

On the second virial coefficients of polymers of various architectures

M. K. Kosmas and A. M. Kosmas

Chemistry Department, University of Ioannina, Ioannina, Greece

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The osmotic pressure second virial coefficients A_2 of linear, ring, regular star and regular comb homopolymers are studied in the Gaussian model including excluded-volume interactions. A perturbation theory scheme is used where the space dimensionality d is considered as a continuous variable and the final conclusions are based on calculations done at the critical dimensionality $d=4$. For chains of intermediate molecular weight, a function F can be defined which depends on the various architectures. The second virial coefficients are smaller for larger values of F . In the case of linear and ring polymers of simple architecture, the F are pure numbers, whereas they depend on the specific characteristics in the cases of more complicated architectures. For star polymers, F is a function of the number f of the branches and, in the case of combs, it depends both on f and on the ratio ρ of the molecular weight of a branch to that of the backbone. In the limit of large molecular weights, A_2 becomes independent of the architecture and a closed form is proposed for it consistent with higher-order calculations.

(Keywords: virial coefficient; linear chains; rings; stars; combs)

INTRODUCTION

The osmotic pressure Π of a polymer solution is a basic property^{1,2} useful for the detection and characterization of the architecture of polymeric chains. In the virial expansion in powers of polymer concentration c (mass/volume), it can be written as

$$(\Pi/RT) = (c/M) + A_2 c^2 + \dots \quad (1)$$

where T is the absolute temperature, R is the gas constant and M is the molecular weight of the polymer. A_2 is the second virial coefficient, and describes the average interactions between two polymeric chains¹⁻³. It is determined from measurements of the osmotic pressure at various concentrations in the limit of infinite dilution as

$$A_2 = \lim_{c \rightarrow 0} \frac{d[\Pi/(RTc)]}{dc}$$

and early studies have shown that it can take both positive and negative values depending on the temperature and the quality of the solvent. A regularity found in the limit of large molecular weights is that A_2 depends on M in a power-law form³⁻⁶:

$$A_2 \sim M^{-\gamma} \quad (2)$$

where γ is a characteristic exponent independent of the nature of the polymer and the solvent. For polymers of various architectures, though, like rings^{7,8}, stars^{9,10} or combs¹¹, A_2 is found to take values different from those of linear chains of the same molecular weight.

The present work was undertaken for two reasons: first to explain the regularities observed, like the power-law dependence of A_2 on M , by describing the conditions under which equation (2) is valid; secondly to explain the

differences observed for polymers of various architectures, thereby producing the quantitative dependence of A_2 on the characteristics of the various architectures.

In the model to be used each chain consists of N segments and a specific configuration is defined if all the $N+1$ position vectors $\{\underline{R}_i | i=1, 2, \dots, N+1\}$ of the ends of the segments are given. The probability $P_0\{\underline{R}_i\}$ of such a configuration, for an ideal chain without excluded-volume interactions, is given in the Gaussian model as the product of N Gaussian functions, one for each segment². The position of the i th segment is determined by means of the position vectors of each beginning \underline{R}_i and its end \underline{R}_{i+1} so that $P_0\{\underline{R}_i\}$ can be written as:

$$P_0\{\underline{R}_i\} = (d/2\pi l^2)^{Nd/2} \exp\left(-\frac{d}{2l^2} \sum_{i=1}^N (\underline{R}_i - \underline{R}_{i+1})^2\right) \quad (3)$$

where l is the length of the segment, d is the dimensionality of the space and the summation runs over all successive position vectors in a way depending on the architecture of the chain. Since the end of a segment coincides with the beginning of each neighbour, the expression in (3) ensures the connectivity of the chain. This Gaussian model, though inadequate to describe quantitatively special effects in the limit of small chains^{6,12}, has been applied with considerable success in the study of larger chains^{2,10}. For the study of a real chain the two-body interactions from segments far apart along the contour length of the chain but capable of coming close in space have to be included. The form of these interactions for two chain points at position vectors \underline{R}_i and \underline{R}_j is approximated with a d -dimensional delta function pseudopotential $2u'\delta^d(\underline{R}_i - \underline{R}_j)$ which takes nonzero values only when \underline{R}_i is close to \underline{R}_j . The intensity of the interaction is proportional to the excluded-volume parameter u' , which can be written in terms of the mean average potential $V(r)$

between the two chain points at positions separated by the vector \underline{r} as

$$u' = \frac{1}{2} \int d\underline{r} \{1 - \exp[-V(\underline{r})/kT]\}$$

The probability of a specific configuration can then be written as

$$P\{\underline{R}_i\} = P_0\{\underline{R}_i\} \exp\left(-u' \sum_{\substack{i=1 \\ i \neq j}}^{N+1} \sum_{\substack{j=1 \\ j \neq i}}^{N+1} \delta^d(\underline{R}_i - \underline{R}_j)\right) \quad (4)$$

where the factor $\frac{1}{2}$ necessary for the proper counting of distinguishable pairs is absorbed in the definition of u' for simplicity. The second virial coefficient A_2 is a property of two chains and the probability of the configuration of two chains has to be used. For a configuration where the ends of the segments of the two chains are at the position vectors $\{\underline{R}_i\}$ and $\{\underline{R}'_j\}$ respectively, the probability is given by:

$$P\{\underline{R}_i, \underline{R}'_j\} = P_0\{\underline{R}_i, \underline{R}'_j\} \exp\left(-u' \sum_{\substack{i=1 \\ i \neq j}}^{N+1} \sum_{\substack{j=1 \\ j \neq i}}^{N+1} \delta^d(\underline{R}_i - \underline{R}_j) - u' \sum_{\substack{i=1 \\ i \neq j}}^{N+1} \sum_{\substack{j=1 \\ j \neq i}}^{N+1} \delta^d(\underline{R}'_i - \underline{R}'_j) - 2u \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \delta^d(\underline{R}_i - \underline{R}'_j)\right) \quad (5)$$

and includes both intra- and interchain interactions, considered to be of the same intensity. $P_0\{\underline{R}_i, \underline{R}'_j\}$ stands for the probability of the two ideal noninteracting chains.

When the number of segments N of the chain is large, the local structure of the chain is irrelevant for the description of its macroscopic properties. In this limit chains with discrete units can be approximated with continuous lines of contour length of measure N and the model described by means of equation (4) and (5) is equivalent to the continuous model introduced some time ago by Edwards¹³. Summations over the units of the chains appearing in the evaluation of the diagrams of perturbation theory are equivalent to integrations over the contour lengths of the chains, which are easier to handle. The only problem in this simplification arises from the vanishing loops, the lengths of which according to equation (14) appear in the denominator and produce infinities in the limit of zero lengths. This is an artifact of the continuous line approximation and it does not change the long-chain character of the chains. It does not cause any real trouble because the infinities can be isolated and ignored (see Appendix).

Previous studies¹⁴ have shown that the dimensionality d of the space plays a dominant role in the behaviour of chains. On increasing d the effects from two-body interactions diminish and $d=4$ is a critical dimensionality above which such effects cease to exist. The study at $d=4$ is the easiest possible and though $d=4$ is a fictitious dimensionality it helps in understanding the behaviour of chains at the real dimensionalities $d=3, 2$ or 1 . The connection between the dimensionality 4 and the rest of the dimensionalities d is done via the parameter $\varepsilon = 4 - d$, which in this analysis is treated as a small quantity. By means of one-loop perturbation theory, we can determine both the structure of the second virial coefficient in the

limit of large molecular weights and the differences due to the various architectures, more evident in the range of intermediate molecular weights.

In the next section the general formalism for the evaluation of A_2 is given, while in the subsequent section the results for the various architectures are discussed. Finally an Appendix follows where the evaluation of the diagrams is explained. Throughout the paper N stands for the total number of segments of the chain while $M = N\mu_0$, with μ_0 the molecular weight of a segment, stands for the total molecular weight of the chain.

EVALUATION OF A_2

A_2 is a property of two chains and in units of volume/(mass)² it can be expressed as^{3,15}:

$$A_2 = -\frac{VN_A}{2M^2} \frac{(C_2 - C_1^2)}{C_1^2} \quad (6)$$

where V is the volume of the system, N_A is Avogadro's number and M is the molecular weight of the chain in units of mass. C_1 is the configurational partition function of a single chain and is the sum of the probabilities of all possible configurations. It can be defined in terms of the probability of a single chain, equation (4), as

$$C_1 = \int \prod_{i=1}^{N+1} d^d \underline{R}_i P\{\underline{R}_i\} \quad (7)$$

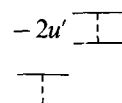
C_2 is the configurational partition function of the system of two chains defined in terms of the probability of two chains, equation (5), as

$$C_2 = \int \prod_{i=1}^{N+1} d^d \underline{R}_i \prod_{j=1}^{N+1} d^d \underline{R}'_j P\{\underline{R}_i, \underline{R}'_j\} \quad (8)$$

To evaluate C_2 from this equation, $P\{\underline{R}_i, \underline{R}'_j\}$ is substituted from equation (5). In the resulting expression the third exponential factor is approximated with its expansion form up to the square term in the interexcluded-volume parameter u' . The result is

$$C_2 = \int \prod_{i=1}^{N+1} d^d \underline{R}_i \prod_{j=1}^{N+1} d^d \underline{R}'_j P_0\{\underline{R}_i, \underline{R}'_j\} \exp\left(-u' \sum_{\substack{i=1 \\ i \neq j}}^{N+1} \sum_{\substack{j=1 \\ j \neq i}}^{N+1} \delta^d(\underline{R}_i - \underline{R}'_j) - u' \sum_{\substack{i=1 \\ i \neq j}}^{N+1} \sum_{\substack{j=1 \\ j \neq i}}^{N+1} \delta^d(\underline{R}'_i - \underline{R}'_j)\right) \left[1 - 2u' \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \delta^d(\underline{R}_i - \underline{R}'_j) + 2u'^2 \left(\sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \delta^d(\underline{R}_i - \underline{R}'_j)\right)^2\right] \quad (9)$$

The first term in the expansion represents the product from two independent chains and it is equal to C_1^2 . The second u' term represents two chains intersected at their i th and j th points due to the action of the $\delta^d(\underline{R}_i - \underline{R}'_j)$ function. It can be written as



where



represents the two intersected chains. The full lines

represent the chains while the broken line represents the delta function which brings them in contact. The point of intersection runs through all the positions of the two chains so that the double summation of the term is produced. The third u'^2 term represents two chains intersected at two different points due to the action of the two delta functions. It is equal to

$$2u'^2 \text{---} \text{---}$$

and again the points of intersection of the two chain runs through all the positions of the chains so that the four summations of the term are produced. By means of these diagrammatic expressions, equation (9) becomes

$$C_2 = C_1^2 - 2u' \text{---} \text{---} + 2u'^2 \text{---} \text{---} \quad (10)$$

so that A_2 , equation (6), takes the form

$$A_2 = u'(N_A V / M^2 C_1^2) \left(\text{---} \text{---} - u' \text{---} \text{---} \right) \quad (11)$$

In the first-order diagram



the single point of intersection does not change the intrachain character so that each chain produces a C_1 factor. The difference from the case of two independent chains is that the two intersected chains move together in all available space of volume V so that a factor V less is produced and appears in the denominator of the expression of the diagram. If we approximate the double summation with a double integration in the limit of large N , the diagram becomes equal to

$$\text{---} \text{---} = (C_1^2 / V) \int_0^N di \int_0^N dj = C_1^2 N^2 / V \quad (12)$$

The second-order diagram



has a u'^2 prefactor and since the overall calculation is up to the second order in u' its value has to be found only up to zeroth u'^0 order. This is the case of ideal chains for which $C_1 = V$ for an open chain and $C_1 = V/N^{d/2}$ for a chain forming a ring. The two points of intersection of the diagram form a loop which determines the form of the diagram. Since the probability of a part of a chain or intersected chains of length $N_p l$ having its two ends at the points \underline{R}_1 and \underline{R}_2 is

$$P(\underline{R}_1, \underline{R}_2; N_p l) = (d/2\pi N_p l^2)^{d/2} \exp[-d(\underline{R}_2 - \underline{R}_1)^2 / 2N_p l^2] \quad (13)$$

the probability of a loop of length $N_p l$ for which $\underline{R}_1 = \underline{R}_2$ is equal to

$$P(\underline{R}_1 = \underline{R}_2; N_p l) = (d/2\pi N_p l^2)^{d/2} \quad (14)$$

After this the value of the second-order diagram



can be found straightforwardly. For its evaluation four length variables are needed: two i_1, j_1 on the first and two i_2, j_2 on the second chain. The form of the diagram depends on the architecture of the chain. In an abstract form it can be written as

$$\text{---} \text{---} = V \int_N di_1 \int_N dj_1 \int_N di_2 \int_N dj_2 (d/2\pi l \times \text{length of loop})^{d/2} \quad (15)$$

where the length of the loop formed by the two points of intersection, the one at the points i_1 of the first and i_2 of the second chain and the second at the points j_1 of the first and j_2 of the second chain, varies as the four length variables run throughout all the contour lengths of the chains. In the easiest case of linear polymers, equation (15) takes the form

$$\text{---} \text{---} = V(d/2\pi l^2)^{d/2} 4 \text{---}$$

with

$$\text{---} = \int_0^N di_1 \int_{i_1}^N dj_1 \int_0^N di_2 \int_{i_2}^N dj_2 1/(j_1 - i_1 + j_2 - i_2)^{d/2} \quad \text{linear chains} \quad (16)$$

The number 4 is a symmetry number and comes from the fact that the cases of $j_1 > i_1$ ($j_2 > i_2$) and $j_1 < i_1$ ($j_2 < i_2$) yield identical results. For the cases of complex architecture this dependence is more complicated. In the case of rings, equation (15) takes the form

$$\text{---} \text{---} = V(d/2\pi l^2)^{d/2} 4 \text{---}$$

with

$$\text{---} \text{---} = \int_0^N di_1 \int_{i_1}^N dj_1 \int_0^N di_2 \int_{i_2}^N dj_2 1/[N(j_1 - i_1)(N - j_1 + i_1) + N(j_2 - i_2)(N - j_2 + i_2)]^{d/2} \quad \text{rings} \quad (17)$$

where the form of the diagram



has been taken from ref. 16. It is equal to $1/(l_1 l_2 l_3 + l_1 l_2 l_4 + l_1 l_3 l_4 + l_2 l_3 l_4)^{d/2}$ where l_1, l_2, l_3 and l_4 are the four lengths joined at the two points. For rings $l_1 + l_2 = N$ and $l_3 + l_4 = N$ so that the simple form $1/[N l_1 (N - l_1) + N l_2 (N - l_2)]^{d/2}$ is obtained. In the case of regular stars of f equal branches, three different diagrams can appear where different numbers of branches from the two chains intersect. When there are two intersected branches the form of the diagram is



When there are three the diagram takes the form



and when there are four the form



When the four length indices i_1, j_1, i_2 and j_2 of equation (15), measured from the centre of the star, run over all the contour lengths of the two chains, $4f^2$ of the first diagram are produced, $4f^2(f-1)$ of the second and $f^2(f-1)^2$ of the third, so that for stars equation (15) takes the form

$$\overline{\Gamma\Gamma} = V(d/2\pi l^2)^{d/2} \left(4f^2 \Psi \leftarrow + 4f^2(f-1) \Psi \leftarrow \leftarrow + f^2(f-1)^2 \Psi \leftarrow \leftarrow \leftarrow \right)$$

with

$$\Psi \leftarrow = \int_0^{N_{br}} di_1 \int_0^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 1/(j_1 - i_1 + j_2 - i_2)^{d/2}$$

$$\Psi \leftarrow \leftarrow = \int_0^{N_{br}} di_1 \int_0^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 1/(j_1 - i_1 + j_2 + i_2)^{d/2}$$

$$\Psi \leftarrow \leftarrow \leftarrow = \int_0^{N_{br}} di_1 \int_0^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 1/(j_1 + i_1 + j_2 + i_2)^{d/2}$$

$N_{br} = N/f$ regular stars

where N_{br} is the branch contour length and N the total contour length of the macromolecule. In the case of regular combs (Figure 1) made from f equal branches of length N_{br} built at equal distances on a backbone of length N_{bb} the points of intersection of the two chains may be either on the backbones of the two chains or on the branches. If we use full lines for the backbones and broken lines for the branches, equation (15) takes the form

$$\overline{\Gamma\Gamma} = V(d/2\pi l^2)^{d/2} \left(4 \Psi \leftarrow + 4 \Psi \leftarrow \leftarrow + 8 \Psi \leftarrow \leftarrow \leftarrow + 8 \Psi \leftarrow \leftarrow \leftarrow \leftarrow + 8 \Psi \leftarrow \leftarrow \leftarrow \leftarrow \leftarrow + 4 \overline{\Gamma\Gamma} + 4 \overline{\Gamma\Gamma} + 4 \overline{\Gamma\Gamma} + 4 \overline{\Gamma\Gamma} + 4 \overline{\Gamma\Gamma} + \overline{\Gamma\Gamma} \right)$$

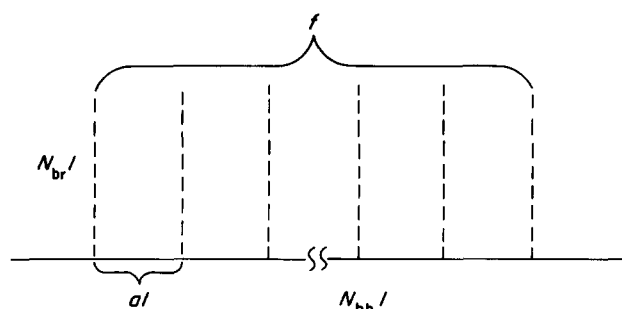


Figure 1 A regular comb polymer with f branches. N_{bb} and N_{br} are the contour lengths, proportional to the molecular weights of the backbone and the branch respectively, $a = N_{bb}/(f+1)$, $\rho = N_{br}/N_{bb}$

with

$$\Psi \leftarrow = \int_0^{N_{bb}} di_1 \int_{i_1}^{N_{bb}} dj_1 \int_0^{N_{bb}} di_2 \int_{j_2}^{N_{bb}} dj_2 1/(j_1 - i_1 + j_2 - i_2)^{d/2}$$

$$\Psi \leftarrow \leftarrow = \sum_{i=1}^f \sum_{j=1}^f \int_0^{N_{br}} di_1 \int_{i_1}^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_{i_2}^{N_{br}} dj_2 1/(j_1 - i_1 + j_2 - i_2)^{d/2}$$

$$\Psi \leftarrow \leftarrow \leftarrow = \sum_{i=1}^f \int_0^{N_{bb}} di_1 \int_{i_1}^{N_{bb}} dj_1 \int_0^{N_{br}} di_2 \int_{i_2}^{N_{br}} dj_2 1/(j_1 - i_1 + j_2 - i_2)^{d/2}$$

$$\Psi \leftarrow \leftarrow \leftarrow \leftarrow = 2 \sum_{i=1}^f \int_0^{N_{bb}} di_1 \int_{i_1}^{N_{bb}} dj_1 \int_0^{N_{br}} di_2 \int_{i_2}^{ia} dj_2 1/(j_1 - i_1 + j_2 + i_2)^{d/2}$$

$$\Psi \leftarrow \leftarrow \leftarrow \leftarrow \leftarrow = 2 \sum_{i=1}^f \sum_{j=1}^f \int_0^{N_{br}} di_1 \int_{i_1}^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_{i_2}^{ia} dj_2 1/(j_1 - i_1 + j_2 + i_2)^{d/2}$$

$$\overline{\Gamma\Gamma} = \sum_{i=1}^f \sum_{j=1}^f \int_0^{N_{bb}} di_1 \int_{i_1}^{N_{bb}} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 \times 1/(|j-i|a + j_1 - i_1 + j_2 + i_2)^{d/2}$$

$$\overline{\Gamma\Gamma} = \sum_{i=1}^f \sum_{j=1}^f \sum_{k=1}^f \int_0^{N_{br}} di_1 \int_{i_1}^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 \times 1/(j-k|a + j_1 - i_1 + j_2 + i_2)^{d/2}$$

$$\overline{\Gamma\Gamma} = 4 \sum_{i=1}^f \sum_{j=1}^f \int_0^{N_{br}} di_1 \int_{i_1}^{ia} dj_1 \int_0^{N_{br}} di_2 \int_0^{ja} dj_2 1/(j_1 + i_1 + j_2 + i_2)^{d/2}$$
















$$\overline{\Gamma\Gamma} = 2 \sum_{i=1}^f \sum_{j=1}^f \sum_{k=1}^f \int_0^{N_{br}} di_1 \int_{i_1}^{ia} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 1/(|j-k|a + j_1 + i_1 + j_2 + i_2)^{d/2}$$

$$\overline{\Gamma\Gamma} = \sum_{i=1}^f \sum_{j=1}^f \sum_{k=1}^f \sum_{l=1}^f \int_0^{N_{br}} di_1 \int_{i_1}^{N_{br}} dj_1 \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 \times 1/(|j-i|a + |l-k|a + j_1 + i_1 + j_2 + i_2)^{d/2}$$

regular combs (19)

In the definitions of the comb diagrams the summations over the f branches are included and ia , $a = N_{bb}/(f+1)$ being the distance between the branches, denotes the position of the branches on the backbone. The finite values of the diagrams for all architectures are given in Table 1 and a demonstration of their evaluation is given in the Appendix.

Table 1 The values for $d=4$ of the first-order diagrams for the various architectures

Linear		$= N^2(\ln N - 2 \ln 2 - \frac{1}{2})$
Ring		$= N^{-2}(\ln N + \frac{1}{2} \ln 2)$
Star		$= N_{br}^2(\ln N_{br} - 2 \ln 2 - \frac{1}{2})$
		$= N_{br}^2(8 \ln 2 - \frac{9}{2} \ln 3)$
		$= N_{br}^2(18 \ln 3 - 28 \ln 2)$
Comb		$= N_{bb}^2(\ln N_{bb} - 2 \ln 2 - \frac{1}{2})$
		$= f^2 N_{br}^2(\ln N_{br} - 2 \ln 2 - \frac{1}{2})$
		$= f[N_{bb}F_0(N_{br}) + \frac{1}{2}F_1(N_{br}) - \frac{1}{2}F_1(N_{bb} + N_{br}) + N_{br}F_0(N_{bb})$ $+ \frac{1}{2}F_1(N_{bb}) - \frac{1}{2}N_{bb}N_{br}]$
		$= -fF_1(N_{br}) - 2N_{bb}fF_0(N_{br}) + fF_1(N_{bb} + N_{br}) - fF_1(N_{bb})$ $+ \sum_{i=1}^f [2N_{bb}F_0(N_{br} + ia) - 2N_{bb}F_0(ia) - F_2(ia) + F_2(N_{bb} + ia)]$
		$= f \sum_{i=1}^f [-F_3(ia) + 2N_{br}F_0(N_{br} + ia) - 2N_{br}F_0(ia) + 4N_{br}^2 \ln 2]$
		$= \sum_{i=1}^f (f-i) \{-F_3(N_{bb} + ia) + F_2(ia) + 2N_{bb}[F_0(2N_{br} + ia)$ $- 2F_0(N_{br} + ia) + F_0(ia)]\}$
		$= f \sum_{i=1}^f (f-i) \{F_4(ia) + 2N_{br}[F_0(2N_{br} + ia) - 2F_0(N_{br} + ia)$ $+ F_0(ia)]\}$
		$= -4f^2F_0(N_{br}) - 8f^2N_{br}^2 \ln 2 - 2fF_3(N_{bb})$ $+ 2 \sum_{i=1}^f [(2f-i+1)F_3(ia) - (f-i)F_3(N_{bb} + ia)]$
		$= f(f-1)F_4(N_{bb}) + \sum_{i=1}^f [(-2f^2 + 4fi - i^2 - 2f + i)F_4(ia)$ $+ (f-i)(f-i-1)F_4(N_{bb} + ia)]$
		$= (-f^2/3 + f^2 - 2f/3)F_5(N_{bb}) + \sum_{i=1}^f \{(-2if^2 + 2fi^2 - i^3/3 + 2f^2$ $- 2fi + i/3)F_5(ia) + \frac{1}{3}[-(f-i)^3 + 12f^2 - 6fi + 3i^2$ $- 2(f-i)]F_5(N_{bb} + ia)\}$
where		
	$F_0(x) = x \ln x$	$F_1(x) = x^2 \ln x$
	$F_2(x) = x^2 \ln x - (x + N_{br})^2 \ln(x + N_{br})$	
	$F_3(x) = x^2 \ln x - 2(x + N_{br})^2 \ln(x + N_{br})$ $+ (x + 2N_{br})^2 \ln(x + 2N_{br})$	
	$F_4(x) = x^2 \ln x - 3(x + N_{br})^2 \ln(x + N_{br})$ $+ 3(x + 2N_{br})^2 \ln(x + 2N_{br}) - (x + 3N_{br})^2 \ln(x + 3N_{br})$	
	$F_5(x) = x^2 \ln x - 4(x + N_{br})^2 \ln(x + N_{br}) + 6(x + 2N_{br})^2 \ln(x + 2N_{br})$ $- 4(x + 3N_{br})^2 \ln(x + 3N_{br}) + (x + 4N_{br})^2 \ln(x + 4N_{br})$	

RESULTS AND DISCUSSION

Linear polymers

By means of the values of the integrals of Table 1 and equations (11), (12) and (16), the dependence of the second virial coefficient A_{2L} of linear chains, on the molecular weight M of the chain and the interaction parameter u' is found as:

$$A_{2L} = (u'N_A/\mu_0^2)[1 - 4u(\ln N + F_L)] \quad N = M/\mu_0$$

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

$$F_L = -2 \ln 2 - \frac{1}{2} = -1.89 \quad d=4 \quad (20)$$

Here μ_0 , in units of mass, is the molecular weight of the segment, u is a dimensionless excluded-volume parameter and N , being proportional to the molecular weight and the contour length of the chain, stands for the number of segments of the chain. F_L is a pure number and in the limit of large molecular weights it is negligible with respect to $\ln N$ so that it can be ignored, while in the limit of intermediate chains it is comparable to $\ln N$ and characterizes the linear chains. Calculations up to u^3 have been done previously³ for the limit $N \rightarrow \infty$, according to which A_{2L} can be written as:

$$A_{2L} = (u'N_A/\mu_0^2)(1 - 4u \ln N + 24u^2 \ln^2 N) \quad (21)$$

As we have shown for the case of the partition function of a chain¹⁶ the series of $u \ln N$ in parentheses is of the general form $(1 + au \ln N)^b$. The parameters a and b have been determined from the first two terms of the series and their values were consistent with the third-order term. Similarly in the expansion (21) a and b can be determined from the coefficients of $u \ln N$ and $u^2 \ln^2 N$ terms as $ab = -4$, $b(b-1)a^2/2 = 24 \Rightarrow a = 8$ and $b = -\frac{1}{2}$, giving for A_{2L} the closed form

$$A_{2L} = (u'N_A/\mu_0^2)(1 + 8u \ln N)^{-1/2} \quad d=4 \quad N \rightarrow \infty \quad (22)$$

Previous studies at $d=3$ ^{17,18} found that A_{2L} is proportional to a function $F_1(z)$ where the parameter z is defined as $z = 2uN^{1/2}$. The solution as a function of dimensionality d shows that z can be defined in any dimensionality as $z = (2u/\epsilon)(N^{\epsilon/2} - 1)$, $\epsilon = 4 - d$, which of course for $d=3$ ($\epsilon=1$) and $N \rightarrow \infty$ is equal to the three-dimensional expression. For $\epsilon \rightarrow 0$, $z \rightarrow u \ln N$ and this is the parameter which appears in equation (22). The classical function $F_1(z)$ has an asymptotic expansion giving information only for small z . Because it is proportional to $N^{1/2}$, a large number, z is small only for u close to zero so that the study at $d=3$ cannot describe A_{2L} far from the θ point. The situation becomes better as we increase d since the dependence of z on N becomes weaker. The best situation is at the critical dimensionality $d=4$ where $z = u \ln N$ obtains the smallest possible values for the same molecular weight permitting the study for larger u values. This is the reason for the success in the determination of the closed form, equation (22), from the first few terms of perturbation theory.

Equation (22) provides the analytic dependence of A_{2L} on the molecular weight $M = N\mu_0$ and the excluded-volume parameter u and by means of it a study over a wide range of conditions can be done. Though it is valid for $d=4$ it permits the derivation of conclusions for smaller

dimensionalities $d = 4 - \epsilon$ via the limit¹⁶ $\ln N = (2/\epsilon)(N^{\epsilon/2} - 1)$ as $\epsilon \rightarrow 0$. It is consistent with experiments and it predicts correctly the form and the critical exponent of A_{2L} in the limit of large molecular weights. In the good solvent region, where u' is positive, the increase of u' by increasing the temperature or the quality of the solvent causes A_{2L} to increase sharply initially and gradually for larger values of u' (ref. 19). On increasing the molecular weight of the chain the second virial coefficient decreases^{4,6,20} and in the good solvent region and the limit of large molecular weights this dependence becomes a power law^{4,5} of the form $A_{2L} \sim M^{-\gamma}$. This behaviour is explained by means of equation (22) and an evaluation of γ up to order ϵ is provided. Indeed for large molecular weights and u positive the second term of equation (22) is more dominant over the first and since $\ln N = (2/\epsilon)N^{\epsilon/2}$ the second virial coefficient becomes

$$A_{2L} = (u' N_A / \mu_0^2) [(16u/\epsilon) N^{\epsilon/2}]^{-1/2} \sim N^{-\epsilon/4} \sim M^{-\epsilon/4}$$

and $\gamma = \epsilon/4$ in agreement with other theories^{5,21}. The same exponent can also be determined from first-order perturbation theory, equation (20), using the fixed point value¹⁴ $u^* = \epsilon/16$. At this point $A_{2L} \sim \exp(-4u^* \ln N) = N^{-\epsilon/4}$, yielding the same critical exponent. For $d = 3$ ($\epsilon = 1$) the value of the exponent is 0.25 and though calculations to higher order in ϵ would yield better estimates of γ it is interesting to notice that the value of $\gamma = \epsilon/4$ is a limit for $N \rightarrow \infty$. For N finite

$$A_{2L} = (u' N_A / \mu_0^2) [1 + (16u/\epsilon) N^{\epsilon/2}]^{-1/2}$$

so that

$$\gamma = -d \ln A_{2L} / d \ln N = (\epsilon/4) \{1 - 1/[1 + (16u N^{\epsilon/2}/\epsilon)]\}$$

is smaller and closer to the value 0.20 found recently for the system of polystyrene in toluene²⁰.

Ring polymers

The value of the diagram



(Table 1) is obtained by means of the integrals of Table 1. Using this value in equations (17) and (11) we obtain for ring polymers the expression

$$A_{2R} = (u' N_A / \mu_0^2) [1 - 4u(\ln N + F_R)]$$

with $F_R = \ln 2/2 = 0.35$ $d = 4$ (23)

For large molecular weights F_R is negligible with respect to $\ln N$ and the second virial coefficient for a ring approaches that of a linear chain. As we will see this applies to all architectures and admits a physical interpretation. The effect of the architecture on the chains is of local character so that in the limit of huge molecular weights, $N \rightarrow \infty$, it disappears from the macroscopic properties of the chain. This result goes beyond the results of first-order classical perturbation theory at $d = 3$, according to which different coefficients for the first-order z terms are found for polymers of different architectures^{22,23} and the above limiting behaviour cannot be seen.

For smaller chains, where the function F_R is comparable to $\ln N$, equation (23) permits comparison between ring and linear chains of the same molecular weight. $F_R > F_L$ so that $A_{2R} < A_{2L}$ in agreement with experimental findings^{7,8}.

Regular star polymers

In the case of regular stars of f branches²¹, use of the integrals of Table 1 in equations (18) and (11) yields the expression

$$A_{2S} = (u' N_A / \mu_0^2) [1 - 4u(\ln N + F_S)]$$

with

$$F_S = -2 \ln 2 - \frac{1}{2} - \ln f + (-7f^2 + 22f - 15) \ln 2 + (\frac{9}{2}f^2 - \frac{27}{2}f + 9) \ln 3 \quad d = 4 \quad (24)$$

The overall form of A_{2S} is the same as that of previous architectures and again for $\ln N \gg F_S$ the behaviour of linear chains is recovered. The difference is that F_S depends on the number of branches, f . Some characteristic values are: for $f = 1, 2, F_S = F_L = -1.89$; the case of linear chain is taken as expected. For $f = 5, F_S = 0.38$; for $f = 10, F_S = 8.65$; for $f = 20, F_S = 39.65$; and for $f = 30, F_S = 89.30$. See also Figures 2 and 3 where the F values of various architectures are compared. We see that F_S increases with f and it can reach very large values. The larger is F_S , the larger are the molecular weights needed to reach linear chain behaviour. This property, like that of the mean square radius of gyration of stars²⁴, expresses the influence of the core, which is larger for larger number of branches⁹.

For stars of the same molecular weight the second virial coefficient according to equation (24) becomes smaller as f increases, in agreement with experiment^{9,12}.

Regular comb polymers

Regular combs (Figure 1) consist of a backbone of length N_{bb} and f branches of length N_{br} each equally distanced along the length of the backbone. In this case the architecture is more complicated and three parameters are needed for its description. For a better

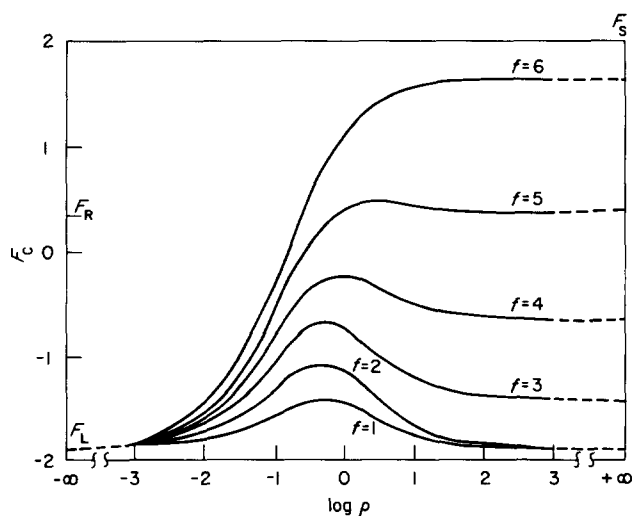


Figure 2 The function F_C for regular combs of $f < 7$ as a function of $\log \rho$. The corresponding F values of linear, ring and regular star chains are also shown

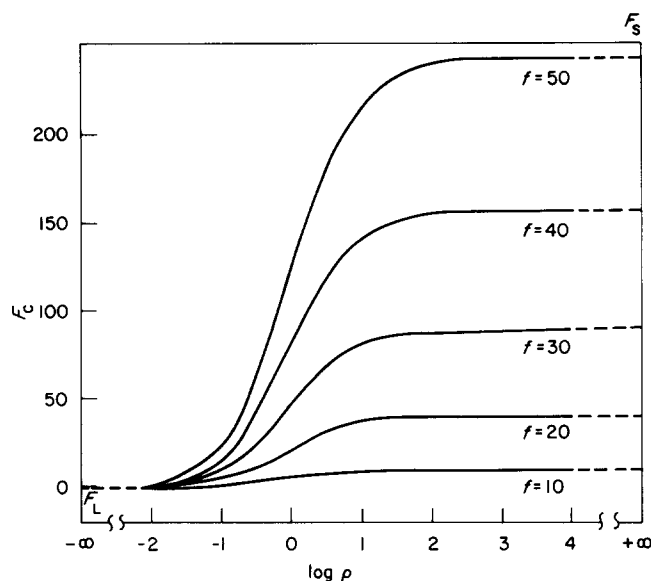


Figure 3 F_C for regular combs of various $f > 6$ as a function of $\log \rho$. For larger f the transition from linear to star behaviour becomes sharper

comparison with the other types of chain the three parameters are chosen to be: (a) the number f of branches, (b) the contour length of the chain, $N = N_{bb} + fN_{br}$, proportional to the molecular weight of the polymer and (c) the ratio $\rho = N_{br}/N_{bb}$ of the molecular weights of the branch and the backbone. As $\rho \rightarrow 0$ the linear chain is obtained while for $\rho \rightarrow \infty$ the regular star is recovered.

Following the same route as in the previous cases we obtain for the comb an expression of the same structure:

$$A_{2c} = (u' N_A / \mu_0^2) [1 - 4u(\ln N + F_C)] \quad d = 4 \quad (25)$$

Again for large N , in the region where $\ln N$ is dominant over F_C , linear chain behaviour results. For smaller chains, F_C determines the value of A_{2c} and larger values of F_C mean smaller values of A_{2c} . The difference now is that F_C describes a complex architecture and is more complicated. It depends on both ρ and f . Generally the effects from four different branches have to be considered so that the expression of F_C includes summations over four different indices as the diagrams of equation (19) indicate. These summations have been converted into a simple summation over one index. Owing to the simplicity of the problem at $d = 4$ compared with that at $d = 3^{25}$, a final expression results with

$$\begin{aligned} F_C = & -\ln(1+f\rho) - \frac{1}{2} + [1/4(1+f\rho)^2] \{ -8(1+f^2\rho^2)\ln 2 \\ & -4f(3f+1)\rho^2 \ln \rho - 8f\rho \ln \rho \\ & + \frac{4}{3}f(f^2 - 12f + 26)(1+\rho)^2 \ln(1+\rho) \\ & - 2f(f^2 - 9f + 12)(1+2\rho)^2 \ln(1+2\rho) \\ & + \frac{4}{3}f(f^2 - 6f + 5)(1+3\rho)^2 \ln(1+3\rho) \\ & - \frac{1}{3}f(f^2 - 3f + 2)(1+4\rho)^2 \ln(1+4\rho) + \sum_{i=1}^f [(-x/3 \\ & - 2f^2 + 10fi - 4i^2 + 4f - \frac{23}{3}i)i^2 \mu^2 \ln(i\mu) + (\frac{4}{3}x + 4f^2 - 28fi + 12i^2 \\ & + \frac{32}{3}i - 8)(i\mu + \rho)^2 \ln(i\mu + \rho) - (2x - 24fi + 12i^2 \end{aligned}$$

$$\begin{aligned} & + 12f - 2i - 8)(i\mu + 2\rho)^2 \ln(i\mu + 2\rho) + (\frac{4}{3}x - 4f^2 \\ & - 4fi + 4i^2 + 8f - \frac{16}{3}i)(i\mu + 3\rho)^2 \ln(i\mu + 3\rho) \\ & - (x/3 - 2f^2 + 2fi - i/3)(i\mu + 4\rho)^2 \ln(i\mu + 4\rho) \\ & - (y^3/3 - 5y^2 + \frac{50}{3}y - 8)(1+i\mu)^2 \ln(1+i\mu) \\ & + (\frac{4}{3}y^3 - 16y^2 + \frac{116}{3}y - 8)(1+i\mu + \rho)^2 \ln(1+i\mu + \rho) \\ & - (2y^3 - 18y^2 + 28y)(1+i\mu + 2\rho)^2 \ln(1+i\mu + 2\rho) \\ & + (\frac{4}{3}y^3 - 8y^2 + \frac{20}{3}y)(1+i\mu + 3\rho)^2 \ln(1+i\mu + 3\rho) \\ & - (y^3/3 - y^2 + \frac{2}{3}y)(1+i\mu + 4\rho)^2 \ln(1+i\mu + 4\rho) \\ & + 8(f^2\rho - fi\rho - 2f\rho + f - i - 2)i\mu \ln(i\mu) \\ & - 16(f^2\rho - fi\rho - f\rho + f - i - 1)(i\mu + \rho) \ln(i\mu + \rho) \\ & + 8(f^2 - fi\rho + f - i)(i\mu + 2\rho) \ln(i\mu + 2\rho)] \} \\ x = & 6f^2i - 6fi^2 + i^3 \quad y = f - i \quad \mu = 1/(f+1) \quad (26) \end{aligned}$$

F_C as a function of ρ and f describes regular comb polymers. Linear and star polymers can be considered as special cases of comb polymers in the limits of $\rho \rightarrow 0$ and $\rho \rightarrow \infty$ respectively. Indeed F_C tends to F_L for $\rho \rightarrow 0$ and to F_S for $\rho \rightarrow \infty$. Another check on the validity of equation (26) can be made for the case of $\rho = \frac{1}{2}$ and $f = 1$ where F_C of a comb with one branch does go to F_S of a star with $f = 3$. Equation (26) permits the study of F_C as a function of ρ and f . Using a small routine, the values of F_C have been found for a large range of ρ and for 11 representative f values and the results are plotted in Figures 2 and 3. For small ρ , less than 10^{-3} , the linear chain behaviour is obtained, while for ρ larger than 10^2 , the star behaviour is produced. For $f \leq 5$ a maximum in F_C appears (a minimum in A_{2c})²⁵ which moves to larger values of ρ as f increases. For $f > 5$ the maximum disappears and a smooth change from linear to star behaviour occurs which becomes sharper as the number f of branches increases.

CONCLUSIONS

The osmotic pressure second virial coefficients A_2 of homopolymers of various architectures have been studied in a perturbation theory scheme. A function F is found which characterizes each architecture and determines the value of A_2 . Analytic expressions of F for the architectures considered are given which allow the comparison of second virial coefficients of polymers of the same molecular weight but of different architectures. The second virial coefficients of linear chains have the largest values and then stars with number of branches $f = 3, 4$ follow. The second virial coefficients of ring polymers are close to those of stars with $f = 5$. Smaller values of A_2 follow for stars of larger values of f . The second virial coefficients of combs depend on the ratio $\rho = N_{br}/N_{bb}$ of the molecular weight of the branch to that of the backbone and change from those of linear chains to those of star chains as ρ increases. For number of branches $f \leq 5$ a maximum in F_C (minimum in A_{2c}) appears (Figure 2), moving to larger values of ρ for larger f . For $f > 5$, on increasing ρ a monotonic change from linear to star

behaviour takes place. This change becomes sharper as the number f of branches increases.

In the limit of large molecular weights ($M \rightarrow \infty$) the specific architecture is irrelevant and a closed form of A_2 as a function of the molecular weight M and the excluded-volume parameter u valid for all polymers is proposed. Larger values of F require larger molecular weights to reach independence from the architecture, which means that for larger values of F the characteristics of the architecture are more persistent.

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APPENDIX

Evaluation of characteristic diagrams for $d=4$ will be demonstrated. For the diagram



defined in equation (16), we make the substitution $j_1 - i_1 \rightarrow l_1$, $i_1 \rightarrow i_1$, $j_2 - i_2 \rightarrow l_2$, $i_2 \rightarrow i_2$ and after integrating over the i_1 and i_2 variables it becomes:

$$\text{Ring} = \int_0^N dl_1 \int_0^N dl_2 (N-l_1)(N-l_2)/(l_1+l_2)^2 \quad (A.1)$$

The l_2 integration is done first so that

$$\begin{aligned} \text{Ring} &= \int_0^N dl_1 [(N^2/l_1) - N - N \ln(N+l_1) + l_1 \ln(N+l_1) \\ &\quad + N \ln l_1 - l_1 \ln l_1] \\ &= [N^2 \ln l_1 - \frac{1}{2} N l_1 - N l_1 \ln(N+l_1) \\ &\quad - \frac{3}{2} N^2 \ln(N+l_1) + \frac{1}{2} l_1^2 \ln(N+l_1) + N l_1 \ln l_1 \\ &\quad - \frac{1}{2} l_1 \ln l_1]_{l_1=0}^{l_1=N} \end{aligned} \quad (A.2)$$

As we have explained in the paper the singularity of the term $N^2 \ln l_1$ in the limit $l_1 \rightarrow 0$ can be ignored and the value of the diagram, quoted in Table 1, is taken from (A.2).

A similar route is followed for the diagram



equation (17), of rings and the form

$$\text{Two Rings} = \frac{1}{N^2} \int_0^N dl_1 \int_0^N dl_2 \frac{(N-l_1)(N-l_2)}{[l_1(N-l_1) + l_2(N-l_2)]^2} \quad (A.3)$$

is obtained. The substitution $N-l_1 \rightarrow l_1$, $N-l_2 \rightarrow l_2$ does not change the demoninator so that

$$\text{Two Rings} = (1/N^2) \int_0^N dl_1 \int_0^N dl_2 l_1 l_2 / [-l_2^2 + N l_2 + l_1(N-l_1)]^2 \quad (A.4)$$

The l_2 integration is done first and we take

$$\begin{aligned} \text{Two Rings} &= (1/N^2) \int_0^N dl_1 \left[\frac{N^2}{(N-l_1)[N^2 + 4l_1(N-l_1)]} \right. \\ &\quad \left. + \frac{2Nl_1}{[N^2 + 4l_1(N-l_1)]^{3/2}} \right] \\ &\quad \times \ln \left(\frac{[N^2 + 4l_1(N-l_1)]^{1/2} + N}{[N^2 + 4l_1(N-l_1)]^{1/2} - N} \right) \end{aligned} \quad (A.5)$$

The first integral is straightforward while the second one is done by parts. The final result is

$$\begin{aligned} \text{Two Rings} &= \left[(1/2N^2) \ln l_1 + (1/4N^2)(2l_1 + N)[N^2 + 4N(N-l_1)]^{-1/2} \ln \left(\frac{[N^2 + 4N(N-l_1)]^{1/2} + N}{[N^2 + 4N(N-l_1)]^{1/2} - N} \right) \right]_{l_1=N}^{l_1=N} \end{aligned} \quad (A.6)$$

and its finite part is the value written in Table 1.

The diagram



equation (18), of stars, after the substitution $j_1 - i_1 \rightarrow l_1$

takes the form

$$\begin{aligned} \times \leftarrow &= \int_0^{N_{br}} dl_1 (N_{br} - l_1) \int_0^{N_{br}} di_2 \int_0^{N_{br}} dj_2 1/(l_1 + i_2 + j_2)^2 \\ &= \int_0^{N_{br}} dl_1 (N_{br} - l_1) [-\ln(2N_{br} + l_1) + 2\ln(N_{br} + l_1) - \ln(l_1)] \end{aligned} \quad (A.7)$$

The substitution $N_{br} - l_1 \rightarrow l_1$ simplifies the integrals which are straightforward and give

$$\begin{aligned} \times \leftarrow &= \frac{1}{2} [(9N_{br}^2 - l_1^2) \ln(3N_{br} - l_1) - 2(4N_{br}^2 - l_1^2) \ln(2N_{br} - l_1) \\ &+ (N_{br}^2 - l_1^2) \ln(N_{br} - l_1)]_{l_1=0}^{l_1=N_{br}} \end{aligned} \quad (A.8)$$

The value of



is written in Table 1.
The diagram



equation (18), of stars, after integrating over the variables i_2 and j_2 takes the form

$$\begin{aligned} \times \times &= \int_0^{N_{br}} di_1 \int_0^{N_{br}} dj_1 [-\ln(2N_{br} + i_1 + j_1) \\ &+ 2\ln(N_{br} + i_1 + j_1) - \ln(i_1 + j_1)] \\ &= \int_0^{N_{br}} di_1 [-(3N_{br} + i_1) \ln(3N_{br} + i_1) \\ &+ 3(2N_{br} + i_1) \ln(2N_{br} + i_1) \ln(2N_{br} + i_1) \\ &- 3(N_{br} + i_1) \ln(N_{br} + i_1) + i_1 \ln(i_1)] \end{aligned} \quad (A.9)$$

The final integration is straightforward and the expression

$$\begin{aligned} \times \times &= \frac{1}{4} [-2(3N_{br} + i_1)^2 \ln(3N_{br} + i_1) + 6(2N_{br} + i_1)^2 \\ &\times \ln(2N_{br} + i_1) - 6(N_{br} + i_1)^2 \ln(N_{br} + i_1) \\ &+ 2i_1^2 \ln(i_1)]_{i_1=0}^{i_1=N_{br}} \end{aligned} \quad (A.10)$$

is obtained, with the value quoted in Table 1.

The diagram



equation (19), of combs, has similar integrations and after their performance it becomes

$$\begin{aligned} \times \leftarrow &= \sum_{i=1}^f \{ [(N_{bb} + N_{br} + ia)^2 - l_1^2] \ln(N_{bb} + N_{br} + ia - l_1) \\ &- [(N_{bb} + N_{br})^2 - l_1^2] \ln(N_{bb} + N_{br} - l_1) \\ &- [(N_{bb} + ia)^2 - l_1^2] \ln(N_{bb} + ia - l_1) \\ &+ (N_{bb}^2 - l_1^2) \ln(N_{bb} - l_1) \}_{l_1=0}^{l_1=N_{bb}} \end{aligned} \quad (A.11)$$

which leads to the value in Table 1.

The final demonstration, concerns the diagram



equation (19), of combs. The double summation

$$\sum_{\substack{i=1 \\ i \neq j}}^f \sum_{\substack{j=1 \\ j \neq i}}^f$$

can be converted into a single one as $2 \sum_{i=1}^f (f-i)$ so that the expression of the diagram after the i_2 and j_2 integrations and the substitution $j_1 - i_1 \rightarrow N_{bc} - l_1$ becomes

$$\begin{aligned} \text{Diagram} &= 2 \sum_{i=1}^f (f-i) \int_0^{N_{bb}} dl_1 l_1 [-\ln(N_{bb} + 2N_{br} + ia - l_1) \\ &+ 2\ln(N_{bb} + N_{br} + ia - l_1) - \ln(N_{bb} + ia - l_1)] \\ &= \sum_{i=1}^f (f-i) \{ [(N_{bb} + 2N_{br} + ia)^2 - l_1^2] \ln(N_{bb} + 2N_{br} + ia - l_1) \\ &- 2[(N_{bb} + N_{br} + ia)^2 - l_1^2] \ln(N_{bb} + N_{br} + ia - l_1) \\ &+ [(N_{bb} + ia)^2 - l_1^2] \ln(N_{bb} + ia - l_1) \}_{l_1=0}^{l_1=N_{bb}} \end{aligned} \quad (A.12)$$

and the value in Table 1 is obtained.