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A General Formalism of Deriving the Pair Potential of Polymer Chains for Arbitrary Interaction Potentials Between Isolated Chain Segments at and Close to the Theta-Point**

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A formalism has been worked out which allows to transform any non-punctiform segment-segment potential of isolated polymer segments ε of fairly short-ranged character into the pair-potential U operating between linear polymer chains with a certain reference to the arguments as they have been originally put forward by *Flory* and *Krigbaum*. Although no restrictions are made in the derivation as to the repulsive or attractive contribution of the segment-segment potential ε because of some known general deficiencies of the *Flory-Krigbaum* treatment for exclusively repulsive interaction, the resulting equations are primarily intended to describe the thermodynamic situation at and close to the θ-point where repulsion and attraction—though working at different ranges of segment separation—cancel. As the equation derived is somewhat complicated two different approximate forms have been developed: The first one is based on a *Taylor* series expansion retaining terms up to the fourth order which allows to characterize U by the second and the fourth moment of the pair segment-segment distribution function, β and γ (β being the so-called binary cluster integral of segment-segment interaction, which is considered to be zero for θ-conditions). In this case U may be represented by an expression of the general form

$$U/kT = A(1 - BR^2)\exp\{-bR^2\}.$$

The second method is based on a separate integration over the repulsive and attractive ranges of ε giving the repulsive (U_+) and the attractive (U_-) part of U finally after some approximations leading to an equation of the general form

$$U/kT = (U_+ + U_-)/kT = A_1\exp\{-b_1R^2\} - A_2\exp\{-b_2R^2\}.$$

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In both cases the knowledge of the exact form of ε is dispensable, only β and γ—or for the second case their repulsive (β_+ and γ_+) and attractive (β_- and γ_-) parts have to be known. It is shown that the approximations are in excellent accordance with the exact form so that they may be conveniently used to describe pair potentials of polymer chains and to analyze pair potentials of segment-segment interactions under the limitations and conditions indicated.

(Keywords: Polymer pair distribution function; Polymer pair potential; Thermodynamics and statistical mechanics of polymer solutions; Theta-systems)

Ein allgemeiner Formalismus zur Ableitung des Paarpotentials zwischen Polymerketten aus beliebigen Wechselwirkungspotentialen zwischen isolierten Segmenten am und nahe dem Theta-Punkt

In gewisser Anlehnung an Vorstellung von *Flory* und *Krigbaum* wurde ein Formalismus entwickelt, der es erlaubt, beliebige nichtpunkförmige zwischen den isolierten Segmenten von Polymerketten wirkenden Wechselwirkungspotentiale ε von einigermaßen beschränkter Reichweite in das zwischen Polymerketten herrschende Paarpotential U zu überführen. Obwohl dabei hinsichtlich des abstoßenden und anziehenden Beitrags zu ε keinerlei besondere Annahmen eingehen, ist die resultierende Gleichung in erster Linie zur Beschreibung der am θ-Punkt bzw. in dessen Nähe vorliegenden Situation gedacht; der Grund dafür ist in gewissen bekannten Mängeln des *Flory-Krigbaum*-Konzepts bei der Beschreibung einer rein repulsiven Wechselwirkung zu suchen. Wegen der relativ komplizierten Form der ermittelten Gleichung für U wurden zur Erleichterung der praktischen Handhabung zwei Näherungsformen konzipiert: Die erste beruht auf einer *Taylor*-Entwicklung unter Berücksichtigung der Terme bis zur vierten Ordnung, die eine Beschreibung von U durch das zweite und das vierte Moment der Segment-Segment-Paarverteilungsfunktion, β und γ erlaubt (β ist dabei das sogenannte binäre Clusterintegral der Segment-Segment-Wechselwirkung, das unter θ-Bedingungen den Wert Null annimmt). In diesem Fall läßt sich U durch einen Ausdruck der allgemeinen Form

$$U/kT = A(1 - BR^2)\exp\{-bR^2\}$$

darstellen. Die zweite Methode geht von einer getrennten Integration über die abstoßenden und anziehenden Bereiche von ε aus und liefert nach einigen Näherungen den abstoßenden (U_+) und den anziehenden (U_-) Teil von U. Dabei entsteht eine Gleichung der allgemeinen Form

$$U/kT = (U_+ + U_-)/kT = A_1\exp\{-b_1R^2\} - A_2\exp\{-b_2R^2\}.$$

In beiden Fällen bedarf es keiner genauen Kenntnis von ε; lediglich β und γ, bzw. im zweiten Fall deren abstoßende (β_+, γ_+) und anziehende (β_-, γ_-) Anteile müßten bekannt sein. Es läßt sich numerisch zeigen, daß die beiden Näherungsgleichungen nur geringfügig von der exakten Gleichung abweichen, so daß sie unter den genannten Bedingungen in bequemer Weise sowohl zur Beschreibung der Paarpotentiale von Polymerketten als auch zur Analyse von Segment-Segment Wechselwirkungspotentialen herangezogen werden können.

Introduction

For quite a long time apparently the best available way to describe the separation dependent interaction between two linear macromolecules has been the *Flory-Krigbaum* potential[1, 2] U_{FK}

$$\frac{U_{FK}(R)}{kT} = n^2 \left(\frac{V_{\text{seg}}}{V_{\text{solv}}}\right) V_{\text{seg}} \left(\frac{3}{4\pi s^2}\right)^{3/2} (1 - 2\chi) \exp\left[-\frac{3R^2}{4s^2}\right] \tag{1}$$

Here n is the number of segments of each polymer molecule, s^2 its mean square radius of gyration, V_{seg} and V_{solv} the volumes of a chain segment and a solvent molecule, respectively, R the separation between the centers of gravity of the two polymer molecules, and χ the *Flory-Huggins* interaction parameter. Eq. 1 also is often written with $(1 - \theta/T)$ instead of $(1 - 2\chi)$ where θ is the so-called *Flory* θ-temperature. In other representations[3] $V_{\text{seg}}(1 - 2\chi)$ is substituted by a quantity β (the so-called binary cluster integral of segment-segment interaction) which may be considered to be the volume excluded by one isolated chain segment to any other one.

If, for sake of simplicity, the factor $V_{\text{seg}}/V_{\text{solv}}$ which in real systems has to cater for an eventual difference in size between solvent molecules and polymer segments, is assumed to be unity, putting $3/4s^2 = b$, eq. 1 takes the form

$$U_{FK}(R)/kT = n^2 \beta \left(\frac{b}{\pi}\right)^{3/2} \exp[-bR^2] \tag{1a}$$

Eq. 1 implies that for θ-conditions ($\chi = 1/2$, $\beta = 0$, or $T = \theta$) U should be zero for all intermolecular separations R. Numerical calculations, however, carried out with four way[4] and five way[5] cubic lattice *Monte Carlo* chains have revealed that this is clearly not the case, U actually being positive (repulsive) for small separations and negative (attractive) for longer ones, before asymptotically rising to zero for very large values of R. In an attempt to provide a tentative explanation for this behaviour it could be shown[6] that for a *Gauss*ian chain the sites which are to be occupied by the segments of a second chain in order to give an attractive segment-segment interaction between segments of different chains actually have a broader distribution than those sites leading to a repulsive interaction. As a consequence the net pair potential between two polymer molecules in general may be well represented by the difference between two *Gauss*ian functions rather than by the single one suggested by eq. 1

$$\frac{U(R)}{kT} = n^2 V \left\{ \left(\frac{3}{4\pi s^2}\right)^{3/2} \exp\left[-\frac{3R^2}{4s^2}\right] - z\Phi \left(\frac{3}{4\pi s''^2}\right)^{3/2} \exp\left[-\frac{3R^2}{4s''^2}\right] \right\} \tag{2}$$

Here z is the maximum number of attractive contacts of energy ΦkT one segment may form and s''^2 is the mean square radius of gyration of these attractive sites, where s''^2 should equal $s^2 + (\delta^2/2)$, δ being the distance between the centers of the segments when forming such an attractive contact.

As eq. 2 which has been found to be obeyed by *Monte Carlo* cubic lattice chains, at least in type, had been derived with some reference to the lattice models used in [4, 5] it seemed desirable to rederive eq. 2 (or an equivalent to it) in a new general way for a continuum model.

Derivation of the Formalism

According to the superposition principle frequently used in statistical mechanics the *Boltzmann* factor for the interaction between two linear macromolecules A and B, each consisting of n segments, $\exp[-U/kT]$, is given by

$$e^{-U/kT} = \prod_{i=1}^{i=n} \prod_{j=1}^{j=n} e^{-\varepsilon/kT} \tag{3}$$

i.e., by the product of the *Boltzmann* factors characterizing the average pairwise interaction between any chain segment of chain A and any chain segment of chain B, ε being the energy of the segment-segment interaction in any pair ij. As we are interested in an average effective potential U (potential of mean force), however, we have to take care of averaging over all possible configurations.

So we may proceed as follows:

The probability density (averaged over all i) of finding a specific segment i of chain A at the location of some volume element dv, *Gauss*ian behaviour of the overall segment distribution assumed, is given by

$$\rho(r') = \left(\frac{3}{2\pi s^2}\right)^{3/2} \exp\left[-\frac{3r'^2}{2s^2}\right] = \left(\frac{a}{\pi}\right)^{3/2} e^{-ar'^2} \tag{3a}$$

r' being the distance between dv and the center of gravity of chain A. On the other hand we need the average probability density $\rho(r'')$ of finding a specific segment of a chain at some volume element dv' apart by a distance r from dv, averaged over all dv' fulfilling this condition. This, in correspondence to the derivation given earlier[6], is

$$\rho(r'') = \frac{1}{4\pi r'' r}\left(\frac{a}{\pi}\right)^{1/2} \{\exp[-a(r''-r)^2] - \exp[-a(r''+r)^2]\} \tag{4}$$

with r'' being the distance between the volume element $\mathrm{d}v$ under consideration and the center of gravity of the chain. Now we have to ask for the differential probability δp_r that a segment i of chain A is at $\mathrm{d}v$ and simultaneously a segment j of chain B is at a distance r around $\mathrm{d}v$, when the centers of chains A and B are at a distance R. This will be given by

$$\delta p_r(r, R) = 4\pi \rho(r') \rho'(r'', r) r^2 \,\mathrm{d}r\, \mathrm{d}v \tag{5}$$

where r'' denotes the distance between $\mathrm{d}v$ and the center of mass of chain B (r', r'', and R of course are not independent of each other, but are connected through the vector equation $\vec{r}' = \vec{r}'' + \vec{R}$).

Using the same principles which have been successfully applied in the course of the numerical calculations[4, 5], averaging over the *Boltzmann* factors of all the $\int \delta p_r$ belonging to "interfering" configurations ($f = \exp[-\varepsilon(r)/kT]$) and the $1 - \int \delta p_r$ "non-interfering" configurations ($f = 1$) yields

$$\begin{aligned} \bar{f} &= \left(1 - \int \delta p_r\right) \cdot 1 + \int \delta p_r \exp[-\varepsilon(r)/kT] \\ &= 1 - \int \delta p_r \left(1 - \exp[-\varepsilon(r)/kT]\right) \end{aligned} \tag{6}$$

We may note that $\exp[-\varepsilon(r)/kT]$ actually is the distribution function for a pair of isolated segments, with $\varepsilon(r)$ being the appropriate pair potential.

Due to the short range character of $\varepsilon(r)$ it follows $\int \delta p_r(1 - \exp[-\varepsilon(r)/kT]) \ll 1$. Thus we may approximate $\bar{f}$ by

$$\bar{f} \approx \exp\left[-\int \delta p_r \left(1 - e^{-\varepsilon(r)/kT}\right)\right] \tag{6a}$$

In order to evaluate the *Boltzmann* factor characterizing the overall average interaction between segments i and j we have to take the product of all $\bar{f}$; this means that after taking logarithms we shall obtain the corresponding average potential U_{ij} by integrating over all volume elements $\mathrm{d}v$

$$U_{ij}/kT = 4\pi \int_{\mathrm{d}v} \int_{r=0}^{r=\infty} \rho \rho' r^2 \left(1 - e^{-\varepsilon(r)/kT}\right) \mathrm{d}r\, \mathrm{d}v \tag{7}$$

As the two integration variables are independent of each other we are free to reverse the order of integrations. Carrying out the integration over $\mathrm{d}v$ separately yields

$$\begin{aligned} \int \rho(r') \rho'(r, r'')\, \mathrm{d}v &= \left(\frac{a}{2\pi}\right)^{1/2} \frac{1}{4\pi r R} \left\{ \exp\left[-\frac{a}{2}(R - r)^2\right] - \exp\left[-\frac{a}{2}(R + r)^2\right] \right\} \\ &\equiv \rho''(r, R) \end{aligned} \tag{8}$$

As we have n segments in chain A and n segments in chain B the *Boltzmann* factor for the overall intermolecular interaction will be the product of n^2 *Boltzmann* factors $\exp[-U_{ij}/kT]$ so that

$$e^{-U/kT} = (e^{-U_{ij}/kT})^{n^2}$$

or

$$U/kT = n^2\, U_{ij}/kT = n^2\, 4\pi \int_0^\infty \rho''(r, R)\,(1 - e^{-\varepsilon(r)/kT})\, r^2\, \mathrm{d}r$$

$$= n^2 \left(\frac{3}{4\pi s^2}\right)^{1/2} \frac{1}{R} \int_0^\infty r \left\{\exp\left[-\frac{3}{4s^2}(R-r)^2\right] - \exp\left[-\frac{3}{4s^2}(R+r)^2\right]\right\} \cdot (1 - e^{-\varepsilon(r)/kT})\, \mathrm{d}r \qquad (9)$$

$$= n^2 \left(\frac{b}{\pi}\right)^{1/2} \frac{1}{R} \int_0^\infty r\, \{\exp[-b(R-r)^2] - \exp[-b(R+r)^2]\} \cdot (1 - e^{-\varepsilon(r)/kT})\, \mathrm{d}r$$

$$\left(b \equiv \frac{a}{2}\right)$$

Eq. 9 constitutes a perfect mathematical tool of transforming any pair potential of segment-segment interaction into the pair potential of interaction between two chain molecules, within the frame of the limitations imposed by the derivation. These limitations, however, are essentially the same as in the derivation of the *Flory-Krigbaum* potential, eq. 1. The most remarkable feature in eq. 9 is the appearance of $4\pi \int r^2 \rho''(r, R)\,(1 - \exp[-\varepsilon/kT])\,\mathrm{d}r$, an expression very similar to the binary cluster integral of the isolated segments, $\beta = 4\pi \int r^2 (1 - \exp[-\varepsilon/kT])\,\mathrm{d}r$. It will be clear at once that this integral, due to the presence of $\rho''(r, R)$ in the integrand, in no way can be zero in general for all intermolecular separations R even if the binary cluster integral of the free segments should be zero, provided only that ε does not vanish for *any* value of r (ideal gas like behaviour of the free segments). It is thus confirmed that an expression as in eq. 1, consisting of one *Gauss*ian function only, must be inappropriate in general for $U(R)$ at least for θ-conditions.

Development of Approximations

In principle any reasonable expression for $\varepsilon(r)$ can be inserted into eq. 9, *e.g.*, square well or triangle potentials, even the use of more elaborated potentials (*e.g.*, the 6,12-*Lennard-Jones* potential) should be possible. However, except for the simplest types of potentials no closed solutions of the integrals in eq. 9 are available so that usually refuge has to be taken in numerical methods in these cases. For must purposes a less complicated approach will be satisfactory: Assuming $r \ll R$, which due to the short range character of $\varepsilon(r)$ is well fulfilled except for very small separations ($R \to 0$), where the distance between the centers of mass of the two chains is of the same order of magnitude as the segment diameter, expansion of the two potentials in eq. 9 into *Taylor* series around R, formally retaining terms up to the fourth order (all even order terms cancel), leads to

$$U/kT = n^2 \left(\frac{b}{\pi}\right)^{1/2} e^{-bR^2} \left\{ 4b \int_0^\infty r^2 (1 - e^{-\varepsilon/kT})\, \mathrm{d}r + \left(\frac{8}{3} b^3 R^2 - 4b^2\right) \cdot \int_0^\infty r^4 (1 - e^{-\varepsilon/kT})\, \mathrm{d}r \right\} \tag{10}$$

Introducing the binary cluster integral β as the integrated second moment of the segment-segment interaction and a quantity $\gamma = 4\pi \int_0^\infty r^4 (1 - e^{-\varepsilon/kT})\, \mathrm{d}r$ as the corresponding integrated fourth moment, eq. 10 transforms into

$$\begin{aligned} U/kT &= n^2 \left(\frac{b}{\pi}\right)^{3/2} e^{-bR^2} \beta - n^2 \left(\frac{b}{\pi}\right)^{3/2} e^{-bR^2} (b - \frac{2}{3} b^2 R^2)\gamma \\ &= n^2 (b/\pi)^{3/2} e^{-bR^2} \left(\beta - (b - \frac{2}{3} b^2 R^2)\gamma\right) \end{aligned} \tag{11}$$

Comparison shows that the first part of the rhs of eq. 11 is identical with the *Flory-Krigbaum* equation in its version of eq. 1a which actually would correspond to taking into account terms up to the second order only in the *Taylor* series expansion of eq. 9. Apparently, it is the second part of the rhs of eq. 11 originating from the third order terms which—according to its dependence on R—causes eq. 1a to fail for θ-conditions. If the positive and negative parts of ε compensate each other so that $\beta = 0$ (which along with our experience will characterize conditions very close to θ-conditions), then, because repulsion between segments exceeds attraction for small distances r, due to the presence of r^4 in the integrand (instead of r^2 for β) γ must be negative. Therefore, the potential U/kT given by eqs. 10 (or 11) will be positive (repulsive) for $R^2 < 3/(2b) = 2s^2$ and negative (attractive) at higher separations. This is indeed in close agreement with *Monte Carlo* calculations carried out for isolated pairs of model chains[4]. Thus, the conclusions drawn at the top of this paragraph are confirmed in a most instructive manner.

The expression for U/kT given by eqs. 9–11 represent the combined action of attraction and repulsion. For some purposes it may be more convenient to consider the potentials for repulsion (U_+) and attraction (U_-) separately ($U = U_+ + U_-$). The integrand in eq. 9 is seen to assume positive or negative values depending on whether ε is repulsive (positive) or attractive (negative) at the specified intersegment distance r under consideration (the expression within braces always being $\geqslant 0$). As a repulsive interaction between the macromolecules can originate from a repulsive interaction of segments only (overall attraction and segment-segment attraction will be connected in a similar way) this suggests to split U into a repulsive part (U_+) and an attractive one (U_-), just by carrying out the integration separately for this range where the integrand is positive and that where it is negative. As ε will be positive for small r and eventually becomes negative in case of additional attractive interaction between the segments at higher separations, so that the sign of ε, if at all, changes only once, it will be sufficient to integrate from $r = 0$ up to that point where ε turns from positive to negative (r_0) for obtaining U_+, the rest of the integration (from r_0 to infinity) giving U_-.

$$U_+/kT = n^2\left(\frac{b}{\pi}\right)^{1/2}\frac{1}{R}\int_0^{r_0} r\{\exp[-b(R-r)^2] - \exp[-b(R+r)^2]\} \cdot (1 - e^{-\varepsilon/kT})\,\mathrm{d}r \tag{12a}$$

$$U_-/kT = n^2\left(\frac{b}{\pi}\right)^{1/2}\frac{1}{R}\int_{r_0}^{\infty} r\{\exp[-b(R-r)^2] - \exp[-b(R+r)^2]\} \cdot (1 - e^{-\varepsilon/kT})\,\mathrm{d}r \tag{12b}$$

Certainly, similar limitations as for eq. 9 will apply to the direct integrability of eqs. 12a and 12b. In a fully analogous fashion, however, also the approximate expression for U/kT, eq. 10 or 11 can be subjected to the procedure of evaluating the integrals separately for positive and negative ε. Introducing the quantities

$$\beta_+ = 4\pi \int_0^{r_0} r^2 (1 - e^{-\varepsilon/kT})\,\mathrm{d}r$$

$$\beta_- = 4\pi \int_{r_0}^{\infty} r^2 (1 - e^{-\varepsilon/kT})\,\mathrm{d}r$$

$$\gamma_+ = 4\pi \int_0^{r_0} r^4 (1 - e^{-\varepsilon/kT})\,\mathrm{d}r$$

$$\gamma_- = 4\pi \int_{r_0}^{\infty} r^4 (1 - e^{-\varepsilon/kT})\,\mathrm{d}r$$

we obtain

$$U_+/kT = n^2 \left(\frac{b}{\pi}\right)^{3/2} e^{-bR^2} \left\{\beta_+ - \gamma_+ b\left(1 - \frac{2}{3} bR^2\right)\right\} \tag{13a}$$

$$U_-/kT = n^2 \left(\frac{b}{\pi}\right)^{3/2} e^{-bR^2} \left\{\beta_- - \gamma_- b\left(1 - \frac{2}{3} bR^2\right)\right\} \tag{13b}$$

Defining the average squares of the segment-segment separations, ${r_+}^2$ and ${r_-}^2$, at which repulsive and attractive segment-segment interaction takes place, respectively,

$${r_+}^2 = \gamma_+/\beta_+ \qquad {r_-}^2 = \gamma_-/\beta_-$$

eqs. 13a, b take the form

$$U_+/kT = n^2 \left(\frac{b}{\pi}\right)^{3/2} e^{-bR^2} \beta_+ \left\{1 - {r_+}^2 b\left(1 - \frac{2}{3} bR^2\right)\right\} \tag{14a}$$

$$U_-/kT = n^2 \left(\frac{b}{\pi}\right)^{3/2} e^{-bR^2} \beta_- \left\{1 - {r_-}^2 b\left(1 - \frac{2}{3} bR^2\right)\right\} \tag{14b}$$

Under the conditions $b{r_+}^2 \ll 1$ (corresponding to ${r_+}^2 \ll {s_-}^2$), and $b{r_-}^2 \ll 1$ (corresponding to ${r_-}^2 \ll s^2$), which due to the short range character of segment-segment interaction are fulfilled in all cases (except for very short chain lengths) these eqs. 14a, b can be transformed into

$$U_+/kT = n^2 \beta_+ \left(\frac{3}{4\pi s_+{}^2}\right)^{3/2} \exp[-3R^2/4s_+{}^2] \equiv n^2 \beta_+ (b_+/\pi)^{3/2} \exp[-b_+R^2] \tag{15a}$$

$$U_-/kT = n^2 \beta_- \left(\frac{3}{4\pi s_-{}^2}\right)^{3/2} \exp[-3R^2/4s_-{}^2] \equiv n^2 \beta_- (b_-/\pi)^{3/2} \exp[-b_-R^2] \tag{15b}$$

$$[b_+ \equiv 3/(4s_+{}^2);\ b_- \equiv 3/(4s_-{}^2)]$$

were $s_+{}^2 = s^2 + r_+{}^2/2$ and $s_-{}^2 = s^2 + r_-{}^2/2$.

In combined form, eqs. 15 will correspond to an overall potential $U(= U_+ + U_-)$ composed of two exponentials

$$U/kT = n^2 \pi^{-3/2} \{\beta_+ b_+{}^{3/2} \exp[-b_+R^2] - \beta_- b_-{}^{3/2} \exp[-b_-R^2]\} \tag{16}$$

as it has been proposed earlier in form of eq. 2 which has been shown to furnish an excellent description of the pair potential operating within a pair of model lattice chains[4].

At the first sight it may be surprising that quite the same approximations lead to the mathematically different expressions of eqs. 11 and 16 which both claim to be adequate representations of U/kT. Apart from the fact that the two types of equations may be easily interconverted for not too large values of R (depending on whether the second term of the expression within braces of eqs. 13 or 14 is absorbed into the exponential as in eq. 15 or not) the difference is mainly a matter of the view which is taken of the problem: If it is preferred to have the contributions of segment repulsion and segment attraction to the overall potential U/kT clearly separated from each other then eq. 16 will be the better representation. If, on the other side, special emphasis is laid on the non-punctiform character of the segment-segment interaction eq. 11 will be the more instructive version. In any case, eq. 11 provides an interesting and new basis of testing pair potentials of chain molecules.

Tests of the Equations and Approximations

a) Model and Basic Data

In correspondence with calculations to be carried out for off-lattice chains[7] the following square-well potential has been chosen for the segment-segment interaction (Fig. 1) with r_0 being the "bond length" (twice the radius of the "hard-sphere" part of the segments): $\varepsilon = \infty$ for $0 \leqslant r/r_0 < 1$; $\varepsilon = \varphi$ for $1 \leqslant r/r_0 \leqslant 1.3$. The chains were considered as freely rotating chains consisting of $n = 50$ segments each with a bond angle of 109°28′ ($s^2 = 2(n-1)r_0^2/6 = 16.33\, r_0^2$). The constant $b = 0.75/s^2$ therefore will have a numeric value of $0.04592\, r_0^{-2}$. With this square well potential a

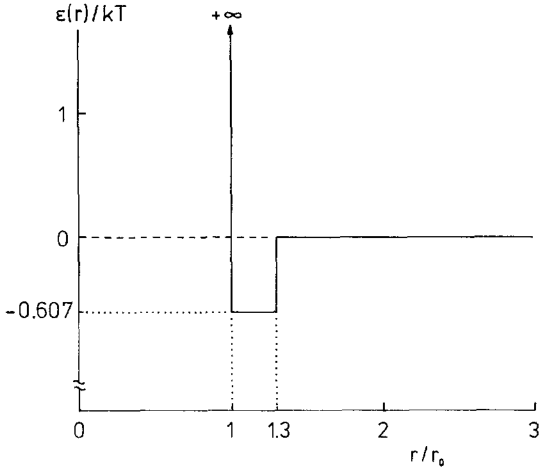

Fig. 1. Schematic representation of the square well potential used in the model calculations

value of $\varphi = -0.6073$ is necessary to make the binary cluster integral of segment-segment interaction β vanish according to

$$\beta = 4\pi \int_0^\infty r^2 (1 - e^{-\varepsilon(r)/kT})\, dr \equiv$$

$$= (4\pi/3)\, r_0^3 + (4\pi/3)\, r_0^3 (1 - e^{-\varphi})(1.3^3 - 1) \equiv 0$$

with $\beta_+ \equiv -\beta_- = 4.189\, r_0^3$.

This is very close to the value of φ ($\varphi = -0.6066$) which has been found to bring the excluded volume between chain molecules

$$u = 4\pi \int_0^\infty R^2 (1 - e^{-U(R)/kT})\, dR$$

down to zero if $U(R)$ is calculated from (the exact) eq. 9 thus proving the correctness of the implication that—at least in the frame of the concept

Table 1. *Pair potential U/kT of model chains ($n = 50$) calculated according to (exact) eq. 9 and approximate eqs. 11 and 16*

R/r_0	U/kT eq. 9	U/kT eq.16	U/kT eq. 11
0.00	0.64476	0.62671	0.67250
1.00	0.59859	0.58234	0.62349
2.00	0.47635	0.46472	0.49405
3.00	0.31835	0.31222	0.32751
4.00	0.16904	0.16742	0.17130
5.00	0.05857	0.05949	0.05703
6.00	—0.00457	—0.00293	—0.00710
7.00	—0.02899	—0.02769	—0.03091
8.00	—0.03025	—0.02959	—0.03117
9.00	—0.02221	—0.02205	—0.02241
10.00	—0.01329	—0.01337	—0.01316
11.00	—0.00681	—0.00694	—0.00662
12.00	—0.00306	—0.00316	—0.00291
13.00	—0.00122	—0.00127	—0.00113
14.00	—0.00043	—0.00046	—0.00039
15.00	—0.00014	—0.00015	—0.00012
16.00	—0.00004	—0.00004	—0.00003

adopted—$\beta = 0$ produces a zero excluded volume u. Using $\varphi = -0.607$ the following values are calculated for γ_+, γ_-, and γ

$$\gamma_+ = (4\pi/5)\,r_0^{\,5} = 2.51\,r_0^{\,5}$$

$$\gamma_- = (4\pi/5)r_0^{\,5}\,(1.3^5 - 1)\,(1 - e^{-\varphi}) = -5.69\,r_0^{\,5}$$

$$\gamma = \gamma_+ + \gamma_- = 4\pi \int_0^\infty r^4\,(1 - e^{-\varepsilon(r)/kT})\,\mathrm{d}r = -3.18\,r_0^{\,5}.$$

b) Numeric and Graphic Tests

Table 1 gives the results of the calculation of U/kT carried out according to (exact) eq. 9 (second column) the integrations being carried out numerically. The results of the corresponding calculations for the approximate forms, eq. 16 (difference of two exponentials) and eq. 11 [single exponential × $(1 - \text{constant} \cdot R^2)$] are shown in columns 3 and 4. It is seen that the agreement is slightly better for eq. 16 but satisfactory also for eq. 11. The point where U passes from positive (repulsive) to negative (attractive) in all three cases is somewhat below $6\,r_0$ [expected value $(2\,s^2)^{1/2} = 5.72\,r_0$]. The overall situation can be depicted most conveniently from Fig. 2 where all the three functions are plotted vs. R/r_0. As the

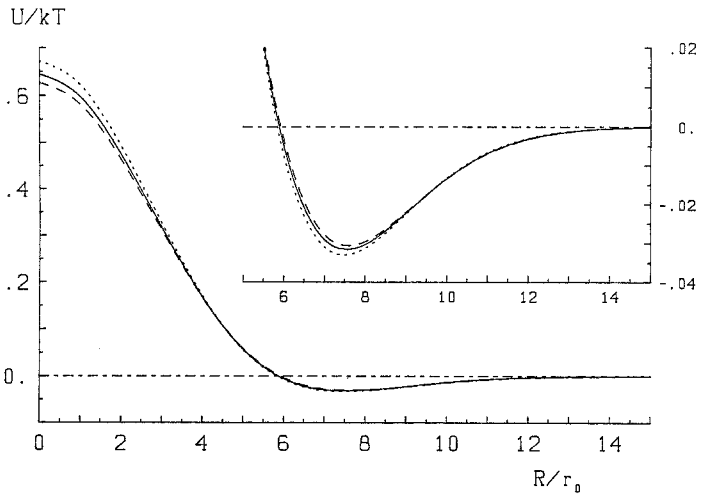

Fig. 2. Pair potential U/kT of freely rotating model chains as calculated by: exact eq. 9 ————; approximate eq. 11 ·········; approximate eq. 16 — — — —

Table 2. *Pair distribution function $G(R)$ and excluded volume u of model chains ($n = 50$) calculated according to (exact) eq. 9 and (approximate) eqs. 11 and 16*

R/r_0	$G(R)$ eq. 9	$G(R)$ eq. 16	$G(R)$ eq. 11
0.00	0.52479	0.53435	0.51043
1.00	0.54959	0.55859	0.53607
2.00	0.62105	0.62831	0.61015
3.00	0.72735	0.73182	0.72072
4.00	0.84448	0.84585	0.84257
5.00	0.94311	0.94225	0.94457
6.00	1.00458	1.00293	1.00712
7.00	1.02942	1.02808	1.03140
8.00	1.03071	1.03003	1.03167
9.00	1.02246	1.02229	1.02266
10.00	1.01338	1.01346	1.01325
11.00	1.00684	1.00697	1.00664
12.00	1.00306	1.00316	1.00291
13.00	1.00122	1.00127	1.00113
14.00	1.00043	1.00046	1.00039
15.00	1.00014	1.00015	1.00012
16.00	1.00004	1.00004	1.00003
	eq. 9	eq. 16	eq. 11
u/r_0^3	0.0	0.55	—0.9

differences can no longer be resolved for $R > 6\,r_0$ on the normal scale an insert to Fig. 2 has been drawn for that range with an enlarged ordinate scale. For better understanding also the pair distribution function $G(R) = \exp(-U/kT)$ for the pairs of chains in its low density limit has been tabled and presented in the same way (Table 2, Fig. 3). Again it is seen that the agreement is very good: The deviations have a maximum order of magnitude of 0.01 in the range of low separations ($R < 3\,r_0$) and are of the order of 0.001 (maximum) for separations where $G(R)$ exceeds unity ($R > 6\,r_0$). It should be noticed that over the whole range of separations the results obtained for (exact) eq. 9 are always *between* those of (approximate) eqs. 11 and 16. Table 2 also contains the volumes u excluded between the model chain molecules which may be calculated according to eq. 17 from $G(R)$: u is found to be very close to zero for the approximate forms (columns 3 and 4), too.

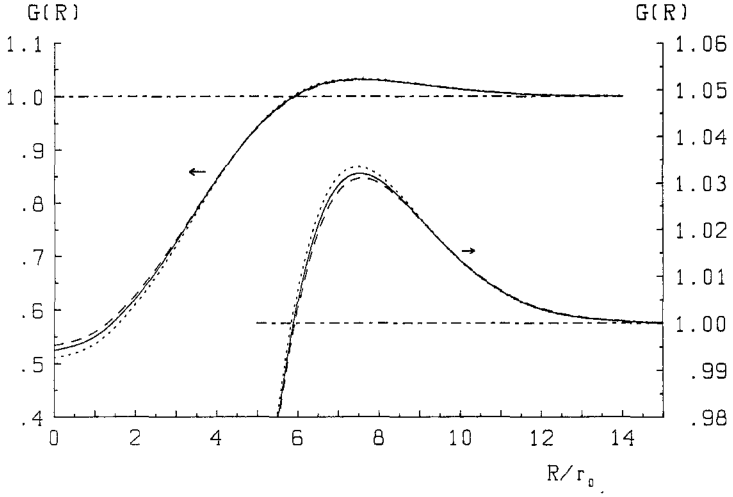

Fig. 3. Pair distribution function $G(R)$ of freely rotating model chains as calculated by: exact eq. 9 ————; approximate eq. 11 ··········; approximate eq. 16 — — — —

A second interesting point will be to check how close the repulsive (U_+) and attractive (U_-) components of the exact form of U (evaluated by carrying out the integration over r separately for the ranges $r = 0$ to $r = r_0$ and $r = r_0$ to $r = \infty$, as indicated in eqs. 12a and 12b) will be to *Gauss*ian behaviour separately. As shown in Fig. 4 no significant deviations from linearity can be detected from a plot of $\ln U_+/kT$ and $\ln U_-/kT$, respectively, vs. R^2. According to the fact that the approximate

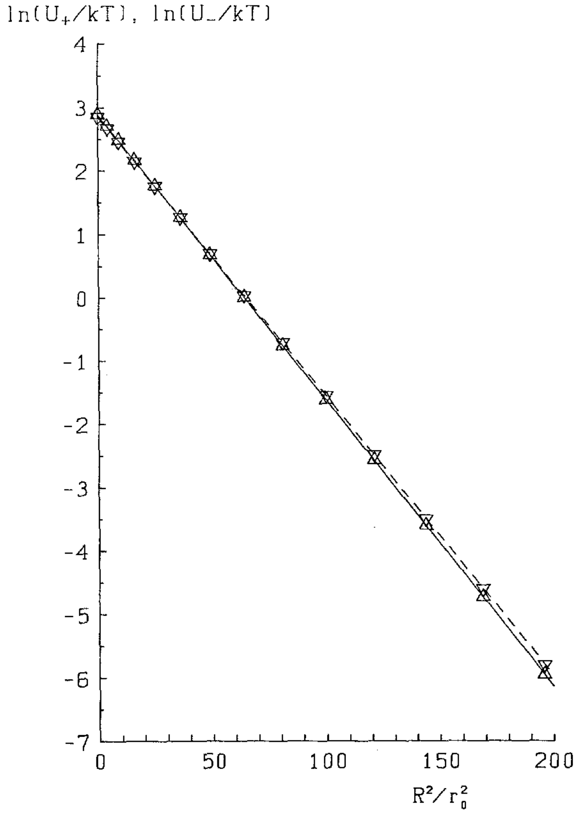

Fig. 4. Logarithmic plot of repulsive and attractive parts of U/kT, U_+/kT, and U_-/kT vs. squared chain separation $(R/r_0)^2$: U_+/kT (eq. 9) △; U_-/kT (eq. 9) ▽; U_+/kT (eq. 15a) ————; U_-/kT (eq. 15b) — — — —

form of U_+/kT and U_-/kT values given in eqs. 15a and 15b by definition is an exponential a plot of these ln U_+/kT or ln U_-/kT values vs. R^2 has to be linear at any rate and may serve as a standard straight line for comparison.

A further point of interest is to analyse exact eq. 9 in the frame of approximate eq. 11. This can be conveniently done by plotting (exact) U/kT values multiplied by e^{bR^2} vs. R^2 according to eq. 11 with $\beta = 0$

$$(U/kT)\, e^{bR^2} = n^2 (b/\pi)^{3/2} [- b\gamma + (2/3)\, b^2 \gamma R^2] \qquad (11\,\text{a})$$

As may be seen from Fig. 5 there are practically no significant deviations from the straight line required by eq. 11a for $R/r_0 > 10$ while according to the expectations (see comments at the end of the deduction section) deviations become feasible at $R/r_0 > 12$. Fortunately, however, as may be seen from Table 1, this range does not contribute very much to the overall interaction of the chains as $[1 - G(R)]$ has come down to -0.003 at $R = 12r_0$. Nevertheless, this plot offers elegant facilities of testing pair potentials of chain pairs and allows to draw conclusions on the nature and structure of the segment-segment interaction potential.

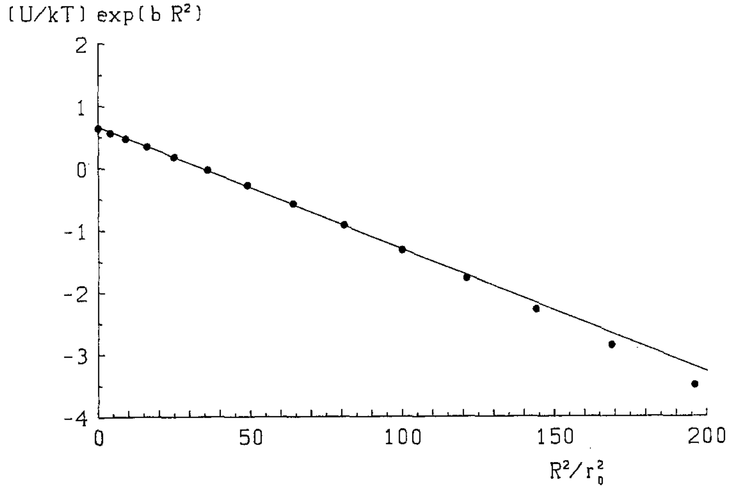

Fig. 5. Plot of $e^{bR^2} \cdot U/kT$ vs. squared chain separation $(R/r_0)^2$: U/kT (eq. 9) ●; U/kT (eq. 11) ———

Needless to say that in all cases where linear regressions are carried out using the points resulting from the exact eq. 9 the parameters of the equations (s^2, ${r_+}^2$, ${r_-}^2$, β, β_+, β_-, γ, γ_+, γ_-) or their combinations are recovered with very good accuracy. This is particularly the case with plots of $\ln U_+/kT$ or $\ln U_-/kT$ vs. R^2.

Concluding Remarks

a) Achievements

The foregoing chapters have shown that it is possible to derive an expression which is able to transform *any* pair potential of fairly short-ranged character operating between segments into the pair potential U describing the interaction between polymer chains along similar ideas as put forward by *Flory* and *Krigbaum*. As this expression (eq. 9) may be too complicated for practical purpose it is profitable to use the approximate forms developed afterwards (eqs. 11 and 16) which describe the segment-segment pair potential in terms of the volume excluded between segments β and the corresponding fourth moment γ of the pair distribution of the segments due to $\varepsilon(r)$, only. β as well as γ may be separated into the contributions arising from repulsion (β_+, γ_+) and attraction (β_-, γ_-) between segments ($\beta = \beta_+ + \beta_-$, $\gamma = \gamma_+ + \gamma_-$). The pairs ($\beta_+$, γ_+) and β_-, γ_-) define mean radii of repulsive ($r_+{}^2 = \gamma_+/\beta_+$) and attractive ($r^2_- = \gamma_-/\beta_-$) interaction between segments which appear to be the most convenient parameters in describing the repulsive (U_+) and attractive (U_-) part of the overall potential between polymer chains ($U = U_+ + U_-$). The excellent accordance between the results obtained for a model potential with the exact eq. 9 on the one hand and the approximate forms based on the characterization of ε by β (β_+, β_-) and γ (γ_+, γ_-) only on the other leads to the conclusion that the knowledge of the exact form of ε is dispensible. In other words this means that taking into account higher moments of the segment-segment pair distribution function (beyond γ, γ_+, γ_- or $r_+{}^2$, $r_-{}^2$, respectively) can give a marginal improvement of the accordance only and will not be worth the effort.

b) Limitations

While it thus has been shown that those difficulties inherent in the original *Flory-Krigbaum* treatment may be removed which arise from the fact that segment attraction and segment repulsion are absorbed into β without taking into account that they are effectuated at quite different segment-segment separations all the other objections which have been raised against the *Flory-Krigbaum* treatment still have to be borne in mind. So it is established that at the level of the second virial coefficients (or the excluded volume between polymer chains) the *Flory-Krigbaum* theory (in its *Flory-Orofino* version[8]) does not agree with the results of the perturbation theory not even to the first order[3]. Furthermore, severe criticism has been put forward against the *Flory-Krigbaum* theory by ourselves[9] at it fails to describe the pair distribution function $G(R)$ correctly for athermal model chains (subject to repulsive segment-segment interaction only). It could be shown[9] that this shortcoming is caused by the assumption implicitely inherent in the *Flory-Krigbaum* treatment all segment-segment interactions between the two chains forming the chain pair are independent of each other. It may be removed, however, by substituting n, the number of real segments by a smaller quantity n' which gives the effective number of segments ("segment clusters") which may be considered to behave independently of each other as required by the *Flory-Krigbaum* theory. This procedure alters the pre-exponential factor of U

only without affecting the exponential. This is in agreement with the findings obtained for model chains[9].

Although all the equations in this communication were originally derived without making any restriction as to the size (or even sign) of β and γ it is clear from the results obtained in [9] that a straightforward application of the equation to athermal chains must fail, too. However, the equations *should* work when n' and β' (and γ' defined in an analogous fashion for segment clusters) are used instead of n, β, and γ. As to the applicability of our equations to θ-systems ($\beta = 0$) it may be well argued that passing to the (unperturbed) θ-state together with many other types of perturbation also the perturbation in form of the interdependence of segment-segment interaction in the chain pair as it was observed for athermal chains will vanish so that our equations will be fully applicable under these conditions. A check of this argument will be given in a forthcoming paper[7].

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