# On the Three-Segment Interactions in Polymer Solutions near the Θ Point

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Long flexible polymer chains in a good solvent are self-avoiding. When the temperature is lowered, the excluded-volume becomes small. At the Θ temperature, the chains are no longer self-avoiding and have a nearly Gaussian behavior. However, it must be realized that the Θ point is defined as an overall compensation point for the second virial coefficient. As a consequence, the polymer chains have strong effective interactions with either positive or negative signs near the Θ point.

Relevant to the physics of polymer solutions near the Θ temperature is a model of the continuous chain with local two-body and three-body interactions. It is described by the model Hamiltonian[1] (in appropriate units)

$$H = \frac{1}{2}\int ds \left(\frac{d\mathbf{r}}{ds}\right)^2 + \frac{b}{2}\int ds \int ds'\, \delta(\mathbf{r}(s) - \mathbf{r}(s')) + \frac{c}{6}\int ds \int ds' \int ds''\, \delta(\mathbf{r}(s)-\mathbf{r}(s'))\, \delta(\mathbf{r}(s')-\mathbf{r}(s'')) \quad (1)$$

where $\mathbf{r}(s)$ represents a configuration of the chain at the contour position $s$ ($0 \le s \le S$, $S$ being the polymerization degree). Coefficients $b$ and $c$ are the two- and three-body interaction parameters, respectively. One may have an arbitrary sign for $b$, while $c$ is positive for stability. (In this paper we restrict our treatment to flexible chains with large molecular weight and neglect the effect of chain ends.[2]) Dimensional analysis readily shows that we have two dimensionless interaction parameters. They are defined by

$$z = (2\pi)^{-3/2} b S^{1/2}, \quad y = (2\pi)^{-3} c \quad (2)$$

Very recently Norisuye and Nakamura[3,4] performed perturbation calculations of the second and third virial coefficients ($A_2$ and $A_3$) and the expansion factor of the end-to-end distance for long flexible chains. When the chains are submitted to three-body interactions, combination of the three-body interactions generates cutoff ($s_0$) dependent (divergent as $s_0 \to 0$) two-body interactions. It is a well-known fact in the renormalization theory that such short-range divergences can be absorbed by a renormalization of the two-body interaction.[1] In fact, the above authors introduced the effective binary cluster integral by measuring $z$ with respect to its value at the Θ point of an infinite chain, an operation which is equivalent to a renormalization (more precisely regularization) of $z$[5]. They found that properties of the long chain other than $A_3$ were expressed solely by the renormalized two-body interaction parameter. They thereupon claimed that the three-body interaction was immaterial for those properties.

We show here that their affirmation above is incorrect. Paraphrased in the context of the renormalization method, their argument runs as follows. The *renormalized* perturbation result for $A_3$ reads

$$A_3 = y(1 + z + y + z^2 + zy + y^2) + z^3 + \ldots \quad (3)$$

where the ellipsis represents fourth and higher order contributions, and we have not written down numerical coefficients explicitly, which are not needed for the present purpose. (The contribution of second order in $z$ is made of only reducible parts with respect to interactions and hence drops out from the final result.) The variable $z$ in eq 3 is the renormalized one to regularize the ultraviolet divergence. It can be identified with the value measured with respect to the Θ point of an infinite chain[5] and is identical to Norisuye's[3] $Z$. At this juncture it is erroneously argued in refs 3 and 4 that, since $z/y \sim S^{1/2}$, terms involving $y^2$, $zy^2$, and $y^3$ were negligible in eq 3 in the long chain limit. In other words, it is assumed $y \ll z^2$. However, we remark first that, in the renormalization of infrared divergence (the long chain limit) for a polymer chain near the Θ point, $z$ must be considered as a constant and it is necessary to perform the renormalization with $c$ and $bS^{1/2}$ fixed constant.[6] This fact shows the limits of the procedure taken in refs 3 and 4. Moreover, the Θ region (tricritical domain) is defined by the so-called tricritical condition[7] $y \gg z^2$ (note we may still take $y \sim |z| \ll 1$ so that the perturbation theory, eq 3, may be valid). Hence, we see the perturbation theory in refs 3 and 4 is not valid for temperatures near the Θ point, contrary to the claim of the authors. After all, $z$ (with the shifted $b$) is small in the Θ domain and the physics of long chains is dominated by the large parameter $y \ln(S/s_0)$, the contributions of which have to be resummed[8] (see the next but one paragraph).

Their calculation of $A_2$ presents the same difficulty. They obtained for $\mathcal{A}_2 \equiv M^{1/2} A_2$, to second order in $z$ and $y$,

$$\mathcal{A}_2 = z(1 - C_1 z) \quad (4)$$

with $C_1 = (32/15)(7 - 2^{5/2})$ and $M$ being the molecular weight of the polymer chain. Here in eq 4 we have used, for simplicity, the unit with which the proportionality constant between the left-hand and right-hand sides is unity. The above is to be compared with the renormalized first-order perturbation result[1,5]

$$\mathcal{A}_2 = z - 8y \quad (5)$$

Furthermore, the result (4) implies that, when plots of $M^{1/2} A_2$ against $z$ are made for the data with different molecular-weight samples, all the data should collapse upon a single curve. This is in sharp contrast to the observed behavior (see Figure 5 of ref 2).

One must note that the space dimension $d = 3$ is the upper critical dimensionality for tricriticality.[8] It is well-known in the theory of tricritical points that at the upper critical dimension the mean-field theory acquires logarithmic corrections. A brief summary of this fact is in order here. When $S \to \infty$ (and for $d = 3$), there appear large logarithmic (in $S$) terms in the expansion of physical quantities (say, vertex functions) in powers of $y$. These so-called tricritical divergences come from the three-body interactions and differ from the usual critical divergences (coming from the excluded-volume interaction, which are thus associated with the parameter $z$). Thus the physics of long chains is dominated by the large parameter $y \ln(S/s_0)$, the contributions of which have to be resummed if one tries to go beyond the first-order approximation near the Θ-point. Such

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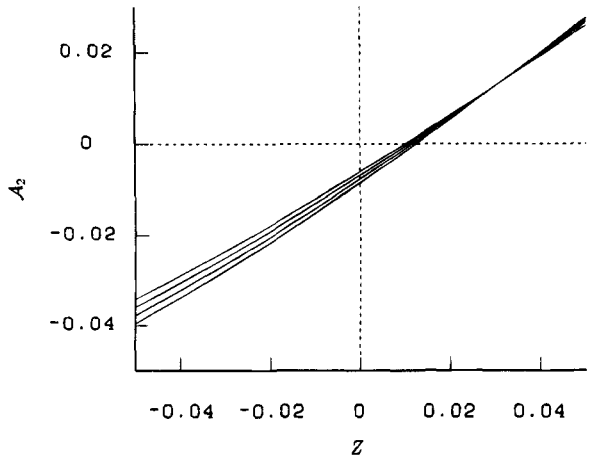


**Figure 1.** Variation of $\mathcal{A}_2$ against $z$ for polystyrene (PS) in cyclohexane. We have used the following values of $s_0$ and $y$ which have been estimated by Duplantier et al.:[9] $s_0 = 0.173$ (nm$^2$), $y = 0.0029$. The curves represent, in order of decreasing depth at $z = -0.005$, the values of $S/s_0 = M/m = 1.21 \times 10^4$, $4.06 \times 10^3$, $1.64 \times 10^3$, $7.88 \times 10^2$; $M$ and $m$ are molecular weights of PS and its monomer.

resummation [of all orders in $y \ln(S/s_0)$] renormalizes $y$ into

$$h \equiv \frac{y}{1 + 44\pi y \ln(S/s_0)} = \frac{1}{44\pi \ln(S/s_0)} \qquad (6)$$

where the last equality follows in the tricritical limit $y \ln(S/s_0) \gg 1$. Similarly, $z$ itself is renormalized by resummation into $z(h/y)^{4/11}$.

Such tricritical renormalization calculation[6b,8] replaces the result (5) by

$$\mathcal{A}_2 = \left[z\left(\frac{h}{y}\right)^{4/11} - 8h\right]\left[1 - \frac{148\pi}{33}h + \frac{4}{3}z\left(\frac{h}{y}\right)^{4/11}\right]^{3/2} \qquad (7)$$

demonstrating the distinctive role played by the three-body interaction ($y$). Figure 1 illustrates the result (7) for $|z| \leq 0.05$, which is the estimated range of validity of the tricritical theory (7). Although our concern in this paper is not the interpretation of a specific experimental result, it is worth noting that the variation of $\mathcal{A}_2$ as a function of $z$ against various molecular weights is consistent with the experimental finding referred to above. However, we remark that the result (7) predicts $\mathcal{A}_2$ is negative at $z = 0$, which does not conform to the experiment where it is found that $\mathcal{A}_2$ of short chains is positive at the $\Theta$ temperature.

In this connection, it is also of interest to see that the same tricritical theory has provided a good quantitative explanation for the observed deswelling of a chain near the $\Theta$ temperature[9] and the measured $M$-dependence of $\Theta$ temperature[10] as well. In particular, the latter measurement unambiguously demonstrates the observability of the three-segment interaction. Thus it is expected that the renormalization method, which has been so successful in elucidating the solution properties of polymers in a good solvent, may resolve the serious problems[11] that the current theory of $\Theta$ region faces.

## References and Notes

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