will be presented in a later publication.) The result is interesting and possibly indicative. The effect of the writhe term is to expand the chain as

$$\langle R^2 \rangle_\Phi = sb^2 \left(1 + \sqrt{\frac{s}{\delta}} - \frac{1}{3\pi} \ln \left(\frac{s}{\delta} \right) + \cdots \right) \tag{7.1}$$

where only the leading terms in $s \sim N$ have been included. δ is a short length ($\sim$ bond length) cut-off which must be introduced to regularize the integrals that occur in the perturbation theory. This result demonstrates that a normalization calculation is required similar to that required for a self-avoiding random walk. This is under consideration and will be reported on; however, it is interesting to note that a similar calculation performed for the self-inductance term leads to a contraction of the chain, given by

$$\langle R^2 \rangle_L = sb^2 \left(1 - \sqrt{\frac{s}{b}} \right). \tag{7.2}$$

In this case no cut-off is required but again the separate result shows that perturbation theory is not valid since $s/b \gg 1$. However, if the two results are combined, then the leading terms can be made to cancel each other if the arbitrary cut-off term δ is suitably chosen so that

$$\langle R^2 \rangle = \langle R^2 \rangle_\Phi + \langle R^2 \rangle_L = sb^2 \left(1 - \frac{1}{3\pi} \ln \left(\frac{s}{\delta} \right) \right). \tag{7.3}$$

This could be regarded as the first two terms of an expansion which re-sums as

$$\langle R^2 \rangle \cong sb^2 \left(s^{-1/3\pi} \right) = s^{1-1/3\pi} = s^{0.89}. \tag{7.4}$$

The exponent is pleasingly close to the value 0.9 found in computer simulations.

8. Conclusions

Topological restrictions can be introduced into a melt of polymer loops by specifying the linking number between each pair of loops. This leads to significant differences in the configurational statistics of the loops as compared to a melt of chains with free ends. A method has been developed to incorporate into the partition-sum factors which conserve the topology. For the case of a single chain in a melt of unlinked polymer loops new statistical weighting factors were found which lead to non-trivial statistical mechanical problems. These factors weight the single chain configurations by terms which depend on the geometric properties of the *writhe* and *self-inductance* of the configurations. The separate effect of these terms is extreme, with the writhe promoting a random coil-to-rod transition, while the inductance tends towards a collapsed coil. Evidence was presented in perturbation theory that in the combined effect largely they tend to cancel each other. The result is that the exponent describing the expansion of the configuration with the number of segments is perturbed from the Gaussian result of 0.5 to 0.45.

Acknowledgment

MGB would like to express his appreciation for the financial support and hospitality of the MPI für Polymerforschung Mainz, where part of this work was completed.

Appendix 1. The statistical calculation of $Z(\{C_\alpha\};\{g_{\beta\beta'}\})$

The essential calculation is the evaluation of (3.11) using the distribution function (3.12), i.e.

$$Z(\{C_\alpha\};\{s_{\beta\beta'}\}) = \sqrt{\det(\Gamma^{-1})}\int \mathrm{D}\Psi_\beta \exp -\frac{1}{\Omega}\sum_{q,\beta,\beta'}\{\Psi_\sigma(-q)\cdot[\Gamma^{-1}]_{\beta\beta'}\cdot\Psi_{\beta'}(q)\}$$
$$\times \exp\frac{1}{\Omega}\sum_{\substack{\beta\neq\alpha\\ q}}\left\{\frac{\Psi_\beta(q)\times\Psi_{\beta'}(-q)\cdot q}{q^2}\delta_{\beta\beta'} + 2\eta_{\alpha\beta}\frac{u^\alpha(q)\times\Psi_\beta(-q)\cdot q}{q^2}\right\}. \tag{A1.1}$$

Since we are dealing with closed loops there is the constraint

$$q\cdot\Psi_\beta(q) = 0.$$

This can be included as a term

$$\exp -\frac{1}{\Omega}\sum_q C(q\cdot\Psi_\beta(q))^2 \qquad \text{where } C\to\infty.$$

The problem (A1.1) has the matrix form

$$Z(\{C_\alpha\};\{s\}) = \sqrt{\det\Gamma^{-1}}\int \mathrm{D}\{\Psi\}\exp -\frac{1}{\Omega}\sum_q \Psi(q)M^{-1}(q)\Psi(q) + 2\sum_q \Psi(-q)\cdot J(q) \tag{A1.2}$$

where

$$[M^{-1}(q)]_{ij,\beta\beta'} = [\Gamma^{-1}(q)]_{\beta\beta'}\delta_i^j + \delta_{\beta\beta'}\frac{\varepsilon_{ijk}q^k}{q^2} + Cq_iq_j$$

and

$$J_{\alpha\beta}(q) = \eta_{\alpha\beta}\frac{u^\alpha(q)\times q}{q^2}.$$

The integrals can be performed to give

$$Z(\{C_\alpha\};\{g\}) = \frac{\sqrt{\det\Gamma^{-1}}}{\sqrt{\det M^{-1}}}\exp -\frac{1}{\Omega}\sum_{q,\beta\beta',ij} J_{i,\alpha\beta'}(-q)M_{ij,\beta\beta'}(q)J_{j,\alpha\beta'}(q). \tag{A1.3}$$

To find the matrix M it is convenient to write the inverse as

$$[M^{-1}(q)]_{ij} = \Gamma^{-1}(q)\left[\delta_{ij} + \Gamma(q)Cq_iq_j + \Gamma(q)\frac{\varepsilon_{ijk}q^k}{q^2}\right]. \tag{A1.4}$$

The matrix in the [ ] bracket has the form

$$Q_{\beta\beta'} = \delta_{\beta\beta'}\delta_i^j + \Gamma_{\beta\beta'}(q)Cq_iq_j + \Gamma_{\beta\beta'}\frac{\varepsilon_{ik}^j q^k}{q^2}.$$

In the limit $C \to \infty$ this has an inverse:

$$Q^{-1} = U_{\beta\beta'}(\delta_{ij} - \hat{q}_i\hat{q}_j) + V_{\beta\beta'}\varepsilon_{ijk}q^k \tag{A1.5}$$

where

$$U = q^2[q^2 + \Gamma^2]^{-1}$$

and

$$V = -\Gamma[q^2 + \Gamma^2]^{-1}$$

These are to be regarded as matrix equations, e.g.

$$V_{\beta\beta'} = -\sum_{\beta''=1}^{N_c}\Gamma_{\beta\sigma}[(q^2 + \Gamma^2)^{-1}]_{\sigma\beta'}$$

and the matrix Γ is related to the original integration variables by (3.13).

Written out in full the matrix product $\sum_{ij,\beta\beta'} J_{i,\alpha\beta'}(-q)M^{-1}_{ij,\beta\beta'}(q)J_{j,\alpha\beta'}(q)$ becomes

$$\begin{aligned}\sum_{ij,\beta\beta'} & J_{i,\alpha\beta}(-q)M^{-1}_{ij,\beta\beta'}(q)J_{j,\alpha\beta'}(q) \\ &= \sum_{\beta\beta'}\eta_{\alpha\beta}\{\Gamma[q^2 + \Gamma^2]^{-1}\}_{\beta\beta'}\eta_{\beta'\alpha}\frac{\{\boldsymbol{u}^\alpha(-q)\times -\boldsymbol{q}\}\cdot\{\boldsymbol{u}^\alpha(q)\times \boldsymbol{q}\}}{q^2} \\ &\quad + \sum_{\beta\beta'}\eta_{\alpha\beta}\{\Gamma^2[q^2 + \Gamma^2]^{-1}\}_{\beta\beta'}\eta_{\beta'\alpha}\frac{\{\boldsymbol{u}^\alpha(-q)\times -\boldsymbol{q}\}\times\{\boldsymbol{u}^\alpha(q)\times \boldsymbol{q}\}\cdot \boldsymbol{q}}{q^4}\end{aligned} \tag{A1.6}$$

where we have used the loop constraint

$$\boldsymbol{q}\cdot\boldsymbol{u}(q) = 0$$

and the use of some vector identities, together with

$$\Gamma_{\beta\beta'} = \frac{1}{N_c}\gamma(q)\sum_\sigma \eta_{\beta\sigma}\eta_{\sigma\beta'}.$$

These manipulations enable the JMJ term to be written as

$$\begin{aligned}\sum_{ij,\beta\beta'} J(-q)M^{-1}(q)J(q) = -\frac{N_c}{\gamma(q)}\Bigg[\Gamma^2[q^2 + \Gamma^2]^{-1}\Bigg\{\boldsymbol{u}^\alpha(-q)\cdot\boldsymbol{u}^\alpha(q) \\ + \Gamma\frac{(\boldsymbol{u}^\alpha(-q)\times\boldsymbol{u}^\alpha(q)\cdot\boldsymbol{q})}{q^2}\Bigg\}\Bigg]_{\alpha\alpha}\end{aligned}$$

which is essentially the form quoted in the paper.

It remains to show that the determinant factors in (A1.3) cancel each other. From (A1.4)

$$\det(M^{-1}) = \det(\Gamma^{-1})\det\left(\left[\delta_{ij} + \Gamma Cq_iq_j + \Gamma\frac{\varepsilon_{ijk}q^k}{q^2}\right]\right).$$

However, since $\Gamma \approx N_c^{-1}$, then $\det(M^{-1}) \approx \det(\Gamma^{-1})$ and the two determinant factors cancel each other.

Appendix 2. The Fourier transform $Z(\{C_\alpha\};\{s\}) \rightarrow Z(\{C_\alpha\};\{m\})$

The transform to be evaluated is

$$Z(\{C_\alpha\}) = \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^\pi \mathrm{d}a \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'} Z(\{C_\alpha\}; s_{\beta\beta'}) \tag{A2.1}$$

where $Z(\{C_\alpha\};\{s_{\beta\beta'}\})$ is given by (3.15) and can be written in the form

$$Z(\{C_\alpha\}; s_{\beta\beta'}) = \exp \Xi(\{C_\alpha\}; s_{\beta\beta'}) \tag{A2.2}$$

with

$$\Xi(\{C_\alpha\}; s_{\beta\beta'}) = -\frac{1}{\Omega} \sum_q [A_{\alpha\alpha}(q;\{s_{\beta\beta'}\}) l_{\alpha\alpha}(q) + B_{\alpha\alpha}(q;\{s_{\beta\beta'}\}) \phi_{\alpha\alpha}(q)].$$

The exponential factor in (A2.2) is expanded and the integrals are done term by term so that

$$Z(\{C_\alpha\}) \cong \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^\pi \mathrm{d}a \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'} [1 + \Xi(\{C_\alpha\}; s_{\beta\beta'}) + \cdots]. \tag{A2.3}$$

For the moment we concentrate on the linear terms in Ξ in this expansion, then

$$Z(\{C_\alpha\}) = 1 - \frac{1}{\Omega} \sum_q [A_{\alpha\alpha}(q^2) l_{\alpha\alpha}(q) + B_{\alpha\alpha}(q^2) \phi_{\alpha\alpha}(q) + \cdots] \tag{A2.4}$$

where

$$A_{\alpha\alpha}(q^2) = \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^\pi \mathrm{d}a \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'} A_{\alpha\alpha}(q;\{s_{\beta\beta'}\})$$

and

$$B_{\alpha\alpha}(q^2) = \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^\pi \mathrm{d}a \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'} B_{\alpha\alpha}(q;\{s_{\beta\beta'}\}).$$

We first consider the integral $B_{\alpha\alpha}(q^2)$, then

$$\begin{aligned} B_{\alpha\alpha}(q^2) &= \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^\pi \mathrm{d}a \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'} B_{\alpha\alpha}(q;\{s_{\beta\beta'}\}) \\ &= \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^\pi \mathrm{d}a \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} \mathrm{d}s_{\beta\beta'} \frac{N_c}{\gamma(q)} \left[\frac{\Gamma^3}{q^2} \left[1 + \frac{\Gamma^2}{q^2} \right]^{-1} \right]_{\alpha\alpha}. \end{aligned} \tag{A2.5}$$

The matrix term is expanded

$$\frac{\Gamma^3}{q^2} \left[1 + \frac{\Gamma^2}{q^2} \right]^{-1} = \frac{1}{q^2} \Gamma^3 \left[1 - \frac{\Gamma^2}{q^2} + \frac{\Gamma^4}{q^4} - \cdots \right]. \tag{A2.6}$$

Recall that $\Gamma_{\beta\beta'} = (\gamma(q)/N_c)s_{\beta\beta'}$ and so, for example, the first term in (A2.5) involves the multiple integrals

$$\prod_{\beta\beta'=1}^{N_c} \frac{1}{\pi^2} \int_0^{\pi} da_{\beta\beta'} \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} ds_{\beta\beta'} \cdots \left[\frac{1}{N_c^2} \prod_{\beta\beta'=1}^{N_c} s_{\alpha\beta} s_{\beta\beta'} s_{\beta'\alpha} \right]. \tag{A2.7}$$

The presence of the macroscopically large term N_c (the number of chains in the system) is now vital since it ensures that the most dominant term occurs when all the variables are different, $\beta \neq \beta'$. The integrals factorize into

$$\frac{1}{N_c^2} \sum_{\beta\beta'} \left[\frac{1}{\pi^2} \int_0^{\pi} da_{\beta\beta'} \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} ds_{\beta\beta'} s_{\beta\beta'} \right]^3 = \frac{1}{N_c^2} \sum_{\beta\beta'} \pi^3 = \pi^3. \tag{A2.8}$$

This result generalizes to any power. Hence

$$\begin{aligned} B_{\alpha\alpha}(q^2) &= \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^{\pi} da_{\beta\beta'} \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} ds_{\beta\beta'} B_{\alpha\alpha}(q; \{s_{\beta\beta'}\}) \\ &= \frac{1}{q^2} \gamma^2 \pi^3 \left[1 - \frac{\pi^2}{q^2} \gamma^2 + \frac{\pi^4}{q^4} \gamma^2 - \cdots \right] \\ &= \frac{\gamma^2 \pi^3}{q^2 + \pi^2 \gamma^2}. \end{aligned} \tag{A2.9}$$

$\gamma = \gamma(q)$ is the bond-vector correlation function given by

$$\gamma(q) = \rho \oint \langle d\boldsymbol{r} \cdot d\boldsymbol{r}' \exp i\boldsymbol{q} \cdot (\boldsymbol{r} - \boldsymbol{r}') \rangle_0$$

where ρ is the number density of monomer units.

This has been evaluated in [26] and a good approximation can be represented by the form

$$\gamma(q) = \rho b^2 \frac{q^2 N b^2}{q^2 N b^2 + \kappa} \tag{A2.10}$$

where κ is a numerical constant ≈ 6. Hence for $q^2 < (Nb^2)^{-1}$, that is for scales of the order of the size of a polymer chain, $\gamma(q)$ can be approximated by a constant

$$\gamma(q) = \rho b^2 \approx \frac{1}{b}$$

since for a melt $\rho b^3 \approx 1$. Then for the range of q values of interest

$$\frac{\gamma^2 \pi^3}{q^2 + \pi^2 \gamma^2} \approx \pi \qquad \text{and} \qquad B_{\alpha\alpha}(q^2) = \pi. \tag{A2.11}$$

It is noteworthy that in this limit the result is exactly π and is independent of γ and hence of the density of the melt. The coefficient $A_{\alpha\alpha}(q^2)$ of the self-inductance term can be treated similarly

$$\begin{aligned} A_{\alpha\alpha}(q^2) &= \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^{\pi} da \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} ds_{\beta\beta'} A_{\alpha\alpha}(q; \{s_{\beta\beta'}\}) \\ &= \prod_{\beta\beta'} \frac{1}{\pi^2} \int_0^{\pi} da \int_{a_{\beta\beta'}}^{2\pi - a_{\beta\beta'}} ds_{\beta\beta'} \frac{N_c}{\gamma(q)} \left[\Gamma^2 \left[1 + \frac{\Gamma^2}{q^2} \right]^{-1} \right]_{\alpha\alpha}. \end{aligned}$$

The matrix term can be expanded and integrated term by term to give

$$A_{\alpha\alpha}(q^2) = \left[\gamma\frac{7\pi^2}{6} - \gamma^3\frac{\pi^4}{q^2} + \gamma^5\frac{\pi^6}{q^4}\cdots\right] = \gamma\frac{7\pi^2}{6} - \frac{\gamma^3\pi^4}{q^2+\gamma^2\pi^2} = \frac{\gamma\pi^2}{6} = \frac{\rho b^2\pi^2}{6} \tag{A2.12}$$

in the physically significant q range of $qb < 1$.

The factorization and resummation can be extended to the higher order terms in the expansion of (A2.3). The final result is equivalent to replacing the matrix factors

$$\begin{aligned} &A_{\alpha\alpha}(q;\{s_{\beta\beta'}\}) \to \pi \\ &B_{\alpha\alpha}(q;\{s_{\beta\beta'}\}) \to \rho b^2\pi^2/6 \end{aligned} \tag{A2.13}$$

in (A2.2) for $Z(\{C_\alpha\}; s_{\beta\beta'})$ to get $Z(\{C_\alpha\})$.

Appendix 3.

The evaluation of

$$Z(\boldsymbol{R}, s) = \left\langle \delta\left(\int_0^s \mathrm{d}s'\, \boldsymbol{e}(s') - \boldsymbol{R}\right)\delta\left(\int_0^L \mathrm{d}s'\, \boldsymbol{e}(s')\right)\exp\left(\frac{-\mathrm{i}}{2}\int_0^L \mathrm{d}s'\,\frac{\boldsymbol{e}\cdot\dot{\boldsymbol{e}}\times\ddot{\boldsymbol{e}}}{|\dot{\boldsymbol{e}}|^2}\right)\right\rangle. \tag{A3.1}$$

The average $\langle\ldots\rangle$ over random walk configurations constructed from unit tangent vectors is achieved by allowing each tangent vector $\boldsymbol{e}(s)$ to randomly point anywhere in space.

In order to make use of a relevant literature result [27], the torsion term must be expressed as the area A enclosed by the curve swept out by the unit tangent vectors to the original curve C. A simple geometry exercise gives

$$A = 2\pi(\text{integer}) - \oint_C \mathrm{d}s\,\tau(s). \tag{A3.2}$$

Hence the weighting factor due to the writhe of the curve becomes

$$\exp \mathrm{i}\pi\Phi = \exp\frac{\mathrm{i}}{2}\oint_C \mathrm{d}s\,\tau(s) = \exp\frac{\mathrm{i}A(\{e\})}{2}.$$

Again the integer factors do not contribute except for a further sign ambiguity that has been ignored.

The delta functions in (A3.1) can be parametrized in the usual way, so that

$$Z(\boldsymbol{R}, s) = \int \mathrm{d}^3k\,\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R})\int \mathrm{d}^3q\, Z(\boldsymbol{k}, q; \boldsymbol{R}, s) \tag{A3.3}$$

where

$$Z(\boldsymbol{k}, q; \boldsymbol{R}, s) = \int D\boldsymbol{e}\,\delta(e^2-1)\exp -\tfrac{1}{2}\int_0^L \mathrm{d}s'\,\boldsymbol{e}(s')\cdot\boldsymbol{B}(s', s) + \mathrm{i}A(\{e\}) \tag{A3.4}$$

and

$$\boldsymbol{B}(s', s) = \begin{cases} -2\mathrm{i}\{\boldsymbol{k}+q\} & s' < s \\ -2\mathrm{i}q & \text{otherwise.} \end{cases}$$

The meaning of equation (A3.4) is transformed by using the identity [27]

$$\int \mathrm{D}e\,\delta(e^2-1)\exp im\int_0^L \mathrm{d}s'\,e(s')\cdot B(s',s)\exp(-imA(\{e\})) = \mathrm{Tr}\left[\exp\int \mathrm{d}s'\,B(s',s)\cdot J\right] \tag{A3.5}$$

where J is the rotation operator and the trace operation is performed in the (j,m) representation.

In this problem m is identified as $m = 1/2$ (this can be traced back to the fact that the coefficient in front of the writhe term in the weighting factor was π). Therefore J can be identified with the spinor representation of the rotation group and J represented by the Pauli spin matrices $J = \sigma/2$. Hence

$$Z(k, q; R, s) = \mathrm{Tr}[\exp \mathrm{i}(ks + qL)\cdot\sigma]$$

and

$$Z(R, s) = \mathrm{Tr}\int \mathrm{d}^3k \exp(-\mathrm{i}k\cdot R)\int \mathrm{d}^3q\ \exp \mathrm{i}\sigma\cdot(Lq + sk). \tag{A3.6}$$

Using the properties of the Pauli spin matrices

$$(k\cdot\sigma)^{2n} = k^{2n} \qquad (k\cdot\sigma)^{2n+1} = (k\cdot\sigma)k^{2n} \qquad \text{and} \qquad \mathrm{Tr}\,\sigma = 0$$

equation (A3.6) becomes

$$Z(R, s) = 2\int \mathrm{d}^3k \exp(-\mathrm{i}k\cdot R)\int \mathrm{d}^3q\ \cos(|Lq + sk|). \tag{A3.7}$$

The factor 2 comes from $\mathrm{Tr}\,1 = 2$ for the $m = 1/2$ representation. For large L, the integral can be evaluated as

$$Z(R, s) = \frac{32\pi^2 f(L)}{Rs}\delta(R = s) \tag{A3.8}$$

where

$$f(L) = \int_{\cong\frac{1}{L}}^{\infty} q^2\,\mathrm{d}q\cos(Lq).$$

The exact value is not important because it can be accounted for by correctly normalizing the final propagator.

Appendix 4. Configurational collapse

The partition sum for the polymer loop in the presence of the self-inductance term can be written as the path integral

$$Z = \int \mathrm{D}r(s)\exp\left[-\frac{2}{3b}\int \mathrm{d}s\,\dot{r}^2(s) - \frac{1}{l}\oint\!\!\oint \mathrm{d}s\,\mathrm{d}s'\,\frac{\dot{r}(s)\cdot\dot{r}(s')}{|r(s) - r(s')|}\right] \tag{A4.1}$$

where the first term is the Wiener measure describing the random walk statistics of the unperturbed chain and the second term is the self-inductance.

A rough argument to show how the inductance term can lead to a configurational collapse of the free chain can be produced by replacing

$$\frac{1}{|r(s)-r(s')|} \rightarrow \left\langle \frac{1}{|r(s)-r(s')|} \right\rangle \rightarrow K\delta(s-s'). \tag{A4.2}$$

Then the partition function (A4.1) becomes

$$Z\{r^{\alpha}\} \propto \exp\left[-\frac{2}{3b}\left(1+\frac{3Kb}{2l}\right)\int \mathrm{d}s\, \dot{r}^2(s)\right] \tag{A4.3}$$

which describes a new random walk configuration with an effective step length b^* given by

$$b^* = b \Big/ \left(1+\frac{7\pi\rho b^3 K}{24}\right) \tag{A4.4}$$

and where the distance between two points on the walk is given by the usual result

$$\left\langle (r(s)-r(s'))^2 \right\rangle = b^*|s-s'|. \tag{A4.5}$$

A crude self-consistent estimate for K can be made by taking the original ansatz (A4.2) and integrating both sides, so that

$$\int_0^L \int_0^L \mathrm{d}s\, \mathrm{d}s' \left\langle \frac{1}{|r(s)-r(s')|} \right\rangle = KL. \tag{A4.6}$$

The expression (A4.5) for $|r(s)-r(s')|$ is used in (A4.6) to determine K self-consistently, i.e.

$$\int_0^L \int_0^L \mathrm{d}s\, \mathrm{d}s' \frac{1}{(b^*|s-s'|)^{1/2}} = KL.$$

Using (A4.4) for b^* gives

$$\left(\frac{1}{b}+\frac{3K}{2l}\right)^{1/2} \kappa L^{3/2} = KL$$

where κ is a numerical constant. Hence

$$K \approx \frac{L}{l} \qquad \text{and} \qquad b^* \approx \frac{b}{K} \approx \frac{bl}{L}. \tag{A4.7}$$

The size of the chain is given by

$$R^2 = b^*L \approx bl \approx b^2 \tag{A4.8}$$

i.e. completely collapsed.

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