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Are sliplink models dangerous?*

T.A. Vilgis

Max-Planck-Institute für Polymerforschung, Postfach 3148, D-6500 Mainz,
Federal Republic of Germany

Summary

It has been reported recently that the use of sliplink models in the theory of polymer dynamics and rubber elasticity is dangerous because they might cause a spontanous conformational symmetry breaking. In this note it is shown that this result is not correct, and no symmetry breaking occurs.

Introduction

Sliplinks are mean field models to account for the effect of entanglements in dense polymer systems, such as concentrated polymer solutions, melts, or rubbers. A number of theoretical results have been derived in polymer dynamics (see the book of Doi and Edwards [1]) or in rubber elasticity (see the review of Edwards and Vilgis [2]). The most simplified picture of a sliplink is given by a polymer chain passing through rings [1,2,3], and has been investigated in detail in refs [2,3,4].
Rieger speculated recently [5] that these type of models are wrong and useless, because they exhibit spontanous symmetry breaking in close analogy to second order phase transitions. Considering one chain which has to pass through a ring, which is fixed in space he concluded that the parts of a chain on both sides of the ring are not random walks, but something different, if the end to end distance exceeds some critical value (see ref [5] for all details and notation which we are following closely). This result was derived by the condition that the entropy of the chain under such conditions has a maximum. The entropy was derived from the number of configurations

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$$\Omega_N(n_1, n_2, R) \sim z^N[n_1 n_2]^{-3/2} \exp\{-\frac{3}{2}\frac{X^2}{n_1 n_2}\} \tag{1}$$

where n_1 is the number of Kuhn segments on one side of the ring, n_2 the number on te other side, N the total number of Kuhn steps, and $X^2 \equiv N(R/\ell)^2$. ℓ is the length of one Kuhn segment. In ref [5] $n \equiv n_1$ and $n_2 \equiv N-n$ has been used directly. By maximization with repect to n of the Boltzmann entropy, which is $\log\Omega_N(n,R)$ it was derived that the maximum of the entropy is not given by $n_0=N/2$, as it was assumed in refs [1-4]. The result from [5] is

$$n_0 = \begin{cases} N/2 & \text{for } R \geq R_c \\ N/2 \pm \{N^2/4-X^2\} & \text{for } R \leq R_c \end{cases} \tag{2}$$

with $R_c^2 = N\ell^2/4$.

Maximization with a Lagrangian Multiplyer

In the following we show that by a modified calculation this result is not correct. The reason for this modification is that we have to use the constraint $N=n_1+n_2$ for the determination of the maximum of the entropy. This condition gives rise to a Lagrangian multiplyer g. The true maximum is given by considering the "modified entropy"

$$\tilde{S} = \log\Omega_N(n_1, n_2, R) + g\{N-(n_1+n_2)\} \tag{3}$$

Simple algebra leads to

$$\begin{aligned} (3/2)(X^2 - n_1 n_2) - g n_1^2 n_2 &= 0 \\ (3/2)(X^2 - n_1 n_2) - g n_1 n_2^2 &= 0 \end{aligned} \tag{4}$$

which has to be solved. This is quite simple and apart from the trivial solutions $n_1=0$ and $n_2=0$ we find for all $g>0$

$$n_1 = n_2 = N/2 \tag{5}$$

Note that this solution is valid for <u>all values</u> of X. Thus we conclude that no spontanous symmatry breaking occurs.

Discussion

In the present note we show that the result of ref [5] is not valid. Therefore the chain between the sliplinks is roughly a random walk, which has been used and derived in [2,4] by pure geometrical arguments. This is, however, in agreement with neutron scattering experiments on the labelled path in dense polymer systems, i.e. form factor of the chain is proportional to scattering vector to the power -2 over a wide range of Q values, indicating the random walk nature of the chain.
Moreover if the amount of chain between the sliplinks would exhibits the conformational symmetry breaking as proposed by Rieger [5] strange instabilities (not the spurt effect!) in the Doi - Edwards model on a macroscopic level would be the consequence. This has not been observed experimentally, theoretically, or by computer simulation, so far.
As a minor consequence of the symmetry breaking the equivalence of the sliplink and tube model would be destroyed.
The solution given by eq(5) can be proven rigorously by a functional integral approach, but this would be beyond the scope of this communication and is left for an extended and more mathematical paper, where further consequences and applications will be discussed.

References

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