Third Virial Coefficient for 4-Arm and 6-Arm Star Polymers

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Abstract

We discuss the computation of the third virial coefficient in polymer systems, focusing on an additional contribution absent in the case of monoatomic fluids. We determine the interpenetration ratio and several quantities that involve the third virial coefficient for star polymers with 4 and 6 arms in the good-solvent regime, in the limit of a large degree of polymerization.
1 Introduction

In the dilute regime the osmotic pressure of a polymer solution can be predicted successfully by using the virial expansion, which we write as

\[ Z \equiv \frac{M \Pi}{RT \rho} = \frac{\Pi}{k_B T c} = 1 + \sum_{n=1} B_{n+1} c^n, \tag{1} \]

where \( c \) is the polymer number density, \( \rho \) the weight concentration, \( M \) the molar mass of the polymer, \( T \) the absolute temperature, and \( k_B \) and \( R \) the Boltzmann and the ideal-gas constant, respectively. The virial coefficients \( B_n \) depend on the degree of polymerization \( N \) and on the chemical details. However, in the good-solvent regime renormalization-group arguments [1–3] indicate that, for \( N \to \infty \), the ratios

\[ A_{n+1} \equiv B_{n+1} \hat{R}_g^{-3n}, \tag{2} \]

where \( \hat{R}_g \) is the zero-density radius of gyration, approach universal constants \( A^*_n \) that are independent of chemical details and depend only on the polymer large-scale structure.

Much numerical and experimental work has been devoted to the calculation of the second virial coefficient \( B_2 \). Results for the higher-order coefficients are instead rare, both experimentally and numerically. In recent years some numerical computations of the third osmotic virial coefficient for solutions of polymers of different architecture have been reported. [4–11] However, in essentially all works an incorrect expression for the third virial coefficient was used. The correct expression, which is valid for any fluid of flexible molecules, was derived in ref. [9], and used to determine the universal ratio \( A^*_3 \) for linear polymers in the good-solvent regime. Let us report here the result. Let us consider a molecular fluid in which each molecule is formed by \( N \) units interacting by means of an intramolecular potential \( V_{\text{intra}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \), where \( \mathbf{r}_1, \ldots, \mathbf{r}_N \) are the unit positions. Molecules \( i \) and \( j \) interact by means of an intermolecular potential \( V_{\text{inter}} \) that depends on the positions \( \{ \mathbf{r}_a^{(i)} \} \) and \( \{ \mathbf{r}_a^{(j)} \} \). Given a quantity \( \mathcal{O} \) which depends on the coordinates of two molecules, we define a zero-density average \( \langle \cdot \rangle^0 \) as

\[ \langle \mathcal{O} \rangle^0_{\mathbf{r}_1^{(1)}, \mathbf{r}_2^{(2)}} \equiv \frac{1}{Q_2} \int d\mathbf{r}_2^{(1)} \ldots d\mathbf{r}_N^{(1)} d\mathbf{r}_2^{(2)} \ldots d\mathbf{r}_N^{(2)} \mathcal{O} \exp[-\beta V_{\text{intra}}(\{ \mathbf{r}_1^{(1)} \}) - \beta V_{\text{intra}}(\{ \mathbf{r}_2^{(2)} \})], \]

\[ Q_2 \equiv \int d\mathbf{r}_2^{(1)} \ldots d\mathbf{r}_N^{(1)} d\mathbf{r}_2^{(2)} \ldots d\mathbf{r}_N^{(2)} \exp[-\beta V_{\text{intra}}(\{ \mathbf{r}_1^{(1)} \}) - \beta V_{\text{intra}}(\{ \mathbf{r}_2^{(2)} \})]. \tag{3} \]

The meaning of this average is easily understood: we fix the position of the first unit of the two molecules to avoid irrelevant volume factors and average over all possible conformations, weighting each conformation with the intramolecular Hamiltonian only (which correspond to consider the zero-density limit). Analogously, given a quantity \( \mathcal{O} \) that depends on the coordinates of three molecules, we define an average \( \langle \mathcal{O} \rangle^0_{\mathbf{r}_1^{(1)}, \mathbf{r}_2^{(2)}, \mathbf{r}_3^{(3)}} \) as follows: it corresponds to averaging over all possible conformations of the three molecules keeping the first unit of the three molecules fixed in \( \mathbf{r}_1^{(1)}, \mathbf{r}_2^{(2)}, \mathbf{r}_3^{(3)} \). In terms of these quantities we define

\[ I_2 \equiv \int d^3\mathbf{r}_{12} \langle f_{12} \rangle^0_{0, \mathbf{r}_{12}}, \tag{4} \]
\[ I_3 \equiv \int d^3r_{12}d^3r_{13} \langle f_{12}f_{13}f_{23} \rangle_{0,r_{12},r_{13}}^0, \]  
\[ T_1 \equiv \int d^3r_{12}d^3r_{13} \langle f_{12}f_{13} \rangle_{0,r_{12},r_{13}}^0 - \left[ \int d^3r_{12} \langle f_{12} \rangle_{0,r_{12}}^0 \right]^2, \]

where \( f_{ij} = \exp(-\beta V_{\text{inter}}) - 1 \) is the Mayer function. The third virial coefficient is then given by:

\[ B_3 = \frac{1}{3} I_3 - T_1. \]

This expression contains two terms: the first one, proportional to \( I_3 \), corresponds to the usual term that gives the third virial coefficient in monoatomic fluids. In addition, there is a second term that is not present in monoatomic fluids and is related to the flexibility of the polymer molecule. This additional term was neglected in refs. [4–8, 10], and thus the corresponding estimates of the third virial coefficient are incorrect. Bruns, [4] starting from a general expression given in Yamakawa’s book, [12] derives the correct expression for \( B_3 \), but then he neglects \( T_1 \) in the numerical calculation, stating incorrectly that it can be shown that such term vanishes for hard-core systems. The derivation of \( B_3 \) given in ref. [9] does not give a physical interpretation to the additional term \( T_1 \). Here we present a different derivation that follows the approach of ref. [5]. It clarifies the physical meaning of \( T_1 \) and explains why this term is necessarily present and non-vanishing.

For linear polymers, even though \( T_1 \) does not vanish, its contribution is small. Indeed, the results of refs. [8, 9] provide the estimates

\[ A_3^* = 9.80 \pm 0.02, \]
\[ \hat{A}_3^* = \lim_{N \to \infty} \left( -\frac{1}{3} I_3 R_g^{-6} \right) = 10.60 \pm 0.04, \]
\[ \lim_{N \to \infty} T_1 R_g^{-6} = 0.80 \pm 0.05. \]

Thus, the contribution \( T_1 \) lowers the third virial coefficient only by 8%.

In this paper, we extend the calculations of ref. [9] to regular star polymers in which \( f \) branches of equal molecular weight are connected to a single branching unit. [13, 14] This type of polymers is particularly interesting. First, they have several technological applications. [13] Second, they show a quite different behavior depending on the number \( f \) of branches, interpolating between linear polymers and hard colloids. Here we shall focus on the cases \( f = 4 \) and \( f = 6 \) with the purpose of investigating the quantitative role of the additional term \( T_1 \) for a different polymer conformation. For both values of \( f \) we find that the additional contribution \( T_1 \) is small: our results show that, for large \( N \), \( T_1/B_3 \approx 0.065 \) and 0.05 for \( f = 4, 6 \), respectively. Note that the relative importance of \( T_1 \) decreases as \( f \) is increased, indicating that star polymers become increasingly more rigid as \( f \) goes to infinity.

The paper is organized as follows. In Section 2 we give a new derivation of the expression (7). In Section 3 we explain the model we use and the simulation method, while in Section 4 we present our results and compare them with the existing literature.
2 A New Derivation of the Third Virial Coefficient for Flexible Molecules

Equation (7) was obtained in ref. [9] by first performing an activity expansion in the grand-canonical ensemble. A different derivation is reported in ref. [4]. None of these two derivations gives any physical insight on the origin of the term $T_1$ and indeed Bruns [4] concluded incorrectly that $T_1 = 0$. Here we present a new derivation that clarifies that $T_1$ vanishes only if the molecules are rigid, i.e. if the probability of each conformation is density independent.

We consider the general case of molecules that have many different internal conformations, labelled by an index $\alpha$. Each conformation has a Boltzmann weight $p_\alpha$, $p_\alpha \propto \exp(-\beta V_{\text{intra}})$, normalized so that $\sum_\alpha p_\alpha = 1$. For convenience, we assume that the number of conformations is finite, as it occurs in lattice models, but the results are clearly valid also in the general case in which there is an infinite number of conformations (it is enough to replace sums by integrals). Particles interact by means of a pairwise potential $V(r,\alpha,\beta)$ that depends on the relative distance $r$ (we fix a reference point on each molecule) and on the internal conformations. As usual, we introduce the Mayer function

$$f_{ij}(r,\alpha_i,\alpha_j) \equiv \exp[-\beta V(r,\alpha_i,\alpha_j)] - 1.$$  \hfill (11)

Let us now assume that the number fraction $x_\alpha$ of each conformation $\alpha$ is fixed. Then, the fluid can be seen as a multicomponent mixture of simple molecules. In this case the virial expansion can be written as [15]

$$Z = 1 - \frac{c}{2} \sum_{\alpha,\beta} x_\alpha x_\beta I_{2,\alpha\beta} - \frac{c^2}{3} \sum_{\alpha,\beta,\gamma} x_\alpha x_\beta x_\gamma I_{3,\alpha\beta\gamma} + O(c^3),$$  \hfill (12)

where

$$I_{2,\alpha\beta} \equiv \int d^3r f_{12}(r,\alpha\beta),$$  \hfill (13)

$$I_{3,\alpha\beta\gamma} \equiv \int d^3r_{12}d^3r_{13} f_{12}(r_{12},\alpha\beta)f_{13}(r_{13},\alpha\gamma)f_{23}(|r_{12} - r_{13}|,\beta\gamma),$$  \hfill (14)

and $c$ is the number density. If the molecules are rigid the number fraction $x_\alpha$ is density independent and equal to the zero-density probability $p_\alpha$. Thus, if we define

$$I_2 = \sum_{\alpha,\beta} p_\alpha p_\beta I_{2,\alpha\beta} \quad I_3 = \sum_{\alpha,\beta,\gamma} p_\alpha p_\beta p_\gamma I_{3,\alpha\beta\gamma},$$  \hfill (15)

we obtain

$$Z = 1 - \frac{c}{2} I_2 - \frac{c^2}{3} I_3 + O(c^3),$$  \hfill (16)

which is the usual virial expansion, with $T_1 = 0$. On the other hand, for flexible molecules $x_\alpha$ is density dependent (if $x_\alpha$ were density-independent, single-molecule properties, for instance the radius of gyration, would not depend on density, which is clearly unphysical). To derive the $c$ dependence of $x_\alpha$ we proceed as in ref. [16], Section II. We consider a quantity $R^{(\alpha)}$ that
assumes the value 1 if the conformation one is considering is the $\alpha$ one, and zero otherwise. Explicitly, given a configuration $\beta$, the value $R^{(\alpha)}_\beta$ of $R^{(\alpha)}$ on this configuration is

$$R^{(\alpha)}_\beta = \delta_{\alpha \beta} = \begin{cases} 1 & \text{if } \beta = \alpha \\ 0 & \text{if } \beta \neq \alpha \end{cases}.$$  \hfill (17)

By definition

$$x_\alpha = \langle R^{(\alpha)} \rangle.$$ \hfill (18)

In order to compute the virial expansion of the right-hand side, we consider $L$ molecules in a volume $V$ and write

$$x_\alpha = \frac{\sum_{\beta_1, \ldots, \beta_L} \int d\mathbf{r}_1 \cdots d\mathbf{r}_L R^{(\alpha)}_{\beta_1} p_{\beta_1} \cdots p_{\beta_L} \prod_{i<j}[1 + f_{ij}(|\mathbf{r}_i - \mathbf{r}_j|; \beta_i, \beta_j)]}{\sum_{\beta_1, \ldots, \beta_L} \int d\mathbf{r}_1 \cdots d\mathbf{r}_L p_{\beta_1} \cdots p_{\beta_L} \prod_{i<j}[1 + f_{ij}(|\mathbf{r}_i - \mathbf{r}_j|; \beta_i, \beta_j)]}. \hfill (19)$$

Expanding the numerator we obtain

$$V^L \sum_{\beta_1} R^{(\alpha)}_{\beta_1} p_{\beta_1} + (L - 1)V^{L-1} \sum_{\beta_1, \beta_2} R^{(\alpha)}_{\beta_1} p_{\beta_1} p_{\beta_2} I_{2, \beta_1 \beta_2} + \left(\begin{array}{c} L - 1 \\ 2 \end{array}\right) V^{L-1} \sum_{\beta_1, \beta_2, \beta_3} R^{(\alpha)}_{\beta_1} p_{\beta_1} p_{\beta_2} p_{\beta_3} I_{2, \beta_1 \beta_2 \beta_3} + \ldots$$

$$= V^L p_\alpha + (L - 1)V^{L-1} p_\alpha \sum_{\beta} p_\beta I_{2, \alpha \beta} + \left(\begin{array}{c} L - 1 \\ 2 \end{array}\right) V^{L-1} p_\alpha I_2 + \ldots \hfill (20)$$

Analogously, for the denominator we obtain

$$V^L + \left(\begin{array}{c} L \\ 2 \end{array}\right) V^{L-1} I_2 + \ldots \hfill (21)$$

Then, in the thermodynamic limit, $L, V \to \infty$ at fixed $c \equiv L/V$, we obtain

$$x_\alpha = p_\alpha + c p_\alpha \sum_{\beta} p_\beta I_{2, \alpha \beta} - c p_\alpha I_2 + O(c^2). \hfill (22)$$

In order to check the correctness of this result we have verified that the condition $\sum x_\alpha = 1$ is satisfied by our expression. If we now substitute this result for $x_\alpha$ into Equation (12), we obtain for $B_3$

$$B_3 = -\frac{1}{3} I_3^2 - \sum_{\alpha \beta \gamma} p_\alpha p_\beta p_\gamma I_{2, \alpha \beta} I_{2, \alpha \gamma} + I_2^2. \hfill (23)$$

It is easy to recognize that

$$T_1 = \sum_{\alpha \beta \gamma} \int d^3 \mathbf{r}_{12} d^3 \mathbf{r}_{13} p_\alpha p_\beta p_\gamma f_{12}(r_{12}, \alpha \beta) f_{13}(r_{13}, \alpha \gamma) - I_2^2,$$

$$= \sum_{\alpha \beta \gamma} p_\alpha p_\beta p_\gamma I_{2, \alpha \beta} I_{2, \alpha \gamma} - I_2^2, \hfill (24)$$
so that we reobtain (7). Note that $T_1$ can also be written as

$$T_1 = \frac{1}{2} \sum_{\alpha \beta} p_\alpha p_\beta \left( \sum_\gamma p_\gamma I_{2,\alpha \gamma} - \sum_\gamma p_\gamma I_{2,\beta \gamma} \right)^2. \quad (25)$$

This relation shows that $T_1 \geq 0$ and that $T_1$ vanishes only if

$$\sum_\gamma p_\gamma I_{2,\alpha \gamma} = \sum_\gamma p_\gamma I_{2,\beta \gamma} \quad (26)$$

for any pair $\alpha$ and $\beta$. Therefore, $T_1 = 0$ only if $\sum_\gamma p_\gamma I_{2,\alpha \gamma}$ is independent of $\alpha$. If this condition is satisfied, we have $\sum_\gamma p_\gamma I_{2,\alpha \gamma} = I_2$, so that the density correction that appears in Equation (22) vanishes. Therefore, $T_1$ vanishes only if $x_\alpha$ does not depend on $c$, that is if the molecules are rigid.

### 3 Model and Simulation Details

We are interested in determining universal properties in the good-solvent regime, in the limit in which the degree of polymerization $N$ goes to infinity. We can thus use any model that captures the basic polymer properties. For computational convenience we consider the well-known self-avoiding walk (SAW) model on a cubic lattice. A star polymer with $f$ branches is represented by $f$ SAWs starting at a common point. A regular star is given by the center $r_0$ and by $f$ branches $r_{i,j}$, $i = 1, \ldots, f$, $j = 1, \ldots, N_f$, such that $|r_0 - r_{i,1}| = 1$, $|r_{i,j} - r_{i,j+1}| = 1$, and all lattice sites are visited at most once. The total number of monomers is $N = fN_f + 1$.

This model is well defined up to $f = 6$. For larger values of $f$, one should use a larger core or a model with soft interactions as in ref. [17].

We simulate the model by using different types of moves:

(i) We consider pivot moves [18–20] applied to a single arm (analogous moves were used on the tetrahedral lattice in ref. [21]). These moves have been shown to be very efficient in simulations of linear polymers. [20] In star-polymer simulations they are not equally efficient since they are rarely accepted when the pivot is close to the center of the star.

(ii) We consider cut-and-permute moves [22] applied to a single arm (see Figure 1). They have been shown to be quite effective in simulations of polymers grafted to impenetrable surfaces and speed up the conformational changes close to the center of the star.

(iii) We use local moves that involve moving one or two monomers of the walk.

For $f \leq 5$ one can generalize the arguments given in ref. [20] to show that this algorithm is ergodic. No such proof is available for $f = 6$, though we expect that the combination of local and non-local moves makes the algorithm ergodic in this case, too.

The virial coefficients are determined by using the hit-or-miss algorithm discussed in refs. [9, 23].
4 Results and Discussion

We perform simulations of star polymers for \( f = 4 \) and \( f = 6 \) with \( 50 \leq N_f \leq 2000 \) and \( 50 \leq N_f \leq 1000 \) in the two cases, respectively. Since \( N = f N_f + 1 \), the total number of monomers is quite large; this should allow us to probe the universal large-\( N \) regime. Results for the constants \( A_2, A_3 \), and for \( \hat{A}_3 \equiv -\frac{1}{3} I_3 \hat{R}_g^{-6} \) are reported in Table 1. In all cases the additional term \( T_1 \) gives a small negative contribution. Quantitatively we find \( T_1/B_3 \approx 0.065, 0.05 \) for \( f = 4, 6 \). This is consistent with the idea that star polymers are less and less flexible as \( f \) increases, so that we expect \( T_1/B_3 \to 0 \) as \( f \to \infty \).

The data reported in Table 1 show a systematic dependence on \( N_f \), see Figure 2, and thus a proper extrapolation is needed in order to obtain the large-\( N \) constants \( A^*_2 \) and \( A^*_3 \). We use the same procedure illustrated in ref. [8], fitting the data to

\[
A(N_f) = A^* + a N_f^{-\Delta} + b N_f^{-\Delta_2},
\]

where \( \Delta \) is a universal exponent whose best estimate is [24] \( \Delta = 0.515 \pm 0.017 \) (other results are reported in ref. [25]). The exponent \( \Delta_2 \) is an effective one that takes into account several correction-to-scaling terms: as in ref. [8], we take \( \Delta_2 = 1.0 \pm 0.1 \). Of course, the previous expression is only the leading part of an expansion in inverse (non-integer) powers of \( N_f \). To monitor the role of the neglected terms, we have repeated the fit several times, each time including only the data satisfying \( N_f \geq N_{f,\text{min}} \). Stable results for \( A^*_2 \) are obtained by using all data, while good fits of \( A^*_3 \) require \( N_{f,\text{min}} = 100 \). The corresponding results are:

\[
A^*_2 = \begin{cases} 
9.979 \pm 0.009 & f = 4, \\
14.174 \pm 0.016 & f = 6;
\end{cases}
\]

Figure 1: The cut-and-permute move applied to a star polymer with \( N_f = 8 \) and \( f = 3 \). One first chooses an arm and a pivot point \( P \). The new arm is obtained by connecting the subwalk \( PE \) to the center \( C \) and then the subwalk \( CP \) to the translated point \( E \).
Table 1: Estimates of $A_2$, $A_3$, and of $\hat{A}_3 \equiv -\frac{1}{3}I_3 \hat{R}^{-6}$.

| $N_f$ | $A_2$  | $\hat{A}_3$ | $A_3$  | $A_2$  | $\hat{A}_3$ | $A_3$  |
|-------|--------|-------------|--------|--------|-------------|--------|
| 50    | 10.899(2) | 52.48(4)  | 49.75(3) | 15.280(2) | 113.43(6) | 108.79(6) |
| 100   | 10.620(2) | 49.16(4)  | 46.40(3) | 14.953(2) | 107.55(6) | 102.95(7)  |
| 150   | 10.497(2) | 47.64(4)  | 44.98(5) | 14.809(2) | 105.10(6) | 100.33(6)  |
| 250   | 10.379(2) | 46.33(4)  | 43.57(3) | 14.666(3) | 102.60(6) | 97.78(6)   |
| 500   | 10.257(2) | 44.98(4)  | 42.24(4) | 14.515(3) | 99.99(6)  | 95.45(6)   |
| 1000  | 10.173(2) | 44.13(4)  | 41.48(5) | 14.416(3) | 98.38(8)  | 93.72(8)   |
| 2000  | 10.115(2) | 43.47(4)  | 40.82(4) | 14.325(3) | 97.38(8)  | 92.72(8)   |

Figure 2: Third virial invariant ratio $A_3$ for $f = 4$ and $f = 6$ versus $N^{-\Delta}$, $\Delta = 0.515$. We also report the extrapolation function $A_3^* + aN_f^{-\Delta}$, $\Delta = 0.515$, determined in the fit.
\[ A_3^* = \begin{cases} 39.56 \pm 0.16 & f = 4, \\ 90.1 \pm 0.4 & f = 6. \end{cases} \] (29)

The errors we quote include the statistical uncertainty and the systematic error due to the uncertainty on \( \Delta \) and \( \Delta_2 \). To compare with the literature it is useful to define the interpenetration ratio \( \Psi \equiv 2(4\pi)^{-3/2}A_2 \) and \( g \equiv B_3/B_2^2 = A_3/A_2^2 \). We obtain

\[ \Psi^* = \begin{cases} 0.4480 \pm 0.0004 & f = 4, \\ 0.6364 \pm 0.0007 & f = 6; \end{cases} \] (30)

\[ g^* = \begin{cases} 0.397 \pm 0.002 & f = 4, \\ 0.449 \pm 0.002 & f = 6. \end{cases} \] (31)

For comparison we quote \( \Psi^* \) and \( g^* \) for \( f = 1 \): [9]

\[ \Psi^* = 0.24693 \pm 0.00013, \] (32)

\[ g^* = 0.3240 \pm 0.0007. \] (33)

Other estimates of \( \Psi^* \) and \( g^* \) for \( f = 1 \) are quoted in refs. [9, 25, 26].

There are no numerical results for \( g^* \). Our estimates increase with \( f \) as expected, but, for \( f = 6 \), \( g^* \) is still far from the hard-sphere value \( 5/8 = 0.625 \), which should be valid for \( f \to \infty \) (a discussion of the behavior of \( g^* \) for large values of \( f \) is reported in ref. [27]). Our results for \( \Psi^* \) are in reasonable agreement with the numerical ones reported in the literature. For \( f = 4 \), refs. [28–30] quote \( \Psi^* = 0.46, 0.467, 0.453 \pm 0.007 \), while for \( f = 6 \) they quote \( \Psi^* = 0.64, 0.665, 0.63 \pm 0.01 \). The results of ref. [29] are those that differ more significantly. Note, however, that in this work much smaller values of \( N_f \) are used: moreover, no proper extrapolation is performed. Field theory results differ instead quite significantly, predicting \( \Psi^* = 0.517, 0.798 \) for \( f = 4, 6 \), respectively. [31] Recent experimental results for star polystyrene in benzene are reported in refs. [32, 33]. They quote \( 0.43 \lesssim \Psi \lesssim 0.46 \) for \( f = 4 \) and \( \Psi \approx 0.60 \) for \( f = 6 \), in reasonable agreement with our results. They also estimate the factor \( g \). The results show a strong dependence on the molecular weight: the two samples with highest molecular weight \( M_w \) give \( g \approx 0.40, g \approx 0.43 \) for \( f = 4 \) and \( g \approx 0.39, g \approx 0.50 \) for \( f = 6 \), with \( g \) increasing with \( M_w \). These results are close to our estimates, even though the experimental results apparently prefer somewhat larger values.

Note that similar discrepancies are observed for linear polymers, see the experimental results cited in refs. [32–34] and references therein. Older results for \( \Psi^* \) are cited in ref. [35]. The experimental estimates of the interpenetration ratio for star polystyrene in toluene show a significant dependence on the molecular weight \( M_w \): for the largest values of \( M_w \) experiments give \( \Psi \approx 0.46, 0.55 \) for \( f = 4 \) and \( \Psi \approx 0.65 \) for \( f = 6 \). These results are reasonably close to our estimates. The experimental values of \( \Psi \) for polybutadiene in cyclohexane quoted in ref. [35], \( 0.42 \lesssim \Psi \lesssim 0.47 \), are also consistent.

In conclusion, we have shown that \( T_1 \) is small but not negligible: if \( T_1 \) is neglected the error is of 6.5% and 5% for \( f = 4, 6 \), respectively. Moreover, our results allow us to compute the osmotic pressure in the dilute regime with good precision (we expect the error to be of order of a few percent below the overlap concentration, see ref. [9]). We find:

\[ Z = \begin{cases} 1 + X + 0.397X^2 + \ldots & f = 4, \\ 1 + X + 0.449X^2 + \ldots & f = 6, \end{cases} \] (34)

where \( X \equiv B_2c \).
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