

Molecular Modeling and Process Simulation: Real Possibilities and Challenges

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The state of the art of molecular modeling with particular attention to the possibilities of application to process simulation is reviewed in this paper. The basic principles of molecular modeling are presented, as well as the recent achievements in direct applications of the methods. Modeling in process engineering is discussed, showing how different models and theories must be applied for different times and lengths of the process of interest. Finally a selected series of examples of application of molecular modeling to problems of interest to process engineering is presented, showing that molecular modeling is a mature technique to be used for generating information to be used in process engineering.

Keywords:

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Introduction

The chemical industry faces considerable economic, environmental and societal challenges as the 21st century approaches. Technology research, development and deployment will be of paramount importance in meeting these challenges and seizing opportunities for future growth. Increased globalization of markets, for example, will create many new market opportunities, but will require the development of advanced technology to ensure the industry is globally competitive and that the resulting industrial development is environmentally sustainable. Manufacturing processes that are resource efficient, cost-effective, and environmentally sound will be a cornerstone in maintaining this balance.

In the *Technology Vision 2020: The U.S. Chemical Industry*,¹ a visionary document that identifies major needs and challenges over the next two decades, it is stressed that “an important element of chemical science and engineering is the development of enabling technologies (technologies that improve the application of fundamental chemical sciences) throughout the industry’s process environment”. The “enabling technologies” identified as essential to the industry’s future (see figure 1) include process science and engineering (e.g. engineering scale-up and design, thermodynamics and kinetics, reaction engineering); chemical measurement; and computational technologies (e.g., computational chemistry, simulation of processes and operations, smart systems, computational fluid dynamics).

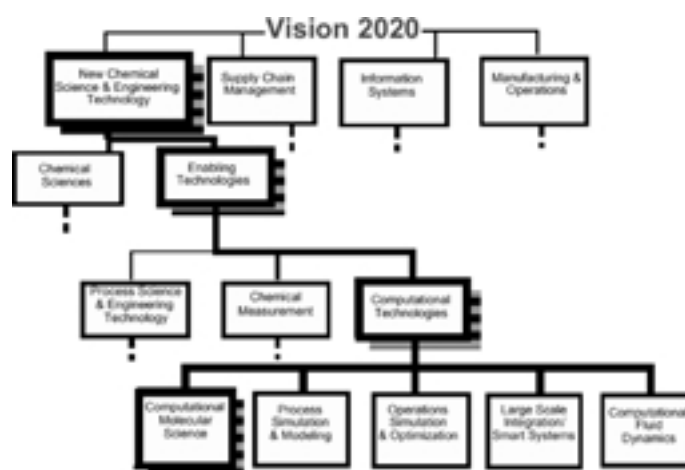


Fig. 1 – The technology vision 2020.

The aspects of computational technology that are most critical to the chemical industry include computational molecular science, process modeling and simulation, optimization of operations, process control, and computational fluid dynamics.

Molecular modeling can, in principle, predict the properties of any material, and consequently can be applicable ‘a priori’ to the design of chemical plants without the need of experimental data. In 1929 Dirac wrote:² “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”. Chemical engineering research and design has traditionally been

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experimentally based: Prausnitz,³ during a conference on process design, said “It is sobering to remember that successful oil refineries were built many years before chemical engineers used chemical potentials or fugacities and that sulfuric acid and nitric acid plants existed long before the Debye-Huckel equation”. Both citation are reported by Mathias et al.⁴ in his paper on molecular modeling in engineering design and material developments and even if some years are passed since then, they are still up to date.

The situation of today is that process simulation tools and process modeling in general are commonly used in process design and chemical engineering practice: thermodynamic and kinetic models are readily available in commercial process simulators and open standard for the development of specific models are available⁵ (Cape Open and Global Cape Open). But still, the thermo physical properties and kinetic models are strongly dependent on experimental measurements. Unfortunately, the different CPU time scale of process simulation and molecular modeling did not allow a direct integration of the method so that molecular-level simulation code cannot be included in process simulators for direct calculation of thermo physical properties, which could be desirable and, in principle, feasible.

Moore’s law allows us to be optimistic as far as the computational power is concerned and we may foresee that in some years the computer power will be high enough that the direct integration will be possible.⁶ However, even with an increasing computing power, some molecular simulation will not be possible even in the future and in presence of optimistic prediction of raise of computer power, due for examples to the introduction of nanotechnology for the production of computer chips: the protein folding and unfolding and the simulation in the vicinity of critical points are examples of such situations.⁶

Petaflop computers (Figure 2) anticipated to be built in the next ten years should maintain the growth rates in these in Moore Law,⁷ making it possible to perform 10^{12} -atom classical and 10^7 -atom quantum MD simulations on such computers around year 2010. Multiresolution approaches used algorithms, combined with cache-conscious techniques, will be essential to achieve scalability on petaflop architectures. Ingenious use of multiscale FE/MD/QM simulations implemented with such scalable algorithms will play a significant role in materials research at the nanoscale.

At the same time, however, notwithstanding the extraordinary evolution of computing power, it is not currently possible to perform reliable atomistic MD simulations of polymers containing

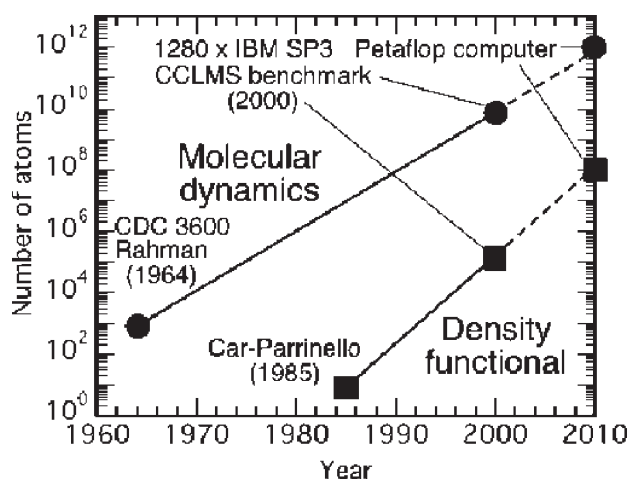


Fig. 2 – Moore’s law for Molecular Dynamics: The number of atoms in classical MD simulations (circles) has doubled every 18 months in the past 36 years, while that in quantum mechanical MD simulations (squares) has doubled every 13 months in the past 15 years. Petaflop computers anticipated to be built in the next ten years should maintain these rates.

more than 10^4 atoms for times of the order of nanoseconds, even on powerful workstations. Nevertheless, by trying to make the structural polymer 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.

Benefits from the coupling of molecular modeling with process simulation and design include but are not limited to (i) shortened product-process development cycles, (ii) optimization of existing processes to improve energy efficiency and minimize production of waste, (iii) efficient design of new products and processes; and (iv) improvements in health, safety, and environment.

Applications for Computational Chemistry in Chemical Processing are readily available in the following fields: new bioprocesses, catalyst design, improved reaction mechanisms, product development (polymers, pharmaceuticals), efficient process design, materials and polymer design, polymer processing and environmental modeling and remediation.

Chemical engineering modeling and time-space relationship

Figure 3 shows the applicability of different modeling techniques in chemical, material and process engineering. It is evident that the same methods cannot be applied to different time and space scale, due to limitation of computer power and to possibility of application of ‘simple enough’ equations in that area. The area of process design, tradi-

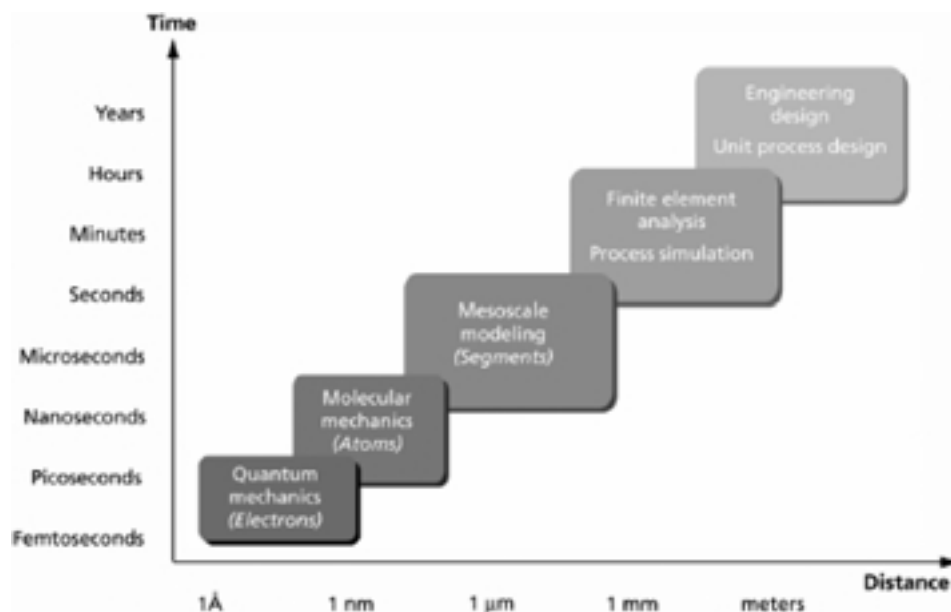


Fig. 3 – Time and Distance in modeling for process engineering

tionally covered by robust and reliable computer code is now in the DNA of chemical engineers in all the countries of the world. Process simulation models for analysis, and synthesis of chemical processes is becoming more and more familiar and common in the developed countries, but still remain a lot to be done in the emerging and in the developing countries.⁵ We are confident that these tools will have more and more penetration in the chemical industries in the future.

Computational molecular science, sometimes called molecular modeling, involves models of chemical systems at the molecular or atomistic level, as well as predictions of quantum effects. At the most basic molecular level, this involves the solution of the Schrodinger equation for electronic (and nuclear) motion or the solution of Newton's equations of motion.⁸

Among other applications, it supplies quantitative estimates of engineering parameters such as heats of formation and heats of reaction, entropies and heat capacities, reaction rate constants, and transport properties like viscosity and thermal conductivity that are needed to construct macro-scale models of complete chemical processes. And molecular modeling gives valuable insight into the properties of new materials so necessary for the efficient design of new products.

In particular, mesoscale simulation methods allow studying inclusions in substratum (e.g. inclusion of materials in polymeric matrix), focusing the subject of modeling from the typical microscopic modeling techniques to the mesoscale approach for representing complex solid and liquid materials. Mesoscale models represent solid materials, fluids,

and gases using larger fundamental units than molecular models, which require atomistic detail and function for larger systems over far longer length and time scales than molecular simulation. Computer simulation determines the structure, properties and dynamics of complex liquids, polymer blends, and structured materials on the nanometer to micron scale.⁹

As already mentioned in the introduction, process simulation and design tools have been traditionally based on experimental information. In the old days, chemical and process engineers used to apply polynomial expression to the interpolation (and sometimes to the extrapolation) of experimental data with almost no statistical treatment and judgment. At a certain point in the history of process engineering, more theoretical models started to be applied for the calculation of thermo physical properties by selecting models available in the literature and by concentrating on the statistical treatment of the experimental data, the reliability of data fitting and the significance of the adjustable parameters. Cubic equations of state and Excess Gibbs Energy models¹⁰ are widespread examples generated by the capacity of the chemical engineering community to apply and further develop concepts and models originally conceived in the chemistry and theoretical physics literature. This operation resulted in the use of more realistic models, with less empiricism and with reference terms more close to the reality. This tendency is auspiciously ongoing and for example now the theoretical (and practical) supremacy of non cubic equations of state^{11,12} (PHCT, PHSCT, SAFT) with respect to the old cubic equation is recognized in the process industry

and in the chemical engineering environment. This result has been achieved again by applying theories and concepts developed years before in the scientific literature. Continuing in this line, now it is time for process and chemical engineers to look at computational chemistry, aiming at applying theoretically consolidated concepts and tools to real products and to real processes for a better understanding of the existing processes and for the possibility of producing new materials.

Computational Chemistry

Computational chemistry involves a mathematical description of systems of chemical species. The goal is to solve the complex equations such as the Schrödinger equation for electronic and nuclear motion which accurately describe natural phenomena. In a practical application of computational chemistry, mathematical equations or algorithms are devised to quantitatively describe the physical and chemical phenomena (e.g., energy states, structures, reactivity, positions and momenta of atoms) that occur in a particular system.⁸ These algorithms are then programmed in the appropriate computer languages and linked together so that the many millions of calculations required to effectively describe the phenomena can be quickly computed.¹³ There are many potential applications of computational chemistry in chemical processes where predicting the characteristics and behavior of a system may be beneficial. By predicting a system's behavior, computational chemistry can potentially be used to improve the efficiency of existing operating systems as well as the design of new systems. It can help to shorten product and process development cycles, optimize processes to improve energy efficiency and environmental performance, and solve problems as they arise in plant operations.

Computational chemistry can also play an important role in the design of molecules (e.g., new chemical products, materials, catalysts). For example, by reliably predicting thermo chemistry (the energy associated with the chemical reaction), it is possible to examine the feasibility of reaction pathways to determine whether a reaction is thermodynamically allowed. Computational chemistry can also be used to reliably predict a wide range of spectroscopic properties (IR, Raman, UV-Vis, NMR, EPR, photoelectron) to aid in the identification of chemical species (e.g., reaction intermediates). Electronic structure calculations can also provide useful insights into bonding, orbital energies and shapes, which can be used to target the design of new molecules with selective reactivity.

As already emphasized, computational chemistry involves calculations at the quantum, atomistic or molecular, and mesoscales, as well as methods that form “bridges” between scales.

At the **quantum scale**, computations seek to solve the Schrödinger equation and describe the ground state (and sometimes the excited state) energies of chemical species. Other properties (e.g., molecular geometry, vibrational and NMR spectroscopic data, multipolar moments) can be obtained from the quantum level energy calculation. Quantum effects are particularly important in chemical reactions and spectroscopy, and provide the basis for predicting interactions at the atomic and molecular scale. The results of quantum mechanical calculations are often used in the design of molecular force fields providing a connection to the next scale, that of atomistic simulations.

The **atomistic or molecular scale** encompasses a wide variety of computations. Calculations are usually done by molecular dynamics or Monte Carlo methods using classical “ball and spring” force fields. Properties described at this scale might range from thermodynamic properties (critical points, pressures) to transport properties (mass and heat transfer) and phase equilibria. Using statistical mechanics, the results of atomistic or molecular scale calculations can then be applied to describe behavior at the mesoscopic and macroscopic scale (e.g., process or bulk properties).

Mesoscale computations describe behavior and properties of systems that reflect the molecular composition of materials, but consist of far too many atoms to compute atom by atom.

Finally, **bridging** techniques attempt to provide continuity and interface between the various scales, allowing the results of calculations at one scale to be used as input parameters to calculations at another scale.

Bridge between molecular modeling and process simulation

More than seventy five per cent of the code in process simulators is dedicated to physical properties estimation, calculation and predictions. Data banks storing pure component parameters and binary interaction parameters for phase equilibrium calculation are extensively used and continuously implemented in modern process simulators. This gives an idea of the important role that physical property availability plays in process simulation. This role become of paramount importance when dealing with new products, with new processes and/or with the revamping, in terms of more sustainability, of existing processes. In most cases substances are used or produced whose

physical properties are not known and in some cases are not even measurable.

Molecular modelling can be seen as a very useful tool to process engineers, by providing the results of virtual experiments, pure components physical properties in a wide range of process conditions, phase equilibrium and kinetic data as well as an interesting tool for screening new and interesting products and reaction schemes.

There are several possibilities for coupling molecular modelling and process simulation. Among them a very interesting one has been proposed for combining molecular modelling and chemical engineering oriented semi-empirical models such as equations of state and excess Gibbs energy models.^{14,15} The general idea here is to use molecular dynamics and Monte Carlo methods for generating the parameters of an equation of state that will subsequently be used in process simulation. In this way one can still perform process simulation with a reasonable hardware (a PC, as well as a workstation) and with a reasonable CPU consumption. In fact, the present computer technology does not allow us to perform a process simulation with integrated molecular modelling tools. The general scheme is reported in figure 3, in which two possibilities are shown:

- Generation of thermo-physical data by means of virtual experiments
- Generation of parameters to be used in semi-empirical model built in process simulators.

Traditionally experimental work has been and is still carried out to provide information to process engineers. The cost of collecting one vapour-liquid equilibria (VLE) data point (i.e., one temperature and composition for just one binary mixture) has been estimated to be around \$ 2,600 and to take 2 days.¹⁶ Thus, we can reasonably hope to perform an experimental characterization of VLE for a small fraction of the total possible mixtures, temperatures and compositions.

With the computing power and technology available nowadays, computer molecular simulations can be considered cheaper and faster than true experiments, especially for simple molecular fluids. 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.

Indeed, during the last decades virtual experiments based on quantum/molecular (QM/MM) me-

chanics calculations and molecular dynamics (MD) simulation techniques have opened avenues in the estimation and prediction of thermo physical properties (both under equilibrium and non-equilibrium conditions) of simple molecular fluids.^{17,18} The treatment of molecular systems in the vapour/gas phase by quantum mechanics is quite simple, due to the possibility of reducing the many-particle problem to a few-particle one based on the low density of a system in the gas phase. If the classical statistical mechanics approximation is permitted, the problem becomes even simpler. Nevertheless, for both amorphous solid states and liquid systems such as solutions and polymers we remain faced with an essentially many-particle system, for which no simple reduction to a few degrees of freedom is possible, and a full treatment of many degrees of freedom is necessary to adequately describe the properties of molecular systems in the fluid-like state. In such cases, to obtain reliable estimations of dynamic and non-equilibrium properties dynamic simulation methods that produce trajectories in the phase space are to be used. The method of MD solves Newton's equation of motion for a given molecular system, which results in space trajectories for all atoms in the system. From these atomic trajectories, a plethora of thermo physical properties can then be calculated as time averages from the relevant microscopic relationships expressed in terms of molecular positions and momenta.

As mentioned above, the aim of computer simulations of molecular systems is to compute macroscopic behaviour from microscopic interactions. The major contributions a microscopic consideration can afford are (i) the understanding and (ii) interpretation of experimental results; (iii) semiquantitative estimates of experimental results and, last but not least, (iv) the possibility to interpolate or extrapolate experimental data into regions that are only difficultly realizable, if at all, in the laboratory.

Figure 4 shows the general connection scheme and the possible interactions between molecular

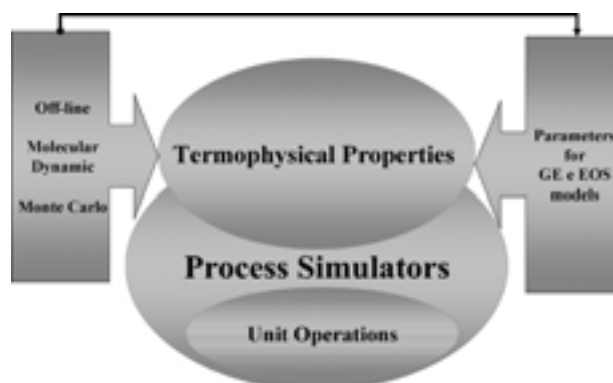


Fig. 4 – Process simulation and molecular modelling

modelling and process simulation. The fundamental starting point of the scheme is the Quantum chemistry and the quantum mechanics ab-initio calculation. Fundamental studies in this field are of paramount importance for defining a theoretical framework within which to develop expressions and parameters for the interaction potential and force fields. Structure and properties of simple materials are used both for developing methods and for the validation of the obtained force fields. Structure and properties may directly be used for defining reaction mechanism and kinetics, which are one of the key inputs to any process simulation run involving reactions and chemical transformation.

Force fields, on the other hand, has a direct application to molecular dynamics and Monte Carlo calculations which are the key techniques for determining pure component and phase equilibrium properties for simple and complex substances. These calculations may be directly applied to the design of new materials and new drugs, to the calculation of parameters of semi empirical models such as equations of state and excess Gibbs energy models or the model development and model validation. Parameters obtained by this procedure are then stored in data base and used by process simulation coupled with semi empirical models, which are by far computationally simpler than any molecular dynamic or Monte Carlo method and therefore affordable in a process simulation.

The boxes depicted in figure 4 rely on the availability of data that are necessary in different parts of the scheme: force fields and model validation, reac-

tion modelling, process simulation etc. A service database is provided for the entire process containing data on thermodynamic properties, phase equilibrium, kinetics, costs and profits, structure and geometry. Furthermore another general service to scheme should contain subroutines implementing all the numerical methods needed for parameter estimation and for solving differential and algebraic equation.

Another traditional method to obtain physico-chemical properties used for screening different possibilities in process synthesis is based on the approach belonging to the group of methods called Computer aided molecular design.¹⁹ It provides a means for determining molecules (CAMD) or mixtures of molecules (CAMMD) having a desirable set of physico-chemical properties. As the physico-chemical properties are directly or indirectly related to the structure of the molecule(s), methodologies for CAMD and CAMMD are typically based on "exploiting" these relationships. Currently, CAMD/CAMMD has found useful industrial applications. However, the application range is restricted because of the limitations on the complexity of the generated molecular structures and on the availability of suitable models for property prediction. Recently, molecular-level information has been combined with the current group contribution based methods for opening new horizons of applicability and accuracy of CAMD. At the same time, CAMD approaches, including molecular mechanics, are extensively used for interpretation of molecular structure and properties and design of new molecules with the desired properties (drugs, agrochemicals, new materials etc).

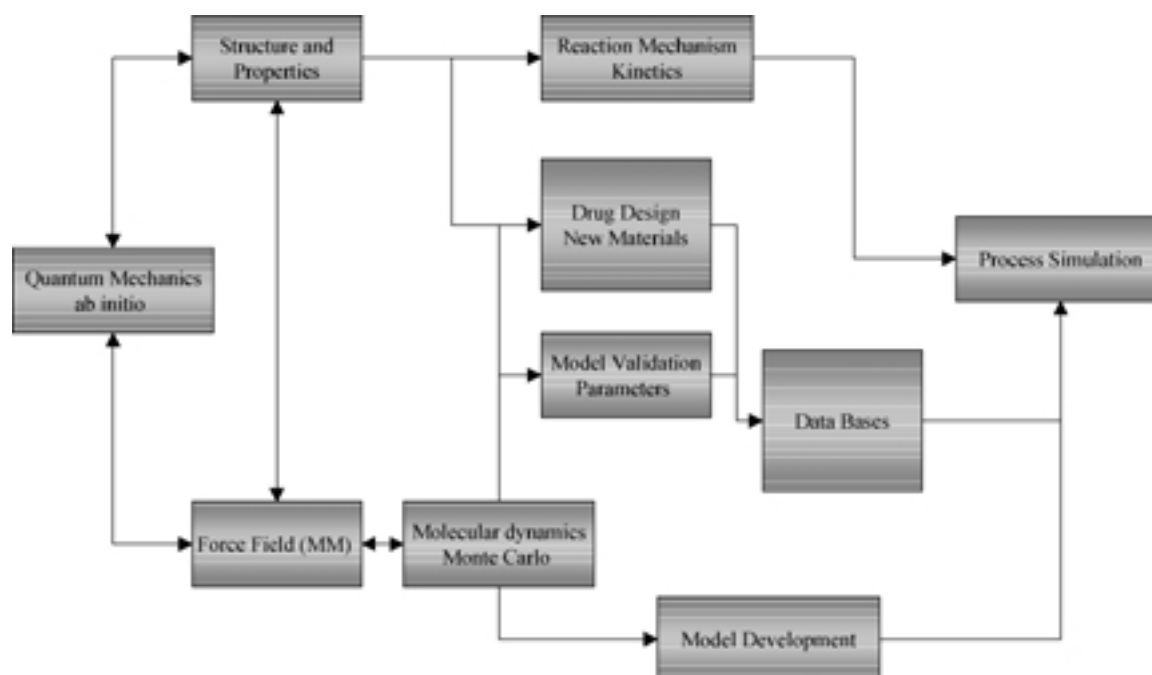


Fig. 5 – General scheme of bridging molecular modelling and process simulation

Examples

Engineering correlations and estimation methods

A route to thermo physical properties of fluids is either via empirical correlations used by engineers for decades or via modern molecular theories of fluids. With respect to inherent limits of the former approach there is no doubt that the future development will go via the molecular approach. Although molecular theories of fluids have made considerable progress over the last decades, their impact on chemical engineering practice has been rather small, particularly because of their usual mathematical complexity and inevitable uncertainty of the proper description of intermolecular interactions. However, the situation has started changing in the last decade with the wide – spread use of theoretically based models which represent a successful semi empirical application of some theoretical ideas.

Phenomenological models will probably remain in industrial practice for the foreseeable future. But we should recognize that these models are simply a physically reasonable way to represent experimental data for the purposes of chemical engi-

neering design and that may not work reliably outside the range of the underlying data. Such models can be applied with success in process analysis, since a direct comparison with real data is possible, but it should be used with caution on process synthesis. And process synthesis is particularly applied in new industries, such as food, pharmaceuticals and metallurgy, where molecules are large, multi functional, strongly polar and ionic. In recent years, models with a stronger theoretical basis (PHSCT, SAFT, ...) have been applied particularly to these industrial environments.

Experimental information needed by such more sophisticated models are less numerous than for previous models, and in those cases molecular modeling have been successfully applied to generate data to be directly used for the calculation of parameters of semi empirical models or directly for determining such parameters. An example of such approach is reported in²⁰ in which pure component parameters of a theoretically based equation of state (PHSCT) are calculated by molecular modeling. The results obtained by this procedure are very interesting and are summarized in Table 1, in which vapor pressure and volumetric properties for refrigerants are predicted.

Table 1 – Predicted vapor pressure P^0 , saturated liquid volume V_L and volumetric properties ρ for selected Chloro Fluoro Hydrocarbons

$$AAD = \text{Absolute Average Deviation} = 100 \cdot \frac{1}{N} \sum_i \left| \frac{M^{\text{exp}} - M^{\text{calc}}}{M^{\text{exp}}} \right|$$

CFHs	PVT	VLE				
	P range (10 ² kPa)	T range (K)	AAD ρ (%)	P ⁰ range (10 ² kPa)	AAD P ⁰ (%)	AAD V _L (%)
R13	5 – 20	150 – 240	1.79	0.03 – 15.93	3.36	2.35
R14	6 – 20	110 – 200	1.93	0.07 – 15.50	1.71	2.27
R21	3 – 10	220 – 310	1.69	0.03 – 23.96	3.08	3.05
R22	5 – 20	250 – 340	1.59	1.77 – 19.82	4.62	1.16
R23	2 – 10	200 – 290	1.65	0.03 – 20.02	5.98	1.78
R32	12 – 98	253 – 333	3.74	3.47 – 8.64	4.33	2.66
R113	1 – 8	270 – 360	3.09	0.10 – 15.03	3.12	5.24
R114	1 – 8	300 – 390	1.16	0.11 – 8.67	4.43	2.91
R115	1 – 8	210 – 300	2.11	0.20 – 10.88	2.17	2.97
R123	1.013	203 – 393	0.622	0.12 – 21.022	3.30	4.29
R134a	8 – 20	285 – 374	1.79	2.16 – 4.27	5.34	0.722
R142b	1.03 – 3.45	266 – 350	1.90	1.14 – 6.20	2.10	1.01
R143a	5.74 – 8.26	274 – 364	2.66	0.25 – 17.5	2.37	3.76
R152a	1.03 – 3.10	266 – 350	1.01	1.09 – 14.3	1.42	1.61

A similar approach has been also applied to PVT properties of pure polymers:²¹ the equations of state used in this case are PHSC and Lattice Fluid model of Sanchez and Lacombe.²² Table 2 shows results obtained in the prediction of PVT properties. For both models the adjustable parameters of the pure polymers have been calculated from molecular modeling directly.

Table 2 – Comparison in terms of root mean squared deviations (RMSD) between experimental data and PHSC and Sanchez Lacombe (LF) equations of state predictions for selected polymers

Polymer	P range (MPa)	T range (K)	RMSD % PHSC	RMSD % LF
<i>a</i> -poly(propylene)	0–196	446.66–571.63	2.5	5
poly(vinyl chloride)	0–200	373.35–423.15	1.1	7
Poly(epichloridrine)	0–200	333.15–413.15	2.5	7
Poly(<i>ε</i> -caprolactone)	0–200	373.75–421.35	1.7	5

A similar approach for the estimation of parameters of Excess Gibbs Energy model was followed in¹⁵ where ab initio quantum mechanics methods are used to obtain a solution of the Schrodinger equation and determine the molecular interaction energies resulting from hydrogen-bonding and van der Waals interactions. In particular, the Hartree–Fock HF method is used to determine the interaction energy between molecular pairs in clusters, and this information is then used in the UNIQUAC model to successfully predict the phase behavior. Examples given in the article are for the methanol water, ethanol water, acetic acid water, and formic acid water mixtures.

Property prediction by molecular modeling in the industrial world

Westmoreland et al. presented a very interesting and rather complete survey of molecular modeling applications in different countries.²³ It is interesting to note only some applications of molecular modeling for calculations of properties in different companies. Notable examples of development of products and processes are the following:

- Bio-active materials like pharmaceuticals (Merck, Novartis, Takeda Chemicals) and crop-protection chemicals (DuPont, Sumitomo Chemical)
- Polymers, glass, and structural materials (Asahi Chemicals, Owens Corning, Rhône Poulenc / Rhodia, W.R. Grace)
- Electronic and photonic materials (Motorola, Toshiba, Lucent)
- Homogeneous and heterogeneous catalysts (Ford, Haldor Topsøe, Ube Industries)

- Sorbents for gas separations (BG Technologies / Advantica Technologies Ltd., Air Liquide, Air Products and Chemicals)
- Personal-care, food, and consumer products (Colgate Palmolive, Unilever, Kellogg, 3M)
- High-volume chemicals and materials (Dow, BASF, Rohm & Haas)
- Dyes and pigments (Bayer, Mitsubishi)
- Films and imaging (Fuji Photo Film, Xerox)
- Fuels and automotive chemicals (Chevron, TotalFina / TotalFinaElf, Lubrizol)
- Commercial software and hardware for calculations (MSI / Accelrys / Pharmacopeia, Gaussian, COSMOlogic, Fujitsu).

Molecular modeling methods have gained acceptance as practical tools in a variety of industries. Tables in Chapter 10 of the ITRI Report²³ list 55 U.S. companies that have made use of molecularly based modeling limited to companies making use of modeling specialists (undoubtedly an incomplete list). The tables list an additional 265 companies, universities, or other organizations elsewhere throughout the world in many different industry sectors, ranging from pharmaceuticals to polymers, personal care and food products.

Force Field for alternative refrigerant

The air-conditioning and refrigeration industry is in the midst of an unprecedented transition, catalyzed by environmental concerns with the impacts of refrigerant emissions. Attention is now focused on ozone depletion and global warming, with a view toward reducing greenhouse gas emissions but the number of suitable elements that can be combined at the molecular level is small. Consequently, the probability of finding an ideal refrigerant is practically zero and greater attention is needed in addressing both environmental and safety concerns by containment, particularly for compounds with minimal adverse impact, rather than phase out. Several HFCs, and particularly their binary and/or ternary mixtures have been recently reconsidered as promising candidates to replaced (to be) banned refrigerants. In this respect, simulation studies and force field developments for perfluorinated compounds are very promising and challenging, but to be useful, the accuracy of calculation should be rather high. Force field and simulation studies for such compounds are limited and a lot of attention is given to generalized force fields which may not be very accurate for a given component. Recently²⁴, during a Workshop on Alternative refrigerants an all-atom model for HFCs, which is able to reproduce accurately experimental PVT and phase equilibrium data has been proposed. An idea of the performances obtainable in the prediction of thermo physical properties is reported in Table 3.

Table 3 – Absolute average deviation (AAD – see table 1) between experimental and predicted values of saturated liquid (SLD) and vapour (SVD) density for some refrigerants.

Compound	AAD SLD	AAD SVD
R32	1.13	3.29
R161	1.22	3.65
R152a	1.49	3.69
R143	2.06	3.70
R143a	2.24	5.51
R134	2.27	4.29
R134a	2.35	4.15
R125	2.11	3.77

COSMO-RS for the prediction of mixture properties

There are rapid improvements in modeling solvation and nonideal mixing properties through combinations of electronic-structure calculations with continuum solvation models (e.g., Tomasi's PCM and subsequent models, the COSMO-RS method developed at Bayer and spun off to a start-up company, COSMOlogic).

Several papers appeared in the literature in the last years^{25, 26} based on variation and refinements of the same basic theory. In all cases it is shown that models based on continuum solvation methods are capable to predict mixture properties with reasonable accuracy starting from quantum chemistry calculations and introducing a parameterization at element level. The basic theory of such models is a unimolecular quantum chemical calculations that provide the necessary information for the evaluation of molecular interactions in liquids. Combined with a very fast and accurate statistical thermodynamics, the new method is an alternative to structure-interpolating group contribution methods. The most important advantages are the essentially general applicability, the sound physical basis.

The overall quality of the results obtained in the literature, both in terms of VLE prediction capabilities for several classes of compounds and computational time involved, allow us to conclude that bridging between molecular and process simulation has achieved a very good impulse in becoming a reality.

Prediction of polymer properties by QSPR

The prediction of thermo physical properties of polymers is extremely important in polymer processing technology, particularly when dealing with

co polymers. For such applications molecular dynamics methods can be applied to the properties prediction, but more effective and efficient results can be obtained by a quantitative relation between structure and properties (QSPR). The method is based on the determination of specific group contribution values for certain classes of polymers²⁷ for amorphous and not cross-linked conditions. Those group contribution values can applied subsequently to copolymers and homo polymers in different conditions. Table 4 reports a comparison between experimental and predicted values for some relevant property for homo polymers.

Table 4 – Comparison among heat capacity calculated by QSPR, molecular dynamic and experimental value for some polymers at different temperatures.

Polymer	T (K)	Cp QSPR (J/mole K)	Cp MD (J/mole K)	Cp EXP (J/mole K)
poly(butylene terephthalate)	150	154	143	135
poly(butylene terephthalate)	200	196	190	182
poly(butylene terephthalate)	400	422	415	401
poly(butylene adipate)	150	160	165	175

Table 5 reports results obtained for copolymers in terms of glass transition temperature. The agreement obtained can be considered very good.

Table 5 – Comparison between experimental and predicted glass transition temperature for copolymers.

Copolymer	T _g (K) QSPR	T _g (K) EXP
poly(butylene adipate) 20 % poly(butylene isophthalate) 80 %	296	281
poly(butylene adipate) 50 % poly(butylene isophthalate) 50 %	274	251
poly(butylene adipate) 80 % poly(butylene isophthalate) 20 %	251	228
poly(butylene isophthalate) 20 % poly(butylene terephthalate) 80 %	339	311
poly(butylene isophthalate) 40 % poly(butylene terephthalate) 60 %	332	305
poly(butylene isophthalate) 60 % poly(butylene terephthalate) 40 %	324	303
poly(butylene isophthalate) 80 % poly(butylene terephthalate) 20 %	317	302

Gas separation by adsorption

Molecular simulations are an effective and complementary tool for studying the sorption thermodynamics of zeolitic systems. In particular, Grand Canonical Monte Carlo (GCMC) techniques are well suited for this purpose.

Recently, GCMC simulations of sorption equilibria of methane, ethane, propane, butane, hexane, cyclohexane, benzene and toluene were performed in a silicate-1 type zeolite.²⁸ The results obtained show good agreement with the corresponding experimentally available sorption isotherms and isosteric heats. Further, they indicate that the considered hydrocarbons behave ideally within the zeolite pores, and that each species prefers to locate at different positions within the zeolite pore framework, in harmony with theoretical predictions.

Nanotechnology

Polymer/organoclay nanocomposites have emerged as a new class of materials in the last decade of the 20th century. They have superior properties, such as higher tensile strength, heat resistance, and are less permeable to gas at a lower level of loading compared with traditional composites. In the formation of nylon 6/organoclay nanocomposites, platelets initially stacked together to form clay particles are intercalated with polymer, exfoliated and dispersed into the nylon matrix. A single platelet is sheetlike, having a thickness of only about 10 Å and 1×1 μm² width. The resulting aspect ratio of about 1000 is a contribution reinforcement factor, since, according to classical theories of filler reinforcement, the volume fraction and the aspect ratio are the key parameters governing the mechanical properties of the resulting nanocomposites. Indeed, such theories predict that only a few percent of clay by volume could double or triple the modulus of layered clay nanocomposites.

Molecular mechanics/dynamics computer simulations are used to explore the atomic scale structure and to predict binding energy values for polymer/clay nanocomposites based on nylon-6, montmorillonite and several, different quaternary ammonium (quat) salts.²⁹ Results reveal that the energy of binding between the polymeric matrix and the montmorillonite platelet shows a decreasing trend with increasing molecular volume V of the quaternary ammonium salt used as surfactant. On the other hand, both the binding energy between the polyamide and the quat, and between the quat and the montmorillonite increase with increasing V , although with a different slope. Shorter hydrocarbonic chains are more effective in producing favorable binding energies with respect to longer ones, and the substitution of hydrogen atoms with polar

groups, such as -OH or -COOH on the quaternary ammonium salt generally results in a greater interaction of the quat with the polymer. Under the hypothesis that the clay platelets are uniformly dispersed within the polymer matrix, the pristine clay still yields a high interfacial strength between MMT and nylon-6. This study is an example of application of mesoscale modelling for the prediction of the property – structure relationship.

Conclusions

The principal role of molecular and materials modelling in the chemical industry is to speed product development and guide experiment.

From the examples reported in this paper we can conclude that even though the phenomenological models will remain relevant to engineering design, they will be more and more coupled and ‘fed’ by virtual experiments and by information generated by molecular modelling. To be effective in the short period of time for material and process design, molecular modelling must serve as an ‘alternative’ laboratory tool’. Examples are reported of direct integration of process modelling with molecular modelling through a physically based thermodynamic model whose parameters are directly calculated from quantum mechanics or molecular dynamics. This approach seems to be very interesting and directly usable for bridging the two modelling tools.

Improvements in molecular modelling simulation require reliable force fields developed from quantum chemistry information and checked versus real engineering oriented experimental data.

Molecular modelling methods have gained acceptance as practical tools in a variety of industries: these methods have been used because they have proved their value with success. Recently²³ a study identified three major success areas for molecular modelling as drug discovery, development of homogeneous catalysts, and thermochemistry. In his overall conclusion,²³ Phil Westmoreland found a “strong evidence that in the next ten years molecularly based modeling will profoundly affect how chemistry, biology, and materials physics are understood, communicated, and transformed to technology, both intellectually and in commercial applications. Molecularly based modeling is a basis for communicating, understanding, and developing new technologies like nanotechnology. It creates new ways of thinking- and of achieving.”

In summary, even though molecular and process modeling deal with different time and length scales, an indirect integration between the two area of modeling is available today and will be more and more direct in the future. This conclusion may be

interpreted as a suggestion to consider, in process modeling, molecular modeling techniques for the direct determination of physical properties of pure components and mixtures already today, to gain familiarity with terms and techniques that will certainly be used in chemical engineering practice tomorrow.

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List of symbols

- AAD – absolute average deviation
 C_p – specific heat (J/mole K)
 P – pressure (kPa)
 PVT – pressure volume temperature
 RMSD – root mean squared deviation
 T – temperature (K)
 T_g – glass transition temperature (K)
 V_L – saturated liquid volume (m³/mole)
 VLE – vapour liquid equilibrium
 ρ – density (kg/m³)

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