Question of excluded volume in polymer chains

1968 J. Phys. A: Gen. Phys. 2 14

(http://iopscience.iop.org/0022-3689/2/1/003)

J. PHYS. A (GEN. PHYS.), 1969, SER. 2, VOL. 2. PRINTED IN GREAT BRITAIN

Question of excluded volume in polymer chains

A. KYSELKA
Jan Šverma Works, Brno, Czechoslovakia
MS. received 3rd July 1968

Abstract. The problem of the excluded volume in a polymer chain is studied with the aid of a function which approximates to the Heaviside step function. This step function excludes the inhibited configurations of the chain by not allowing the distance of the end points of its ith link and $i+s$th link ($1 \leqslant s \leqslant N-1$, $i = 1, \ldots, N-s$) to be smaller than the chosen $\delta > 0$, $0 < \delta < a$, where $a^2 = \frac{2}{3}\langle \boldsymbol{r}_i^2 \rangle$, $\langle \boldsymbol{r}_i^2 \rangle$ is the mean square of link length.

In a single-contact approximation, the limiting case $\delta \to 0$ leads to an asymptotic relation proportional to the relation from Fixman's perturbation theory of the first order. The cause of the disagreement lies in the approximate character of the step function used.

1. Introduction

Rubin (1952) used the approximate step function

$$\Delta_{jk} = 1 - \exp\left\{\frac{1}{\delta^2}\left(\sum_{i=j+1}^{k} \boldsymbol{r}_i\right)^2\right\}$$

for excluding the inhibited configurations of the polymer chains, where

$$\left(\sum_{i=j+1}^{k} \boldsymbol{r}_i\right)^2 = \boldsymbol{R}_{j+1,k}^2$$

is the square of the distance of the $j+1$th link of the chain from the kth link and δ is a chosen number, $0 < \delta < a$. The end points of chain links are then the centres of spheres with a radius $\frac{1}{2}\delta > 0$ which must not overlap. With the aid of this step function Rubin determined the upper limit of the mean square of the polymer chain length by a procedure, the mathematical side of which has been criticized by James (1953).

It is the purpose of our paper to show that in a single-contact approximation this approximate step function will provide in the case of small volume effects the correct asymptotics, identical, apart from the numerical constant, with Fixman's perturbation theory of the first order.

It should be noted that the equation (23) in Rubin's paper also employs asymptotic properties of series which appear in the same paper in equation (12). The equation (23), however, does not give in a single-contact approximation the correct result in the limiting case $\delta \to 0$.

2. Calculation

In agreement with Rubin (1952) the unnormalized random walk distribution function with regard to the excluded volume is defined by

$$P_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \exp\left(-\frac{1}{a^2}\sum_{i=1}^{N} \boldsymbol{r}_i^2\right) \prod_{j=0}^{N-1} \prod_{k=j+1}^{N} \theta_{jk}; \qquad (1)$$

the exponential term on the right-hand side of equation (1) is the unnormalized Gaussian random walk distribution without the excluded volume, $a^2 = \frac{2}{3}\langle \boldsymbol{r}_i^2 \rangle$, $\boldsymbol{r}_i$ is the ith vector displacement of the link and θ_{jk} is the Heaviside step function which, in the distribution function (1), excludes the inhibited random walk configurations.

The function θ_{jk} is replaced according to Rubin's paper by an approximate function

$$\Delta_{jk} = 1 - \exp\left\{-\frac{1}{\delta^2}\left(\sum_{i=j+1}^{k} \boldsymbol{r}_i\right)^2\right\} \tag{2}$$

which for $\boldsymbol{R}^2_{j+1,k} \gg \delta^2$ or $\boldsymbol{R}^2_{j+1,k} \ll \delta^2$ accurately replaces the Heaviside step function θ_{jk}. $\delta > 0$ is the chosen number which according to (2) is a measure of the minimum distance of non-neighbouring chain segments, in which occurs the exclusion of the inhibited volume. For the mean-square length of the chain it is true that

$$\langle \boldsymbol{R}_N^2 \rangle = \frac{\int_{-\infty}^{\infty} \dots \int \left(\sum_{i=1}^{N} \boldsymbol{r}_i\right)^2 P_N(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)\, \mathrm{d}\boldsymbol{r}_1 \dots \mathrm{d}\boldsymbol{r}_N}{\int_{-\infty}^{\infty} \dots \int P_N(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)\, \mathrm{d}\boldsymbol{r}_1 \dots \mathrm{d}\boldsymbol{r}_N} \tag{3}$$

which can formally be written (Rubin 1952)

$$\langle \boldsymbol{R}_N^2 \rangle = -\frac{\mathrm{d}}{\mathrm{d}\alpha} \ln I(\alpha)|_{\alpha=0} \tag{4}$$

where

$$I(\alpha) = \int_{-\infty}^{\infty} \dots \int P_N(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) \exp\left\{-\alpha\left(\sum_{i=1}^{N} \boldsymbol{r}_i\right)^2\right\} \mathrm{d}\boldsymbol{r}_1 \dots \mathrm{d}\boldsymbol{r}_N. \tag{5}$$

The function $P_N(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)$ permits the following 'cluster development':

$$P_N(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) = \exp\left(-\frac{1}{a^2}\sum_{i=1}^{N} \boldsymbol{r}_i^2\right)\left(1 - \sum_{j<k} \Omega_{jk} + \sum_{j<k}\sum_{r<s} \Omega_{jk}\Omega_{rs} - \dots\right) \tag{6}$$

where

$$\Omega_{jk} = \exp\left\{-\frac{1}{\delta^2}\left(\sum_{i=j+1}^{k} \boldsymbol{r}_i\right)^2\right\}. \tag{7}$$

Then in a single-contact approximation

$$P_N(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) = \exp\left(-\frac{1}{a^2}\sum_{i=1}^{N} \boldsymbol{r}_i^2\right)\left[1 - \sum_{j=0}^{N-1}\sum_{k=j+1}^{N} \exp\left\{-\frac{1}{\delta^2}\left(\sum_{i=j+1}^{k} \boldsymbol{r}_i\right)^2\right\}\right] \tag{8}$$

and

$$\begin{aligned} I(\alpha) = {} & \int_{-\infty}^{\infty} \dots \int \exp\left\{-\frac{1}{a^2}\sum_{i=1}^{N} \boldsymbol{r}_i^2 - \alpha\left(\sum_{i=1}^{N} \boldsymbol{r}_i\right)^2\right\} \\ & \times \left[1 - \sum_{j<k} \exp\left\{-\frac{1}{\delta^2}\left(\sum_{i=j+1}^{k} \boldsymbol{r}_i\right)^2\right\}\right] \mathrm{d}\boldsymbol{r}_1 \dots \mathrm{d}\boldsymbol{r}_N \\ = {} & \left\{\int_{-\infty}^{\infty} \dots \int \exp\left\{-\frac{1}{a^2}\sum_{i=1}^{N} x_i^2 - \alpha\left(\sum_{i=1}^{N} x_i\right)^2\right\} \mathrm{d}x_1 \dots \mathrm{d}x_N\right\}^3 \\ & - \sum_{j=0}^{N-1}\sum_{k=j+1}^{N}\left\{\int_{-\infty}^{\infty} \dots \int \exp\left\{-\frac{1}{a^2}\sum_{i=1}^{N} x_i^2 - \alpha\left(\sum_{i=1}^{N} x_i\right)^2 - \frac{1}{\delta^2}\left(\sum_{i=j+1}^{k} x_i\right)^2\right\} \mathrm{d}x_1 \dots \mathrm{d}x_N\right\}^3. \end{aligned} \tag{9}$$

Using Rubin's approximate step function, all the integrals are of Gaussian type and, therefore, the Rubin theory may, in principle, be applied to any desired number of contacts.

The evaluation of the integrals which appear in the right-hand side of the equation (9) is given in Rubin's work. By substituting their values into (9), after rearrangement, one obtains

$$I(\alpha) = (\pi a^2)^{3N/2}\left[\frac{1}{(1+Na^2\alpha)^{3/2}} - \sum_{j=0}^{N-1}\sum_{k=j+1}^{N} \frac{\delta^3}{\{a^2\alpha(N\delta^2 + Na^2p - p^2a^2) + \delta^2 + pa^2\}^{3/2}}\right] \tag{10}$$

where $p = k-j$, $k > j$, $j = 0, 1, \ldots, N-1$. Then

$$\ln I(\alpha) = \ln(\pi a^2)^{3N/2} + \ln\left[\frac{1}{(1+Na^2\alpha)^{3/2}} - \sum_{j<k} \frac{\delta^3}{\{a^2\alpha(N\delta^2+Na^2p-p^2a^2)+\delta^2+pa^2\}^{3/2}}\right]$$

and

$$\langle \boldsymbol{R}_N{}^2 \rangle = \frac{\frac{3}{2}Na^2 - \frac{3}{2}\delta^3 a^2 \sum_{j=0}^{N-1} \sum_{k=j+1}^{N} \left\{\frac{N}{(pa^2+\delta^2)^{3/2}} - \frac{p^2a^2}{(pa^2+\delta^2)^{5/2}}\right\}}{1 - \sum_{j=0}^{N-1} \sum_{k=j+1}^{N} \frac{\delta^3}{(\delta^2+pa^2)^{3/2}}}. \tag{11}$$

In the case of small volume effects ($\delta \ll 1$) in the denominators of the fractions in (11) it is possible to neglect δ^2 compared with pa^2. Then the numerator of the right-hand side of (11) is multiplied by the sum of the infinite geometrical series with the quotient

$$\delta^3 \sum_{j=0}^{N-1} \sum_{k=j+1}^{N} \frac{1}{a^3 p^{3/2}}.$$

Up to terms of order δ^3, we have

$$\langle \boldsymbol{R}_N{}^2 \rangle = \tfrac{3}{2}Na^2 + \tfrac{3}{2}\frac{\delta^3}{a} \sum_{j=0}^{N-1} \sum_{k=j+1}^{N} \frac{1}{(k-j)^{1/2}}. \tag{12}$$

According to Fixman (1955)

$$\sum_{j<k} \frac{1}{(k-j)^{1/2}} \sim \tfrac{4}{3}N^{3/2} \quad \text{for} \quad N^{1/2} \gg 1.$$

Now it is possible to show (see e.g. Volkenstejn 1959) that the factor δ in the theory presented is connected with the parameter β of the excluded volume (Fixman's binary cluster integral) in Fixman's perturbation theory in this way:

$$\beta = \int_0^\infty [1 - \exp\{-V(r)/kT\}] 4\pi r^2 \, \mathrm{d}r$$
$$= \tfrac{4}{3}\pi\delta^3. \tag{13}$$

This imposes a certain limitation on the interaction potential $V(r)$. This is in contrast with the Ursell–Mayer theory of imperfect gases, for which we can have either $\beta < 0$ or $\beta > 0$. For the sake of formal agreement let us now introduce into (12) $\frac{3}{2}a^2 = b^2$ and finally, in a single-contact approximation, we obtain

$$\langle \boldsymbol{R}_N{}^2 \rangle = Nb^2 + \sqrt{\pi}\left(\frac{3}{2\pi b^2}\right)^{3/2} b^2 N^{3/2}\beta - \ldots. \tag{14}$$

3. Conclusion

Our paper represents an addendum to Rubin's (1952) paper in which he determined the upper limit of the quantity $\langle \boldsymbol{R}_N{}^2 \rangle \sim N^{3/2}$. The procedure given in that paper was not, however, mathematically correct as was shown by James (1953).

The author's result (14) is in agreement with Rubin's result, but it differs from Fixman's perturbation theory of the first order by a constant factor. The ratio between the constants is $\frac{4}{3}/\sqrt{\pi} = 0{\cdot}75$. This is apparently caused by the fact that the step function Δ_{jk} used by Rubin has, for the distance $\boldsymbol{R}_{j+1,k}{}^2 \simeq \delta^2$, a rounding off of the corner which leads in the case of small volume effects to an enlargement of its mean square length $\langle \boldsymbol{R}_N{}^2 \rangle$ compared with exact perturbation theory according to Fixman (1955).

References

Fixman, M., 1955, *J. Chem. Phys.*, **23**, 1656–9.
James, H. M., 1953, *J. Chem. Phys.*, **21**, 1628–36.
Rubin, R. J., 1952, *J. Chem. Phys.*, **20**, 1940–5.
Volkenstejn, M. V., 1959, *Konfiguracionnaja Statistika Polimernych Cepej* (Leningrad: Moskva).