Experimental realization of true self-avoiding walks

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We show that the statistics of a linear polymer in an extremely polydispersed solution with a broad distribution of chain sizes is the same as that of a true self-avoiding walk. We also develop a Flory theory for a true self-avoiding walk and determine the upper critical dimension d_c and the correlation-length exponent ν. We find $d_c=2$ and $\nu=2/(d+2)$, in agreement with previous estimates.

Recently, Amit, Parisi, and Peliti[1] have introduced the "true" self-avoiding walk (TSAW) model which describes the path of a random walker that is constrained to avoid visiting a given point in space with a probability that is proportional to the number of times this point has already been visited. This constraint leads to a reduced excluded volume interaction as compared with the usual self-avoiding walk. The net effect is that the chain is less expanded and, in fact, its upper critical dimension d_c is found[1] to be 2 instead of $d_c=4$ for excluded volume self-avoiding walks.[2] Although TSAW has been extensively studied recently,[3-6] thus far it has been thought that it is only a statistical model without any relation to a real physical system. The main theoretical interest in this model stems from its unusual critical properties.[1,3-6]

In this Rapid Communication we show that, in fact, true self-avoiding walks describe the statistics of a special type of linear polymers in solution and their properties can be investigated experimentally by means of neutron and light scattering techniques. We also develop a Flory theory[2,7] for the TSAW and determine the upper critical dimension d_c and the exponent ν.

Before we discuss the physical realization of the TSAW, let us first discuss the difference between this model and the excluded volume problem, i.e., the usual self-avoiding walks.[2] In the TSAW the probability of moving to a new site depends on the number of times this site has already been visited.[1] In contrast, in the self-avoiding walk the probability of visiting a given site depends on the total number of self-intersections.[1,2] The net effect is that if we approximate each chain with a cloud of uniform density, then the repulsive energy in the TSAW is proportional to the density of the chain, whereas for the self-avoiding walk this interaction energy is proportional to the square of the chain density. Thus, with the use of a Flory-type theory[2,7] the interaction free energy for the TSAW can be written as

$$F_{\rm int}\sim N/R^d \ , \tag{1}$$

where N is the number of steps in the walk and R is its end-to-end length. Equation (1) should be contrasted with $F_{\rm int}\sim N^2/R^d$ for self-avoiding walks.[2,7]

An important remark at this point concerns the upper critical dimension d_c of TSAW. We can estimate the maximum repulsive energy by letting R have its minimum value corresponding to an unperturbed chain, i.e., $R\sim N^{1/2}$. The repulsive energy for the TSAW is thus proportional to $N^{1-d/2}$. The dimension above which this repulsive energy, i.e., the excluded volume effect, is negligible is $d_c=2$, in agreement with previous estimates.[1,3,4]

To obtain the total Flory free energy for the TSAW we add the elastic free energy[2,7] $F_{\rm el}\sim R^2/N$ to $F_{\rm int}$ and find

$$F\sim R^2/N+N/R^d \ , \tag{2}$$

where we have omitted all the unimportant constants in (2). Minimizing (2) with respect to R we find

$$R\sim N^{\nu} \ , \tag{3}$$

with

$$\nu=2/(d+2) \ . \tag{4}$$

Equation (4) is the same as the result obtained by Pietronero[4] using a self-consistent-field approach and shows that, as expected,[2] these two approaches are very similar.

Now let us consider the physical situation where the TSAW may be realized. Consider a melt made initially of bifunctional monomers in a vessel. These monomers are allowed to react with each other, thus leading to a very polydispersed condensate. Let us focus attention on a single polymer chain. It has been argued[8] that two different cases must be considered: (i) a *typical chain* with a molecular weight of the order of the weight-average molecular weight N_w, and (ii) a very *long chain,* much longer than the typical one.

The very long chain locally feels the presence of the other monomers. On a larger scale, however, the large chain interacts with itself and excluded volume effects are present. The other chains act just as a good solvent. Hence polydispersity has no effect on long chains. Thus, assuming $F_{\rm int}\sim N^2/R^d$, Flory theory gives $\nu=3/(d+2)$ for the very long chain where the excluded volume effect is present.

For the typical chain the excluded volume interaction is screened by the other chains.[8] As shown by Edwards[9] and de Gennes,[10] the degree of screening is proportional to the weight-average molecular weight N_w. In a polycondensed melt of linear polymers one finds $N_w\sim N$.[7] Thus the in-

teraction free energy for the typical chain is given by[8]

$$F_{\text{int}} \sim N^2/N_w R^d \sim N/R^d \ . \tag{5}$$

Equation (5) implies that the interaction energy instead of being proportional to the square of the monomer density—as for the excluded volume chain or self-avoiding walks—is directly proportional to the monomer density. Since the interaction energy is also proportional to the density in the TSAW model, then typical chains in a condensate have the statistics of the TSAW. In particular, for typical chains $d_c = 2$ and $\nu = 2/(d+2)$.[8]

In conclusion, the statistics of the TSAW are shown to be related to those of what we[8] have called "typical" chains in condensate. Properties of these chains can be measured in neutron or light scattering experiments. We have also presented a Flory theory for the TSAW. We find $d_c = 2$ and $\nu = 2/(d+2)$, in agreement with previous estimates.[1,3-6]

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