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LETTER TO THE EDITOR

Physical bound on the excluded-volume exponent of a polymer

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Abstract. A simple physical argument restricts the value of the excluded-volume exponent ν of a polymer. The result is $\nu < \frac{2}{3}$ in three dimensions.

Recently the statistical mechanics of a macomolecule in solution exhibiting the excluded-volume effect has been extensively reinvestigated (see, e.g., Yamakawa 1974, Burch and Moore 1976, McKenzie 1976, de Gennes 1977, Khoklov 1977, Schäfer and Witten 1977, Lax *et al* 1978, Oono and Oyama 1978, Odijk and Houwaart 1978). Nevertheless, as far as the author is aware, the following simple argument providing a bound for the excluded-volume exponent ν has not yet been presented.

Let the polymer have N Kuhn segments each of length A, and an excluded volume β between segments.

Statement 1. In the limit of a large excluded-volume parameter z, the mean-square extension length approaches a power of z:

$$z \sim A^{-3}\beta N^{1/2} \tag{1}$$

$$\lim_{z\to\infty} \langle R^2\rangle \sim NA^2 z^{2(2\nu-1)}. \tag{2}$$

Statement 2. The principle of universality holds.

This means (2) is valid for a class of flexible models having a long-range excluded-volume effect. One particular model is a chain consisting of N loosely attached cylinders each of length A, each cylinder having a very small but finite thickness D (contour length $l = NA$, N is very large, $A \gg D$). Then the excluded-volume is given by the usual Zimm expression

$$\beta \sim A^2 D. \tag{3}$$

Hence,

$$\lim_{N\to\infty} \langle R^2\rangle \sim l^{2\nu} A^{4-6\nu} D^{4\nu-2}. \tag{4}$$

Statement 3. For this model,

$$\left(\frac{\partial\langle R^2\rangle}{\partial A}\right)_l > 0. \tag{5}$$

This can be seen as follows. Let us compare model 1 having the parameters $(A_1, N_1, D_1 \ll A_1)$ with model 2 $(A_2 = 2A_1, N_2 = \frac{1}{2}N_1, D_1 = D_2)$. Then $\langle R^2 \rangle_2 > \langle R^2 \rangle_1$ since we can obtain model 2 from model 1 by switching on a hypothetical, short-range repulsive potential which stiffens consecutive pairs of thin cylinders.

Therefore inequality (5) restricts ν to a narrow range.

$$\tfrac{1}{2} \leqslant \nu < \tfrac{2}{3}. \tag{6}$$

Note that we have considered an extreme case for the dependence of the excluded volume on the segment length. Other models would give a more complicated dependence and inequality (5) would be difficult to prove. Finally, it is pertinent to remark that the increase in Kuhn length can actually occur, namely in the excluded-volume theory of polyelectrolytes when the salt concentration decreases (Odijk 1977, Skolnick and Fixman 1977, Odijk and Houwaart 1978).

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