THE EFFECT OF EXCLUDED VOLUME INTERACTIONS UPON THE MEAN SQUARE LENGTH OF A POLYMER CHAIN

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Asymptotic behaviour of the mean square length $\langle \vec{R}_N^2 \rangle$ of a discrete freely linked chain with a fixed valence angle α has been examined numerically considering excluded volume interactions with only first nearest neighbours in the links sequence of polymer chain. These interactions have no asymptotic effect upon the chain length (N). For the case of $N \to \infty$ the value of $\langle \vec{R}_N^2 \rangle$ approaches that of N.

It is well known that in the case of continuous models of polymer chains the mean square chain length can be expressed as $\langle \vec{R}_N^2 \rangle \sim N$ when $N \to \infty$ assuming that excluded volume interactions affect only the nearest neighbours of the polymer chain[1]. Montroll[2] has long ago attempted, though not quite successfully, to solve this problem using a discreet three-dimensional simple cubic model. Applying the Markoff chain theory and excluding the first few adjacent nodes of polymer chain he raised a hypothesis that these first nearest interactions are the primary source of deviations from random models[2]. Since the connection between the theory of continuous models and that of discrete lattice chain is at present questionable[3] it is not possible to apply

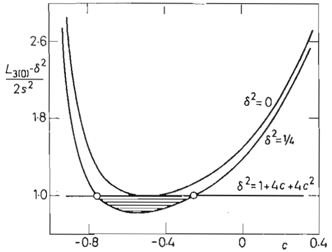

FIG. 1

Graphical Solution of Inequality (*I*)

When first adjacent nodes are excluded the allowed values of α will lie in the hatched area.

automatically the conclusion valid for asymptotic behaviour of the value of $\langle \overrightarrow{R_N^2} \rangle$ in the case of continuous chain to the model examined by Montroll. Tschen[4] investigated the asymptotic behaviour of $\langle \overrightarrow{R_N^2} \rangle$ on a model consisting of chains with a fixed valence angle and hindered internal rotation and assuming interactions of the

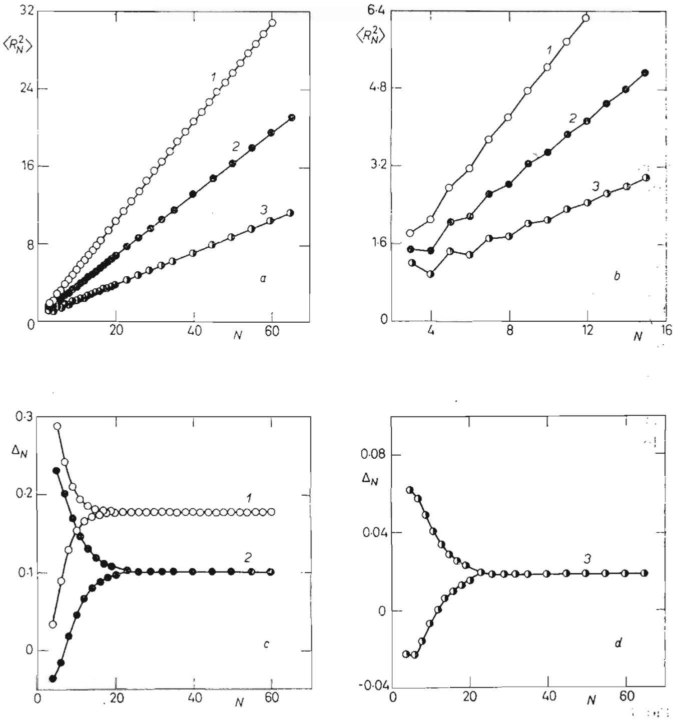

FIG. 2

The Dependence of $\langle \overrightarrow{R_N^2} \rangle$ and Δ_N on the Number of Links N

(*a*) $\overrightarrow{R_N^2}$ *vs* N: *1* $\alpha = 120°$, $\delta = 0{\cdot}485$; *2* $\alpha = 130°$, $\delta = 0{\cdot}485$; *3* $\alpha = 138°$, $\delta = 0{\cdot}500$; (*b*) detail of $\overrightarrow{R_N^2}$ *vs* N before achieving asymptotic values of $\langle \overrightarrow{R_N^2} \rangle$; (*c*, *d*) Δ_N *vs* N.

first nearest neighbours in sequence of chain links he came to the known Debye formula, where $\langle \vec{R}_N^2 \rangle \sim N$ for $N \to \infty$. Recently Dvořák[5] analysed the Tschens's model but considered more precisely the effect of excluded volume for every four adjacent nodes of the chain and came to a very complicated analytical relation between $\langle \vec{R}_N^2 \rangle$ and N. This relation, with regard to the above mentioned facts, is worth of numerical analysis.

The Method of Calculation and Results

The equation for the corrected mean square length with regard to the interactions of the first nearest neighbours was programmed and fed into a small MINSK 22 computer. The allowed values of the valence angle 180°-α and of the parameter δ obey the following relationship:

$$L_3(0) - 2s^2 \sin \delta_0 < \vartheta^2 , \quad (1)$$

when $0 \leqq \delta \leqq \frac{1}{2}$. The allowed values of the above mentioned parameters of the chain are given in Fig. 1. Assuming that the inequality (1) holds, it was possible to vary the parameters α and δ. For selected values of these parameters the quantities $\langle \vec{R}_N^2 \rangle$ — mean square chain length and $\Delta_N = 2s^2 w/(1 - c)^2 . (S_N - S_{N-1})$ — called difference[5] for $N = 4, \ldots, 65$, were computed. With respect to a rather limited storage capacity of the MINSK 22 computer the computation up to $N = 65$ was possible without the storage overflow. The typical computation results of the dependence $\langle \vec{R}_N^2 \rangle$ on N are given in Figs 2*a* and 2*b*. The dependence of the difference Δ_N on N is shown in Figs 2*c* and 2*d*. The notation is the same as in ref.[5].

DISCUSSION

The difference $\Delta_N = 2s^2 w/(1 - c)^2 . (S_N - S_{N-1})$ is the most important of the followed quantities which describes the behaviour of the chain mean square length $\langle \vec{R}_N^2 \rangle$; the correction was made by including of the volume effect upon every four adjacent chain nodes. The computations indicate quite unambiguously that the correction to the value $\langle \vec{R}_N^2 \rangle$ is, with great accuracy, constant for N greater than 20. It is thus possible to assume that $\langle \vec{R}_N^2 \rangle \sim N$, when $N \to \infty$. At the same time this accuracy is quite sufficient to conclude that asymptotic behaviour of $\langle \vec{R}_N^2 \rangle$ has been, within the followed region (from $N = 3$ to $N = 60$), attained and that a computation of the same type on a larger computer considering more links would not yield new results. The quantity Δ_N is in fact an alternating series which, according to the described calculations, converges very quickly to the constant (above $N = 20$). If we apply the results valid for the continuous model, including all the interactions, following *e.g.* from the SCF theory of Edwards[6] (*i.e.* that $\langle \vec{R}_N^2 \rangle \sim N^{6/5}$ for $N \to \infty$), to the discrete chain, then the Montroll hypothesis is not valid. The excluded volume is thus substantially influenced by more distant interactions in the sequence of polymer chain and not only those being considered more probable because of their occurence in close vicinity. As it was said above the application of conclusions obtained on continuous model to discrete model is not justified[3] at present. The validity of global theories of continuous models is itself questionable[7] (different results obtained for $\gamma(1 < \gamma < 2)$). At the moment it is thus possible neither to confirm nor to disprove the Montroll hypothesis.

LIST OF SYMBOLS

$\langle \vec{R_N^2} \rangle \equiv \langle R_N^2 \rangle$ mean square length of polymer chain
N number of chain links
$180°\text{-}\alpha$ valence angle; symbol α can also be used [grad]
δ excluded volume parameter
$L_3(0)$ mean square length uncorrected for the excluded volume effect
s $\sin \alpha$

$$\vartheta_0 = \arcsin\left[\min\left(1, \frac{L_3(0) - \delta^2}{2s^2}\right)\right]$$

Δ_N difference

$$\Delta_N = \frac{2s^2 w}{(1 - c)^2} (S_N - S_{N-1})$$

c $\cos \alpha$

$$w = \frac{2 \cos \vartheta_0}{\pi + 2\vartheta_0}$$

$$S_N = \sum_{p=0}^{N-3} \sum_{\nu=0}^{p} \sum_{\lambda=1}^{N-p-\nu-2} (-1)^{p+\nu} s^{2\nu} c^{N-2-2\nu-\lambda} w^p \binom{p}{\nu} \binom{N-p-\lambda-3}{N-p-\lambda-\nu-2} \left[\lambda(1 + c^{\lambda+1}) - \frac{2c}{1-c}(1 - c^\lambda)\right]$$

γ critical exponent $\langle R_N^2 \rangle \sim N^\gamma$

REFERENCES

1. Flory P. J.: *Statistical Mechanics of Chain Molecules.* Interscience, New York 1969.
2. Montroll E. W.: J. Chem. Phys. *18*, 734 (1950).
3. Yamakawa H.: *Modern Theory of Polymer Solutions.* Harper and Row, New York 1971.
4. Tchen C. M.: J. Chem. Phys. *20*, 214 (1952).
5. Dvořák S.: This Journal *33*, 3254 (1968).
6. Edwards S. F.: Proc. Phys. Soc. (London) *85*, 613 (1965).
7. Torrens McC. I.: J. Chem. Phys. *48*, 1488 (1968).

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