# Molecular Simulation of the thermophysical properties of fluids : from understanding toward quantitative predictions

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Molecular simulation refers to methods in which the individual positions and conformations of the molecules are explicitly accounted for. Over the last decades, algorithms have made numerous progress in this field, and the increase of computer capacity at has made many realistic systems accessible to simulation. What kind of thermophysical properties can be addressed with molecular simulation ? Does it provide qualitative understanding or quantitative predictions ? We provide tentative answers to these questions.

In a first part, the main types of molecular simulation methods are introduced. Molecular dynamics (MD), which consists in solving Newton's equations of motion with time, can be used to address equilibrium properties and dynamic behaviour as well. Monte Carlo simulation (MC), which relies on statistical methods, is particularly adapted to phase equilibria or physisorption. Both methods require to represent the potential energy, which is classically decomposed into intramolecular (bond stretching, bending, etc. ) and intermolecular (dispersion, repulsion, electrostatic, polarisation) contributions.

In a second part, the prediction of fluid properties is reviewed. Statistical averages can be used to address phase properties (PVT relationships, enthalpy). Thermodynamic derivative properties (heat capacity, compressibility, Joule-Thomson coefficient….) can be determined by analysing fluctuations. Either MC or MD can be used to get a very good understanding of the relations between properties and molecular structure, as shown by examples like high pressure hydrocarbon gases, CFCs, acid gases, and natural gases.

Fluid phase equilibria are discussed in a third part. MC simulation can be used to represent the vapour-liquid equilibrium of pure substances in a large range of temperatures and molecular structures. Examples are given in which it is used to provide pure component properties when pure chemicals are not commercially available, such as heavy hydrocarbons of complex structure. MC simulation is also capable of predicting phase behaviour for mixtures with little (or no) calibration on binary system data. This aspect is illustrated by the prediction of Henry constants of gases in polar liquids and by the prediction of phase diagrams of acid gases (H2S, CO2) with water, methanol or hydrocarbons. These examples provide an opportunity to show that molecular simulation is able to reproduce detailed features, such as the self-association of polar molecules and the critical scaling behaviour.

The fourth part of the talk is devoted to the prediction of transport properties. A very important advantage of molecular simulation is that it encompasses the prediction of equilibrium properties and dynamic properties in a single theoretical framework. Viscosity, diffusion coefficients and thermal conductivity may be derived consistently by MD and the role of the various interactions can be separated. For many systems, very good predictions are obtained, and simulation is shown to predict detailed features such as the differences in viscosity between isomers.

In a fifth section, other successful applications of molecular simulation are presented with a special emphasis on interfacial properties, where it allows to account for the amphiphile role of surfactants. Adsorption in microporous adsorbents and solubility in polymer materials are also briefly mentioned.

In the conclusion, the current limitations of molecular simulation methods are mentioned. Future improvements are expected in several ways : more powerful statistical bias algorithms, more accurate intermolecular potentials and more systematic use of parallel computers.