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1987 J. Phys. A: Math. Gen. 20 1471

(http://iopscience.iop.org/0305-4470/20/6/030)

J. Phys. A: Math. Gen. **20** (1987) 1471-1483. Printed in the UK

Conformational properties of regular comb polymers

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Received 8 April 1986, in final form 30 June 1986

Abstract. Regular comb polymers with excluded volume interactions are studied and compared with regular star and linear polymers. First-order calculations in the excluded volume parameter, at the critical dimensionality $d=4$, yield the characteristic exponents of the macroscopic properties to order $\varepsilon = 4-d$. The number of total configurations and the number of configurations with the backbone forming a ring are found. The evaluation of the mean end-to-end square distances of the backbone and the branches give an insight to the spatial distribution of the macromolecule.

1. Introduction

Previous studies on the excluded volume problem of polymers of various architectures (Miyake and Freed 1983, Vlahos and Kosmas 1984, Kosmas and Kosmas) are extended to include regular comb polymers, made from a backbone and f identical branches built at uniform intervals along the backbone (Berry and Orofino 1964, Berry 1971). The polymer chain (figure 1) consists of N segments, N_{bb} of which belong to the backbone and N_{br} to each of the f branches, $N = N_{\mathrm{bb}} + fN_{\mathrm{br}}$. The contour lengths, proportional to the molecular weights of the chain, the backbone and the branch are Nl, $N_{\mathrm{bb}}l$ and $N_{\mathrm{br}}l$, respectively, and the distance between two successive branches is $\alpha' = N_{\mathrm{bb}}l/(f+1)$. Another characteristic quantity of combs is the ratio $\rho = N_{\mathrm{br}}/N_{\mathrm{bb}}$ of the lengths of the branch and the backbone and the two natural limits of linear ($N_{\mathrm{br}} \to 0$) and regular star ($N_{\mathrm{bb}} \to 0$) chains are recovered as the limits of small and large values of ρ, respectively.

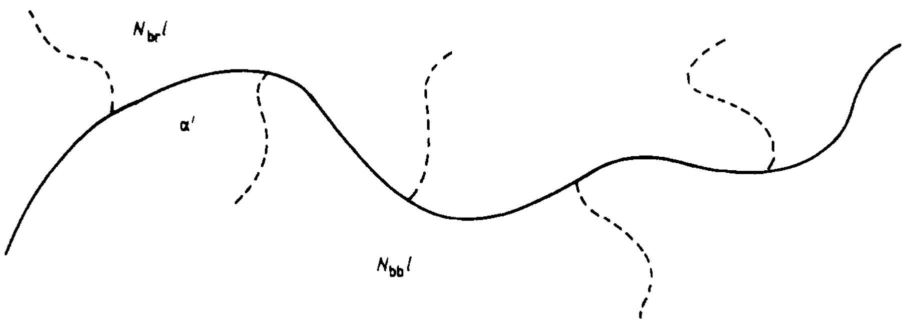


Figure 1. A regular comb polymer. $N_{\mathrm{bb}}l$ and $N_{\mathrm{br}}l$ are the lengths of the backbone and a branch, respectively. α' is the distance between two successive branches.

A configuration of the chain in space is determined if all the $N+1$ position vectors $\boldsymbol{R}_i$, $i=1,2,\ldots,N+1$ of the ends of the segments are given. The probability $P\{\boldsymbol{R}_i\}$ of the specific configuration $\{\boldsymbol{R}_i\}$ is given by

$$P\{\boldsymbol{R}_i\}=P_0\{\boldsymbol{R}_i\}\exp\left(-u'\sum_{\substack{i=1\\ i\neq j}}^{N+1}\sum_{j=1}^{N+1}\delta^d(\boldsymbol{R}_i-\boldsymbol{R}_j)\right) \tag{1.1}$$

where

$$P_0\{\boldsymbol{R}_i\}=(d/2\pi l^2)^{dN/2}\exp\left(-(d/2l^2)\sum_{\substack{\text{successive}\\ \text{position}}}(\boldsymbol{R}_i-\boldsymbol{R}_{i'})^2\right) \tag{1.2}$$

is the probability of an ideal chain in the space of dimensionality d, with the summation running over all successive chain positions i, i', ensuring the connectivity of the chain. The exponential term of (1.1) represents the two-body long-range interactions and $u'=\frac{1}{2}\int \mathrm{d}\boldsymbol{r}[\exp(-V(\boldsymbol{r})/kT)-1]$ is the excluded volume parameter written in terms of the average two-body potential $V(\boldsymbol{r})$. A prefactor $\frac{1}{2}$ in the definition of u' is used for the proper counting of distinguishable pairs in the two-body interaction term of (1.1). A convenient way, in the case of combs, of realising the summations of (1.1) is to employ another index m which describes whether the chain point lies on the backbone or on one of the f branches. It takes the value 0 for the backbone points and the integer values from 1 to f for the points on the f branches, respectively. Each chain point is characterised by two indices m and i, the first one denoting whether it lies on the backbone or on one of the f branches and the second denoting its exact position on the backbone or the branches. In this notation the double summation of (1.1) becomes a summation over four indices, two, m and n, denoting whether the two points lie in the backbone or the branches, and two, i and j, denoting the exact positions of the chain points:

$$\sum_{\substack{i=1\\ i\neq j}}^{N+1}\sum_{j=1}^{N+1}\equiv\sum_{m=0}^{f}\sum_{n=0}^{f}\sum_{\substack{i\\ \text{in the}\\ m,n\text{ set}}}\sum_{j}. \tag{1.3}$$

As in recent studies of star polymers (Vlahos and Kosmas 1984), first-order calculations in u' are made at the critical dimensionality $d=4$ in order to describe basic macroscopic properties of combs. By means of the fixed point value $u^*=\varepsilon/16$, $\varepsilon=4-d$ (Kosmas 1981), which is universal, not depending on the architecture of the chain, the characteristic exponents of the macroscopic properties of combs are found to order ε. We thus study (in § 2) the total number C of the configurations of the chain as well as the number U of the configurations with the comb backbone forming a ring. In the limit of large molecular weights the exponent ν for the sizes of the various parts of the chain remains the same as that of linear chains. However, the present first-order calculations yield the results for smaller chains, permitting the study of the sizes of the various parts of the combs which give an insight to the spatial distribution of the macromolecule. We thus find, in § 3, the mean end-to-end square distance of the backbone $\langle R^2\rangle_{\mathrm{bb}}$ and also those of the branches $\langle R^2\rangle_{\mathrm{br},k}$ ($k=1,2,\ldots,f$). Conclusions and an appendix follow.

2. The number C of total configurations and the number U of configurations with the backbone forming a ring

The number C of total configurations is proportional to the configurational partition function. Employing the two indices for each position vector it can be evaluated from the probability, (1.1), if we integrate over all position vectors R_{mi}:

$$C = \mu_0^N \int \prod_m \prod_i \mathrm{d}^d \boldsymbol{R}_{mi}\, P\{\boldsymbol{R}_{mi}\} \qquad \mu_0 = (d/2\pi l^2)^{d/2}. \tag{2.1}$$

First-order calculations in u' are made after $P\{\boldsymbol{R}_{mi}\}$ is approximated with its expansion form up to u' as

$$P\{\boldsymbol{R}_{mi}\} = P_0\{\boldsymbol{R}_{mi}\}\left(1 - u' \sum_{m=0}^{f} \sum_{n=0}^{f} \underset{\substack{\text{in the}\\ m,n \text{ set}}}{\sum_i \sum_j} \delta^d(\boldsymbol{R}_{mi} - \boldsymbol{R}_{nj})\right). \tag{2.2}$$

Employing (2.2) in (2.1) we take for C the expression

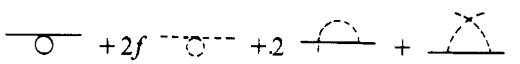
$$C = \mu_0^N\left(1 - u' \sum_{m=0}^{f} \sum_{n=0}^{f} \underset{\substack{\text{in the}\\ m,n \text{ set}}}{\sum_i \sum_j} \langle \delta^d(\boldsymbol{R}_{mi} - \boldsymbol{R}_{nj})\rangle\right) \tag{2.3}$$

where $\langle\ \rangle$ means an average with respect to the ideal probability $P_0\{R_{mi}\}$, equation (1.2). The effect of the delta function is to bring in contact two points of the chain forming a loop with a probability of occurrence depending on the length of the loop,

$$\text{probability of a loop} = (d/2\pi l \times \text{length of loop})^{d/2}. \tag{2.4}$$

In the limit of large number of chain points, the i and j summations of equation (2.3) can be approximated with integrations over the contour length of the chain. The two points of contact may belong to the backbone or the branches so that four different cases appear. In the first one both points belong to the backbone, in the second both points belong to the same branch, in the third, one is on the backbone and one on a branch while in the fourth case the two points belong to two different branches. If we use a full line to represent the backbone and broken lines to represent the branches, the four cases can be represented in a diagrammatic language as

$$C = \mu_0^N\left[1 - u\left(2 \quad + 2f \quad + 2 \quad + \quad \right)\right]$$



$$u = u'(d/2\pi l^2)^{d/2} \tag{2.5}$$

where the $(d/2\pi l^2)^{d/2}$, factor in front of u' comes from the prefactor of the loop probability, equation (2.4), u is a dimensionless excluded volume parameter and the diagrams are defined to be dimensionless. The number 2 in front of the backbone diagram and the f branch diagrams is a symmetry number and comes from the fact that the cases $i<j$ and $i>j$ yield identical results. The number 2 at the third diagram comes from the double $\Sigma_m\, \Sigma_n$ summation which brings a branch into contact with the backbone twice. The forms of the diagrams can be found by means of the loop probability, equation (2.4), and they are

 $$=\int_0^{N_{\rm bb}}\mathrm{d}i\int_i^{N_{\rm bb}}\mathrm{d}j\;1/(j-i)^{d/2} \qquad (2.6a)$$

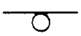
 $$=\int_0^{N_{\rm br}}\mathrm{d}i\int_i^{N_{\rm br}}\mathrm{d}j\;1(j-i)^{d/2} \qquad (2.6b)$$

 $$=2\sum_{m=1}^{f}\int_0^{N_{\rm br}}\mathrm{d}i\int_0^{m\alpha}\mathrm{d}j\;1/(i+j)^{d/2} \qquad \alpha=N_{\rm bb}/(f+1) \qquad (2.6c)$$

 $$=\sum_{\substack{m=1\\ m\neq n}}^{f}\sum_{n=1}^{f}\int_0^{N_{\rm br}}\mathrm{d}i\int_0^{N_{\rm br}}\mathrm{d}j\;1/(j+i+|n-m|\alpha)^{d/2}. \qquad (2.6d)$$

The double summation over m and n in equation (2.6d) depends only on the difference $m-n$ so it can be converted into a single summation over $\lambda=m-n$. The final values of the diagrams are quoted in table 1 and a demonstration of their evaluation is given

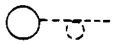
Table 1. The values of the diagrams for $d=4$.

 $=-\ln N_{\rm bb}$

 $=-\ln N_{\rm br}$

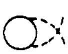
 $=\sum_{m=1}^{f}[\ln(N_{\rm bb}-m\alpha)-\ln(N_{\rm bb}+N_{\rm br}-m\alpha)+2\ln N_{\rm br}+\ln(m\alpha)-\ln(N_{\rm br}+m\alpha)]$

 $=2\sum_{\lambda=1}^{f}(f-\lambda)[-\ln(2N_{\rm br}+\lambda\alpha)+2\ln(N_{\rm br}+\lambda\alpha)-\ln(\lambda\alpha)]$

 $=-(1/N_{\rm bb}^2)\ln N_{\rm br}$

 $=(2/N_{\rm bb}^2)\ln N_{\rm bb}$

 $=f\{[2/N_{\rm bb}\sqrt{\Delta}]\ln[(\sqrt{\Delta}-N_{\rm bb})/(\sqrt{\Delta}+N_{\rm bb})]+(2/N_{\rm bb}^2)\ln N_{\rm bb}\} \qquad \Delta=N_{\rm bb}^2+4N_{\rm bb}N_{\rm br}$

 $=(2/N_{\rm bb}^2)\sum_{\lambda=1}^{f}(f-\lambda)[-\ln(2N_{\rm bb}N_{\rm br}+N_{\rm bb}\lambda\alpha-\lambda^2\alpha^2)+2\ln(N_{\rm bb}N_{\rm br}+N_{\rm bb}\lambda\alpha-\lambda^2\alpha^2)$
$-\ln(N_{\rm bb}\lambda\alpha-\lambda^2\alpha^2)]$

 $R_{\rm bb}^2=N_{\rm bb}-N_{\rm bb}\ln N_{\rm bb}$

 $R_{\rm bb}^2=\sum_{m=1}^{f}[N_{\rm br}-N_{\rm br}^2/(N_{\rm br}+\mathrm{m}\alpha)-2N_{\rm br}\ln(N_{\rm br}+m\alpha)+2N_{\rm br}\ln N_{\rm br}]$

 $R_{\rm bb}^2=2N_{\rm br}^2\sum_{\lambda=1}^{f}(f-\lambda)[1/(N_{\rm br}+\lambda\alpha)-2/(2N_{\rm br}+\lambda\alpha)]$

 $R_{{\rm br},k}^2=N_{\rm br}-N_{\rm br}\ln N_{\rm br}$

 $R_{{\rm br},k}^2=\frac{1}{2}[2N_{\rm br}-N_{\rm br}^2/(N_{\rm bb}+N_{\rm br}-k\alpha)-N_{\rm br}^2/(N_{\rm br}+k\alpha)+2(N_{\rm bb}-k\alpha)\ln(N_{\rm bb}-k\alpha)$
$-2(N_{\rm bb}-k\alpha)\ln(N_{\rm bb}+N_{\rm br}-k\alpha)+2k\alpha\ln(k\alpha)-2k\alpha\ln(N_{\rm br}+k\alpha)]$

 $R_{{\rm br},k}^2=\frac{1}{2}\sum_{m=1\neq k}^{f}[N_{\rm br}^2/(N_{\rm br}+\lambda\alpha)-N_{\rm br}^2/(2N_{\rm br}+\lambda\alpha)+2(N_{\rm br}+2\lambda\alpha)\ln(N_{\rm br}+\lambda\alpha)$
$-2(N_{\rm br}+\lambda\alpha)\ln(2N_{\rm br}+\lambda\alpha)-2\lambda\alpha\ln(\lambda\alpha)] \qquad \lambda=|m-k|$

in the appendix. Using their values in equation (2.5) we obtain the following expression for C:

$$C=\mu^N\{1-u[2(f-1)\ln N+F_c(f,\rho)]\} \qquad \mu=\mu_0\,\mathrm{e}^{-2uN} \tag{2.7a}$$

where

$$\begin{aligned}F_c(f,\rho)={}&-2(f-1)\ln(1+f\rho)+2f\ln\rho\\&+2\sum_{\lambda=1}^{f}\{-(f-\lambda)\ln[2\rho(f+1)+\lambda]-(f-\lambda-2)\ln\lambda\\&+2(f-\lambda-1)\ln[\rho(f+1)+\lambda]\}\end{aligned} \tag{2.7b}$$

and μ is the non-ideal value of μ_0 found as before (Kosmas 1981). For large molecular weights N in the region where $\ln N \gg F_c(f,\rho)$, $F_c(f,\rho)$ can be ignored as negligible and C behaves as a power law of the form $C=\mu^N N^{\gamma-1}$. The exponent γ can be determined from the coefficient of $\ln N$ in equation (2.7a) and the universal fixed point value $u^*=\varepsilon/16$ which does not depend on the architecture of the chain:

$$C=\mu^N N^{-u^*2(f-1)}=\mu^N N^{\gamma-1} \qquad N\to\infty \qquad u^*=\varepsilon/16 \tag{2.8}$$

so that

$$\gamma=1-2u^*(f-1)=1-(f-1)\varepsilon/8. \tag{2.9}$$

γ is a new exponent and characterises comb chains of f branches. For the chain without branches, $f=0$, the case of the linear chain is obtained with $\gamma=1+\varepsilon/8$. For combs of one branch, $f=1$, the exponent $\gamma=1$ does not depend to first order on ε, and the case is close to that of an ideal chain. On increasing f the exponent γ decreases showing a decrease of the number of total configurations C and a freezing of the macromolecule. This decrease of γ goes for large f as the first power of f and comparing the exponent γ of combs, equation (2.9), with $\gamma=1-f(f-3)\varepsilon/16$ of stars (Vlahos and Kosmas 1984), where the decrease of γ goes as f^2, we see that the freezing of stars is larger than that of combs. This is reasonable because stars, having all branches starting from a common origin, are of larger compactness than combs (Roovers 1979).

Equation (2.7a) with $F_c(f,\rho)$ (equation (2.7b)) is a general expression and describes all regular combs of various f and ρ including linear and star chains which can be obtained from combs as the limits of small and large ρ respectively. In the limit of small $\rho=N_{\mathrm{br}}/N_{\mathrm{bb}}$, the branch length N_{br} is much smaller than the length N_{bb} of the backbone, $N_{\mathrm{br}}\ll N_{\mathrm{bb}}$, and the backbone length approaches the total contour length of the chain $N_{\mathrm{bb}}\sim N$. In this limit, $\ln\rho=\ln N_{\mathrm{br}}-\ln N_{\mathrm{bb}}\to -\ln N_{\mathrm{bb}}\sim -\ln N$. In the expression of $F_c(f,\rho)$, equation (2.7b), only the second $\ln\rho$ term survives, so that

$$F_c(f,\rho)=-2f\ln N \qquad \text{for small } \rho. \tag{2.10}$$

Using this expression in equation (2.7a), the results of the linear chain are recovered:

$$C=\mu^N[1+2u\ln N]=\mu^N N^{2u^*}=\mu^N N^{\gamma-1} \qquad \gamma=1+\varepsilon/8 \qquad \text{for linear chains.} \tag{2.11}$$

In the other limit of large ρ, N_{bb} is negligible, $N_{\mathrm{br}}\to N/f$ and $\ln\rho=\ln N_{\mathrm{br}}-\ln N_{\mathrm{bb}}\to \ln N_{\mathrm{br}}\sim\ln N-\ln f\sim\ln N$. In equation (2.7$b$), in the limit of large ρ all the terms which have ρ in the ln function yield $\ln N$ while the rest of the terms are negligible. The summation over λ is trivial and $F_c(f,\rho)$ becomes of the form

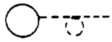
$$F_c(f,\rho)=(f^2-5f+2)\ln N \qquad \text{for large } \rho. \tag{2.12}$$

By means of this expression and equation (2.7*a*), the star exponent is obtained

$$C = \mu^N[1 - u(f^2 - 3f)\ln N]$$
$$= \mu^N N^{-u^*(f^2-3f)} = \mu^N N^{\gamma-1} \qquad \gamma = 1 - f(f-3)\varepsilon/16 \qquad \text{for stars} \tag{2.13}$$

as expected.

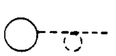
Another example of evaluation of macroscopic properties from the probability distribution $P\{\boldsymbol{R}_{mi}\}$, equation (1.1), is the number U of configurations  with the backbone forming a ring. In a diagrammatic language, U up to first order in u can be written as

$$U = \mu_0^N (d/2\pi l^2)^{d/2}\Big[$$  $$- u\Big(2$$  $$+ 2f$$  $$+ 2$$  $$+$$  $$\Big)\Big] \qquad u = (d/2\pi l^2)^{d/2}u' \tag{2.14}$$

with the diagrams having the forms

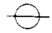
 $$= 1/N_{\mathrm{bb}}^{d/2} \tag{2.15a}$$

 $$= \int_0^{N_{\mathrm{bb}}} \mathrm{d}i \int_i^{N_{\mathrm{bb}}} \mathrm{d}j\, 1/[(j-i)(N_{\mathrm{bb}} - j + i)]^{d/2} \tag{2.15b}$$

 $$= (1/N_{\mathrm{bb}}^{d/2}) \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_i^{N_{\mathrm{br}}} \mathrm{d}j\, 1/(j-i)^{d/2} \tag{2.15c}$$

 $$= 2\sum_{m=1}^{f} \int_0^{m\alpha} \mathrm{d}i \int_0^{N_{\mathrm{br}}} \mathrm{d}j\, 1/[ij + (N_{\mathrm{bb}} - i)(j+i)]^{d/2} \tag{2.15d}$$

 $$= \sum_{\substack{m=1 \\ m \neq n}}^{f} \sum_{n=1}^{f} \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{N_{\mathrm{br}}} \mathrm{d}j\, 1/[N_{\mathrm{bb}}(i+j) + |m-n|\alpha(N_{\mathrm{bb}} - |m-n|\alpha)]^{d/2}. \tag{2.15e}$$

The last two diagrams are isomorphic with the diagram  used before (Kosmas 1982) which has the form $1/(l_1l_2 + l_1l_3 + l_2l_3)^{d/2}$ with l_1, l_2 and l_3 the three lengths joint at the two points. The values of the diagrams found after the performance of the integrals are shown in table 1. In the appendix the evaluation of the diagram  is given as an example. By means of the values of the diagrams, U obtains the form

$$U = \mu^N (d/2\pi l^2 N_{\mathrm{bb}})^{d/2}\{1 - u[2(f+2)\ln N_{\mathrm{bb}} + F_\upsilon(f, \rho)]\} \tag{2.16a}$$

with

$$F_\upsilon(f,\rho) = -2f\ln\rho + (4f/\sqrt{1+4\rho})\ln[(\sqrt{1+4\rho}-1)/(\sqrt{1+4\rho}+1)]$$
$$+ 2\sum_{\lambda=1}^{f}(f-\lambda)\ln\{[\rho(f+1)^2 + \lambda(f+1) - \lambda^2]^2/[2\rho(f+1)^2 + \lambda(f+1) - \lambda^2]$$
$$\times[\lambda(f+1) - \lambda^2]\}. \tag{2.16b}$$

In the limit of large molecular weights where $\ln N_{\mathrm{bb}} \gg F_\upsilon(f,\rho)$, the latter can be ignored and U becomes a power law of the form

$$U \sim N_{\mathrm{bb}}^{-(d/2) - u^*2(f+2)} \sim N_{\mathrm{bb}}^{\beta} \qquad \beta = -2 + (\varepsilon/2) - (\varepsilon/8)(f+2). \tag{2.17}$$

The exponent β is another characteristic exponent of combs and decreases with the increase of the number f of branches, expressing the increasing difficulty of the backbone to close as the amount of repulsion from more branches increases. For $\rho \to 0$, $\ln \rho \to -\ln N_{bb}$ so that $F_\upsilon(f, \rho)$ goes to $F_\upsilon(f, \rho) = -2f \ln \rho + 4f \ln \rho = -2f \ln N_{bb}$. In this limit the linear chain behaviour $U \sim N_{bb}^{-d/2}(1 - 4u \ln N_{bb}) \sim N_{bb}^{-2+(\varepsilon/4)}$ is obtained. For $\rho = \frac{1}{2}$ and $f = 1$ U becomes equal to the U_{12} of stars of $f = 3$ (Vlahos and Kosmas 1984) giving another check on the validity of equation (2.16).

3. The mean end-to-end square distances of the backbone and the branches

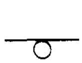
The backbone is one of the two characteristic parts of the comb and the study of its size as a function of f and ρ reveals the conditions under which the backbone is stretched or coiled. The mean end-to-end square distance of the backbone $\langle R^2 \rangle_{bb}$ expresses the square of its size and in terms of the probability $P\{\boldsymbol{R}_{mi}\}$, equation (1.1), can be written as

$$\langle R^2 \rangle_{bb} = \int \prod d^d\boldsymbol{R}_{mi}\, P\{\boldsymbol{R}_{mi}\} R_{bb}^2 \left(\int \prod d^d\boldsymbol{R}_{mi}\, P\{\boldsymbol{R}_{mi}\} \right)^{-1} \tag{3.1}$$

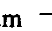
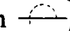
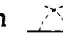
where R_{bb}^2 is the end-to-end square distance of the backbone for each configuration. If we use the expansion (2.2) in equation (3.1), u' appears both in the numerator and the denominator. To first order in u', this ratio is equivalent to a difference of two terms coming from the numerator and the denominator respectively. It can be written as

$$\begin{aligned}\langle R^2 \rangle_{bb} = \langle R_{bb}^2 \rangle_0 - u' \Bigg(&\int \prod d^d\boldsymbol{R}_{mi}\, P_0\{\boldsymbol{R}_{mi}\} R_{bb}^2 \sum_m \sum_n \sum_i \sum_j \delta^d(\boldsymbol{R}_{mi} - \boldsymbol{R}_{nj}) \\ &- \int \prod d^d\boldsymbol{R}_{mi}\, P_0\{\boldsymbol{R}_{mi}\} R_{bb}^2 \int \prod d^d\boldsymbol{R}_{mi}\, P_0\{\boldsymbol{R}_{mi}\} \sum_m \sum_n \sum_i \sum_j \delta^d(\boldsymbol{R}_{mi} - \boldsymbol{R}_{nj}) \Bigg).\end{aligned} \tag{3.2}$$

The summations are the same for the two terms and diagrams including both terms can be defined. Equation (3.2) becomes

$\langle R^2 \rangle_{bb} = \langle R_{bb}^2 \rangle_0 - u\Big(2$  $_{R_{bb}^2} + 2$  $_{R_{bb}^2} +$  $_{R_{bb}^2}\Big)$ (3.3)

$$u = u'(d/2\pi l^2)^{d/2} \qquad \langle R_{bb}^2 \rangle_0 = N_{bb}$$

where the diagrams with R_{bb}^2 subscripts express the backbone mean end-to-end square distance $\langle R^2 \rangle_{bb}$ for the configurations denoted by the diagrams. In the diagram  $_{R_{bb}^2}$ two backbone points are connected, in the diagram  $_{R_{bb}^2}$ a branch and the backbone intersect while in the diagram  $_{R_{bb}^2}$ the two connected points come from two different branches. Their forms can be found by means of equation (3.2) which includes the difference of two terms. Performing the integrations over the $\boldsymbol{R}_{mi}$ a simple rule comes out which permits the evaluation of the forms of the diagrams as $-$(length of the backbone in the loop)^2/(length of loop)$^{(d/2)+1}$. For the diagram $_{R_{bb}^2}$ the length of the backbone in the loop is the same with the loop and it is equal to $(j-i)$. The diagram can be written as

$$R^2_{\mathrm{bb}} = -\int_0^{N_{\mathrm{bb}}} \mathrm{d}i \int_i^{N_{\mathrm{bb}}} \mathrm{d}j \; 1/(j-i)^{(d/2)-1}. \tag{3.4a}$$

For the diagrams  R^2_{bb} and  R^2_{bb} the lengths of the backbone in the loops are j and $|n-m|\alpha$, respectively, while the lengths of the loops are $(i+j)$ and $(i+j+|n-m|\alpha)$ respectively. They can be written as

$$R^2_{\mathrm{bb}} = -2\sum_{m=1}^{f} \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{m\alpha} \mathrm{d}j\, j^2/(i+j)^{(d/2)+1} \tag{3.4b}$$

$$R^2_{\mathrm{bb}} = -\sum_{m=1\neq n=1}^{f}\sum^{f} \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{N_{\mathrm{br}}} \mathrm{d}j (n-m)^2\alpha^2/[i+j+|n-m|\alpha]^{(d/2)+1} \tag{3.4c}$$

and their values are found and listed in table 1. By means of equation (3.3) and the values of the diagrams the mean end-to-end square distance of the backbone becomes

$$\langle R^2\rangle_{\mathrm{bb}} = N_{\mathrm{bb}}\{1+u[2\ln N_{\mathrm{bb}} + F_{\mathrm{bb}}(f,\rho)]\} \tag{3.5a}$$

with

$$\begin{aligned} F_{\mathrm{bb}}(f,\rho) = {} & -2-2f\rho-2\rho^2 f(f+1)-2\rho\sum_{m=1}^{f}\{[f-1+\rho(f+1)]/[1+m/\rho(f+1)]\} \\ & +4\rho\sum_{m=1}^{f}[f+2\rho(f+1)]/[2+m/\rho(f+1)]+4\rho\sum_{m=1}^{f}\ln[1+m/\rho(f+1)]. \end{aligned} \tag{3.5b}$$

In the limit of large backbone lengths N_{bb} and when $\ln N_{\mathrm{bb}} \gg F_{\mathrm{bb}}(f,\rho)$ the latter can be ignored and $\langle R^2\rangle_{\mathrm{bb}} = N_{\mathrm{bb}}(1+2u\ln N_{\mathrm{bb}})$ becomes a power law of the form $\langle R^2\rangle_{\mathrm{bb}} = N_{\mathrm{bb}}^{2\nu}$. The exponent ν can be found from the u dependence of $\langle R^2\rangle_{\mathrm{bb}}$ and the universal fixed point value $u^* = \varepsilon/16$ as $\langle R^2\rangle_{\mathrm{bb}} = N_{\mathrm{bb}}^{1+2u^*} = N_{\mathrm{bb}}^{2\nu} \Rightarrow \nu = \frac{1}{2}+u^* = \frac{1}{2}+(\varepsilon/16)$ and coincides with the exponent ν of linear chains (de Gennes 1972, Kosmas 1982). $\langle R^2\rangle_{\mathrm{bb}}$, (equation (3.5$a$)), which shows whether the backbone is extended or not increases as $F_{\mathrm{bb}}(f,\rho)$ increases. Plots of $F_{\mathrm{bb}}(f,\rho)$ are given in figure 2 for $f = 1$, 5, 10, 15, 20 and 25 as a function of $\ln\rho$. What we see from these figures is that on increasing ρ, by increasing the branch length N_{br}, the extension of the backbone increases until a limiting value is reached which depends on f. The interpretation of this behaviour can be made taking account the interactions between the branches and the backbone. The presence of the branches leads to an expansion of the backbone which is larger for larger masses of branches in the vicinity of the backbone. On increasing ρ by increasing the length N_{br} of the branches the mass of the branches close to the backbone increases and therefore the expansion of the backbone increases. Increasing ρ further the branches extend away from the backbone and they cannot influence it any more. In this region the limiting behaviour of F_{bb} is reached. The limiting values of F_{bb} for $\rho\to\infty$ can be found from equation (3.5b). They are

$$\underset{\rho\to\infty}{F_{\mathrm{bb}}} = -2+\tfrac{5}{6}f+\tfrac{1}{6}f^2 \tag{3.6}$$

and show how the increase of f increases the limiting extension of the backbone.

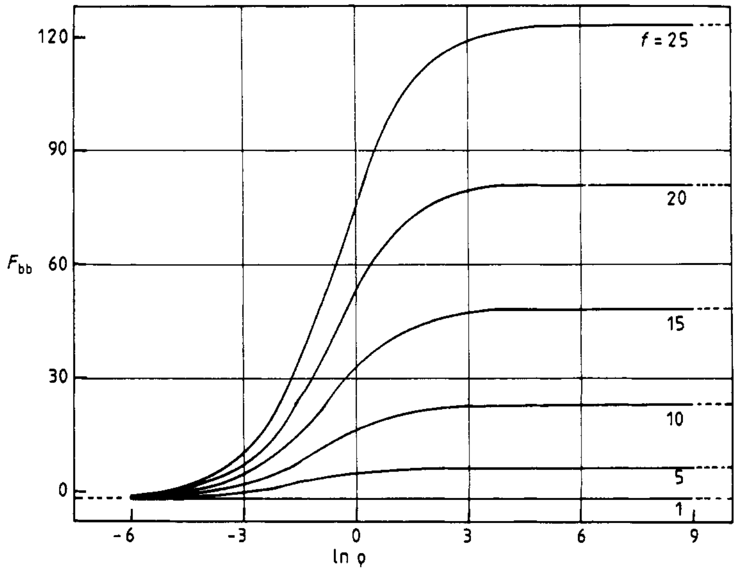


Figure 2. The function $F_{bb}(f, \rho)$ which determines the extension of the backbone as a function of $\ln \rho$ for $f = 1$, 5, 10, 15, 20 and 25.

The mean end-to-end square distance $\langle R^2 \rangle_{br,k}$ of the kth branch ($k = 1, 2, \ldots, f$) can be defined in terms of the probability distribution $P\{\boldsymbol{R}_{mi}\}$, equation (1.1), as

$$\langle R^2 \rangle_{br,k} = \int \prod \mathrm{d}^d \boldsymbol{R}_{mi} P\{\boldsymbol{R}_{mi}\} R^2_{br,k} \left(\int \prod \mathrm{d}^d \boldsymbol{R}_{mi} P\{\boldsymbol{R}_{mi}\} \right)^{-1} \tag{3.7}$$

where $R^2_{br,k}$ is the end-to-end square distance of the kth branch for each configuration. Employing equation (2.2), we take

$$\begin{aligned} \langle R^2 \rangle_{br,k} = \langle R^2_{br,k} \rangle_0 - u' \bigg(& \int \prod \mathrm{d}^d \boldsymbol{R}_{mi} \, P_0\{\boldsymbol{R}_{mi}\} R^2_{br,k} \sum_m \sum_n \sum_i \sum_j \delta^d (\boldsymbol{R}_{mi} - \boldsymbol{R}_{nj}) \\ & - \int \prod \mathrm{d}^d \boldsymbol{R}_{mi} \, P_0\{\boldsymbol{R}_{mi}\} R^2_{br,k} \int \prod \mathrm{d}^d \boldsymbol{R}_{mi} \, P_0\{\boldsymbol{R}_{mi}\} \sum_m \sum_n \sum_i \sum_j \delta^d (\boldsymbol{R}_{mi} - \boldsymbol{R}_{nj}) \bigg). \end{aligned} \tag{3.8}$$

Defining diagrams to include both terms of equation (3.8), the mean end-to-end square distance of the branch becomes

$$\begin{aligned} \langle R^2 \rangle_{br,k} &= \langle R^2_{br,k} \rangle_0 - u \left(2 \quad R^2_{br,k} + 2 \quad R^2_{br,k} + 2 \quad R^2_{br,k} \right) \\ \langle R^2_{br,k} \rangle_0 &= N_{br}. \end{aligned} \tag{3.9}$$

After the performance of the integrations of equation (3.8), the forms of the diagrams come out to be

$$R^2_{br,k} = - \int_0^{N_{br}} \mathrm{d}i \int_i^{N_{br}} \mathrm{d}j \; 1/(j - i)^{(d/2)-1} \tag{3.10a}$$

$$R^2_{\mathrm{br},k} = -\int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{N_{\mathrm{bb}}-k\alpha} \mathrm{d}j\, i^2/(i+j)^{(d/2)+1} - \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{k\alpha} \mathrm{d}j\, i^2/(i+j)^{(d/2)+1} \tag{3.10b}$$

and

$$R^2_{\mathrm{br},k} = -\sum_{m=1\neq k}^{f} \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{N_{\mathrm{br}}} \mathrm{d}j\, i^2/(i+j+|m-k|\alpha)^{(d/2)+1} \tag{3.10c}$$

and obey the general rule of being equal to $-$(length of the k branch in the loop)^2/(length of the loop)$^{(d/2)+1}$. The values of the diagrams are shown in table 1 and using them in equation (3.9) we obtain for the mean end-to-end square distance of the kth branch the expression

$$\langle R^2_{\mathrm{br},k}\rangle = N_{\mathrm{br}}\{1+u[2\ln N_{\mathrm{br}} + F_{\mathrm{br},k}(f,\rho)]\} \tag{3.11a}$$

with

$$\begin{aligned} F_{\mathrm{br},k}(f,\rho) = {}& -4+\{\rho(f+1)/[(\rho+1)(f+1)-k)\}+\rho(f+1)/[\rho(f+1)+k] \\ & -[2/\rho(f+1)](f+1-k)\ln\{(f+1-k)/[(\rho+1)(f+1)-k]\} \\ & -[2k/\rho(f+1)]\ln\{k/[\rho(f+1)+k]\} \\ & -\sum_{m=1\neq k}^{f}(-\rho(f+1)/[2\rho(f+1)+|m-k|]+\rho(f+1)/[\rho(f+1)+|m-k|] \\ & +2\{[\rho(f+1)+|m-k|]/\rho(f+1)\}\ln\{[\rho(f+1) \\ & +|m-k|]/(2\rho(f+1)+|m-k|)\} \\ & -2[|m-k|/\rho(f+1)]\ln[(|m-k|)/[\rho(f+1)+|m-k|]\}). \end{aligned} \tag{3.11b}$$

From this analytic expression we choose and plot F_{br} as a function of $\ln\rho$ for all k of f from 1 to 5 in figure 3, and for the end and middle branches for $f=5$, 10, 15

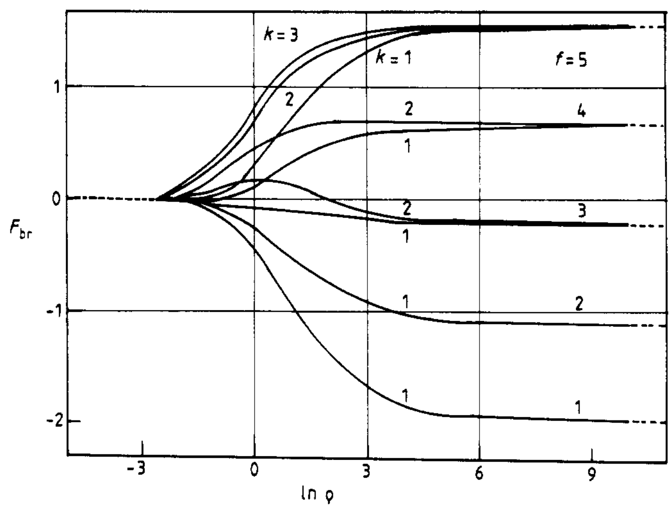


Figure 3. The function $F_{\mathrm{br},k}(f,\rho)$ which determines the extension of the branches as a function of $\ln\rho$, for all k of $f=1$, 2, 3, 4 and 5.

and 20 in figure 4. Larger values of $F_{br,k}$ mean a larger extension of the kth branch. The influence of the backbone on the branches can be seen in figure 3 from the study of the case $f = 1$ of a single branch. On increasing ρ by decreasing the backbone length N_{bb}, F_{br} decreases which means that the extension of the branch decreases. This decrease reaches a limiting value for large ρ where the mass of the branch starts being away from the reducing backbone. The influence of the other branches on a specific branch is of an opposite nature to that of the backbone on the branch. Increasing ρ, the part of F_{br} of a branch coming from the interactions of the other branches increases, showing that the influence of the other branches is to increase the extension of a branch. These two competitive effects can be seen even in the case $f = 2$, (figure 3). The decrease of F_{br} in this case is less than that of the case $f = 1$ and this happens because of the presence of the second branch which, tending to extend the first branch, lessens the predominant effect of the backbone. In the case $f = 3$ two different kinds of branches exist, the end branches with $k = 1$ and the central branch with $k = 2$. In this case the effects of the two end branches on the central one appear explicitly in figure 3. An increase of $F_{br,2}$ is observed in the beginning where the effects from the end branches overcome that of the backbone, a maximum is reached where the two opposite effects cancel and then a decrease starts where the effect of the backbone dominates. For $f \geq 4$ the effects of the branches dominate and an increase of F_{br} as a function of ρ is observed except an imperceptible decrease for the two end branches ($f = 1$) on which the effects of the other branches are slightly weaker. From figures 3 and 4, comparing the extension of the internal branches with those of the externals, we see that the internal ones extend more. The reason for this is that the internal branches, because of their symmetrical position, interact more with the other branches. In the limit $\rho \to 0$ where the backbone becomes of infinite length, $F_{br,k}$ tends to the same limit for all k, showing that in the limit of infinite backbone length the

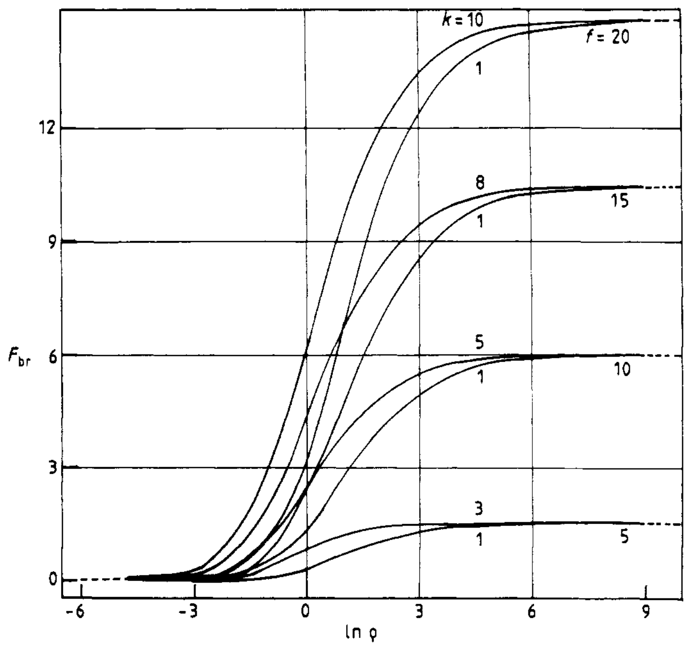


Figure 4. The function $F_{br,k}(f, \rho)$ of the end and middle branches for $f = 5$, 10, 15 and 20.

branches become equivalent. In the other limit of a star, $\rho \to \infty$, all the branches again become equivalent having the same F_{br} for each case of f (figures 3 and 4).

4. Conclusions

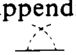
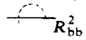
The conformational properties of regular comb polymers have been studied at the critical dimensionality $d = 4$ by means of first-order perturbation theory in the excluded volume parameter u. The critical characteristic exponents of combs for the total number of configurations C and the number U of configurations with the backbone forming a ring have been determined to order ε. The exponents of these two quantities decrease linearly as the number f of the branches of the comb increases, which expresses a freezing of the macromolecule. This freezing is less than the corresponding freezing of stars of larger compactness for which the corresponding exponents decrease as f^2. The critical exponent ν which characterises the sizes of parts of the macromolecule in the limit of infinite lengths is the same as that of linear chains. In finite chains the presence of the branches extend the backbone and a specific branch more. The backbone on the other hand, decreases the extension of the branches. These results found from first-order ε calculations describe an overall solution to the problem at the fictitious dimensionality $d = 4 - \varepsilon$. The value of the exponents and the prefactors admit small corrections from higher-order calculations, but the general trends in the behaviour of the comb are well described by the non-ideal solution at $d = 4 - \varepsilon$ (ε small).

The present work should stimulate further studies on comb polymers. Synthesis of model combs with varying ρ and f will test the above results experimentally. Further studies with enumeration techniques will be able to check the properties of the macromolecule and the transition from linear-like to star-like behaviour of combs with increasing $\rho = N_{\mathrm{br}}/N_{\mathrm{bb}}$.

Acknowledgment

We are grateful to Mr E E Mariakakis for his help in creating the computer programs.

Appendix

In this appendix we demonstrate the evaluation of three characteristic diagrams, the diagram  of C, equation (2.6d), the diagram  of U, equation (2.15d), and the diagram  of $\langle R^2\rangle_{\mathrm{bb}}$, equation (3.4$b$), for $d = 4$.

Starting from equation (2.6d) and converting the double summation into a single one over the variable $\lambda = m - n$ we take for the first diagram

$$
\begin{aligned}
&= 2\sum_{\lambda=1}^{f} (f-\lambda) \int_0^{N_{\mathrm{br}}} \mathrm{d}i \int_0^{N_{\mathrm{br}}} \mathrm{d}j\, 1/(j+i+\lambda\alpha)^2 \\
&= 2\sum_{\lambda=1}^{f} (f-\lambda) \int_0^{N_{\mathrm{br}}} \mathrm{d}i[-1/(N_{\mathrm{br}}+i+\lambda\alpha)+1/(i+\lambda\alpha)] \\
&= 2\sum_{\lambda=1}^{f} (f-\lambda)[-\ln(2N_{\mathrm{br}}+\lambda\alpha)+2\ln(N_{\mathrm{br}}+\lambda\alpha)-\ln(\lambda\alpha)] \qquad \text{(A1)}
\end{aligned}
$$

which is the value quoted in table 1.

The 2 in front of the summation in the diagram  (equation (2.15*d*)) accounts for the fact that the i integration on the ring between 0 and $m\alpha$ (the position of the branch) and between $m\alpha$ and the end of the ring give identical results. The j integration is performed first:

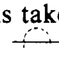
$$=2\sum_{m=1}^{f}\int_0^{m\alpha} \mathrm{d}i\{-1/[N_{\mathrm{bb}}(N_{\mathrm{bb}}j+N_{\mathrm{bb}}i-i^2)]\}\big|_0^{j=N_{\mathrm{br}}}$$

$$=2\sum_{m=1}^{f}\int_0^{m\alpha} \mathrm{d}i\{-1/[N_{\mathrm{bb}}(N_{\mathrm{bb}}N_{\mathrm{br}}+N_{\mathrm{bb}}i-i^2)]+1/[N_{\mathrm{bb}}i(N_{\mathrm{bb}}-i)]\}. \tag{A2}$$

The i integration yields an expression including $\Delta=N_{\mathrm{bb}}^2+4N_{\mathrm{bb}}N_{\mathrm{br}}$ and we take

$$=2\sum_{m=1}^{f}\{(1/N_{\mathrm{bb}}^2)\ln N_{\mathrm{bb}}-(1/N_{\mathrm{bb}}\sqrt{\Delta})\ln[(\sqrt{\Delta}+N_{\mathrm{bb}})/(\sqrt{\Delta}-N_{\mathrm{bb}})]\}. \tag{A3}$$

The m dependence disappears in equation (A3) because all positions on the ring are equivalent, so that the result of table 1 is taken.

For the evaluation of the diagram  $_{R_{\mathrm{bb}}^2}$ we start from equation (3.4*b*), with $d=4$. The i integration is done first and we take

$$_{R_{\mathrm{bb}}^2}=\sum_{m=1}^{f}\int_0^{m\alpha}\mathrm{d}j[-2N_{\mathrm{br}}/(j+N_{\mathrm{br}})+N_{\mathrm{br}}^2/(j+N_{\mathrm{br}})^2]. \tag{A4}$$

The j integration is trivial and the result is

$$_{R_{\mathrm{bb}}}=\sum_{m=1}^{f}[-2N_{\mathrm{br}}\ln(N_{\mathrm{br}}+m\alpha)+2N_{\mathrm{br}}\ln N_{\mathrm{br}}-N_{\mathrm{br}}^2/(N_{\mathrm{br}}+m\alpha)+N_{\mathrm{br}}]. \tag{A5}$$

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