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LETTER TO THE EDITOR

A configurational phase transition induced by topological entanglements between long chain molecules

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Abstract. A critical linking number, m_c, is defined, and an expression is obtained for the mean square size, R^2, of an entangled polymer loop. For linking numbers m_c, the existence of a configurational phase transition is demonstrated by the occurrence of a collapsed state in the polymer molecule.

The properties of topologically entangled polymer molecules have attracted much interest in recent years. The initial mathematical formulation of the problem is due to Edwards (1967, 1968). More recently, in a previous paper (Brereton and Shah 1980; hereafter referred to as I), the statistical mechanics of two long chain polymer molecules subject to a topological constraint in the form of a linking number was formulated (see I for further references). The criterion for deciding whether the molecules, described by space curves $r_\alpha(s)$ and $r_\beta(t)$, were linked or not was provided by the Gauss integral

$$I_{\alpha\beta}[c_\alpha, c_\beta] = \frac{1}{4\pi} \oint_{c_\alpha} \oint_{c_\beta} ds \, dt \, \dot{r}_\alpha(s) \cdot \dot{r}_\beta(t) \times \nabla[1/(r_\alpha - r_\beta)] \tag{1}$$

where $\dot{r}(s) = dr(s)/ds$.

$I_{\alpha\beta}$ takes integer values depending on the linking of the two curves. In I, one of the loops, say c_β, was allowed to fill a macroscopic volume at a finite density and an average was then performed over all the configurations of this 'background' molecule subject to the constraint that $I_{\alpha\beta} = m$, where m is some definite linking number. Then the constraint ($I_{\alpha\beta} = m$), averaged over the background chain, can be expressed as

$$\langle \delta(I_{\alpha\beta} - m) \rangle_{[c_\beta]} = \left(\frac{1}{2\pi W[c_\alpha]}\right)^{1/2} \exp\left(-\frac{m^2}{2W[c_\alpha]}\right) \tag{2}$$

where

$$W[c_\alpha] = \oint_{c_\alpha} ds \, ds' \, \dot{r}(s) \cdot \mathbf{T}[r(s) - r(s')] \cdot \dot{r}(s'). \tag{3}$$

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

$$\mathbf{T}(R) = \frac{\rho l^2}{12R}\left(\mathbf{1} + \frac{RR}{R^2}\right). \tag{4}$$

ρ is the number density of background monomers and l the step length of the chain.

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Thus the effect on the configuration c_α of a topological entanglement with the chain c_β, resulting in a definite linking number m, is expressed by assigning the weighting factor (2) to each configuration c_α.

This weighting factor has a maximum for those configurations $\{c_\alpha^*\}$ for which $W\{c_\alpha^*\} = m^2$. It is interesting to note that if only the unit tensor part of T, equation (4), is used then

$$W \simeq \frac{\rho l^2}{12\pi} \int ds \, ds' \frac{\dot{r}(s) \cdot \dot{r}(s')}{|r - r'|}, \tag{5}$$

the integral part of which is essentially the inductance of a loop. For solenoidal configurations, the inductance depends on the (number of turns)^2. The weighting factor (2) can clearly be optimised by solenoidal configurations adapting the number of turns equal to the linking number. However, for polymer configurations this weight factor due to the topological constraint must be offset against the natural tendency of the molecule to adopt essentially a random walk configuration. The weighting factor (2) can be parameterised as

$$(2\pi W)^{-1/2} \exp(-m^2/2W) = \frac{1}{2\pi} \int dg \, \exp(-\tfrac{1}{2}q^2 W + igm). \tag{6}$$

The random walk aspect of the configuration is described by using a Gaussian distribution of step lengths, or in a continuum notation, the Wiener measure

$$\int D\{r\} \exp\left(-\frac{3}{2l} \int_0^L \dot{r}^2(s) \, ds \right). \tag{7}$$

Thus in the presence of entanglements the complete statistical weight factor to be used in performing averages over the c_α configurations is

$$\int \frac{dg}{2\pi} e^{+igm} \int D\{r\} \exp\left(-\frac{3}{2l} \int ds \, \dot{r}^2 - \tfrac{1}{2}g^2 \int ds \, ds' \, \dot{r} \cdot \mathbf{T}(r - r') \cdot \dot{r} \right). \tag{8}$$

In I this problem was transformed into a gauge field theoretic formalism. However, in this Letter we wish to report on an alternative approach obtained by replacing the tensor $\mathbf{T}(r - r')$ by its pre-averaged value, i.e.

$$\mathbf{T}[r(s) - r(s')] \rightarrow \langle \mathbf{T}(r - r') \rangle = T(s - s')\mathbf{I}. \tag{9}$$

This approximation is familiar in the dynamics of polymer molecules in solution, where a tensor similar to $\mathbf{T}$ naturally arises from hydrodynamic interactions and is known as the Oseen tensor (see e.g. Yamakawa (1971)). Ideally the average occurring in (9) should be self-consistently calculated. That calculation will be presented in detail elsewhere. The main features of our result can be arrived at by using the unperturbed chain configurations. The result is

$$T(s - s') = \tfrac{2}{9}(2\pi)^{-3/2} \left(\frac{L}{|s - s'|(L - |s - s'|)} \right)^{1/2} \tag{10}$$

where $L = Nl$.

The weight factor can now be written as

$$\int \frac{dg}{2\pi} \int D\{\dot{r}\} \exp\left(-\frac{3}{2l} \int ds \, ds' \, \dot{r}(s) \cdot \dot{r}(s')h(s - s') \right) \tag{11}$$

where

$$h(s - s') = \delta(s - s') + \tfrac{1}{3}g^2 l T(s - s'). \tag{12}$$

The functional integral in (11) looks like the distribution function for a Gaussian random walk governed by a correlated step length: $\langle \dot{r}(s) \cdot \dot{r}(s') \rangle = |h(s - s')|^{-1}$. The extent of the correlation contained in $h(s - s')$ depends on g, which is the variable conjugate to the linking number m. The functional integral (11) can be performed exactly.

The probability $p(m)$ of finding the two loops c_α and c_β entangled with a linking number m is given by

$$p(m) = \langle \delta(I_{\alpha\beta}\{c_\alpha, c_\beta\} - m) \rangle_{[c_\alpha, c_\beta]}. \tag{13}$$

Using (11) this has been evaluated as

$$p(m) = (1/2\pi\bar{m}^2)^{1/2} \exp(-m^2/2\bar{m}^2) \tag{14}$$

where the average (linking number)^2, $\bar{m}^2$, is given by

$$\bar{m}^2 \sim \rho l^3 (l/d)^{1/2} N. \tag{15}$$

d is a cut-off necessitated by the breakdown of the Gaussian random-walk model on scales of the order of monomer units $d \sim l$. The mean square size $R^2(s, m)$ of the c_α loop linked m times is measured by

$$R^2(s, m) = \langle \delta(I_{\alpha\beta} - m)(r_\alpha(s) - r_\alpha(0))^2 \rangle_{[c_\alpha][c_\beta]} \tag{16}$$

which can be evaluated using (11). The result can be written as

$$\frac{R^2(s)m}{R_0^2(s)} = \left(\frac{NL}{s_0}\right)^{1/4} \left\{ f\left[\left(\frac{NL}{s_0}\right)^{1/4}\left(1 - \frac{m}{m_c(s_0)}\right)\right] + f\left[\left(\frac{NL}{s_0}\right)^{1/4}\left(1 + \frac{m}{m_c(s_0)}\right)\right] \right\} \tag{17}$$

where s_0 is the measure of arc length appropriate for a loop, i.e. $s_0 = s(1 - s/L)$ and $R_0^2(s)$ is the unperturbed Gaussian result for a loop of length L:

$$R_0^2 = s_0 l.$$

The function f has the following limiting properties:

$$f(0) = 1, \qquad f(x) \sim 1/x, \qquad x > 1, \tag{18}$$

and the critical linking number m_c is given by

$$m_c^2(s_0) \simeq \rho l^3 (l/d) N^{3/2} (L/s_0)^{1/2} \tag{19}$$

and depends on the arc length s_0 over which the size of the molecule is being measured. For $m \ll m_c$, equation (17) together with (18) simplifies to

$$R^2(s, m) \simeq R_0^2(s)(1 + m^2/m_c^2(s_0)). \tag{20}$$

If we average $R^2(s, m)$ over m using (14), then

$$R^2(s) = \langle R^2(s, m)_m = R_0^2(s)(1 + \bar{m}^2/m_c^2(s_0)).$$

We have, using (15) and (19), that $\bar{m}^2/m_c^2 \sim N^{-1/2}$ and consequently the correction to the Gaussian result is negligible. At $m = m_c(s_0)$ the chain is expanded as $R^2/R_0^2 \sim N^{1/4}$ and for $m > m_c(s)$, the chain collapses with increasing linking number as

$$R^2/R_0^2 \sim m_c(s)/m. \tag{21}$$

These results show that for $m < m_c(s_0)$ the entropy of the chain still dominates over the linking number constraint, and an approximate random walk configuration results. For $m > m_c(s_0)$ the constraint dominates and some kind of partially collapsed solenoidal state occurs. The linking number is a global constraint which affects the largest-scale features of the molecule first. Thus for $m < m_c(L)$ no part of the molecule will be dominated by the linking number constraint. However, when $m > m_c(L)$ there will still be shorter arc lengths $0 < s_0 < s_0^*$ for which $m < m_c(s_0^*)$, and consequently over these arc length scales the molecule will still be approximately Gaussian. However, for arc lengths $s_0 > s_0^*$ the constraint dominates and some collapsed state prevails at these scales. From (19) the criterion $m < m(s_0^*)$ can be rewritten as

$$s_0^* < L m_c^4 (L/2)/m^4. \tag{22}$$

We can picture the highly entangled state of the molecule as still being composed of Gaussian subunits on some arc length scale $0 < s_0 < s_0^*$, but overall these units are connected in a partially collapsed non-Gaussian manner.

It is interesting to note that Elderfield (1980) has examined this problem in the gauge field theoretic formalism to see if the critical exponents of the unconstrained polymer system are changed by entanglements. He uses the $d = 4 - \varepsilon$ expansion technique familiar in critical phenomena problems and finds that for m less than a critical value the entanglements do not alter the universality class. His expression for the critical linking number in three dimensions is essentially the same as ours, i.e. $m_c^2 \sim N^{3/2}$.

A more detailed picture of the entangled state, including a self-consistent calculation, will be presented in a full paper. We will also give the mechanical properties of the model and possible applications to molecules such as the DNA.

References

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