ELSEVIER

Polymer 43 (2002) 591–597

polymer

www.elsevier.com/locate/polymer

Pair-wise additivity for potentials of mean force in dilute polymer solutions ☆

A. Striolo[a,b,1], D. Bratko[a], J.M. Prausnitz[a,b,*]

[a]Chemical Engineering Department, Gilman Hall, University of California, Berkeley CA 94720, USA
[b]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Abstract

Standard Monte Carlo techniques were used to compute the potential of mean force between pairs and between triplets of freely jointed hard-sphere polymers in dilute solutions. Segment–segment interactions at poor solvent conditions were represented by square-well potentials. Well width equaled half a segment diameter and well depth was either zero or $-0.30\ k_BT$. Polymer chains contained 25 segments.

For polymer triplets at a set of selected two-body distances, the pair-wise additivity of the potential of mean force provides a reasonable approximation for the three-body potential of mean force. At athermal conditions, the error introduced by assuming additivity is generally less than 10–15% of the total three-body interaction, while for well depth $-0.30\ k_BT$, the error rises, but is still generally less than 20–30%. Deviations from the calculated three-body potential of mean force are a function of solvent conditions and of relative positions of the interacting polymers. For polymer chains containing 15, 25 or 30 segments, simulation results do not depend significantly on polymer length.

Keywords: Monte Carlo simulation; Pair-wise additivity; Potential of mean force

1. Introduction

In typical molecular-thermodynamic calculations it is common practice to assume that the three-body potential is given by the sum of the two body potentials:

$$\Gamma^{(2)}_{123} = \Gamma^{(2)}_{12} + \Gamma^{(2)}_{13} + \Gamma^{(2)}_{23} \tag{1}$$

where $\Gamma^{(3)}_{123}$ is the potential of three particles denoted by subscripts 1, 2 and 3. When generalized to any number of multi-body potentials, Eq. (1) expresses the pair-wise additivity assumption; it provides an approximation that is often adopted in statistical mechanics of simple fluids [1,2]. For three interacting particles, Eq. (1) introduces a relatively small uncertainty when applied to monatomic or simple fluids [3–7]. Triple-dipole interactions contribute between two to nine percent of the cohesive energy of the crystals of rare gases [8]. Upon considering the effect of three-body interactions, it is possible to improve the prediction of density of the liquid branch in vapor–liquid phase equilibria for argon [9].

Little is known about uncertainties in applying the pair-wise additivity assumption to potentials of mean force, i.e. to systems where the interacting molecules are not in vacuum but in a solvent. For a three-body potential of mean force, $W^{(3)}_{123}$, the additivity assumption is:

$$W^{(3)}_{123} = W^{(2)}_{12} + W^{(2)}_{13} + W^{(2)}_{23}; \tag{2}$$

where superscripts 1, 2 and 3 denote the interacting particles. Because the radial distribution function, g_{ij}, is directly related to the potential of mean force [1,10], $W^{(2)}_{ij}$, according to

$$g_{ij} = \exp\left(\frac{-W^{(2)}_{ij}}{k_BT}\right), \tag{3}$$

Eq. (2) is equivalent to Kirkwood's superposition approximation of pair distribution functions [11]. When this approximation is generalized to any number of multi-body potentials, calculations of fluid properties ignore the contributions of three- and higher many-body interactions. For two-dimensional simple fluids, the superposition approximation introduces an uncertainty of only a few percent when compared to molecular-simulation results [12].

☆ This paper was originally submitted to *Computational and Theoretical Polymer Science* and received on 31 July 2000; received in revised form on 18 December 2000; accepted on 18 December 2000. Following the incorporation of *Computational and Theoretical Polymer Science* into *Polymer*, this paper was consequently accepted for publication in *Polymer*.

* Corresponding author. Tel.: +1-510-642-3592; fax: +1-510-642-4778.
E-mail address: prausnit@cchem.berkeley.edu (J.M. Prausnitz).

[1] Currently at Dipartimento di Principi e Impianti di Ingegneria Chimica, Via Marzolo 9, 35131 Padova, Italy.

0032-3861/02/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S1089-3156(01)00003-4

Some empirical corrections have been proposed to improve predictions for Lennard-Jones fluids [13], or for hard-sphere fluids [14]. Triple-dipole interactions increase the density difference between two equilibrium liquid phases for binary mixtures of Lennard-Jones atoms [15], and by including three-body interactions, better prediction was obtained for phase behavior of highly polar multicomponent liquid mixtures [16]. The three-body term is also important in systems containing ionic micelles or globular proteins with long-ranged double-layer interactions [17].

In phase-equilibrium calculations for polymer solutions, e.g. Refs. [18–20], additional caution is required. In this case, potentials of mean force are not only solvent-averaged McMillan–Mayer potentials between individual polymer segments [21], but, in addition, they are integrals over the conformations of the polymers. In practical calculations, the possible error introduced by assuming pair-wise additivity can sometimes be overcome by adjusting model parameters. To improve fundamental calculations of polymer-solution properties, it will be useful to have some estimate of the error introduced by the pair-wise additivity assumption.

This work is concerned with the pair-wise additivity of conformational averages for the potential of mean force between macromolecules in dilute solutions. Toward that end, the calculations performed here are within the McMillan–Mayer framework for segments with pair-wise additivity for the solvent-averaged potential of mean force between segments.

2. Model and simulation details

The polymer is represented by a chain of 25 freely jointed hard spheres. Time-consuming calculations of the three-body potential of mean force preclude calculations for significantly longer chains. Fortunately, preliminary simulations for chains with 15 and 30 segments do not show appreciable differences from the simulations obtained for 25-segment chain.

Two different scenarios were considered: purely self-avoiding chains with no attraction between the hard-sphere segments, and chains with weak attraction between non-bonded segments. In the latter case, the attraction was represented by a square-well potential with well width equal to one half of the segment diameter σ, well depth ϵ, was set to $-0.30\ k_B T$. The segment–segment square-well potential, ϕ, as a function of the center-to-center segment-segment distance, d, is represented by:

$$\phi(d) = \begin{cases} \infty & d < \sigma \\ \epsilon & \sigma \le d \le 1.5{\cdot}\sigma \end{cases}. \tag{4}$$

Both intra- and inter-segment interactions were considered for non-bonded polymer segments. For a square-well chain with given well width, the theta condition corresponds to a well-depth equal to $-0.32\ k_B T$ [22]. Computer-simulations show that, for linear chains with segments interacting with the given square-well potential, the coil size scales as random walk, and the second osmotic virial coefficient equals zero [22]. Therefore, our calculations correspond to dilute polymer solutions spanning good solvent conditions from athermal (hard-core with no attraction) to near-theta conditions. Because solvent molecules were not considered explicitly, our segment–segment potentials correspond to solvent-averaged potentials of mean force.

Standard Monte Carlo techniques were used to compute the potential of mean force between pairs or triplets of polymers. Isolated conformations of the linear polymer were generated with the Pivot algorithm [23,24]. The simulation was initiated with a fully stretched chain that was allowed to equilibrate within 1,500,000 moves. In the production run, one out of every few thousand successive configurations was recorded and used to compute the radius of gyration and the potential of mean force. Equilibration was verified by repeating the calculations at least three times. Table 1 shows radii of gyration for the chains considered here. To compute the potential of mean force between polymer pairs, we adopted the algorithm proposed by Hall and coworkers [22,25]. The pair potential of mean force, $W^{(2)}(r)$, as a function of the separation between the centers of mass of the polymers, r, is obtained by:

$$\frac{W^{(2)}(r)}{k_B T} = -\ln \frac{\sum_{i=1}^{M_P} U_i^{(2)}(r)}{M_P}, \tag{5}$$

where M_P is the total number of polymer pairs used at each distance and $U_i^{(2)}(r)$ is the statistical weight of each pair at given separation and configuration. This quantity is obtained by:

$$U_i^{(2)}(r) = \exp\left(-\Phi_i^{(2)}(r)/k_B T\right) \tag{6}$$

where $\Phi_i^{(2)}(r)$ is the potential between two polymer molecules for a particular configuration:

$$\Phi_i^{(2)} = \sum_{k=1}^{n} \sum_{l=1}^{n} \phi(d_{kl}) \tag{7}$$

The subscript i specifies a particular interacting polymer pair. The summation is over all segment pairs, and d_{kl} is

Table 1
Reduced sample-average radii of gyration squared, $\langle R_g^2 \rangle$, computed for linear polymers at different well depth. The reducing factor is σ^2, where σ is the diameter of a polymer segment

Number of segments	Well depth, $k_B T$	$\langle R_g^2 \rangle / \sigma^2$
15	0	4.75 ± 0.4
15	−0.30	4.1 ± 0.3
25	0	10.0 ± 0.5
25	−0.30	7.6 ± 0.3
30	0	12.1 ± 0.7
30	−0.30	9.3 ± 0.3

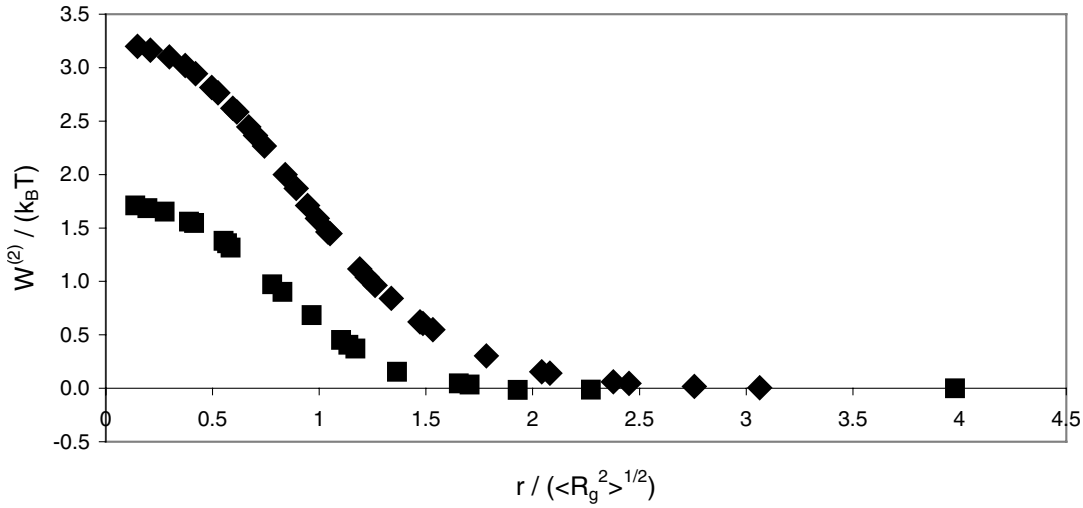

Fig. 1. Pair-potential of mean force as a function of the distance between centers of mass of the polymers for 25-segment chains. Diamonds are for athermal conditions, squares for well depth $-0.30\ k_BT$. Symbols are larger than statistical uncertainties.

the center-to-center distance of segment k belonging to the first polymer chain, to segment l of the second chain. This potential diverges if at least two segments belonging to interacting polymers overlap. If there are no overlaps, the total potential equals the number of segment pairs belonging to the two interacting polymers separated by less than 1.5 times the segment diameter σ, multiplied by the well depth. One thousand different conformations of the polymer were used to sample a total of one million polymer pairs at each separation r.

The algorithm has been generalized to compute the potential of mean force for triplets. The three-body potential of mean force, $W^{(3)}$, is obtained by:

$$\frac{W^{(3)}(r_{AB}, r_{BC}, r_{AC})}{k_BT} = -\ln \frac{\sum_{i=1}^{M_T} U_i^{(3)}(r_{AB}, r_{BC}, r_{AC})}{M_T}, \qquad (8)$$

where M_T is the total number of polymer triplets tested, r_{AB}, r_{BC}, r_{AC} the distances between the centers of mass of the polymers A and B, B and C, A and C, respectively; and $U_i^{(3)}$ is the statistical weight of each triplet. Analogous to Eq. (2), the statistical weight of a polymer triplet i is given by:

$$U_i^{(3)}(r_{AB}, r_{BC}, r_{AC}) = \exp\left(-\Phi_{ABC}^{(3)}/k_BT\right), \qquad (9)$$

where

$$\Phi_{ABC}^{(3)} = \Phi_{AB}^{(2)}(r_{AB}) + \Phi_{BC}^{(2)}(r_{BC}) + \Phi_{AC}^{(2)}(r_{AC}) \qquad (10)$$

To investigate the effect of the relative positions of different polymer chains on the three-body interaction, the three molecules were displaced in space to form different triangles. The center of mass of the first molecule, A, is placed at the origin and the second, B, at a fixed distance. The third molecule, C, is placed consecutively in four different positions such that the distance r_{AC} always equals r_{BC}. The four

Table 2
Three-body potential of mean force, $W^{(3)}$, for linear polymer chains, 25 segments each, at athermal conditions

r_{AB}/σ	$(r_{AC} = r_{BC})/\sigma$	$W^{(3)}$, k_BT
0.94	0.47	9.1 ± 0.2
1.88	0.94	8.4 ± 0.2
2.35	1.18	7.9 ± 0.15
3.13	1.57	6.95 ± 0.15
3.76	1.88	6.14 ± 0.05
4.23	2.12	5.5 ± 0.1
4.70	2.35	4.87 ± 0.05
5.64	2.82	3.7 ± 0.1
6.58	3.29	2.8 ± 0.1
7.52	3.76	2.05 ± 0.1
0.94	0.66	9.0 ± 0.2
1.88	1.33	8.10 ± 0.15
2.35	1.66	7.45 ± 0.1
3.13	2.22	6.25 ± 0.1
3.76	2.66	5.19 ± 0.05
4.23	2.99	4.40 ± 0.1
4.70	3.32	3.65 ± 0.05
5.64	3.99	2.35 ± 0.1
6.58	4.65	1.45 ± 0.1
0.94	0.94	8.8 ± 0.2
1.88	1.88	7.5 ± 0.1
2.35	2.35	6.6 ± 0.1
3.13	3.13	4.92 ± 0.05
3.76	3.76	3.55 ± 0.05
4.23	4.23	2.65 ± 0.1
4.70	4.70	1.97 ± 0.05
5.64	5.64	0.95 ± 0.1
6.58	6.58	0.45 ± 0.05
0.94	1.94	7.84 ± 0.15
1.88	3.88	4.81 ± 0.05
2.35	4.84	3.50 ± 0.05
3.13	6.46	1.99 ± 0.05
3.76	7.75	1.25 ± 0.05
4.23	8.72	0.89 ± 0.05
4.70	9.69	0.64 ± 0.05

Table 3
Three-body potential of mean force, $W^{(3)}$, for linear polymer chains, 25 segments each, at well depth $-0.30\ k_BT$

r_{AB}/σ	$(r_{AC} = r_{BC})/\sigma$	$W^{(3)}$, k_BT
0.76	0.38	5.05 ± 0.25
1.52	0.76	4.70 ± 0.25
2.28	1.14	4.05 ± 0.20
3.04	1.52	3.35 ± 0.15
4.56	2.28	1.78 ± 0.05
0.76	0.54	5.00 ± 0.25
1.52	1.07	4.70 ± 0.15
2.28	1.61	3.70 ± 0.10
3.04	2.15	2.65 ± 0.10
4.56	3.22	0.92 ± 0.02
0.76	0.76	5.10 ± 0.25
1.52	1.52	4.35 ± 0.20
2.28	2.28	2.95 ± 0.15
3.04	3.04	1.60 ± 0.05
4.56	4.56	0.180 ± 0.005
0.76	1.57	4.55 ± 0.20
1.52	3.13	2.42 ± 0.10
2.28	4.70	1.05 ± 0.05
3.04	6.27	0.44 ± 0.02

positions [3] of the center of mass of the polymer C are such that in the first configuration, $r_{AC} = 0.5{\cdot}r_{AB}$; in the second, $r_{AC} = (\sqrt{2}/2){\cdot}r_{AB}$. in the third, $r_{AC} = r_{AB}$; and in the fourth, $r_{AC} = (\sqrt{17}/2){\cdot}r_{AB}$. At every distance r_{AB}, the three-body potential of mean force is computed for each of the four spatial arrangements. These arrangements are shown in Fig. 6, Appendix A.

3. Results and discussion

Fig. 1 shows the pair potential of mean force as a function of the center-to-center distance computed for 25-segment chains. Diamonds represent results for athermal chains ($\epsilon = 0$), while squares represent results for $\epsilon = -0.30\ k_BT$. The distance r is normalized by the radius of gyration of the polymer. For the polymer pair at athermal conditions, the potential of mean force is positive at all separations. At $\epsilon = -0.30\ k_BT$ the potential of mean force is generally less repulsive, and becomes weakly attractive at distances of about 2.5 times the radius of gyration.

The triplet potential of mean force, $W^{(3)}$, was computed at different separations between chains A, B and C. Table 2 gives calculated triplet potentials of mean force obtained for 25-segment athermal chains at different center-to-center distances. Table 3 shows the triplet potential of mean force obtained for 25-segment chains at different center-to-center separations for $\epsilon = -0.30\ k_BT$. The 'excess' potential of mean force, $\Delta W^{(3)}$, was computed from:

$$\Delta W^{(3)}(r_{AB}, r_{BC}, r_{AC}) = W^{(3)}(r_{AB}, r_{BC}, r_{AC}) - [W^{(2)}(r_{AB}) + W^{(2)}(r_{BC}) + W^{(2)}(r_{AC})]. \quad (11)$$

Fig. 2 shows the excess potential of mean force as a function of reduced composite distance between polymers, r', at athermal conditions. The reduced composite distance is defined as:

$$r' = \frac{(r_{AB}{\cdot}r_{BC}{\cdot}r_{AC})^{(1/3)}}{\langle R_g^2\rangle^{(1/2)}}. \quad (12)$$

For the 25-segment chains, Fig. 2b–d show similar behavior: the excess three-body potential is repulsive at high separations, while it is weakly attractive at composite distances lower than the radius of gyration of the interacting polymers. Fig. 2a, however, shows that the excess potential remains negative at all separations. The weak attraction is attributed to several effects: the excluded volume of two

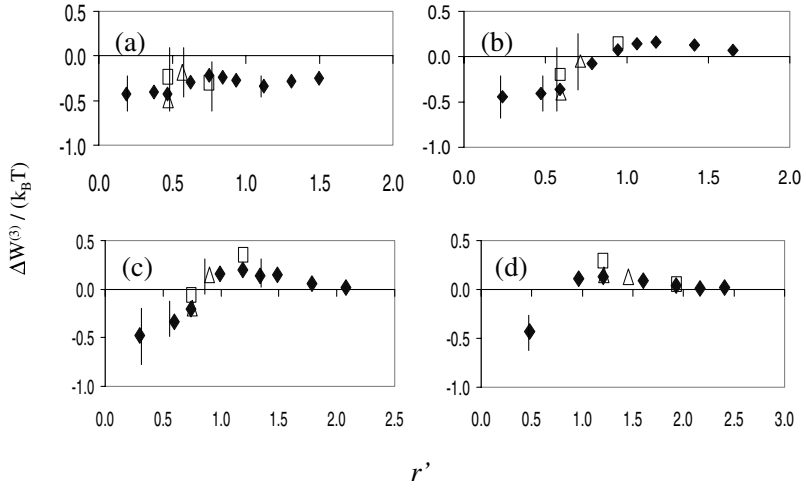

Fig. 2. Excess potential of mean force as a function of reduced composite distance between polymers. Results are for athermal conditions: (a) is for $r_{AC} = 0.5\ r_{AB}$; (b) is for $r_{AC} = 0.7071\ r_{AB}$; (c) is for $r_{AC} = r_{AB}$ and (d) is for $r_{AC} = 2.0616\ r_{AB}$. Diamonds are for 25-segment chains, squares for 15-segment chains, and triangles for 30-segment chains. Only some representative error bars are shown.

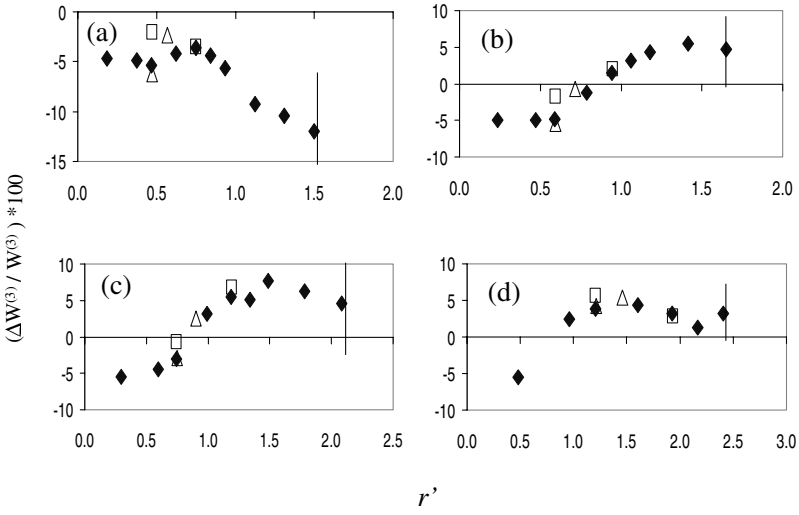

Fig. 3. Percentage of the excess potential of mean force relative to the three-body potential as a function of the reduced composite distance between polymers. Results are for athermal conditions: (a) is for $r_{AC} = 0.5\ r_{AB}$; (b) is for $r_{AC} = 0.7071\ r_{AB}$; (c) is for $r_{AC} = r_{AB}$ and (d) is for $r_{AC} = 2.0616\ r_{AB}$. Results are for athermal conditions. For clarity, error bars are omitted.

interpenetrating chains experienced by the third molecule generally lies below the sum of contributions from two independent chains, and available space is increased due to orientational correlations between the molecules. This situation is, however, reversed at composite separations exceeding the radius of gyration of isolated chains because polymer interpenetration leads to a moderate increase in the radius of gyration of adjacent chains. Due to excluded volume effects, an excess repulsion rises. The dependence of $\Delta W^{(3)}$ on triplet geometry is due to changes in the shielding of interactions between molecules A and B by molecule C; this shielding is most pronounced in the configuration shown in Fig. 2a where the third molecule (C) is placed between A and B. Results obtained for 15- and 30-segment chains agree with these observations, within statistical uncertainty.

Fig. 3 shows the excess potential of mean force as a percentage of the three-body potential of mean force, $W^{(3)}$, at different reduced composite distances at athermal conditions. In most cases in athermal dilute polymer solutions, the error introduced by Eq. (2) is less than 10–15% of the three-body potential. Therefore, pair-wise additivity of potentials of mean force provides a reasonable approximation at these conditions. Fig. 3a suggests that upon increasing the reduced composite distance, the absolute value of the percent error introduced by Eq. (2) also increases. However, at reduced composite distances larger than 1.20, for athermal dilute polymer solutions, the three-body potential of mean force, $W^{(3)}$, is small and the error is not significant.

Fig. 4 shows the excess potential of mean force as a function of reduced composite distance between weakly attractive polymers at $\epsilon = -0.30\ k_B T$. When there is a net

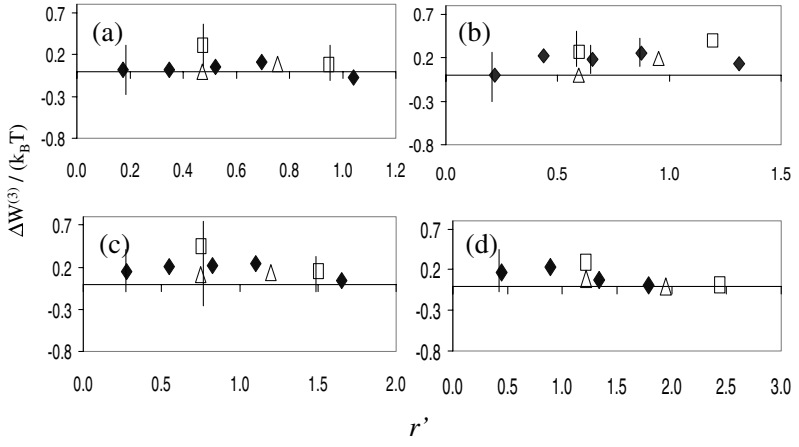

Fig. 4. Excess potential of mean force as a function of the reduced composite distance between polymers. Results are for theta conditions: (a) is for $r_{AC} = 0.5\ r_{AB}$; (b) is for $r_{AC} = 0.7071\ r_{AB}$; (c) is for $r_{AC} = r_{AB}$ and (d) is for $r_{AC} = 2.0616\ r_{AB}$. Diamonds are for 25-segment chains, squares for 15-segment chains, and triangles for 30-segment chains. Only some representative error bars are shown.

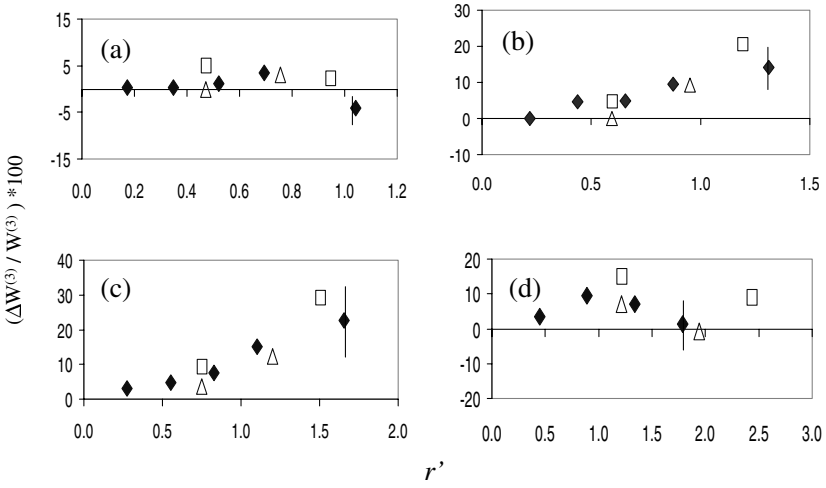

Fig. 5. Percentage of the excess potential of mean force relative to the three-body potential as a function of the reduced composite distance between polymers at theta conditions. (a) is for $r_{AC} = 0.5\ r_{AB}$; (b) is for $r_{AC} = 0.7071\ r_{AB}$; (c) is for $r_{AC} = r_{AB}$ and (d) is for $r_{AC} = 2.0616\ r_{AB}$. Diamonds are for 25-segment chains, squares for 15-segment chains, and triangles for 30-segment chains. For clarity, error bars are omitted.

attraction between non-bonded polymer segments, we expect a positive excess three-body potential of mean force because attracting segments from distinct chains compete for favorable interactions. Upon addition of the third polymer, a fraction of contacts between segments belonging to the other two macromolecules is replaced by contacts with segments from the third. Further, when two polymer chains, A and B, are close to each other, their conformations differ from the conformations of non-interacting polymers. Segments of different chains are attracted by each other, and the segment density in the region between the centers of mass of the two chains exceeds the sum of densities of two uncorrelated chains. Therefore, the volume available to segments of the third polymer chain, C, is smaller than expected, producing a net three-body repulsion. All our results agree with this phenomenological explanation.

Fig. 5 shows the excess potential of mean force as a percentage of the three-body potential of mean force at different reduced composite distances for $\epsilon = -0.30\ k_B T$. The error introduced by Eq. (2) is typically less than twenty percent of the total interaction. The percent error is higher for $\epsilon = -0.30\ k_B T$ than that for athermal conditions. Fig. 5b and c suggest that upon increasing the reduced composite distance, the relative error introduced by Eq. (2) rises. However, at reduced composite distances larger than 1.20, $W^{(3)}$ is small, and the error is not significant.

4. Conclusions

The pair-wise additivity assumption for a three-body potential of mean force provides a reasonable approximation in dilute polymer solutions at good-solvent conditions.

At athermal conditions, the error introduced by the additivity approximation is generally below 10–15% of the three-body potential of mean force. At small separations, the excess three-body potential of mean force is negative indicating an excess three-body attraction between polymer triplets at small separations. However, due to swelling of interpenetrating chains beyond the radius of gyration of isolated polymer molecules, the excess three-body potential of mean force can be positive at higher separations depending on the relative positions of the three interacting polymer chains.

At well depth $-0.30\ k_B T$, the excess three-body potential of mean force is always positive, showing an excess repulsion between polymer triplets. At these solvent conditions, the excess three-body potential of mean force is less than 20–30% of the three-body potential of mean force.

Results obtained with polymers of 15 and 30 segments indicate that our calculations do not change with polymer length.

Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Science Division of the US Department of Energy under Contract Number DE-AC03-76SF00098. D.B. acknowledges support from the National Science Foundation. Calculations were performed with the CRAY T3E supercomputers at the NPACI (San Diego, CA) and at the NERSC (Lawrence Berkeley National Laboratory, Berkeley, CA) supercomputing centers. The authors are grateful to N. Elvassore, C.K. Hall, L. Lue, D.N. Theodorou, and J.Z. Wu for helpful discussions. A.S. thanks R. Wimberly for encouragement.

Appendix A (Figure 6)

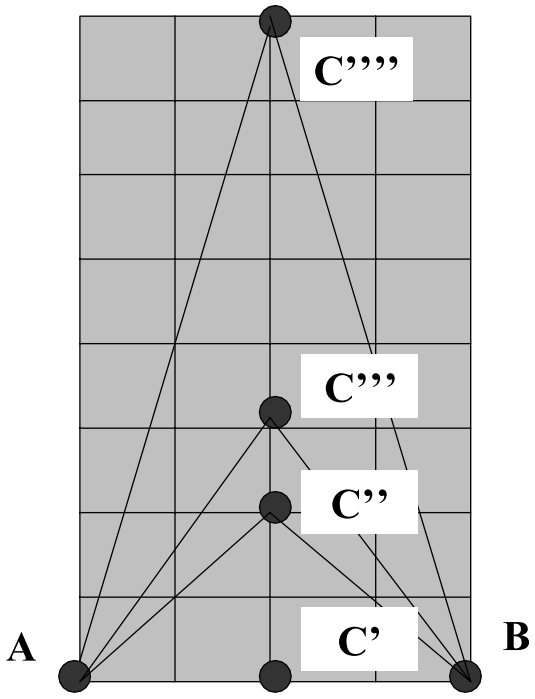

Fig. 6. Trial arrangements considered in calculation of conformational averages for three-body interactions. In the figure, the points represent the position of the centre of mass of each polymer coil. The centre of mass of the first molecule, A, is placed at the origin and the second, B, at a fixed distance. The third molecule, C, is placed consecutively in four different positions. In the first configuration, C', $r_{AC} = 0.5 \cdot r_{AB}$; in the second, C'', $r_{AC} = (\sqrt{2}/2) \cdot r_{AB}$; in the third, C''', $r_{AC} = r_{AB}$; and in the fourth, C'''', $r_{AC} = (\sqrt{17}/2) \cdot r_{AB}$.

References

[1] Hill TL. Statistical mechanics. New York: McGraw-Hill, 1956.
[2] Hansen JP, McDonald I. Theory of simple liquids. 2nd ed. London: Academic Press, 1986.
[3] Axilrod BM, Teller E. J Chem Phys 1943;11:299.
[4] Axilrod BM. J Chem Phys 1951;19:719.
[5] Alder BJ. Phys Rev Lett 1964;12:317.
[6] Rahman A. Phys Rev Lett 1964;12:575.
[7] Barker JA, Henderson D, Smith WR. Phys Rev Lett 1968;21:134.
[8] Axilrod BM. J Chem Phys 1951;19:724.
[9] Sadus RJ, Prausnitz JM. J Chem Phys 1996;104:4784.
[10] Chandler D. Introduction to modern statistical mechanics. New York: Oxford University Press, 1987.
[11] Kirkwood JG. J Chem Phys 1935;3:300.
[12] Guevara-Rodriguez FDeJ, Medina-Noyola M. Mol Phys 1998;95: 621.
[13] Hernando JA, Gamba Z. J Chem Phys 1992;97:5142.
[14] Taylor MP, Lipson JEG. J Chem Phys 1993;99:5625.
[15] Sadus RJ. Fluid Phase Equilibria 1998;150:63.
[16] Benmekki E-H, Mansoori GA. Fluid Phase Equilibria 1988;41:43.
[17] Wu JZ, Bratko D, Blanch HW, Prausnitz JM. J Chem Phys 2000;113:3360.
[18] King RS, Blanch HW, Prausnitz JM. AIChE J 1988;34:1585.
19 Haynes CA, Benitez FJ, Blanch HW, Prausnitz JM. AIChE J 1993;39:1539.
[20] Lue L, Blankschtein D. Ind Engng Chem Res 1996;35:3032.
[21] McMillan WG, Mayer JE. J Chem Phys 1945;13:276.
[22] Dautenhahn J, Hall CK. Macromolecules 1994;27:5399.
[23] Lal M. Mol Phys 1969;17:57.
[24] Zifferer G. Macromolecules 1990;23:3166.
[25] Yethiraj A, Hall CK. J Colloid Interface Sci 1992;151:102.