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Excluded volume in polymer chains

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Abstract. There the theory of the excluded volume effect for a polymer chain is given. The mutual interaction of the monomer units is approximated by the repulsive potential of hard spheres.

In a single-contact approximation formulae were obtained, for small volume effects, which were identical with the Fixman perturbation theory of the first order. The theory can be extended, in principle, to models of a chain with a larger number of contacts.

1. Introduction

The Ursell–Mayer statistical theory of imperfect gases has been applied by many authors (e.g. Fixman 1955, Grimley 1959, Alexandrowicz 1967, etc.) to various models of polymer chains with a variable link length. Their theory emanates from the assumption that the factor $\Pi^{N}{}_{k} \exp\{-V(R_{jk})/kT\}$, which considers the interaction between the gas particles, may be replaced by the expression $\Pi^{N}_{j<k} \exp\{-\beta\delta(\boldsymbol{R}_{jk})\}$, where $V(R_{jk})$ is the interaction potential between the jth and kth particle, the distance between which is $R_{jk} = |\boldsymbol{R}_{jk}|$, β is the effective excluded volume and $\delta(\boldsymbol{R}_{jk})$ is the three-dimensional Dirac δ-function. The said assumption means that the authors consider the volume effects as small *a priori*.

On the other hand, James (1953) took into consideration the number of ways in which the chain, described in the said model, may be extended if there is one link added to it without violating the condition of the excluded volume. In this way he came to the conclusion that his theory probably overestimates the effect of the excluded volume.

Rubin (1952) estimated the upper limit of the quantity $\langle \boldsymbol{R}_N{}^2 \rangle$—the mean-square length of polymer chain—using the assumption that the interaction potential between the monomer units can be approximated by the repulsive potential of hard spheres with a radius $\frac{1}{2}\delta > 0$. Owing to difficulties of a mathematical character this estimate has not been carried out in Rubin's (1952) paper for the three-dimensional case. The theory, resulting from Rubin's assumption, completes evidently the two said theories in the sense that it operates only with the permissible configurations in which the condition $|\boldsymbol{R}_{jk}| > \delta$ is fulfilled.

This work aims to show that in the single-contact approximation the Rubin assumptions lead to the Fixman perturbation theory of first order.

2. Calculation

According to Rubin (1952), the mean-square length of the chain can be formally written as

$$\langle \boldsymbol{R}_N{}^2 \rangle = -\left.\frac{I'(\alpha)}{I(\alpha)}\right|_{\alpha=0} \tag{1}$$

where

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

where $P_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ is the unnormalized random walk distribution function of the chain, in which is included the repulsive interaction of hard spheres:

$$P_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \exp\left(-\frac{1}{a^2}\sum_{i=1}^{N} \boldsymbol{r}_i{}^2\right) \prod_{j=0}^{N-1} \prod_{k=j+1}^{N} \theta_{jk}. \tag{3}$$

The exponential factor on the right-hand side of expression (3) is the Gaussian distribution of N random walks, $a^2 = \frac{2}{3}\langle \boldsymbol{r}_i^2\rangle$, and the second factor modifies this distribution with respect to the excluded volume effect. θ_{jk} is the Heaviside step function, which, according to Kyselka (1968), can be written

$$\theta_{jk} = \lim_{\epsilon \to 0_+} \frac{\mathrm{i}}{2\pi} \int_{-\infty}^{\infty} \frac{\exp\{-\mathrm{i}\tau(\boldsymbol{R}_{jk}^2 - \delta^2)\}}{\tau + \mathrm{i}\epsilon} \mathrm{d}\tau = \begin{array}{ll} 1 & \text{for } \boldsymbol{R}_{jk}^2 > \delta^2 \\ \frac{1}{2} & \text{for } \boldsymbol{R}_{jk}^2 = \delta^2 \\ 0 & \text{for } \boldsymbol{R}_{jk}^2 < \delta^2. \end{array} \tag{4}$$

The step function θ_{jk} is a special case of the characteristic function and thus

$$\begin{aligned} \prod_{j<k}^{N} \theta(\boldsymbol{R}_{jk}^2 - \delta^2) &= \prod_{j<k}^{N} \{1 - \theta(\delta^2 - \boldsymbol{R}_{jk}^2)\} \\ &= 1 - \sum_{j<k} \Omega_{jk} + \sum_{j<k} \sum_{r<s} \Omega_{jk}\Omega_{rs} - \ldots \\ \Omega_{jk} &= \theta(\delta^2 - \boldsymbol{R}_{jk}^2) \end{aligned} \tag{5}$$

is valid.

In the Ursell–Mayer theory, the following potential corresponds to the approximation of the repulsion of monomer units by hard spheres:

$$V(R_{jk}) = \begin{cases} \infty & \text{for } R_{jk} < \delta \\ 0 & \text{for } R_{jk} > \delta. \end{cases} \tag{6}$$

These conditions are satisfied only for small values of R_{jk} which in actual fact influence the choice of the positive number δ. Under the conditions (6) the effective excluded volume (Fixman's binary cluster integral) is

$$\beta = 4\pi \int_0^{\infty} \left[1 - \exp\left\{-\frac{V(R_{jk})}{kT}\right\}\right] \boldsymbol{R}_{jk}^2 \, \mathrm{d}R_{jk} = \tfrac{4}{3}\pi\delta^3. \tag{7}$$

In a single-contact approximation,

$$\prod_{j=0}^{N-1} \prod_{k=j+1}^{N} \theta_{jk} \simeq 1 - \sum_{j=0}^{N-1} \sum_{k=j+1}^{N} \Omega_{jk}$$

according to (5). This expression will be substituted into (2) and the integration over the space variables can be preceded by the integration over the variable τ. The integral over the space variables is given in Rubin (1952). One may then obtain

$$\begin{aligned} I(\alpha) &= \frac{(\pi a^2)^{3N/2}}{(1 + Na^2\alpha)^{3/2}} \left\{1 - \sum_{j=0}^{N-1} \sum_{k=j+1}^{N} \lim_{\epsilon \to 0_+} \frac{\mathrm{i}}{2\pi} \int_{-\infty}^{\infty} \frac{\exp(-\mathrm{i}\delta^2\tau)}{\tau + \mathrm{i}\epsilon} \frac{\mathrm{d}\tau}{(1 + \mathrm{i}\lambda\tau)^{3/2}}\right\} \\ \lambda &= pa^2 \left(1 - \frac{pa^2\alpha}{1 + Na^2\alpha}\right) > 0. \end{aligned} \tag{8}$$

The validity of the single-contact approximation is determined by the condition $I(0) > 0$; from this follows the magnitude of the parameter δ. Should this condition not be satisfied, expression (8) could, for large values of N, assume negative values. The limiting expression in the curly bracket of relation (8) has the value (see appendix)

$$W\left(\frac{\delta^2}{\lambda}\right) = \frac{2}{\sqrt{\pi}} \int_0^{\delta^2/\lambda} \sqrt{t}\, \mathrm{e}^{-t} \, \mathrm{d}t \tag{9}$$

and for the expansion factor of the chain, $\alpha^2 = \langle \boldsymbol{R}_N^2 \rangle / \frac{3}{2} N a^2$, we have according to (2)

$$\alpha^2 = 1 + \frac{4\gamma^{3/2}}{3N\sqrt{\pi}} \frac{\sum_{s=1}^{N} (N-s+1) \frac{e^{-\gamma/s}}{\sqrt{s}}}{1 - \frac{2}{\sqrt{\pi}} \sum_{s=1}^{N} (N-s+1) \int_0^{\gamma/s} \sqrt{\tau}\, e^{-\tau}\, d\tau} \tag{10}$$

$\gamma = \delta^2/a^2$ and the double summation has been replaced by a single one. In the hard-sphere approximation the excluded volume is characterized by the parameter z

$$z = \frac{4\gamma^{3/2}}{3\sqrt{\pi}} \sqrt{N} = \left(\frac{3}{2\pi b^2}\right)^{3/2} \beta\sqrt{N}, \qquad a^2 = \tfrac{2}{3} b^2.$$

By rearranging expression (10) we obtain in the expansion in terms of γ, in the lowest power of γ,

$$\alpha^2 = 1 + \frac{4\gamma^{3/2}}{3\sqrt{\pi}} \left(\sum_{s=1}^{N} \frac{1}{\sqrt{s}} + \frac{1}{N} \sum_{s=1}^{N} \frac{1}{\sqrt{s}} - \frac{1}{N} \sum_{s=1}^{N} \sqrt{s} \right). \tag{11}$$

By using the asymptotic expansion of the function $\Sigma_{s=1}^{N} 1/s^n$ we obtain after introducing the parameter z

$$\alpha^2 = 1 + \tfrac{4}{3} z \left(1 + \frac{\frac{3}{4}\zeta(\frac{1}{2})}{\sqrt{N}} + \ldots \right)$$

where $\zeta(n)$ is Riemann's ζ-function. The linear approximation in the parameter z is

$$\alpha^2 = 1 + \tfrac{4}{3} z \tag{12}$$

which is valid for

$$z\sqrt{N} \ll 1. \tag{13}$$

5. Conclusion

The result of this paper is a re-evaluation of the results of Rubin (1952) who was concerned with estimating the upper limit of the quantity $\langle \boldsymbol{R}_N^2 \rangle$. Rubin obtained explicit estimates in the following cases: (i) a Gaussian repulsion of monomer units and (ii) a hard-sphere repulsion of monomer units. In case (i) these estimates were given by Rubin in 2, 3 and 4 dimensions, in the case (ii) in 2 and 4 dimensions only. The important case of a three-dimensional space remained unsolved. In the paper by Kyselka (1969 a) a single-contact approximation was calculated under assumption (i) and it was found that for small volume effects the result differs from the Fixman perturbation theory by a constant factor. For case (ii) the author, in a single-contact approximation for small volume effects, obtained a result that was identical with the Fixman perturbation theory of the first order. Therefore, it is possible to employ assumption (i) to estimate the upper limit of the quantity $\langle \boldsymbol{R}_N^2 \rangle$, but a more accurate estimate can be obtained by using the assumption (ii).

Appendix

1. *Integral*:

$$I = \int_{-\infty}^{\infty} \cdots \int \exp\left\{ -\alpha \left(\sum_{i=1}^{N} x_i \right)^2 - \beta \sum_{i=1}^{N} x_i^2 - \gamma \left(\sum_{i=j+1}^{k} x_i \right)^2 \right\} dx_1 \ldots dx_N.$$

Solution: Let A denote the quadratic form in the exponent. Then A is positive definite, and thus there exists the linear transformation

$$x_i = \sum_{\nu=1}^{N} t_{i\nu} \xi_\nu, \qquad i = 1, 2, \ldots, N$$

which transforms the quadratic form to a sum of squares

$$\sum_{i,j} a_{ij}x_i x_j = \sum_k \xi_k^2$$

where a_{ij} denotes the coefficients of the quadratic form A. Thus

$$\sum_{\nu}\sum_{\lambda}\sum_{ij} a_{ij}t_{i\nu}\xi_\nu t_{j\lambda}\xi_\lambda = \sum_k \xi_k^2$$

i.e.

$$\sum_{\nu\lambda} (\tilde{T}AT)_{\nu\lambda}\xi_\nu\xi_\lambda = \sum_{\nu\lambda} \delta_{\nu\lambda}\xi_\nu\xi_\lambda$$

i.e.

$$\tilde{T}AT = E$$

and because $|\tilde{T}| = |T|$ is $|T|^2|A| = 1$, $|T| = |A|^{-1/2}$, and therefore

$$\mathrm{d}x_1 \dots \mathrm{d}x_N = \frac{\partial(x_1, \dots, x_N)}{\partial(\xi_1, \dots, \xi_N)}\mathrm{d}\xi_1 \dots \mathrm{d}\xi_N = |T|\,\mathrm{d}\xi_1 \dots \mathrm{d}\xi_N$$

and finally

$$I = \int_{-\infty}^{\infty}\dots\int \exp\Big(-\sum_i \xi_i^2\Big)\frac{\mathrm{d}\xi_1 \dots \mathrm{d}\xi_N}{|A|^{1/2}} = \frac{1}{|A|^{1/2}}\left\{\int_{-\infty}^{\infty}\exp(-\xi^2)\,\mathrm{d}\xi\right\}^N = \frac{\pi^{N/2}}{|A|^{1/2}}.$$

It is thus sufficient to find the determinant of the quadratic form A equal to

$$|A| = \begin{array}{cc} & \begin{array}{ccccccccccc} & & & & j+1 & & k & & & & \end{array} \\ \begin{array}{c} \\ \\ \\ \\ j+1 \\ \\ \\ k \\ \\ \\ \\ \end{array} & \begin{vmatrix} \alpha+\beta & \alpha & \dots & \alpha & \alpha & \dots & \alpha & \alpha & \dots & \alpha \\ \alpha & \alpha+\beta & \dots & \alpha & \alpha & \dots & \alpha & \alpha & \dots & \alpha \\ \vdots & & \ddots & \vdots & \vdots & & \vdots & \vdots & & \vdots \\ \alpha & \alpha & \dots & \alpha+\beta & \alpha & \dots & \alpha & \alpha & \dots & \alpha \\ \alpha & \alpha & \dots & \alpha & \alpha+\beta+\gamma & \alpha+\gamma \dots & \alpha+\gamma & \alpha & \dots & \alpha \\ \vdots & \vdots & & \vdots & \alpha+\gamma & \alpha+\beta+\gamma \dots & \alpha+\gamma & \vdots & & \vdots \\ \vdots & \vdots & & \vdots & \vdots & \ddots & & \vdots & & \vdots \\ \alpha & \alpha & \dots & \alpha & \alpha+\gamma & \dots & \alpha+\beta+\gamma & \alpha & \dots & \alpha \\ \alpha & \alpha & \dots & \alpha & \alpha & \dots & \alpha & \alpha+\beta & \dots & \alpha \\ \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots & \ddots & \vdots \\ \alpha & \alpha & \dots & \alpha & \alpha & \dots & \alpha & \alpha & \dots & \alpha+\beta \end{vmatrix} \end{array}.$$

By elementary transformations of this determinant we obtain

$$|A| = \beta^{N-j-1}\begin{vmatrix} N\alpha+\beta & \alpha & \dots & \alpha & p\alpha \\ 0 & \beta & \dots & 0 & 0 \\ \vdots & & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & \beta & 0 \\ p\gamma & 0 & \dots & 0 & \beta+p\gamma \end{vmatrix}$$

$$= \beta^{N-j-1}\{(N\alpha+\beta)\beta^{j-1}(\beta+p\gamma)+(-1)^{j+2}p\gamma(-1)^{j+1}p\alpha\beta^{j-1}\}$$

therefore

$$|A| = \beta^{N-2}\{(N\alpha+\beta)(\beta+p\gamma)-p^2\alpha\gamma\}, \qquad p = k-j.$$

For the integral we obtain

$$I = \frac{\pi^{N/2}}{[\beta^{N-2}\{(N\alpha+\beta)(\beta+p\gamma)-p^2\alpha\gamma\}]^{1/2}}$$

2. *Integral*:

$$\lim_{\epsilon\to 0_+} \frac{1}{2\pi \mathrm{i}} \int_{-\infty}^{\infty} \frac{\mathrm{d}\tau}{\tau+\mathrm{i}\epsilon} \frac{\exp(-\mathrm{i}\delta^2\tau)}{(1-\mathrm{i}\lambda\tau)^{3/2}}.$$

Solution:

$$I = \int_{-\infty}^{\infty} \frac{\mathrm{d}\tau}{\tau+\mathrm{i}\epsilon} \frac{\exp(-\mathrm{i}\delta^2\tau)}{(1-\mathrm{i}\lambda\tau)^{3/2}} = \frac{\mathrm{i}}{\lambda^{3/2}} \int_{-\infty}^{\infty} \frac{\mathrm{d}\tau}{\mathrm{i}\tau-\epsilon} \frac{\exp(-\mathrm{i}\delta^2\tau)}{(\rho-\mathrm{i}\tau)^{3/2}}$$

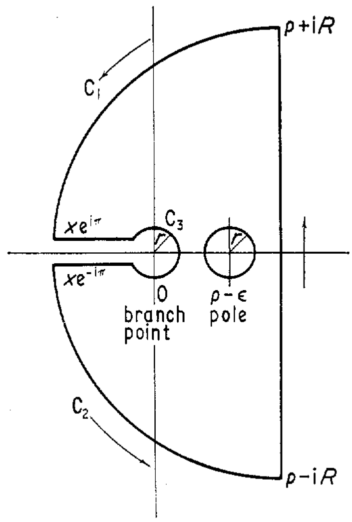
$$= -\frac{2\mathrm{i}}{\lambda^{3/2}} \frac{\mathrm{d}}{\mathrm{d}\rho} \int_{-\infty}^{\infty} \frac{\mathrm{d}\tau}{\mathrm{i}\tau-\epsilon} \frac{\exp(-\mathrm{i}\delta^2\tau)}{(\rho-\mathrm{i}\tau)^{1/2}}\bigg|_{\rho=1/\lambda}$$

Set $\rho-\mathrm{i}\tau = z$; then $\rho - z = \mathrm{i}\tau$, $\mathrm{i}\,\mathrm{d}\tau = -\mathrm{d}z$ and

$$I = \frac{2}{\lambda^{3/2}} \frac{\mathrm{d}}{\mathrm{d}\rho} \int_{\rho-\mathrm{i}\infty}^{\rho+\mathrm{i}\infty} \frac{\mathrm{d}z \exp\{-\delta^2(\rho-z)\}}{(z-\rho+\epsilon)\sqrt{z}}\bigg|_{\rho=\lambda^{-1}}$$

$$= \frac{2}{\lambda^{3/2}} \frac{\mathrm{d}}{\mathrm{d}\rho} \left\{\exp(-\delta^2\rho) \int_{\rho-\mathrm{i}\infty}^{\rho+\mathrm{i}\infty} \frac{\exp(\delta^2 z)\,\mathrm{d}z}{(z-\rho+\epsilon)\sqrt{z}}\right\}.$$

By integrating $\exp(\delta^2 z)/(z-\rho+\epsilon)\sqrt{z}$ along the path C



we obtain

$$\int_{\rho-\mathrm{i}R}^{\rho+\mathrm{i}R} + \int_{C_1} + \int_{C_2} + \int_{C_3} + \mathrm{i}\int_0^R \frac{\exp(-\delta^2 x)\,\mathrm{d}x}{(x+\rho-\epsilon)\sqrt{x}} + \mathrm{i}\int_0^R \frac{\exp(-\delta^2 x)\,\mathrm{d}x}{(x+\rho-\epsilon)\sqrt{x}} = 2\pi\mathrm{i}\frac{\exp\{\delta^2(\rho-\epsilon)\}}{(\rho-\epsilon)^{1/2}}.$$

In the limit $\epsilon\to 0_+$, $R\to\infty$, $r\to 0$ is

$$\int_{\rho-\mathrm{i}\infty}^{\rho+\mathrm{i}\infty} \frac{\exp(\delta^2 z)\,\mathrm{d}z}{(z-\rho+\epsilon)\sqrt{z}} = 2\mathrm{i}\left\{\frac{\pi\exp(\delta^2\rho)}{\sqrt{\rho}} - \int_0^{\infty} \frac{\exp(-\delta^2 x)}{(x+\rho)\sqrt{x}}\,\mathrm{d}x\right\}.$$

Thus

$$I = \frac{4\mathrm{i}}{\lambda^{3/2}} \frac{\mathrm{d}}{\mathrm{d}\rho} \left\{\frac{\pi}{\sqrt{\rho}} - \exp(-\delta^2\rho) \int_0^{\infty} \frac{\exp(-\delta^2 x)}{(x+\rho)\sqrt{x}}\,\mathrm{d}x\right\}.$$

Now we have

$$\frac{\exp\{-\delta^2(x+\rho)\}}{x+\rho} = \int_{\delta^2}^{\infty} \exp\{-(x+\rho)t\}\,\mathrm{d}t$$

i.e.

$$I = \frac{4\mathrm{i}}{\lambda^{3/2}}\frac{\mathrm{d}}{\mathrm{d}\rho}\left[\frac{\pi}{\sqrt{\rho}} - \int_0^{\infty}\frac{\mathrm{d}x}{\sqrt{x}}\int_{\delta^2}^{\infty}\exp\{-(x+\rho)t\}\,\mathrm{d}t\right]$$

$$= \frac{4\mathrm{i}}{\lambda^{3/2}}\frac{\mathrm{d}}{\mathrm{d}\rho}\left\{\frac{\pi}{\sqrt{\rho}} - \int_{\delta^2}^{\infty}\exp(-\rho t)\,\mathrm{d}t\int_0^{\infty}\frac{\exp(-xt)}{\sqrt{x}}\,\mathrm{d}x\right\}.$$

The inner integral is changed by the substitution $xt = \xi^2$ into the integral

$$\frac{2}{\sqrt{t}}\int_0^{\infty}\exp(-\xi^2)\,\mathrm{d}\xi = \left(\frac{\pi}{t}\right)^{1/2}$$

so that

$$I = \frac{4\mathrm{i}}{\lambda^{3/2}}\frac{\mathrm{d}}{\mathrm{d}\rho}\left\{\frac{\pi}{\sqrt{\rho}} - \sqrt{\pi}\int_{\delta^2}^{\infty}\frac{\exp(-\rho t)}{\sqrt{t}}\,\mathrm{d}t\right\}, \qquad \rho = \lambda^{-1}.$$

Subsequently

$$I = 4\mathrm{i}\lambda^{-3/2}\left\{-\tfrac{1}{2}\pi\rho^{-3/2} + \sqrt{\pi}\int_{\delta^2}^{\infty}\exp(-\rho t)\sqrt{t}\,\mathrm{d}t\right\}$$

$$= -2\pi\mathrm{i} + 4\mathrm{i}\sqrt{\pi}\int_{\delta^2/\lambda}^{\infty} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t$$

i.e.

$$I = -2\pi\mathrm{i}\left(1 - \frac{2}{\sqrt{\pi}}\int_{\delta^2/\lambda}^{\infty} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t\right)$$

$$= -2\pi\mathrm{i}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\infty} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t + \frac{2}{\sqrt{\pi}}\int_0^{\delta^2/\lambda} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t\right).$$

Since

$$\frac{2}{\sqrt{\pi}}\int_0^{\infty} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t = \frac{2}{\sqrt{\pi}}\Gamma(\tfrac{3}{2}) = 1$$

we obtain finally

$$I = -2\pi\mathrm{i}\frac{2}{\sqrt{\pi}}\int_0^{\delta^2/\lambda} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t$$

i.e.

$$\lim_{\epsilon\to 0+}\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{\infty}\frac{\mathrm{d}\tau}{\tau+\mathrm{i}\epsilon}\frac{\exp(-\mathrm{i}\delta^2\tau)}{(1-\mathrm{i}\lambda\tau)^{3/2}} = -\frac{2}{\sqrt{\pi}}\int_0^{\delta^2/\lambda} t^{1/2}\,\mathrm{e}^{-t}\,\mathrm{d}t.$$

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