

# The $\theta$ -behaviour of heterogeneous macromolecules

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A polymer chain consisting of  $N_r$  segments with a repulsive interaction (binary cluster integral  $\beta_r$ ) and  $N_a \ll N_r$  segments with a stronger, attractive and pairwise saturable interaction ( $\beta_a$ ), which is at the averaged  $\theta$ -point  $N_r^2\beta_r + N_a^2\beta_a = 0$  deviations from the predictions of the two parameter theory:  $\alpha_{R/S}^2 - 1 \sim -\Delta z_r < 0$  and  $A_2 \sim \Delta z_r > 0$  with  $\Delta z_r \sim \beta_r(N_a/N_r)^{1/2}$ . It is shown that the deviations from the universal behaviour are due to the existence of an intermediate length scale  $\sim N_a/N_r$ .

(Keywords:  $\theta$  behaviour; saturable attractive interaction; expansion factor; second virial coefficient; deviation from universality)

## INTRODUCTION

The 'two-parameter concept' (see ref. 1) can be characterized in the vicinity of the  $\theta$ -point by the following expressions for the expansion factors of the mean square end-to-end distance and the radius of gyration and for the second virial coefficient of the osmotic pressure

$$\alpha_{R/S}^2 - 1 \sim z \quad (1a)$$

$$A_2 \sim \beta h(z); \quad h(z) \rightarrow 1 \quad (1b)$$

$$z \sim \beta \rightarrow 0 \quad (1c)$$

This is the common basis for the interpretation of equilibrium properties of dilute polymer solutions. Within the 'two-parameter concept' the effects of intra- and intermolecular interaction between macromolecular segments are controlled by the excluded volume parameter  $z = (3/2\pi)^{3/2} \beta N^2 / \langle R^2 \rangle_0^{3/2}$ . This is the ratio between the strength of the interaction  $\beta N^2$  and the volume of the unperturbed coil  $\langle R^2 \rangle_0^{3/2} = N^{3/2} l^3$ . The usual symbols  $\beta$ ,  $l$  and  $N$  are used for the binary cluster integral, the statistical segment length and the number of statistical segments respectively. Experimental results for a number of polymers (see ref. 1) and the universality principle<sup>2</sup> or the scaling concepts<sup>3,4</sup> emerging from the relationship between physics of critical phenomena and polymer physics confirm equations (1a) and (1b), which were first of all derived by several approximate theories<sup>1</sup>. From equations (1a) and (1b) it follows that at the  $\theta$ -point ( $\beta = z = 0$ ) the molecular dimensions have their unperturbed values and  $A_2$  disappears. This picture may be slightly perturbed by the influence of the three segment interaction<sup>5</sup>, but at least for linear polymers in three dimensions the three segment interaction may be absorbed in an effective two segment interaction and equations (1a) and (1b) remain valid in the vicinity of  $T = \theta$ . Thus the two parameter theory for long flexible macromolecules appears to be supported theoretically by introducing a renormalized pairwise segment-segment interaction

parameter, with its zero at the experimentally observable  $\theta$ -point<sup>7</sup>.

However, the experimental results for a number of polymer-solvent systems are not in agreement with the predictions of the 'two-parameter concept'<sup>8</sup>. Typical common features of such systems which often tend to associations of macromolecules too, may be characterized by equations (2a) and (2b)

$$\alpha_{R/S}^2 \sim N^{2\nu-1} \text{ with } 1/3 \lesssim \nu \lesssim 1/2 \text{ which implies } \alpha_{R/S}^2 \lesssim 1 \quad (2a)$$

$$A_2 \gtrsim 0 \quad (2b)$$

in a certain temperature interval ('theta-region'). It may be concluded from equation (2a) that the resulting interaction between segments is attractive, while  $A_2 \gtrsim 0$  points to a repulsive intermolecular interaction. Equations (2a) and (2b) are in qualitative disagreement with the results of the 'two-parameter concept' (1a) and (1b). Thus we have to expect qualitatively different properties for polymer-solvent systems obeying equations (1) or (2). We have learned from the scaling approach that the universal behaviour (equation (1)) is caused by the existence of long ranged correlations which are large in comparison with any molecular scales. Consequently, it may be expected that weak deviations from the universal behaviour are caused by the existence of an intermediate length scale which is large in comparison with the molecular level (the statistical segment length) but much smaller than the chain length. Examples of such polymer systems may be expected being random copolymers with very different comonomer content and with different interactions between the comonomers. The interaction between segments may depend on the configuration or the conformation of the segments of homopolymers, too. Examples of such interactions are chain defects, stereocomplexes, configuration-dependent dipole moments for polar macromolecules or 'microcrystallites' formed by bundlelike short regular sequences of conformations (e.g. all-trans) of

different chains or different parts of one chain. We investigated a chain model where most of the segments show a weak repulsive interaction, while a few segments possess a stronger, attractive and pairwise saturable interaction. The intermediate length scale is then the average distance between the 'attractive' segments. Similar models are considered (in refs. 5, 9 and 10) within the framework of the Lifshitz-theory. In ref. 9 the coil-globule transition is investigated for saturable attractive interaction, whereas in refs. 5a and 10 the shift of the  $\theta$ -temperature caused by three segment interactions is considered. In these works the case of infinite dilution is only investigated and effects resulting from an intermediate length scale cannot be taken into account, since in the mean-field Lifshitz-approach all properties are controlled by an averaged interaction energy.

### DESCRIPTION OF THE MODEL

We will investigate a freely jointed chain of Gaussian statistical segments with the following properties:

1. The chain consists of  $N_r \simeq N$  segments with a weak repulsive interaction (binary cluster integral  $\beta_r$ ) with all segments and of  $N_a \ll N$  segments which show a pairwise saturable, attractive interaction (binary cluster integral  $\beta_a$ ). Both types of segments have the same statistical segment length  $l$ .
2. All sequences of segments for given numbers  $N_r$  and  $N_a$  are of equal probability.
3. Very long chains are considered here. The conditions  $N_r/N_a \gg 1$  and  $N_a \gg 1$  are fulfilled simultaneously.
4. The influence of three segment interactions will be absorbed into renormalized binary cluster integrals (compare equations (5), (6) and (7)).

### THEORY

#### Expansion factor

An attractive interaction causes an enhanced contact probability of the corresponding segments. If the attractive, saturable interaction of a small number of segments  $N_a \ll N$  is strong enough that the contact probability of all of these segments is comparable with one, then a coil-globule transition may occur<sup>9</sup>. In the  $\theta$ -region  $\alpha_{S/R}^2 \simeq 1$  the effects of attractive and repulsive interactions nearly compensate each other. Then only the contact probability of 'attractive' segments neighbouring along the chain is significantly enhanced. This contact probability is given by

$$P(O_{i,j_a}) = \beta_a p'(O_{i,j_a}) \leq \beta_a p_0(O_{i,j_a}) \leq \beta_a / (3/2\pi l^2 |j_a - i_a|)^{3/2} \quad (3)$$

$p'$  denotes the probability density for the distance between the segments  $i_a$  and  $j_a$ , where the interaction between the segments  $i_a$  and  $j_a$  must not be taken into account. The attractive interaction of the segments under consideration in equation (3) is contained in  $\beta_a$ . As a consequence  $p'$  is determined mainly by the interaction of the 'repulsive' segments between segments  $i_a$  and  $j_a$  and the ones on the adjacent parts of the chain. In our investigation of the  $\theta$ -region,  $p'$  will be approximated by the random walk distribution  $p_0$ . The explicit expression shows a fast

decrease of the contact probability for increasing chain length between the 'attractive' segments  $i_a$  and  $j_a$  (compare to equation (3)).

The distribution function  $p(R)$  of the chain end-to-end distance is given by

$$p(R) = Z^{-1} \int d^3\{r\} \delta(R - (r_N - r_1)) p_0(\{r\}) \times \prod_{i_r < j_r} (1 + f_{i,j_r}) \prod_{k_a < l_a} (1 + f_{k,l_a}) \quad (4)$$

$p_0(\{r\})$  is the random walk distribution of the Gaussian segments.  $f_{i,j_r}$  and  $f_{k,l_a}$  are the Mayer's  $f$ -functions of the repulsive and the attractive interaction, respectively.  $Z$  is the normalizing partition function. On account of the enhancement of the contact probability for adjacent 'attractive' segments it seems reasonable to take into consideration explicitly the loops formed by contacts of these segments. Splitting up the product of the  $f_{k,l_a}$  and regarding the contribution of single loops only ( $(P(O_{k,k+l_a}))^2 \ll P(O_{k,k+l_a})$ ) yields

$$\prod_{k_a < l_a} (1 + f_{k,l_a}) = \prod_{k_a} (1 + f_{k,k+l_a}) \prod_{k_a, l_a > k+l_a} (1 + f_{k,l_a}) \simeq (1 + \sum_{k_a} f_{k,k+l_a}) \prod_{k_a, l_a > k+l_a} (1 + f_{k,l_a}) \quad (5)$$

and

$$p(R) = (p_{nl}(R) + \beta_a \sum_{k_a} p'(O_{k,k+l_a}) p(R|O_{k,k+l_a})) / (1 + \beta_a \sum_{k_a} p'(O_{k,k+l_a})) \quad (6)$$

for the distribution function of the end-to-end distance for a chain with a given sequence of 'attractive' and 'repulsive' segments.  $p_{nl}(R)$  and  $p(R|O_{k,k+l_a})$  are the distribution functions of the end-to-end distance for the chain under consideration without contacts of adjacent 'attractive' segments and with contact of the  $k$ -th and the  $k+1$ -th 'attractive segment' respectively. In equation (6) we have to sum up over all contacts of neighbouring 'attractive' segments. According to our model we have to investigate an ensemble of chains with randomly distributed attractive segments. The ensemble average of the distribution function (6) is approximated by

$$\langle p(R) \rangle = (1 - P_0) p_{nl}(R) + P_0 p(R|O_{\Delta k_a}) \quad (7)$$

with

$$P_0 = N_a P(O_{\Delta k_a}) / (1 + N_a P(O_{\Delta k_a}))$$

and

$$\Delta k_a = N/N_a \simeq N_r/N_a \ll N$$

The approximation may be justified by the following considerations

1. All quantities in equation (6) depend in the case of short loops only on the length of the loop and are independent on the position of the loop within the chain.
2. We work in the  $\theta$ -region and are interested mainly in the sign of  $\alpha_R^2 - 1$  and  $A_2$ . Interaction effects may be considered in this case in linear order and the in-

roduction of averaged values into equation (6) yields equation (7).

Using the method of hierarchy equations for the distribution functions  $p_{nl}(R)$  and  $p(R|O_{\Delta k_a})$  (see ref. 1) we obtain

$$p_{nl}(R) = Z_1^{-1} p_0^{(N)}(R) \exp(-V^{(N)}(R)/kT) \quad (8)$$

$$p(R|O_{\Delta k_a}) = Z_2^{-1} p_0^{(N-\Delta k_a)}(R) \exp(-V(R|O_{\Delta k_a})/kT) \quad (9)$$

with the ensemble averaged potentials of mean forces

$$V^{(N)}(R)/kT \approx (\beta_r + \beta_a(N_a/N_r)^2) \sum_{k < 1} p(O_{kl}|R) \quad (10)$$

$$V(R|O_{\Delta k_a})/kT = V^{(N-\Delta k_a)}(R)/kT + V_{lr,\Delta k_a}(R)/kT \quad (11)$$

$$V_{lr,\Delta k_a}(R)/kT \approx \beta_r \sum_{\substack{k \in \text{loop} \\ l \in \text{tails}}} p(O_{kl}|R)$$

The upper index in equations (8)–(11) is introduced for convenience and denotes the number of segments of linear chains figuring in the expressions for the needed distribution functions.

In equations (10) and (11) we have now to sum up the contributions of all segment pairs with exclusion of the neighbouring ‘attractive’ segments. Concentrating our interest on the vicinity of the  $\theta$ -region we may replace the conditional distribution functions on the right hand side of equations (10) and (11) by the unperturbed functions  $p_0$ . Then it is useful to perform all further investigations at the ‘averaged two parameter  $\theta$ -point’  $T = \langle \theta \rangle$  where the  $R$ -dependent part of  $V(R) \sim -(N_r^2 \beta_r + N_a^2 \beta_a)|R|$  vanishes. Then the  $R$ -dependent part of  $V^{(N-\Delta k_a)}(R)$  originating from the segments in the tails outside the loop vanishes as well, and it remains as the pure repulsive contribution  $V_{lr,\Delta k_a}(R)$  of the interaction of the segments in the loop with the segments in the tails.  $V_{lr,\Delta k_a}(R)$  may be approximated<sup>11</sup> for  $\Delta k_a \ll N$  by

$$V_{lr,\Delta k_a}(R)/kT = -1.2z_r(\Delta k_a/N)X \quad (12)$$

with  $z_r = (3/2\pi l^2)^{3/2} \beta_r N_r^{1/2}$  and  $X = (R^2/Nl^2)^{1/2}$ . From equations (7)–(12) it follows for the ensemble averaged mean square end-to-end distance

$$\langle \langle R^2 \rangle \rangle = (1 - P_0) \langle R^2 \rangle_0 + R_0 \langle R^2 \rangle_0 \alpha^2(\Delta k_a) \quad (13)$$

$\alpha^2(\Delta k_a)$  contains the contraction due to the loop formation and the expansion caused by the repulsive potential  $V_{lr,\Delta k_a}$ . Using the Heermans–Overbeck procedure we obtained an estimate for  $\alpha^2(\Delta k_a)$

$$\alpha^2(\Delta k_a) \approx 1 - \frac{1}{3} \frac{\partial}{\partial X} V(X) \Big|_{X=1} \approx 1 - \frac{\Delta k_a}{N} (1 - 0.4z_r) \quad (14)$$

and finally

$$\alpha_R^2 = \langle \langle R^2 \rangle \rangle / \langle R^2 \rangle_0 = 1 - P_0 \frac{\Delta k_a}{N} (1 - 0.4z_r) \quad (15)$$

Due to the restriction to  $T = \langle \theta \rangle$  the attractive and the repulsive interactions are related by the definition of  $\langle \theta \rangle$ . Thus  $\alpha_R^2$  may be expressed by  $\beta_r$  alone

$$\alpha_R^2 = 1 - \frac{\Delta z_r (1 - 0.4z_r)}{1 + N_a^{1/2} z_r}; \quad \Delta z_r = (3/2\pi l^2)^{3/2} \beta_r \Delta k_a^{1/2} \quad (16)$$

Equation (16) shows that for  $z_r \gtrsim 1$  the heterogeneity of the intramolecular interaction leads to a contraction of the coil at  $T = \langle \theta \rangle$ . We get a deviation from a simple extrapolation of the results of the two-parameter concept which is controlled, as mentioned already above, by an additional length scale above the molecular level  $l$ ,  $\Delta z_r$  turns out to be the measure of the influence of this heterogeneity on the molecular dimensions.

### Second virial coefficient

We start from the MacMillan–Mayer theory

$$A_2 = -N_A/2VM^2 \int d^3(\{r\}_1) d^3(\{r\}_2) P(\{r\}_1) P(\{r\}_2) [\exp(-W(\{r\}_1, \{r\}_2)/kT) - 1] \quad (17)$$

Expansion of the intermolecular interaction term  $\exp(-W(\{r\}_1, \{r\}_2)/kT)$  to first order into Mayer’s  $f$ -functions and introduction of equation (5) for the contribution of the attractive intramolecular interaction into  $p(\{r\}_1)$  and  $p(\{r\}_2)$ , respectively, gives

$$A_2 = N_A/2M^2 \left[ \sum_{i_1, j_2} \beta_r + \sum_{k_1, k_2} \beta_a (1 - P(O_{k_1, k+1, i_1}) - P(O_{k_1, k-1, i_1})) (1 - P(O_{k_2, k+1, j_2}) - P(O_{k_2, k-1, j_2})) \right] \quad (18)$$

We get a weighted sum over all possible contributions of the intermolecular interaction. The weights  $(1 - P(O_{k, k \pm 1}))$  are the result of the assumed saturability of the attractive interaction in our model. Ensemble averaging gives then at  $T = \langle \theta \rangle$

$$\langle A_2 \rangle = N_A/2m^2 \cdot N_a^2/N^2 (-\beta_a) \cdot 4P(O_{\Delta k_a}) = N_A/2m^2 \cdot 4\beta_r \cdot \Delta z_r \quad (19)$$

$\langle A_2 \rangle$  is greater than zero at  $T = \langle \theta \rangle$  because a part of the intermolecular attractive interaction may be realized by breaking up the intramolecular interactions only. Consequently, the repulsive intermolecular interactions are only partially compensated by the interactions of the ‘attractive’ segments.

### CONCLUSIONS

A simple model for heterogeneous macromolecules was investigated. It was assumed that among segments with a weak repulsive interaction (the solvent was a moderately good one for these segments). A few segments with a stronger attractive, saturable interaction are rarely mixed.

Approximate expressions for the expansion factor and the second virial coefficient are derived. The main results  $\alpha_R^2 \lesssim 1$  and  $A_2 > 0$  at  $T = \langle \theta \rangle$  are independent on the used approximations. The deviations from the results of the ‘two-parameter concept’ are controlled by  $\Delta z_r$ , the measure of strength and extension along the chain of the heterogeneity of the segment–segment interaction. The deviation from the ‘two-parameter-theory’ and with it from the universality principle is in agreement with the

physical foundation of this principle itself. For non-zero heterogeneity  $\Delta z_r > 0$  an intermediate length scale between the molecular (the segment length  $l$ ) and the macromolecular scale (e.g.  $\langle R^2 \rangle$ ) exists. Hence the universality principle based on the existence of one characteristic length only may not be valid. On the other hand we have to expect a behaviour according to the 'two-parameter-theory' if a heterogeneous interaction is averaged out over distances along the chain which are comparable with the statistical segment length. Examples are alternating copolymers or random copolymers with a comonomer ratio nearly one. The general results are in agreement with the scaling results in ref. 12, where for copolymers more complicated scaling relations for  $\langle R^2 \rangle$  are deduced than in the case of homopolymers.

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