

Remarks on smoothed-density theories for flexible chains with three-segment interactions

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(Received 9 April 1992; revised 6 May 1992)

The Orofino–Flory (OF) type smoothed-density theories for the end-distance expansion factor α_R and the second virial coefficient A_2 of flexible chains with three-segment interactions are inconsistent with first-order perturbation calculations unless the ternary cluster integral β_3 is zero. It is shown in the present paper that the inconsistency arises from the factorization approximation to segment density distribution functions invoked in the smoothed-density model and that a proper treatment of such functions leads to expressions consistent with the perturbation calculations but different from the OF type equations. Thus, for non-zero β_3 and near the Θ point the previous smoothed-density or mean-field theories retain no valid place, even though those for A_2 account for a few experimental findings (at or below the Θ temperature) that two-parameter theories fail to explain. In particular, the prediction of a coil–globule transition by the OF type equations has no theoretical significance. It is also shown by a perturbation calculation that when both binary and ternary cluster integrals are vanishingly small, α_R for an infinitely long chain is expressed in terms of a single excluded-volume variable up to second order in β_3 with the same numerical coefficients as those in the two-parameter theory.

(Keywords: excluded-volume effect; expansion factor; second virial coefficient; smoothed-density theory; three-segment interaction; coil–globule transition)

INTRODUCTION

Recent experiments^{1–4} have shown that the ternary cluster integral β_3 for the interaction among three segments in flexible chains generally remains positive at the Θ point where the second virial coefficient A_2 vanishes. This suggests the breakdown of the binary cluster approximation to polymer properties in dilute solution near Θ . In fact, two important experimental findings are available which can hardly be explained in the framework of two-parameter theory. One is the molecular weight independent behaviour of A_2 below Θ ^{5–7}, and the other, positive A_2 values for very low molecular weight samples at the Θ temperature at which A_2 for high molecular weight samples vanishes^{8–10}. These findings were qualitatively explained^{8,11} by the Orofino–Flory (OF) smoothed-density theory¹² with non-zero β_3 or essentially the same theory of Tanaka¹¹.

However, the explanation does not seem conclusive, since, as pointed out by Yamakawa¹³, the OF theory is inconsistent with a seemingly more correct first-order perturbation calculation¹³ unless β_3 happens to be zero. The inconsistency is serious in that the two types of theory give different interpretations³ of Θ . Yamakawa¹³ also found a similar inconsistency to exist in the end-distance expansion factor. Thus, the present study was undertaken to find the origin of these inconsistencies, confining itself to infinitely long chains.

SECOND VIRIAL COEFFICIENT

We consider two identical, long flexible chains of molecular weight M each of which is Gaussian in the unperturbed state. Given an average intermolecular potential V_{12} as a function of the distance S_{12} between the centres of mass of the two chains, A_2 may be expressed by:

$$A_2 = \frac{N_A}{2M^2} \int \{1 - \exp[-V_{12}(S_{12})/k_B T]\} dS_{12} \quad (1)$$

where N_A is the Avogadro constant, k_B the Boltzmann constant and T the absolute temperature. Taking two- and three-segment interactions into account, we may express V_{12} in the smoothed-density model as¹⁴:

$$V_{12}(S_{12})/k_B T = \beta_2 \sum_{i_1}^n \sum_{i_2}^n \int P_{i_1}(s) P_{i_2}(s - S_{12}) ds \\ + 2\beta_3 \sum_{i_1 < j_1}^n \sum_{i_2}^n \int P_{i_1 j_1}(s, s) P_{i_2}(s - S_{12}) ds \quad (2)$$

Here, $P_{i_1}(s)$ [or $P_{i_2}(s)$] denotes the distribution function for the distance vector s of segment i_1 in chain 1 (or segment i_2 in chain 2) from the centre of mass, and $P_{i_1 j_1}(s, s)$, the bivariate distribution function associated with a pair of segments i_1 and j_1 belonging to chain 1; β_2 and n denote, respectively, the binary cluster integral and the number of segments in each chain.

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We consider no intramolecular excluded-volume effect. Then, the distribution functions $P_{0i_1}(s)$ and $P_{0i_1j_1}(s, s)$ in the unperturbed state are obtained by the standard method¹⁴ as:

$$P_{0i_1}(s) = (3/2\pi\langle S_{i_1}^2 \rangle_0)^{3/2} \exp(-3s^2/2\langle S_{i_1}^2 \rangle_0) \quad (3)$$

$$P_{0i_1j_1}(s, s) = [3/2\pi b^2(j_1 - i_1)]^{3/2} (3/2\pi\langle D_{i_1j_1}^2 \rangle_0)^{3/2} \times \exp(-3s^2/2\langle D_{i_1j_1}^2 \rangle_0) \quad (\text{for } j_1 > i_1) \quad (4)$$

where

$$\langle S_{i_1}^2 \rangle_0 = \frac{nb^2}{3} \left(1 - \frac{3i_1}{n} + \frac{3i_1^2}{n^2} \right) \quad (5)$$

$$\langle D_{i_1j_1}^2 \rangle_0 = \frac{nb^2}{3} \left[1 - \frac{3j_1}{n} + \frac{3j_1^2}{n^2} - \frac{3(j_1^2 - i_1^2)(j_1 + i_1)}{4n^3} \right] \quad (6)$$

and b is the segment length. The segment density distribution function $\sum_{i_1} P_{0i_1}(s)$ may be replaced in a good approximation¹⁴ by:

$$\sum_{i_1} P_{0i_1}(s) = n(3/2\pi\langle S^2 \rangle_0)^{3/2} \exp(-3s^2/2\langle S^2 \rangle_0) \quad (7)$$

with $\langle S^2 \rangle_0$ being the mean-square radius of gyration of the unperturbed chain considered, i.e. $\langle S^2 \rangle_0 = nb^2/6$. To evaluate $\sum_{i_1 < j_1} P_{0i_1j_1}(s, s)$ we introduce a cut-off parameter σ so that $i_1 \leq j_1 - \sigma$. Thus, σ represents the minimum number of consecutive segments needed for the formation of a loop in one chain; it should be much smaller than n . With this parameter, $\sum P_{0i_1j_1}(s, s)$ for very large n may be evaluated first by integration over i_1 by part and then by use of the above Gaussian approximation to $\sum_{j_1} P_{0j_1}(s)$ [i.e. equation (7) with the sum replaced by an integral]. The result thus obtained reads:

$$\sum_{i_1 < j_1} P_{0i_1j_1}(s, s) = \frac{2n^{5/2}}{6^{3/2}\sigma^{1/2}} \left(\frac{3}{2\pi\langle S^2 \rangle_0} \right)^3 \exp\left(-\frac{3s^2}{2\langle S^2 \rangle_0}\right) \quad (n^{1/2} \gg \sigma^{1/2} > 1) \quad (8)$$

Substitution of equations (7) and (8), together with a similar expression for $P_{0i_2}(s - S_{12})$, into equation (2), followed by integration, yields:

$$V_{12}(S_{12})/k_B T = 3^{3/2} \left[z_2 + 4 \left(\frac{n}{\sigma} \right)^{1/2} z_3 \right] \exp(-3S_{12}^2/4\langle S^2 \rangle_0) \quad (9)$$

where

$$z_2 = (3/2\pi b^2)^{3/2} \beta_2 n^{1/2} \quad (10)$$

$$z_3 = (3/2\pi b^2)^3 \beta_3 \quad (11)$$

The integral in equation (1) with equation (9) is approximately evaluated by the OF procedure¹² to give:

$$A_2 = \frac{16\pi N_A \langle S^2 \rangle_0^{3/2}}{3^{3/2} M^2} \ln \left\{ 1 + \frac{3^{3/2} \pi^{1/2}}{4} \left[z_2 + 4 \left(\frac{n}{\sigma} \right)^{1/2} z_3 \right] \right\} \quad (12)$$

for positive or small negative A_2 . If the intramolecular excluded-volume effect is introduced by invoking the uniform expansion approximation, $\langle S^2 \rangle_0^{3/2}$, z_2 and z_3 in this expression are replaced by $\langle S^2 \rangle_0^{3/2} \alpha^3$, z_2/α^3 and z_3/α^6 , respectively, with α being an expansion factor.

When $z_2 + 4(n/\sigma)^{1/2} z_3$ is much smaller than unity, equation (12) gives:

$$A_2 = \frac{N_A n^2}{2M^2} \left[\beta_2 + \frac{4}{\sigma^{1/2}} \left(\frac{3}{2\pi b^2} \right)^{3/2} \beta_3 + \dots \right] \quad (13)$$

which agrees with the first-order perturbation calculation¹³ for infinite n ; note that σ is set equal to unity in reference 13. The first-order calculation for finite n shows that an additional term $-8(3/2\pi b^2)^{3/2} \beta_3/n^{1/2}$ exists in the square brackets of equation (13)^{3,15}. The expression including this term can be derived from equation (1) with equations (2)–(6) (or even by use of the Gaussian approximation for $\sum P_{0i_1}$). Either equation (12) or (13) indicates that Θ_∞ (Θ for infinite n) is the temperature at which $\beta_2 + 4\sigma^{-1/2}(3/2\pi b^2)^{3/2} \beta_3 = 0$.

If $P_{0i_1j_1}(s, s)$ is approximated by $P_{0i_1}(s)P_{0j_1}(s)$ and if equation (7) is used, V_{12} is obtained as:

$$V_{12}(S_{12})/k_B T = 3^{3/2} [z_2 \exp(-3S_{12}^2/4\langle S^2 \rangle_0) + 8z_3 \exp(-S_{12}^2/\langle S^2 \rangle_0)]$$

This is the OF potential and leads to the OF expression¹² (without intramolecular excluded volume):

$$A_2 = \frac{16\pi N_A \langle S^2 \rangle_0^{3/2}}{3^{3/2} M^2} \ln \left[1 + \frac{3^{3/2} \pi^{1/2}}{4} (z_2 + 3^{3/2} z_3) \right] \quad (\text{OF}) \quad (14a)$$

Note that the parameters X_1 and X_2 in equation (17) of reference 12 are equal to $3^{3/2} z_2$ and $8 \times 3^{3/2} z_3$, respectively¹³. In the vicinity of Θ , equation (14a) gives:

$$A_2 = \frac{N_A n^2}{2M^2} \left[\beta_2 + 3^{3/2} \left(\frac{3}{2\pi b^2} \right)^{3/2} \frac{\beta_3}{n^{1/2}} + \dots \right] \quad (14b)$$

which indicates that the condition for Θ_∞ is given by $\beta_2 = 0$.

The OF equation (14a) differs from equation (12) in the ternary cluster term. Apparently, this discrepancy results from the above replacement of $P_{0i_1j_1}(s, s)$ by $P_{0i_1}(s)P_{0j_1}(s)$. Thus, we find that the inconsistency of the OF theory with the first-order perturbation calculation arises from this factorization approximation, i.e. ignoring the effect of chain connectivity on the probability of segment collision in one of the two interacting chains. From this, two points may be made. First, the explanation^{8,11} of the behaviour^{5–10} of experimental A_2 at and below Θ , mentioned in the Introduction, has little theoretical significance. Second, the vanishing of β_2 cannot be regarded as the Θ condition for long chains unless β_3 happens to be zero.

END-DISTANCE EXPANSION FACTOR

As mentioned in the Introduction, the smoothed-density¹² and perturbation¹³ theories of the expansion factor α_R for the mean-square end-to-end distance $\langle R^2 \rangle$ are also inconsistent. The former leads to:

$$\alpha_R^2 = 1 + d_1 z_2 + d_2 z_3 + \dots \quad (\text{smoothed-density}) \quad (15)$$

with d_1 and d_2 being positive constants, while the latter is shown to give for large n :

$$\alpha_R^2 = 1 + \frac{4}{3} \left[z_2 + 4 \left(\frac{n}{\sigma} \right)^{1/2} z_3 \right] + \dots \quad (\text{perturbation}) \quad (16)$$

Thus, apart from the numerical constants, the two expressions differ again in the ternary cluster term.

The end-to-end distance of a smoothed-density chain may be calculated from:

$$\langle R^2 \rangle = \int R^2 P_0(\mathbf{R}) e^{-V(\mathbf{R})/k_B T} d\mathbf{R} / \int P_0(\mathbf{R}) e^{-V(\mathbf{R})/k_B T} d\mathbf{R} \quad (17)$$

using the unperturbed distribution function $P_0(\mathbf{R})$ for the end-to-end vector \mathbf{R} and the intramolecular potential $V(\mathbf{R})$ given, respectively, by:

$$P_0(\mathbf{R}) = (3/2\pi n b^2)^{3/2} \exp(-3R^2/2nb^2) \quad (18)$$

$$V(\mathbf{R})/k_B T = \beta_2 \sum_{i < j} \int P_{ij}(s, s|\mathbf{R}) ds + \beta_3 \sum_{i < j < k} \int P_{ijk}(s, s, s|\mathbf{R}) ds \quad (19)$$

In equation (19), $P_{ij}(s, s|\mathbf{R})$ denotes the conditional probability density of finding segments i and j in the volume element ds under the condition that the end-to-end vector of the chain is fixed to \mathbf{R} ; $P_{ijk}(s, s, s|\mathbf{R})$ is self-explanatory. We evaluated these functions first in the unperturbed state (see reference 14 for the procedure) and then transformed them to those in the perturbed state using the uniform expansion approximation. The result thus obtained for $V(\mathbf{R})$ is written as:

$$\begin{aligned} \frac{V(\mathbf{R})}{k_B T} = & \frac{z_2}{\alpha_R^3} \sum_{i < j} \frac{n}{[(j-i)(n-j+i)]^{3/2}} \\ & \times \exp \left[-\frac{3(j-i)R^2}{2nb^2 \alpha_R^2 (n-j+i)} \right] \\ & + \frac{z_3}{\alpha_R^6} \sum_{i < j < k} \frac{n^{3/2}}{[(k-j)(j-i)(n-k+i)]^{3/2}} \\ & \times \exp \left[-\frac{3(k-i)R^2}{2nb^2 \alpha_R^2 (n-k+i)} \right] \quad (20) \end{aligned}$$

Using the Hermans–Overbeek approximation¹⁶ after substitution of equations (18) and (20) into equation (17), we get:

$$\alpha_R^5 - \alpha_R^3 = \left(\frac{2\pi}{3} \right)^{1/2} \left[z_2 + 4 \left(\frac{n}{\sigma} \right)^{1/2} \frac{z_3}{\alpha_R^3} \right] \quad (21)$$

This equation is consistent with the first-order perturbation calculation [equation (16)]; the slight difference between the numerical constants $(2\pi/3)^{1/2}$ [in equation (21)] and $4/3$ [in equation (16)] is due to the Hermans–Overbeek approximation. Equation (21) differs in the z_3 term from the OF type equation¹²:

$$\alpha_R^5 - \alpha_R^3 = d_1 z_2 + d_2 \frac{z_3}{\alpha_R^3} \quad (\text{OF type}) \quad (22)$$

The latter can be derived when $P_{ij}(s, s|\mathbf{R})$ and $P_{ijk}(s, s, s|\mathbf{R})$ in equation (19) are approximated by $P_i(s|\mathbf{R})P_j(s|\mathbf{R})$ and $P_i(s|\mathbf{R})P_j(s|\mathbf{R})P_k(s|\mathbf{R})$, respectively. Thus, as is the case with A_2 , the factorization approximation is responsible for the discrepancy between the z_3 terms of the OF and perturbation equations.

DISCUSSION

We have shown that chain connectivity plays a crucial role in the ternary cluster terms of A_2 and α_R^2 . As may be seen from the present calculation and also from perturbation calculations by others^{13,15,17}, a pair of

segments at a short contour distance in one chain contributes primarily to these terms. Since a chain portion consisting of a small number of segments, say t , may not fully be perturbed, the uniform expansion approximation invoked in deriving equation (21) is likely to be invalid for the ternary cluster term of α_R at least near Θ . If t segments are unperturbed and if $n^{1/2} \gg t^{1/2} \gg \sigma^{1/2}$, it can be shown that z_3 replaces z_3/α_R^3 in equation (21). This suggests that α_R near Θ should read:

$$\alpha_R^5 - \alpha_R^3 = \frac{4}{3} Z \quad (23)$$

where

$$Z = z_2 + 4 \left(\frac{n}{\sigma} \right)^{1/2} z_3 \quad (24)$$

In equation (23) we have replaced the numerical coefficient $(2\pi/3)^{1/2}$ by $4/3$. In the vicinity of $\alpha_R = 1$, this equation gives $\alpha_R^2 = 1 + (4/3)Z - (8/3)Z^2 + \dots$, whereas equation (21) leads to $\alpha_R^2 = 1 + (4/3)Z - (8/3)Z^2 - (32/3)(n/\sigma)^{1/2} z_3 Z + \dots$ if the coefficient $(2\pi/3)^{1/2}$ is again replaced with $4/3$. Hence, the difference between these equations appears in the second and higher orders of z_3 in the expansion.

To confirm the relevance of equation (23) near Θ , we have made a second-order perturbation calculation of α_R^2 (to order in β_2^2 , $\beta_2\beta_3$, and β_3^2) for an infinitely long chain assuming that both β_2 and β_3 are vanishingly small. The calculation is laborious but elementary (see reference 14), and only the result is presented here. It reads:

$$\alpha_R^2 = 1 + \frac{4}{3} Z - \left(\frac{16}{3} - \frac{28}{27} \pi \right) Z^2 + \dots \quad (25)$$

This expression is in line with the Z expansion of equation (23), leading to the conclusion that the uniform expansion approximation is invalid near Θ . This should also be the case for A_2 .

Importantly, equations (23) and (25) are formally identical, respectively, to the modified Flory equation and the z_2 expansion of α_R^2 , both in the binary cluster approximation¹⁴. If, as is often assumed in the vicinity of Θ , β_2 varies linearly with $1/T$ while β_3 is independent of T , the relation $Z = \text{constant} \times M^{1/2}(1 - \Theta/T)$ holds in a fixed solvent at temperatures close to Θ . As T is removed from Θ , however, this relation should become inadequate and z_3 in equation (24) may be expected to approach z_3/α_R^3 eventually. Equation (21) corresponding to the fully perturbed state indicates that the ternary cluster term is insignificant for large α_R^3 .

The OF type equation (22) for α_R (or more correctly for the radius expansion factor) predicts a coil–globule transition to occur in a single chain far below Θ , provided that $d_2 z_3$ is larger than a certain positive value^{18,19}. However, this prediction is incorrect, since the theory ignores the effect of chain connectivity on segment density distribution. For $\alpha_R \ll 1$, our equation (21) gives $\alpha_R^3 = \text{constant}$. This result is odd and incompatible with the prevailing notion^{20,21} that a long flexible chain should collapse to a globule far below Θ . Probably, we should take into account segment interactions higher than the ternary one to discuss the dimensions of a collapsed coil. Sanchez's theory²² incorporates such interactions but neglects chain connectivity.

In conclusion, the factorization approximation to segment density distribution functions associated with three-segment interactions is responsible for the inconsistency of the OF smoothed-density theories¹² for A_2 and α_R with the first-order perturbation calculations¹³. Thus,

analyses based on the OF theories or similar mean-field theories have little significance unless β_3 is zero. After the completion of the present study, reference was made to work by Yamakawa^{2,3}, who explained the positive A_2 of short chains at Θ_∞ as being due to effects of chain ends.

ACKNOWLEDGEMENT

We are very grateful to Professor W. H. Stockmayer for valuable comments on this manuscript.

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