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Configurational properties of dilute polymer solutions, dimensionality and perturbation theory

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Abstract. We present a technique for calculation of configurational properties of dilute polymer solutions. By using second-order perturbation theory in the small parameter $\varepsilon = 4 - d \to 0$, we are able to determine a specific value of the excluded volume parameter u equivalent to the fixed point value given by renormalisation group theory. For this value of the excluded volume parameter each expansion series in ε can be summed to an exponential function. We thus study the total number of configurations, C, the number of configurations returning to the origin, U, and the mean square end-to-end distance, $\langle R^2 \rangle$, of the polymer coil. An interdimensional relationship previously developed is used to extrapolate the present results to lower dimensions. Finally, we compare our results with those of previous theories and lattice enumerations, discussing possible differences between the Gaussian excluded volume model used here and the self-avoiding walk model, close to dimensionality $d = 1$.

1. Introduction

In dilute polymer solutions the various polymer chains are on the average far apart from each other, and thus the interactions between them can be neglected. Consequently, the study of dilute polymer solutions reduces to that of isolated polymer coils. But although intermolecular interactions are negligible in this limit, intramolecular ones must be considered. Under specific conditions of temperature, solvent and molecular weight, called θ conditions, long-range interactions are cancelled by solvent effects. In this case, the only remaining interactions are those of adjacent monomer units. The problem can then be described by a Markoff process and is equivalent to a random walk on a lattice. If N is the number of the segments of the chain, proportional to the molecular weight of the polymer, the mean end-to-end square distance of the coil behaves as

$$\langle R^2 \rangle \sim N. \tag{1.1}$$

Under conditions other than the θ conditions, the interactions between non-adjacent segments are switched on and the behaviour of the polymer can no longer be represented by a Markoff process. In the good solvent case these interactions are repulsive and the chain expands. The mean square end-to-end distance then becomes

$$\langle R^2 \rangle \sim N^{2\nu} \qquad (\nu > \tfrac{1}{2} \text{ good solvent}). \tag{1.2}$$

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For a linear polymer starting at the origin **0** and ending at $\boldsymbol{R}$, the distribution function of $\boldsymbol{R}$ in the Gaussian model with excluded volume is given by the expression (Fixman 1955, Kosmas and Freed 1978b, Yamakawa 1971)

$$P[\boldsymbol{R}, N] = \left(\frac{3}{2\pi l}\right)^{dN/2} \int \prod_{i=1}^{N} \mathrm{d}^d \boldsymbol{r}_i \delta^d(\boldsymbol{r}_1) \delta^d(\boldsymbol{r}_N - \boldsymbol{R}) \times \exp\left(-\frac{3}{2l^2} \sum_{i=1}^{N-1} (\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2 - \frac{B}{2} \sum_{\substack{i=1 \\ i \neq j}}^{N} \sum_{j=1}^{N} V(\boldsymbol{r}_i - \boldsymbol{r}_j)\right). \tag{1.3}$$

Here d is the dimensionality of the system, l is an effective segment length, the vector $\boldsymbol{r}_i$ points to the ith segment or link, N is the number of segments proportional to the molecular weight, and B is proportional to the inverse of temperature. $V(\boldsymbol{r}_i - \boldsymbol{r}_j)$ is the non-bonded interaction between the segments i and j and, as is customary (Fixman 1955, Yamakawa 1971), is taken to be $V(\boldsymbol{r}_i - \boldsymbol{r}_j) = (2u/B)\delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j)$ where u is the binary cluster integral. The first term in the Boltzmann factor represents a connectivity term which guarantees that the segments form a chain and do not behave like the molecules of a fluid. The second excluded volume term relates to a two-body potential arising when segments remote along the chain approach in space. It carries all the physics and the difficulty of the problem. The approximation of $V(\boldsymbol{r}_i - \boldsymbol{r}_j)$ with the delta function pseudopotential has also been used in the continuous model (des Cloizeaux 1980, Edwards 1965b, Freed 1972), according to which the polymer chain is approximated by a continuous line. The present model is equivalent to the continuous model. As a matter of fact, the perturbation expansions of § 2 are the same as those coming from the continuous model (Edwards 1975) in the limit of large N. The differences of the two models are different values of normalisation constants and the necessary introduction of proper cut-offs in the continuous model.

Flory (1949) used mean field arguments to approximate the solution of the problem. He considers the free energy of the system to consist of two terms, an elasticity term and an interaction energy term. He expresses the free energy as a function of the expansion factor of the coil and obtains this expansion factor by minimising the free energy. He gives for the mean end-to-end square distance of the coil the form

$$\langle R^2 \rangle \sim N^{2\nu}, \qquad \nu = 3/(2+d), \tag{1.4}$$

where d stands for the dimensionality of the system. For a critique of Flory's method see des Cloizeaux (1970). Edwards (1965b) replaces the two-body potential between the segments with random fields (Freed 1972, Kosmas and Freed 1978a) and he finds the most dominant field in a self-consistent way. His results, although of mean field accuracy, give some corrections to Flory's formula, equation (1.4), and criteria of where they are valid. A different approach is used by Domb (1969) who attacks the excluded volume problem with enumerations of self-avoiding walks on lattices. He gives results for the mean end-to-end square distance of the walk, the number of total walks (Edwards 1965a) and the number of walks returning to the origin. De Gennes (1972) notices the equivalence of the self-avoiding walk to the n-component Ising model in the limit $n \to 0$. Using the results of the renormalisation group theory of Wilson and Kogut (1974), he applies the Ginsburg–Landau–Wilson model describing second-order phase transitions to the polymer study.

Recently (Kosmas and Freed 1978b) we have shown how the solutions of the problem at different dimensionalities are related, and we have demonstrated with

scaling arguments the criticality of dimensionality four in agreement with previous findings (Wilson and Kogut 1974, de Gennes 1972). For dimensions above four the excluded volume effects are negligible and the chain behaves like an ideal one. We gave formulae relating the solutions at different dimensionalities and, using the results for the one-dimensional rigid rod as a boundary solution, we have recovered Flory's formula, equation (1.4).

In this work, following Wilson and Kogut's (1974) ε expansion used in connection with renormalisation group theory, we solve the problem in a perturbation scheme (des Cloizeaux 1980) close to four dimensions. We only need the solution for $\varepsilon = 4-d \to 0$, since with the relations connecting the various properties at different dimensionalities (Kosmas and Freed 1978b) given here, we can jump from $4-\varepsilon$ to $3-\varepsilon$ etc. With second-order perturbation theory in ε we are able to determine a specific value of the interaction parameter u, equivalent to the fixed point value of the renormalisation group theory, for which the various series can be summed to exponential functions. This requirement is in accord with renormalisation group theory which postulates that the step by step elimination of the several degrees of freedom of a system, close to a critical point, preserves the form of the free energy (here an exponential function in u^*) (Wilson and Kogut 1974).

In § 2 we define the characteristic quantities of the polymer chain such as the number of total configurations, C, the number of configurations returning to the origin, U, and the mean end-to-end square distance, $\langle R^2 \rangle$, in terms of the distribution function of equation (1.3). We then calculate these quantities close to four dimensions. Section 3 demonstrates how we derive the results for $d = 3, 2, 1$, using as a boundary solution the one developed for $d = 4-\varepsilon$ ($\varepsilon \to 0$). In the last section we discuss our results and compare the present treatment with previous theories. The Appendix illustrates the evaluation of various diagrams.

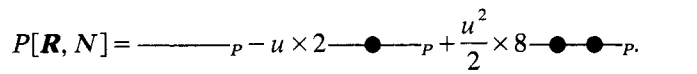
2. Evaluation of the quantities close to four dimensions

In what follows we take for simplicity the effective length $l = 1$ and assume that all the other parameters bear proper units. Employing the delta function pseudopotential in equation (1.3) and expanding the distribution function in powers of u, we have the form

$$P[\boldsymbol{R}, N] = \left(\frac{3}{2\pi}\right)^{dN/2} \int \prod_{i=1}^{N} \mathrm{d}^d \boldsymbol{r}_i \, \delta^d(\boldsymbol{r}_1)\, \delta^d(\boldsymbol{r}_N - \boldsymbol{R}) \exp\left(-\frac{3}{2}\sum_{i=1}^{N-1} (\boldsymbol{r}_i - \boldsymbol{r}_{i+1})^2\right)$$
$$\times \left[1 - u \sum_{\substack{i=1 \\ i\neq j}}^{N} \sum_{j=1}^{N} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j) + \frac{u^2}{2}\left(\sum_{\substack{i=1 \\ i\neq j}}^{N} \sum_{j=1}^{N} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j)\right)^2 - \cdots\right]. \tag{2.1}$$

The first term in the expansion represents the distribution function of an ideal chain, the u term is the result for a chain with one 'knot' arising from the delta function constraint and the u^2 term is the result with two knots arising from the two delta functions of this term.

Denoting the ideal chain by a horizontal line and the knots by dots, equation (2.1) can be written in a diagrammatic language as



(2.2)

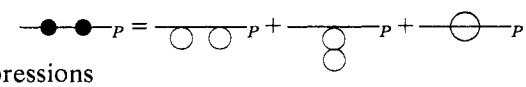
The subscript refers to the property in question, for example, P stands for the distribution function and the numbers 2 and 8 are the symmetry numbers of the corresponding diagrams. The explanation of the symbols in equation (2.2) is as follows:

$$= (3/2\pi N)^{d/2} \exp(-\tfrac{3}{2}R^2/N); \tag{2.3}$$

gives rise to only one kind of diagram,

$$= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(\frac{3}{2\pi(j-i)}\right)^{d/2} \left(\frac{3}{2\pi(N-j+i)}\right)^{d/2} \times \exp\left(-\frac{3}{2}\frac{R^2}{(N-j+i)}\right); \tag{2.4}$$

gives rise to three different kinds of diagrams,



with the expressions

$$= \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \left(\frac{3}{2\pi(j-i)}\right)^{d/2} \left(\frac{3}{2\pi(l-k)}\right)^{d/2} \times \left(\frac{3}{2\pi(N-j+i-l+k)}\right)^{d/2} \exp\left(-\frac{3}{2}\frac{R^2}{(N-j+i-l+k)}\right), \tag{2.5a}$$

$$= \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \left(\frac{3}{2\pi(l-i-k+j)}\right)^{d/2} \times \left(\frac{3}{2\pi(k-j)}\right)^{d/2} \left(\frac{3}{2\pi(N-l+i)}\right)^{d/2} \exp\left(-\frac{3}{2}\frac{R^2}{(N-l+i)}\right), \tag{2.5b}$$

$$= \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \left(\frac{3}{2\pi}\right)^{d} \frac{l_{\text{eff}}^{d/2}}{l_1^{d/2} l_2^{d/2} l_3^{d/2}} \times \left(\frac{3}{2\pi(N-l_1-l_2-l_3+l_{\text{eff}})}\right)^{d/2} \exp\left(-\frac{3}{2}\frac{R^2}{(N-l_1-l_2-l_3+l_{\text{eff}})}\right). \tag{2.5c}$$

In equation (2.5) $l_1 = j-i$, $l_2 = k-j$, $l_3 = l-k$, $l_{\text{eff}}^{-1} = l_1^{-1} + l_2^{-1} + l_3^{-1}$ and i, j, k, l measure contour lengths along the polymer chain (Fixman 1955). Throughout the rest of this work l_1, l_2, l_3, l_{eff}, i, j, k, l will have the same meaning as in equation (2.5).

The distribution function $P(\boldsymbol{R}, N)$ as expressed in equation (2.2), with the meaning of the various diagrams given by equations (2.3)–(2.5), will be used to study the various coil properties.

2.1. Number of total configurations

The number of total configurations is defined as

$$C = \mu_0^N \int \mathrm{d}^d \boldsymbol{R}\, P[\boldsymbol{R}, N], \tag{2.6}$$

where μ_0 represents the activity for an ideal chain. For the present theory this is the normalisation factor of equation (1.3), $\mu_0 = (3/2\pi)^d$, while for walks on a lattice this is the lattice coordination number. Lattice enumerations for self-avoiding walks have

found that C depends on N in the limit of large N, in the form

$$C = \mu^N N^{a_d}, \tag{2.7}$$

where μ is an effective coordination number depending on the lattice used and a_d is a critical index independent of the lattice, depending only on the dimensionality of the system. It was found to be close to $\frac{1}{6}$ for $d = 3$ and close to $\frac{1}{3}$ for $d = 2$.

In order to evaluate the number of total configurations, we begin with the definition (2.6) where the distribution function $P(\boldsymbol{R}, N)$ is expressed by the expansion of equation (2.2). Thus equation (2.6) becomes

$$C = \mu_0^N \int \mathrm{d}^d \boldsymbol{R} \Big(\text{——}_P - u \times 2 \text{—●—}_P + \frac{u^2}{2} \times 8 \text{—●—●—}_P \Big). \tag{2.8}$$

Using the expressions (2.3), (2.4), and (2.5) in equation (2.8) for the several P diagrams and absorbing factors of $(3/2\pi)^{d/2}$ in u, we find for C

$$C = \mu_0^N \Big[\text{——}_C - u \times 2 \text{—○—}_C + \frac{u^2}{2} \times 8 \Big(\text{—○○—}_C + \text{—⊗—}_C + \text{—⊖—}_C \Big) \Big], \tag{2.9}$$

with

$$\text{——}_C = 1, \tag{2.10a}$$

$$\text{—○—}_C = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{(j-i)^{d/2}}, \tag{2.10b}$$

$$\text{—○○—}_C = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \frac{1}{(j-i)^{d/2}} \frac{1}{(l-k)^{d/2}}, \tag{2.10c}$$

$$\text{—⊗—}_C = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \frac{1}{(l-i-k+j)^{d/2}} \frac{1}{(k-j)^{d/2}}, \tag{2.10d}$$

$$\text{—⊖—}_C = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \frac{l_{\mathrm{eff}}^{d/2}}{l_1^{d/2} l_2^{d/2} l_3^{d/2}}, \tag{2.10e}$$

and l_{eff}, l_1, l_2, l_3, i, j, k, l defined in equation (2.5). The diagrams (2.10) have been calculated for $d = 4 - \varepsilon$ in the limit of $\varepsilon \to 0$ and $N \to \infty$ and collected in table 1. Examples of these calculations are given in the Appendix. Using the values of these

Table 1. Values of the various diagrams.

	C	U	$\langle R^2 \rangle$
—○—	$N - \ln N + \frac{1}{2}\varepsilon(N - \frac{1}{2}\ln^2 N)$	$N^{-2}[N + 2\ln N + \frac{1}{2}\varepsilon(3\ln^2 N + N \ln N)]$	$N \ln N - N + \frac{1}{4}\varepsilon N \ln^2 N$
—○○—	$\frac{1}{2}N^2 - 2N \ln N + \ln^2 N$	$N^{-2}(\frac{1}{2}N^2 - \ln N)$	$2N \ln^2 N - N^2 \ln N + \frac{3}{2}N^2$
—⊗—	$N \ln N - \ln^2 N - N$	$N^{-2}(3\ln^2 N + 2N \ln N)$	$3N \ln N - N \ln^2 N - \frac{1}{2}N^2$
—⊖—	$-\frac{3}{2}\ln^2 N$	$3N^{-2}\ln^2 N$	$-\frac{3}{2}N \ln^2 N$

diagrams in the expression (2.9), we obtain for the number of total configurations

$$C = \mu_0^N\{1 - u[2N - 2\ln N + \varepsilon(N - \tfrac{1}{2}\ln^2 N)] + \tfrac{1}{2}u^2 8[(\tfrac{1}{2}N^2 - 2N\ln N + \ln^2 N) + (N\ln N - \ln^2 N - N) + (-\tfrac{3}{2}\ln^2 N)]\}, \tag{2.11}$$

which after ordering powers of u and ε in the limit of large N leads to

$$C = \mu_0^N[1 - u(2N - 2\ln N) + u\varepsilon(\tfrac{1}{2}\ln^2 N) + u^2(2N^2 - 4N\ln N - 6\ln^2 N)]. \tag{2.12}$$

We now search for a specific value $u = u^*$ that converts the series (2.12) to an exponential function. We thus obtain the characteristic relation

$$\tfrac{1}{2}u^{*2}(2N - 2\ln N)^2 = u^*\varepsilon(\tfrac{1}{2}\ln^2 N) + u^{*2}(2N^2 - 4N\ln N - 6\ln^2 N), \tag{2.13}$$

which as a quadratic equation has two solutions, $u^* = 0$ corresponding to the trivial ideal solution and $u^* = \varepsilon/16$ corresponding to a non-ideal solution describing the expanded coil. These two values are identical to the values given by renormalisation group theory, as expected, since renormalisation group theory is exact in the limit $\varepsilon \to 0$. For $u = u^*$ the series given by equation (2.12), although it has two different functional forms N and $\ln N$, sums to an exponential function of the form

$$C = \mu_0^N\, e^{-\varepsilon N/8} N^{\varepsilon/8} = \mu^N N^{\varepsilon/8}, \qquad \mu = \mu_o e^{-\varepsilon/8} < \mu_0, \tag{2.14}$$

which is identical to the form that lattice enumerations yield. So we see that equation (2.14) represents a solution of the problem close to four dimensions and for a specific value of $u = u^*$.

The new thing to emerge from the complete expression equation (2.14) is the effective activity μ. According to renormalisation group theory, this result is valid for a larger area of points in the proximity of the fixed point. Therefore, equation (2.14) is expected to be valid independently of u as long as we do not fall in the neighbourhood of the other, trivial fixed point, $u^* = 0$, where the expanded chain becomes a Gaussian ideal coil. In § 3 equation (2.14) is used in the limit $\varepsilon \to 0$ to obtain useful results for the real dimensionalities $d = 3, 2, 1$.

2.2. Configurations returning to origin

The second quantity that we study in this work is the number of configurations returning to the origin, given by

$$U = \mu_0^N P[\mathbf{0}, N]. \tag{2.15}$$

Lattice enumerations of self-avoiding walks yield for U in the limit of large N the form

$$U = \mu^N N^{b_d}, \tag{2.16}$$

where b_d is a critical exponent depending only on the dimensionality and found to be close to $-\frac{7}{4}$ for $d = 3$ and close to $-\frac{3}{2}$ for $d = 2$. The parameter μ is the same as in the definition of C.

The same treatment is followed for the evaluation of U as previously for the evaluation of the number of total configurations. Using equation (2.2) for the probability distribution in equation (2.15), we obtain

$$U = \mu_0^N\Big(\text{———}_P - u \times 2\text{—●—}_P + \frac{u^2}{2} \times 8\text{—●—●—}_P\Big)_{R=0}. \tag{2.17}$$

Again using the expressions (2.3), (2.4) and (2.5) for the P diagrams, we obtain for the number of configurations returning to the origin the expression

$$U = \mu_0^N \Big[\text{———}_U - u \times 2 \text{———○———}_U + \frac{u^2}{2} \times 8 \Big(\text{———○○———}_U + \text{———⊗———}_U + \text{———⊖———}_U \Big) \Big], \tag{2.18}$$

with

$$\text{———}_U = 1/N^{d/2}, \tag{2.19a}$$

$$\text{———○———}_U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{(j-i)^{d/2}} \frac{1}{(N-j+i)^{d/2}}, \tag{2.19b}$$

$$\text{———○○———}_U = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \frac{1}{(j-i)^{d/2}} \frac{1}{(l-k)^{d/2}} \frac{1}{(N-j+i-l+k)^{d/2}}, \tag{2.19c}$$

$$\text{———⊗———}_U = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \frac{1}{(l-i-k+j)^{d/2}} \frac{1}{(k-j)^{d/2}} \frac{1}{(N-l+i)^{d/2}}, \tag{2.19d}$$

$$\text{———⊖———}_U = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^{N} \frac{l_{\text{eff}}^{d/2}}{l_1^{d/2} l_2^{d/2} l_3^{d/2}} \frac{1}{(N-l_1-l_2-l_3+l_{\text{eff}})^{d/2}}, \tag{2.19e}$$

where the symbols have the same meaning as before. Using the values of the diagrams (2.19) from table 1 in equation (2.18), we find for U

$$\begin{aligned} U = \mu_0^N \{ & N^{-(4-\varepsilon)/2} - u(1/N^2)[2N + 4 \ln N + \varepsilon(3 \ln^2 N + N \ln N)] \\ & + \tfrac{1}{2} u^2 (8/N^2)[(\tfrac{1}{2}N^2 - \ln N) + (3 \ln^2 N + 2N \ln N) + (3 \ln^2 N)]\}, \end{aligned} \tag{2.20}$$

which upon ordering powers of u and ε in the limit $N \to \infty$ leads to

$$\begin{aligned} U = (\mu_0^N/N^2)\{1 + [\tfrac{1}{2}\varepsilon \ln N - u(2N + 4 \ln N)] + [\tfrac{1}{8}\varepsilon^2 \ln^2 N - u\varepsilon(3 \ln^2 N + N \ln N) \\ + 4u^2(\tfrac{1}{2}N^2 + 6 \ln^2 N + 2N \ln N)]\}. \end{aligned} \tag{2.21}$$

Again looking for the values of u which make the series (2.21) sum to an exponential function, we recover the same values $u^* = 0, \varepsilon/16$ found in the study of the number of total configurations C. This demonstrates that the results of renormalisation group theory about the existence of a unique fixed point apply correctly to the study of polymers. Using the non-trivial value $u^* = \varepsilon/16$ in equation (2.21), we obtain the number of configurations returning to the origin as

$$U = \mu_0^N \, \mathrm{e}^{-\varepsilon N/8} N^{-2+\varepsilon/4} = \mu^N N^{-2+\varepsilon/4}, \qquad \mu = \mu_0 \, \mathrm{e}^{-\varepsilon/8}. \tag{2.22}$$

Equation (2.22) has the same form that lattice enumerations yield, with μ being the same as in the expression (2.14) for the number of total configurations. Equation (2.22) will also be used in the next section as a boundary solution in the limit $\varepsilon \to 0$ in order to derive results for the real dimensionalities $d = 3, 2, 1$.

2.3. Mean end-to-end square distance

We now proceed to study the property most studied previously, the mean end-to-end square distance of the coil, $\langle R^2 \rangle$, defined as the second moment of the distribution

function equation (1.3),

$$\langle R^2\rangle = \int \mathrm{d}^d\boldsymbol{R}\, R^2 P[\boldsymbol{R}, N] \Big/ \int \mathrm{d}^d\boldsymbol{R}\, P[\boldsymbol{R}, N]. \tag{2.23}$$

It physically represents the dimensions of the polymer coil. In the limit of large N, $\langle R^2\rangle$ behaves as

$$\langle R^2\rangle \sim N^{2\nu_d}, \tag{2.24}$$

where ν_d is a third critical exponent believed to be close to $\frac{3}{5}$ for $d=3$ and close to $\frac{3}{8}$ for $d=2$. The evaluation proceeds in exactly the same way. Equation (2.2) for the probability distribution is substituted into equation (2.23) to yield

$$\langle R^2\rangle = \Big[\int \mathrm{d}^d\boldsymbol{R}\, R^2 \Big(\text{———}_P - u\times 2\text{—●—}_P + \frac{u^2}{2}\times 8\text{—●—●—}_P \Big)\Big]$$
$$\times \Big[\int \mathrm{d}^d\boldsymbol{R} \Big(\text{———}_P - u\times 2\text{—●—}_P + \frac{u^2}{2}\times 8\text{—●—●—}_P \Big)\Big]^{-1}. \tag{2.25}$$

Using again the expressions (2.3), (2.4) and (2.5) for the P diagrams, we obtain

$$\langle R^2\rangle = \text{———}_{\langle R^2\rangle} + u\times 2\text{—○—}_{\langle R^2\rangle} + \frac{u^2}{2}\Big[8\text{—○—}_C \times \text{—○—}_{\langle R^2\rangle}$$
$$+8\Big(\text{—○○—}_{\langle R^2\rangle} + \text{—⊗—}_{\langle R^2\rangle} + \text{—◯—}_{\langle R^2\rangle}\Big)\Big], \tag{2.26}$$

with

$$\text{———}_{\langle R^2\rangle} = N, \tag{2.27a}$$

$$\text{—○—}_{\langle R^2\rangle} = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \frac{1}{(j-i)^{d/2-1}}, \tag{2.27b}$$

$$\text{—○○—}_{\langle R^2\rangle} = -\sum_{i=1}^{N-3}\sum_{j=i+1}^{N-2}\sum_{k=j+1}^{N-1}\sum_{l=k+1}^{N} \Big(\frac{1}{(j-i)^{d/2-1}(l-k)^{d/2}} + \frac{1}{(j-i)^{d/2}(l-k)^{d/2-1}}\Big), \tag{2.27c}$$

$$\text{—⊗—}_{\langle R^2\rangle} = -\sum_{i=1}^{N-3}\sum_{j=i+1}^{N-2}\sum_{k=j+1}^{N-1}\sum_{l=k+1}^{N} \Big(\frac{(l-i)}{(l-i-k+j)^{d/2}(k-j)^{d/2}}\Big), \tag{2.27d}$$

$$\text{—◯—}_{\langle R^2\rangle} = -\sum_{i=1}^{N-3}\sum_{j=i+1}^{N-2}\sum_{k=j+1}^{N-1}\sum_{l=k+1}^{N} \Big(\frac{l_1+l_2+l_3-l_{\mathrm{eff}}}{l_1^{d/2}l_2^{d/2}l_3^{d/2}}\Big). \tag{2.27e}$$

The diagrams (2.27) are also calculated and listed in table 1. Using their values in equation (2.26), we take for the mean end-to-end square distance

$$\langle R^2\rangle = N + u(2N\ln N - 2N + \tfrac{1}{2}\varepsilon N\ln^2 N) + \tfrac{1}{2}u^2\{8(N-\ln N)(N\ln N - N)$$
$$+8[(2N\ln^2 N - N^2\ln N + \tfrac{3}{2}N^2)$$
$$+(3N\ln N - N\ln^2 N - \tfrac{1}{2}N^2) - \tfrac{3}{2}N\ln^2 N]\}, \tag{2.28}$$

which upon ordering powers of u and ε gives in the limit $N\to\infty$ the expression

$$\langle R^2\rangle = N[1 + 2u\ln N + (\tfrac{1}{2}u\varepsilon - 6u^2)\ln^2 N]. \tag{2.29}$$

Values of u that convert the series to an exponential function are the ones found before, namely $u^* = 0, \varepsilon/16$. For $u^* = -\varepsilon/16$ relation (2.29) becomes

$$\langle R^2 \rangle = N^{1+\varepsilon/8}, \tag{2.30}$$

giving the value for the critical exponent

$$\nu_{4-\varepsilon} = \tfrac{1}{2}(1+\varepsilon/8) \qquad \text{as} \quad \varepsilon \to 0. \tag{2.31}$$

The above result is identical to the renormalisation group result in the limit $\varepsilon \to 0$.

3. Interdimensional relationships

In this section we give the expressions which relate the various properties at different dimensionalities. They will help us to obtain useful results for the real dimensionalities $d = 3, 2, 1$ using as a known boundary solution the one found in the previous section for $d = 4 - \varepsilon$ $(\varepsilon \to 0)$.

The main quantity in this treatment is the mean end-to-end square distance, $\langle R^2 \rangle$, equivalent to the inverse of the square of the correlation length in critical phenomena. It physically represents the square of the physical length of the coil. In a previous article (Kosmas and Freed 1978b) we considered the polymer chain between two hyperplanes (Daoud and de Gennes 1977) and we were able to correlate the solution at two different dimensionalities d and $d-1$. For the exponents ν_d and ν_{d-1} the relation

$$2 - \frac{1}{\nu_d} = \frac{4-d}{5-d}\left(2 - \frac{1}{\nu_{d-1}}\right)$$

was found. Writing this relation in a more suitable form, we notice that

$$\frac{2-1/\nu_d}{4-d} = \frac{2-1/\nu_{d-1}}{4-(d-1)} = \frac{2-1/\nu_{d-2}}{4-(d-2)} = \cdots = C_\nu, \tag{3.1}$$

where C_ν is a constant of the problem independent of the dimensionality. The invariant C_ν may be evaluated by means of the solution close to four dimensions previously developed in § 2, and consequently ν_d can be determined as a function of the dimensionality of the system. Employing equation (2.31), C_ν is calculated as

$$C_\nu \underset{\varepsilon \to 0}{=} \frac{2-1/\nu_{4-\varepsilon}}{4-(4-\varepsilon)} = \frac{2-2(1+\varepsilon/8)^{-1}}{\varepsilon} = \frac{2-2(1-\varepsilon/8)}{\varepsilon} = \frac{1}{4}. \tag{3.2}$$

Combining equations (3.1) and (3.2), we determine the critical exponent ν_d as

$$\nu_d = 4/(4+d). \tag{3.3}$$

The above treatment demonstrates that the solution of the problem close to the critical dimensionality $d = 4$, in connection with the interdimensional relation (3.1), leads to an expression for the critical exponent ν_d slightly different from that given by Flory's formula, equation (1.4). Thus for $d = 3$ and 2 equation (3.3) yields $2\nu_3 = 1.143$ and $2\nu_2 = 1.333$ respectively, in fair agreement with the corresponding results obtained from equation (1.4), $2\nu_3 = 1.2$ and $2\nu_2 = 1.5$. But the difference becomes pronounced at dimension $d = 1$, where the present result gives $2\nu_1 = 1.60$ compared with $2\nu_1 = 2$ of the previous theory. Possible explanations for this discrepancy are discussed in the next section.

We now proceed to find how the expressions that give a certain property of the polymer chain at different dimensionalities correlate with each other. Let us consider a general property E with an ideal exponent e_d^0 ($u = 0$), and write a general expression for E in the form (Kosmas and Freed 1978b)

$$E = N^{e_d^0} f_E(uN^{(4-d)/2}). \tag{3.4}$$

If we confine the polymer between two hyperplanes a distance D apart, we take

$$E = N^{e_d^0} f'_E(uN^{(4-d)/2}, D/N^{1/2}). \tag{3.5}$$

The effect of the parameter $uN^{(4-d)/2}$ is to combine with the rest of the parameters of the problem to give the non-ideal results. Defining a non-ideal exponent e_d for the dimensionality d, we find from equation (3.5) that

$$\begin{aligned} E &= N^{e_d^0}(uN^{(4-d)/2})^{2(e_d-e_d^0)/(4-d)} f_1\left(\frac{D}{N^{\nu_d} u^{(2\nu_d-1)/(4-d)}}\right) \\ &= N^{e_d} u^{2(e_d-e_d^0)/(4-d)} f_1\left(\frac{D}{N^{\nu_d} u^{(2\nu_d-1)/(4-d)}}\right). \end{aligned} \tag{3.6}$$

Accepting a power law dependence of f_1 on its argument for $D \to 0$, we recover the $d-1$ problem so that

$$\begin{aligned} E &= N^{e_d} u^{2(e_d-e_d^0)/(4-d)} (N^{\nu_d} u^{(2\nu_d-1)/(4-d)})^{-w} D^w \\ &= cN^{e_{d-1}} u^{2(e_{d-1}-e_{d-1}^0)/[4-(d-1)]}, \end{aligned} \tag{3.7}$$

where c is a constant independent of u and N.

Equating the exponents of the variables N and u in the two members of equation (3.7), we take two relations including the unknown w. Eliminating w, we obtain

$$\frac{2}{4-d}(e_d - e_d^0) - e_d\left(\frac{2-1/\nu_d}{4-d}\right) = \frac{2}{4-(d-1)}(e_{d-1} - e_{d-1}^0) - e_{d-1}\left(\frac{2-1/\nu_d}{4-d}\right). \tag{3.8}$$

But $(2-1/\nu_d)/(4-d)$ is a constant of the problem, and thus after using equation (3.2) we find another constant of the problem independent of the dimensionality, namely

$$\frac{2}{4-d}(e_d - e_d^0) - \frac{e_d}{4} = \frac{2}{4-(d-1)}(e_{d-1} - e_{d-1}^0) - \frac{e_{d-1}}{4} = \cdots = C_e. \tag{3.9}$$

The C_e is to be determined for each property from the solution close to dimensionality four.

As a first example we study the number of total configurations C for which $a_d^0 = 0$. Equation (3.9) then becomes

$$\frac{2}{4-d}(a_d) - \frac{a_d}{4} = C_a. \tag{3.10}$$

The solution close to four dimensions gives (see equation (2.14)) $a_{4-\varepsilon} = \varepsilon/8$, which substituted in equation (3.10) gives $C_a = \frac{1}{4}$. This information is enough to determine a_d as a function of dimensionality:

$$a_d = (4-d)/(4+d). \tag{3.11}$$

This equation gives the following results for the various dimensionalities: $a_3 = 0.143$,

$a_2 = 0.333$, $a_1 = 0.600$. They are slightly different at $d = 3$ from what lattice enumerations studies (Domb 1969) have found ($a_3 = 0.167$, $a_2 = 0.333$).

For the walks returning to the origin $b_d^0 = -d/2$ and so equation (3.9) becomes

$$\frac{2}{4-d}\left(b_d + \frac{d}{2}\right) - \frac{b_d}{4} = C_b. \tag{3.12}$$

From the solution close to four dimensions (see equation (2.22)) we have $b_{4-\varepsilon} = -2 + \varepsilon/4$ which, used in (3.12), gives $C_b = 0$. This determines b_d as a function of dimensionality:

$$b_d = -4d/(4+d). \tag{3.13}$$

The corresponding indices at $d = 3, 2, 1$ are $b_3 = -1.714$, $b_2 = -1.333$ and $b_1 = -0.800$ respectively, again slightly different from results yielded by lattice enumerations studies ($b_3 = -1.750$, $b_2 = -1.500$). Possible explanations of these differences between the present Gaussian model with excluded volume and the self-avoiding walk model are discussed in the next section.

4. Discussion

We have given a solution to the configurational problem of dilute polymer solutions close to four dimensions. We have determined a specific value of the interaction parameter u completely equivalent to the fixed point value in renormalisation group theory. For the fixed point value of the interaction parameter, the various series that describe the properties of the system can be summed to exponential functions. The solution for $d = 4 - \varepsilon$ is important, since it bears all the characteristics of the problem at real dimensionalities; additional information is obtained by using it as a boundary solution in interdimensional relationships to derive results for $d = 3$, 2 and 1.

The results of the present work are very close to those of renormalisation group theory of the Ginzburg–Landau–Wilson model. The agreement becomes exact in the limit of small ε where the ε expansion of renormalisation group theory tends to a correct limit. As we have already mentioned, the present method also confirms the uniqueness of the fixed point regardless of the property that we study, as has been well demonstrated from the independent calculations of C, U, and $\langle R^2 \rangle$. The main advantage of the method is its simplicity. We arrive at results analogous to those of the renormalisation group using a simple perturbation scheme, and this fact enables the adoption of the present technique to more complicated problems.

The interdimensional relationship given by equation (3.1) is a general law describing the non-ideal behaviour of a polymer chain under the present Gaussian model with excluded volume. To give useful results it must be combined with a solution at a specific dimensionality. This is because we need to determine the invariant of the problem, C_ν of equation (3.1), in order to express ν_d as a function of the dimensionality. Kosmas and Freed (1978b) have used the one-dimensional rigid rod $\nu_1 = 1$ in equation (3.1) as a known solution, and have recovered in this way the mean field results given by equation (1.4). Their result, together with the result of the present model, $\nu_1 = 0.8$ obtained by using the correct boundary solution $\nu_{4-\varepsilon} = \frac{1}{2}(1 + \varepsilon/8)$ in equation (3.1), indicate some possible differences between the Gaussian excluded volume model and the self-avoiding walk model for low dimensionalities. The former model allows crossings of the polymer chain whereas the self-avoiding walk model forbids such configurations.

Of course, for higher dimensionalities the difference is negligible, since both models for d approaching four converge to ideal ones. As we have seen, the present results are good compared with lattice enumerations studies of self-avoiding walks for $d = 2$ and 3. The question then posed is whether the lack of identity between the two models is the cause of the more pronounced difference in the exponents for $d = 1$.

For $d = 1$ the conformation in the self-avoiding walk model is that of a rigid rod, clearly yielding $\langle R^2 \rangle = N^{2\nu_1}$, $\nu_1 = 1$. The situation is different in the Gaussian model with excluded volume. This model for $d = 1$ deals with the distribution of N segments $X_1, X_2, \ldots, X_N$ lying on a line. The segments interact with an energy expressed by the Boltzmann factor of equation (1.3). Such an interaction does not prevent permutations of the segments along the line in which the two segments X_1 and X_N, the two physical ends of the chain, are not the two ends of the permutation. Physically, such permutations represent configurations of the polymer in which folding occurs. The mean end-to-end square distance of folded configurations is less than N^2, which is the corresponding value for the full extended chain. The problem under these conditions is a one-dimensional long-range problem, and bears all the characteristics of the two- and three-dimensional analogues, in contrast with the self-avoiding walk problem which at $d = 1$ allows only the rigid rod configuration. By taking into account the folded configurations, the Gaussian model with excluded volume necessarily yields mean end-to-end distance less than that of the rigid rod, $\langle R^2 \rangle \sim N^2$, but at the same time larger than the ideal coil answer, $\langle R^2 \rangle \sim N$. It is clear that the correct answer must lie somewhere between these two limits, having the form $\langle R^2 \rangle \sim N^{2\nu_1}$ with ν_1 between $\frac{1}{2}$ and 1, presumably close to our result 0.8. Analogous differences can be detected for higher dimensionalities, though the non-ideality of the chain reduces as the dimensionality of the space increases.

Concluding, we mention that beyond the insight we have gained from the solution of the polymer conformational problem at $d = 4 - \varepsilon$, which exhibits all the important features of the solution at real dimensionalities, we have confirmed the uniqueness of the fixed point for the several properties of the polymer coil. We have found the exponents ν_d, a_d and b_d as functions of the dimensionality and we have determined the activity μ of a real chain. Finally we have questioned possible differences between the present Gaussian model with excluded volume and the self-avoiding walk model close to dimensionality $d = 1$.

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Appendix

Here we give examples of evaluation of diagrams. We will evaluate ———_C and $\text{○—○}_{\langle R^2 \rangle}$. For $d = 4 - \varepsilon$,

$$\text{○—}_C = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{(j-i)^{(4-\varepsilon)/2}}, \tag{A1}$$

which upon making the substitution $i-j=k$ for small ε gives

$$\text{—○—}_C = \sum_{k=1}^{N-1} (N-k)\left(\frac{1}{k^2}+\frac{\varepsilon}{2}\frac{\ln k}{k^2}\right). \tag{A2}$$

At this stage we convert the summation into an integration to obtain

$$\text{—○—}_C = N\int_1^{N-1}\frac{\mathrm{d}k}{k^2}-\int_1^{N-1}\frac{\mathrm{d}k}{k}+\frac{\varepsilon}{2}\left(N\int_1^{N-1}\frac{\mathrm{d}k}{k^2}\ln k-\int_1^{N-1}\frac{\mathrm{d}k}{k}\ln k\right). \tag{A3}$$

The integrals of A3 are trivial, and give in the limit $N\to\infty$ the final form

$$\text{—○—}_C = N-\ln N+\tfrac{1}{2}\varepsilon(N-\tfrac{1}{2}\ln^2 N), \tag{A4}$$

which is listed in table 1.

The second-order diagrams are lengthier. We need second-order diagrams only in order ε^0 so $d/2=2$.

$$\text{—○○—}\langle R^2\rangle = -\sum_{i=1}^{N-3}\sum_{j=i+1}^{N-2}\sum_{k=j+1}^{N-1}\sum_{l=k+1}^{N}\left(\frac{1}{(j-i)(l-k)^2}+\frac{1}{(j-i)^2(l-k)}\right). \tag{A5}$$

Upon making the substitution $j-i=k_1$, $l-k=k_2$ we convert (A5) into

$$\text{—○○—}\langle R^2\rangle = -\frac{1}{2}\sum_{k_2=1}^{N-3}\sum_{k_1=1}^{N-2-k_2}(N-k_1-k_2)^2\left(\frac{1}{k_1k_2^2}+\frac{1}{k_1^2k_2}\right). \tag{A6}$$

Converting the summations into integrations, and taking into account the fact.that the two sums of (A6) give the same result, we obtain

$$\text{—○○—}\langle R^2\rangle = -\int_1^{N-3}\mathrm{d}k_2\int_1^{N-2-k_2}\mathrm{d}k_1(N-k_1-k_2)^2\frac{1}{k_2^2k_1}. \tag{A7}$$

The integrations of (A7) are straightforward and in the limit of $N\to\infty$ give the result

$$\text{—○○—}\langle R^2\rangle = 2N\ln^2 N-N^2\ln N+\tfrac{3}{2}N^2, \tag{A8}$$

also listed in table 1.

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