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An example of spontaneous symmetry breaking in polymer physics

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Summary

A polymer chain subject to certain constraints (slip-link plus fixed end points) is considered. It is shown that this system exhibits spontaneous symmetry breaking when the end-to-end distance of the chain is lowered below a certain critical value. Various implications of this effect are mentioned.

Introduction

When considering the conformational properties of polymer molecules on length scales much larger then the distance between two monomers it is common practice to model the chain by a random walk (RW) (1). Neglecting self-avoidance effects the number of different configurations of one chain with fixed end-to-end distance $\underline{R}$ is given by

$$\Omega_n(\underline{R}) \simeq z^n n^{-3/2} \exp(- \frac{3}{2} R^2/na^2) \qquad /1/$$

where a is the length of one RW step, n is the number of steps, and z is a coordination number. Taking into account only entropic contributions Eq. /1/ yields the following expression for the free energy of the chain

$$F(n,R) \simeq \frac{3}{2} R^2/na^2 + \frac{3}{2} \ln(n) - \ln(z) \qquad /2/$$

All factors which are irrelevant in our calculation have been omitted. As can be seen F is just the potential of a Hookian spring. This potential is the basic ingredient in the Rouse chain model which describes the polymer as a succession of beads connected by ideal springs (1).

The issue of this note is to show that despite the trivial appearance of Eq. /2/ there are some unexpected and intriguing properties of a constrained polymer chain with subchains obeying Eq. /1/.

Theory

Take a polymer chain with its end points being fixed a distance 2R apart. Impose on this system the condition that the chain has to pass through a slip-link which is located at a distance R from the end points.

In Fig. 1a this system is depicted in the Rouse chain approach. In Fig. 1b our approach is shown which seems to be more realistic as the topological constraints which reduce the region of the phase space accessible to this system are fixed in space and not relative to the center of mass of the chain under consideration.

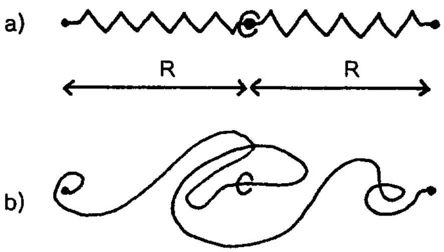

Figure 1 The polymer chain with its two end points fixed has to pass through a slip-link between the end points. The spring bead (Rouse) model (a) and our approach (b) are depicted.

The number of configurations is now given by

$$\Omega_N(n,R) \simeq z^N(n(N-n))^{-3/2}\exp(- \frac{3}{2}\frac{N}{n(N-n)} R^2/a^2) \qquad /3/$$

where n is the number of steps on one side of the slip-link. Eq. /3/ holds if the area spanned by the slip-link is very small compared to the volume filled by the chain. The Boltzmann entropy is the logarithm of $\Omega_N(n,R)$

$$S \simeq - \frac{3}{2} \ln(n(N-n)) - \frac{3}{2}\frac{N}{n(N-n)} R^2/a^2 \qquad /4/$$

(k is set to unity).

It can be shown that the value of n for which S is a maximum depends on the end-to-end distance in a non-trivial way. We find the following relations

$$n_o = N/2 \qquad \text{for } R \geqslant R_c := Na^2/4 \qquad /5/$$

$$n_o = N/2 \pm (N^2/4 - NR^2/a^2)^{1/2} \qquad \text{for } R < R_c \qquad /6/$$

where n_o is the value which yields the maximum of S.
In Fig. 2 the dependence of n_o on R is depicted.

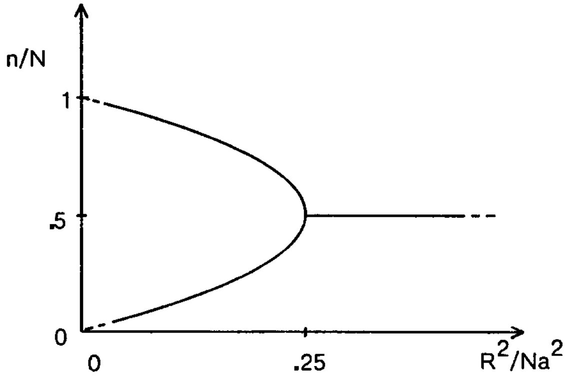

Figure 2 The number of RW steps between one end point of the chain and the slip-link for which the Boltzmann entropy is maximum is depicted as a function of the squared distance between these two points.

The use of the Boltzmann entropy implies that we do not consider fluctuations of n about n_o. For $R \geqslant R_c$ these fluctuations take place about $n_o = N/2$ as in the Rouse model. But for $R < R_c$ this symmetry is broken with regard to short time scales because the system is sure to be found near one of the two states which give a maximum of S. As the free energy assumes a finite value at n=N/2 for $R < R_c$ there is a non-zero transition rate for the transition from one n_o state to the other one. On averaging n over times which are much larger than the inverse of the transition rate we regain the symmetry of the system with <n> = N/2.

For a more complete description of the system the Gibbs entropy has to be evaluated. But in this case the problem becomes less trivial because a weighted sum over all possible states (i.e. values of n) is required and the Gaussian form in Eq. /1/ has to be replaced by a function involving the inverse Langevin function which holds also for n = R/a.

Discussion

In the following we mention some points for which the above considerations are relevant:
a. The slip-link approach is used in models describing the rheological properties of polymers (2) and describing the behaviour of polymeric networks (3). The result which we derived above shows that the concept of slip-links must not be taken to literally.
b. Antionetti et al (4) used the picture of strangled polymers. This might be an example of a true slip-link. We speculate that these strangled states also occur in cross-linked systems under load where the described effect might play a certain role.
c. There is some interest in simple models exhibiting bifurcation (5). Here we gave another example of such a simple system.
d. It will be interesting to examine the behaviour of systems with several slip-links and the dynamics of these systems (6).

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References

1. deGennes, P.G., "Scaling concepts in polymer physics," Cornell University Press, Ithaca (1979)
2. Doi, M., Edwards, S.F., J. Chem. Soc. Farad. Trans. II 74, 1802 (1978)
3. Ball, R.C., Doi, M., Edwards, S.F., Warner, M., Polymer 22, 1010 (1981)
4. Antonietti, M., Sillescu, H., Macromolecules 18, 1162 (1985)
5. Nicolis, J.S., "Dynamics of hierarchichal systems," Springer-Verlag Berlin, Heidelberg, New York (1986)
6. Rieger, J., in preparation

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