Molecular Dynamics Simulation of Realistic Systems

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Molecular dynamics simulation is a powerful tool for understanding and predicting thermophysical properties in systems both at equilibrium and away from equilibrium and composed of molecules ranging in complexity from spherically symmetric monatomic molecules to polymers. The widespread utilization of low-cost high performance engineering workstations has permitted the application of molecular dynamics and Monte Carlo simulation techniques to proliferate at an astounding rate. High-performance massively-parallel supercomputers (such as the Intel Paragon and IBM SP/2) permit the simulation of systems with an unprecedented degree of complexity. As computing costs continue to decline, molecular simulation of systems modeled to a high degree of accuracy promises to become an equal partner with experiment for the prediction of thermophysical properties for industrial purposes. Several examples of the use of molecular dynamics simulation to predict the properties of highly realistic systems are described.

1. OVERVIEW OF MOLECULAR DYNAMICS SIMULATION

The rapidly increasing speed of computing over the past decade, combined with its equally rapidly decreasing cost, is revolutionizing science and engineering, so much so that computational science is increasingly regarded by many as the equal partner of the two traditional sciences, theory and experiment. In the realm of physical properties prediction, the primary impact of this development has been the evolution of molecular simulation methods into essential and ubiquitous tools for the calculation of the thermophysical properties of fluid and solid systems\textsuperscript{1}.

Molecular simulation can be performed in two main domains. One is in the time domain (molecular dynamics, in which the solution of dynamical differential equations of motion describing the classical mechanical motion of the individual molecules is averaged over time to obtain time-averaged measures of macroscopic thermophysical properties). The other is in configurational space (Monte Carlo, in which configurations of the system of interest are generated by a Markov chain process designed to asymptotically generate a succession of configurations distributed according to a prescribed probability distribution - such as the Boltzmann distribution...
for a canonical ensemble system at fixed temperature, volume and molecule number - from which configurational averages of macroscopic thermophysical properties can be obtained. Additionally, molecular simulation can be performed by some hybrid of these two methods (such as Brownian dynamics in which the motion of the Brownian molecules is handled dynamically while the solvent is handled statistically). This paper will be devoted to molecular dynamics (MD) while Monte Carlo simulation are be the subject of the paper by Smit.

1.1 Molecular Dynamics Ensembles

MD simulations are conceptually straightforward: The non-linear ordinary differential equations of motion for the dynamics of the molecules of interest, usually Newton’s equations of motion, or a variant thereof, are solved using standard numerical methods for initial-value problems and the trajectories of the molecules are calculated as functions of time. Thermophysical properties (such as pressure, energy and shear viscosity) are calculated as time averages from microscopic expressions given in terms of the positions and momenta of the individual molecules. Newton’s equations of motion yield a simulated system at constant energy \( (E) \), number of molecules \( (N) \) and volume \( (V) \). Thus, Newtonian molecular dynamics yields a realization of the microcanonical (or isoenergetic-isochoric) ensemble of statistical mechanics. [Strictly speaking, such a simulated system satisfies one additional constraint because the total momentum is preserved under Newton’s laws, prompting some to call the ensemble generated by Newton’s equations the MD ensemble.] The isoenergetic-isochoric ensemble is not a particularly convenient ensemble because the temperature is not prescribed. Beginning in the early 1980’s, considerable theoretical progress was made in developing methods for either constraining the temperature (essentially the average kinetic energy per molecule)\(^2\), \(^3\) or the kinetic energy\(^4\) of the system (isothermal and isokinetic methods respectively) to a prescribed value. The recognition that Newton’s equations of motion could be rigorously modified to enable the simulation of other ensembles (including constant pressure\(^5\)) has led to a proliferation of new ensembles for MD, including the grand canonical ensemble\(^6\), the Gibbs-Duhem ensemble for extending phase equilibria calculations\(^7\) and an MD version of the Gibbs ensemble for direct computation of phase equilibria\(^8\).

1.2. Molecular Dynamics Simulation Algorithms

In addition to the ensembles involved, MD simulations can be broken up into three broad categories based on the nature of the molecules: spherically symmetric molecules, rigid non-spherical polyatomic molecules, and flexible polyatomic molecules (including polymers). Rigid polyatomic molecules are handled either by augmenting the translational equations of motion with Eulerian rotational equations of motion (typically solved using the quaternion formalism introduced to molecular simulation by Evans\(^9\)) or via constraint dynamics to impose rigid bond length and/or fixed bond angle constraints\(^10\)-\(^12\). The simulation of non-rigid molecules can be made efficient by the use of multitime step methods that treat the short time scale internal degrees of freedom related to bonded pair interactions on a different basis than the motion induced by intermolecular and non-bonded intramolecular interactions\(^13\). Finally, MD simulations differ on the basis of the numerical scheme used to integrate the non-linear ordinary differential equations resulting from the ensemble used and the molecular model employed. The numerical methods range from the simple but effective Verlet methods to Runge-Kutta and predictor-corrector algorithms. Many of the basics of MD simulation are described in the fine monograph by Allen and Tildesley\(^1\),
although many of the more recent developments - particularly the proliferation of ensembles now possible in MD - have been published since completion of this book.

1.3. Non-Equilibrium Molecular Dynamics

Non-equilibrium molecular dynamics (NEMD) has been developed over the past three decades, with the most important developments in the last decade including the derivation of rigorous nonlinear response theories to theoretically characterize the methods for the first time. Many of these developments are covered in the monograph by Evans and Morriss\cite{14} and recent review articles\cite{15,16}. NEMD permits the simulation of a system at steady state away from equilibrium, such as a system subject to homogenous planar Couette flow. In NEMD, an external field, either physically realizable (as in the case of planar Couette flow) or synthetic (as in the case of the color field algorithm), is applied to a system so as to be consistent with periodic boundary conditions. The field induces a current so that the ratio of the current to the applied field provides a measure of a transport coefficient (e.g., shear viscosity in the case of planar Couette flow and diffusivity in the case of the color field algorithm). The planar Couette flow algorithm (known as isokinetic SLLOD\cite{4}) is exact to all orders of the field and so is in principle applicable to both the linear and non-linear regimes, while for synthetic algorithms the correspondence between the quantity calculated by NEMD and the corresponding transport coefficient is only valid in the linear regime (limit of zero applied field).

1.4. \textit{Ab initio} Molecular Dynamics

A recent development in MD that deserves brief mention is the use of \textit{ab initio} methods, pioneered by Car and Parrinello, in which the electronic degrees of freedom are solved using density functional theory simultaneously with the classical motion of the atoms in the system. While originally focused on materials exhibiting a band gap, the method has recently been applied to water\cite{17,18} with some success. Because it is essentially an \textit{N}-body simulation technique, it involves prohibitively long computation times compared to ordinary classical MD for the same number of molecules. Alternatively, the technique is limited to small system sizes, such as 32 molecules in the water study cited above. However, it offers the possibility of eliminating our reliance on effective two-body intermolecular potentials that are limited to various regions of the phase diagram. For example, intermolecular pair potentials for water fitted to ambient conditions (and which thus effectively account in their parametrizations for multi-body effects such as polarizability) do not work as well outside this regime.

1.5. Parallel Molecular Dynamics

The advent of massively parallel machines has driven the extension of all the methods described above to forms suitable for execution on parallel machines, the most powerful of which (e.g., the Intel Paragon family, the IBM SP/2, and the Cray T3D) utilize the message-passing paradigm. For MD, the most efficient implementations on parallel machines have largely focused on domain decomposition where each processor handles the molecules located in a particular region of physical space\cite{19}. In our laboratory, we have undertaken the development of a large number of message-passing parallel MD codes for the equilibrium and non-equilibrium MD simulation of aqueous solutions and polymeric fluids. Information about these developments is provided by a World Wide Web server located at URL http://flory.engr.utk.edu/ldrd/w.html.
This very brief summary of the status of MD simulation is by no means comprehensive and is intended simply as an overview to provide the background for a discussion of the uses of MD to model substances with a high degree of realism. Provided that the intermolecular potentials are known, MD now provides us with a highly-refined tool for predicting many thermophysical properties (thermodynamic and transport properties, phase equilibria and dynamical properties) of real systems. In fact, knowledge of the intermolecular potential is frequently the major limitation in the application of MD simulation techniques.

We will consider several cases in which the availability of accurate intermolecular potentials has made it possible to predict the properties of real systems with a high degree of accuracy or, as in one case, to provide definitive verification of the predictions of theory. The problems we shall consider are ion-pairing in supercritical aqueous electrolyte systems, the Newtonian transport properties of low molecular weight fluids, and the scaling behavior of transport properties of polymeric fluids.

2. ION PAIRING IN SUPERCritical WATER

Supercritical fluids have generated considerable interest in recent years because of their application as solvents in supercritical solvent extraction processes and supercritical fluid chromatography and as reaction media. The unique combination of the dissolving power of a liquid combined with the transport properties of a gas and the ability to cause large density changes with small pressure and/or temperature changes are the main reasons for much of the interest in supercritical fluids and their mixtures.

Dilute supercritical mixtures present serious challenges to molecular simulation for several reasons. First, the diluteness is itself a problem: to study a mixture in which the solute species is at a mole fraction of \( x_U \leq 10^{-3} \), the typical upper limit for supercritical solutions of practical interest, requires performing a simulation containing at least \( 10^3 \) molecules, and may require \( 10^4 \) to \( 10^5 \) to obtain good statistical averages on solute-solute interactions\(^{20}\). (We use the notation that the subscript \( U \) denotes solute, subscript \( V \) denotes solvent.) Second, simulations performed at near-critical states require that the dimensions of the simulation cell are large in comparison to the correlation length \( \xi \) which diverges at the critical point\(^{21,22}\). A third difficulty is that in order to perform simulations at near-critical and supercritical state points, the critical point for the model must be determined. The most efficient method for doing so is to perform a Gibbs ensemble Monte Carlo (GEMC)\(^{23,24}\) to determine the phase envelope. GEMC estimates for the critical point are, like any other simulation-derived property, dependent on details of the simulation (such as the method used for truncating the intermolecular potential and possible finite size effects) so that precise critical point estimates (to within 1% or less) are very difficult to obtain. Finally, so-called "infinitely dilute" molecular simulations are typically performed at finite dilutions of \( x_U = 10^{-2} - 10^{-3} \) (one solute molecule in 200-1000 solvent molecules with solute-solute interactions eliminated). Thermodynamically, this solute mole fraction is sufficient to cause a significant shift of the mixture critical point away from the solvent critical point, complicating further the interpretation of the nearness of the simulated system to criticality. Although there has been considerable focus on performing MD simulation on near critical supercritical mixtures\(^{20-22,25-27}\) (at temperatures and densities within 5% of the critical values), our present understanding is that the
important processes in supercritical fluid solvation are associated with short-range solute-solvent structure and that the dramatic long-ranged effects associated with near criticality (such as the large magnitude of the solute partial molar volume) are primarily solvent effects and of secondary importance\(^\text{28}\).

The near-critical properties of dilute aqueous electrolyte solutions are extremely difficult to determine with precision due to the simultaneous existence of long-ranged density/composition fluctuations and long-ranged Coulombic interactions. For the particular case of highly dilute NaCl in water, this situation translates into a rapid change in the slope of the \(T - x\) and \(P - x\) critical lines\(^\text{29, 30}\). Since in the highly compressible near-critical region large changes in the solvent dielectric constant dramatically affect screening of the Coulombic interactions, and consequently, the degree of ionic association, modeling of dilute high temperature and near-critical electrolyte solutions is extremely difficult.

In order to understand ion pairing in dilute supercritical aqueous solutions, we have undertaken a program of molecular dynamics simulations of dilute aqueous NaCl solutions in near-critical water, particularly focusing on the \(\text{Na}^+ / \text{Cl}^-\) association process which can be envisioned as

\[
\text{Na}^+ + \text{Cl}^- \leftrightarrow \text{Na}^+ \| \text{Cl}^- \leftrightarrow \text{Na}^+ \text{Cl}^- \leftrightarrow \text{NaCl} \tag{1}
\]

where NaCl is the product of the "reaction" between the \(\text{Na}^+\) and \(\text{Cl}^-\) ions, and \(\text{Na}^+ \| \text{Cl}^-\) and \(\text{Na}^+ \text{Cl}^-\) represent the solvent separated ion pair (SSIP) and contact ion pair (CIP) states, respectively. Experimental evidence indicates that these two ion-paired states might act as reaction intermediates\(^\text{31-35}\). We determine the anion-cation potential of mean force by molecular simulation\(^\text{36}\) complementing other results at higher temperature\(^\text{37, 38}\) and ambient conditions\(^\text{39}\).

Technical details of the simulation are provided elsewhere\(^\text{36}\). Here, we summarize only the most pertinent information. The water-water interactions were described by the simple point charge (SPC) model of Berendsen et al.\(^\text{40}\), the ion-water interactions were modeled using the Pettitt-Rossky model\(^\text{41}\) while for the ion-ion interaction we used the Fumi-Tosi model for alkali-halide interactions\(^\text{42, 43}\). All simulations were performed with the ions at "infinite dilution" in the isokinetic-isochoric ensemble, with \(N = 256\) molecules, \(N - 2\) water molecules plus an anion and a cation. The method used to calculate the potential of mean force is the constraint technique of Cicotti et al.\(^\text{44}\). A series of simulations are performed with the ions constrained in each simulation to remain a fixed distance \(r\) apart. In each simulation, the solvent contribution to the force between the ions, \(\Delta F(r)\), is calculated from the force exerted on each ion by the solvent, \(F_{\text{wI}}\) for \(I = \text{Na}, \text{Cl}\) corresponding to sodium and chloride respectively according to

\[
\Delta F(r) = 0.5\left(\hat{r}_{\text{NaCl}} \cdot (F_{\text{wI}} - F_{\text{wNa}})\right) \tag{2}
\]

where \(\hat{r}_{\text{NaCl}}\) is the unit vector along the direction of the anion-cation interaction. The solvent contribution is added to the direct Coulombic force to give the total ion-ion force \(F_{\text{NaCl}}(r)\) and integrated from a large distance \(r_0\) to \(r\) to calculate the potential of mean force, \(W_{\text{NaCl}}(r)\), via

\[
W_{\text{NaCl}}(r) = W_{\text{NaCl}}(r_0) - \int_{r_0}^{r} F_{\text{NaCl}}(r')dr' \tag{3}
\]
From this, the NaCl radial distribution function is calculated by $g_{\text{NaCl}}(r) = \exp[-W_{\text{NaCl}}(r)/k_B T]$ where $k_B$ is Boltzmann's constant and $T$ is the absolute temperature. The equilibrium constants can be evaluated from $g_{\text{NaCl}}(r)^{45}$. The simulations were performed at a state condition corresponding to $T_c = 1.05$, $\rho_c = 1.0$ based on the critical conditions for the SPC water model$^{46}$. Standard periodic boundary conditions were used along with the minimum image criterion and a spherical cutoff with reaction field for the truncated intermolecular interactions$^1$. The accuracy of the reaction field was assessed by performing Ewald summation simulations for a few typical constrained configurations$^{45}$. The production runs for thermodynamic and structural properties comprised $3 \times 10^4$ time steps (30 psecs) while those for mean-force calculations were extended to $10^5$ time-steps for each constrained ion-pair distance.

We comment first of all about the accuracy of the molecular dynamics simulation for pure supercritical water. In one sense, SPC is typical of rigid, non-polarizable models fitted to the ambient behavior of water, in that the accuracy of the model deteriorates as one moves away from ambient conditions. In particular, the dipole moment of SPC water is 2.274 D for the SPC, considerably larger than 1.85D, the dipole moment of the isolated water molecule. The larger value employed by the SPC is obtained by fitting to ambient condition properties and is an effective value which takes into account the many-body polarizability at the pair interaction level. Since the degree of polarizability is a state-dependent quantity, it is not surprising that several pieces of evidence, ranging from phase equilibria$^{47}$ to neutron scattering at supercritical conditions$^{48,49}$ suggest that the high value of the effective dipole moment of SPC is inaccurate in supercritical states. The result is that the critical properties predicted by the SPC ($T_c = 587K$ and $\rho_c \approx 0.27gm/cc$)$^{46}$ differs significantly from that of real water ($T_c = 647.1K$ and $\rho_c = 0.322gm/cc$).

A variant of the SPC, SPCE$^{50}$, has excellent phase equilibrium and critical properties$^{51}$ but, since its effective dipole moment is larger than SPC's, it predicts structure in the supercritical state less accurately than SPC. It is clear that an intermolecular potential that will predict the properties of water throughout the phase diagram will require true accounting for polarizability effects$^{52}$. Nevertheless, the thermodynamic properties of the SPC model in supercritical states are predicted quite accurately at corresponding states (same $\rho_r = \rho / \rho_c$ and $T_r = T / T_c$), as shown by Cummings et al.$^{21}$. 
Figure 1. Potential of mean force (left) and radial distribution function (right) between sodium and chloride ions at infinite dilution in supercritical water ($T_r = 1.05$, $\rho_r = 1.0$) calculated by simulation (-----) and using the continuum theory given by Eq. (4).

The potential of mean force and NaCl radial distribution function at infinite dilution at $T_r = 1.05$, $\rho_r = 1.0$ are shown in Figure 1. The simulation results are compared to the continuum theory in which the potential of mean force is assumed to be given by the bare potential between the ions, $u_{NaCl}(r)$, screened by the dielectric constant of the solvent, $\varepsilon$,

$$W_{NaCl}^{\text{continuum}}(r) = \frac{u_{NaCl}(r)}{\varepsilon} \quad (4)$$

The equilibrium constant for association is given by

$$K_a^M = \frac{\rho_{\text{CI}^-}}{\rho_{Na^+}\rho_{\text{CI}^-}} \quad (5)$$

where the superscript $M$ denotes units of liter/mole and $\rho_{\text{CI}^-}$, $\rho_{Na^+}$, and $\rho_{\text{CI}^-}$ are the density of contact ion pairs, unassociated $Na^+$ ions and unassociated $CI^-$ ions respectively while the equilibrium between SSIP and CIP is given by
\[ K_s = \frac{\rho_{\text{SIF}}}{\rho_{\text{CIF}}} \]  

(6)

To eliminate uncertainties associated with the calculation of the dielectric constant of SPC, it turns out to be more appropriate to consider the related quantity \( I_a = K_a^M \exp(q_{\text{ion}} q_{\text{cl}} / e r_0 k_b T) \) where \( q_a \) is the charge on ion \( \alpha, \alpha = Na, Cl \). This quantity is a very sensitive function of the state conditions. For example, simulation results indicate that \( \log I_a = 4.3 \) at \( \rho = 0.1252 \text{ g/cm}^3 \) and \( T = 800 \text{ K} \), \( \log I_a = 5.6 \) at \( \rho = 0.0832 \text{ g/cm}^3 \) and \( T = 800 \text{ K} \), and \( \log I_a = -1.38 \) at ambient conditions. For the state point under consideration here, the simulation predicts \( \log I_a = 1.07 \pm 0.3 \) and \( K_s = 0.32 \). Experimentally\(^{45, 53} \), one obtains \( \log I_a = 1.23 \pm 0.2 \), so that the experimental and simulation values are within the uncertainty of each quantity. This is remarkably good agreement given both the difficulties of the experimental measurement and the various approximations involved in the simulation model. We are currently evaluating the accuracy of the predictions in other regions of the phase diagram and the use of more accurate models for the water-water interaction.

3. NEMD PREDICTION OF TRANSPORT PROPERTIES

A very successful application of molecular dynamics is the use of NEMD to predict transport properties in real systems, as described in a recent review by Cummings and Evans\(^{54} \). As examples, we note that the viscosity of supercritical methane\(^{54, 55} \) has been predicted using NEMD to within 0.3% of experimental measurements using an atomistically detailed model\(^{56} \). The same model predicts the viscosity along the saturated liquid line less accurately, with errors varying from 2% to 33%. The viscosity of liquid rubidium\(^{57, 58} \) has been predicted using an effective density-dependent ion-ion potential to within 7%-11% of experiment while for liquid sodium the error is 4%-18% . The SPC model for liquid water was found by NEMD to underpredict viscosity at ambient conditions by a factor of two\(^{59} \) but recent equilibrium simulations with SPCE find excellent agreement with experiment\(^{60} \). The transport properties of supercritical carbon dioxide\(^{61, 62} \) were studied by NEMD and found to be predicted quite accurately. In a related study\(^{63} \), Wang and Cummings found that the unusual composition of the shear viscosity of
ethane/alkane liquid mixtures was predicted well by NEMD. This mixture is one for which extended corresponding states methods have proven inadequate. Many researchers have contributed to the growing literature on the prediction of alkane viscosity using NEMD.

Recently, Cui et al. reported NEMD simulations of the shear viscosity of \( n \)-decane, shown in Figure 2, using the intermolecular potential developed in the Shell group to describe the phase behavior of normal alkanes. The extrapolated Newtonian shear viscosity of \( n \)-decane at absolute temperature, \( T = 480 \text{ K} \) and density of \( 0.6136 \text{ g/cm}^3 \), the same state condition as in the equilibrium molecular dynamics simulations of Mundy et al., was found to be \((197 \pm 3) \times 10^{-6} \text{ Pa s}\). This compares very favorably with the experimental result, \((196 \pm 5) \times 10^{-6} \text{ Pa s}\) and with the equilibrium molecular dynamics result, \((191 \pm 12) \times 10^{-6} \text{ Pa s}\), of Mundy et al. Cui et al. are currently extending these results to higher alkanes where the rheology is considerably more complex and equilibrium methods are extremely limited in their effectiveness due to the very long rotational relaxation times which characterize the higher \( n \)-alkanes.

4. MOLECULAR DYNAMICS OF MODEL POLYMER MELTS

An interesting application of equilibrium molecular dynamics has been to verify some of the predictions of scaling theories for polymer dynamics. Using a very simple model for a polymer chain (soft spheres connected by finitely-extensible springs), Kremer and Grest performed equilibrium molecular dynamics simulations of systems of chains composed of 25-400 monomeric units. The diffusion constant \( D \) as measured by the mean squared displacement of the center of mass is predicted to vary as \( 1/N \), where \( N \) is the number of beads in the chain, for \( N \leq N_e \), where \( N_e \) is the value of \( N \) at which chain entanglement begins. Experimentally, for \( N \gg N_e \), it is found that \( D \approx 1/N^2 \). As shown in Figure 3, the simulations demonstrate that a crossover from Rouse dynamics \((D \approx 1/N)\) to the \( D \approx 1/N^2 \) regime is observed in the simulations, verifying one of the predictions of scaling theories.
Acknowledgments

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. I am especially indebted to my colleagues, Ariel Chialvo and Shengteng Cui, for their assistance in preparing this manuscript, and to Carol Hall, for her helpful comments on an earlier draft of the manuscript.

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