On the Many-Chain Problem: A Class of Skeleton Diagrams. From a Dilute to a Semidilute System, to the Flory–Huggins Limit

M. K. Kosmas

Chemistry Department, University of Ioannina, Ioannina, Greece.

Received December 28, 1987; Revised Manuscript Received January 4, 1988

ABSTRACT: We study the problem of many interacting polymer chains and a class of basic diagrams is found to govern the behavior of the system. The values of these diagrams can be summed up and the contributions from the rest diagrams can be incorporated, so that the properties of the system can be found in all regions of concentration, molecular weight, and intensity of excluded-volume interactions. Closed functions up to an integral are given for the osmotic pressure and the mean end-to-end square distance of a coil which are capable of describing the regions of dilute, semidilute, and concentrated solutions. The characteristic exponents of all virial coefficients of these properties are calculated to the order $\epsilon = 4 - d$ (d is the dimensionality of space), and an alternating rule for their signs is found. The transition from the semidilute region where the properties depend on the ratio C_m/C_m^*, the solution monomer concentration to the local coil concentration, to the concentrated solution where the properties depend on the monomer concentration C_m is analyzed.

1. Introduction

The understanding of polymer solutions with variable amounts of polymer dissolved in a solvent has to pass through the problem of many interacting chains.[1] Beyond its importance for the description of concentrated polymer solutions[2] the many-chain problem is the initial step toward more complicated systems of polymers. Such systems can be systems of polymers of various architectures[3] such as rings, stars, or combs where the architecture is an extra factor to be considered or systems of polymers at interfaces where the presence of a surface interacting with the macromolecules is of dominant importance.[4] The difficulties and the interest of a system of many polymer chains arise from the existence of two kinds of interactions:[5] the intrachain interactions between units belonging to the same chain, which describe isolated coils in dilute solutions and to which much study has been devoted,[6-8] and the interchain interactions between units belonging to different chains, which become important as the concentration of the polymer in the solution increases.[1,2]

If the concentration of macromolecules in the solution is varied, three main regions can be realized.[1,9] The first one is the dilute region of small concentration where the polymer coils are on the average far apart and the behavior of isolated macromolecules determines the macroscopic properties of the system. Increasing the concentration, the coils approach each other and the interactions between them start becoming important. In this region the concentration of the polymer can be treated as a small parameter and the macroscopic properties can be expressed in virial expansions in powers of the concentration of macromolecules, C_p = number of chains/volume. The corresponding monomer concentration is equal to $C_m = C_pN$, where N stands for the number of monomers per chain and it is proportional to the molecular weight and the contour length of the chains. The actual dependence of the properties on the concentration comes from the ratio C_m/C_m^* of the global monomer concentration C_m to the local coil concentration of monomers C_m^*, expressing the ratio of the volume occupied by each coil to the volume available to each of them. With further increase in concentration, the space available to each chain becomes less than its own volume and the chains start to interpenetrate. This is the onset of semidilute solution where the macroscopic properties are still described by means of the ratio C_m/C_m^*.[9-11] The dependence of C_m^* on N has as a result the explicit appearance in the macroscopic properties up to the semidilute solution of both the concentration C_m of monomers and the molecular weight N of the chains. Further increase in concentration leads to more dense systems, where a monomer sees other monomers coming from its own or other chains in the same way, resulting in the loss of the meaning of the chains and of their lengths. The parts of the properties coming from the interactions of many chains do not have an explicit dependence on the molecular weight N in this limit, but they depend only on the monomer concentration C_m. Such behavior starts at the end of semidilute solution where proper power laws with respect to the large ratio C_m/C_m^* yield the independence on N. This region can be considered as the beginning of the concentrated solution where mean-field arguments can be applied.

Previous theoretical studies on the subject include the works of Huggins and Flory who describe the concentrated region.[12-14] On the basis of mean-field arguments applicable in this region, they give a theoretical derivation of the linear relationship between the osmotic pressure Π and C_m^2, observed experimentally. Edwards[1] defines the regions of dilute, semidilute, and concentrated polymer solutions and by means of his continuous model and self-consistent field theories describes the semidilute region, giving an expression of the osmotic pressure in terms of the concentration, the molecular weight, and the excluded-volume parameter. Though the proper strong concentration dependence $\Pi \sim C_m^{9/4}$ of the semidilute region, as well as the dependence $\Pi \sim C_m^2$ of the concentrated region, is found,[15] the right C_m/C_m^* dependence of less dense systems and the way of going from the C_m/C_m^* dependence to the C_m dependence are not given. des Cloizeaux[10] uses diagrams irreducible with respect to the interaction lines, and eliminating the short-range divergences derives the scaling law[16,17] correlating the osmotic pressure with the product $C_p\langle R^2\rangle^{d/2}$ ($\langle R^2\rangle$ is the mean end-to-end square distance of a coil and d is the dimensionality of the space) proportional to the ratio C_m/C_m^*. He also uses diagrams with one loop and describes the region of small excluded-volume interactions, giving a parametric representation of osmotic pressure and the size of the coil in terms of fugacities.[18] Duplantier[19] treats the problem at $d = 4$ and describes the semidilute region, giving expressions for small second virial coefficient. Freed and co-workers,[20,21] by means of direct *renormalization*, describe semidilute solutions and extend the study of linear chains to rings and stars. Ohta and Oono[22-24] use Edward's

0024-9297/89/2222-0720$01.50/0

method and give closed forms for Π and the mean end-to-end square distance $\langle R_1^2 \rangle_c$ of a coil in the semidilute region, to order $\epsilon = 4 - d$. These previous theories either focused on the C_m/C_m^* dependence capable of describing the dilute and the semidilute solutions or establish the C_m dependence without an appearance of N describing the high concentration limit. No theory studies the transition from the one behavior to the other.

Experimentally, Noda et al.[25] determine the osmotic pressure of polystyrene for a large range of concentrations starting from dilute up to semidilute solutions. In the dilute region they find that Π/C_m is smaller for larger N in accordance with the ideal relation of the dilute system, Π/C_m - $(1/N)$. Their results fit a universal graph up to moderate concentrations in accordance with the scaling law $\Pi N/C_m = F(C_m/C_m^*)$, and the proper power law dependence describing the beginning of dense systems where Π does not depend on N is also well described. With further increase in concentration, the concentrated region is reached where C_m determines the osmotic pressure in a $\Pi \sim C_m^2$ law (see Flory 1942, Huggins 1942, and references therein).

The previous theories do not describe all chain behaviors in a unified way. In this work we make such an effort and describe all regions of concentration, excluded-volume interactions, and molecular weights in a unified way, extending previous results of semidilute solutions in order to describe concentrated solutions as well. The technique and the results of the present work can also be applied to the study of more complicated problems of many chains met in systems of chains of various architectures[3,21] or systems of chains interacting with substrates.[4] The class of the basic skeleton diagrams (loop diagrams of des Cloizeaux) used to build macroscopic properties (see sections 2A and 2B) can also be employed for the description of these complicated but more useful cases.

An important parameter in the study of the macroscopic properties of chains is the dimensionality d of space.[7] Its role has been explained previously where techniques based on its importance have been applied with success to few chain problems. The combination $uN^{(4-d)/2}$, with u the excluded-volume parameter, expresses the nonidealities and governs the conformational behavior of the chains. For $d > 4$ this combination becomes negligible for large N, meaning that nonidealities do not contribute for dimensionalities $d > 4$. For $d \leqslant 4$, $uN^{(4-d)/2}$ becomes important and it becomes larger as d decreases. The existing nonidealities for $d < 4$ are smaller for larger d, which implies that the difficulties faced for solving the problems get less for larger d. At $d = 4$, $N^{(4-d)/2}$ is equivalent to $\ln N$ with the smallest possible values which makes $d = 4$ the best dimensionality to work at because the chains behave nonideally, while the difficulties faced for their description are the least possible to overcome. It is characteristic for example that the critical exponents and the general structure of the various properties can be found from first-order perturbation theory at $d = 4$. Properties concerning isolated chains behave at $d = 4$ as[7]

$$P = P_0[1 + xu \ln N + ...] \sim P_0 N p \qquad (1.1)$$

The exponent p can be found from the number x of first-order calculations, and the fixed point value $u^* = \epsilon/16$ as $p = xu^* = x\epsilon/16$ ($\epsilon = 4 - d$). The quantity inside the brackets in eq 1.1 at $d = 4$ behaves like $[1 + 8u \ln N]^a$ with a capable of being determined also from x as $a = x/8$. The same general rules apply to systems of more chains. The second virial coefficient, for example, concerning two chains behaves like[26] $A_2 \sim uN^2(1 - 4u \ln N + ...) \sim uN^2[1 + 8u \ln N]^{-1/2}$ at $d = 4$, which means that the critical exponent δ of $A_2 \sim uN^\delta$, valid to the large molecular weight limit $N \rightarrow \infty$, is equal to $\delta = 2 - 4u^* = 2 - (\epsilon/4)$, while the structure of the solution at $d = 4$ is of the general form $A_2 \sim uN^2(1 + 8u \ln N)^a$, with $a = -1/2$.

The appearance of $\ln N$ in the one-loop first-order calculations of the various properties at $d = 4$ means a strong contribution of the nonidealities, accompanying the change of the ideal values of the critical exponents to their nonideal ones. On the other hand, if a $\ln N$ does not appear in the first-order u term of a property, its ideal exponent does not change and the effects of the excluded-volume interactions on the specific property in the limit of large molecular weights are negligible. This last criterion can be used to check the cancellation of excluded-volume effects coming from different sources such as intra- and interexcluded-volume interactions, both present in systems of many chains.

Having these observations in mind we proceed to study a system of many chains at $d = 4 - \epsilon$ (ϵ small), aiming at the description of the general structure of the solution and the behavior of systems of many chains. In the next section a canonical ensemble is used where a class of important diagrams is found to determine the behavior of the system. The osmotic pressure and the mean end-to-end square distance of a coil are given as expressions including an integral, capable of describing the system as a function of concentration, molecular weight, and excluded-volume interactions. In section 3 we find the values of the diagrams and we study the overall solution for $d = 4$. The regions of dilute and semidilute solutions and the limiting concentrated region are properly described in section 4. In the final section 5 a brief conclusion is given.

2. Formulation in a Canonical Ensemble

In a canonical ensemble the probability distribution $P\{r_{im}\}$ of the system of n chains in a volume V is given by

$$P\{r_{im}\} = P_0\{r_{im}\} \exp\{-u \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m=1}^{n} \delta^d(r_{im} - r_{jm}) \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m=1}^{n} \sum_{m'=1}^{n} \delta^d(r_{im}{}^n - r_{jm'}{}^n)\}; \qquad i \neq j, \quad m \neq m' \qquad (2.1)$$

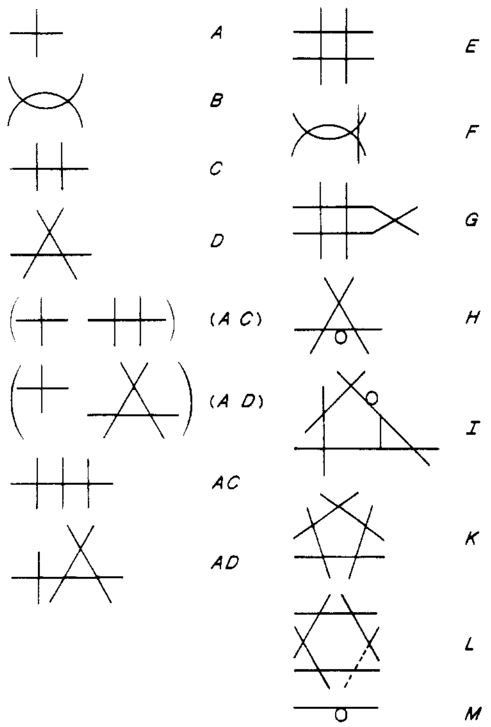
with $P_0\{r_{im}\} = \exp\{-(d/2\pi l^2)\sum_{i=1}^{N}\sum_{m=1}^{n}(r_{im} - r_{i+1,m})^2\}$ the ideal probability expressing the connectivity terms of the n chains each made of N units. u is the excluded-volume parameter describing both intra- and interexcluded-volume interactions, considered to be of equal intensity, and the first and the second parts of the exponential term represent the intra- and interexcluded-volume interactions, respectively.

2A. The Osmotic Pressure. In order to find the osmotic pressure $\Pi = kT\partial \ln Z/\partial V$ of the system, the configurational partition function Z is needed. Z is a central quantity in the canonical ensemble and it can be found after the performance of a multiple integral of the probability distribution $P\{r_{im}\}$ over all nN positions $r_{im}\{i = 1, 2, ..., N;\ m = 1, 2, ..., n\}$ of all the units of the chains.

$$Z = \int \prod_{i=1}^{N} \prod_{m=1}^{n} d^d r_{im} P\{r_{im}\} \qquad (2.2)$$

A way to calculate Z and the rest correlated quantities is to use initially a perturbation theory with respect to interexcluded-volume interactions, hiding for a later step the intraexcluded-volume interactions. In this procedure the various order diagrams taken in the first step from the interexcluded-volume interactions will refer to chains with intraexdluded-volume interactions. Expanding $P\{r_{im}\}$ of

Chart I



eq 2.1 with respect to interexcluded-volume interactions we take the expression

$$Z = \langle 1 - u[\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m=1}^{n} \sum_{m'=1}^{n} \delta^d(r_{im} - r_{jm'})] + (1/2!)u^2[\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m=1}^{n} \sum_{m'=1}^{n} \delta^d(r_{im} - r_{jm'})]^2 + \sum_{i>2}[(-u)^i/i!][\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m=1}^{n} \sum_{m'=1}^{n} \delta^d(r_{im} - r_{im'})]^i\rangle, \qquad m \neq m' \tag{2.3}$$

where the brackets $\langle\ \rangle$ denote the average over all positions of units with respect to the rest part $P_0\{r_{im}\}$ $\exp\{-u\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{m=1}^{n}\delta^d(r_{im} - r_{jm})\}$ $(i \neq j)$ of the probability which includes the remaining intraexcluded-volume interactions. Each δ function of equation 2.3 brings in contact two polymeric units from two different chains. In the first- and second-order diagrams, for example, of the form A and B (Chart I), the two nonideal chains are joined in one and two points due to the action of one and two δ functions, respectively. In the evaluation of physical properties like the osmotic pressure Π or the mean end-to-end square distance of a chain in the presence of other chains $\langle R_1^2\rangle_c$, disconnected diagrams like (A C) or (A D) or diagrams with open structures like AC or AD cancel (see ref 10). The rest diagrams contribute to the various orders of concentration depending on the number of the chains involved in them. Let us concentrate on the diagrams of i chains which contribute to the C_p^i terms. These diagrams can have in general m contacts between pairs of chains. The cases $m < i$ correspond to open structures which do not contribute, with an exception of the simple first-order diagram A, which contributes to the osmotic pressure. The rest diagrams have either $m = i$ or $m > i$. The cases with $m = i$ gives rise to ring-type diagrams (loop diagrams of ref 18) like D ($m = i = 3$) or E ($m = i = 4$), which are the simplest diagrams with structure and play a dominant role in the determination of the macroscopic properties. For $m > i$ the connections are more than the chains and examples are F ($m = 4$, $i = 3$) and G ($m = 5$, $i = 4$). These diagrams with $m > i$ together with the corresponding intraexcluded-volume diagrams of the same number of chains can be treated as derivative diagrams of the corresponding ring diagrams. Examples of derivative diagrams are H, which can be considered as a derivative diagram of the three-chain D ring diagram with an extra intrainteraction beyond the three-chain system, and I as a derivative diagram of the five-chain K ring diagram, with two extra contacts beyond the contacts of the five-chain ring. So in general each C_p^i term is described by a *skeleton* diagram of the ring type[27] and its *derivative* diagrams having the same number of chains but a larger number of contacts. Derivative diagrams alter the coefficients of the various powers of concentration in a simple regular way which is analyzed below.

For each macroscopic property of the system a skeleton expression can be given, initially coming from the contributions of the ring diagrams, and the effects of the derivative diagrams can then be incorporated, yielding the final expressions. In the case of the osmotic pressure Π the diagram B can be considered as a derivative diagram of the simple A diagram which survives. In the general $\langle[\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^i\rangle$ term, i δ functions act simultaneously on i chains so the ring diagram made from i chains is of the form L (i chains). The number of the ith ring diagrams equals the ways i chains can be taken out of n chains and form a ring and it comes out to be $n(n-1)(n-2)\ldots(n-i+1)2^{i-1}(i-1)!$. In the thermodynamic limit of $n \to \infty$, $V \to \infty$, and $n/V = C_p$ going to a constant, the term $\langle[\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^i\rangle$ yields the following number of ring diagrams

$$\langle[\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m=1}^{n} \sum_{m'=1}^{n} \delta^d(r_{im} - r_{jm'})]^i\rangle_{\mathrm{s}} = (n^i/V^{i-1})2^{i-1}(i-1)!2^iL, \qquad i \neq j \tag{2.4}$$

An s subscript is used from now on to denote the skeleton expression of a quantity coming from the contributions of the ring diagrams only. The form of the ring diagrams having a loop is equal in the Gaussian model to $(d/2\pi l \times \text{length of loop})^{d/2}$ which upon absorbing the $(d/2\pi l)^{d/2}$ constants in u's we take for their values

$$L = \int_0^N \mathrm{d}i_1 \int_{i_1}^N \mathrm{d}j_1 \int_0^N \mathrm{d}i_2 \int_{i_2}^N \mathrm{d}j_2 \ldots \int_0^N \mathrm{d}i_i \int_{i_i}^N \mathrm{d}j_i\ 1/(\text{length of loop})^{d/2} = \int_0^N \mathrm{d}l_1 \int_0^N \mathrm{d}l_2 \ldots \int_0^N \mathrm{d}l_i\ (N - l_1)(N - l_2) \ldots (N - l_i)/(l_1 + l_2 + \ldots + l_i)^{d/2};$$
$$\text{with} \quad l_1 = j_1 - i_1,\ l_2 = j_2 - i_2,\ \ldots,\ l_i = j_i - i_i \tag{2.5}$$

where the factor 2^i in eq 2.4 is separated from the definition of the ring diagram and comes from the two equivalent cases $i_i < j_i$ and $i_i > j_i$, for each chain. A factor of $1/V^{i-1} = V^{n-i+1}/V^n$ also appears because the average is taken over the positions of all the chains. In the denominator all of them move independently producing a V^n factor, while in the numerator, because of the presence of the ring, i chains move together producing a V factor times a V^{n-i} factor from the rest $n - i$ chains.

The structure of the form of the ring diagrams permits their evaluation up to an integral. Employing the dimensionless variables $x_i = l_i/N$ we take

$$L = N^{2i-(d/2)} \int_0^1 \mathrm{d}x_1 \int_0^1 \mathrm{d}x_2 \ldots \int_0^1 \mathrm{d}x_i\ (1 - x_1) \times (1 - x_2) \ldots (1 - x_i)/(x_1 + \ldots + x_i)^{d/2} \tag{2.6}$$

and if we write the denominator as $1/(x_1 + x_2 + \ldots + x_i)^{d/2}$

$= [1/\Gamma(d/2)]\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}e^{-p(x_1+x_2+...+x_i)}$, the i × integrations become separable and equivalent, yielding the expression

$$L = [N^{2i-(d/2)}/\Gamma(d/2)]\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}\left[\int_0^1 \mathrm{d}x\ (1-x)e^{-px}\right]^i \tag{2.7}$$

Calling

$$J = \int_0^1 \mathrm{d}x\ (1-x)e^{-px} = (e^{-p} - 1 + p)/p^2 \tag{2.8}$$

we see that the ring diagrams can be evaluated up to an integral as

$$L = [N^{2i-(d/2)}/\Gamma(d/2)]\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}J^i \tag{2.9}$$

The evaluation of the ring diagrams up to an integral permits the evaluation of the skeleton partition function corresponding to these diagrams up to an integral. Using the values of the ring diagrams as well as that of the two chain diagram $A = (un^2N^2/V)$ in eq 2.4 and 2.3, we take for the logarithm of the skeleton partition function of the ring diagrams, that is without taking account of the contributions of the derivative diagrams, the expression

$$[\ln Z]_s = n \ln V - (un^2N^2/V) + [N^{-d/2}/2\Gamma(d/2)]\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}\sum_{i=3}^{\infty}(-4uN^2nJ)^i(iV^{i-1}) \tag{2.10}$$

The skeleton osmotic pressure of the system can then be found as

$$\Pi_s/(kT) = \partial \ln Z_s/\partial V = C_p + uC_p^2N^2 + [N^{-d/2}/2\Gamma(d/2)]\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}\sum_{i=3}^{\infty}(-4uN^2JC_p)^i \times [-1 + (1/i)], \qquad C_p = n/V \tag{2.11}$$

The summation in eq 2.11 is trivial, leading to $\Pi_s/(kT) = C_p\{1 + (\lambda/4) + [2uN^{(4-d)/2}/\Gamma(d/2)]\lambda F_\pi(\lambda)\}$, where

$$F_\pi(\lambda) = (1/\lambda^2)\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}[(1/2)(\lambda J)^2 + (\lambda J)/(1 + \lambda J) - \ln(1 + \lambda J)], \qquad \lambda = 4uC_pN^2 \tag{2.12}$$

in accord with the results from other methods.[19,21,22] Analogous expressions of the function $J = (e^{-p} - 1 + p)/p^2$ have been given previously in the treatment of semidilute solutions. Duplantier[19] working at $d = 4$ and for a small second virial coefficient gives an $F_\pi(\lambda)$ function which includes only the first expansion term of $(\lambda J)/(1 + \lambda J)$. The function $F_\pi(\lambda)$ is the same as that given by Freed et al.[21] (see also ref 22) in their treatment up to order ϵ, but their expressions meant to describe the $\epsilon > 0$ region do not give the zeroth order ($\epsilon = 0$, ± > 0) limit given by means of eq 2.12 (see also ref 19). Moreover, these theories explaining the C_m/C_m^* dependence of semidilute solutions do not describe concentrated solutions where the dependence on N through C_m^* ceases to be valid. Equation 2.12 includes only the contribution from ring diagrams, while the contribution from the rest of the derivative diagrams have to be incorporated. The easiest way to do this is through the virial expansion of $\Pi_s/(kT)$. In an expansion in powers of λ (proportional to C_p) the function $F_\pi(\lambda)$ goes as

$$F_\pi(\lambda) = \int_0^\infty \mathrm{d}p\ p^{(d/2)-1}[(2/3)\lambda^1J^3 - (3/4)\lambda^2J^4 + (4/5)\lambda^3J^5 + ... + (-1)^{i-1}((i-1)/i)\lambda^{i-2}J^i + ...] = \sum_{i=3}^{\infty}\alpha_i\lambda^{i-2}, \qquad \alpha_i = (-1)^{i-1}[(i-1)/i]\int_0^\infty \mathrm{d}p\ p^{(d/2)-1}J^i \tag{2.13}$$

permitting the evaluation of the virial expansion of Π_s to various orders of C_p. The structure of Π_s resulting after the integrations is the following:

$$\Pi_s/(kT) = C_p\{1 + A_{2s}C_p + A_{3s}C_p^2 + A_{4s}C_p^3 + ... + A_{is}C_p^{i-1} + ...\} = C_p + A_{2s}C_p^2 + \sum_{i=3}^{\infty}A_{is}C_p^i \tag{2.14}$$

with

$$A_{2s} = uN^2, \quad A_{3s} = [2uN^{(4-d)/2}/\Gamma(d/2)]\alpha_3(4uN^2)^2, \quad A_{4s} = [2uN^{(4-d)/2}/\Gamma(d/2)]\alpha_4(4uN^2)^3, ..., \quad A_{is} = [2uN^{(4-d)/2}/\Gamma(d/2)]\alpha_i(4uN^2)^{i-1}, ...$$

The derivative diagrams change the skeleton virial coefficients of a property to their final forms. For the osmotic pressure we take for example that

$$A_{is} + \text{(action of derivative diagrams)} \rightarrow A_i \tag{2.15}$$

so that the final form of the property becomes

$$\Pi/(kT) = C_p + A_2C_p^2 + \sum_{i=3}^{\infty}A_iC_p^i \tag{2.16}$$

providing, after the evaluation of A_i by means of eq 2.15, a general expression of the property in terms of C_p, N, and u.

2B. Mean End-to-End Square Distance of a Coil. The mean end-to-end square distance $\langle R_1^2\rangle_c$ of a coil, expressing its size in the presence of other chains, is the second property that we study. It can be written in terms of the probability $P\{r_{im}\}$, eq 2.1, as

$$\langle R_1^2\rangle_c = \int\prod_{i=1}^{N}\prod_{m=1}^{n}\mathrm{d}^dr_{im}\ P\{r_{im}\}R_1^2 \Big/ \int\prod_{i=1}^{N}\prod_{m=1}^{n}\mathrm{d}^dr_{im}\ P\{r_{im}\} \tag{2.17}$$

We treat eq 2.17 in a similar fashion as eq 2.2 of the partition function. In the first step we find the skeleton expression from the contributions of the ring diagrams. If it is expanded with respect to interexcluded-volume interactions, all disconnected diagrams as well as diagrams with open structures cancel and leave for the skeleton property the expression

$$\begin{aligned}\langle R_1^2\rangle_{cs} = \langle R_1^2\rangle_{0s} - u\{&\langle R_1^2[\textstyle\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]\rangle - \langle R_1^2\rangle\langle[\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]\rangle\}_s + \\ (1/2)u^2\{&\langle R_1^2[\textstyle\sum\sum\sum\sum\delta^d(r_{im} - r_{im'})]^2\rangle - \langle R_1^2\rangle\langle[\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^2\rangle\}_s + \\ ... + [(-u)^i/i!]\{&\langle R_1^2[\textstyle\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^i\rangle - \langle R_1^2\rangle\langle[\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^i\rangle\}_s + ...\end{aligned} \tag{2.18}$$

The first-order u term vanishes while in the thermodynamic limit, $n \rightarrow \infty$, $V \rightarrow \infty$, $n/V = C_p$ finite, the u^i term is proportional to C_p^{i-1}

$$\{\langle R_1^2[\textstyle\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]\rangle - \langle R_1^2\rangle\langle[\delta^d(r_{im} - r_{jm'})]\rangle\}_s = 0$$

$$\{\langle R_1^2[\textstyle\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^i\rangle - \langle R_1^2\rangle\langle[\sum\sum\sum\sum\delta^d(r_{im} - r_{jm'})]^i\rangle\}_s = C_p^{i-1}2^{i-1}i!2^iL_R \tag{2.19}$$

The diagram L_R is made of i chains and its form can be found from the difference of the two terms of eq 2.19. It is equal to $-$(part of chain 1 in the loop)^2/(length of the loop)$^{(d/2)+1}$.

$$L_R = \int_0^N \mathrm{d}i_1 \int_{i_1}^N \mathrm{d}j_1 \int_0^N \mathrm{d}i_2 \ldots \int_0^N \mathrm{d}i_i \int_{i_i}^N \mathrm{d}j_i \, (-)(j_1 - i_1)^2 / (\text{length of the loop})^{(d/2)+1} = \int_0^N \mathrm{d}l_1 \int_0^N \mathrm{d}l_2 \ldots \int_0^N \mathrm{d}l_i \, (N - l_1)(N - l_2) \ldots (N - l_i)(-l_1^2) / (l_1 + l_2 + \ldots + l_i)^{(d/2)+1} = -[N^{2i+1-(d/2)} / \Gamma((d/2) + 1)] \int_0^1 \mathrm{d}x_1 \int_0^1 \mathrm{d}x_2 \ldots \int_0^1 \mathrm{d}x_i \, x_1^2(1 - x_1)(1 - x_2) \ldots (1 - x_i)$$

$$\int_0^\infty \mathrm{d}p \, p^{(d/2)} \exp\{-p(x_1 + x_2 + \ldots + x_i)\} = -[N^{2i+1-(d/2)} / \Gamma((d/2) + 1)] \int_0^\infty \mathrm{d}p \, p^{d/2} \left[\int_0^1 \mathrm{d}x \, (1 - x)x^2 \exp\{-px\} \right] \left[\int_0^1 \mathrm{d}x_1 \, (1 - x_1) \exp\{-px_1\} \right]^{i-1} = -[N^{2i+1-(d/2)} / \Gamma((d/2) + 1)] \int_0^\infty \mathrm{d}p \, p^{d/2} \phi J^{i-1} \quad (2.20)$$

with $\phi = \int_0^1 \mathrm{d}x \, (1 - x)x^2 \exp(-px) = (6/p^4)e^{-p} + (4/p^3)e^{-p} + (1/p^2)e^{-p} - (6/p^4) + (2/p^3)$ and the same J defined previously in eq 2.8. This evaluation of the ring diagrams up to an integral permits the evaluation of $\langle R_1^2 \rangle_{\mathrm{cs}}$ of eq 2.18 up to an integral.

$$\langle R_1^2 \rangle_{\mathrm{cs}} = \langle R_1^2 \rangle_{0\mathrm{s}} - [N^{1-(d/2)} / 2\Gamma((d/2) + 1)C_\mathrm{p}] \int_0^\infty \mathrm{d}p \, p^{(d/2)} (\phi / J) \sum_{i=2}^{\infty} (-\lambda J)^i = \langle R_1^2 \rangle_{0\mathrm{s}} - [8N^{5-(d/2)} u^2 C_\mathrm{p} / \Gamma((d/2) + 1)] \int_0^\infty \mathrm{d}p \, p^{(d/2)} \phi J / (1 + \lambda J) = \langle R_1^2 \rangle_{0\mathrm{s}} \{1 - [2uN^{2-(d/2)} / \Gamma((d/2) + 1)] F_\mathrm{R}(\lambda)\}; \qquad F_\mathrm{R}(\lambda) = \lambda \int_0^\infty \mathrm{d}p \, p^{(d/2)} \phi J / (1 + \lambda J), \quad \lambda = 4uC_\mathrm{p}N^2 \quad (2.21)$$

The negative term in eq 2.21 expresses the decrease of the size of the coil with the increase of concentration; it is bounded though by the value of u, which being of order $u^* = \epsilon/16$ ($\epsilon \to 0$) does not permit $\langle R_1^2 \rangle_{\mathrm{cs}}$ to obtain unphysical negative values (see also ref 22 where such terms are exponentiated). The function $F_\mathrm{R}(\lambda)$ can be expanded in powers of λ as

$$F_\mathrm{R}(\lambda) = \int_0^\infty \mathrm{d}p \, p^{(d/2)} \phi [\lambda J - (\lambda J)^2 + \ldots + (-1)^{i-1} (\lambda J)^i + \ldots] = \sum_{i=1}^{\infty} \beta_i \lambda^i, \qquad \beta_i = (-1)^{(i-1)} \int_0^\infty \mathrm{d}p \, p^{(d/2)} \phi J^i \quad (2.22)$$

permitting $\langle R_1^2 \rangle_{\mathrm{cs}}$ to be expressed as a virial expansion in powers of C_p.

$$\langle R_1^2 \rangle_{\mathrm{cs}} = \langle R_1^2 \rangle_{0\mathrm{s}} + B_{1\mathrm{s}} C_\mathrm{p} + B_{2\mathrm{s}} C_\mathrm{p}^2 + \ldots + B_{i\mathrm{s}} C_\mathrm{p}^i + \ldots = \langle R_1^2 \rangle_{0\mathrm{s}} + \sum_{i=1}^{\infty} B_{i\mathrm{s}} C_\mathrm{p}^i \quad (2.23)$$

with

$$B_{i\mathrm{s}} = -[2uN^{3-(d/2)} / \Gamma((d/2) + 1)] \beta_i (4uN^2)^i$$

The virial coefficients $B_{i\mathrm{s}}$ of the skeleton expression can yield the true virial coefficients B_i after the incorporation of the contributions of the derivative diagrams, as for the case of the virial coefficients of the osmotic pressure.

$$B_{i\mathrm{s}} + (\text{action of derivative diagrams}) \to B_i \quad (2.24)$$

Equation 2.23 becomes then

$$\langle R_1^2 \rangle_\mathrm{c} = \langle R_1^2 \rangle_0 + \sum_{i=1}^{\infty} B_i C_\mathrm{p}^i \quad (2.25)$$

and this is an expression which after the evaluation of B_i by means of the eq 2.24 can describe the size of a coil as a function of u, N, and C_p.

3. Calculations at $d = 4 - \epsilon$

In the model described above, the replacement of the real summations over the units of the chain with the easier to be found integrations over the contour length of the chains makes the model equivalent to continuous line models.[1,6] The application of perturbation theory in these continuous models suffers from divergences coming from zeros in the denominators appearing in the small length limits. To avoid this, renormalization theories[10,19,20] have been developed which in a systematic way treat the divergences which are irrelevant in the final physical result. In the exponentiation techniques which we have used[7] we have isolated these divergences and the analysis has been based on terms surviving in the limit of large molecular weights. A way to avoid the zeros in the denominators is to add to them a small positive constant x equivalent to a physical small-length cutoff, which though necessary for the existence of the integrals is not expected to affect the long-range macroscopic properties. In this way the divergences can be isolated from the rest useful results. The first-order diagram M, for example, which appears in the evaluation of the partition function of a chain

$$Z_1 = \mu_0^N [1 - 2uM + \ldots] \quad (3.1)$$

is equal at $d = 4$ to

$$M = \int_0^N \mathrm{d}i \int_i^N \mathrm{d}j \, 1/(j - i)^2 = \int_0^N \mathrm{d}l \, (N - l)/l^2, \quad l = j - i \quad (3.2\mathrm{a})$$

and is divergent. But the diagram

$$M = \int_0^N \mathrm{d}l \, (N - l)/(l + x)^2 = \int_0^1 \mathrm{d}y \, (1 - y)/(y + \delta)^2, \qquad \delta = x/N \quad (3.2\mathrm{b})$$

is not. It is equal to

$$M = \int_0^1 \mathrm{d}y \, (1 - y)/(y + \delta)^2 = (1/\delta) - \ln(1 + \delta) + \ln(\delta) = (1/\delta) + \ln(\delta) = (N/x) + \ln x - \ln N, \quad \delta \to 0 \quad (3.2\mathrm{c})$$

and the benefit of writing it in the form (3.2b) is that the x divergent parts and the ln N are separated (eq 3.2c). Knowing that the x parts of the integral, due to the existence of the physical cutoff, do not influence the long-range properties of the chain at the limit $N \to \infty$ but just alter the exponential prefactor μ_0 of eq 3.1, we concentrate on the ln N part, which gives for the partition function of an isolated chain the form

$$Z_1 = \mu^N [1 + 2u \ln N + \ldots\} \quad (3.3)$$

Such forms yield the power laws with respect to N, the critical exponents, and other useful information as has been discussed in the Introduction.[7]

3A. Osmotic Pressure. In the case of the ring diagrams of osmotic pressure, eq 2.5, in order to avoid the divergences we add similarly a small x in the denominator, indicating in this case the existence of a physical cutoff in the loops among the chains. This interchain cutoff saves, for example, the approach to the closed-packed density $\sim 1/x^{d/2}$, which of course the present analysis does not reach. The model though is capable of describing the limit of high concentrations,[15] at which the existence of the cutoff though necessary like in the isolated chains is irrelevant for the description of long-range properties. Following similar steps as those leading to eq 2.9, we take instead that at $d = 4$

$$L = [N^{2i-2}/\Gamma(2)]\int_0^\infty \mathrm{d}p\, p e^{-p\delta} J^i, \qquad \text{with} \quad \delta = x/N \tag{3.4}$$

The action of the derivative diagrams is to change the virial coefficients A_{is} in a simple way, clear even from the full evaluation of the first member of the series. For the second virial coefficient A_{2s}, previous results[26] show that its uN^2 form after the action of the derivative diagrams becomes $uN^2[1 - 4u \ln N + 24(u \ln N)^2 + ...] = uN^2(1 + 8u \ln N)^{-(1/2)}$, amounting to multiplying A_{2s} by the factor $(1 + 8u \ln N)^{-1/2}$. This is general and the contributions of the derivative diagrams amount to multiplying the virial coefficients by factors of the form $(1 + 8u \ln N)^{x_i}$ with x_i unknown exponents. The exponents x_i can be determined by means of the previous well-established result that in the semidilute excluded-volume limit the osmotic pressure Π obeys the relation $\Pi/(KT) = C_p F(C_m/C_m{}^*)$.[10,16] The ratio $C_m/C_m{}^*$ is equal to the ratio of the monomer concentration in the solution C_pN to the local monomer concentration of a coil proportional to $N/\langle R^2\rangle^{d/2}$. At $d = 4$ the mean end-to-end square distance behaves like $\langle R^2\rangle = N(1 + 8u \ln N)^{1/4}$,[8] and the ratio $C_m/C_m{}^*$ comes out to be proportional to $u^{1/2}$ for large u, $C_m/C_m{}^* \sim u^{1/2}$. Therefore the action of the derivative diagrams is to multiply the terms of the osmotic pressure, eq 2.14, with powers of $(1 + 8u \ln N)$ in such a way that they becomes powers of $u^{1/2}$ in the full excluded-volume limit. The term $A_{2s}C_p$, for example, incorporating the effects of the derivative diagrams, becomes

$$A_2C_p = A_{2s}C_p(1 + 8u \ln N)^{x_2} = C_p uN^2(1 + 8u \ln N)^{x_2} \sim u^{1/2} \Rightarrow u^{1+x_2} \sim u^{1/2}, \qquad x_2 = -\tfrac{1}{2} \tag{3.5}$$

in agreement with previous calculations of the contributions from both the skeleton and the derivative diagrams.[26] In general for $i > 2$, A_{is} proportional to u^i, eq 2.14, is a coefficient of a $C_p{}^{i-1}$ term, which means that after the contribution of the derivative diagrams A_{is} has to become proportional to $(u^{1/2})^{i-1}$. This determines the exponent x_i and yields for A_i the final form

$$A_i = A_{is}(1 + 8u \ln N)^{x_i} = [2uN^{(4-d)/2}/\Gamma(d/2)]\alpha_i(4uN^2)^{i-1}(1 + 8u \ln N)^{x_i} \sim u^{i+x_i} = u^{(i-1)/2} \Rightarrow x_i = -(i + 1)/2 \quad \text{for} \quad i > 2 \tag{3.6}$$

By means of the $\lim_{\epsilon\to 0} \ln N = (2/\epsilon)(N^{\epsilon/2} - 1) \sim N^{\epsilon/2}$, we see that A_i goes in the limit of large molecular weights as

$$A_i \sim N^{h_i}, \quad h_i = (\epsilon/2) + 2i - 2 - (\epsilon/4)(i + 1) \quad \text{for} \quad i > 2 \tag{3.7}$$

determining so for the first time the critical exponents h_i of all virial coefficients to order ϵ. Resumming now the terms, eq 2.16, with the new final forms of A_i, we take an expression for the osmotic pressure of the same structure as that of the skeleton expression eq 2.12, which includes the contributions from all diagrams.

$$\Pi/(kT) = C_p\{1 + (\lambda'/4) + [2uN^{\epsilon/2}(1 + 8u \ln N)^{-1}/\Gamma(2 - (\epsilon/2))]\lambda' F_\pi(\lambda')\} \tag{3.8}$$

but with a new

$$\lambda' = \lambda(1 + 8u \ln N)^{-1/2} = 4uC_pN^2(1 + 8u \ln N)^{-1/2} \sim C_m/C_m{}^*$$

$$F_\pi(\lambda') = \sum_{i=3}^{\infty} \alpha_i \lambda'^{\,i-2} = (1/\lambda'^2)\int_0^\infty \mathrm{d}p\, p e^{-p\delta}[(1/2) \times (\lambda' J)^2 + (\lambda' J)/(1 + \lambda' J) - \ln(1 + \lambda' J)] \tag{3.9a}$$

and

$$\alpha_i = (-1)^{i-1}[(i - 1)/i]\int_0^\infty \mathrm{d}p\, p e^{-p\delta} J^i \tag{3.9b}$$

are the same as those of eq 2.12 with $d = 4$. The cutoff term $\delta = x/N$ takes care of the divergences as has been explained in the beginning of the section. Equation 3.9 is a general expression of the osmotic pressure as a function of concentration C_p the molecular weight N, and the intensity of the excluded-volume interactions u and can be used for the study of various interesting regions.

3B. The Size of a Coil. As far as the size of the coil is concerned, eq 2.18–2.25 of the mean end-to-end square distance of a coil are employed, where the evaluation of the diagrams, eq 2.20, are necessary. The forms of these diagrams after the addition of the small positive constant x in their denominators, following the same route as in the case of osmotic pressure, become at $d = 4$

$$L_R = -[N^{2i-1}/\Gamma(3)]\int_0^\infty \mathrm{d}p\, p^2 e^{-p\delta}\phi J^{i-1} \tag{3.10}$$

changing the values of β_i, eq 2.22, to

$$\beta_i = (-1)^{(i-1)}\int_0^\infty \mathrm{d}p\, p^2 e^{-p\delta}\phi J^i, \qquad d = 4 \tag{3.11}$$

which changes also accordingly the values of the virial coefficients B_{is} of eq 2.23.

The virial coefficients B_{is} of the skeleton expression can yield the true virial coefficients B_i after the incorporation of the contributions of the derivative diagrams. As for the virial coefficients of the osmotic pressure, the contributions of the derivative diagrams of the mean end-to-end square distance amount in multiplying B_{is} by a function $(1 + 8u \ln N)^{y_i}$ with y_i unknown exponents,

$$B_i = B_{is}(1 + 8u \ln N)^{y_i} \tag{3.12}$$

The exponents y_i can be determined by means of the requirement that in the scaling region $\langle R_1{}^2\rangle_c$ has to be of the form[28]

$$\langle R_1{}^2\rangle_c = \langle R_1{}^2\rangle_0 F(C_m/C_m{}^*) = \langle R_1{}^2\rangle_0[1 + d_1(C_m/C_m{}^*) + d_2(C_m/C_m{}^*)^2 + ...] \tag{3.13}$$

By means of eq 2.25 and 3.13 we see that the $C_p{}^i$ term of the expansion of $\langle R_1{}^2\rangle_c$ behaves like

$$B_iC_p{}^i \sim \langle R_1{}^2\rangle_0(C_m/C_m{}^*)^i \sim N(1 + 8u \ln N)^{1/4} \times (u^{1/2}C_pN^2)^i \sim u^{(i/2)+(1/4)}C_p{}^i \Rightarrow B_i \sim u^{(i/2)+(1/4)} \tag{3.14}$$

On the other hand, by means of eq 2.23 B_i is seen to behave like

$$B_i = B_{is}(1 + 8u \ln N)^{y_i} = -[2uN^{3-(d/2)}/\Gamma((d/2) + 1)]\beta_i(4uN^2)^i(1 + 8u \ln N)^{y_i} \sim u^{i+1+y_i} \tag{3.15}$$

Equating the exponents of u from eq 3.14 and 3.15, $(i/2) + (1/4) = i + 1 + y_i$, we determine $y_i = -(i/2) - (3/4)$. The virial coefficients B_i are then given by

$$B_i = -[2uN^{1+(\epsilon/2)}/\Gamma(3 - (\epsilon/2))]\beta_i(4uN^2)^i(1 + 8u \ln N)^{-(i/2)-(3/4)} \tag{3.16}$$

By means of the limit as $\epsilon \to 0$ of $\ln N = (2/\epsilon)(N^{\epsilon/2} - 1)$,

Table I
Ten First α_i and β_i Coefficients, Eq 3.9 and 3.18, for the Evaluation of ${}^{v}F_{\pi}(\lambda')$ and ${}^{v}F_{R}(\lambda')$ of the Virial Expansion of Π and $\langle R_1^2\rangle_c$, Respectively

i	α_i	β_i
1		3.863×10^{-1}
2		-5.019×10^{-2}
3	2.174×10^{-1}	1.011×10^{-2}
4	-4.683×10^{-2}	-2.523×10^{-3}
5	1.358×10^{-2}	7.172×10^{-4}
6	-4.489×10^{-3}	-2.229×10^{-4}
7	1.601×10^{-3}	7.393×10^{-5}
8	-6.013×10^{-4}	-2.576×10^{-5}
9	2.343×10^{-4}	9.329×10^{-6}
10	-9.395×10^{-5}	-3.486×10^{-6}
11	3.852×10^{-5}	
12	-1.609×10^{-5}	

B_i are seen to behave in the limit of large molecular weights N like

$$B_i \sim N^{k_i} \sim N^{(8-\epsilon)i/4+(\epsilon/8)+1} \Rightarrow k_i = (8-\epsilon)(i/4) + (\epsilon/8) + 1 \quad (3.17)$$

We determine for the first time both the structure of all virial coefficients of the coil size and their critical exponents up to order ϵ. By means of the true virial coefficients B_i, eq 3.16, and β_i, eq 3.11, the mean end-to-end square distance $\langle R_1^2\rangle_c = \langle R_1^2\rangle_0 + \sum_{i=1}^{\infty} B_i C_p^{\,i}$ of a coil becomes

$$\langle R_1^2\rangle_c = \langle R_1^2\rangle_0 \{1 - [2uN^{\epsilon/2}/\Gamma(3 - (\epsilon/2))](1 + 8u \ln N)^{-1} F_R(\lambda')]\} \quad (3.18)$$

with

$$\lambda' = \lambda(1 + 8u \ln N)^{-1/2} = 4uC_pN^2(1 + 8u \ln N)^{-1/2} \sim C_m/C_m^*$$

and

$$F_R(\lambda') = \sum_{i=0}^{\infty} \beta_i \lambda'^{\,i} = \lambda' \int_0^{\infty} \mathrm{d}p\, p^2 e^{-p\delta} \phi J/(1 + \lambda' J),$$

$$\beta_i = (-1)^{(i-1)} \int_0^{\infty} \mathrm{d}p\, p^2 e^{-p\delta} \Phi J^i, \qquad d = 4$$

where λ of eq 2.21 has been substituted with λ' as in the case of osmotic pressure. Equation 3.18 is a general expression describing the size of the coil in all regions of concentration, molecular weight, and excluded-volume interactions.

4. Dilute, Semidilute, and Concentrated Solutions

Equation 3.8 and 3.18 are general expressions and describe the osmotic pressure and the mean end-to-end square distance of a coil, respectively, in terms of the concentration C_p, the molecular weight N, and the intensity of the excluded-volume interactions u. They can be used for the study of various interesting regions. We start with the osmotic pressure of a dilute solution.

4A. Osmotic Pressure. (a) Dilute Solution. In the dilute solution where the chains on average are far apart the concentration $C_m = C_pN$ of the monomers in the solution is much less than the local monomer concentration C_m^* of the coils. In this region the ratio C_m/C_m^* is small compared to unity and the quantity $\lambda' \sim C_m/C_m^*$ is small so a Taylor expansion of $F_\pi(\lambda')$ with respect to λ' can be made and the virial expansion of Π up to any order of concentration can be achieved. The virial coefficients can be found by means of eq 3.6 once the coefficients α_i, eq 3.9, have been found. $J = (e^{-p} - p + 1)/p^2$, as a function of p, behaves normally. It is equal to $^1/_2$ for $p = 0$, decreases with p, and for $p \rightarrow \infty$ goes as $J \rightarrow (1/p)$. The integral $\int_0^\infty \mathrm{d}p\, pJ^ie^{-p\delta}$, eq 3.9, exists for $i > 1$ even for $\delta = 0$ so that all the coefficients α_i, $i > 1$, can be calculated analytically. The J^i factor yields terms of the form $p^{-n}e^{-p}$, which by means of eq 4.4 can be evaluated giving the values of the virial coefficients. The first ten α_i have been found and quoted in Table I. We notice that they have alternating signs, establishing a rule of alternating signs for the virial coefficients of the osmotic pressure. This is in accord with Duplantier's finding of a negative fourth virial coefficient. As we will see in section 4B the same rule applies to the coefficients of $\langle R_1^2\rangle_c$ as well. The truncation ${}^{v}F_\pi(\lambda')$ of the virial expansion up to the tenth power of λ' is plotted in Figure 1 and compared with the full function $F_\pi(\lambda')$ taken after evaluating numerically the integral of eq 3.9. We see that the expansion up to the tenth power of λ' describes well the full function $F_\pi(\lambda')$ up to values of $\lambda' \sim 1.7$.

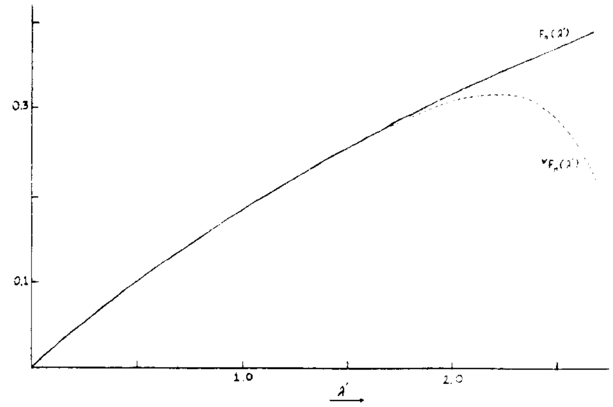


Figure 1. Plots of the full function $F_\pi(\lambda')$, eq 3.9, of the osmotic pressure, eq 3.8, and of its expansion ${}^{v}F_\pi(\lambda') = \sum_{i=3}^{12} \alpha_i \lambda'^{\,i-2}$ up to the $\lambda'^{\,10}$ term.

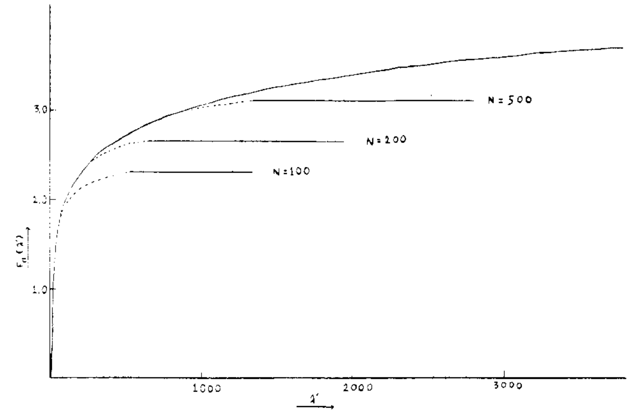


Figure 2. Master curve $F_\pi(\lambda')$, eq 3.9, for a large range of $\lambda' \sim C_m/C_m^*$ values. The horizontal lines represent regions of high concentration ($\lambda' \rightarrow \infty$) for various molecular weights N, eq 4.10.

(b) Semidilute Region. Equation 3.9 can describe osmotic pressure for higher values of C_p as well, therefore describing the semidilute region. In the full excluded-volume limit and $\epsilon > 0$, $(1 + 8u \ln N)^{-1}$ behaves like $[1 + (16u/\epsilon)(N^{\epsilon/2} - 1)]^{-1} \sim N^{-\epsilon/2}$, so that the osmotic pressure, eq 3.8, becomes independent of the molecular weight N and depends only on λ', which is proportional to the characteristic ratio C_m/C_m^*. Such dependence has been tested and agrees with experiments up to semidilute solution.[17,20] By means of a numerical evaluation of the integral of eq 3.9 we can find this dependence for a large range of λ' values. The corresponding plot of the master curve $F_\pi(\lambda')$ up to values of $\lambda' \sim 3600$ is shown in Figure 2, where the concentrated regions for various molecular weights are also shown. A thing to notice from this graph is that with increasing concentration the slope of the curve reduces, showing that a stronger dependence on C_m occurs in semidilute than in concentrated solution, in accordance with the $\Pi \sim C_m^{9/4}$ and $\Pi \sim C_m^2$ dependences in the two regions, respectively.[15]

(c) Concentrated Solution. An interesting result is that eq 3.9 can also describe regions of high concentration. In the high-concentration limit λ' is a large number so that $F_\pi(\lambda')$, eq 3.9, can be expanded in powers of $1/\lambda'$ as

$$F_\pi(\lambda') = (1/2)\int_0^\infty \mathrm{d}p\ pe^{-p\delta}J^2[1 + O(\ln \lambda'/\lambda')] \tag{4.1}$$

and the osmotic pressure at $d = 4$ becomes, in the limit of large concentrations, of the form

$$\Pi/(kT) = C_p\{1 + uC_pN^2(1 + 8u \ln N)^{-1/2} + \Big[2u(1 + 8u \ln N)^{-1}(1/2)\lambda' \int_0^\infty \mathrm{d}p\ pe^{-p\delta}J^2\Big\}, \quad J = (e^{-p} - 1 + p)/p^2 \tag{4.2}$$

Now the integral $\int_0^\infty \mathrm{d}p\ pe^{-p\delta}J^2$ exists only for positive values of the cutoff parameters $\delta = x/N > 0$, which means that in the region of high concentration an extra δ dependence and through it an N dependence enter. The osmotic pressure, contrary to what happens in the semidilute region, is no more a universal function of the ratio C_m/C_m^*. We can find the new dependence by finding the integral $\int_0^\infty \mathrm{d}p\ pe^{-p\delta}J^2$ as a function of $\delta = x/N$. Substituting J from eq 2.8 we take

$$\int_0^\infty \mathrm{d}p\ pe^{-p\delta}J^2 = \int_{a\to 0}^\infty \mathrm{d}p\ [p^{-3}e^{-p(2+\delta)} - 2p^{-3}e^{-p(1+\delta)} + 2p^{-2}e^{-p(1+\delta)} + p^{-3}e^{-p\delta} - 2p^{-2}e^{-p\delta} + p^{-1}e^{-p\delta}] \tag{4.3}$$

By means of the general formula

$$\int_a^\infty \mathrm{d}p\ p^{-n}e^{-kp} = e^{-ka}\{[1/(n-1)a^{n-1}] + [(-k)^1/(n-1)(n-2)a^{n-2}] + [(-k)^2/(n-1)(n-2)(n-3)a^{n-3}] + \ldots + [(-k)^{n-2}/(n-1)!a]\} + [(-k)^{n-1}/(n-1)!]\int_a^\infty \mathrm{d}p\ p^{-1}e^{-kp} = e^{-ka}\{[1/(n-1)a^{n-1}] + [(-k)^1/(n-1)(n-2)a^{n-2}] + [(-k)^2/(n-1)(n-2)(n-3)a^{n-3}] + \ldots + [(-k)^{n-2}/(n-1)!a]\} + [(-k)^{n-1}/(n-1)!][-\underline{C} - \ln(ka) + O(ka)] \tag{4.4}$$

where the limit for small a of the exponential integral $\int_a^\infty \mathrm{d}p\ p^{-1}e^{-kp} = -\underline{C} - \ln(ka) + O(ka)$ ($\underline{C}$ is Euler's constant) has been used, we can find all terms of eq 4.3 in terms of a and take in the end the limit $a \to 0$. The overall result if finite for $\delta > 0$, and it is equal to

$$\int_0^\infty \mathrm{d}p\ pe^{-p\delta}J^2 = -2 \ln 2 - (1/2) - \ln \delta + O(\delta \ln \delta) = -2 \ln 2 - (1/2) - \ln x + \ln N + O(\ln N/N) \tag{4.5}$$

The constants and x parts, like in the case of the isolated chain (see section 3), are irrelevant and the osmotic pressure in the limit of very high concentrations takes at $d = 4$ the form

$$\Pi/(kT) = C_p\{1 + uC_pN^2(1 + 8u \ln N)^{-1/2} + u(1 + 8u \ln N)^{-1}(\lambda') \ln N\}; \quad \epsilon = 0, \quad C_p \to \infty, \quad \lambda' = 4uC_pN^2(1 + 8u \ln N)^{-1/2} \tag{4.6}$$

which can be written as

$$\Pi/(kT) = C_p\{1 + uC_pN^2(1 + 8u \ln N)^{-1/2} + u(1 + 8u \ln N)^{-1}4uC_pN^2(1 + 8u \ln N)^{-1/2} \ln N\} \tag{4.7}$$

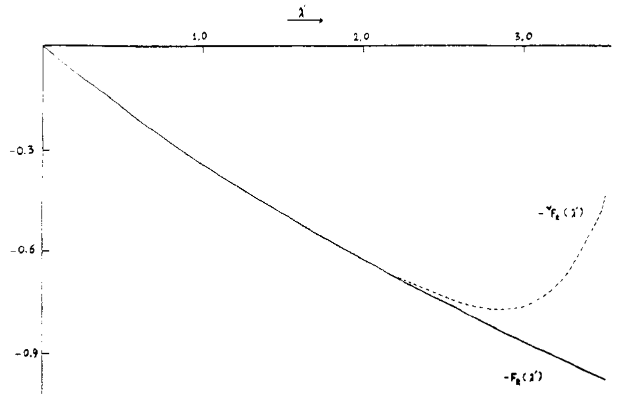


Figure 3. Plots of the full function $F_R(\lambda')$ of the mean end-to-end square distance of a coil, eq 3.18, and its expansion ${}^vF_R(\lambda') = \sum_{i=1}^{10}\beta_i\lambda'^i$ up to the λ'^{10} term.

As we have explained in the introduction, the first-order $u \ln N$ term shows among other things the importance of excluded-volume interactions from various sources. To first order in $u \ln N$, $(1 + 8u \ln N)^{-1/2} = (1 - 4u \ln N)$, so we take for the behavior of the osmotic pressure up to first order in $u \ln N$ the expression

$$\Pi/kT = C_p\{1 + uC_pN^2(1 - 4u \ln N + \ldots) \times (1 + 4u \ln N + \ldots)\} = C_p\{1 + uC_pN^2[1 + O(u \ln N)]\} \tag{4.8}$$

This proves that in the limit of high concentrations the two opposite excluded-volume effects represented by the factors $(1 - 4u \ln N + \ldots)$ and $(1 + 4u \ln N + \ldots)$ of eq 4.8 cancel exactly. The net first order $u \ln N$ is zero and the effects of the overall excluded-volume interactions are negligible. The osmotic pressure can be written in this region of high concentrations as

$$\Pi/kT = C_p\{1 + uC_pN^2[1 + O(u \ln N)]\} \sim uC_m^2 \tag{4.9}$$

a result which agrees with the previous findings of Flory and Huggins[15] from mean-field calculations. Beyond this analytic approach to the high-concentration limit where mean-field arguments apply another thing to notice is that in this limit, where the meaning of the chains is lost as expected, the osmotic pressure depends solely on C_m, a result which has not been taken from the C_m/C_m^* dependence of previous theories. $F_\pi(\lambda')$ at the concentrated region is also shown in Figure 2, where according to eq 4.1 and 4.5 it goes in the limit of high concentration to the value

$$F_\pi(\lambda') = (1/2) \ln N, \qquad \lambda' \to \infty \tag{4.10}$$

and ceases to be a function of $\lambda' \sim C_m/C_m^*$. Of course eq 4.10 is the limit of $F_\pi(\lambda')$ for large λ', eq 4.1, while terms of smaller λ' can be calculated in a systematic way from the $1/\lambda'$ expansion of eq 3.9. The description, therefore, of the analytic way of going from the semidilute solution to the concentrated solution (dashed curve of Figure 2) can be done to any order of accuracy.

4B. The Size of a Coil. (a) Dilute Solution. In the regions of small concentrations an expansion of $F_R(\lambda')$, eq 3.18, can be performed and the virial coefficients can be determined. The ten first of them are found analytically and quoted in Table I. Their signs also alternate, establishing an alternate rule for the signs of the coefficients of $\langle R_1^2\rangle_c$ like that of Π. The plot of ${}^vF_R(\lambda')$ based on these first ten terms is shown in Figure 3 and compared with the plot taken after the numerical evaluation of the integral of $F_R(\lambda')$. The virial expansion ${}^vF_R(\lambda')$ of $F_R(\lambda')$ describes the curve well up to values $\lambda' \sim 2.1$. Figure 3 shows that

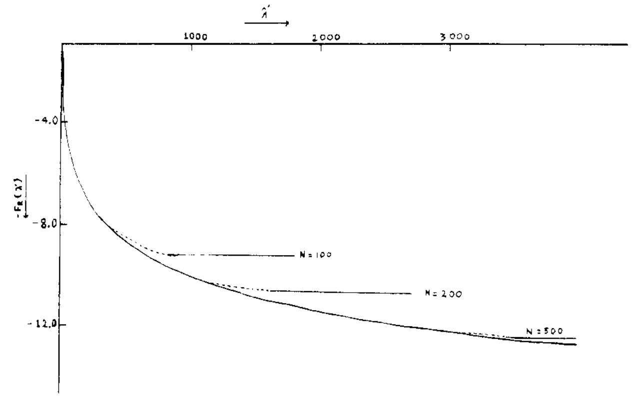


Figure 4. Master curve $F_R(\lambda')$, eq 3.18, for a large range of $\lambda' \sim C_m/C_m{}^*$ values. The horizontal lines represent regions of high concentration ($\lambda' \rightarrow \infty$) for various molecular weights N, eq 4.12.

the size $\langle R_1{}^2\rangle_c$ of a coil decreases as the concentration of polymers increases.

(b) Semidilute Region. With increase of C_p, the semidilute region is reached, where the master curve of $F_R(\lambda')$ is followed and the ratio $\langle R_1{}^2\rangle_c/\langle R_1{}^2\rangle_0$ is a function solely of the ratio $C_m/C_m{}^*$.[28] $-F_R(\lambda')$ after the numerical evaluation of the integral of eq 3.18, for $\delta = 0$ is plotted in Figure 4 up to values of $\lambda' \sim 3900$. The plot of Figure 4 shows that the decrease of $\langle R_1{}^2\rangle_c$ gets smaller as the concentration increases, ending in an independence from C_m in accord with the results of Muthukumar and Edwards,[15] who find that the scaling result of a strong decrease like $\sim C_m{}^{-1/4}$ in the semidilute region ends up with an independence from C_m in the concentrated solution.

(c) Concentrated Region. An analytic study of eq 3.18 can be done in the high-concentration limit where $F_R(\lambda')$ can be expanded by powers of $1/\lambda'$ in a systematic way as

$$F_R(\lambda') = \lambda' \int_0^\infty \mathrm{d}p\, p^2 e^{-p^\delta}(\phi J/\lambda' J)[1 + (1/\lambda' J)]^{-1} = \int_0^\infty \mathrm{d}p\, p^2 e^{-p^\delta}\phi[1 - (1/\lambda' J) + (1/\lambda' J)^2 - \ldots], \quad d = 4 \tag{4.11}$$

The evaluation of the first term $\int_0^\infty \mathrm{d}p\, p^2 e^{-p^\delta}\phi$ of eq 4.11 will give us some insight to the behavior of the size of the coil in the high-concentration limit. This first term exists only for $\delta > 0$, which means that in the high-concentration limit the function $F_R(\lambda')$ is not only a function of $C_m/C_m{}^*$ anymore, a thing which is true in the semidilute region. The extra dependence on N can be found after the evaluation of the first term of eq 4.11. This can be done by means of the general formula, eq 4.4, as for eq 4.5.

$$F_R(\lambda')_{\lambda' \to \infty} = \int_0^\infty \mathrm{d}p\, p^2 e^{-p^\delta}\phi = -2 \ln \delta - 6 + 2 \ln (1 + \delta) + 6\delta \ln (1 + \delta) + [1/(1 + \delta)] - 6\delta \ln \delta = 2 \ln N - 2 \ln x + O(\text{constants}) \tag{4.12}$$

Ignoring the constant and the ln x parts as irrelevant, we can find $\langle R_1{}^2\rangle_c$ in the limit $C_p \rightarrow \infty$, for $d = 4$, from eq 3.18. It is of the form

$$\langle R_1{}^2\rangle_c = N[1 + 2u \ln N + \ldots][1 - 2u \ln N + \ldots] = N[1 + O(u \ln N)] \tag{4.13}$$

which again shows that a cancellation of intra- and interexcluded-volume effects occurs in this limit of high concentrations and that the ratio $\langle R_1{}^2\rangle_c/\langle R_1{}^2\rangle_0$, because of this cancellation, does not show a dependence on N. In Figure 4, the limit $F_R(\lambda') = 2 \ln N$ of high concentrations ($\lambda' \rightarrow \infty$) is also shown. The analytic way of going from the semidilute to the concentrated solution (dashed lines) can be found to any order of accuracy after the evaluation of the higher order terms of eq 4.11.

5. Conclusions

We have studied a system of many polymer chains. By means of the class of skeleton diagrams of the ring type we have given closed expressions up to an integral for the osmotic pressure and the size of a coil, capable of describing all regions of polymer concentration, intensity of excluded-volume interactions, and molecular weight of the chains. From these expansions the three characteristic regions of dilute solutions where virial expansions can be used, the semidilute solution where the properties are functions of the ratio $C_m/C_m{}^*$ of the global to the local monomer concentration and the concentrated solution where inter- and intraexcluded-volume effects cancel and the chains tend to behave ideally, are properly described. A rule of alternating signs for the virial coefficients of the osmotic pressure and the size of a coil is given, and a systematic way of going from the $C_m/C_m{}^*$ dependence of the semidilute solution to the C_m dependence of the concentrated region is analyzed.

References and Notes

(1) Edwards, S. F. *Proc. Phys. Soc., London* **1966**, *88*, 265.
(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, London, 1978. Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971. De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979. Freed, K. F. *Renornalization Group Theory of Macromolecules*; Wiley: New York, 1987.
(3) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228. Vlahos, C. H.; Kosmas, M. K. *Polymer* **1984**, *25*, 1607; *J. Phys. A: Math. Gen.* **1987**, *20*, 1471. Kosmas, M. K.; Kosmas, A. M. *Polymer* **1986**, *27*, 1359.
(4) Whittington, S. G. *J. Chem. Phys.* **1975**, *63*, 79. Kosmas, M. K. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 563; *J. Phys. A: Math. Gen.* **1985**, *18*, 539; **1986**, *19*, 3087. Eisenriegler, E.; Kremer, K.; Binder, K. *J. Chem. Phys.* **1982**, *77*, 6298. Douglas, J. F.; Wang, S. Q.; Freed, K. F. *Macromolecules* **1986**, *19*, 2207.
(5) Wolf, B. A. *Macromolecules* **1985**, *18*, 2474.
(6) Edwards, S. F. *Proc. Phys. Soc., London* **1965**, *85*, 613. Domb, C. *Adv. Chem. Phys.* **1969**, *15*, 229. Freed, K. F. *Adv. Chem. Phys.* **1975**, *22*, 1.
(7) Kosmas, M. K. *J. Phys. A: Math. Gen.* **1981**, *14*, 931.
(8) Kosmas, M. K. *J. Phys. A: Math. Gen.* **1982**, *15*, 1667.
(9) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(10) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1980**, *41*, 749.
(11) Ferry, J. D. *Macromolecules* **1980**, *13*, 1719.
(12) Huggins, M. L. *J. Phys. Chem.* **1942**, *46*, 151. Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51. Edwards, S. F. *J. Phys. A: Math. Gen.* **1975**, *8*, 1670.
(13) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(14) Moore, M. A.; Wilson, C. A. *J. Phys. A.: Math. Gen.* **1980**, *13*, 3501.
(15) Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* **1982**, *76*, 2720.
(16) Ottinger, H. C. *Macromolecules* **1985**, *18*, 93.
(17) Schafer, L. *Macromolecules* **1981**, *14*, 668; **1984**, *17*, 1357.
(18) Des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1980**, *41*, 761.
(19) Duplantier, B. N. *Physics* **1986**, *B275*, 319.
(20) Oono, Y.; Ohta, T.; Freed, K. F. *J. Chem. Phys.* **1981**, *74*, 6458.
(21) Cherayil, B. J.; Bawendi, M. G.; Miyake, A.; Freed, K. F. *Macromolecules* **1986**, *19*, 2770.
(22) Ohta, T.; Oono, Y. *Phys. Lett.* **1982**, *89A*, 460.
(23) Ohta, T.; Nakanishi, A. *J. Phys. A: Math. Gen.* **1983**, *16*, 4155.
(24) Oono, Y. *Adv. Chem. Phys.* **1985**, *61*, 301.
(25) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, *14*, 668. Noda, I.; Higo, Y.; Veno, N.; Fujimoto, T. *Macromolecules* **1984**, *17*, 1055.
(26) Kosmas, M. K. *J. Phys. (Les Ulis, Fr.)* **1984**, *45*, L889.
(27) Miyakawa, H.; Mono, K.; Saito, N. *Macromolecules* **1984**, *17*, 388.
(28) Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978**, *69*, 3647.