ESTIMATION OF EXCESS VOLUMES AND CHEMICAL REACTION PARAMETERS BY COMPUTER SIMULATIONS USING FUSED-HARD-SPHERE POTENTIALS

Ulrich K. Deiters
Institute of Physical Chemistry
University at Cologne
Luxemburger Str. 116
D-50939 Köln
Germany

Isobaric (NpT) Monte Carlo simulations of several mixtures consisting of fused-hard-sphere molecules have been performed from gas-like to liquid-like densities. For mixtures mimicking (xenon + alkane) mixtures thus excess volumes could be estimated. It turns out that a part of the experimentally observed excess volumes must be attributed to packing effects, and that these effects are sensitive to details of the geometric model.
It is demonstrated that Monte Carlo simulations of fused-hard-sphere molecules can be used to qualitatively predict reaction and activation volumes of some simple reactions, thus explaining the pressure dependence of product ratios.

Estimation de volumes d'excès et de paramètres de réaction par simulations numériques en utilisant les potentiels des sphères dures fondues

Les simlations numériques de Monte Carlo dans l'ensemble isobarique-isothermique NpT pour plusieurs mélanges constitués de molécules à sphères dures fondues ont été réalisées pour un domaine de densités allant du gaz au liquide. Donc, les volumes d'excès peuvent être estimés sur les mélanges que l'on identifie aux mélanges (xénon + paraffine). Il en résulte qu'une partie de volume d'excès observé expérimentalement doit être attribuée aux effets de tassement des molécules et que ces effets sont sensibles au modèles géométrique.
On démontre que les simulations Monte Carlo avec des molécules aux sphères dures fondues peuvent être utilisées pour des prévisions qualitatives des volumes de réaction et des volumes d'activation pour des réactions simples, en élucidant de cette façon la dépendance de la pression sur les rapports de produits.

Symbols

B	second virial coefficient
K	number of reactants
k	chemical reaction rate constant
N	number of particles
n	amount of substance
p	pressure
$\tilde{p}$	dimensionless pressure
R	gas constant
T	temperature
u	unit length of simulation (1 Å)
V	volume
$\Delta_r V$	reaction volume
x	mole fraction
ν_i	stoichiometric factor of species i
Z	compression factor
ξ_i	reduced density
σ	hard sphere diameter
Superscripts	
E	excess function
$\neq$	activation property
Subscripts	
e	educt; state before reaction
i	belonging to compound i
m	molar property
p	product; state after reaction
R	reactant
S	solvent

1. INTRODUCTION

While the early computer simulations were based on spherically symmetrical interaction potentials, nonspherical, more realistic potentials were tried out as soon as the computer power became sufficient. Thus a large amount of computer simulation data has become available over the years for simple electrostatic potentials (e.g., dipolar spheres, quadrupolar spheres). It was realized later that such models, while describing well some properties of polar fluids, usually failed to represent dielectric constants and other properties of dense liquids. This can be attributed to shape effects: Real molecules cannot rotate freely and align theirelectrical momenta in dense liquids. As soon as computer simulations take molecular shape into account, the prediction of electrostatic properties even of liquids becomes possible [1, 2].

Another branch of statistical thermodynamics has studied extensively convex bodies, and this has indeed become a very fruitful field of science [3-5]. Convex body fluids have been used to describe liquid crystals and polymer systems, to name only a few applications.

However, real molecules can usually not be regarded as convex bodies. On the other hand, because molecules are built of atoms, the geometric shape of many molecules can be represented reasonably well by fused-hard-sphere models. Since at high densities the structure of liquids is known to be dominated by repulsion forces, it should be possible to ne-

MOTS-CLÉS thermodynamique / thermodynamique statistique / simulation numérique utilisant les fused-hard-sphere potentiels / volume d'excès / volumes de réaction et d'activation

KEYWORDS thermodynamics / statistical thermodynamics / Monte Carlo computer simulation / fused-hard-sphere potentials / excess volume / reaction and activation volumes

glect attraction forces to some extent. Hence it should be possible to study packing efficiencies of liquid mixtures by computer simulations of fused-hard-sphere model fluids. Such calculations should give informations about the size of the contribution of geometry effects to the liquid excess volume, and about the degree of sophistication required in a molecular model to show these effects.

This work does not aim at the accurate reproduction of experimental liquid properties at low pressures; for such an attempt attractive forces have to be taken into account, e.g. in the form of multi-center Lennard-Jones potentials. It has to be noted, however, that the published interaction potentials usually treat a methyl or methylene group as a single interaction site (e.g. [6], thus simplifying molecular structure to some extent, and the effect of this simplification will be studied here.

2. EXCESS VOLUMES

2.1 Systems studied and models

In order to investigate shape effects on thermodynamic properties simple systems are probably most appropriate. Here mixtures of a spherical and a triangular molecule were chosen for which experimental data were available, namely (xenon + propane) and (xenon + cyclopropane). Xenon had been chosen as mixing partner, because its polarizability and attractive interaction potential corresponds to that of a methyl or methylene group; thus the influence of attractive forces on the liquid structure was minimized.

As explained above, the molecules of the mixtures studied here were represented by fused-hard-sphere models. Three different levels of detail were considered :

- level 1 : Whole molecules are represented by hard spheres.
- level 2 : In cyclopropane and propane each methyl or methylene group is represented by a hard sphere.
- level 3 : Each atom is represented by a hard sphere.

The coordinates of the atoms were obtained from empirical force-field calculations (program MM3 by Allinger et al. [7-9]). For the hard-sphere radii van der Waals radii by Ewsley [10] were used, reduced by approximately 10%. Previous simulations had shown that the densities calculated with these radii agreed best with the experimentally observed liquid densities.

For the simplified models 1 and 2 the hard-sphere radii were chosen in such a way that the volume of the resulting body was the same as that of the fused-hard-sphere body of the detailed approach 3. The hard-sphere radii used in this work are given in Table 1, the atom coordinates in Table 5.

atom/group	r^{hs}/ *A
C	1.800
H	1.170
He	1.200
Rn	3.000
CH_2, CH_3	1.916
C_3H_6	2.396

Table 1. Hard sphere (van der Waals) radii used in the simulations.

2.2 Simulation technique

The computer simulations were carried out by isobaric Monte Carlo technique with periodic boundary conditions [11]. The ensemble sizes were 256 or 512 molecules. After combined translation/rotation attempts for all molecules one volume change was attempted. The maximum displacements were automatically adjusted to maximize the mean square displacement, which usually led to acceptance ratios near 30%. In a similar way the maximum volume changes were optimized to give large volume fluctuations.

At the beginning of a simulation the molecules were placed at random into the simulation box at very low density; then the pressure was raised to a finite value, and the sample compressed to its equilibrium density. This way orientational correlation with the start configuration was completely avoided.

The orientational correlation between the molecules was also monitored in order to recognize states which no longer represented a true fluid.

A special problem of isobaric Monte Carlo simulations is the calculation of the average density, which is a fluctuating property. Here a block averaging method was used : The running density values were combined into blocks, with the block size being estimated from the number of Monte Carlo steps required for a density fluctuation. An average over all block densities was formed. The oldest block of the simulation run was compared to this average; if t-statistics showed it to be incompatible to the overall average, it was discarded. By this technique the equilibration phase was kept from influencing the final results.

The simulations were terminated when the statistical uncertainty of the density had dropped below a preselected margin. Typically the simulations required 2-3x10^5 Monte Carlo cycles, a cycle consisting of attempted displacements of all molecules and one volume change.

2.3 Results

In an isobaric Monte Carlo simulation of hard-body fluids the system pressure can be specified by the dimensionless reduced pressure

$$\tilde{p} = \frac{pu^3}{k_B T} \quad (1)$$

where u is the length unit (e.g., 1 Å). Evidently only the pressure/temperature ratio is significant for this kind of molecules. Another important property is the compression factor

$$Z = \frac{pV}{Nk_B T} = \tilde{p}\,\frac{V}{Nu^3} \qquad (2)$$

The last factor represents a volume per molecule, made dimensionless by the length unit. Introducing the hard-body van der Waals volume v^* then leads to

$$Z = \frac{\tilde{p}}{\xi}\,\frac{v^*}{u^3} \qquad (3)$$

where

$$\xi = \frac{Nv^*}{V} = \frac{N_A v^*}{V_m} \qquad (4)$$

is the reduced density.

The calculation of excess volumes requires simulations of the mixture with mole fraction x_1 and the pure fluids at the same reduced pressure :

$$V^E = V_{m,mix}(\tilde{p}) - \left(x_1 V_{m,1}(\tilde{p}) - x_2 V_{m,2}(\tilde{p})\right) \qquad (5)$$

The calculations are naturally very time-consuming.

The results are shown in Table 2. The excess volumes obtained from the detail level 2 and 3 models are very similar, but not the same. This shows that modelling atomic groups instead of single atoms is a simplification which does affect thermodynamic properties.

The level 1 model, which neglects all molecular shape, yields rather different excess volumes. Evidently, the shape of molecules has a strong influence on liquid structure.

For mixtures of hard spheres (the level 1 model) an equation of state has been derived from integral equation theory by Mansoori et al. [12]:

$$Z = 1 + \frac{E\xi + (2 - E + 3F)\xi^2 - F\xi^3}{(1-\xi)^3} \qquad (6)$$

with

$$E = 3\frac{h_1 h_2}{h_3} + 1$$

$$F = \frac{h_2^3}{h_3^2} - 1$$

$$h_k = \sum_i x_i \sigma_i^k$$

where σ is the particle diameter. This equation predicts that excess volumes should always be negative and approach zero with increasing pressure. The low-pressure limit of the excess volume can be derived from this equation via the second virial coefficients; for a binary mixture it amounts to

$$\lim_{\tilde{p}\to 0} V^E = x_1 x_2 (2B_{12} - B_{11} - B_{22})$$

$$= -\frac{\pi}{2} N_A x_1 x_2 (\sigma_2 - \sigma_1)^2 (\sigma_2 + \sigma_1) \qquad (7)$$

system	exp.	detail level → / $\tilde{p}$	3	2	1
			V^E/cm³ mol⁻¹		
xenon + cyclo-propane	0.76	0.001	− 0.15		− 0.30
		0.010	− 0.03		− 0.03
		0.020	− 0.16	− 0.10	
		0.050	− 0.18	− 0.10	0.01
		0.100	− 0.12	− 0.07	0.01
		0.200	− 0.10	0.01	
xenon + propane	− 0.30	0.020	− 0.04		
		0.050	− 0.16		
		0.100	− 0.02		
		0.200	− 0.07		

Table 2. Excess volumes of equimolar (xenon + hydrocarbon) mixtures. Experimental data taken at 183 K and ambient pressure (liquid phase).

and is evidently always negative.

A comparison with the simulation results in Table 2 and in Fig. 1 reveals that the simulations at detail level 1 agree well with Eqns. (7-6), but that the other simulations seem to deviate significantly at high pressures.

From this one has to conclude that equations of state which are based on the hard-sphere mixture theory do not capture details of liquid structure well enough to predict excess volumes of dense mixtures of nonspherical molecules.

There is a small, but significant difference between the results for detail levels 2 and 3: Combining groups of atoms into spheres does affect the simulations.

It must be noted that none of the models agrees fully with the experimental observations [13]. A part of the measured excess volumes can be attributed to packing effects, as shown by our simulations with fused-hard-sphere models; the larger part, however, is probably due to effects of attractive intermolecular forces.

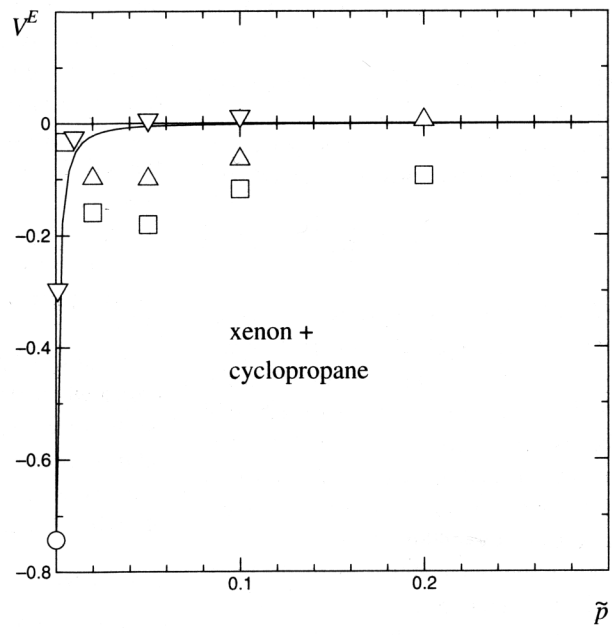

Fig. 1 *Excess volumes of equimolar (xenon + cyclopropane) mixtures: simulation results for fused-hard-sphere models. : – hard-sphere mixture equation of state, Eqn. (6), ○: theoretical limiting value, Eqn. (7), ▽ : simulation using single sphere model (detail level 1), △ : sphere per group model (detail level 2), □: sphere per atom model (detail level 3).*

Conversely, a theory or an equation of state that ignores the shape of molecules will probably fail to account fully for the experimentally observed values of excess volumes.

It is remarkable that the systems (xenon + propane) and (xenon + cyclopropane) have rather different excess volumes (0.30 and 0.76 $cm^3 mol^{-1}$, resp.), although the sizes and the shapes of the hydrocarbons are rather similar. These experimental observations are not reflected by the simulations at detail level 2 and 3 : The simulated excess volumes are always close to 0.1 $cm^3 mol^{-1}$ for both systems. One has to conclude that shape effects are probably responsible for a small part of the experimentally observed excess volumes. Furthermore, detail level 2 does not make any distinction between staggered conformations (as in propane) and eclipsed conformations (as in cyclopropane). It must be concluded therefore that these conformational details are of minor importance to computer simulations.

3. ACTIVATION VOLUMES

3.1 Volume effects in chemical reactions

An especially useful application of Monte Carlo simulation is the calculation of volume changes and activation volumes of chemical reactions — or at least the part of these volumes which can be related to packing effects. Because the concentrations in a reacting mixture cannot be changed freely and some constituents may be short-lived, the experimental determination of volume effects is sometimes rather difficult.

Generally, a chemical reaction between K species A_i can be written as

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightarrow \ldots + \nu_{K-1} A_{K-1} + \nu_K A_K \quad (8)$$

where the ν_i denote the stoichiometric coefficients (negative for educts, positive for products).

An important intermediate property for calculations of reaction parameters is the partial molar volume of a component i

$$V_i = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{k\neq i}} \quad (9)$$

which is related to the reaction volume by

$$\Delta_r V_m = \sum_i^K \nu_i V_i \quad (10)$$

where the summation involves all species connected by the reaction.

It is formally possible to regard the transition state of a chemical reaction as a (shortlived) chemical species. Hence it is possible to assign a reaction volume to the activation step of a chemical reaction. This transitional reaction volume is also known as the activation volume of the reaction, which is experimentally accessible through the pressure dependence of reaction rate constant :

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{V^{\neq}}{RT} \quad (11)$$

An important point is now that the partial molar volumes, which are underlying the reaction volume as well as the activation volume, are not necessarily identical with the molar volumes, van der Waals volumes or similar characteristics of the pure species. Instead they are configurational properties, which can be obtained through computer simulations.

3.2 Systems studied and simulation technique

An interesting system, which has been studied experimentally by Klärner et al. [14] in great detail, is the dimerization of 1,3-butadiene, which can take place either as a synchronous pericyclic reaction leading to 4-vinylcyclohexene, or as a sequential reaction involving a diradical intermediate and producing divinylcyclobutane or cyclooctadiene (see Fig. 2 for the structural formula). By isotopic substitution it could furthermore be shown that there are, in fact, two different reaction paths for the synchronous reaction, one having an *exo* configuration of the transition state, the other one an *endo* configuration. All these products are observed, with vinylcyclohexene being the dominant species at ambient pressure.

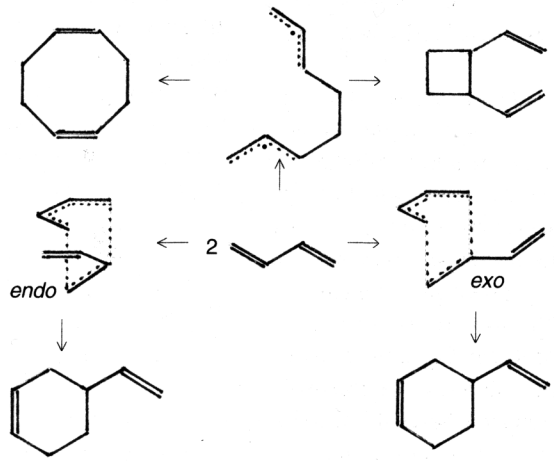

Fig. 2 Reaction paths of the dimerization of 1,3-butadiene

The van der Waals volumes of the transition states were calculated by a bisection algorithm. It turns out that they are almost the same (compare Table 3), and one might expect from this that the product ratio is little affected by pressure. This, however, is in contrast to the experimental observations : At pressures around 600 MPa the product reached via the *endo*-shaped transitional state is clearly favoured.

In order to explain this effect, isobaric Monte Carlo simulations of various reaction mixtures were performed. Again the molecules involved were represented by fused-hardsphere models, with each atom represented by a hard sphere. The molecular structures were obtained from a semiempirical force-field program [7-9] ; the

atom coordinates are given in Table 5 Because of the relatively small number of molecules in the simulations only conformers of minimal energy were used (e.g., butadiene assumed to be in s-trans conformation), and no attempt was made to account for conformer equilibria.

The simulation ensembles contained $N_S = 208$ solvent molecules and either $2N_R = 48$ butadiene molecules (in s-trans conformation) or $N_R = 24$ dimers (transition states or product molecules). Activation or reaction volumes were then estimated by

$$\Delta V = \frac{1}{N_R}\Big(\big(N_R + N_S\big)V_{m,p} - \big(2N_R + N_S\big)V_{m,e}\Big) \quad (12)$$

where $V_{m,e}$ and $V_{m,p}$ denote the molar volumes of the educt mixture (solvent + butadiene) or of the product mixture, respectively.

Further details of the simulation and of the estimation of partial molar volumes have been given elsewhere [14].

3.3 Results

Two series of computer simulations were carried out for the butadiene dimerization study: In the first series it was assumed that the solvent is butadiene, too, i.e., the reaction takes place in compressed butadiene. In the second series a noble gas (modelled as single hard spheres) was used as solvent.

The results are shown in Table 4 for a reduced pressure of $\tilde{p} = 0.1$, which corresponds to a dense liquid state : The reaction volumes are strongly negative, which explains why this type of reaction is best carried out at high pressures. The simulated activation volumes differ from the experimental values systematically, which is to be expected from the too simple interaction model. But it is evident that the simulations indicate that the *endo* transition state has the smallest activation volume and that hence this reaction path it the most favoured at high pressures.

The simulations furthermore predict that the dominance of the *endo* reaction path will practically vanish, if the reaction is carried out in a solution with spherical solvent molecules. Here helium as well as radon were used in the simulations. The latter is not expected to be a practically useful solvent ; it was merely chosen because it is the biggest spherical molecule. It is interesting to observe that the size of the solvent molecules has little effect on the stereospecificity of the reaction path : The *endo* state is only preferred if the solvent is nonspherical. Unfortunately, experimental results for the butadiene dimerization in noble gases as solvents have not been reported in literature, yet.

molecule	V_{vdW}/Å^3
1,3-butadiene	72.27
endo transition state	135.25
exo transition state	135.33
diradical transition state	137.07
4-vinylcyclohexene	128.70
1,2-divinylcyclobutane	131.62
1,5-cyclooctadiene	127.25

Table 3. Van der Waals volumina of the fused-hard-sphere models.

4. SUMMARY

Simulations using fused-hard-sphere molecular models are easier to carry out and use less computer time than simulations with realistic attractive interactions potentials, but nevertheless are able to account for a small, but significant part of excess volumes in liquid mixtures. It is shown that the simulation results deviate from equation of state calculations at high densities: These predict that excess volumes should vanish for high pressures, which is not confirmed by the simulations. Evidently hard-sphere mixture equations of state cannot represent the fluid structure well enough to give reliable predictions of excess volumes at high pressures.

It is possible to estimate partial molar volumes, reaction volumes, and activation volumes of chemically reacting systems. Again, the simulations cannot capture all contributions to these properties, but it is possible to judge from differences of activation volumes, which reaction paths become more favoured at high pressures. It is furthermore possible to assess the effect of solvent shapes on activation and reaction volumes, which opens ways to control the product spectra of chemical reactions.

product	$\Delta_r V_m$/cm^3 mol^{-1} simulated	$\Delta_r V_m$/cm^3 mol^{-1} experimental
	solvent : butadiene	
endo transition state	– 32.8	– 27.9
exo transition state	– 30.8	– 25.4
diradical transition state	– 13.5	– 14.6
4-vinylcyclohexene	– 35.4	– 33.5
1,2-divinylcyclobutane	– 29.8	– 24.2
1,5-cyclooctadiene	– 40.0	– 43.5
	solvent : helium	
endo transition state	– 12.8	
exo transition state	– 12.8	
diradical transition state	– 11.8	
	solvent : radon	
endo transition state	– 13.9	
exo transition state	– 13.3	
diradical transition state	– 12.8	

Table 4. Activation and reaction volumes of the butadiene dimerization. Simulated: isobaric Monte Carlo simulation at reduced pressure $\tilde{p}$ = 0.1; experimental: at 393 K [1].

x/Å	y/ Å	z/Å	r/Å
	helium		
0.00000	0.00000	0.00000	1.200
	xenon		
0.00000	0.00000	0.00000	2.100
	radon		
0.00000	0.00000	0.00000	3.000
	cyclopropane (level 1)		
0.00000	0.00000	0.00000	2.396
	cyclopropane (level 2)		
– 0.14992	– 0.62676	0.40787	1.916
– 0.14991	0.87186	0.40787	1.916
– 0.58252	0.12255	0.81574	1.916
	cyclopropane (level 3)		
– 0.14992	– 0.62676	0.40787	1.800
– 0.14991	0.87186	0.40787	1.800
– 0.58252	0.12255	– 0.81574	1.800
– 0.88798	– 1.17410	1.00399	1.170
0.79881	– 1.17410	0.40763	1.170
0.79882	1.41920	0.40762	1.170
– 0.88797	1.41921	1.00399	1.170
0.05020	0.12255	– 1.70980	1.170
– 1.63659	0.12255	– 1.11343	1.170
	propane (level 3)		
– 0.70744	– 0.86237	0.00000	1.800
– 0.73664	0.64958	0.00000	1.800
– 2.15240	1.18109	0.00000	1.800
0.32183	– 1.24295	0.00000	1.170
– 1.21078	– 1.27610	0.88396	1.170
– 1.21079	– 1.27610	– 0.88396	1.170
– 0.18928	1.03663	0.88190	1.170
– 0.18927	1.03663	– 0.88189	1.170
– 2.16813	2.27837	0.00000	1.170
– 2.71024	0.84445	– 0.88396	1.170
– 2.71025	0.84445	0.88396	1.170
	s-trans-1,3-butadiene		
0.00000	0.00000	0.00000	1.170
0.00000	0.00000	5.59363	1.170
1.56929	0.00000	1.04303	1.170
– 0.46830	0.00000	4.59573	1.800
0.46830	0.00000	0.99789	1.800
0.28217	0.00000	3.47794	1.800
– 1.38129	0.00000	2.02000	1.170
1.38130	0.00000	3.57362	1.170
– 0.28216	0.00000	2.11568	1.800
– 1.56928	0.00000	4.55059	1.170
	exo transition state		
– 1.81943	0.64905	0.21782	1.800
– 1.80496	1.05761	– 1.12734	1.800
– 0.63762	1.43263	– 1.76540	1.800
0.50996	– 0.55014	– 1.29974	1.800
0.44173	– 0.90303	0.05677	1.800
– 0.67124	0.59734	0.98701	1.800
1.67862	– 0.79979	0.88866	1.800
1.79552	– 1.41775	2.06463	1.800
– 2.77460	0.31819	0.65831	1.170
– 2.74516	1.03459	– 1.70241	1.170
– 0.59383	1.36849	– 2.86396	1.170
0.02657	2.16838	– 1.28691	1.170
1.45374	– 0.13721	– 1.68822	1.170
– 0.07107	– 1.15910	– 2.01074	1.170
– 0.24987	– 1.72708	0.30054	1.170
0.01860	1.45358	0.93314	1.170
– 0.77452	0.15842	1.99239	1.170
2.52309	– 0.19100	0.52262	1.170
0.97398	– 2.03267	2.46638	1.170
2.72047	– 1.32050	2.65646	1.170

Table 5. Atom or group coordinates and radii of the fused-hard-sphere molecular models used in the simulations

5. ACKNOWLEDGMENTS

The author wishes to thank Dr. E. J. M. Filipe, Instituto Superior Técnico, Lisbon (Portugal), and Prof. Dr. F.-G. Klärner, University of Essen (Germany) for granting access to unpublished material and for helpful discussions. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] Hloucha, M. and Deiters, U. K., *Monte Carlo simulations of acetonitrile with an anisotropic polarizable molecular model*. Mol. Phys. 90 (1997) 593-597.

[2] Hloucha, M. and Deiters, U. K., *Monte Carlo study of the thermodynamic properties and the static dielectric constant of liquid trifluoromethane*. Fluid Phase Equil. 149 (1998) 41-56.

[3] Boublik, T., *Equation of state for hard convex body fluids*. Mol. Phys. 42 (1981) 209-216.

[4] Boublik, T., *Statistical thermodynamics of nonspherical molecule fluids*. Ber. Bunsenges. Phys. Chem. 85 (1981) 1038-1041.

[5] Boublik, T., *Third virial coefficient and the hard convex body equation of state*. Mol. Phys. 83 (1994) 1285-1297.

[6] Jorgensen, W. L., Madura, J. D., and Swenson, C. J., *Optimized interaction potential functions for liquid hydrocarbons*. J. Amer. Chem. Soc. 106 (1984) 6638-6646.

[7] Allinger, N. L., Yuh, Y. H., and Lii, J.-H., *Molecular Mechanics. The MM3 force field for hydrocarbons*. 1. J. Amer. Chem. Soc. 111 (1989) 8551-8566.

[8] Lii, J.-H. and Allinger, N. L., *Molecular Mechanics. The MM3 force field for hydrocarbons. 2. Vibrational frequencies and thermodynamics*. J. Amer. Chem. Soc. 111 (1989) 8566-8575.

[9] Lii, J.-H. and Allinger, N. L., *Molecular Mechanics. The MM3 force field for hydrocarbons. 3. The van der Waals' parameters and crystal data for aliphatic and aromatic hydrocarbons*. J. Amer. Chem. Soc. 111 (1989) 8576-8582.

[10] Ewsley, J., *Die Elemente*. de Gruyter, Berlin, 1994.

[11] Allen, M. P. and Tildesley, D., *Computer Simulation of Liquids*. Clarendon Press, Oxford, 1987.

[12] Mansoori, G. A., Carnahan, N. F., Starling, K. E., and Leland, T. W., *Equilibrium properties of the mixture of hard spheres*. J. Chem. Phys. 54 (1971) 1523-1525.

[13] Filipe, E. J. M., Pereira, L. A. M., Dias, L. M. B., Calado, J. C. G., Sear, R. P., and Jackson, G., *Shape effects in molecular liquids: Phase equilibria of binary mixtures involving cyclic molecules*. J. Phys. Chem. B 101 (1997) 11243-11248.

[14] Klärner, F.-G., Krawczyk, B., Ruster, V., and Deiters, U. K., *Evidence for pericyclic and stepwise processes in the cyclodimerization of chloroprene and 1,3-butadiene from pressure-dependence and stereochemistry. Experimental and theoretical volumes of activation and reaction*. J. Amer. Chem. Soc. 116 (1994) 7646-7657.

x/Å	y/ Å	z/Å	r/Å
	endo transition state		
1.71861	4.42937	2.82541	1.800
2.38227	4.73129	1.62395	1.800
3.75479	4.47239	1.44736	1.800
3.83246	2.40643	1.60010	1.800
3.20265	1.94847	2.76762	1.800
2.39132	3.84602	3.91570	1.800
1.88468	1.26779	2.77862	1.800
0.96908	1.35450	1.81261	1.800
0.63320	4.60662	2.89788	1.170
1.79993	5.14038	0.78212	1.170
4.15789	4.59765	0.42978	1.170
4.43998	4.77607	2.25347	1.170
4.92978	2.30886	1.57850	1.170
3.35540	2.16150	0.63972	1.170
3.85927	1.73430	3.62724	1.170
3.34689	4.27916	4.24788	1.170
1.79533	3.32996	4.68454	1.170
1.64546	0.64890	3.66063	1.170
1.13123	1.96280	0.90970	1.170
0.01360	0.81296	1.90794	1.170
	diradical transition state		
2.26801	4.85614	6.58984	1.800
3.09090	5.78321	7.25067	1.800
4.45881	5.57709	7.50752	1.800
5.20860	4.33287	7.10250	1.800
6.71228	4.40422	7.41633	1.800
7.44336	5.41343	6.56724	1.800
8.83026	5.63735	6.64034	1.800
9.68959	4.95459	7.51679	1.800
2.64292	3.88814	6.22262	1.170
1.20189	5.07783	6.42013	1.170
2.62811	6.72696	7.58608	1.170
5.00670	6.36555	8.04876	1.170
5.06760	4.14573	6.01197	1.170
4.76617	3.47074	7.65581	1.170
6.86026	4.64641	8.49509	1.170
7.16238	3.40071	7.22799	1.170
6.86290	6.00671	5.84205	1.170
9.27820	6.39314	5.97289	1.170
9.33031	4.18534	8.21799	1.170
10.76905	5.17646	7.52584	1.170
	4-vinylcyclohexene		
0.04697	0.01293	– 0.00025	1.800
– 0.33979	– 0.48688	1.40228	1.800
0.85757	– 0.72266	2.28378	1.800
2.11482	– 0.79250	1.82235	1.800
2.46659	– 0.64511	0.36715	1.800
1.23377	– 0.80468	– 0.53334	1.800
0.37038	1.48855	– 0.00180	1.800
0.17499	2.28889	– 1.05493	1.800
– 0.82711	– 0.13913	– 0.68047	1.170
– 0.87968	– 1.46003	1.32425	1.170
– 1.03562	0.23889	1.88555	1.170
0.67105	– 0.84986	3.36440	1.170
2.94503	– 0.95703	2.53112	1.170
2.93942	0.35414	0.22029	1.170
3.22432	– 1.41641	0.09129	1.170
1.48264	– 0.50554	– 1.57985	1.170
0.93899	– 1.88125	– 0.56693	1.170
0.80292	1.91724	0.91834	1.170
– 0.24629	1.90031	– 2.00027	1.170
0.43256	3.35979	– 1.01864	1.170
	trans-1,2-divinylcyclobutane		
0.00000	0.00000	0.00000	1.170
0.00000	0.00000	6.98409	1.170
4.11324	0.00000	2.34166	1.170
1.23911	– 0.13244	5.26660	1.800
3.92936	0.69172	3.95109	1.170
3.36689	– 1.67594	4.66489	1.170
0.56355	– 1.24007	3.75230	1.170
2.21596	– 0.21756	0.66591	1.170
3.41705	0.04895	3.20495	1.800
– 0.64218	– 1.07000	5.55722	1.170
2.89736	– 1.30787	3.72873	1.800
1.94998	0.42954	2.87376	1.800
0.26677	0.23461	1.04101	1.800
0.13763	– 0.41664	5.97545	1.800
1.53454	0.12059	1.46047	1.800
2.96716	– 2.15834	3.01867	1.170
1.60253	1.47232	2.91700	1.170
– 0.52251	0.56421	1.73262	1.170
1.92520	0.53058	5.81402	1.170
1.49345	– 0.66691	3.88181	1.800
	1,5-cyclooctadiene (chair)		
– 1.36895	– 0.38726	0.84424	1.800
– 0.71793	1.09573	– 1.20741	1.800
0.98280	– 0.79516	– 1.06705	1.800
1.08035	0.01398	1.41663	1.800
– 2.23367	– 0.60840	1.50432	1.170
– 2.26715	1.47074	0.20214	1.170
– 0.81148	2.05106	– 1.74462	1.170
0.14218	– 1.51083	– 0.95080	1.170
2.70636	– 0.12434	0.05120	1.170
1.64483	0.50048	2.22575	1.170
– 1.78135	0.58866	– 0.26504	1.800
0.45078	0.52757	– 1.54515	1.800
1.75680	- 0.66366	0.25076	1.800
– 0.23141	0.14410	1.67185	1.800
– 1.08206	– 1.36719	0.40862	1.170
– 2.57629	0.11343	– 0.87706	1.170
0.99762	1.17565	– 2.24585	1.170
1.63063	– 1.23800	– 1.85226	1.170
2.06611	– 1.67698	0.58218	1.170
– 0.38103	0.71220	2.60184	1.170

Table 5. (Continued) Atom or group coordinates and radii of the fused-hard-sphere molecular models used in the simulations