Effects of the excluded volume interactions on the conformational properties of star polymers

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The effects of the excluded volume interactions on the conformational properties of star polymers have been studied. First order calculations at the critical dimensionality $d=4$ yield the critical exponents of the average quantities up to first order in $\varepsilon = 4-d$. We thus find the partition function, the probability of the end of a branch to reach the central core and the probability of contact of the ends of two branches. The size of the macromolecule, expressed by the mean square radius of gyration $\langle s^2 \rangle_{star}$ is studied in the region where the interactions between the polymeric units repel one another and in the region where the units attract one another. The results are compared with the results of previous works and with experiments.

INTRODUCTION

A determining factor for the macroscopic behaviour of macromolecules is their structure. The synthesis and characterization of polymers of specific structures is completed with theoretical studies which aim to explain and predict their properties. Star molecules are composed of f polymeric chains, the branches being joined together to a common junction (*Figure 1*). The synthesis of star polymers of different number of branches and of different molecular weights is possible[1] and stars with $f = 18$ have recently been synthesized[2]. Their theoretical study started long ago. Zimm and Stockmayer[3] used the random walk model to find the mean square radius of gyration $\langle s^2 \rangle_{star}$ and they calculated the ratio

$$g = \frac{\langle s^2 \rangle_{star}}{\langle s^2 \rangle_{linear}} = \frac{3f-2}{f^2}$$

(the ratio of the radius of a star to that of a linear polymer of the same molecular weight). The random walk model built to describe long ideal chains falls short of describing specific effects like the stiffness of the chain[4] or close packing of the monomers. In stars the density of the segments at the core of the molecule is high and the effects due to the close packing of the monomers is easily detected[5,6]. The size of the molecules and the temperature where the second virial coefficient of their solutions vanishes are found experimentally to differ from the results taken from the model of random walk[5,7,8]. Core effects are more evident in stars of short chains and many branches. They become less important for larger molecular weights and smaller number of branches where the size of the core compared to the size of the molecule is small. The random walk model is more able to describe such cases[9-12].

Other effects not included in the random walk model are those coming from the variation of temperature and the quality of the solvent. These effects can be studied by including in the model the long range interactions due to the units far away along the chain but close in space. The excluded volume parameter u describes the strength of these interactions and it increases generally with the increase of temperature and the quality of the solvent. Repulsions between the monomers occur when u is positive; attractions occur when u becomes negative, and when $u = 0$ the net long range interactions vanish. Previous work on the subject[13,14] include the work of Daoud and Cotton[15] who used a phenomenological model with a close-packed core of constant monomer density and describe the cases of large number of branches and short chains where core effects are important. Recently Miyake and Freed[16] incorporated excluded volume effects on the Gaussian model in a rigorous way. They studied the average properties using the chain conformational renormalization group method. Their solution, given in terms of renormalized quantities, described chains of large molecular weights in good solvents where the exponentiation condition incorporated in renormalization group theory together with the
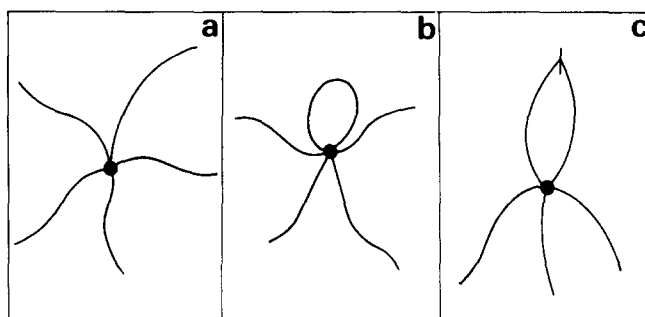

Figure 1 a) A star polymer illustrated for $f=5$, b) The end of a branch in contact with the central core, c) The end of two branches in contact

meaning of the critical exponents, is valid. In this work we employ the Gaussian model with excluded volume interactions in order to study the effects of the quality of the solvent and the temperature, on the conformational behaviour of stars. Previous results on linear chains[17,18] are extended to polymers of different structure. Simple first order calculations at the critical dimensionality $d=4$ determine the structure of the average quantities and the critical exponents to order $\varepsilon = 4 - d$. The radius of gyration of a star is expressed in terms of the molecular weight of the chain the number of branches f and the excluded volume parameter u in an analytic way. This permits the study of the size of the molecule in both regions, under good solvent conditions where $u > 0$ but also under poor solvent conditions $(u < 0)$ where attractions occur between the polymeric units, and the shrinkage of the molecule starts[19]. For large chains and for $u > 0$ the meaning of the critical exponent is valid, while for smaller chains the macroscopic behaviour is competitively determined from the molecular weight or the number of branches of the star. Where possible a comparison is made between the present results and the up to date experimental findings.

THEORETICAL BACKGROUND AND DEFINITIONS

If we consider the centre of the molecule to be fixed at the origin (*Figure 1*), we need two indices for the determination of the position vectors R_{n_i} of the units of the chain. The first index n determines the branch on which the unit lies and varies from 1 to f, while the second index i indicates the position of the unit from the centre of the molecule along the specific branch, and varies from 1–N. The probability distribution $P\{R_{n_i}\}$ for the positions of the units is given by

$$P\{R_{n_i}\} = P_0\{R_{n_i}\}\exp\left\{-u\sum_{n=1}^{f}\sum_{n'=1}^{f}\ \sum_{i=1}^{N}\sum_{j=1}^{N}\delta^d(R_{n_i} - R_{n_j})\right\} \tag{1}$$

$P_0\{R_{n_i}\}$ is an ideal distribution without long range interactions and in the Gaussian model it is given by[20]

$$P_0\{R_{n_i}\} = [d/2\pi]^{dfN/2}\exp\left\{-(d/2)\sum_{n=1}^{f}\sum_{i=1}^{N}(R_{n_i} - R_{n_{i+1}})^2\right\} \tag{2}$$

The exponential term represents long range pair interactions between all the units of the star. For simplicity the unit length of the chain has been taken equal to unity, while the units of the excluded volume parameter u, being equal to double the binary cluster integral[20], are defined so that the exponential term is dimensionless. $P\{R_{n_i}\}$ is a central quantity and all thermodynamic properties can be defined in terms of it. In this work we study the following properties:

(1) The partition function, related to the free energy of the system and taken from $P\{R_{n_i}\}$ by integration in the positions of all units. It is proportional to the configurational integral

$$C = \mu_0^{Nf}\int\prod_{n=1}^{f}\prod_{i=1}^{N}d^dR_{n_i}P\{R_{n_i}\},\ \mu_0 = (d/2\pi)^{d/2} \tag{3}$$

(2) The probability $P_1 = U_1/C$ for the end of the branch 1 to reach the centre of the molecule. U_1 is the number of configurations with the end of the specific branch at the centre written as:

$$U_1 = \mu_0^{fN}\int\prod_{n=1}^{f}\prod_{i=1}^{N}d^dR_{n_i}P\{R_{n_i}\}\delta^d(R_{1_N}) \tag{4}$$

where δ^d is the d dimensional Dirac delta function.

(3) The probability $P_{12} = U_{12}/C$ for the ends of the branches 1 and 2 to be in contact. U_{12} is the number of configurations with the ends of the two branches in contact, expressed as:

$$U_{12} = \mu_0^{fN}\int\prod_{n=1}^{f}\prod_{i=1}^{N}d^dR_{n_i}P\{R_{n_i}\}\delta^d(R_{1N} - R_{2N}) \tag{5}$$

(4) The mean square radius of gyration

$$\langle s^2\rangle_{\text{star}} = (1/2M^2)\sum_{n=1}^{f}\sum_{n'=1}^{f}\ \sum_{l=1\neq}^{N}\sum_{k=1}^{N}\langle(R_{nl} - R_{n'k})^2\rangle,$$
$$M = f\cdot N \tag{6}$$

written in terms of the mean square distances between the units and expressing the square of the size of the star. First order calculations are made, which means that the exponential term of equation (1) will be approximated with its expansion form to first order in u.

THE PARTITION FUNCTION AND THE PROBABILITIES P_1 AND P_{12}

By means of the Gaussian distribution (equation (2)), after the performance of all R_{n_i} integrations[17], C assumes the following form written in terms of diagrams.

$$C = \mu_0^{fN}\left\{1 - u\left[2f\ \diagramright + f(f-1)\ \diagramright\right]\right\} \tag{7}$$

A factor equal to $(d/2\pi l^2)^{d/2}$ coming from the integrations is absorbed in u making it dimensionless. The expressions of the two different first order diagrams are given in *Table 1*. They are derived from the presence of the delta function which brings into contact two different polymeric units. In the first diagram the two units belong to the same branch while in the second the two units come from two different branches. Their values for $d = 4$ are given in *Table 1* and using them C becomes

$$C = \mu_0^{fN}\{1 - u[2f(N - \ln N) + f(f-1)\ln N]\} \tag{8}$$

$$= \mu_0^{fN}\cdot e^{-2uNf}\{1 + (3f - f^2)u\ln N\}$$

In the good solvent region $(u > 0)$ and for large molecular weights the $\ln N$ series give rise to expressions of the form N^a. The characteristic exponent a, as in the case of linear chains can be determined from the fixed point value u^*. Second order calculations on stars yield the same fixed point value u^* as for linear chains indicating that u^* is a universal number not depending on the specific architecture of the molecule. It is equal to $u^* = \varepsilon/16$[17]. By means of this value equation (8) becomes

$$C = [\mu_0 e^{-2u}]^{fN}N^{(\varepsilon/16)(3-f)f},\ u > 0,\ \text{large } N \tag{9}$$

Table 1. First order diagrams for star molecules.

Diagram	Expression	Value for $d = 4$
	$\sum\limits_{i=1}^{N-1} \sum\limits_{J=i+1}^{N} (J-i)^{-(d/2)}$	$N - \ln N$
	$\sum\limits_{i=1}^{N} \sum\limits_{J=1}^{N} (i+J)^{-(d/2)}$	$\ln N$
	$\sum\limits_{i=1}^{N} \sum\limits_{J=1}^{N} [ij + (N-i)(i+j)]^{-(3/2)}$	$2N^{-2}\ln N$
	$\sum\limits_{i=1}^{N} \sum\limits_{J=1}^{N} [(J-i)(N-J+i)]^{-(d/2)}$	$N^{-2}[N + 2\ln N]$
	0	0
	$\sum\limits_{i=1}^{N} \sum\limits_{J=K}^{l} \dfrac{-(K-J)^2}{(J+i)^{(d/2)+1}}$	$\dfrac{1}{2}\left[\dfrac{(k-l)^2}{l} + 2K\ln\dfrac{l}{K} - \dfrac{(k-l)^2}{N+l} + 2(K+N)\ln\dfrac{K+N}{l+N} \right]$
	$\sum\limits_{i=1}^{l} \sum\limits_{J=1}^{N} \dfrac{-(l-K)^2}{(J+i)^{(d/2)+1}}$	$\dfrac{1}{2}\left[\dfrac{-1}{2N} + \dfrac{1}{N+l} + \dfrac{1}{N} - \dfrac{1}{l} \right](l-k)^2$
	$\sum\limits_{i=1}^{l} \sum\limits_{J=1}^{N} \dfrac{-i^2}{(J+i)^{(d/2)+1}}$	$-\dfrac{l^2}{2(N+l)} + \dfrac{l}{2} + N\ln\dfrac{N}{N+l}$
	$\sum\limits_{i=l}^{N} \sum\limits_{J=1}^{N} \dfrac{-i^2}{(J+i)^{(d/2)+1}}$	$\dfrac{1}{2}\dfrac{l^2}{2N} + \dfrac{l^2}{N+l} - l$
	$\sum\limits_{i=1}^{N-1} \sum\limits_{J=i+1}^{N} [(J-i)(2N-J+i)]^{-(d/2)}$	$\dfrac{1}{4N}$
	$\sum\limits_{i=1}^{N} \sum\limits_{J=1}^{N} [(i+J)(2N-i-j)]^{-(d/2)}$	$\dfrac{1}{2}\,N^{-2}\ln N$
	$\sum\limits_{i=1}^{N} \sum\limits_{J=1}^{N} [ij + (2N-i)(i+j)]^{-(d/2)}$	$\dfrac{1}{4}\,N^{-2}\ln N$

determining in this way the value of the critical exponent a, in agreement with the results of renormalization group theory[16]. On increasing f the exponent a becomes zero at f=3 and then negative showing the freezing in of the stars of many branches.

More light on the structure of the stars will be shed from the probability P_1 for the end of the branch 1 to reach the core and the probability P_{12} for the ends of two branches to come in contact (*Figure 1*).

$$P_1 = U_1/C = N^{-(d/2)} - u\left\{ 2\left[\text{⟨diagram⟩} - N^{-(d/2)}\text{⟨diagram⟩} \right] \right.$$

$$\left. + 2(f-1)\left[\text{⟨diagram⟩} - N^{-(d/2)}\text{⟨diagram⟩} \right] \right\} \tag{10}$$

The differences in the diagrams come from the ratio U_1/C and all the diagrams not involving branch 1 are cancelled. The expressions and the values of these diagrams are given in *Tables 1*. By means of these values P_1 takes the form

$$P_1 = N^{-(4-\epsilon)/2} - u(2f+4)N^{-2}\ln N \sim N^{-2+(\epsilon/4)-(\epsilon/8)f}, \quad u>0 \tag{11}$$

On increasing the value of f, P_1 drops very quickly, which means that the presence of the other branches prevents the end of a branch from reaching the core. For the probability P_{12} we take

$$P_{12} = U_{12}/C = (2N)^{-(d/2)} - u\left\{ 4\left[\text{⟨diagram⟩} - (2N)^{-(d/2)} \right] \right.$$

$$\left.\vdots\right]+4(f-2)$$

$$\tag{12}$$
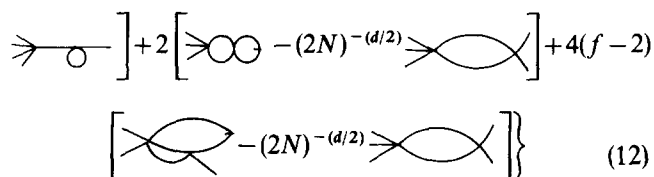
Using the values of the diagrams from *Table 1* we take for $u^* = \varepsilon/16$ that

$$P_{12} = (2N)^{-(4-\varepsilon)/2} - 6u(2N)^{-2}\ln N \sim N^{-2+(\varepsilon/8)} \tag{13}$$

giving rise to an exponent independent of f. This means that the number U_{12} of configurations with the two ends in contact and C depend in the same way on the number of branches f for large molecular weights and under good solvent conditions. The various effects of the other $f-2$ branches on the probability P_{12} are cancelled.

THE RADIUS OF GYRATION AND COMPARISON WITH EXPERIMENTS

The mean square distances in the definition of $\langle s^2 \rangle_{\text{star}}$ (equation (6)) can either be distances between units of the same branch $\langle (\mathcal{L}_{1l} - \mathcal{L}_{1k})^2 \rangle$ or distances between units from different branches $\langle (\mathcal{L}_{1l} - \mathcal{L}_{2k})^2 \rangle$. In terms of these distances $\langle s^2 \rangle_{\text{star}}$ can be written as

$$\langle s^2 \rangle_{\text{star}} = (1/(2M^2)) \left[f \sum_{k=1}^{N} \sum_{l=1}^{N} \langle (\mathcal{L}_{1l} - \mathcal{L}_{1k})^2 \rangle + \right.$$

$$\left. f(f-1) \sum_{k=1}^{N} \sum_{l=1}^{N} \langle (\mathcal{L}_{1l} - \mathcal{L}_{2k})^2 \rangle \right] \tag{14}$$

For the calculation of the distance $\langle (r_{1l} - r_{1k})^2 \rangle$ between units on the same branch interactions coming from units of the same branch and interactions coming from other branches have to be considered. The first kinds of interaction have been calculated previously for the linear chain[18] and they are to order u

$$A = -2k\ln\frac{l}{k} - 2(N-l)\ln\frac{(N-k)}{(N-l)} - 2(l-k)\ln(l-k)$$

$$-\frac{(l-k)^2}{N} + 3(l-k) \tag{15}$$

$$\langle (\mathcal{L}_{1l} - \mathcal{L}_{1k})^2 \rangle = (l-k) - u \left\{ A + 2(f-1) \left[\right. \right.$$

$$\tag{16}$$

The diagrams in equation (16) represent the interactions from other branches and their expressions and values are given in *Table 1*. Using these values we take for the mean square distance between units of the same branch the expression

$$\langle (\mathcal{L}_{1l} - \mathcal{L}_{1k})^2 \rangle = (l-k) + u \left\{ \left[2k\ln\frac{l}{k} + 2(N-l)\ln\frac{(N-k)}{(N-l)} \right. \right.$$

$$+ 2(l-k)\ln(l-k) + \frac{(l-k)^2}{N} - 3(l-k) \right] - 2(f-1)\left[\frac{(l-k)^2}{4N} \right.$$

$$\left. + k\ln\frac{l}{k} - (N+k)\ln\frac{(N+l)}{(N+k)} \right] \right\}, \quad l > k \tag{17}$$

When $f = 1$ or 2 the cases of linear chain with molecular weights N or $2N$ are recovered. The effects of the other branches on the l to k distance can be quantitively determined from the f dependent part of the u term. It is seen, for example, that in the good solvent region $(u > 0)$, other branches expand more segments which are closer to the core. Opposite effects are expected when u is negative. For the mean square distance between units on different branches we have

$$\langle (\mathcal{L}_{1l} - \mathcal{L}_{2k})^2 \rangle = (l+k) - u \left\{ B + 2(f-2) \left[\right. \right.$$

$$\tag{18}$$

l and k measure the distances of the lth and kth units from the centre of the star, while B represents the contributions from the units of the two branches considered as a linear chain with double length. The rest of the u term represents the interactions from the remaining $(f-2)$ branches, B can be found from A with the substitutions $N \rightarrow 2N$, $l \rightarrow N + l$, $k \rightarrow N - k$. The last two diagrams in equation (18) are symmetrical with the first two from which they can be found if we interchange l and k. The expressions and the values of the diagrams are quoted in *Table 1*. For the mean square distance of units from different branches we take the expression

$$\langle (\mathcal{L}_{1l} - \mathcal{L}_{2k})^2 \rangle = (l+k) + u \left\{ \left[2(N-k)\ln\frac{(N+l)}{(N-k)} \right. \right.$$

$$+ 2(N-l)\ln\frac{(N+k)}{(N-l)} + 2(l+k)\ln(l+k) + \frac{(l+k)^2}{2N} - 3(l+k) \right]$$

$$\left. - 2(f-2)\left[N\ln\frac{(N+l)}{N} + N\ln\frac{(N+k)}{N} - \left(\frac{l^2 + k^2}{4N} \right) \right] \right\} \tag{19}$$

which reveals that the presence of the other branches expands more the l to k distance in a good solvent and shrinks it more under poor solvent conditions. The expressions equations (17) and (19) can be used in equation (14) and after approximating the k and l summations with integrations, we take for the mean square radius of gyration the expression:

$$\langle s^2 \rangle_{\text{star}} = \frac{N(3f-2)}{6f} \left\{ 1 + u \left[2\ln N + 8\frac{(f-1)(3f-5)\ln 2}{(3f-2)} \right. \right.$$

$$\left. - \frac{13}{12}\left(\frac{2 + 6(f-1)(2f-3)}{(3f-2)} \right) \right] \right\}$$

$$= \langle s^2 \rangle_{\text{star},0} \{ 1 + 2u[\ln M + F(f)] \}, \quad M = nf \tag{20}$$

$\langle s^2 \rangle_{\text{star},0}$ is the value of the radius without long range interactions taken into account; for the Gaussian model is equal to $M\left(\frac{3f-2}{6f^2} \right)$. The term in the brackets comes from the long range excluded volume interactions, M is proportional to the total molecular weight of the molecule and

$$F(f) = -\ln f + \frac{4(f-1)(3f-5)\ln 2}{(3f-2)} - \frac{13}{12}\left[\frac{1 + 3(f-1)(2f-3)}{(3f-2)} \right]$$
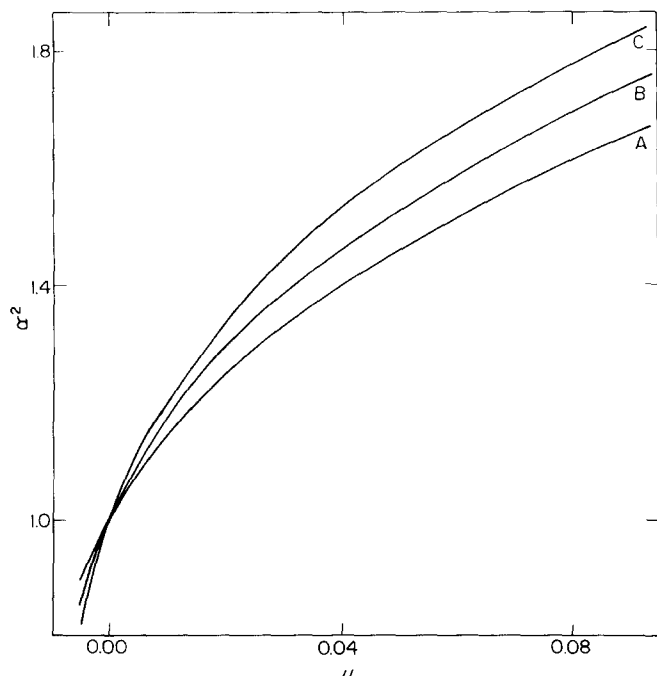
Figure 2 The dependence of the expansion factor α^2 on the excluded volume parameter u for various stars of $M = 10^4$ and different number of branches, A: $f=5$, B: $f=10$, C: $f=15$

is an increasing function of the number f of branches. The excluded volume parameter u depends on the temperature and the quality of the solvent, so that the u term in equation (20) represents the effects which the variation of the temperature and the quality of the solvent bring on the conformational behaviour of the chain. This term depends on both the molecular weight M and on the number f of branches. It has been shown previously by means of third order calculations[19] that the series in $u \ln N$ comes from the expansion of the closed form $\langle s^2 \rangle = (N/6)[1 + 8u(\ln N - \frac{13}{12})]^{1/4}$ where $\ln N = \lim_{\varepsilon \to 0}(2/\varepsilon)(N^{\varepsilon/2} - 1)$ and $\varepsilon = 4 - d$. For large molecular weights the $\ln N$ term dominates over the rest constant terms and the power law dependence of the mean square radius of gyration on the molecular weight $\langle s^2 \rangle \sim N(\ln N)^{1/4} \sim N^{1 + (\varepsilon/8)}$ is recovered. The corresponding expression for stars of f branches includes the function $F(f)$. The expansion factor α^2 takes the form

$$\alpha^2 = \frac{\langle s^2 \rangle_{star}}{\langle s^2 \rangle_{star,0}} = \{1 + 8u[\ln M + F(f)]\}^{1/4} \qquad (21)$$

Analysing equation (21) we see that a third factor, beyond the excluded volume parameter u and the molecular weight M, on which the size of the stars depends is the number f of branches. $F(f)$ is an increasing function of f ($F(1) = F(2) = -1.08$, $F(5) = -0.16$, $F(10) = 2.18$, $F(15) = 4.81$, $F(20) = 7.55$) so that an increase of M or f increases the expansion factor in the good solvent region where u is positive, while a decrease is expected under poor solvent conditions where u is negative (*Figure 2*). Both factors M and f determine α^2 through the u part of equation (21) acting competitively. The region of power law dependence on M is reached when $\ln M$ is dominant over $F(f)$, but $F(f)$ is an increasing function of f so that stars of larger number of branches need larger molecular weights to reach the region of power law dependence

(*Figure 3*). This property goes with the vanishing of core effects which become less important for stars of larger molecular weights and smaller number of branches. For very large molecular weights $F(f)$ becomes negligible with respect to $\ln M$ and the expansion factor α^2 tends to that of a linear chain of the same molecular weight.

For a comparison of the present theoretical results with experimental findings we can refer to the works of Berry[9] and Zillox[5]. Berry finds that under good solvent conditions the expansion factor α^2 for stars where $f \geqslant 3$ is bigger than that of a linear chain of the same molecular weight where $f = 1$ or 2 and this can quantitively be seen from equation (21) where for u positive on increasing f and consequently $F(f)$ larger α^2 are obtained (*Figure 2*). The increase of α^2 with temperature found experimentally[9] is also in agreement with equation (21) since α^2 increases with u which is an increasing function of temperature. Zillox correlated the expansion factor with the combination $uM^{1/2}$, and he has found $\alpha^2 - 1$ to be proportional to $uM^{1/2}$ for small values of $uM^{1/2}$ while this dependence gets weaker for larger values of $uM^{1/2}$. The explanations for these findings come out of equation (21) as follows: For small values of $u \ln M$ equation (21) can be approximated up to first order in the small parameter so that $\alpha^2 - 1 = 2u \ln M \sim 2uM^{\varepsilon/2}$. For $\varepsilon = 1$ the $uM^{1/2}$ dependence is recovered. For larger values of $u \ln M$ the full equation (21) has to be used and a weaker dependence comes out as can be seen from *Figure 2*.

The excluded volume parameter u is an increasing function of T so that the rate of change of the expansion factor with respect to temperature goes as the derivative $d\alpha^2/du$. From the analytic equation (21) all derivatives with respect to u can be taken. For the first derivative we take:

$$\frac{d\alpha^2}{du} = \frac{2[\ln M + F(f)]}{\{1 + 8u[\ln M + F(f)]\}^{3/4}} \qquad (22)$$

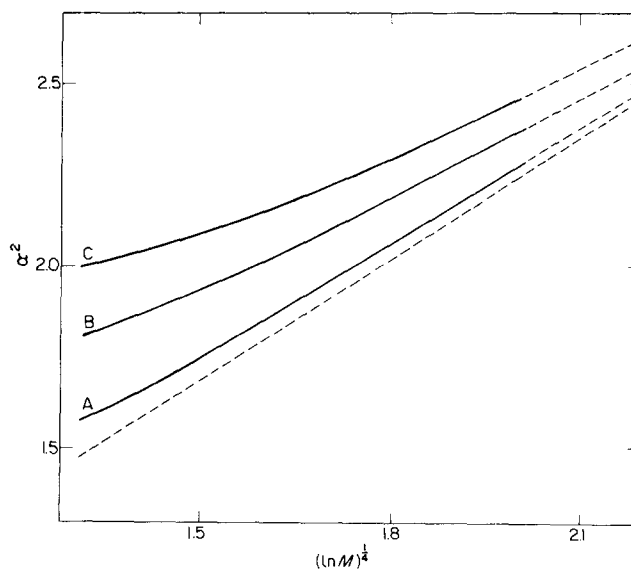It decreases with increase in u and consequently decreases with the increase of T. This contributes to the

Figure 3 The dependence of α^2 on M for stars of different number f branches, A: $f=6$, B: $F=12$, C: $f=18$, $u=0.2$. Stars with larger f need larger molecular weights to reach the region of power law dependence $\alpha^2 = (8u \ln M)^{1/4}$ (represented by the dashed line)

decrease of the rate of change of α^2 with respect to T as the temperature increases. This is in accord with the experimental findings of Berry[9].

The analytic dependence of the rate of change of α^2 with respect to u on M, f and u can be studied from equation (22). We see for example that close to the ideal state where u is negligible $d\alpha^2/du = 2[\ln M + F(f)]$. For large molecular weights where $\ln M$ dominates over $F(f)$ it becomes of the power law form $d\alpha^2/du \sim M^{\varepsilon/2}$ in accordance with Zillox's findings according to which $\alpha^2 - 1 \sim uM^{1/2}$. For more elevated temperatures it becomes

$$\frac{d\alpha^2}{du} = \frac{2}{(8u)^{3/4}}[\ln M + F(f)]^{1/4}$$

which for large molecular weights takes the form $d\alpha^2/du \sim M^{\varepsilon/8}$ showing that the dependence of the rate of change of the expansion factor with respect to temperature becomes weaker for more elevated temperatures.

CONCLUSIONS

The technique used previously for the study of the thermodynamic properties of linear polymer chains has been extended to include the effects coming from the macromolecules with different structures. First order calculations at the critical dimensionality $d = 4$ have been made for star polymers. In the good solvent region and for large molecular weights the average macroscopic properties are characterized by certain critical exponents which have been determined to order $\varepsilon = 4 - d$. The size of the molecule was studied under good and poor solvent conditions and a competition for the determination of macroscopic behaviour was found between the molecular weight M and the number of branches f of the star. Further studies are needed to clarify the analytic dependence of the macroscopic properties of stars on u, f and M and the results of the present work will be of assistance in achieving this aim.

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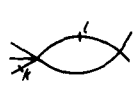20   Yamakawa, H. 'Modern theory of polymer solutions', Harper and Row, New York (1971), Chap. III

APPENDIX

In this appendix we give examples of the evaluation of first order diagrams from *Table 1*, at $d = 4$. The summations are converted into integrations which in the limit of large N's yield the following result

$$\int_1^N di \int_1^N dj \frac{1}{(i+j)^2} = \int_1^N di \left[\frac{-1}{N+i} + \frac{1}{i+1}\right] = \ln N \tag{A1}$$

quoted in *Table 1*.

$$\int_1^N di \int_1^N dj \frac{-l^2}{(i+j)^3} = \frac{l^2}{2} \int_1^N di \left[\frac{1}{(N+i)^2} - \frac{1}{(i+1)^2}\right] \tag{A2}$$

$$= \frac{1}{2}\left[\frac{l^2}{2N} + \frac{l^2}{N+l} - l\right]$$

$$\int_1^N di \int_1^N dj \frac{1}{[ij + (2N-i)(i+j)]^2} \tag{A3}$$

$$= \frac{-1}{2N} \int_1^N di \left[\frac{1}{(2N^2 + 2Ni - i^2)} - \frac{1}{(2Ni - i^2)}\right]$$

The first term of equation (A3) yield negligible contributions while the second gives the result of *Table 1*. All the rest diagrams can be found in the same way and their values are written in *Table 1*.