LBNL-46588
Preprint

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Pair-Wise Additivity for Potentials of Mean Force in Dilute Polymer Solutions

A. Striolo, D. Bratko, and J.M. Prausnitz

Chemical Sciences Division

August 2000

Submitted to
Computational and Theoretical Polymer Science

REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library - Ref.
Lawrence Berkeley National Laboratory

LBNL-46588
Copy 1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBNL-46588

Pair-Wise Additivity for Potentials of Mean Force in Dilute Polymer Solutions

A. Striolo, D. Bratko and J.M. Prausnitz

Department of Chemical Engineering
University of California
and
Chemical Sciences Division
Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720, U.S.A.

August 2000

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

Pair-Wise Additivity for Potentials of Mean Force in Dilute Polymer Solutions

Alberto Striolo[#], Dusan Bratko and John M. Prausnitz*

Chemical Engineering Department

University of California, Berkeley
and

Chemical Sciences Division

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

* to whom correspondence should be addressed

[#] currently at Istituto di Impianti Chimici, Università di Padova, Via Marzolo 9, 35131 Padova, Italy

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.

Key Words: Monte Carlo Simulation, Pair-Wise Additivity, Potential of Mean Force

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:

$$\Gamma_{123}^{(3)} = \Gamma_{12}^{(2)} + \Gamma_{13}^{(2)} + \Gamma_{23}^{(2)} \ , \qquad (1)$$

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, Equation *(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, Equation *(1)* introduces a relatively small uncertainty when applied to monatomic or simple fluids.[3-7] For the simple systems, the error in total potential is usually between 2 and 10%, not enough to explain the crystal structures of rare-gas crystals.[8] However, 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:

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

where subscripts 1, 2, 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

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

Equation *(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 percents when compared to

molecular-simulation results.[12] 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. 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.

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 $-0.30\ k_BT$. The segment-segment square-well potential, ϕ, as a function of the center-to-center segment-segment distance, d, is represented by:

$$\phi(d)=\begin{cases}\infty & d<\sigma \\ \varepsilon & \sigma \le d \le 1.5\cdot\sigma\end{cases} \qquad (3)$$

For a square-well chain with given well width, the theta condition corresponds to a well-depth equal to $-0.32\ k_BT$.[22] Therefore, our calculations correspond to dilute polymer solutions at good solvent conditions.

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 thousands 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:

$$\frac{W^{(2)}(r)}{k_B T} = -\ln \frac{\sum_{i=1}^{M_P} U_i^{(2)}(r)}{M_P} \quad , \qquad (4)$$

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:

$$U_i^{(2)}(r) = \exp^{\frac{-\Phi_i^{(2)}(r)}{k_B T}} \quad , \qquad (5)$$

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

$$\Phi_i^{(2)} = \sum_{k=1}^{n} \sum_{l=1}^{n} \phi(d_{kl}) \ . \qquad (6)$$

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

$$\frac{W^{(3)}(r_{AB}, r_{BC}, r_{AC})}{k_B T} = -\ln \frac{\sum_{i=1}^{M_T} U_i^{(3)}(r_{AB}, r_{BC}, r_{AC})}{M_T} \quad , \qquad (7)$$

where M_T is the total number of polymer triplets tested; r_{AB}, r_{BC}, r_{AC} are 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 Equation *(2)*, the statistical weight of a polymer triplet i is given by:

$$U_i^{(3)}(r_{AB}, r_{BC}, r_{AC}) = \exp^{\frac{-\Phi_{ABC}^{(3)}}{k_B T}} \quad , \qquad (8)$$

where

$$\Phi_{ABC}^{(3)} = \Phi_{AB}^{(2)}(r_{AB}) + \Phi_{BC}^{(2)}(r_{BC}) + \Phi_{AC}^{(2)}(r_{AC}) \quad . \qquad (9)$$

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 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, $r_{AC} = \frac{\sqrt{2}}{2} \cdot r_{AB}$; in the third, $r_{AC} = r_{AB}$; and in the fourth, $r_{AC} = \frac{\sqrt{17}}{2} \cdot r_{AB}$. At every distance r_{AB}, the three-body potential of mean force is computed for each of the four spatial arrangements.

Results and discussion

Figure 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 ($\varepsilon=0$), while squares represent results for $\varepsilon=-0.30\ k_BT$. 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 $\varepsilon=-0.30\ k_BT$ 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-segmnet chains at different center-to-center separations for $\varepsilon=-0.30\ k_BT$. The 'excess' potential of mean force, $\Delta W^{(3)}$, was computed from:

$$\Delta W^{(3)}(r_{AB}, r_{BC}, r_{AC}) = W^{(3)}(r_{AB}, r_{BC}, r_{AC}) - \left[W^{(2)}(r_{AB}) + W^{(2)}(r_{BC}) + W^{(2)}(r_{AC})\right]. \quad (10)$$

Figure 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:

$$r' = \frac{(r_{AB} \cdot r_{BC} \cdot r_{AC})^{1/3}}{\left(\langle R_g^2 \rangle^{1/2}\right)} \quad . \qquad (11)$$

For the 25-segment chains, Figures 2b, 2c, and 2d 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. Figure

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 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 Figure 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.

Figure 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 Equation (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. Figure 3a suggests that upon increasing the reduced composite distance, the percent error introduced by Equation (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.

Figure 4 shows the 'excess' potential of mean force as a function of reduced composite distance between weakly attractive polymers at ε=-*0.30* k_BT. When there is a net 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 of our results agree with this phenomenological explanation.

Figure 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 ε=-*0.30* k_BT. In most cases, the error introduced by Equation (2) is within a few percent of the total interaction. However, the percent error is higher for ε=-*0.30* k_BT than that for athermal conditions. Figures 5b and 5c suggest that upon increasing the reduced composite distance, the relative error introduced by Equation (2) rises. However, at reduced composite distances larger than 1.20, $W^{(3)}$ is small, and the error is not significant.

Conclusions

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

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 $-0.30\ k_BT$, 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.

Acknowledgments

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Science Division of the U.S. 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.

References

1. Hill, T.L. Statistical mechanics, McGraw Hill, New York 1956.
2. Hansen; I.R. McDonald, Theory of simple liquids, 2nd Ed., Academic Press, London 1986.
3. Axilrod, B.M.; Teller, E., J. Chem. Phys. 1943, 11, 299.
4. Axilrod, B.M., J. Chem. Phys. 1951, 19, 719.
5. Alder, B.J., Physical Review Letters 1964, 12, 317.
6. Rahman, A., Physical Review Letters 1964, 12, 575.
7. Barker, J.A.; Henderson, D.; Smith, W.R., Physical Review Letters 1968, 21, 134.
8. Axilrod, B.M., J. Chem. Phys. 1951, 19, 724.
9. Sadus, R.J.; Prausnitz, J.M., J. Chem. Phys. 1996, 104, 4784.
10. Chandler, D., Introduction to modern statistical mechanics, Oxford University Press, New York 1987.
11. Kirkwood, J.G., J. Chem. Phys. 1935, 3, 300.
12. Guevara-Rodriguez, F. De J.; Medina-Noyola, M., Molecular Physics 1998, 95, 621.
13. Hernando, J.A.; Gamba, Z., J. Chem. Phys. 1992, 97, 5142.
14. Taylor, M.P.; Lipson, J.E.G., J. Chem. Phys. 1993, 99, 5625.
15. Sadus, R.J., Fluid Phase Equilibria 1998, 150, 63.
16. Benmekki, E.-H.; Mansoori, G.A., Fluid Phase Equilibria 1988, 41, 43.
17. Wu, J.Z.; Bratko, D.; Blanch, H.W.; Prausnitz, J.M., accepted by J. Chem. Phys. 2000.
18. King, R.S.; Blanch, H.W.; Prausnitz, J.M., AIChE J. 1988, 34, 1585.
19. Haynes, C.A.; Benitez, F.J.; Blanch, H.W.; Prausnitz, J.M., AIChE J. 1993, 39, 1539.
20. Lue, L.; Blankschtein, D., Ind. Eng. Chem. Res. 1996, 35, 3032.
21. McMillan, W.G.; Mayer, J.E., J. of Chemical Physics 1945, 13, 276.
22. Dautenhahn, J.; Hall, C.K., Macromolecules, 1994, 27, 5399.
23. Lal, M., Molecular Physics 1969, 17, 57.
24. Zifferer, G., Macromolecules, 1990, 23, 3166.
25. Yethiraj, A.; Hall, C.K., J. Colloid and Interface Science 1992, 151, 102.

Table1 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_BT	$\langle R_g^2 \rangle / \sigma^2$
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

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

Figure captions

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.

Fig. 2 'Excess' potential of mean force as a function of reduced composite distance between polymers. Results are for athermal conditions. Figure 2a is for r_{AC}=0.5 r_{AB}, Figure 2b is for r_{AC}=0.7071 r_{AB}, Figure 2c is for r_{AC}=r_{AB}, and Figure 2d 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. Figure 3a is for r_{AC}=0.5 r_{AB}, Figure 3b is for r_{AC}=0.7071 r_{AB}, Figure 3c is for r_{AC}=r_{AB}, and figure 3d is for r_{AC}=2.0616 r_{AB}. Results are for athermal conditions. For clarity, error bars are omitted.

Fig. 4 'Excess' potential of mean force as a function of the reduced composite distance between polymers. Results are for theta conditions. Figure 4a is for r_{AC}=0.5 r_{AB}, Figure 4b is for r_{AC}=0.7071 r_{AB}, Figure 4c is for r_{AC}=r_{AB}, and Figure 4d 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. Results are for theta conditions. Figure 5a is for r_{AC}=0.5 r_{AB}, Figure 5b is for r_{AC}=0.7071 r_{AB}, Figure 5c is for r_{AC}=r_{AB}, and Figure 5d 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.

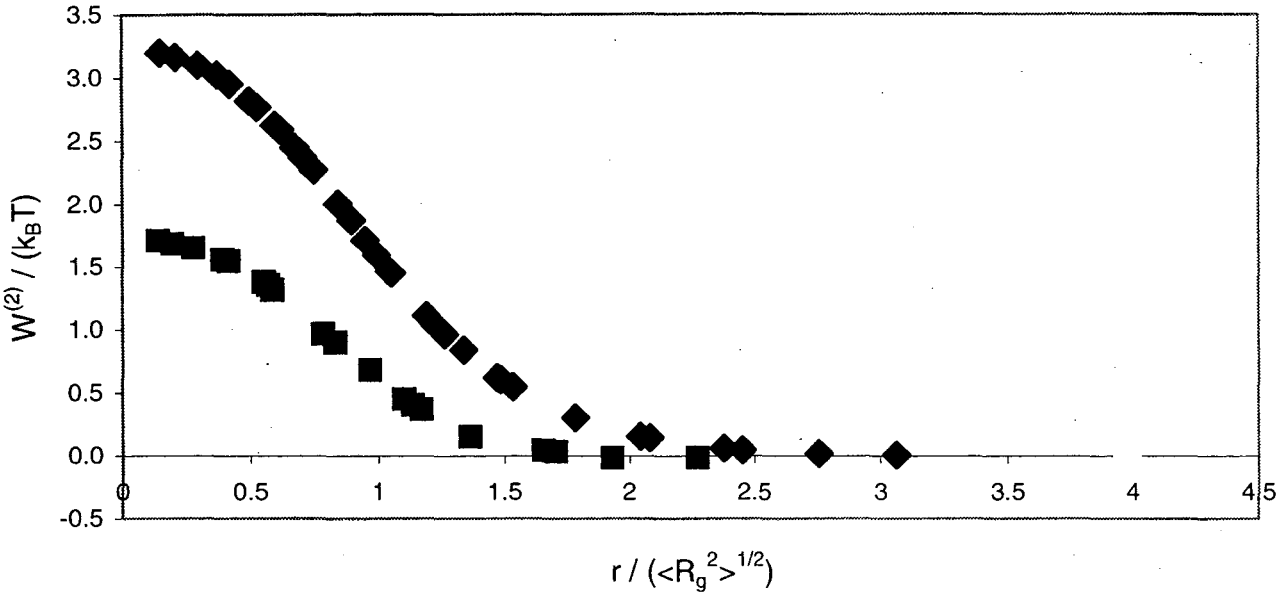

Fig. 1, Striolo et al., Pair-Wise Additivity....

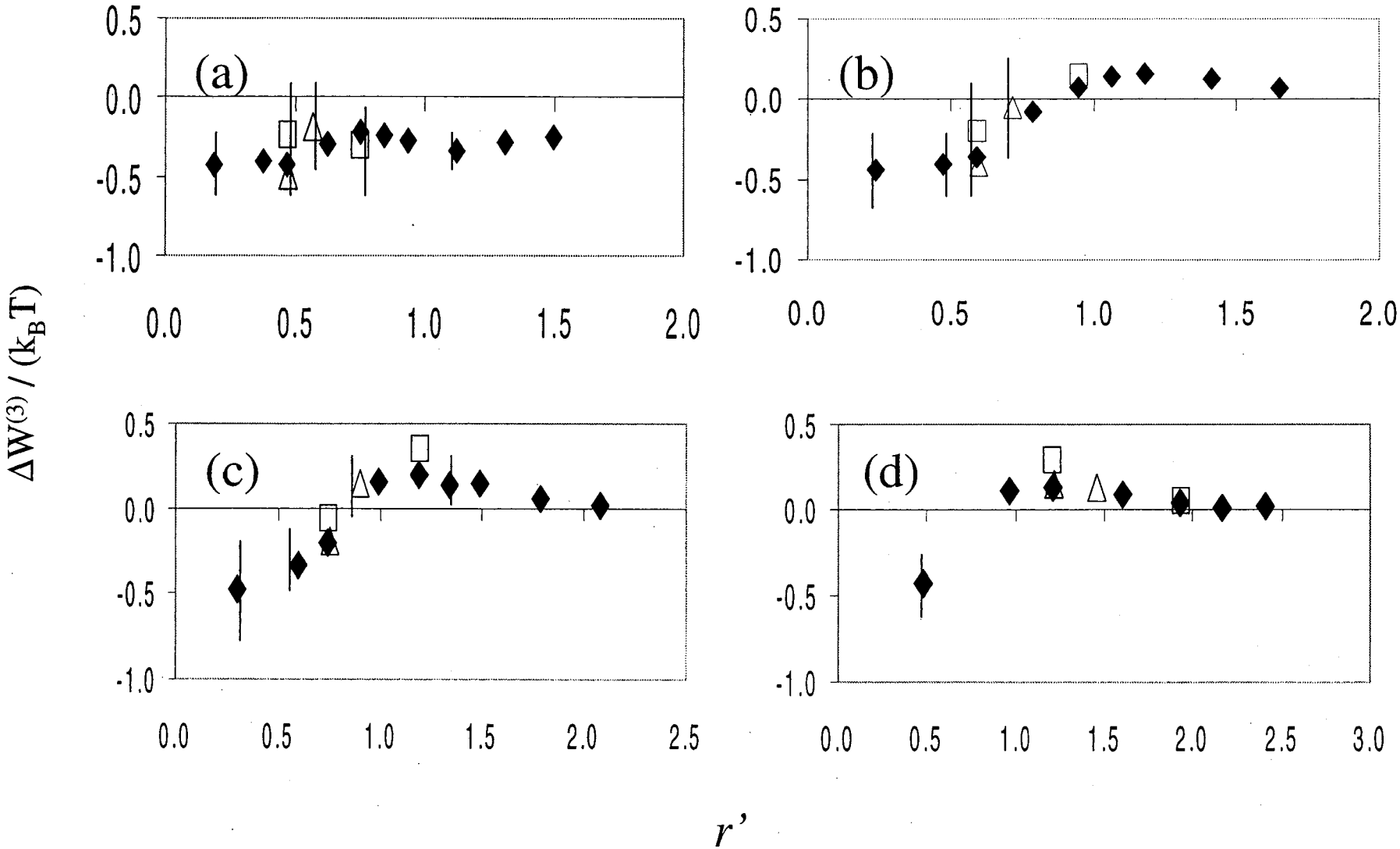

Fig. 2, Striolo et al., Pair-Wise Additivity...

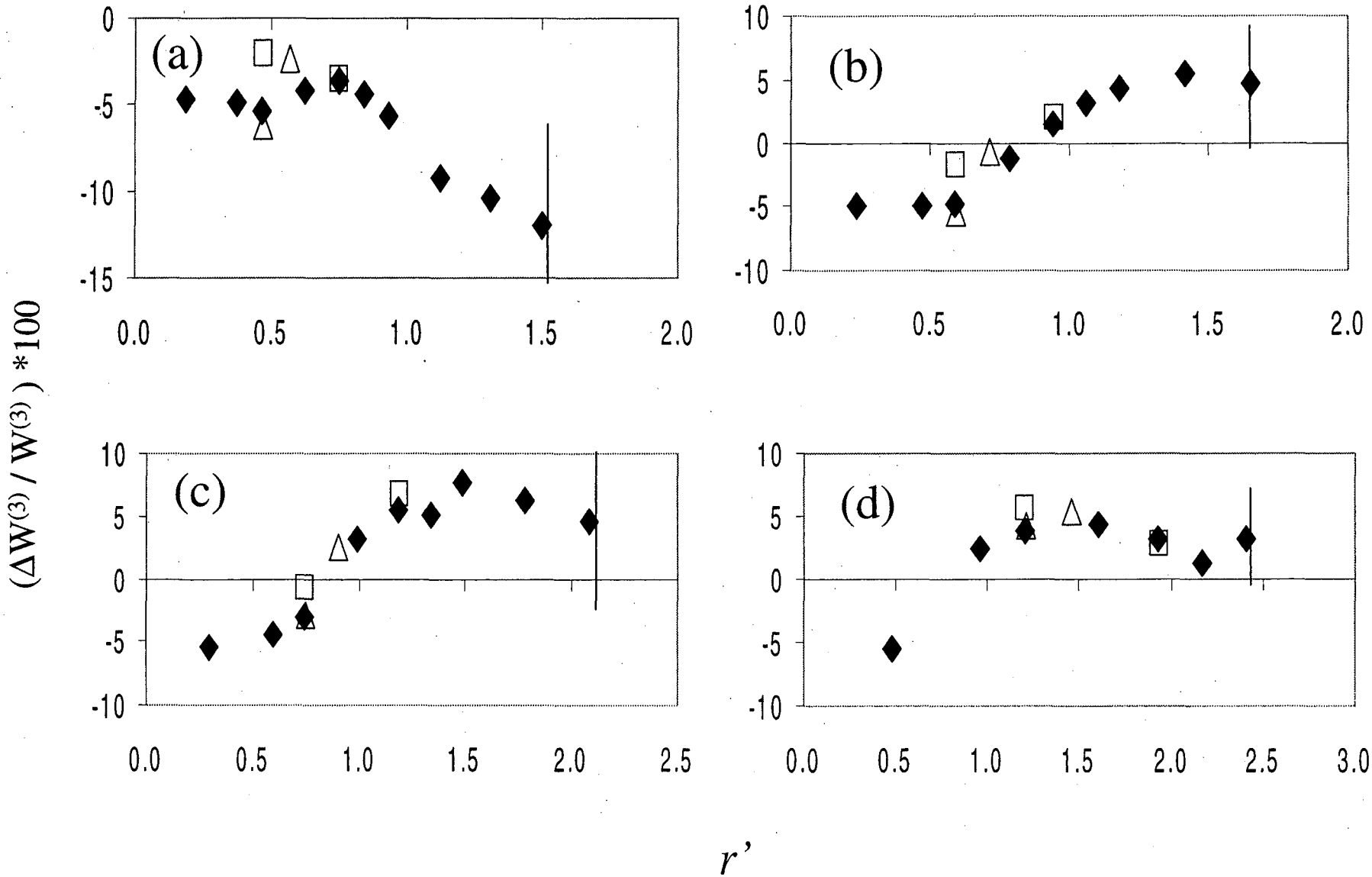

Fig. 3, Striolo et al., Pair-Wise Additivity...

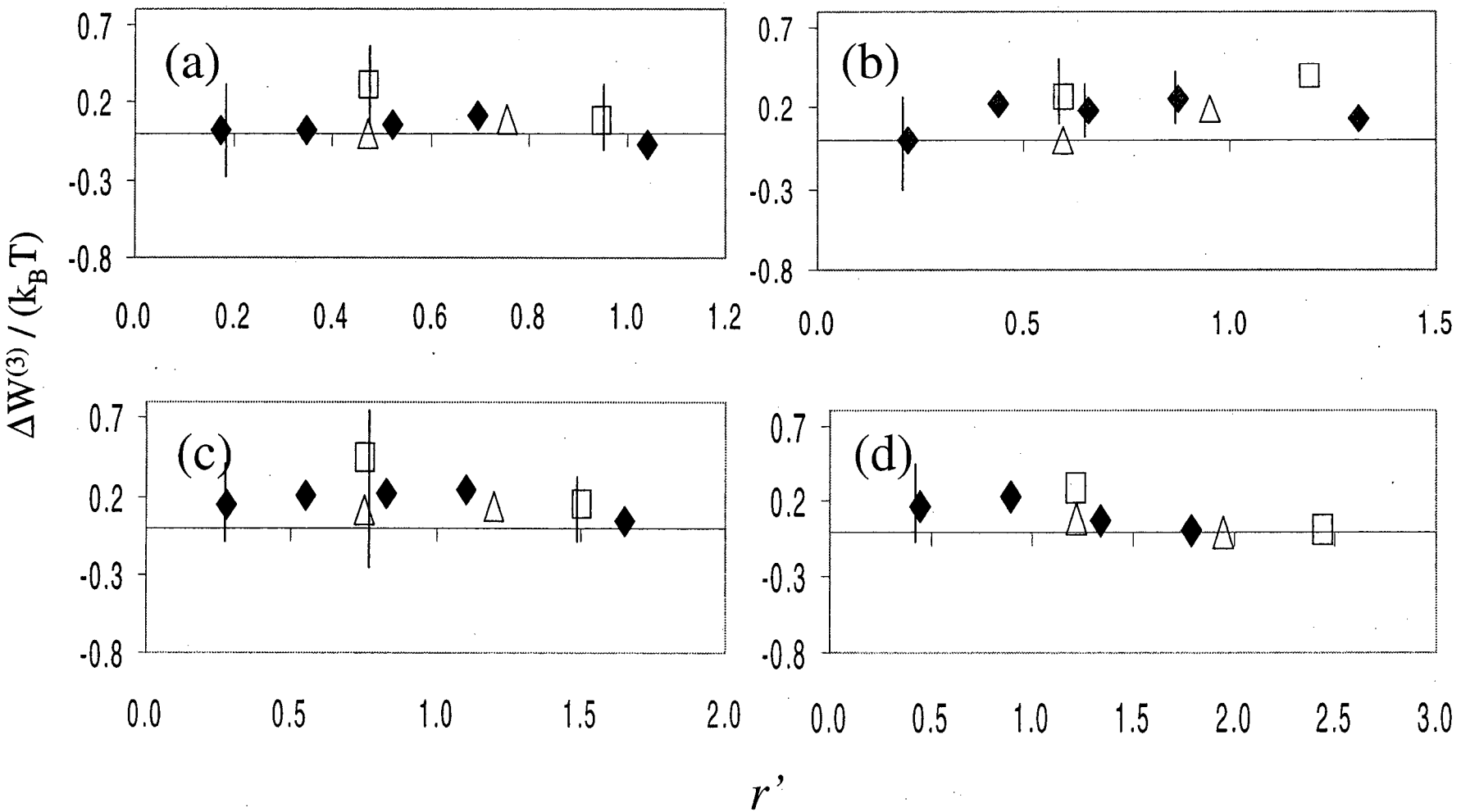

Fig. 4, Striolo et al., Pair-Wise Additivity...

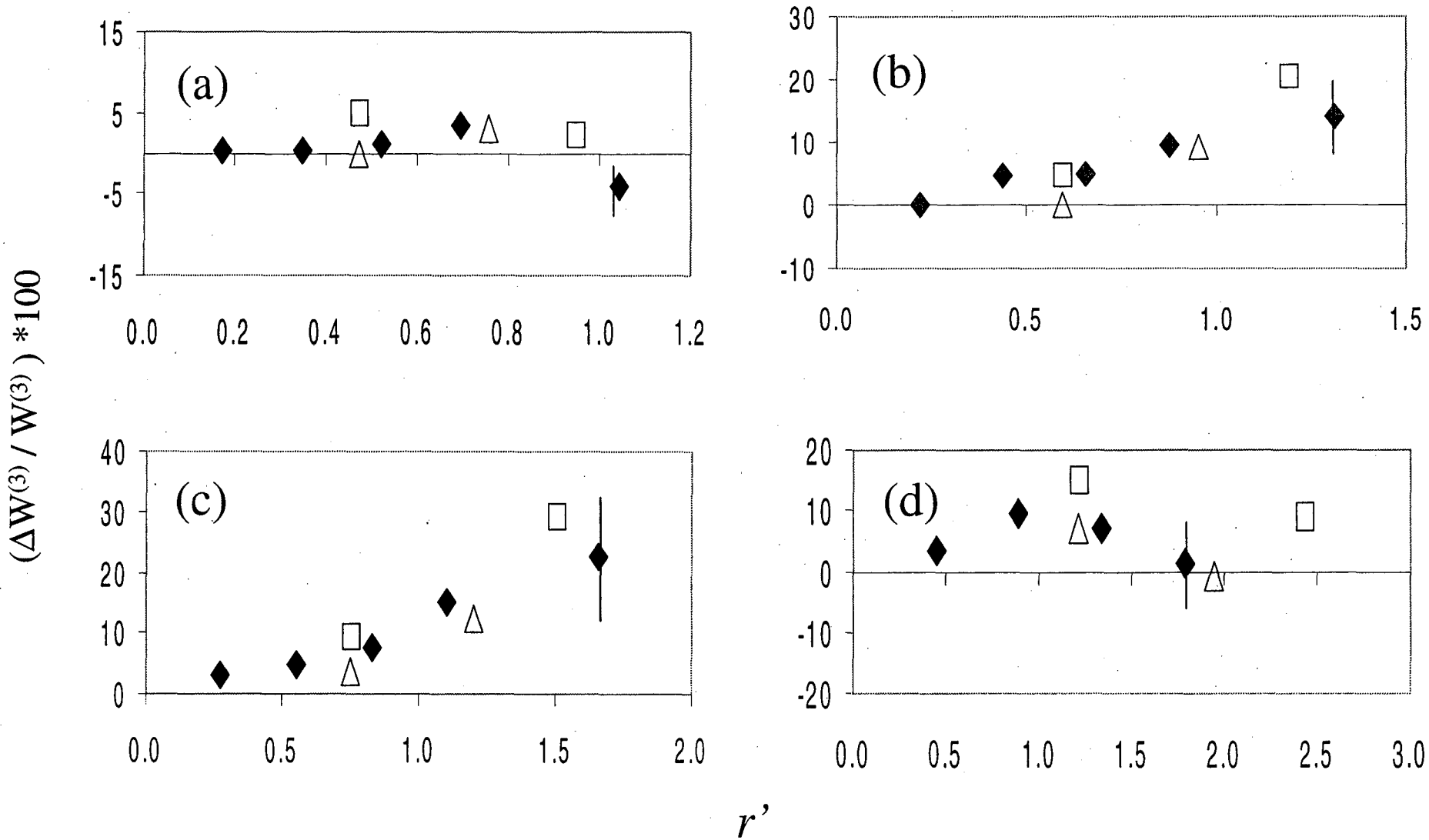

Fig. 5, Striolo et al., Pair-Wise Additivity...

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720

Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098