

Molecular dynamics simulations of real systems: application to chloro-fluoro-hydrocarbons and polymers

Maurizio Fermeglia^{*}, Sabrina Pricl

Department of Chemical, Environmental and Raw Materials Engineering (DICAMP), University of Trieste, Piazzale Europa 1, I-34127 Trieste, Italy

Received 25 May 1998; accepted 9 October 1998

Abstract

The present paper reports the results obtained from MD calculations on the following systems: (1) chloro-fluoro-hydrocarbons (CFHs) of widespread use in the refrigerant industry (e.g., R22, R32, R123, etc.) and (2) selected polymers of industrial applications. In the case of CFHs, force field and quantum-mechanical techniques were employed in molecular modeling and for the calculation of geometrical and chemico-physical parameters. The Connolly surface algorithm, corrected for quantum-mechanical effects, was used in the evaluation of molecular surfaces and volumes. From these data, the parameters of the perturbed hard sphere chain equation of state, V^* and A^* , were obtained. The third parameter, E^* , was calculated from extensive MD simulations under NPT conditions. For polymers, a more complicated preliminary procedure was necessary to model realistic amorphous polymeric chains. The Lattice Fluid equation parameters were then calculated from thorough MD simulations both under NVT and NPT conditions. The predicted thermophysical properties of both classes of substances are then discussed and compared with the relevant experimental data, were available. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Molecular simulation; Equation of state; Molecular dynamics; Refrigerants; Polymers; Thermophysical properties

1. Introduction

During the last decades, computer experiments based on molecular/quantum mechanics (MM/QM) calculations and molecular dynamics (MD) simulation techniques have opened avenues in the calculations and predictions of both equilibrium and nonequilibrium thermophysical properties of small molecules and of long polymeric chains as well. The method of MD solves Newton's equations of motion for a given molecular system, which results in trajectories for all the atoms in the system.

^{*} Corresponding author. Tel.: +39-40-6763438; fax: +39-40-569823; e-mail: mauf@dicamp.univ.trieste.it

From these atomic trajectories, a plethora of thermophysical properties can then be calculated as time averages from the relevant microscopic relationships expressed in terms of molecular positions and momenta.

The major contributions a microscopic consideration can afford are (a) the understanding and (b) interpretation of experimental results; (c) semiquantitative estimates of experimental results and, last but not least, (d) the possibility to interpolate or extrapolate experimental data into regions that are only difficultly realizable, if at all, in the laboratory.

Further, from this type of virtual experiments it should be possible, in principle, to extract the characteristic parameters of some equation of state (EOS), thus avoiding tedious experimental effort for determining PVT isotherms and vapour pressure as a function of temperature. As an exploratory work to combine the technique of molecular mechanics/molecular dynamics techniques and the EOS theory, we developed a strategy to calculate the perturbed hard sphere chain (PHSCT) EOS parameters A^* , V^* and E^* for CFHs and, for polymers, the Lattice Fluid (LF) EOS parameters P^* and ρ^* . Even though specific equations of state have been considered in this work, the proposed procedure holds an absolutely general character and can be applied to any equation of state, provided the pure component parameters have a sound and well defined physical meaning.

In our opinion, this procedure could be of great help in integrating molecular dynamics techniques and process simulators, particularly in those cases where EOS parameters must be obtained for molecules with scarce if not absent experimental data sets available.

2. Experimental

All calculations were run on a Silicon Graphics Origin 200 (microprocessor MIPS RISC 10000, 64 bit CPU, 128 MB RAM). The commercial software *Cerius*² from Molecular Simulation was used for both MM/QM and MD simulations. The CFHs molecules were built and their geometry optimized via MM using the COMPASS force field. The COMPASS FF is an augmented version of the CFF series of forcefields [1], and is the first ab initio forcefield that has been parametrized and validated using condensed-phase properties in addition to various ab initio and empirical data for molecules in isolation. The molecules were modeled to have a total charge equal to zero, and the distribution of the partial charge within each molecule was determined by the charge equilibration method of Rappé et al. [2] Energy was minimized by up to 5000 Newton–Raphson iterations. Following this procedure, the root-mean-square atomic derivatives in the low energy regions were smaller than 0.05 kcal/mole Å. Long-range nonbonded interactions were treated by applying suitable cut-off distances, and to avoid the discontinuities caused by direct cutoffs, the cubic spline switching method was used. Other chemico-physical parameters were obtained by the semi-empirical quantum-mechanical algorithm MOPAC (v. 6.0), using the AM1 method and the BFGS procedure with the PRECISE option selected to ensure an adequate convergence criterion. Following this protocol, the maximum residual internal coordinate forces on the optimized coordinates were always less than 3×10^{-4} hartee/bohr. The stopping criterion for the SCF iterative process required a density matrix convergence of less than 10^{-8} .

The calculation of molecular surfaces were performed using the so-called Connolly dot surfaces algorithm [3]. Accordingly, a probe sphere of a given radius, representing the solvent molecule, is placed tangent to the atoms of the molecule at thousands different positions. For each position in which the probe does not experience van der Waals overlap with the atoms of the molecule, points

lying on the inward-facing surface of the probe sphere become part of the molecule *solvent-accessible surface*. According to this procedure, the molecular surface generated consists of the van der Waals surface of the atoms which can be touched by a solvent-sized probe sphere (thus called *contact surface*), connected by a network of *concave* and *saddle surfaces* (globally called *reentrant surface*), that smooths over crevices and pits between the atoms of the molecule. The sum of the contact and the reentrant surface form the so-called *molecular surface (MS)*; this surface is the boundary of the *molecular volume (MV)* that the solvent probe is excluded from if it is not to undergo overlaps with the molecule atoms, which therefore is also called *solvent-excluded volume*. Finally, performing the same procedure by setting the probe sphere radius equal to zero, the algorithm yields the *van der Waals surface (WS)*.

If the Connolly algorithm can be considered a good technique for calculating molecular surfaces, the same procedure has been proved to be less accurate for the determination of molecular volumes. Indeed, it has been observed that the molecular volumes derived using algorithms based on van der Waals radii are generally 30% lower than the experimentally determined volumes for small molecules [4]. Accordingly, for the calculation of the CFHs molecular volumes, we employed a method based on semiempirical molecular orbital calculations. First, the electron density distribution of the molecule was accomplished using the AM1 algorithm. The software calculates the electron density of the molecule at each point of a grid covering the molecule, allowing the grid size and the space between grid points to be varied. Since the orientation of the molecule within the grid can also be varied, the errors that occur from using a grid of a specific spacing and size can be quantified. The electron density value for each point of the grid was then used to calculate the volume of each molecule as a function of the percentage of the total, calculated electronic density, according to a calculation technique proposed by Rellick and Becktel [4]. In this way, no assumption was made about the value of the radii of individual atoms or groups of atoms. Fig. 1 reports an example of a Connolly surface for the refrigerant R123.

For the calculation of the thermophysical properties of CFHs, 256 molecules were confined in a cubic box with periodic boundary conditions; in order to minimize the artifact of periodicity for liquids and gases, a cut-off distance was set equal to half the box length. The resultant structures were relaxed via MM, using the COMPASS FF; in this case, the Ewald technique was employed in handling nonbonded interactions.

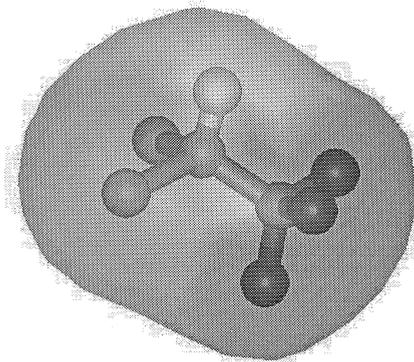


Fig. 1. Connolly surface obtained for R123.

Temperature was controlled via weak coupling to a temperature bath [5], with coupling constant $\tau_T = 0.01$ ps, whereas pressure was kept constant by coupling to a pressure bath [6], with relaxation time $\tau_p = 0.1$ ps. The relevant equations of motion were solved by the Verlet leapfrog algorithm, using an integration step of 1 fs. Each MD run consisted in a system equilibration phase, during which the equilibration process was followed by monitoring the behavior of both kinetic and potential energy and the time evolution of density, and a successive data collection phase. For the CFH liquid state simulation, the energy components as well as density have ceased to show a systematic drift and have started to oscillate about steady mean values around 30 ps. Even smaller times were required to equilibrate the vapor/gas phase. Accordingly, equilibration phases longer than 50 ps and data acquisition runs longer than 300 ps were judged not necessary to enhance data accuracy.

In the case of polymers, the constitutive repeating unit was first built and modeled via the COMPASS FF and then polymerized to a DP = 100. Six different amorphous structures for each polymeric chain were generated via the Rotational Isomeric State algorithm (RIS), at $T = 300$ K, packed into a cubic simulation box with 3-D periodicity and relaxed via the PCFF FF to minimize energy and avoid atom overlaps. The PCFF is an ab initio class 2 forcefield, in which the resulting energy surfaces are scaled using experimental data to reduce the systematic errors due to the approximations in the ab initio methods [7]. The bond terms of the PCFF functional form include a quartic polynomial both for bond stretching and angle bending, a three-terms Fourier expansion for torsions and a Wilson out-of-plane coordinate term. Six crossterms up through 3rd order are present to account for coupling between the intramolecular coordinates. The final two nonbonded terms represent the intermolecular electrostatic energy and the van der Waals interactions, respectively; the latter employs an inverse 9th power term for the repulsive part rather than the more customary 12th power term. The relaxed structures were subjected to simulated annealing (5 repeated cycles from 300 K to 1000 K and back) to overcome the local minimum energy barriers using a NVT-MD conditions. At the end of each annealing cycle, the structures were relaxed via FF, allowing the box dimensions to vary. The conformation corresponding to minimum energy was extracted for further simulation. A long single chain instead of many shorter chains was selected for simulation in order to avoid the unusual distribution of free volumes due to chain several chain ends.

From the fully relaxed models of the corresponding polymeric chains, isothermal-isobaric MD experiments were run from 300 to 50 K at intervals of 50 K; the information at 0 K, needed for the polymer pure component parameters estimation, was then collected by extrapolation. The NPT MD runs at each temperature were performed under the same conditions described for the CFHs molecules. Also in this case, a preliminary run of 50 ps was sufficient to equilibrate the system and a data collection phase extended up to 300 ps was considered adequate to obtain the required information.

3. Theory

A very brief description of the equations of state considered in this work and commonly employed in process simulators (i.e., the simplified PHSC theory and the Lattice Fluid theory) will now be presented.

The equation of state used for CFHs is based on the simplified PHSCT [8–11] in which the molecule is considered being constituted by chains of freely jointed tangent hard spheres. The PHSCT

Table 1

Molecular geometries and general properties for a selected list of CFHs. Available experimental values are reported in parenthesis for comparison

CFHs		I.P. (eV)	μ (D)	ΔH_{form} (kcal/mole)
<i>R32</i>				
C–H	1.099 (1.093)			
C–F	1.355 (1.357)	12.02 (12.71)	2.041 (1.978)	– 106.0 (– 108.0)
FCF	108.3° (108.3°)			
HCF	109.5° (108.7°)			
<i>R143a</i>				
C–H	1.091 (1.081)			
C–F	1.338 (1.340)	13.10 (12.90)	2.329 (2.347)	– 172.6 (– 177.9)
C–C	1.510 (1.494)			
FCF	108.0°			
CCH	111.2° (112°)			
HCH	107.9°			
<i>R22</i>				
C–H	1.267			
C–F	1.368			
C–Cl	1.809	12.3 (12.2)	1.47 (1.42)	– 114.2 (115.3)
FCF	109.2°			
FCCl	112.5°			
HCCl	105.1°			

I.P. = ionization potential.

EOS has been developed starting from the modified Chiew equation of state for hard-sphere chains as the reference term [12], a van der Waals type perturbation term and the Song–Mason method to relate equation of state parameters to the intermolecular potential [8]. More details on this model, as developed for applications to refrigerant and hydrocarbons, we refer to our previous papers [13,14].

The relevant equation in terms of pressure is expressed as:

$$\left(\frac{P}{\rho kT} \right) = 1 + r^2 b \rho g(d^+) - (r-1) [g(d^+) - 1] - \frac{r^2 a \rho}{kT} \quad (1)$$

where P is the pressure, T the absolute temperature, $\rho = N/V$ the number density, N the number of molecules, V the volume of the system, k the Boltzmann's constant, d the hard-sphere diameter and $g(d^+)$ the pair radial distribution function of hard spheres at contact. Three parameters appear in Eq. (1), all with a well defined physical meaning: respectively, the number of effective hard spheres per molecule (r), the intermolecular potential-well depth between a nonbonded pair of segments (a) and the segmental diameter (b). To obtain an engineering-oriented equation of state, a redefinition of the EOS parameters has been performed [13], expressing the parameters with quantities reflecting the size, shape and energetic interactions of the fluids considered as follows:

$$V^* = (\pi/6) r \sigma^3 N_A \quad (2)$$

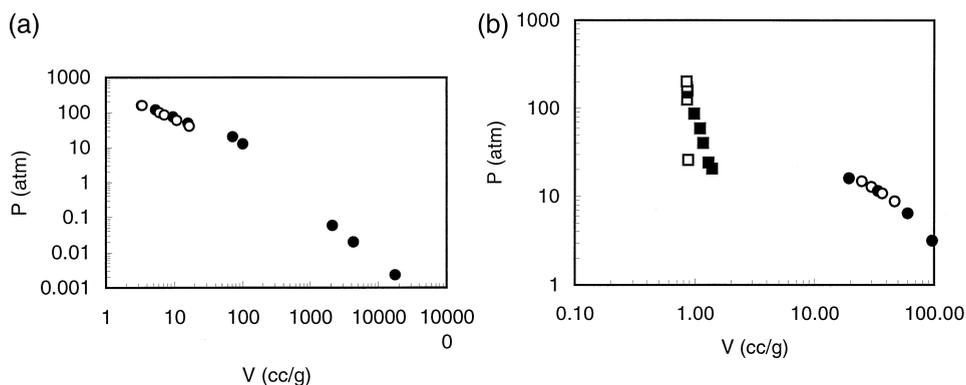


Fig. 2. Comparison between simulated (filled symbols) and experimental (open symbols) PVT behavior for R32. (a) $T = 298.16$ K; (b) 473.16 K. Experimental data from Ref. [20].

where N_A is Avogadro's constant; a characteristic surface area, A^* :

$$A^* = \pi r \sigma^2 N_A \quad (3)$$

and a characteristic 'cohesive' energy, E^*

$$E^* = r(\varepsilon/k)R_g \quad (4)$$

where R_g is the gas constant.

According to our procedure, the three EOS parameters can be estimated as follows: from the values of molecular areas and volumes calculated via the corrected Connolly algorithm and normalized with respect to methane ($r = 1$), the relevant r and σ values can be calculated and, accordingly, A^* and V^* can be obtained by means of Eqs. (2) and (3). The parameter ε/k is obtained from MD as the ratio of the equilibrium value of the potential and kinetic energy at the given temperature; thus, E^* is easily obtained by Eq. (4). An alternative way to estimate E^* is to insert the calculated A^* and V^* into Eq. (1), together with a PVT data set generated by MD.

Table 2

Simulated PVT data for R32 at $T = 298.16$ K and $T = 473.16$ K

$T = 298.16$ K (subcritical)			$T = 473.16$ K (supercritical)	
P (atm)	V (cc/g)	Phase	P (atm)	V (cc/g)
16.1	19.44 ± 0.11	v	121.2	5.30 ± 0.056
11.6	33.78 ± 0.34	v	75.0	9.52 ± 0.14
6.45	60.23 ± 0.72	v	49.6	15.8 ± 0.10
3.17	96.15 ± 1.4	v	20.7	71.4 ± 1.0
1.38	20.76 ± 0.10	l	12.8	100 ± 2.0
1.30	24.30 ± 0.10	l	0.0588	2083 ± 14
1.17	40.24 ± 0.32	l	0.0200	4255 ± 16
1.10	58.57 ± 0.56	l	0.00237	17544 ± 130
0.98	85.70 ± 1.3	l		
0.87	156.5 ± 2.0	l		

Table 3

Calculated molecular areas, volumes and PSHCT EOS parameters for a selected list of CFHs

CFHs	A (Å ²)	V (Å ³)	A^* (10 ⁻⁹ cm ² /mol)	V^* (cm ³ /mol)	E^* (bar dm ³ /mol)	E_1^* (bar dm ³ /mol)
R22	91.1 ± 0.3	58.7 ± 0.2	5.47	36.2	36.80	37.4
R32	69.3 ± 0.1	50.1 ± 0.1	4.16	20.6	32.58	34.8
R123	154 ± 0.3	128 ± 0.2	9.27	54.1	69.94	64.6

In order to assert the general validity and applicability of the procedure proposed in this work, a different equation of state for polymers, i.e., the Lattice Fluid model [15–17], has been used, (although the PHSCCT could be applied also to macromolecules).

The Lattice Fluid theory may be considered a generalization of the classical lattice theory, where vacancies are allowed. The theory gives rise to a compressible equation of state that accounts for lower critical solution temperatures behavior, thus justifying thermally induced phase separations. The equation of state is expressed as follows:

$$\left(\frac{\rho}{\rho^*}\right)^2 + \left(\frac{P}{P^*}\right) + \left(\frac{T}{T^*}\right) \left[\ln\left(1 - \left(\frac{\rho}{\rho^*}\right)\right) + (1 - 1/r) \left(\frac{\rho}{\rho^*}\right) \right] = 0 \quad (5)$$

where T^* , P^* and ρ^* are characteristic parameters and $r \rightarrow \infty$ for polymers: P^* corresponds to the cohesive energy density at 0 K and ρ^* is related to the specific volume at 0 K, v^* . Both values have been calculated by means of the extrapolation procedure describe in the experimental session. The characteristic temperature T^* is obtained by inserting P^* and ρ^* and simulated PVT data in Eq. (5).

4. Results and discussion

Table 1 reports the results obtained from MM/QM calculations for a selected list of the CFHs examined; the experimental data are reported for comparison, where available. As can be seen from this table, the agreement between experimental and calculated values, both in the case of geometrical parameters and of other general chemico-physical properties, is excellent. An example of simulated PVT behavior for a given refrigerant (i.e., R32) is given in Fig. 2(a) and (b), where experimental data are also shown for comparison. Again, the agreement between simulated and experimental data is satisfactory, and seems to confirm the validity of the choice of the simulation conditions and forcefield. For the sake of completeness, Table 2 reports the numerical values of the simulated data.

Table 4

Predicted vapor pressure and volumetric properties for a selected list of CFHs

CFHs	PVT			VLE			Ref.
	P range (MPa)	T range (K)	AD ρ (%)	Range P^0 (MPa)	AD P^0 (%)	AD V_L (%)	
R22	0.5–2.0	250–340	1.59	0.177–1.982	4.62	1.16	[21]
R32	0.12–9.2	253–333	3.74	0.347–2.21	4.33	2.66	[22]
R123	10.1	30–120	–	1.200–210.2	3.30	4.29	[23]

AD = average deviation.

Table 5

Calculated LF EOS parameters for polystyrene and polyethylene. Experimental data from Ref. [24] (PS) and from Ref. [25] (PE)

	Polystyrene	Polyethylene
P^* (MPa)	437	377
v^* (cc/g)	0.861	0.934
T^* (K)	629.57	437.63
P range (MPa)	0.1–200	0.1–200
T range (K)	393–469	413–473
AAD (% volume)	1.15	3.84

AAD = average absolute deviation.

The results of the calculation of PHSCT EOS parameters for three CFHs are reported in Table 3, along with the relevant molecular areas and volumes. The last two columns report the energetic parameter values (E^* and E_1^*) calculated according to the two different procedure described above.

As can be seen in Table 4, which shows the predicted vapor pressure and volumetric properties for a selected list of CFHs by means of the PHSCT EOS, the representation of the experimental data is more than satisfactory. These results were obtained with E_1^* ; in the case of E^* much larger errors, especially for P^0 (up to 80% in the entire T range), were observed. This is essentially due to the degree of empiricism of the equation of state, which is dumped by the small adjustment of the energetic parameter to the simulated data. Similar attempts to predict energetic parameters by means of generalized correlations [14,18] showed comparable results and, in these cases, the energetic parameter was tuned by using true experimental data. In the present procedure no experimental data were used.

4.1. Polymers

Table 5 reports the characteristic parameters obtained for the polymers considered in this work according to the procedure explained in the experimental session. A set of PVT data for different isotherms and different polymers have been generated by means of molecular dynamics [19] and these data have been used for tuning the characteristic temperature T^* . The Lattice Fluid model (Eq. (4)) with the parameters reported in Table 5 has been used for estimating PVT properties in a wide temperature and pressure range, and the percent deviations between the predicted and experimental data are also reported in Table 5. The results obtained can be considered, in our opinion, rather satisfactory.

5. Conclusions

This paper reports results obtained through a new procedure for estimating EOS parameters from computer simulations. The problem of estimating reasonable parameters for EOS is a very important issue in the analysis and synthesis of chemical process and in the use of process simulators. In many cases, for instance, chemical engineers need to input EOS parameters for molecules that have not yet been synthesized (as in the case of a particular chloro-fluoro-hydrocarbon), or for long chain molecules for which experimental data cannot be easily obtained (due to peculiar process or experimental conditions). Furthermore, in the calculation of rate controlled processes, it is sometimes

necessary to estimate the equilibrium condition with a high degree of accuracy, and again experimental data in such conditions may not be available.

The new, original method proposed in this work gives good results and is relatively inexpensive. The suggested procedure is absolutely general and can be applied in principle to any equation of state, provided the parameters have a physical meaning. The tuning of the energetic parameter to a generated data account for the degree of empiricism introduced at a certain stage in the development of any equation of state. Further work is in progress to extend the method to other equation of state and to enlarge the data base test substances.

6. List of symbols

a	intermolecular potential well-depth between a nonbonded pair of segments, Eq. (1)
A^*	characteristic surface area, parameter in PHSCT EOS, $\pi r \sigma^2 N_A$, Eq. (3)
b	segmental diameter, Eq. (1)
d	hard sphere diameter, Eq. (1)
E^*	characteristic cohesive energy, parameter in PHSCT EOS, $r(\varepsilon/k)R_g$, Eq. (4)
$g(d^+)$	pair radial distribution function of hard spheres in contact, Eq. (1)
k	Boltzmann's constant
N_A	Avogadro's number
P	pressure
P^*	cohesive energy density at 0 K, parameter in LF EOS, Eq. (5)
r	number of effective hard spheres per molecule, Eq. (1)
R_g	gas constant
V	volume
V^*	characteristic molecular volume, parameter in PHSCT EOS, $(\pi/6)r\sigma^3 N_A$, Eq. (2)
T	absolute temperature
T^*	characteristic temperature, parameter in LF EOS, Eq. (5)

Greek symbols

ε	intermolecular potential well-depth, Eq. (4)
μ	dipole moment
ν^*	specific volume at 0 K, $1/\rho^*$
ρ	density
ρ^*	density at 0 K, parameter in LF EOS, Eq. (5)
σ	intermolecular potential well-depth distance, Eqs. (2) and (3)
τ_T	temperature bath coupling constant
τ_P	pressure bath relaxation time

Acknowledgements

Authors thank Ministero dell'Università e della Ricerca Scientifica (MURST—Roma) and the University of Trieste (special grant for Scientific Research) for the financial support.

References

- [1] J.R. Maple, T.S. Thacher, U. Dinur, A.T. Hagler, *Chemical Design Automation News* 5 (1990) 5.
- [2] A.K. Rappé, W.A. Goddard, *J. Phys. Chem.* 95 (1991) 3358.
- [3] M.L. Connolly, *J. Appl. Crystallogr.* 16 (1983) 548.
- [4] L.M. Rellick, W.J. Bechtel, *Biopolymers* 42 (1997) 191.
- [5] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, *J. Chem. Phys.* 81 (1984) 3684.
- [6] H.C. Andersen, *J. Chem. Phys.* 72 (1980) 2384.
- [7] J.R. Maple, U. Dinur, A.T. Hagler, *Proc. Nat. Acad. Sci. USA* 85 (1988) 5350.
- [8] Y. Song, E. A. Mason, *J. Chem. Phys.* 12 (1991) 7840.
- [9] Y. Song, S.M. Lambert, J.M. Prausnitz, *Ind. Eng. Chem. Res.* 33 (1994) 1047.
- [10] Y. Song, S.M. Lambert, J.M. Prausnitz, *Chem. Engng. Sci.* 17 (1994) 2765.
- [11] Y. Song, T. Hino, S.M. Lambert, J.M. Prausnitz, *Fluid Phase Equilibria* 117 (1996) 69.
- [12] Y.C. Chiew, *Mol. Phys.* 70 (1990) 129.
- [13] M. Fermeglia, A. Bertucco, D. Patrizio, *Chem. Engng. Sci.* 52 (1997) 1517.
- [14] M. Fermeglia, A. Bertucco, S. Bruni, *Chem. Engng. Sci.* 17 (1998) 3117–3128.
- [15] I.C. Sanchez, R.H. Lacombe, *J. Phys. Chem.* 80 (1976) 2352.
- [16] I.C. Sanchez, R.H. Lacombe, *Macromolecules* 11 (1978) 1145.
- [17] I.C. Sanchez, C.G. Panayiotou, in: S.I. Sandler (Ed.), *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, New York, 1994.
- [18] J. Gregorowicz, M. Fermeglia, G. Soave, I. Kikic, *Chem. Engng. Sci.* 46 (1991) 1427.
- [19] S. Pricl, M. Fermeglia, submitted to *AIChE J.*, 1999.
- [20] P.F. Malbrunot, P.A. Meunier, G.M. Scatena, W.H. Mears, K.P. Murphy, J.V. Sinka, *J. Chem. Eng. Data* 13 (1968) 16.
- [21] B. Platzter, A. Polt, G. Maurer, *Thermophysical Properties of Refrigerants*, Springer, Berlin (FRG), 1990.
- [22] C. Bouchot, D. Richon, *Proc. Int. Conf. CFC's: the Day After*, Padova (I), 1994, p. 517.
- [23] M.O. McLinden, J.S. Gallagher, L.A. Weber, G. Morrison, D. Ward, A.R.H. Goodwin, M.R. Moldover, J.W. Schmidt, H.B. Chae, T.J. Bruno, J.F. Ely, M.L. Huber, *ASHRAE Trans.* 95 (1989) 263.
- [24] A. Quach, R. Simha, *J. Appl. Phys.* 42 (1971) 4592.
- [25] P.J. Zoller, *J. Appl. Polym. Sci.* 23 (1979) 1057.