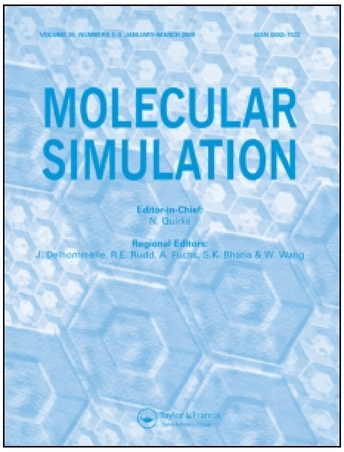

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From Molecular to Process Simulation: Novel Approaches to the Prediction of Phase Equilibria and PVT Behavior Based on Molecular/Quantum Mechanics and Molecular Dynamics Simulations

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FROM MOLECULAR TO PROCESS SIMULATION: NOVEL APPROACHES TO THE PREDICTION OF PHASE EQUILIBRIA AND PVT BEHAVIOR BASED ON MOLECULAR/QUANTUM MECHANICS AND MOLECULAR DYNAMICS SIMULATIONS

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Actually, in modern process simulators, more than 75% of the code implemented is dedicated to physical properties estimation, calculation and predictions. Data banks storing pure component parameters and binary interaction parameters for phase equilibrium calculations are extensively used and continuously implemented in actual process simulators. This gives an idea of the important role physical properties availability plays in process simulation.

In this paper we propose a new way for coupling molecular and process simulation. The basic machinery is to resort to molecular/quantum mechanics and molecular dynamics simulation techniques for generating the parameters of some equations of state that will subsequently be used for the prediction of phase equilibria and PVT behavior of small and polymeric molecules as well. This information, in turn, will be used as input in the process simulator, thus creating a final and well-defined bridge between molecular and process simulations in chemical engineering.

Keywords: Molecular simulation; process simulation; phase equilibrium

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INTRODUCTION

During the last decades, computer experiments based on molecular/quantum mechanics (MM/QM) and molecular dynamics (MD) simulation techniques have opened avenues in the calculations and prediction of both equilibrium and non-equilibrium thermophysical properties of small molecules and long polymeric chains as well [1]. At the same time, notwithstanding the extraordinary evolution of computing power, it is not possible to perform reliable atomistic MD simulations of systems containing more than 10^4 atoms for times of the order of nanoseconds with acceptable times, even on powerful workstations.

Nevertheless, by trying to make the molecular model as realistic as possible, computer simulations can indeed be used to predict molecular properties for which the experimental determination is too costly, time-consuming or even impossible. A clear illustration of this assertion comes immediately to mind when thinking of a research topic peculiar to chemical engineering: the determination of vapor–liquid equilibria for liquid mixtures. If we consider only a small subsection of all possible systems, such as zeotropic mixtures of chloro-fluoro-hydrocarbons to be exploited as alternative refrigerants, it appears evident that the number of potentially useful mixtures is huge, and it would be extremely uneconomical, if not inconceivable, to evaluate experimentally the thermodynamic properties of all possible alternatives.

It might be not so, however, for a computer. In fact, computer experiments provide a direct route from the microscopic details of a system to macroscopic characteristics of experimental interests, such as equations of state, transport properties, and so on. As well as being of academic interest, now virtual experiments are becoming technologically useful since, despite the limitations outlined above, molecular simulations can be considered cheaper and faster than true experiments, especially for simple molecular fluids.

In the chemical engineering practice there is a strong current need of models for describing volumetric and equilibrium properties of novel molecules, small and macro, and their mixtures. Good and reliable methods are available in the literature for describing the behavior of mixtures of both cases, but they necessarily rely on the availability of a set of experimental data both for pure components and the mixtures. Therefore, provided we properly account for the two major problems encountered in any virtual experiment (*i.e.*, the size of the configurational space that is accessible to the molecular system and the accuracy of the molecular model or atomic interaction function or force field that is used to model the molecular system), we can think of computer simulation at least as a first way of screening among the plethora of possible system candidates. In this paper we want to show how, from such virtual experiments, it is possible to extract the characteristic parameters of some equations of state (EOS), thus avoiding the tedious experimental efforts for determining PVT isotherms and/or vapor pressure as a function of temperature. To this aim, we report our recent progress in the attempt of combining the technique of MM/QM and MD simulations and the EOS theory. In summary, these techniques are employed in different ways to obtained different EOS parameter values which, inserted in the corresponding EOS, are then employed to predict the VLE and/or the PVT behavior of the considered systems in a vast range of T and P.

As we shall discuss later in more detail, the quality of the prediction, in conjunction with the relative fast calculation time required for the simulation, can be considered extremely satisfactory. Furthermore, although some specific EOSs have been considered here, the proposed computational procedures hold an absolutely general character and can be applied to any EOS, on condition that its characteristic parameters have a sound and well defined physical meaning [2].

THEORETICAL

Perturbed Hard Sphere Chain Theory (PHSCT) for Low Molecular Weight Molecules

The first equation of state considered in this work is based on the simplified perturbed-hard-sphere-chain theory model (PHSCT) [3–5], in which the molecule is considered being constituted by chains of freely jointed tangent hard spheres (or segments). The PHSCT EOS has been developed starting from the modified Chiew equation of state for hard-sphere chains as the reference term [6], a van der Waals-type perturbation term and the Song–Mason method [3] to relate equation of state parameters to the intermolecular potential.

In term of pressure, the complete equation of state can be expressed as:

$$(P/\rho \mathrm{k}T) = 1 + r^2 b\rho g(d^+) - (r-1)[g(d^+) - 1] - (r^2 a\rho/\mathrm{k}T) \qquad (1)$$

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 constant, d the hard-sphere diameter and $g(d^+)$ the pair radial distribution function of hard spheres at contact. Equation (1) contains three parameters, all with a well-defined physical meaning: the number of effective hard spheres per molecule (r), the intermolecular potential-well depth between a non-bonded pair of segments (a) and the effective hard-sphere diameter (b).

To obtain an engineering-oriented equation of state, a redefinition of the EOS parameters has been performed [3, 7, 8] according to which each pure component was characterized by a set of three segment-based parameters – σ, ε and r – which were combined further to yield three, final characteristic molecular parameters reflecting the size, shape and energetic interactions of the fluids considered as follows. First, a characteristic volume V^* was defined as:

$$V^* = (\pi/6) r \sigma^3 \mathrm{N_A} \tag{2}$$

where $\mathrm{N_A}$ is Avogadro's constant. Second, a characteristic surface area, A^*, was given as:

$$A^* = \pi r \sigma^2 \mathrm{N_A} \tag{3}$$

and finally a characteristic "cohesive" energy, E^*, was introduced as:

$$E^* = r(\varepsilon/\mathrm{k})\mathrm{R_g} \tag{4}$$

where $\mathrm{R_g}$ is the gas constant.

For the determination of the PHSCT EOS parameter values, we propose the following procedure: from the values of molecular areas and volumes calculated *via* a corrected Connolly algorithm (see below) and normalized with respect to methane ($r = 1$), the relevant r and σ values can be calculated and, accordingly, V^* and A^* can be obtained by means of Eqs. (2) and (3). The parameter ε/k is obtained from MD simulations 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) (see below for details).

Perturbed Hard Sphere Chain Theory (PHSCT) for Polymers

The equation of state presented above can be applied also to polymers, provided we consider a polymer molecule as being constituted by a chain of freely jointed tangent hard spheres. If we now accordingly define the polymer segment density ρ_r as:

$$\rho_r = r \times \rho \tag{5}$$

Equation (1) can be rewritten as:

$$(P/\rho_r \mathrm{k}T) = 1 + b\rho_r g(d^+) - (1 - 1/r)[g(d^+) - 1] - a\rho_r/\mathrm{k}T \tag{6}$$

For polymeric chains, $r \rightarrow \infty$ and hence $1 - 1/r \rightarrow 1$; accordingly, Eq. (1) can be finally recast as:

$$(P/\rho_r \mathrm{k}T) = 1 + b\rho_r g(d^+) - g(d^+) - a\rho_r/\mathrm{k}T \tag{7}$$

In perfect analogy with the procedure described for small size molecules, the three EOS parameters V^*, A^* and E^* can be defined in this case as:

$$V^* = (\pi/6)(r/M)M_0\sigma^3\mathrm{N_A} \tag{8}$$

where $\mathrm{N_A}$ is Avogadro's constant, M is the polymer molecular weight and M_0 is the polymer constitutive repeating unit (CRU) molecular weight;

$$A^* = \pi(r/M)M_0\sigma^2\mathrm{N_A} \tag{9}$$

and finally:

$$E^* = (\varepsilon/\mathrm{k})(r/M)M_0\mathrm{R_g} \tag{10}$$

In this case, the procedure for the determination of the EOS parameters we propose is quite similar to that described above, with the difference that the third, energetic parameter E^* can be obtained from MD simulations of the appropriate monomers in the gas state.

Sanchez–Lacombe Lattice Fluid Equation of State (LF) for Polymers

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 [10, 11]. The equation of state is expressed as follows:

$$(\rho/\rho^*) + (P/P^*) + (T/T^*)[\ln(1 - (\rho/\rho^*)) + (1 - 1/r) \times (\rho/\rho^*)] = 0 \tag{11}$$

where T^*, P^* and ρ^* are characteristic parameters and $r \rightarrow \infty$ for large polymers. P^* corresponds to the cohesive energy density at 0 K and ρ^* is related to the specific volume at 0 K. According to our procedure, both P^* and ρ^* values can be calculated *via* MD by means of the extrapolation maneuver describe in the experimental session. The characteristic temperature T^* is finally obtained by inserting P^*, ρ^* and a MD simulated PVT data set in Eq. (11).

SIMULATION DETAILS

All simulations were run on a Silicon Graphics Origin 200 (microprocessor MIPS RISC 10000, 64 bit CPU, 128 MB RAM) and performed by using the commercial software Cerius^2(v. 3.9) from Molecular Simulation Inc. (for both MM/QM and MD simulations) and in-house developed computer programs (stand-alone and add-on to the commercial package). In all virtual experiments, the *ab initio*, second generation COMPASS98 forcefield was used [12], coupled with the charge equilibration method of Rappé and Goddard [13].

PHSCT EOS Parameters for Small Molecules and Polymers

The first procedure proposed was tested on a set of 14 alternative chloro-fluoro-hydrocarbons (CFHs) of very actual interest as potentially useful replacers of ozone-damaging refrigerants. Table I reports the relevant details of the simulations performed on this set of molecules.

The calculation of molecular surfaces were performed using the Connolly dot surfaces algorithm [15, 16], corrected to account for quantum effects

TABLE I Simulation conditions used in the virtual experiments on CFHs

MM calculations	*Convergence criterion*	*Nonbonded interactions*
COMPASS98 forcefield [12] + charge equilibration method of Rappé and Goddard [13]; up to 5000 Newton-Raphson iterations	Root-mean-square (rms) atomic derivatives $\leq$ 0.05 kcal/mole Å	Cut-off + spline method; 6th power combination rule for mixed van der Waals parameters [14]
MD calculations Cubic box with 256 molecules; suitable cut-off; Ewald summation for nonbonded interaction	NPT MD Initial for the atoms assigned according to a Boltzmann distribution at $2 \times T$; weak coupling with temperature bath [18] ($\tau_T = 0.01$ ps) and pressure bath [19] ($\tau_p = 0.1$ ps)	MD runs 50 ps equilibration + 300 ps data aquisition

according to the technique proposed by Rellick and Becktel [17]. In this way, no assumption was made about the value of the radii of individual atoms or groups of atoms.

PHSCT EOS Parameters for Polymers

The procedure proposed for the determination of PHSCT EOS parameters for the four synthetic polymers of industrial application considered, *i.e.*, poly(epichloridrine) (PECH), poly(ε-caprolactone) (PCL), poly(vinylchloride) (PVC) and atactic poly(propylene) (*a*-PP) is quite similar to that described for the small CFH molecules. Indeed, for each polymer, the constitutive repeating unit (CRU) was first built and its geometry optimized by energy minimization using the COMPASS98 force field and the same conditions described for the small molecules a few lines above. On these CRUs, the MD experiments necessary to the determination of the energetic parameter E^* (see Eq. (10)) were conducted according to the same procedure reported in Table I, except that the temperature used was set equal to 1028 K (gas state). The Connolly algorithm was used also in this case for the determination of molecular surfaces and volumes; nevertheless, to the purpose of this procedure, the values of the molecular surface areas and volumes obtained with this technique were reasonable enough and could be used, without resorting to any correction [20, 21], in the calculation of the related EOS parameters.

LF EOS for Polymers

For the prediction of the polymeric properties with the LF EOS, first each model CRU obtained with the procedure described above was polymerized to a conventional degree of polymerization (DP) equal to 100. Explicit hydrogens were used in all model systems, thus bringing the total number of atoms in each polymeric chain to 600 in the case of PVC, 900 for *a*-PP, 1000 for PECH and 1800 for PCL, respectively.

Six different amorphous structures for each polymeric chain were generated *via* the Rotational Isomeric State (RIS) algorithm at $T = 386\,\text{K}$, and packed into a cubic simulation box with 3-D periodicity. The initial density for each chain was set equal to the corresponding available literature values, in order to minimize discrepancies in the final density values obtained from MD simulations. The structures were then relaxed to minimize energy and avoid atom overlaps using the conjugate-gradient method. In each case, the Ewald technique was employed in handling nonbonded interactions and the charge equilibration method was again used to equilibrate the charge distribution.

Such a straightforward molecular mechanics scheme is likely to trap the simulated system in a metastable local high-energy minima. To prevent the system from such entrapments, the relaxed structures were subjected to simulated annealing (5 repeated cycles from 386 K to 1000 K and back) using constant volume/constant temperature (NVT) MD conditions. At the end of each annealing cycle, the structures were again relaxed *via* FF (rms force less than 0.1 kcal/mole Å for the polymer and 0.1 kcal/mole Å^3 for the stresses on the periodic boxes as convergence criteria). From the fully relaxed models of the corresponding polymeric chains, isothermal-isobaric (NPT) MD experiments were run at 386 K (a temperature above the glass transition temperature for all polymers) and from 350 to 50 K at intervals of 50 K; the information at 0 K, needed for the LF EOS parameters estimation, was then collected by extrapolation. The Newton atomic equations of motion were solved under the same conditions reported above for small molecules. In this case, equilibration was reached within 50 ps in all cases, and the data collection phase was extended up to 250 ps.

RESULTS AND DISCUSSION

PHSCT EOS Parameters for Small Molecules

The validity of any molecular simulation rests on the suitability and accuracy of the equations used for the intermolecular potentials. Although the accuracy of a prediction may be estimated by considering the approximations and simplifications of the model and computational procedure, the final test lies in a comparison of theoretically predicted and experimentally measured properties. Table II shows only a very partial set of the results of this comparison in terms of geometrical parameters and of other general chemico-physical properties (such as dipole moment, ionization potential and enthalpy of formation). From an inspection of this table and all other data available [8] we can conclude that, for all the CFHs considered, the agreement is more than satisfactory.

We performed a further check of the agreement between simulation and experiment by comparing the simulated PVT behavior of the CFH molecules with the corresponding experimental data. Figure 1 shows, as an example, the results obtained for the refrigerant R32. Again, the agreement between virtual and real experiment is satisfactory, thus confirming the

TABLE II Structural molecular parameters and selected chemico-physical data for four CFHs. Comparison between calculated and experimental data (in parenthesis, where available)

CFHs	*Bond lengths* (Å),	ΔH_{form} (*kcal/mole*)	*I.P.* (*eV*)	μ(*D*)
R13				
C—F	1.320 (1.325)			
C—Cl	1.750 (1.752)	−162.6 (−168.8)	13.2 (12.4)	0.59 (0.50)
FCF	108.3 (108.6)			
R14				
C—F	1.322 (1.323)	−225.7 (−223.1)	15.3	0
FCF	109.4 (109.5)			
R21				
C—F	1.338			
C—Cl	1.767			
C—H	1.101			
FCCl	110.2	−65.22	12.0 (11.5)	1.39 (1.29)
ClCCl	110.7			
FCH	109.4			
ClCH	108.2			
R22				
C—F	1.337			
C—Cl	1.767			
C—H	1.100			
FCF	109.2	−114.2 (−115.3)	12.3 (12.2)	1.47 (1.42)
FCCl	111.1			
FCH	109.4			
ClCH	108.7			

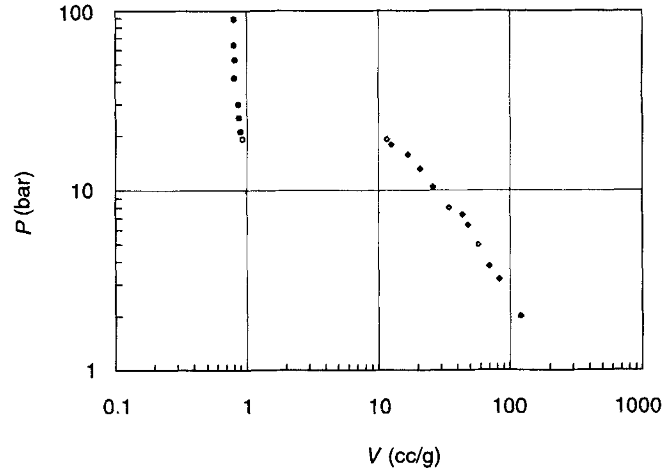

FIGURE 1 Comparison between simulated (filled symbols) and experimental (open symbols) PVT behavior for the refrigerant R22 at 323 K.

validity of the particular forcefield used and the adequacy of the selected simulation conditions.

Once the corrected molecular surface areas A and volumes V are calculated, the determination of the relevant values of the PHSCT EOS parameters V^* (Eq. (2)) and A^* (Eq. (3)) is straightforward. Table III reports the values of A, V and of the corresponding EOS parameters for all 14 CFH molecules considered. The last column of Table III lists the values of the EOS energetic parameter E^*, obtained by Eq. (4). The corresponding values of the parameter ε/k, appearing in Eq. (4), were calculated as:

$$\varepsilon/\mathrm{k} = (E_{\mathrm{pot}}^{\mathrm{nonbond}}/E_{\mathrm{kin}}) \times T \tag{12}$$

in which the equilibrium energy components were obtained, for all CFHs, from NPT MD simulations in the gas state ($T = 600\,\mathrm{K}$). The *a priori* calculated parameters reported in Table III were then inserted in the PHSCT EOS expression and the corresponding thermodynamical properties of the CFHs considered have been predicted. Figures 2(a) and 2(b) show some selected examples of the comparison between the density values and the saturated liquid volumes predicted with the PHSCT EOS using the parameter values reported in Table III and the corresponding experimental data [7].

Even more instructive is to consider a comparison of the results obtained by this procedure with the results obtained for the same refrigerants with the same EOS whose optimal values of the parameters were calculated regressing vapor pressure and PVT data [8, 20]. Table IV shows the results of this comparison in terms of root-mean-square deviation (RMSD).

TABLE III Molecular areas, volumes and PHSCT EOS parameters for the 14 CFHs considered

CFHs	A ($\mathring{A}^2$)	V ($\mathring{A}^3$)	A^* (10^{-9} cm^2/mol)	V^* ($cm^3/mole$)	E^* ($bar\ dm^3/mole$)
R13	103 ± 0.2	73.1 ± 0.1	6.16	38.8	32.52
R14	88.5 ± 0.1	73.4 ± 0.1	5.31	31.0	24.37
R21	113 ± 0.2	84.9 ± 0.1	6.78	41.6	52.14
R22	91.1 ± 0.3	58.7 ± 0.2	5.47	36.2	37.42
R23	50.4 ± 0.1	56.1 ± 0.2	5.22	26.8	36.50
R32	69.3 ± 0.1	50.1 ± 0.1	4.16	20.6	34.76
R113	175 ± 0.3	140 ± 0.1	10.5	62.7	70.72
R114	155 ± 0.3	104 ± 0.2	9.26	59.9	53.10
R115	142 ± 0.2	104 ± 0.2	8.50	52.7	44.85
R123	154 ± 0.3	128 ± 0.2	9.27	54.1	64.61
R134a	112 ± 0.1	84.2 ± 0.1	6.76	41.5	45.12
R142b	125 ± 0.2	90.9 ± 0.2	7.47	46.5	49.14
R143a	112 ± 0.2	96.3 ± 0.2	6.73	38.6	43.20
R152a	107 ± 0.3	101 ± 0.1	6.45	35.4	49.29

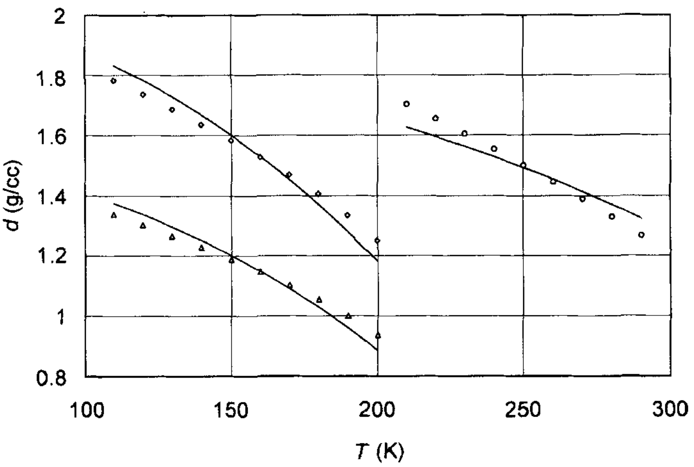

FIGURE 2a Simulated density (continuous lines) as a function of temperature obtained by PHSCT EOS with parameters calculated according to the proposed for a set of CFHs. Symbols (experimental data): diamonds, R14; circles, R115; triangles, R152a.

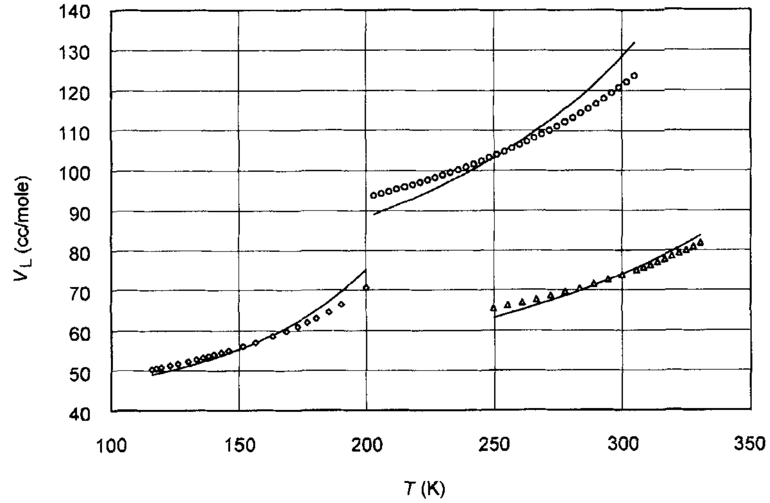

FIGURE 2b Simulated saturated liquid volume (continuous lines) as a function of temperature obtained by PHSCT EOS with parameters calculated according to the proposed for a set of CFHs. Symbols (experimental data): diamonds, R14; circles, R115; triangles, R152a.

If we consider that the uncertainty in the experimental data is of the order of 2%, the *a priori* calculation method proposed in this paper, when compared to pure correlation of experimental data for determining the

TABLE IV Comparison in terms of RMSD between best-fit PHSCT calculations (A) and results from the same EOS with parameter values calculated according to the proposed procedure (B)

	PVT density		*VLE Vapor pressure*		*Saturated liquid density*	
CFHs	*A*	*B*	*A*	*B*	*A*	*B*
R13	1.97	1.99	2.08	3.69	2.76	2.80
R14	2.22	2.24	2.41	2.37	2.62	2.64
R21	2.12	1.96	2.57	3.42	3.54	3.74
R22	2.48	2.16	1.77	5.36	2.09	1.22
R23	2.04	2.09	2.59	6.71	1.88	2.10
R32	4.63	5.08	0.80	5.11	0.39	4.28
R113	2.77	3.78	2.96	4.14	1.00	6.35
R114	1.42	1.70	1.71	4.94	3.18	3.37
R115	2.55	2.53	2.32	2.54	3.43	3.46
R123	1.65	0.70	2.98	4.13	4.74	4.92
R134a	2.09	2.48	1.35	5.48	0.39	0.81
R142b	2.98	2.06	0.98	2.23	2.03	1.19
R143a	2.74	2.98	2.32	2.37	3.65	3.76
R152a	1.08	1.07	1.39	1.64	1.87	1.83
Average	2.02	2.34	2.61	3.87	2.34	3.03

entire set of EOS parameters, introduces only approximately 1% of additional uncertainty. If we take into account the very short times and the low costs required to obtain one set of PHSCT EOS parameters for each CHF molecule (from the molecule building to its MD simulation) and that no one single experimental data is required, even to obtain a prediction of vapor pressure, the quality of the results reported in Table IV are, in our opinion, to be considered more than satisfactory.

PHSCT EOS Parameters for Polymers

According to the procedure described above, the determination of the two PHSCT EOS parameters V^* and A^* is again straightforward. Table V shows the ensamble averaged values of the molecular surface areas and volumes for all the polymers and the relevant CRUs whereas Table VI reports the corresponding calculated values of the PHSCT EOS parameters.

The *a priori* calculated parameters reported in Table VI were then inserted in the PHSCT EOS expression and the corresponding thermodynamical properties of the polymers considered have been predicted and compared with the relevant experimental data [21, 22].

Table VII reports the results of this comparison in terms of root-mean-square deviation, whereas two graphical examples are given by Figures 3(a) and 3(b) for *a*-PP and PVC, respectively (only some selected data sets are reported in each Figure for the sake of clarity).

TABLE V Ensamble averaged molecular surface areas and volumes for the four CRUs and the corresponding polymers

Polymer	A_{CRU} ($\AA^2$)	V_{CRU} ($\AA^3$)	A_p ($\AA^2$)	V_p ($\AA^3$)
a-PP	90.7 ± 0.2	61.0 ± 0.2	6406 ± 15	9396 ± 21
PVC	84.9 ± 0.2	57.9 ± 0.2	5815 ± 12	4793 ± 14
PECH	106 ± 0.3	76.2 ± 0.3	9352 ± 22	7404 ± 39
PCL	170 ± 0.4	124 ± 0.6	10112 ± 34	9687 ± 54

TABLE VI Calculated PHSCT EOS parameters for the four polymers

Polymer	A^* ($10^{-9} cm^2/mol$)	V^* (cm^3/mol)	E^* ($bar\ dm^3/mol$)
a-PP	5.45	40.33	52.67
PVC	5.59	32.93	62.35
PECH	6.34	62.32	60.43
PCL	10.2	166.2	80.25

TABLE VII Comparison in terms of RMSD between experimental data and PHSCT EOS predictions using the parameter values reported in Table VI

Polymer	*P range* (*MPa*)	*T range* (*K*)	*RMSD* (%)
a-PP	0-196	446.66-571.63	2.5
PVC	0-200	373.35-423.15	1.1
PECH	0-200	333.15-413.15	2.5
PCL	0-200	373.75-421.35	1.7

In terms of RMDS, the quality of the results shown in Table VII and in the pertinent Figures is rather good. Nevertheless, the predicted values show, in all cases, a definite trend in the temperature dependence of the thermophysical properties. A cause for this trend can be reasonably ascribed to the oversimplification of the perturbation term in Eq. (7) that includes, with a certain degree of empiricism, both the van der Waals and the electrostatic interactions. This approximation could be accounted for by including a temperature dependence of the EOS parameters or by explicitly adding a term to the EOS expression. Yet, since the purpose of our paper is to present and test a new procedure for the generation of EOS parameters rather than validating or proposing a new thermodynamic model, we can consider the global prediction results listed in Table VII more than satisfactory.

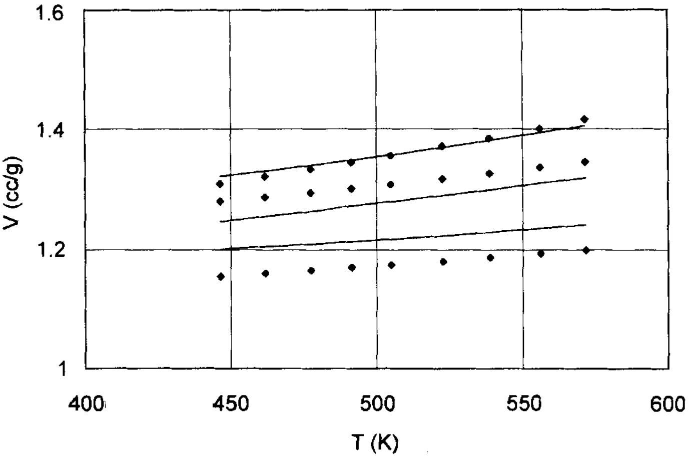

FIGURE 3a Example of the comparison between the experimental (symbols) PVT behavior of a-PP and the corresponding predictions (lines) obtained with the PHSCT EOS using the parameter values calculated in this work and listed in Table VI.

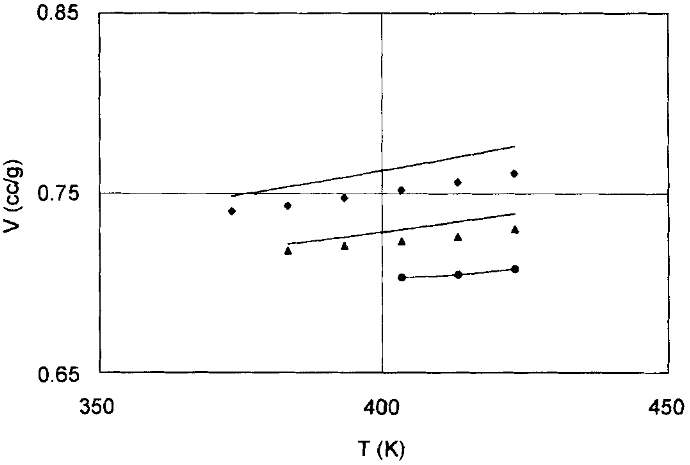

FIGURE 3b Example of the comparison between the experimental (symbols) PVT behavior of PVC and the corresponding predictions (lines) obtained with the PHSCT EOS using the parameter values calculated in this work and listed in Table VI.

LF EOS for Polymers

As briefly mentioned in the theory section, the LS EOS parameter P^* directly corresponds to the cohesive energy density at 0 K. In general, e_{coh} is defined as the ratio of the cohesive energy E_{coh} and the molar volume

V at a given temperature; E_{coh}, in turn, is defined as the increase in internal energy per mole of substance if all intermolecular forces are eliminated. In our simulated systems, each chain is surrounded by other chains that are simply displaced images of the chain itself. The cohesive energy is the energy of interactions between these images. Accordingly, the values of E_{coh} at different temperatures can be obtained from simulation by calculating the difference between the nonbonded energy of the periodic structure and the corresponding value for an isolated parent chain in vacuum. Finally, the value of E_{coh} at 0 K can be gained by extrapolation.

To this purpose, six parent chains for each polymer were generated and their energy minimized according to the procedure described in the simulation details section. The simulated annealing method was again applied as described above to these systems to provide thermal energies to cross energy barriers between conformation local minima. Finally, NVT MD simulations were performed on the single chains (again the six best relaxed chains for each polymer) *in vacuum* at the same temperature conditions applied for the simulations of the relevant periodic systems. As expected, the valence contribution to E_{tot} is nearly the same for both chains, and the major difference is indeed given by the nonbonded term $E_{\mathrm{nb}} = E_{\mathrm{vdw}} + E_{\mathrm{coul}}$. As a matter of fact, it can be easily understood that the reduction in the total energy for the chain in bulk rises solely due to the intermolecular nonbonded attractive interactions between the atoms from neighboring chains [21]. Accordingly, in Table VIII we report the values of the three LF EOS parameters for all polymers. For each macromolecule, P^* is equal to e_{coh} obtained by extrapolation as explained above, ρ^* is the polymer density value at 0 K and T^* is obtained by inserting the corresponding P^*, ρ^* and the simulated P and ρ values at the highest simulated temperatures in Eq. (11) [21].

The PVT data for all polymers were then predicted with Eq. (11) using the appropriate parameter sets listed in Table VIII. Figures 4(a) and 4(b) are two selected example of the comparison between the predicted and the

TABLE VIII Calculated LF EOS parameters for the four polymers

Polymer	P^* (*MPa*)	ρ^* (*g/cc*)	T^* (*K*)
PECH	446.2	1.441	662
PCL	476.0	1.168	613
PVC	463	1.471	711
a-PP	332.0	0.9337	578

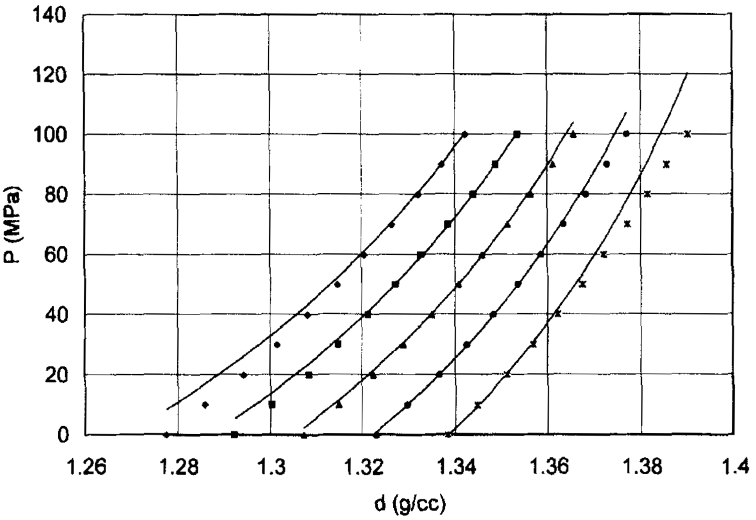

FIGURE 4a Example of the comparison between the experimental (symbols) PVT behavior of PECH and the corresponding predictions (lines) obtained with the LF EOS using the parameter values calculated in this work and listed in Table VIII.

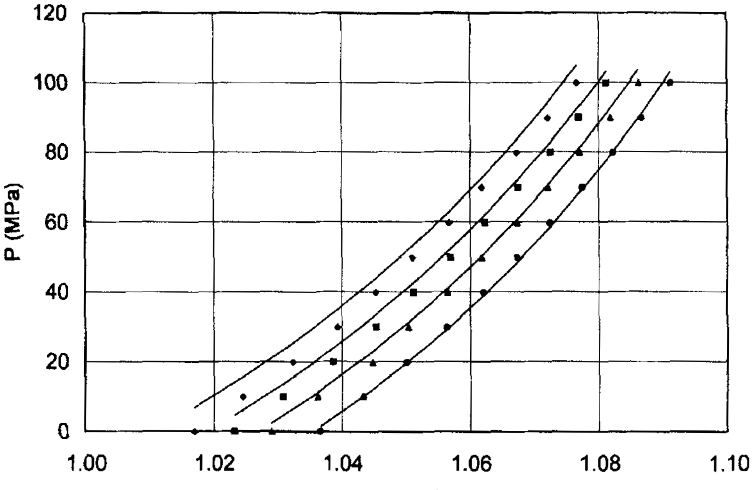

FIGURE 4b Example of the comparison between the experimental (symbols) PVT behavior of PCL and the corresponding predictions (lines) obtained with the LF EOS using the parameter values calculated in this work and listed in Table VIII.

corresponding available experimental values [22]. It may be seen that the agreement between the relevant data sets is more than satisfactory in all cases.

TABLE IX Comparison in terms of RAD between experimental data and LF EOS predictions using the parameter values reported in Table VIII

Polymer	*P range* (*MPa*)	*T range* (*K*)	*RAD* (%)	*RAD* (*Rodgers*, 1993) (%)	*RAD* (*Sanchez and Panayiotou*, 1994) (%)
PECH	0–100	60.0–140.0	7	23	24
PCL	0–100	100.6–148.2	5	9	10
PVC	0–100	100.2–150.0	7	20	7
a-PP	0–100	800–120.0	5	8	7

To quantify the quality of our PVT predictions, in this case we calculated the percent relative average deviations (%RAD). The values of %RAD average over the entire P/T range for each polymer are shown in Table IX, where we also report the %RAD obtained by using Eq. (11) with two other parameters sets available in literature [11, 22]. From an inspection of this Table we can not only conclude that the proposed procedure is indeed useful for the determination of the LF EOS parameters but also that the PVT data prediction quality thus obtained is comparable, if not superior, to that obtainable with the current literature parameter values.

CONCLUSIONS AND FURTHER WORK

This paper reports the results obtained with two new procedures for estimating EOS parameters from computer simulations. The problem of estimating reasonable parameters for EOS is a topical issue in the analysis and synthesis of chemical processes and in the use of process simulators. In this last case, for instance, chemical engineers need to input EOS parameters for small molecules that have not yet been synthesized, or for long chain polymers 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 methods proposed in this work give good results, are relatively inexpensive, absolutely general and can be applied in principle to any equation of state, provided the parameters have a well defined physical meaning. The tuning of one EOS parameter to a generated data accounts 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 equations of state and to enlarge the data base test substances.

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