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The configurational properties of topologically entangled molecules

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Abstract. The statistical mechanical problem of two polymer molecules subject to a linking number constraint is solved in the so-called ‘pre-averaged approximation’, whereby a function of the coordinates of one of the molecules is replaced by its averaged value. For this molecule a critical winding number $m_c(L, s)$ can be identified, depending on the total length L of the molecules and the arc length scale s over which the configurational properties are being investigated. We find that $m_c \sim N^{3/4}(L/s)^{1/4}$ and that for winding numbers $m < m_c(L, L)$ the original entropy of the chain still dominates and the configuration remains approximately Gaussian. For $m > m_c(L, L)$, the constraint dominates and we present evidence to suggest that a partially collapsed solenoidal-like state is adopted, but one which is nevertheless still a Gaussian random coil on a smaller arc length scale $s < s^*$, with $s^* = L(m_c/m)^4$.

1. Introduction

The unusual properties of polymer molecules are a direct result of their chain-like molecular structure which provides the molecules with a vast reserve of conformational entropy. This chain structure can also give rise to another unique feature, that of topologically entangled molecules (figures 1(a), (b)). Clearly the centre of mass of each molecule is restricted as are the configurational degrees of freedom. The two molecules depicted in figure 1(a) cannot adopt the configuration of those in figure 1(b) without breaking their chemical bonds. This restriction in the entropic content of each molecule will modify the physical properties of the molecules, particularly in the concentrated polymeric state where many topological entanglements can be formed. The term ‘entanglement’ has been used by many authors to describe the rather general restrictions on configurational changes that occur in long chain molecules in a concentrated or molten state. For a comprehensive review see Graessley (1974). In this work we deal with the precise notion of a topological entanglement which describes a certain topological relation existing between the molecules, which is necessarily conserved throughout all the configurational changes that the molecule can undergo. Figure 1 illustrates the difference between these two concepts. In figure 1(c) the molecules, having free ends, can eventually be separated whereas in figures 1(a), (b) they cannot.

If the molecules are sufficiently long for the ends not to matter, or the time period of the experiment short enough so that disentanglement does not take place, then the

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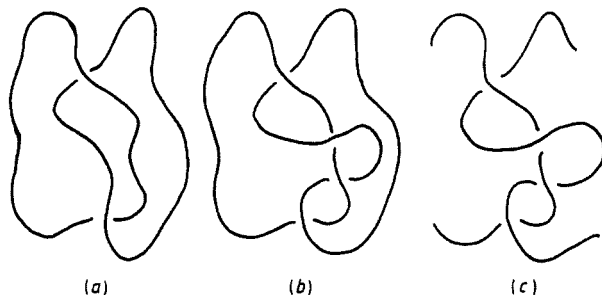


Figure 1. Topologically entangled molecules with winding numbers (a) one and (b) two. (c) These molecules are not topologically entangled and winding numbers are not defined.

situations depicted in figure 1 may all be described as 'entangled'. Physically this situation is observed in dynamic mechanical measurements on polymer melts of linear polymers of different molecular weights, i.e. chain lengths (see e.g. Graessley 1974).

In this paper we shall consider the simplest non-trivial problem of topologically entangled molecules, that of two closed loops. The statistical mechanics of this problem has been formulated in a previous paper (Brereton and Shah 1980) where an isomorphism with a local gauge-invariant field theory was exhibited. It also contains references to the contributions of other authors on this subject. In this paper we shall present an approximate solution to the statistical mechanical problem without using the field theory formalism. A preliminary account of this work has already been given in Brereton and Shah (1981).

2. The statistical weighting due to the topological constraint

The criterion for deciding whether the two molecules, described by the space curves $r_\alpha(s)$ and $r_\beta(t)$, are linked or not is partially provided by the Gauss integral (e.g. Alexandroff and Hopf 1935, Edwards 1967).

$$I_{\alpha\beta}\{C_\alpha, C_\beta\} = \frac{1}{4\pi} \oint_{C_\alpha} ds \oint_{C_\beta} dt \dot{r}_\alpha(s) \cdot \dot{r}_\beta(t) \times \nabla \frac{1}{|r_\alpha - r_\beta|} \quad (2.1)$$

where $\dot{r}(s) = dr(s)/ds$ and s, t are arc length parameters. $I_{\alpha\beta}$ takes integer values m depending on the linking of the two curves. The linking number is only a first-order topological invariant and does not always distinguish between different topological configurations. Figure 2 gives a well known example of the failure of $I_{\alpha\beta}$ as an invariant. Higher-order link invariants, such as the Alexander polynomials, can distinguish between the configurations of figures 2(a) and 2(b) (e.g. Vologodskii *et al* 1974). However, such invariants are algorithmic in nature and not suitable for the analytic approach adopted in the paper.

The physical problem we are going to consider consists of evaluating the statistical average of some configurational property $A\{C_\alpha\}$ of, say, the C_α molecule averaged over all the configurations of the C_α and C_β molecules subject to the constraint that the linking number between the two molecules is m , i.e.

$$\langle A \rangle = \frac{\langle \delta(I_{\alpha\beta} - m) A\{C_\alpha\} \rangle_{\{C_\alpha\}\{C_\beta\}}}{\langle \delta(I_{\alpha\beta} - m) \rangle_{\{C_\alpha\}\{C_\beta\}}} \quad (2.2)$$

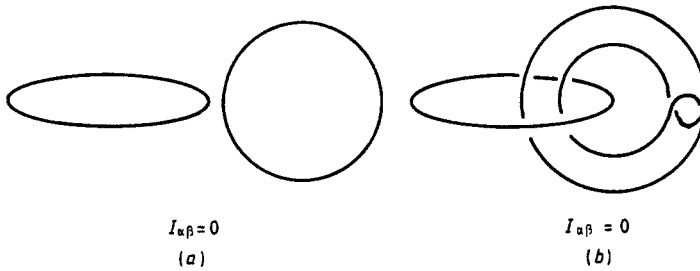


Figure 2. (a) The trivial link. (b) The whitehead link.

By focusing attention on the configurational properties of only one of the molecules C_α , we can attempt to perform the configurational average over the other molecule to obtain the effective weighting factor $E\{C_\alpha\}$

$$E\{C_\alpha\} = \langle \delta(I_{\alpha\beta}\{C_\alpha, C_\beta\} - m) \rangle_{\{C_\beta\}} \tag{2.3}$$

The method was considered in detail in Brereton and Shah (1980). Essentially the constraint $I_{\alpha\beta} = m$ is parametrised by

$$\delta(I_{\alpha\beta} - m) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dg \exp ig(m - I_{\alpha\beta}) \tag{2.4}$$

and the following approximation is used

$$\langle \exp -igI_{\alpha\beta} \rangle_{\{C_\beta\}} \approx \exp -\frac{1}{2}g^2 \langle I_{\alpha\beta}^2 \rangle_{\{C_\beta\}} \tag{2.5}$$

whereby $I_{\alpha\beta}$ is treated as a Gaussian random variable.

The quantity $\langle I_{\alpha\beta}^2 \rangle_{\{C_\beta\}}$ is then evaluated on the basis that the statistical properties of bond vectors $\mathbf{b}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$ comprising the configuration of C_β are described by a Gaussian distribution function, i.e.

$$P\{\mathbf{b}_1, \dots, \mathbf{b}_N\} \prod_i d\mathbf{b}_i \propto \exp -\frac{3}{2l^2} \sum_i \mathbf{b}_i^2 \prod_i d\mathbf{b}_i \tag{2.6}$$

with $\langle \mathbf{b}_i^2 \rangle = l^2$.

In the continuum limit this distribution goes over to the Wiener measure

$$P\{\mathbf{r}(s)\} \mathcal{D}\{\mathbf{r}(s)\} \propto \exp -\frac{3}{2l} \int_0^{L_\beta} \dot{\mathbf{r}}^2(s) ds \mathcal{D}\{\mathbf{r}(s)\} \tag{2.7}$$

In our previous paper we showed that in the limit of $L_\beta \rightarrow \infty$

$$\begin{aligned} \langle I_{\alpha\beta}^2 \rangle_{\{C_\beta\}} &= W\{C_\alpha\} \\ &= \frac{\rho l^2}{24\pi} \oint_{C_\alpha} ds ds' \dot{\mathbf{r}}(s) \cdot \mathbf{T}\{\mathbf{r}(s) - \mathbf{r}(s')\} \cdot \dot{\mathbf{r}}(s') \end{aligned} \tag{2.8}$$

where the tensor $\mathbf{T}(\mathbf{R})$ is given by

$$\mathbf{T}(\mathbf{R}) = \frac{1}{|\mathbf{R}|} (\mathbf{1} + \mathbf{R}\mathbf{R}/|\mathbf{R}|^2) \tag{2.9}$$

and ρ is the number density of the β monomers.

Hence we can write

$$\begin{aligned} E\{C_\alpha\} &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dg \exp(igm - \frac{1}{2}g^2 W\{C_\alpha\}) \\ &= (2\pi W\{C_\alpha\})^{-1/2} \exp -\frac{1}{2}m^2/W\{C_\alpha\}. \end{aligned} \quad (2.10)$$

Thus the effect on the configuration C_α of a topological entanglement with the chain C_β resulting in a linking number m , is expressed by assigning the weight factor $E\{C_\alpha\}$ to each configuration C_α . This gives a maximum weight to those configurations $\{C_\alpha^*\}$ for which $W\{C_\alpha^*\} = m^2$. Part of the expression for $W\{C_\alpha\}$ is familiar from electromagnetism. If only the unit tensor part of \mathbf{T} , equation (2.9), is used then

$$W\{C_\alpha\} = \frac{\rho l^2}{24\pi} \oint_{c_\alpha} ds ds' \frac{\dot{r}(s) \cdot \dot{r}(s')}{|r(s) - r(s')|} \quad (2.11)$$

the integral part of which is essentially the inductance of a loop. This integral is divergent when $r(s) = r(s')$, and in the electrical case the thickness of the wire is introduced to give a finite answer for the inductance. We may therefore anticipate the appearance of an extra parameter in our model in the form of a cut-off, corresponding in some sense to the thickness of the polymer. We shall relate it directly to the average entanglement number of the molecule. For solenoidal configurations, the inductance depends on the (number of turns)². The weight factor (2.10) can clearly be optimised with a solenoidal configuration by adapting the linking number m to the number of turns of the solenoid. However, for polymer molecules this weight factor due to the topological constraint must be offset against the natural tendency of the molecule to adopt an essentially random walk configuration. It is competition between the demands of the linking number constraint and finding the most entropic configuration that constitutes the essence of the statistical mechanical problem. In the previous paper we transformed this into a local gauge invariant field theory. However in the next section of this paper we present an alternative approach based on an approximation familiar in the dynamics of polymer molecules in dilute solution: the so-called pre-averaged approximation.

3. The generating function in the pre-averaged approximation

In the previous section we established that, for two molecules mutually entangled with a linking number m , the average of some configurational property $A\{C_\alpha\}$ is given by

$$\langle A \rangle = \frac{\langle (2\pi W\{C_\alpha\})^{-1/2} \exp(-\frac{1}{2}m^2/W\{C_\alpha\}) A\{C_\alpha\} \rangle_{\{c_\alpha\}}}{\langle (2\pi W)^{-1/2} \exp(-\frac{1}{2}m^2/W) \rangle_{\{c_\alpha\}}} \quad (3.1)$$

with $W\{C_\alpha\}$ given by (2.8). If we choose

$$A\{C_\alpha\} = \exp i\lambda \cdot \{r^\alpha(s_1) - r^\alpha(s_2)\} \quad (3.2)$$

where s_1 and s_2 are any two points on the C_α molecule, then all the configurational properties of interest can be generated from

$$J(\lambda, s_1, s_2, m) = \langle (2\pi W)^{-1/2} \exp -\frac{1}{2}m^2/W + \lambda \cdot \{r(s_1) - r(s_2)\} \rangle. \quad (3.3)$$

The possible configurations of the C_α molecule are generated, as before, by using a Gaussian distribution of step lengths (2.6). It is convenient to reparametrise the

weighting factor in equation (3.3) by (2.10) so that the generating function can be written as

$$\begin{aligned}
 J(\lambda, s_1, s_2, m) &= \int \frac{dg}{2\pi} \exp igm \int_{\text{loops}} \mathcal{D}\{r\} \exp\left(-\frac{3}{2l} \int_0^L \dot{r}^2(s) ds \right. \\
 &\quad \left. - \frac{g^2}{2} \frac{\rho l^2}{24\pi} \int_0^L ds \int_0^L ds' \dot{r}(s) \cdot \mathbf{T}(r-r') \cdot \dot{r}(s') + i\lambda \cdot \int_0^L ds \dot{r}(s) \theta_{12}(s)\right) \quad (3.4)
 \end{aligned}$$

where

$$\theta_{12}(s) \begin{cases} = 1 & s_1 < s < s_2 \\ \neq 0 & \text{otherwise.} \end{cases}$$

The analytic problems posed by (3.4) are still intractable without further approximation. The tensor $\mathbf{T}\{r(s) - r(s')\}$ also occurs in a different context in the hydrodynamics of polymer molecules and is known as the Oseen tensor (see Yamakawa 1971). In these problems considerable analytic progress can be made by means of the pre-averaging approximation whereby we replace

$$\begin{aligned}
 \mathbf{T}\{r(s) - r(s')\} &\rightarrow \langle T\{r(s) - r(s')\} \rangle \\
 &= \left\langle \frac{\mathbf{1}}{|r-r'|} + \frac{(r-r')(r-r')}{|r-r'|^3} \right\rangle \\
 &= T(s-s')\mathbf{1}. \quad (3.5)
 \end{aligned}$$

For an unperturbed Gaussian distribution, the function $T(s-s')$ has been calculated in appendix 1, and we obtain

$$T(s) = \frac{8}{3}(2\pi)^{-1/2} [3/sl(1-s/L)]^{1/2}. \quad (3.6)$$

Ideally the average occurring in these expressions should be self-consistently calculated. We shall discuss this point later; for the moment the principal feature of this approximation is that the part of (3.4) which involves the integration over all the configurations of the molecule can be written as

$$\int_{\text{loops}} \mathcal{D}\{r\} \exp -\frac{3}{2l} \int_0^L \int_0^L ds ds' \dot{r}(s) \cdot \dot{r}(s') h(s-s') + i\lambda \cdot \int_0^L \dot{r}(s) \theta_{12}(s) ds \quad (3.7)$$

where

$$h(t) = \delta(t) + \frac{1}{3}g^2 \rho l^3 T(t)/24\pi. \quad (3.8)$$

The exponent in (3.7) can be diagonalised by a normal mode transformation after which the resulting Gaussian integral can be done. However the amount of algebra has also increased, and so various simplifying mathematical approximations have to be made. We have presented the details of this calculation in appendix 2. Using the results of appendix 2 we can write the generating function (3.3) as

$$J(\lambda, s_{12}, m) = \int \frac{dg}{2\pi} \exp\left(igm - \frac{\beta g^2}{2} - \frac{\lambda^2 l s_{12}}{6} \frac{\gamma^2(s_{12})}{\gamma^2(s_{12}) + g^2}\right) \quad (3.9)$$

where

$$\beta = bN\rho l^3 \sqrt{l/d} \quad \gamma^2(s) = \frac{1}{\rho l^3} \frac{1}{\sqrt{N}} \sqrt{L/s}$$

and a and b are numerical constants

(3.10)

$$a = \frac{27}{2\pi} (2\pi)^{3/2} \quad b = \left(\frac{1}{2\pi}\right)^{3/2} \frac{4}{9}$$

with $N = L/l$, and s_{12} being the arc length, appropriate for a loop, between the points s_1 and s_2

$$s_{12} = (s_1 - s_2)[1 - (s_1 - s_2)/L]. \quad (3.11)$$

The parameter d represents the small distance cut-off necessitated by the fact that we have used a mathematical curve of infinitesimal thickness to represent our model of the polymer molecule. In § 2 we have already commented on the analogy of this calculation with the calculation of the inductance of a loop and how the latter depends on the thickness of the wire. The appearance of the cut-off parameter d is thus expected, and will depend on the local structure of the molecule rather than on any global property such as the molecular weight.

It is interesting to compare the form of the generating function (3.9) with that obtained by a much more direct method—albeit as a result of a gross approximation of the pre-averaged form of the tensor \mathbf{T}

$$\langle \mathbf{T}\{r(s) - r(s')\} \rangle \simeq c \delta(s - s') \mathbf{1} \quad (3.12)$$

where c is a constant to be identified later. Then, the functional integral (3.7) can be written as

$$\int_{\text{loops}} \{r\} \exp\left(-\frac{3}{2} \frac{(1 + g^2 \rho l^3 c)}{l} \int_0^L ds \dot{r}^2(s) + i\lambda \cdot \int_0^L \dot{r}(s) \theta_{12}(s) ds\right) \quad (3.13)$$

where all numerical constants have been incorporated into c . This functional integral is Gaussian with an effective step length of $l/(1 + g^2 \rho l^3 c)$. The path integral can be evaluated to give

$$(1 + g^2 \rho l^3 c)^{-3N/2} \exp\left(-\frac{\lambda^2 l s_{12}}{6} \frac{1}{1 + g^2 \rho l^3 c}\right). \quad (3.14)$$

If we further approximate

$$(1 + g^2 \rho l^3 c)^{-3N/2} \simeq \exp(-\frac{3}{2} N \rho l^3 c) \quad (3.15)$$

then the generating function (3.4) can be written as

$$J(\lambda, s_{12}, m) = \int \frac{dg}{2\pi} \exp\left(igm - \frac{3}{2} N \rho l^3 c g^2 - \frac{\lambda^2 l s_{12}}{6(1 + g^2 \rho l^3 c)}\right). \quad (3.16)$$

This result is similar to (3.9), obtained by detailed calculations in appendix 2. The major difference is that the constant c occurring in the third term of the exponential in (3.16) is replaced by

$$\rho l^3 c \rightarrow [\gamma^2(s_{12})]^{-1} = \pi K \sqrt{N} \sqrt{s_{12}/L} \quad (3.17)$$

with

$$K = (1/2\pi)^{3/2} \frac{2}{27} \rho l^3$$

and the constant c occurring in the second term of the exponential being replaced by

$$c \rightarrow \frac{4}{27}(1/2\pi)^{3/2}\sqrt{l/d}. \tag{3.18}$$

In the next section we shall use the generating function (3.9) to derive and discuss the various configurational properties of the molecule. We shall also obtain a macroscopic representation of the small distance cut-off parameter d .

4. Configurational properties of entangled molecules

4.1. Entanglement probability distribution function

The probability $p(m)$ of finding two polymer molecules mutually entangled with a winding number m is given by

$$p(m) = \langle \delta[I_{\alpha\beta}\{c_\alpha, c_\beta\} - m] \rangle_{(c_\alpha), (c_\beta)} \tag{4.1}$$

and in terms of the generating function (3.3)

$$p(m) = J(\lambda, s_1, s_2, m)|_{\lambda=0}. \tag{4.2}$$

Using equation (3.16) for J we have that

$$\begin{aligned} p(m) &= \int \frac{dg}{2\pi} \exp(-\frac{1}{2}g^2\beta + igm) \\ &= (2\pi\beta)^{-1/2} \exp - m^2/2\beta. \end{aligned} \tag{4.3}$$

Consequently we can immediately identify β as the average (winding number)²

$$\langle m^2 \rangle = \beta = b\rho l^3 N \sqrt{l/d} \tag{4.4}$$

(recall that ρ is the number density of the background molecule and $b = (3/2\pi)^{3/2} \frac{4}{27}$). This result enables us to replace the small distance cut-off parameter d , which represents the ‘thickness’ of the molecule, by a macroscopic physical property of the molecule. It is similar to the relationship between the end-to-end distance $\langle R^2 \rangle$ and the step length parameter l

$$\langle R^2 \rangle = lL. \tag{4.5}$$

This enables the microscopic parameter l to be related to the macroscopic size of the molecule. We also have from (4.4) that $\langle m^2 \rangle \sim N$.

4.2. The size of an entangled molecule

Next we investigate the spatial distance $R(s, m)$ between two points an arc length s apart on the molecule entangled with a winding number m . In terms of the generating function this is given by

$$R^2(s, m) = - \frac{\nabla_\lambda^2 J(\lambda, s, m)}{J(\lambda, s, m)} \Big|_{\lambda=0}. \tag{4.6}$$

Using (3.16) for $J(\lambda, s, m)$ we obtain

$$R^2(s, m) = R_0^2(s) \frac{\int dg \exp(-\frac{1}{2}\beta g^2 + igm) \gamma^2(s) / (\gamma^2(s) + g^2)}{\int dg \exp(-\frac{1}{2}\beta g^2 + igm)} \tag{4.7}$$

where $R_0^2(s) = sl(1 - s/L)$ and is the result for an unconstrained Gaussian loop of length L . The integrals in (4.7) can be evaluated exactly in terms of the error functions and the relevant features of $R(s)$ can be obtained from the properties of these functions.

This calculation is presented in appendix 3; however the qualitative features of this result can be immediately obtained by approximating the term

$$\gamma^2(s)/(\gamma^2(s) + g^2) \approx \exp - g^2/\gamma^2(s). \quad (4.8)$$

Then the integrals are readily evaluated to give

$$R^2(s) = R_0^2(s) \exp[m^2/\beta(\beta\gamma^2 + 2)]. \quad (4.9)$$

Using (3.10) for the definition of β and γ^2 we have that $\beta\gamma^2(s) \gg 1$ for all s , so that we can write

$$R^2(s) = R_0^2(s) \exp(m^2/m_c^2(L, s)) \quad (4.9')$$

where $m_c(L, s)$ is an important grouping of the parameters of the problem, given by

$$m_c(L, s) = \gamma(s)\beta \quad (4.10)$$

$$= \{b^2 a\}^{1/2} \{\rho l^3\}^{1/2} \sqrt{l/d} (L/l)^{3/4} (L/s)^{1/4}. \quad (4.11)$$

The most important features of $m_c(L, s)$ are summarised by

$$m_c(L, s) \sim N^{3/4} (L/s)^{1/4}. \quad (4.12)$$

In particular it increases as the scale s , over which the size of the molecule is being measured, is decreased. Recall $\langle m^2 \rangle \sim N$ and so $m_c^2 \sim N^{3/2}$ for $s \sim L$, i.e.

$$m_c^2 \gg \langle m^2 \rangle. \quad (4.13)$$

For $m \ll m_c(L, s)$ the molecule is expanded over the Gaussian result $R_0^2(s)$ by

$$R^2(s) = R_0^2(s) (1 + m^2/m_c^2(L, s)). \quad (4.14)$$

This result is the same as that obtained in appendix 3 by evaluating the integrals occurring in (4.7) exactly. From the appendix we also have that at $m = m_c(L, s)$

$$R^2(s) = R_0^2(s) (NL/s)^{1/4} \sqrt{3/2} (l/d)^{1/4}.$$

This particular result requires the exact evaluation of the integrals and is lost by the approximation (4.8).

For $m \gg m_c(L, s)$ we have from (4.10) that

$$R^2(s) = R_0^2(s) \exp(m^2/m_c^2(L, s)). \quad (4.15)$$

The exponential term in this result is also obtained with the exact result in appendix 3. However, such an expansion of the molecule is clearly unphysical and this is confirmed by a calculation of the free energy which tends to infinity as $m \rightarrow m_c(L, s)$.

The linking number represented by $m_c(L, s)$ is an important scaling factor for the properties of entangled chains: it represents a state of critical entanglement. For $m < m_c(L, s)$ the molecule still has sufficient configurational freedom to be governed by the Gaussian distribution (2.6) of chain bond vectors. The size of the entangled molecule is only slightly perturbed from the unconstrained state. Consequently the key approximation of this work (3.5), where we effectively replaced $|r - r'|^{-1}$ by its average value based on Gaussian configurational statistics, is reasonably self-consistent. However for $m > m_c(L, s)$ the approximation is clearly no longer self-consistent, and the constraint becomes dominant in determining a new configurational state of the

molecule. To understand the possible nature of the new state when $m > m_c(L, s)$, we may first observe that the critical linking number $m_c(L, s)$ depends on the arc length s over which the size of the molecule is being investigated. From equation (4.12)

$$m_c(L, s) \sim N^{3/4} (L/s)^{1/4} \quad (4.16)$$

and is a minimum for the largest length scale of $s \sim L$. As we might well have anticipated, we see that as m is increased, the entanglements first affect the large scale configurational features of the molecule. This is consistent with them being global rather than local constraints on the chain configuration. However, when $m > m_c(L, L)$ it is still possible to find shorter arc lengths $0 < s < s^*$ for which $m_c(L, L) < m < m_c(L, s^*)$. Consequently over these smaller scales of arc lengths the molecule will still be approximately Gaussian, although it will be non-Gaussian on the larger scale $s > s^*$.

Using (4.16) the condition $m < m_c(L, s^*)$ can be written as

$$s^* < L(m_c/m)^4 \quad (4.17)$$

where we shall denote by m_c the minimum value $m_c(L, L)$ at which critical entanglement first occurs.

In the next section we present an initial attempt to understand the configurational state of the molecule for $m > m_c$. The arguments are far from rigorous but we shall try and show, in accordance with intuition, that for these high entanglements numbers the molecule is in a partially collapsed solenoidal state compared with the unconstrained random coil state.

4.3. The highly entangled state

In § 2 we showed that the weighting factor due to entanglements was given by

$$(2\pi W\{r\})^{-1/2} \exp -\frac{1}{2} m^2 / W\{r\} \quad (4.18)$$

with $W\{r\}$ given by equations (2.8) and (2.9). This factor is a maximum for those configurations $\{r^*\}$ for which $W\{r^*\} = m^2$ and the discussion given in that section indicated that such configurations might be solenoidal. However, in the last section we established that for $m < m_c$ the entropic nature of the random walk statistics was still dominant over the entanglement constraint and the molecule adopted an essentially random coil configuration. For $m > m_c$ the entropic state became non-self-consistent, with the size of the molecule expanding as $\exp m^2/m_c^2$, indicating that the approximation procedure whereby we replace the term $|r - r'|^{-1}$ in the expression (3.5) by an average calculated using random coil statistics was going badly wrong. However, we also established in the last section that for $m > m_c$ we could find smaller arc length scales $(s - s') < s^*$ over which the molecule still behaved like a random coil, and for which this present procedure was still valid. This suggests an alternative approximation whereby we split the original molecule into $r = L/s^*$ submolecules and treat each of these as independent loops but still connected together. The justification for treating the molecule as r independent but connected loops is, admittedly, somewhat *ad hoc* but comes close to some realisation of a solenoidal state.

Each loop of length s^* is, by definition, Gaussian and the maximum winding number it can accommodate and still remain Gaussian is $m_c(s^*, s)$. On a scale $s \sim s^*$ we have from (4.11) that

$$m_c(s^*, s^*) \equiv m_c^* = k(s^*/l)^{3/4} \quad (4.19)$$

where k contains all the other factors. For the entire molecule on a scale $s \sim L$

$$m_c(L, L) \equiv m_c = k(L/l)^{3/4} \tag{4.20}$$

and, of course, $m_c^* < m_c$. However, if we have $r = L/s^*$ of these Gaussian subloops, and consider them as independent, then the maximum winding number that could be accommodated is

$$m_{\max} = rm_c^* = (L/s^*)k(s^*/l)^{3/4}.$$

Using

$$s^* = L(m/m_c)^4$$

we have that

$$m_{\max} = m(kN^{3/4}/m_c) = m > m_c$$

thus confirming the possibility in this model of accommodating a winding number $m > m_c$. We can check the consistency of this picture, of subdividing the entire molecule of length L into r independent loops of length s^* as a means of accommodating this high winding number by an analytic calculation. It proceeds much along the lines we have described already. If we divide the chain into r segments labelled by p and denote by s_p the arc length which lies in the p th segment, i.e. $(p-1)s^* < s_p < ps^*$, then the ‘interaction’ function $W\{c_\alpha\}$, equation (2.8), can be written as

$$\frac{\rho l^2}{24\pi} \sum_{pp'=1}^r \int_{(p-1)s^*}^{ps^*} ds_p \int_{(p'-1)s^*}^{p's^*} ds_{p'} \dot{r}(s_p) \cdot \mathbf{T}[r(s_p) - r(s_{p'})] \cdot \dot{r}(s_{p'}). \tag{4.21}$$

The additional approximation of treating the molecule as r independent loops consists in replacing the tensor \mathbf{T} in equation (4.21) by $\mathbf{T}[r(s_p) - r(s_{p'})] \delta_{pp'}$. The generating function for r independent loops subject to an overall winding number m can be written as

$$J(\lambda, m) = \frac{1}{2\pi} \int dg \exp igm[j(\lambda, m, g)]^r \tag{4.22}$$

where $j(\lambda, m, g)$ is the generating function appropriate for one of the loops. We can use the result derived in appendix 2, equation (A2.18), but with the replacements $L \rightarrow s^*$, $N \rightarrow N^* = s^*/l$ to give

$$j(\lambda, m, g) = \exp - \left(\beta^* \frac{g^2}{2} + \frac{\lambda^2 l s^*}{b} \frac{\gamma^{*2}(s)}{\gamma^{*2}(s) + g^2} \right) \tag{4.23}$$

where β^* and γ^* are obtained from β and γ with the replacements given above, i.e.

$$\beta^* = b\rho l^3 N^* \sqrt{l/d}$$

with

$$\gamma^{*2} = \frac{a}{\rho l^3} \frac{1}{\sqrt{N^*}} \sqrt{s^*/s'}. \tag{4.24}$$

$s' = s$ (modulo s^*), where s is the arc length of the original molecule.

Therefore,

$$[j(\lambda, m, g)]^r = \exp - \left(\beta g^2 + \frac{\lambda^2 l L}{b} \frac{\gamma^{*2}}{\gamma^{*2} + g^2} \right). \tag{4.25}$$

The calculation of the size of the molecule proceeds exactly as before and once again we find a critical winding number m_c^* given by

$$m_c^* = \gamma^* \beta.$$

Using (4.24)

$$m_c^* = (ab^2 \cdot \rho l^3 \cdot l/d)^{1/2} (rn^3)^{1/4} (s^*/s')^{1/4} \quad (4.26)$$

$$m_c^* = r^{1/4} m_c(L, s) (s^*/s')^{1/4} \quad (4.27)$$

where we have used (4.11) for the critical winding number $m_c(L, s)$ of the molecule in the approximately Gaussian state when $m < m_c$. For $s \sim L$, $s' \sim s^*$ we have $m_c^* = r^{1/4} m_c$. Thus by splitting the molecule into r independent subloops as a way of accommodating the winding number $m > m_c$, we find that the critical winding number threshold is raised by the factor $r^{1/4}$. Consequently we can choose the number of loops r so that m never exceeds m_c^* thus ensuring that the subloops remain essentially Gaussian. The condition $m < m_c^*$ gives $r > (m/m_c)^4$ which is entirely consistent with $r > L/s^*$ using (4.17) for s^* and confirms our intuitive picture given earlier.

The size of the entire molecule is the same as the size of any of the subloops. Since $m < m_c^*$, the subloops are always approximately Gaussian; consequently

$$R^2 \sim ls^* \sim lL/r \sim lL(m_c/m)^4.$$

Therefore

$$R^2/lL = (m_c/m)^4 < 1. \quad (4.28)$$

The molecule is partially collapsed by the high entanglement constraint and only remains Gaussian on the scale $s < s^*$.

5. Conclusion

The results obtained in § 4 are the major results of the paper. For a polymer molecule of N links of average length l entangled with an infinitely long background molecule we have identified over an arc length scale s a critical winding number

$$m_c(L, s) \sim \rho l^3 N^{3/4} (L/s)^{1/4}$$

where ρ is the number density of the background molecule and $L = Nl$. For $m < m_c$ the original entropy of the chain still dominates over the winding number constraint, resulting in an approximate random walk configuration. For $m > m_c$, the constraint dominates and a partially collapsed solenoidal state seems most likely. Since the winding number is a global constraint, affecting the largest scale features of the molecule first, we can still find in the collapsed state shorter arc lengths $s < s^*$ over which the molecule is still in a random coil configuration.

We have treated the simplest situation of two entangled chains and dealt only with the configurational properties of one of the chains. In a future publication we shall consider the situation of many entangled chains and, using the same approximations adopted in this paper, calculate the mechanical properties due to the entanglements. The results will be applied to a discussion of the modulus of rubber and of molten polymers in the plateau region.

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Appendix 1

Evaluation of

$$\langle \mathbf{T}(s-s') \rangle = \left\langle \frac{\mathbf{1}}{|\mathbf{r}(s) - \mathbf{r}(s')|} + \frac{(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \right\rangle \tag{A1.1}$$

where the averaging is over a Gaussian distribution of bond vectors. Equation (A1.1) can be parametrised by

$$\langle \mathbf{T}(s-s') \rangle = \int \frac{d^3q}{\pi^2} \frac{1}{q^2} (\mathbf{1} - \mathbf{q}\mathbf{q}/q^2) \langle \exp i\mathbf{q}(\mathbf{r} - \mathbf{r}') \rangle \tag{A1.2}$$

and since we are dealing with Gaussian distributions

$$\langle \exp i\mathbf{q}(\mathbf{r} - \mathbf{r}') \rangle = \exp -\frac{1}{6}q^2 \langle (\mathbf{r} - \mathbf{r}')^2 \rangle \tag{A1.3}$$

and (A1.2) can be integrated to give

$$\langle \mathbf{T}(s-s') \rangle = \frac{8}{3} \left(\frac{3}{2\pi} \frac{1}{\langle (\mathbf{r} - \mathbf{r}')^2 \rangle} \right)^{1/2} \mathbf{1} \tag{A1.4}$$

with

$$\langle (\mathbf{r} - \mathbf{r}')^2 \rangle = (s-s')l[1 - (s-s')/L].$$

Appendix 2

Evaluation of the path integral

$$\mathcal{N}^{-1} \int \mathcal{D}\{r\} \exp -\frac{3}{2l} \int_0^L ds ds' \dot{r}(s) \cdot \dot{r}(s')(s-s') + i\lambda \cdot \int_0^L \dot{r}(s)\theta_{12}(s) ds \tag{A2.1}$$

where \mathcal{N} is the normalisation factor $(2\pi l/3)^{3N/2}$ and

$$h(s) = \delta(s) + g^2 K [ls(1-s/L)]^{-1/2} \tag{A2.2}$$

with

$$K = (1/2\pi)^{3/2} \frac{2}{27} \rho l^3.$$

The exponent in equation (A2.1) can be diagonalised by the normal mode transformation $\dot{r}(s) \rightarrow \dot{r}_n$ where

$$\begin{aligned} \dot{r}(s) &= \sum_{n=-\infty}^{\infty} r_n \exp(2\pi i n s/L) \\ \dot{r}_n &= L^{-1} \int_0^L ds r(s) \exp(-2\pi i n s/L). \end{aligned} \tag{A2.3}$$

Then (A2.1) becomes

$$\mathcal{N}^{-1} \int \mathcal{D}\{r\} \exp -\frac{3L}{2l} \sum_{n \neq 0} |\dot{r}_n|^2 h_n + iL\lambda \cdot \sum_{n \neq 0} \dot{r}_n \theta_{-n} \tag{A2.4}$$

where

$$h_n = \int_0^L ds h(s) \exp(-2\pi ins/L)$$

and

$$\theta_n = \frac{1}{L} \int_0^L ds \theta_{12}(s) \exp(-2\pi ins/L).$$

The path integral can now be done to give

$$\mathcal{N}^{-1} \prod_n \left(\frac{2^{\pi l}}{3h_n} \right)^{3/2} \exp(-\lambda^2 lL/b) \sum_n \frac{|\theta_n|^2}{h_n}. \tag{A2.5}$$

This can be written as

$$\exp \sum_{n \neq 0} \left(-\frac{3}{2} \ln h_n - \frac{\lambda^2 lL}{b} \frac{|\theta_n|^2}{h_n} \right) \tag{A2.6}$$

with

$$h_n = 1 + g^2 K(N/n)^{1/2} \tag{A2.7}$$

and

$$|\theta_n|^2 = \frac{1}{2\pi} \frac{1}{m^2} \sin^2 \frac{\pi m}{L} (s_1 - s_2). \tag{A2.8}$$

The remaining difficulties to be overcome before we achieve an explicit evaluation of this path integral occur in performing the sum over n in (A2.6). We consider first

$$A = \sum_{n \neq 0} \ln h_n = \sum_{n \neq 0} \ln[1 + g^2 K(N/n)^{1/2}]. \tag{A2.9}$$

If the sum is replaced by a integral over dn , the integration can be done to give

$$A = g^4 K^2 N - \ln \left(\frac{1 + g^2 K(N/n)^{1/2}}{g^2 K(N/n)^{1/2}} \right) + \frac{\ln[1 + g^2 K(N/n)^{1/2}]}{g^4 K^2 N/n} + \frac{1}{g^2 K(N/n)}. \tag{A2.10}$$

The upper limit $n \rightarrow \infty$ gives a divergent answer. Normal modes with n large correspond to small distance scales and so if we choose a cut-off distance $s \sim d$ then this is equivalent to a cut-off at large values of $n \sim L/d = Nl/d$. The occurrence of this divergence is due to the singular nature of the entanglement interaction W when $r(s) = r(s')$. By introducing a ‘thick’ polymer we can avoid this singularity, correspondingly we consider d to be some measure of the thickness of the polymer. With this cut-off procedure the integral becomes

$$N\{-g^4 K^2 \ln[1 + (g^2 K)^{-1}(l/d)^{1/2}] + (l/d) \ln[1 + Kg^2(d/l)^{1/2}] + g^2 K(l/d)^2\}. \tag{A2.11}$$

As $d \rightarrow 0$, the leading term is $2g^2 KN(l/d)^{1/2}$. Consequently the first term in (A2.6) can be written as $\exp(-3g^2 KN\sqrt{l/d})$. The second term to be evaluated is

$$B = \sum_{n \neq 0} \frac{|\theta_n|^2}{h_n}. \tag{A2.12}$$

Using (A2.8) for $|\theta_n|^2$ and (A2.7) for h_n

$$B = \frac{1}{2\pi} \int_1^\infty \frac{dn}{n^2} \frac{\sin^2 \pi n s_{12}/L}{1 + g^2 K(N/n)^{1/2}} \tag{A2.13}$$

where $s_{12} = s_1 - s_2$.

Unfortunately this integral cannot be evaluated in any closed form. This is particularly inconvenient as, in order to complete the calculation, we need to know B as a function of g^2 . The integral is a monotonically decreasing function of g^2 and at $g^2 = 0$ and for $g^2 \rightarrow \infty$ it can be exactly evaluated:

at $g^2 = 0$

$$B = \frac{1}{\pi^2} \int_1^\infty \frac{dn}{n^2} \sin^2 \pi n s_{12}/L = s_{12}/L; \tag{A2.14}$$

as $g^2 \rightarrow \infty$

$$B \rightarrow \frac{1}{\pi^2 K N^{1/2}} \frac{1}{g^2} \int \frac{dn}{n^{3/2}} \sin^2 \pi n s_{12}/L = \frac{1}{g^2} \frac{1}{K} \left(\frac{s_{12}}{NL} \right)^{1/2}. \tag{A2.15}$$

We therefore approximate the integral by the form

$$B = \frac{s_{12}}{L} \frac{\gamma^2(s_{12})}{\gamma^2(s_{12}) + g^2} \tag{A2.16}$$

where

$$\gamma^2(s_{12}) = (L/Ns_{12})^{1/2} / \pi K. \tag{A2.17}$$

Hence equation (A2.6) for the path integral can be written as

$$\exp - \left(\frac{g^2}{2} \beta + \frac{\lambda^2 l s_{12}}{b} \frac{\gamma^2(s_{12})}{\gamma^2(s_{12}) + g^2} \right) \tag{A2.18}$$

where

$$\beta = bKN(l/d)^{1/2} = (3/2\pi)^{3/2} \frac{4}{9} \rho l^3 N(l/d)^{1/2}. \tag{A2.19}$$

Appendix 3

Evaluation of

$$R^2(s, m) = R_0^2(s) \frac{\int_{-\infty}^\infty dg \exp(-\frac{1}{2}\beta g^2 + igm)(1 + g^2/\gamma^2)^{-1}}{\int_{-\infty}^\infty dg \exp(-\frac{1}{2}\beta g^2 + igm)}. \tag{A3.1}$$

By symmetry, the integral in the numerator is

$$\int_{-\infty}^\infty dg \cos gm \exp(-\frac{1}{2}\beta g^2) \frac{\gamma^2}{\gamma^2 + g^2} \tag{A3.2}$$

and is evaluated in Gradshteyn and Ryzhik (1980) as

$$\frac{1}{2} \pi \gamma \exp \frac{1}{2} \beta \gamma^2 [2 \cosh m\gamma - \exp(-m\gamma) \Phi(\gamma\sqrt{\beta/2} - m\sqrt{1/2\beta}) - \exp(m\gamma) \Phi(\gamma\sqrt{\beta/2} + m\sqrt{1/2\beta})]. \tag{A3.3}$$

$\Phi(x)$ is the probability integral

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \quad (\text{A3.4})$$

By writing $2 \cosh m\gamma = \exp(m\gamma) + \exp(-m\gamma)$ equation (A3.3) can be rewritten as

$$\frac{1}{2}\pi\gamma \exp(-m^2/2\beta)[\exp(x_+^2)(1 - \Phi(x_+)) + \exp(x_-^2)(1 - \Phi(x_-))] \quad (\text{A3.5})$$

where

$$x_{\pm} = \gamma\sqrt{\frac{1}{2}\beta}(1 \pm m/\gamma\beta). \quad (\text{A3.6})$$

The integral in the denominator of (A3.1) is straightforward and gives

$$\sqrt{2\pi/\beta} \exp(-m^2/2\beta). \quad (\text{A3.7})$$

Therefore (A3.1) can be written as

$$R^2(s, m)/R_0^2(s) = \sqrt{2\pi} \frac{1}{4} \gamma\sqrt{\beta}(u(x_+) + u(x_-)) \quad (\text{A3.8})$$

where

$$u(x) = \exp(x^2)(1 - \Phi(x)). \quad (\text{A3.9})$$

For $m \ll \gamma\beta$, $x_+ \sim x_- \sim \gamma\sqrt{\beta}/2$.

Using the definitions (3.17) for γ and β we have that $\gamma\sqrt{\beta} \sim N^{1/4}$ and so $x_{\pm} \gg 1$. Asymptotically $u(x) \sim (\sqrt{\pi}|x|)^{-1}$ and

$$u(x_+) + u(x_-) = 2\sqrt{2/\pi} \frac{1}{\gamma\sqrt{\beta}} \frac{1}{1 - m^2/(\gamma\beta)^2}. \quad (\text{A3.10})$$

Consequently

$$\frac{R^2(s, m)}{R_0^2(s)} = \frac{1}{1 + m^2/(\gamma\beta)^2} \approx 1 + \frac{m^2}{(\gamma\beta)^2} \quad \text{for } m \ll \gamma\beta. \quad (\text{A3.11})$$

For $m = \gamma\beta$, $x_+ = \gamma\sqrt{2\beta} \gg 1$ and $x_- = 0$. Since $u(0) = 1$, we have

$$\frac{R^2(s, m = \gamma\beta)}{R_0^2(s)} = \frac{1}{4}\sqrt{2\pi}\gamma\sqrt{\beta} = (NL/s)^{1/4} \frac{1}{2}\sqrt{3}(l/d)^{1/4} \quad (\text{A3.12})$$

and for $m \gg \gamma\beta$ the variable x_- becomes negative and large. $\Phi(-x) = -\Phi(x)$ and $u(-x) \sim \exp(x^2)$. Therefore

$$\frac{R^2(s, m)}{R_0^2(s)} = \frac{R^2(s, \gamma\beta)}{R_0^2(s)} \exp(m^2/\gamma\beta). \quad (\text{A3.13})$$

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