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On the mean radius of gyration of a polymer chain

Marios K Kosmas

Chemistry Department, University of Ioannina, Ioannina, Greece

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Abstract. We calculate the intrachain bead-to-bead square distance of a real polymer chain, close to the critical dimensionality $d = 4$. From this we obtain the mean-square radius of gyration $\langle S^2 \rangle$ of the polymer as a function of the molecular weight N of the chain and the excluded volume parameter u. A proportionality relationship between $\langle S^2 \rangle$ and the mean square end-to-end distance $\langle R^2 \rangle$ of the coil, previously suggested by enumerations of self-avoiding walks on lattices, is shown to be true. An estimate of the universal ratio $\langle S^2 \rangle / \langle R^2 \rangle$ is given.

1. Introduction

The mean radius of gyration $\langle S^2 \rangle$ of a polymer coil (Yamakawa 1971) is defined as the average square distance of the chain segments from the centre of the mass of the chain. It characterises the size and shape of the polymer and thus it may be obtained from hydrodynamic measurements. In the limit of small scattering angles it is proportional to the slope of the structure factor with respect to the square of the wavenumber. Therefore it is also directly observable in scattering experiments of dilute polymer solutions.

For an ideal chain, the various statistical averages can be calculated relatively easily (Yamakawa 1971). Both the average radius of gyration $\langle S^2 \rangle$ and the average end-to-end square distance $\langle R^2 \rangle$ are found to be proportional to the molecular weight N and their constant ratio is equal to $1/6$,

$$\langle S^2 \rangle / \langle R^2 \rangle = 1/6 \text{ (ideal chain)}. \tag{1.1}$$

When a real chain is considered though, the excluded volume interactions between all pairs of beads increase the complexity of the problem enormously. In a good solvent these long-range interactions are repulsive and the coil expands (Edwards 1965). The dependence of $\langle S^2 \rangle$ and $\langle R^2 \rangle$ on the molecular weight N, in the limit of $N \to \infty$, becomes of the power law variety,

$$\langle S^2 \rangle \sim N^{2\nu'} \tag{1.2a}$$

$$\langle R^2 \rangle \sim N^{2\nu}. \tag{1.2b}$$

A question which arises immediately is whether ν' and ν are identical and if a proportionality relationship between $\langle S^2 \rangle$ and $\langle R^2 \rangle$, analogous to equation (1.1) is also valid for the non-ideal case.

Classical perturbation expansions give a negative answer to the question of proportionality. Close to the θ point the binary cluster integral u takes small values and the

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parameter $z = (3/2\pi)^{3/2} u N^{1/2} (d = 3)$ is treated as the small perturbation parameter. The first-order perturbation results in the three-dimensional space (Fixman 1955) are

$$\langle S^2 \rangle = (N/6)[1 + (134/105)z] \tag{1.3a}$$

$$\langle R^2 \rangle = N[1 + (4/3)z] \tag{1.3b}$$

from which the ratio $\langle S^2 \rangle / \langle R^2 \rangle$ comes out to depend on the molecular weight N. On the other hand, indications of a proportionality relationship between $\langle S^2 \rangle$ and $\langle R^2 \rangle$ are found by means of enumerations of self-avoiding walks confined on lattices (Domb and Hioe 1969, Lax *et al* 1978). From extrapolations to large values of N it is concluded by these methods that ν and ν' are the same, showing in this way that $\langle S^2 \rangle / \langle R^2 \rangle$ is independent of N.

Classical perturbation theory cannot properly describe the thermodynamic limit since the assumption that $z \sim u N^{1/2}$ is small fails at large N. Recent studies in the field of statistical mechanics have shown that an interesting parameter in the study of polymers is the dimensionality d of the space (de Gennes 1972, Wilson and Kogut 1974). The dimensionality four is a critical one. For dimensionalities above $d = 4$, even chains with large excluded volume behave ideally. This makes the solution for $d > 4$ to represent a good choice as a zeroth-order exact solution. Using then $\varepsilon = 4 - d$ as the small parameter of a perturbation scheme, we approach the real world of dimensionalities smaller than four bringing in evenly the non-idealities of the problem.

In a recent article (Kosmas 1981) we have applied these concepts to study the properties of a polymer coil, associated with the end-to-end distribution function of the chain. Following the ideas of Renormalisation Group (RG) theory (Wilson and Kogut 1974) we have reached the meaning of the fixed point in a simple perturbation scheme. RG theory postulates that successive eliminations of the degrees of freedom of a system close to a critical point, keeps the functional form of the free energy the same. In polymers the Boltzmann factor is an exponential function in the excluded volume parameter u (see equations (2.1) and (2.2)). Thus it has also to be an exponential function in u^* the fixed-point value of u, after the elimination of all degrees of freedom. We solved the problem in a perturbation scheme and by requiring the expansion series to fit into an exponential function, we recovered the fixed-point values $u^* = 0, \varepsilon/16$. These values give the same exponents with those coming from RG theory in the limit $\varepsilon = 4 - d \to 0$.

In the present work we study the mean-square radius of gyration related to the general, two segment, distribution function of the polymer chain (Witten and Schäfer 1978). In § 2 we derive an expression for the mean average bead-to-bead square distance which we use in § 3 to calculate the mean radius of gyration. The interesting ratio $\langle S^2 \rangle / \langle R^2 \rangle$ on which the calculation of $\langle R^2 \rangle$ from the experimental quantity $\langle S^2 \rangle$ is based is also estimated close to $d = 4$ in § 3.

2. The mean bead-to-bead square distance

In the Gaussian model with excluded volume the distribution function $P(\{\boldsymbol{r}_i\})$ for the N beads of the polymer chain, assumed to be located at the points $\boldsymbol{r}_i$, $i = 1, 2, \ldots, N$, is given (Yamakawa 1971) by:

$$P(\{\boldsymbol{r}_i\}) = c \exp\left\{ -\sum_{i=1}^{N-1} (3/2l^2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 - (B/2) \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} V(\boldsymbol{r}_i - \boldsymbol{r}_j) \right\}. \tag{2.1}$$

Here c is a normalisation constant and $B = 1/kT$. The effective segment length l does not affect the present analysis and is taken for simplicity to be equal to 1. The mean potential $V(\boldsymbol{r}_i - \boldsymbol{r}_j)$ between non-bonded pairs of beads is approximated as usual by a delta function pseudopotential,

$$(B/2)\,V(\boldsymbol{r}_i - \boldsymbol{r}_j) = u\delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j), \tag{2.2}$$

where the excluded volume parameter u is the binary cluster integral.

The average radius of gyration can be expressed in terms of the intrachain distances (Domb and Hioe 1969) as

$$\langle S^2 \rangle = (1/2N^2) \sum_{l=1}^{N} \sum_{\substack{k=1 \\ l \neq k}}^{N} \langle (\boldsymbol{r}_1 - r_k)^2 \rangle, \tag{2.3}$$

where $\langle (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \rangle$ is the mean-square distance between the beads l and k. This average is defined by means of the distribution function, equation (2.1) as

$$\langle (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \rangle = \left[\int P[\{\boldsymbol{r}_i\}](\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \prod_{i=1}^{N} d\boldsymbol{r}_i \right] \left[\int P[\{\boldsymbol{r}_i\}] \prod_{i=1}^{N} d\boldsymbol{r}_i \right]^{-1}. \tag{2.4}$$

If we make use of the approximation, equation (2.2) in equation (2.1) and expand the exponential we take up to first order in u that

$$\begin{aligned}
\langle (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \rangle = {} & \left\{ \int \exp\left[-\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right] \left[1 - u \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j) \right] (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right\} \\
& \times \left\{ \int \exp\left[-\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right] \left[1 - u \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j) \right] \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right\}^{-1} \\
= {} & \left\{ \exp\left[-\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right] (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right\} \\
& \times \left\{ \int \exp\left[-\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right] \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right\}^{-1} \\
& - u \left[\left\{ \int \exp\left[-\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right] (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j) \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right\} \right. \\
& \times \left[\int \exp\left\{ -\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right\} \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right]^{-1} \\
& - \left[\int \exp\left\{ -\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right\} (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right] \\
& \times \left[\int \exp\left\{ -\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right\} \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right]^{-1} \\
& \times \left[\int \exp\left\{ -\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right\} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j) \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right] \\
& \left. \times \left[\int \exp\left\{ -\sum_{i=1}^{N-1} (3/2)(\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 \right\} \prod_{i=1}^{N} \mathrm{d}\boldsymbol{r}_i \right]^{-1} \right].
\end{aligned} \tag{2.5}$$

The first term in equation (2.5) is the mean bead-to-bead square distance for an ideal chain and is equal to the length of the segment $(l-k)$ while the u term represents the contribution from chains with a loop coming from the delta function constraint.

In the u term of equation (2.5), the position and the length of the loop is determined by the lengths i and j. The relative magnitude of the lengths i and j with respect to the lengths k and l (the beginning and the end of the segment under study) determines the position of the loop with respect to the k, l segment and hence the final form of the corresponding Gaussian integrals. In a diagrammatic language we can represent the intrachain distance as:

$$\langle (\boldsymbol{r}_l - \boldsymbol{r}_k)^2 \rangle = (l-k) - u\Bigg\{ \sum_{i=1}^{k}\sum_{j=1}^{k} \;\underset{0}{\overset{k\ l}{\bigcirc}}\; + \sum_{i=1}^{k}\sum_{j=k}^{l} \;\underset{k}{\overset{l}{\bigcirc}}\; + \sum_{i=1}^{k}\sum_{j=l}^{N} \;\underset{l}{\overset{}{\bigcirc}}\; k$$

$$+ \sum_{i=k}^{l}\sum_{j=1}^{k} \;\underset{k}{\overset{l}{\bigcirc}}\; + \sum_{i=k}^{l}\sum_{j=k}^{l} \;\underset{}{\overset{k\ \ l}{\bigcirc}}\; + \sum_{i=k}^{l}\sum_{j=l}^{N} \;\underset{l}{\overset{k}{\bigcirc}}\;$$

$$+ \sum_{i=l}^{N}\sum_{j=1}^{k} \;\underset{l}{\overset{}{\bigcirc}}\; k + \sum_{i=l}^{N}\sum_{j=k}^{l} \;\underset{l}{\overset{k}{\bigcirc}}\; + \sum_{i=l}^{N}\sum_{j=l}^{N} \;\underset{0}{\overset{k\ l}{\bigcirc}}\; \Bigg\}, \qquad i \neq j,\ l > k. \tag{2.6}$$

The circle in these diagrams represents the i, j loop and the k and l points the beginning and the end of the segment. In the first and the last diagrams the i, j loop lies outside the k, l segment, while in the $\overset{k\ \ l}{\bigcirc}$ diagram it lies inside the segment. In the diagram $l\bigcirc k$ the segment lies inside the loop and in the rest of the diagrams the loop and the segment have only some of their parts in common.

To evaluate these diagrams we have to go to the corresponding expression of the u term of equation (2.5) where the integration over all $\boldsymbol{r}$'s has to be performed. As a first step we integrate over $\boldsymbol{r}$'s representing the positions of beads between special points. The special points for the first-order diagrams are the end of the chain with a position vector $\boldsymbol{R}_N$, the kth and lth beads at $\boldsymbol{R}_k$ and $\boldsymbol{R}_l$ respectively, and the i, j junction at $\boldsymbol{R}$. These integrations are over Gaussian functions and are trivial. After this part is done we are left with Gaussian probabilities for the several portions of the chain whose positions are defined by the vectors $\boldsymbol{O}$, $\boldsymbol{R}$, $\boldsymbol{R}_k$, $\boldsymbol{R}_l$ and $\boldsymbol{R}_N$. Completion of the integrations over capital $\boldsymbol{R}$'s gives the final form of the diagrams. Two examples will be given for the diagrams $\overset{k\ \ l}{\bigcirc}$ and $\underset{l}{\overset{k}{\bigcirc}}$. For the diagram $\overset{k\ \ l}{\bigcirc}$, before doing the integration over capital $\boldsymbol{R}$'s we take that:

$$\underset{0}{\overset{\boldsymbol{R}\ \boldsymbol{R}_k \boldsymbol{R}_l \boldsymbol{R}_N}{\bigcirc}} = \int \mathrm{d}\boldsymbol{R} \int \mathrm{d}\boldsymbol{R}_k \int \mathrm{d}\boldsymbol{R}_l \int \mathrm{d}\boldsymbol{R}_N (3/2\pi i)^{d/2}$$

$$\times \exp[-3R^2/2i][3/2\pi(j-i)]^{d/2}[3/2\pi(k-j)]^{d/2}$$

$$\times \exp[-3(\boldsymbol{R}_k - \boldsymbol{R})^2/2(k-j)][3/2\pi(l-k)]^{d/2} \exp[-3(\boldsymbol{R}_l - \boldsymbol{R}_k)^2/2(l-k)]$$

$$\times [3/2\pi(N-l)]^{d/2} \exp[-3(\boldsymbol{R}_N - \boldsymbol{R}_l)^2/2(N-l)](\boldsymbol{R}_l - \boldsymbol{R}_k)^2$$

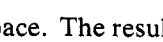
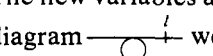
$$- \int \mathrm{d}\boldsymbol{R} \int \mathrm{d}\boldsymbol{R}_k \int \mathrm{d}\boldsymbol{R}_l \int \mathrm{d}\boldsymbol{R}_N (3/2\pi i)^{d/2}$$

$$\times \exp[-3R^2/2i][3/2\pi(j-i)]^{d/2}[3/2\pi(k-j)]^{d/2}$$

$$\times \exp[-3(\boldsymbol{R}_k-\boldsymbol{R})^2/2(k-j)][3/2\pi(l-k)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_l-\boldsymbol{R}_k)^2/2(l-k)][3/2\pi(N-l)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_N-\boldsymbol{R}_l)^2/2(N-l)](l-k). \tag{2.7}$$

The $\boldsymbol{R}$ integrations are over all space and are facilitated by making the linear transformation:

$$\boldsymbol{R}_N \to \boldsymbol{R}_N-\boldsymbol{R}_l, \qquad \boldsymbol{R}_l \to \boldsymbol{R}_l-\boldsymbol{R}_k, \qquad \boldsymbol{R}_k \to \boldsymbol{R}_k-\boldsymbol{R}, \qquad \boldsymbol{R} \to \boldsymbol{R}. \tag{2.8}$$

The new variables are also integrated over all space. The result is  $= 0$. For the diagram  we take:


$$= \int d\boldsymbol{R} \int d\boldsymbol{R}_k \int d\boldsymbol{R}_l \int d\boldsymbol{R}_N (3/2\pi i)^{d/2} \exp\{-3R^2/2i\}[3/2\pi(k-i)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_k-\boldsymbol{R})^2/2(k-i)][3/2\pi(j-k)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_k-\boldsymbol{R})^2/2(j-k)][3/2\pi(l-j)]^{d/2}$$
$$\times \exp -3(\boldsymbol{R}_l-\boldsymbol{R})^2/2(l-j)][3/2\pi(N-l)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_N-\boldsymbol{R}_l)^2/2(N-l)](\boldsymbol{R}_l-\boldsymbol{R}_k)^2$$
$$-\int d\boldsymbol{R} \int d\boldsymbol{R}_k \int d\boldsymbol{R}_l \int d\boldsymbol{R}_N (3/2\pi i)^{d/2} \exp[-3R^2/2i][3/2\pi(k-i)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_k-\boldsymbol{R})^2/2(k-i)][3/2\pi(j-k)]^{d/2}$$
$$\times \exp[-3(\boldsymbol{R}_k-\boldsymbol{R})^2/2(j-k)][3/2\pi(l-j)]^{d/2} \exp[-3(\boldsymbol{R}_l-\boldsymbol{R})^2/2(l-j)]$$
$$\times [3/2\pi(N-l)]^{d/2} \exp[-3(\boldsymbol{R}_N-\boldsymbol{R}_l)^2/2(N-l)](l-k). \tag{2.9}$$

Next we change into the new variables

$$\boldsymbol{R}_N \to \boldsymbol{R}_N-\boldsymbol{R}_l, \qquad \boldsymbol{R}_k \to \boldsymbol{R}_k-\boldsymbol{R}, \qquad \boldsymbol{R}_l \to \boldsymbol{R}_l-\boldsymbol{R}, \qquad \boldsymbol{R} \to \boldsymbol{R} \tag{2.10}$$

and we make use of the identity

$$(\boldsymbol{R}_l-\boldsymbol{R}_k)^2 = (\boldsymbol{R}_l-\boldsymbol{R})^2+(\boldsymbol{R}_k-\boldsymbol{R})^2-2(\boldsymbol{R}_l-\boldsymbol{R})(\boldsymbol{R}_k-\boldsymbol{R}). \tag{2.11}$$

The integrations over Gaussian functions are trivial and they give finally that

 $= -(j-k)^2/(j-i)^{d/2+1}$. (2.12)

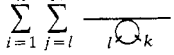
Similarly the forms for the rest of the diagrams can be found. All of them are collected in table 1.

The next thing in order, according to equation (2.6), is to find the summations over i and j for each diagram. We facilitate this by converting these summations into integrations. Examples for $d = 4$ are:

$$\sum_{\substack{i=1 \\ i\neq j}}^{k} \sum_{j=k}^{l} \quad \text{  }$$
$$\simeq \int_1^k di \int_k^l dj[-(j-k)^2/(j-i)^3] \simeq -\int_k^l dj(j-k)^2 \int_1^k di(j-i)^{-3}$$

$$\simeq -(1/2)\int_k^l \mathrm{d}j(j-k)^2[(j-k)^{-2}-j^{-2}] \simeq -(1/2)\int_k^l \mathrm{d}j[2k/j-k^2/j^2]$$

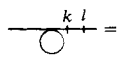
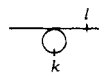
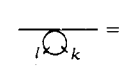
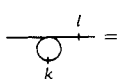
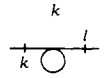
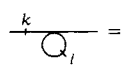
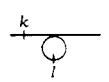
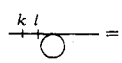
$$\simeq -k\ln(l/k)+k(l-k)/2l, \tag{2.13}$$

$\sum_{i=1}^{k}\sum_{j=l}^{N}$ 

$$\simeq -(l-k)^2\int_1^k \mathrm{d}i\int_l^N \mathrm{d}j(j-i)^{-3} \simeq [(l-k)^2/2]\int_1^k \mathrm{d}i[(N-i)^{-2}-(l-i)^{-2}]$$

$$\simeq [(l-k)^2/2][(N-k)^{-1}-N^{-1}-(l-k)^{-1}+l^{-1}]. \tag{2.14}$$

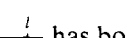
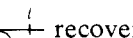
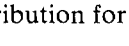
Table 1. First-order diagrams necessary for the evaluation of intrachain distances of a polymer chain.

 $=0$	 $=-\dfrac{(j-k)^2}{(j-i)^{d/2+1}}$	 $=-\dfrac{(l-k)^2}{(j-i)^{d/2+1}}$
 $=-\dfrac{(j-k)^2}{(j-i)^{d/2+1}}$	 $=-\dfrac{1}{(j-i)^{d/2-1}}$	 $=-\dfrac{(l-i)^2}{(j-i)^{d/2+1}}$
$=-\dfrac{(l-k)^2}{(j-i)^{d/2+1}}$	 $=-\dfrac{(l-i)^2}{(j-i)^{d/2+1}}$	 $=0$

The rest i and j summations can be evaluated in a similar way. If we put the results in the same order as in equation (2.6), we take that:

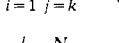
$$\begin{aligned}\langle(\boldsymbol{r}_l-\boldsymbol{r}_k)^2\rangle &= (l-k)-u[\![0+[-k\ln(l/k)+k(l-k)/2l)\\
&\quad+\{[(l-k)^2/2][(N-k)^{-1}-N^{-1}-(l-k)^{-1}+l^{-1}]\}\\
&\quad+[-k\ln(l/k)+k(l-k)/2l]+[-2(l-k)\ln(l-k)+2(l-k)]\\
&\quad+\{(N-l)\ln[(N-l)/(N-k)]+(N-l)(l-k)/2(N-k)\}\\
&\quad+\{[(l-k)^2/2][(N-k)^{-2}-N^{-1}-(l-k)^{-1}+l^{-1}]\}\\
&\quad+\{(N-l)\ln[(N-l)/(N-k)]+(N-l)(l-k)/2(N-k)\}+0]\!]\\
&= (l-k)-u\{-2k\ln(l/k)-2(N-l)\ln[(N-k)/(N-l)]\\
&\quad-2(l-k)\ln(l-k)-(l-k)^2/N+3(l-k)\},\qquad l>k.\end{aligned} \tag{2.15}$$

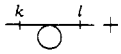
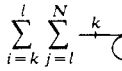
The term of equation (2.15), first order in u, includes both positive and negative parts. A specific combination of the indices l and k is possible for which the u term vanishes. For these values of l and k the portion of the chain starting at the length k and ending at the length l behaves ideally. This condition for intrasegmental ideality does not depend only on the length $(l-k)$ of the segment but also on its position along the chain. After this, a 'blob' picture (Farnoux *et al* 1978, Weill and des Cloizeaux 1979) according to which there are portions of the chain of certain lengths (blobs) with ideal behaviour regardless of their position on the chain, has to be improved.

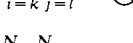
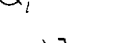
The diagram  has both beads i and j coming from inside the segment (k, l). This is the only diagram with this property and represents intrasegmental excluded volume effects. When $k \to 0$ and $l \to N$ all the rest diagrams give negligible contributions and the diagram  recovers the first-order result of the mean end-to-end square distance of the polymer coil. All the remaining diagrams involve beads from outside the (k, l) segment. A useful observation can be made regarding this partition. We will see that the largest contribution for the evaluation of $\langle S^2 \rangle$ comes from the intrasegmental diagram  while the remaining diagrams can only alter the proportionality constants in the limit of large N's.

3. The mean radius of gyration

In order to evaluate the mean radius of gyration $\langle S^2 \rangle$ up to first order in u we combine equations (2.3) and (2.6) to obtain

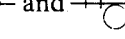
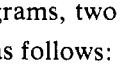
$$\langle S^2 \rangle = N^{-2} \sum_{k=1}^{N-1} \sum_{l=k+1}^{N} \Bigg[(l-k) - u \Bigg(\sum_{i=1}^{k} \sum_{j=1}^{k} \text{} + \sum_{i=1}^{k} \sum_{j=k}^{l} \text{  } + \sum_{i=1}^{k} \sum_{j=l}^{N} \text{  }$$

$$+ \sum_{i=k}^{l} \sum_{j=1}^{k} \text{  } + \sum_{i=k}^{l} \sum_{j=k}^{l} \text{  } + \sum_{i=k}^{l} \sum_{j=l}^{N} \text{  }$$

$$+ \sum_{i=l}^{N} \sum_{j=1}^{k} \text{} + \sum_{i=l}^{N} \sum_{j=k}^{l} \text{  } + \sum_{i=l}^{N} \sum_{j=l}^{N} \text{  } \Bigg) \Bigg], \qquad i \neq j. \tag{3.1}$$

The results of i and j summations have been given in equation (2.15). According to the expression (3.1) the l and k summations are in order. We convert the summations into integrations and we take for the zeroth-order term

$$\sum_{k=1}^{N-1} \sum_{l=k+1}^{N} (l-k) \simeq \int_{1}^{N-1} \mathrm{d}k \int_{k+1}^{N} \mathrm{d}l (l-k) = N^3/6, \qquad N \to \infty. \tag{3.2}$$

The diagrams  and give zero contributions while the calculation for the four equivalent diagrams, two of them of the form  and the other two of the form goes as follows:

$$\sum_{k=1}^{N-1} \sum_{l=k+1}^{N} \sum_{i=k}^{l} \sum_{j=1}^{k} \text{}$$

$$\simeq \int_{1}^{N} \mathrm{d}k \int_{k}^{N} \mathrm{d}l (-k^2/2l + k/2 - k \ln l + k \ln k)$$

$$= -(1/6) \int_{1}^{N} \mathrm{d}l l^2 + (1/2) \int_{1}^{N} \mathrm{d}k (N-k) - (1/2) \int_{1}^{N} \mathrm{d}l \ln l l^2$$

$$+ \int_{1}^{N} \mathrm{d}k \ln k (N-k) k$$

$$= -(1/18) N^3, \qquad N \to \infty. \tag{3.3a}$$

In a similar way the remaining diagrams give:

$$\sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\sum_{i=1}^{k}\sum_{j=l}^{N} \quad l\bigcirc k$$

$$= \sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\sum_{i=l}^{N}\sum_{j=1}^{k} \quad l\bigcirc k = -N^3/72, \tag{3.3b}$$

$$\sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\sum_{\substack{i=k\\ i\neq j}}^{l}\sum_{j=k}^{l} \quad k\ \ l\ \bigcirc = -(N^3/3)\ln N + (11/18)N^3. \tag{3.3c}$$

Using these results in equation (3.1) we obtain an expression for the mean radius of gyration,

$$\langle S^2\rangle = (N/6)[1+2u(\ln N - 13/12)]. \tag{3.4}$$

When $u=0$ equation (3.4) recovers of course the ideal result. The mean square distance $\langle R^2\rangle$ up to first order in u, can be calculated (Kosmas 1981) as the contribution of the intrasegmental diagram $k\ \ l\ \bigcirc$ at the limit $k\to 0$ and $l\to N$. Equation (2.15) then gives

$$\langle R^2\rangle = N[1+2u(\ln N - 1)]. \tag{3.5}$$

First thing to notice comparing equations (3.4) and (3.5) is that in the limit of $N\to\infty$ the proportionality relationship between $\langle S^2\rangle$ and $\langle R^2\rangle$ is still valid up to first order in u, in contrast to the classical perturbation results, equations (1.3a), (1.3b). In the evaluation of $\langle S^2\rangle$ the $N^3\ln N$ term comes only from the intrasegmental diagram $k\ \ l\ \bigcirc$ while the other diagrams contribute N^3 terms of less importance in the limit $N\to\infty$. These terms can only change the overall proportionality constants of the average quantities. This observation about the importance of the intrasegmental diagrams is also true for higher perturbation orders and we will use this fact to show that the proportionality relationship between $\langle S^2\rangle$ and $\langle R^2\rangle$ holds for higher orders. Another useful observation comes out of the form of the u term. The contribution of the terms of lower order than $\ln N$, 13/12 for $\langle S^2\rangle$ and 1 for $\langle R^2\rangle$ (equations (3.4) and (3.5)), is larger in the case of the mean radius of gyration $\langle S^2\rangle$. Therefore it is more difficult for $\langle S^2\rangle$ than for $\langle R^2\rangle$ to reach its thermodynamic form at large N, where the $\ln N$ term dominates over the less important constant terms. This is the analytical version of the result of enumeration techniques (Kumbar and Windwer 1971, Lax and Windwer 1971), according to which the $\langle S^2\rangle$ needs larger values of N in order to obtain its thermodynamic form.

As we mentioned, the dominant contribution in the limit $N\to\infty$ comes from the intrasegmental diagrams only. Neglecting the minor contributions from the other diagrams, $\langle S^2\rangle$ can be obtained from an intrasegmental expression of the (l,k) segment similar to that found (Komas 1981) for the mean end-to-end square distance $\langle R^2\rangle$. In this way we take up to second order that

$$\langle S^2\rangle = N^{-2}\sum_{k=1}^{N-1}\sum_{l=k+1}^{N}[(l-k)+2u(l-k)\ln(l-k)+(u\varepsilon/2-6u^2)(l-k)\ln^2(l-k)]. \tag{3.6}$$

We convert the summations into integrations which can be performed in a straightforward manner. The result up to second order in u and for large N is

$$\langle S^2\rangle = N^{-2}[(N^3/6)+(2u\ln NN^3/6)+(u\varepsilon/2-6u^2)\ln^2 NN^3/6]. \tag{3.7}$$

The corresponding expression for the average end-to-end square distance is

$$\langle R^2\rangle = N[1+2u\ln N+(u\varepsilon/2-6u^2)\ln^2 N]. \tag{3.8}$$

Comparing equations (3.7) and (3.8) we see that the corresponding terms of the two expressions have the same proportionality ratio, revealing that $\langle S^2\rangle$ is proportional to $\langle R^2\rangle$. The interesting thing to notice is that this proportionality is valid regardless of the RG theory and the meaning of the exponent. Its successful proof is only based on the suitable choice of the small perturbation parameter $\varepsilon = 4-d$.

If we now use the meaning of the fixed point in the neighbourhood of which the expansions (3.7) and (3.8) fit into exponential functions, we find (Kosmas 1981) that u^* the fixed point value of u can take the values $u^* = 0, \varepsilon/16$. These values of u^* give, for the average quantities, the expressions (see equations (3.4) and (3.5)),

$$\langle S^2\rangle = (N/6)\exp\{2u^*[\ln N-(13/12)]\} = \exp\{-13u^*/6\}N^{1+2u^*}/6 \tag{3.9a}$$

$$\langle R^2\rangle = N\exp\{2u^*(\ln N-1)\} = \exp\{-2u^*\}N^{1+2u^*} \tag{3.9b}$$

and for their ratio

$$\langle S^2\rangle/\langle R^2\rangle = \exp\{-u^*/6\}/6. \tag{3.10}$$

The present analysis shows that the exponents ν and ν' defined in §1 and characterising the square averages $\langle R^2\rangle$ and $\langle S^2\rangle$ are identical, $\nu = \nu' = (1/2)+u^*$, and estimates the universal ratio $\langle S^2\rangle/\langle R^2\rangle = \exp\{-\varepsilon/96\}/6$ for the non-ideal case. This ratio depends only on the dimensionality of the system and takes smaller values for smaller dimensionalities, in general agreement with previous results (Wall and Erpenbeck 1959). The quantitative outcomes of equations (3.9) and (3.10) are only valid in the limit $\varepsilon \to 0$, and comparison with the results of other techniques for lower dimensionalities is unreliable. The extrapolation of results of first order in ε to lower dimensionalities, with the use of large values of ε underestimates certain quantities. For example, the value of the critical exponent $\nu_{4-\varepsilon} = (1/2)+(\varepsilon/8)$ for $\varepsilon = 1, 2, 3$ becomes $\nu_3 = 0.563$, $\nu_2 = 0.625$ and $\nu_1 = 0.688$, while the more correct values for the exponents coming from interdimensional analysis (Kosmas and Freed 1978) are: $\nu_3 = 0.571$, $\nu_2 = 0.667$ and $\nu_1 = 0.800$. Analogous things happen with the exponent $\varepsilon/96$ of the universal constant $\langle S^2\rangle/\langle R^2\rangle = \exp(-\varepsilon/96)/6$. If we make the simple extrapolation to $d = 3, 2$ and 1 by taking ε to be 1, 2 and 3 respectively the quantity $\varepsilon/96$ takes underestimated values. As a consequence the ratio $\langle S^2\rangle/\langle R^2\rangle = \exp\{-\varepsilon/96\}/6$ takes larger values $\langle S^2\rangle/\langle R^2\rangle = 0.165$ $\varepsilon = 1$, $\langle S^2\rangle/\langle R^2\rangle = 0.163$ $\varepsilon = 2$, than those generally found (Lax *et al* 1978) from lattice enumeration techniques $\langle S^2\rangle/\langle R^2\rangle \simeq 0.155$ $d = 3$, $\langle S^2\rangle/\langle R^2\rangle \simeq 0.140$ $d = 2$.

4. Conclusion

We have worked close to the critical dimensionality $d = 4$ and we have shown that a proportionality relationship exists between the mean radius of gyration and the mean end-to-end square distance of a non-ideal polymer coil in the limit of large molecular

weights. This result is independent from the RG theoretical frame and the meaning of the critical exponent. We have also found the intrachain mean-square distance between any two beads of the chain. The condition of ideal behaviour of a portion of the chain does depend on the position of the segment, contrary to the blob model which accepts that suitable segments (blobs) behave ideally regardless of their chain position. Finally, using the idea of the fixed point, we have calculated the universal ratio $\langle S^2\rangle/\langle R^2\rangle$ in the limit $\varepsilon = 4 - d \to 0$.

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