# POLYMER DIMENSIONS IN
# SOLUTIONS OF FINITE CONCENTRATIONS

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In a good solvent $\langle R^2 \rangle$, the mean square radius of gyration of a flexible polymer molecule, should decrease with increasing polymer concentration. Standard methods in statistical mechanics may be used to express $\langle R^2 \rangle$ as a power series in the concentration $c$. In dilute solutions, $\langle R^2 \rangle = \langle R^2 \rangle_0 (1 + Kc)$, where $\langle R^2 \rangle_0$ is the mean-square-radius of gyration at infinite dilution. If $c$ is expressed in g cm$^{-3}$, an approximate evaluation of $K$ gives $K = (2/3\pi)^{\frac{1}{2}} M^2 (\partial A_2 / \partial M)$, where $M$ is the molecular weight of the polymer, and $A_2$ is the usual second virial coefficient in the osmotic pressure series.

## 1. INTRODUCTION

If the osmotic pressure of a solution of flexible polymer molecules is not proportional to the absolute temperature, the dimensions of the polymer chains must vary with the polymer concentration. This effect will influence many properties of polymer solutions. Obvious ones are the concentration dependence of the viscosity and the light scattered by moderately concentrated solutions. Some recent work by North [1] indicates that an effect of this sort is also important in the kinetics of reactions between polymeric free radicals. In this paper we indicate how the formula expressing the size of a polymer molecule as a power series in the concentration may be derived, and we give an approximate calculation of the coefficient of the term in this series which is linear in the concentration.

## 2. MEAN DIMENSIONS AT FINITE CONCENTRATION

Consider one chain molecule in a large volume $V$ of solvent. Let $f_1(R, \mathbf{X})\mathrm{d}R\mathrm{d}\mathbf{X}$ be the probability that the centre of gravity of the chain is at $\mathbf{X}$ to within $\mathrm{d}\mathbf{X}$, and the radius of gyration $R$ to within $\mathrm{d}R$. Of course, $f_1(R, \mathbf{X}) = V^{-1} f_1(R)$, where $f_1(R)\mathrm{d}R$ is the probability that the chain has radius of gyration $R$ to within $\mathrm{d}R$. Also,

$$\int f_1(R, \mathbf{X})\mathrm{d}\mathbf{X} = f_1(R), \quad \int f_1(R)\mathrm{d}\mathbf{R} = 1.$$

In what follows it will be convenient to replace the pair $(R, \mathbf{X})$ by the single symbol $\mathbf{Q}$ and to refer to $\mathbf{Q}$ as a configurational vector.

Consider now a solution containing $n$ identical chains in a volume $V$. The configuration of the chains is given by the $n$ configurational vectors $\mathbf{Q}_1, \mathbf{Q}_2, \ldots \mathbf{Q}_n$, which we contract to $\mathbf{Q}^n$. The solution is characterized by a potential of mean force $w(\mathbf{Q}^n)$, which depends on the chain configuration, and the configurational partition function $Z_n$ is defined by

$$n! Z_n = V^n \Omega_n,$$

where

$$\Omega_n = \int f_1(\mathbf{Q}^n) W(\mathbf{Q}^n)\mathrm{d}\mathbf{Q}^n. \tag{1}$$

In eqn. (1),

$$f_1(\mathbf{Q}^n) = f_1(\mathbf{Q}_1) \ldots f_1(\mathbf{Q}_n),$$

and

$$W(\mathbf{Q}^n) = \exp\left[-w(\mathbf{Q}^n)/kT\right].$$

If the potential of mean force $w(\mathbf{Q}^n)$ vanishes for all configurations $\mathbf{Q}^n$,

$$\Omega_n = 1, \quad \mathbf{Z}_n = V^n/n!,$$

and the osmotic pressure calculated as $kT \, \partial(\ln Z_n)/\partial V$, follows van't Hoff's law.

The probability $f_n(\mathbf{Q}^m)\mathrm{d}\mathbf{Q}^m$, that with $n$ chains in the volume $V$, a specified set of $m$ chains ($m \leqslant n$) has the configuration $\mathbf{Q}^m$ to within $\mathrm{d}\mathbf{Q}^m$ is given by

$$\Omega_n f_n(\mathbf{Q}^m) = \int f_1(\mathbf{Q}^n)W(\mathbf{Q}^n)\mathrm{d}\mathbf{Q}^{n-m}, \tag{2}$$

where the notation $\mathrm{d}\mathbf{Q}^{n-m}$ means that the integrations over the configurations $\mathbf{Q}^m$ of the specified chains are omitted. We are interested in a special case of eqn. (2), namely that with $m = 1$. We denote the corresponding probability density by $f_n(\mathbf{Q}_1)$ so that

$$\Omega_n f_n(\mathbf{Q}_1) = \int f_1(\mathbf{Q}^n)W(\mathbf{Q}^n)\mathrm{d}\mathbf{Q}^{n-1}. \tag{3}$$

$\langle R_1^2 \rangle$, the mean square radius of gyration of the chain (and of course any chain in the solution) is given by

$$\langle R_1^2 \rangle = \int R_1^2 f_n(\mathbf{Q}_1)\mathrm{d}\mathbf{Q}_1 = \int R_1^2 f_n(R_1)\mathrm{d}R_1. \tag{4}$$

At infinite dilution, $f_n(\mathbf{Q}_1) \to f_1(\mathbf{Q}_1)$ and $\langle R_1^2 \rangle \to \langle R_1^2 \rangle_0$, say, where

$$\langle R_1^2 \rangle_0 = \int R_1^2 f_1(\mathbf{Q}_1)\mathrm{d}\mathbf{Q}_1. \tag{5}$$

Techniques already familiar from the theory of real gases [2] may be used to derive from eqn. (1) and (3), an expansion of $f_n(\mathbf{Q}_1)$ in a power series in the concentration $(n/V)$. The corresponding expansion of $\langle R_1^2 \rangle$ then follows from eqn. (4). We shall derive only the first two terms of these series here. The full series expansions are in any case most easily derived by starting from the grand partition function for the polymer solution.

We need the expansion [2]

$$W(\mathbf{Q}^n) = W(\mathbf{Q}^{n-1}) + \sum_k U_2(\mathbf{Q}_1\mathbf{Q}_k)W(\mathbf{Q}^{n-2}) + \ldots, \tag{6}$$

where

$$U_2(\mathbf{Q}_i\mathbf{Q}_k) = W(\mathbf{Q}_i\mathbf{Q}_k) - 1,$$

and if only the terms written in eqn. (6) are used, the results will be correct in the binary complex approximation in which triple and higher-order complexes of chain molecules are ignored. It is well known that this approximation gives the first two terms in the virial expansion of the osmotic pressure, and in the present problem, it gives the first two terms of the expansion of $f_n(\mathbf{Q}_1)$ as a power series in the concentration. In this binary complex approximation we can replace the second term on the right in eqn. (6) by

$$W(\mathbf{Q}^{n-1})\sum_k U_2(\mathbf{Q}_1\mathbf{Q}_k),$$

so that

$$W(\mathbf{Q}^n) = W(\mathbf{Q}^{n-1})[1 + \sum_k U_2(\mathbf{Q}_1\mathbf{Q}_k)]. \tag{7}$$

Using this in eqn. (3) we have with the aid of eqn. (2),

$$(\Omega_n/\Omega_{n-1})f_n(\mathbf{Q}_1) = f_1(\mathbf{Q}_1)[1 + (n-1)\int f_{n-1}(\mathbf{Q}_2)U_2(\mathbf{Q}_1\mathbf{Q}_2)\mathrm{d}\mathbf{Q}_2]. \tag{8}$$

In the binary complex approximation we can replace $f_{n-1}(\mathbf{Q}_2)$ under the integral sign in eqn. (8) by $f_1(\mathbf{Q}_2)$. Also, since $n$ is large we can replace the factor $(n-1)$ by $n$. Then,

$$(\Omega_n/\Omega_{n-1})f_n(\mathbf{Q}_1) = f_1(\mathbf{Q}_1)[1 + n\int f_1(\mathbf{Q}_2)U_2(\mathbf{Q}_1\mathbf{Q}_2)\mathrm{d}\mathbf{Q}_2]. \tag{9}$$

By integrating this equation over $Q_1$, we prove that

$$(\Omega_n/\Omega_{n-1}) = 1 + (n/V)B, \qquad (10)$$

where

$$\left.\begin{array}{l} B = V\!\int\! f_1(\mathbf{Q}_1)f_1(\mathbf{Q}_2)U_2(\mathbf{Q}_1\mathbf{Q}_2)\mathrm{d}\mathbf{Q}_1\mathrm{d}\mathbf{Q}_2 \\ = \int\! B(R_1R_2)f_1(R_1)f_1(R_2)\mathrm{d}R_1\mathrm{d}R_2. \end{array}\right\} \qquad (11)$$

In the second eqn. (11) we have introduced a quantity $B(R_1,R_2)$ defined by

$$VB(R_1R_2) = \int U_2(\mathbf{Q}_1\mathbf{Q}_2)\mathrm{d}\mathbf{X}_1\mathrm{d}\mathbf{X}_2. \qquad (12)$$

$B(R_1R_2)$ is the excluded volume integral for two chain molecules at infinite dilution with fixed radii of gyration $R_1$ and $R_2$. $B$, which is the mean value of this quantity, is the familiar excluded volume integral which determines the second virial coefficient in the osmotic pressure series. To verify this latter statement, we note that the binary complex approximation is valid if $nB/V \ll 1$, so that the solution of eqn. (10) may be taken as

$$\Omega_n = \exp(\tfrac{1}{2}Bn^2/V).$$

The osmotic pressure follows at once. We have

$$\Pi = kT \,\partial(\ln Z_n)/\partial V = kT(n/V)[1 - \tfrac{1}{2}(n/V)B]. \qquad (13)$$

Returning to eqn. (9), we substitute for $\Omega_n/\Omega_{n-1}$ from eqn. (10) integrate over the translational coordinates $\mathbf{X}_1$ and $\mathbf{X}_2$, and introduce $B(R_1R_2)$ from eqn. (12). Remembering that $nB/V \ll 1$, the result is

$$f_n(R_1) = f_1(R_1)\{1 + (n/V)[\int B(R_1R_2)f_1(R_2)\mathrm{d}R_2 - B]\}, \qquad (14)$$

correct to terms linear in $(n/V)$. If we multiply this equation by $R_1^2$ and integrate over $R_1$, we obtain

$$\langle R_1^2 \rangle = \langle R_1^2 \rangle_0 + (n/V)[\langle R_1^2 B(R_1R_2)\rangle - \langle R_1^2\rangle_0 B], \qquad (15)$$

where

$$\langle R_1^2 B(R_1R_2)\rangle = \int R_1^2 B(R_1R_2)f_1(R_1)f_1(R_2)\mathrm{d}R_1\mathrm{d}R_2. \qquad (16)$$

Eqn. (15) is the fundamental equation expressing the concentration dependence of the size of chain molecules in dilute solutions. The quantity which determines this concentration dependence is seen to be the fluctuation in $R_1^2 B(R_1R_2)$ at infinite dilution. An approximate calculation of this quantity is given in the next section.

### 3. APPROXIMATE EVALUATION OF THE FLUCTUATION TERM

If we represent a chain molecule by a set of $N+1$ beads joined by links of length $l$ which are freely jointed at the beads, a fairly reliable expression for $B(R_1R_2)$ is available.[3, 4] We have

$$B(R_1R_2) = \beta N^2 F(x), \qquad (17)$$

where $\beta$ is the excluded volume integral for a pair of chain beads, and $F$ is a certain function of the variable $x$ defined by

$$x = -[3/2\pi(R_1^2 + R_2^2)]^{\frac{3}{2}}\beta N^2. \qquad (18)$$

Graphs of $F(x)$ have been given.[3, 5] In a good solvent, $x$ is positive and $F(x)$ decreases slowly with $x$, and because of this we can reduce the fluctuation term in eqn. (15) by expanding $B(R_1R_2)$ in a Taylor series about the point $R_1 = (\langle R_1^2\rangle_0)^{\frac{1}{2}}$, $R_2 = (\langle R_2^2\rangle_0)^{\frac{1}{2}}$ and retaining only the leading terms. Of course, $\langle R_1^2\rangle_0 = \langle R_2^2\rangle_0 = \langle R^2\rangle_0$, say, since all chains have the same size. This approximation gives

$$\langle R_1^2 B(R_1R_2)\rangle - \langle R_1^2\rangle_0 B = (\partial B/\partial R_1)^*[\langle R^3\rangle_0 - \langle R\rangle_0\langle R^2\rangle_0], \qquad (19)$$

where the star indicates that the derivative is to be evaluated at $R_1 = R_2 = (\langle R^2 \rangle_0)^{\frac{1}{2}}$. $(\partial B/\partial R_1)^*$ can be expressed in terms of the second virial coefficient $A_2$ in the osmotic pressure series

$$\Pi = \mathbf{R}T[(c/M) + A_2 c^2 + \ldots],$$

where $c$ is the polymer concentration in g cm$^{-3}$, and $M$ its molecular weight. In current theories [3,4] $A_2$ is calculated as

$$A_2 = -\tfrac{1}{2}\beta(\mathbf{N}/M_0^2)F(x^*), \tag{20}$$

where $N$ is Avogadro's number, $M_0$ the molecular weight of a chain bead and

$$x^* = -[3/4\pi\langle R^2 \rangle_0]^{\frac{3}{2}}\beta N^2. \tag{21}$$

$F$ is the same function as in eqn. (17). It follows from eqn. (17), (18), (20) and (21) that

$$(\partial B/\partial R_1)^* = (3M^2/2N)(\langle R^2 \rangle_0)^{-\frac{1}{2}}(\partial A_2/\partial M). \tag{22}$$

It remains therefore to estimate the term in square brackets on the right of eqn. (19). To do this we need the distribution function $f_1(R)$ for the radius of gyration of a single chain in a large volume of solvent. This function is not known because the problem of the " volume effect " has not yet been solved. To complete our approximate calculation, we assume that $f_1(R)$ is Gaussian. In this case,

$$\langle R^3 \rangle_0 - \langle R \rangle_0\langle R^2 \rangle_0 \doteq (2/3\pi^{\frac{1}{2}})^{\frac{3}{2}}(\langle R^2 \rangle_0)^{\frac{3}{2}}. \tag{23}$$

From eqn. (15), (19), (22) and (23), we obtain,

$$\left.\begin{aligned}
\langle R^2 \rangle &= \langle R^2 \rangle_0(1 + Kc), \\
K &= (2/3\pi)^{\frac{1}{2}}M^2(\partial A_2/\partial M)
\end{aligned}\right\} \tag{24}$$

for the mean square radius $\langle R^2 \rangle$ at concentration $c$ in terms of $\langle R^2 \rangle_0$, the mean-square-radius at infinite dilution.

Experimental measurements of the dependence of $A_2$ on molecular weight are represented adequately by the formula

$$A_2 = CM^{-\varepsilon},$$

so that

$$M^2(\partial A_2/\partial M) = -\varepsilon M A_2.$$

Typical values of $\varepsilon$ are 0·11 for polyisobutylene in cyclohexane [6] at 30°C, 0·16 for $\alpha$-methyl styrene in toluene [7] at 25°C and 0·19 for polyisobutylene in toluene [8] at 25°C. The concentration dependence of $\langle R^2 \rangle$ in dilute solutions is therefore less marked than that of $\Pi/c$.

## 4. Discussion

We emphasize again that our formula for $K$ in eqn. (24) is only approximate. Two approximations are involved. First, that $B(R_1 R_2)$ is slowly varying in the neighbourhood of $R_1^2 = R_2^2 = \langle R^2 \rangle_0$, and secondly, that the distribution function $f_1(R)$ is Gaussian. Of these, the first is probably not serious in a good solvent so that from eqn. (19) and (22), we have a fairly reliable formula for $K$, namely,

$$K = (3M^2/2)(\partial A_2/\partial M)(\langle R^2 \rangle_0)^{-\frac{3}{2}}(\langle R^3 \rangle_0 - \langle R \rangle_0\langle R^2 \rangle_0). \tag{25}$$

Our second approximation, namely that $f_1(R)$ is Gaussian, was used to evaluate the last factor on the right of eqn. (25). Until we can solve the problem of the volume effect, the form of $f_1(R)$ remains unknown. With no volume effect, $f_1(R)$ is not Gaussian, but for long chains a relation like eqn. (23) still holds with a different

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numerical factor in place of $(2/3\pi^{\frac{1}{2}})^{\frac{3}{2}}$. Unless therefore the existence of a volume effect modifies the form of eqn. (23) so that the right-hand side depends on the chain length other than through the factor $(\langle R^2 \rangle_0)^{\frac{3}{2}}$, we shall still have eqn. (24) for $K$ but with a different numerical factor in place of $(2/3\pi)^{\frac{1}{2}}$.

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