Molecular simulation of complex systems using massively parallel supercomputers

Peter T. Cummings a,b,*

a Department of Chemical Engineering, University of Tennessee, 419 Dougherty Engineering Building, Knoxville, TN 37996-2200, USA
b Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6181, USA

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Abstract

Massively parallel supercomputers, such as the 150 Gigaflop Intel Paragons located at Oak Ridge National Laboratory and Sandia National Laboratories, make possible molecular simulation of systems of unprecedented complexity and realism. We describe some of the issues related to efficient implementation of molecular dynamics and Monte Carlo simulations on massively parallel supercomputers. The application of these methods to the prediction of the rheology of lubricants, polymer blends and high temperature aqueous electrolyte systems will be described. © 1998 Elsevier Science B.V.

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1. Introduction

For several decades, molecular simulation has played a major role in physical properties research in providing essentially exact quasi-experimental data for comparison to the results of statistical mechanical theories [1]. The advent of massively parallel supercomputers now makes it possible for molecular simulation methods to become the direct route to predicting the properties of many real systems of industrial interest. In particular, the prediction of the properties of bulk fluid-phase and amorphous systems is now within reach, whereas previously molecular simulation was largely restricted to small fluid systems (such as rational drug design, in which 1–2 large biomolecules are suspended in a fluid solvent) or crystalline systems (where the regularity of the structure over very small distance scales renders the problem comparatively straightforward computationally). Using
Molecular simulation can be classified into two broad categories: Molecular dynamics (MD) simulation and Monte Carlo (MC) simulation. In MD, Newton’s equations of motion for the positions and velocities of the molecular units (which may be atoms, molecules or functional groups within molecules) are solved numerically to determine the properties of interest (such as energy, pressure, stress tensor and measures of structure) over a period of time (typically of the order of $10^{15}$ to $10^{8}$ time steps) so that the properties can be averaged over time to yield predictions for the macroscopically observable quantities. Since the time step is determined by the need to represent molecular collisions accurately, it is typically of the order of $10^{-15}$ to $10^{-14}$ seconds, or approximately 1/100th of the mean time between collisions in a liquid. The presence of strong intramolecular forces—such as the carbon–carbon bond stretch in a hydrocarbon chain—can in principle require a much smaller time step due to the characteristic relaxation time for such motions. In MC simulation, configurations of the system (positions only) are generated randomly by a Markov chain process in order to generate configurations distributed according to the relevant probability distribution (e.g., Boltzmann distribution). Properties of interest are then averaged over the configurations generated. MC simulation has the advantage that cleverly constructed Markov chains can explore much wider regions of configurational space than molecular dynamics for an equivalent investment of computing resources. However, unlike molecular dynamics, MC cannot be used to study many dynamical phenomena, such as transport properties, because of its inherent lack of dynamical information. Provided that the intermolecular potentials are known, MD and MC simulation now provide us with highly-refined tools 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 molecular simulation techniques.

The advent of massively parallel supercomputers has led to the development of versions of MD and MC 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 and T3E) utilize the message-passing paradigm. For MD, we note that in principle any method for solving first order, nonlinear ordinary differential equations could be used to solve the dynamical equations (see Eq. (1) below). However, because the evaluation of the force is by far the most time consuming part of the calculation (90–99% of the computer time), only a narrow range of numerical methods are employed in practice [1]. For alkane chains in particular, multi-timestep methods, such as rRESPA [2] that solve the fast intramolecular motion on a shorter time step than the slower intermolecular motion, can be as much as an order of magnitude more efficient than brute force implementations. On massively parallel supercomputers, a strategy must be adopted to distribute the calculation across processors. Several strategies exist. In replicated data, each processor stores a copy of quantities associated with all $N$ atoms (positions, momenta, and higher derivatives as required by the numerical integration method of choice). The force calculation is divided equally across processors to achieve load-balance. The results of the force computation as well as the new updated positions of the atoms must be communicated to all processors at every
timestep. The cost for this global exchange of information scales as the number of atoms \( N \), independent of the number of processors \( P \), and is the reason replicated data does not scale well to large numbers of processors. An enhancement to replicated data, known as force-decomposition \([3,4]\), reduces this communication cost by a factor of \( 1/\sqrt{P} \), allowing more processors to be used effectively on a given size problem. However the nonlocal communication in the method still begins to dominate as machine sizes grow to thousands of processors.

In domain decomposition (mainly applicable to systems with short-ranged interactions), the spatial domain of the central simulation cell is subdivided into cubic sub-domains, each of which is mapped to a processor \([5]\). Thus, each processor is responsible for integrating the equations of motion for the molecules lying within its spatial subdomain. Efficient implementation of domain decomposition relies on eliminating message-passing during the force calculation. The approach of Pinches et al., implemented in domain decomposition MD codes, combines domain decomposition with the link cell method \([6]\) for further subdivision of the spatial domain within each processor. By each processor keeping track of a layer of ‘ghost’ link cells around itself in addition to the real molecules located within the spatial domain of the processor, the information needed to calculate forces at each time step is available without message passing. At the completion of each time step, molecules must be assigned to their correct processor and the layer of ‘ghost’ link cells updated. However, this message passing step between processors is not global and hence can be accomplished reasonably efficiently. Our experience has shown that domain decomposition is an effective strategy for performing simulations on large systems (e.g., > 10,000 atoms) for relatively short times (e.g., < 1 ns), while replicated data is the preferred method for smaller systems (e.g., < 10,000 atoms) simulated for long times (e.g., > 1 ns).

In this paper, 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. The problems we shall consider are the prediction of the rheology of lubricants, the thermodynamic properties of polymer blends and high temperature aqueous electrolyte systems.

2. Rheology of lubricants

The rheological properties of liquid alkanes of intermediate molecular sizes \((C_{20}-C_{40})\) are among the most important properties in the performance of lubricants, since they constitute the lube basestock of all commercially available motor oils. Improved motor oils are produced when long-chain, frequently highly-branched hydrocarbons \((C_{n}, n \geq 100)\) are added at low dilution to improve the viscosity index (a measure of viscosity over a wide range of temperature) of the oil. The next generation of high-efficiency low-pollution automobiles will require engines operating at higher temperature to ensure more complete combustion of fuel. This will put severe demand on lubricants, and oil companies throughout the world are in the process of developing new synthetic lubricants in anticipation of these requirements. Using molecular simulation to predict the rheological properties of synthetic lubricants prior to synthesis is an extraordinarily cost-effective design tool. Using nonequilibrium molecular dynamics (NEMD) and a model for the interaction potential for liquid alkanes recently developed by the molecular modeling group at Shell Research \([7,8]\), Mundy et al. \([9]\) and Cui et al. \([10]\) quantitatively predicted the viscosity of liquid normal decane. The model was assessed by Mondello and Grest \([11]\) for a number of equilibrium properties at near-ambient temperature.
conditions. We have recently implemented a multiple time step algorithm [10,12] to perform molecular simulations for chain molecules undergoing planar Couette flow on massively parallel supercomputers, particularly the Intel Paragon. This allows us to systematically study the rheological properties of liquid alkanes with molecular size of industrial interest.

The viscosity of alkane liquids can be determined using NEMD [13]. As is typical in experimental measurement, the viscosity is measured computationally by subjecting a fluid to planar Couette flow [14]. The NEMD equations of motion used for liquid alkanes under planar Couette flow are the SLLOD [13] equations with Nose dynamics [12]:

\[
\begin{align*}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \gamma \mathbf{y}_i \hat{x}, \quad \mathbf{p} = \mathbf{F}_i - \gamma p y y, \quad \hat{z} = \frac{p_y}{Q}, \quad \dot{p}_z = F_z
\end{align*}
\]

where the dot over a quantity indicates the time derivative of that quantity, \(\mathbf{r}_i\) and \(\mathbf{p}_i\) are the position and momentum coordinates of atom \(a\) in molecule \(i\), \(\gamma\) and \(p_y\) are their y components, \(m_i\) is the mass, and is a unit vector in \(x\)-direction. The quantities \(\zeta\), \(p_z\), and \(Q\) are the variables related to the Nose thermostat, \(F_z = \sum_{i,a} \frac{p_i^2}{m_i} - 3Nk_BT\), \(Q = 3Nk_BT\sigma^2\), \(\tau\) is the Nose thermostat time constant, and \(N\) is the total number of atoms in the system. The strain rate \(\gamma = du_y/dy\) describes the rate at which the velocity in the \(x\)-direction varies with vertical position (\(y\)) in the Couette flow field.

Standard Lees–Edwards boundary conditions [15] are used to drive the planar Couette flow. The strain-rate dependent viscosity \(\eta\) is determined from the constitutive relation:

\[
\eta = -\frac{\langle P_{xy} \rangle + \langle P_{yx} \rangle}{2\gamma}
\]

where \(\langle P_{xy} \rangle\) and \(\langle P_{yx} \rangle\) are averages of the \(xy\) and \(yx\) components of the symmetrized traceless pressure tensor. Further details of the method for calculating the pressure tensor are provided by Cui et al. [12]. Because of a combination of high frequency motions associated with intramolecular bond vibration, bond angle bending and torsional forces and lower frequency motion associated with intermolecular interactions, the equations of motion were solved using a multiple time step technique with Nose constant temperature dynamics [2,16,12]. All internal interactions were treated as fast motions and the intermolecular interaction as the slow motion.

Simulations were performed using a replicated data code developed in our research group. The viscosity is plotted in Fig. 1 for four linear alkanes (decane, hexadecane at two temperatures, and tetracosane) at respective state points as a function of dimensionless strain rate \(\gamma' = \gamma \sqrt{m \sigma^2 / \epsilon}\) where \(\gamma'\), the mass \((m)\), size \((\sigma)\) and energy \((\epsilon)\) parameters are those for a methyl group. Each state point corresponds to the experimental equilibrium density at atmospheric pressure at the respective temperature. The figure is plotted on a log–log scale and the strain rate covers several orders of magnitude. As can be seen from the figure, the viscosity shows shear thinning behavior as a function of strain rate, typically observed in chain molecule fluid systems. At larger shear, the shear thinning follows a power law. The slope of the log–log plot varies from \(-0.33\) to \(-0.41\) for the four linear alkane liquids simulated. This can be compared with the experimentally observed slopes of \(-0.4\) to \(-0.9\) for polymeric fluids. This suggests that even though the alkane chains studied here are very short in comparison to polymer systems, they nevertheless exhibit some of the generality of the
long-chain systems. Another interesting aspect is that the shear viscosities for decane, hexadecane, and tetracosane at high strain rate nearly overlap each other. Intuitively, this behavior should be related to the fact that at high strain rate, these fairly short and stiff alkane chains are well aligned with each other so they can slide past each other easily. In addition, the longer chain systems align with a smaller angle in the flow direction, resulting in a similar viscosity even though the chain lengths are different.

The dimensionless strain rates shown in Fig. 1 correspond to real strain rates in the range $10^8 - 10^{12}$ s$^{-1}$ which, at the low end, correspond to the maximum strain rates experienced by lubricants in automobile engines. On the other hand, laboratory measurements of viscosity cannot be performed at strain rates higher than $10^6 - 10^7$ s$^{-1}$, and for the linear alkanes only Newtonian viscosity measurements (in the limit $\gamma \to 0$) are available from experiment. The experimentally measured Newtonian viscosities of these liquids are shown as horizontal bars perpendicular to the vertical axis of the graph in Fig. 1. Notice that the experimental Newtonian viscosities are always greater than the Newtonian plateaus in the NEMD results (ranging from 35% to 70% larger), but that the order of the experimental and NEMD results is the same. We have also found this to be true in less extensive calculations on branched alkanes. Also, it should be noted that the accuracy of the predicted viscosities is remarkably good given that the intermolecular potentials used in the calculation have not been fitted to any experimental viscosity data.

3. High temperature aqueous electrolyte systems

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,
Fig. 2. Schematic of the SSIP, SSHIP, and CIP configurations.

particularly focusing on the Na\(^{+}\)|Cl\(^{-}\) association process which can be envisioned as involving the following reaction equilibria:

\[
Na^{+} + Cl^{-} \rightleftharpoons Na^{+}Cl^{-} \rightleftharpoons Na^{+}\mid Cl^{-} \rightleftharpoons Na^{+}\mid Cl^{-}
\]

(3)

where Na\(^{+}\)Cl\(^{-}\), Na\(^{+}\)Cl\(^{-}\) and Na\(^{+}\)\|Cl\(^{-}\) represent the contact ion pair (CIP), solvent-shared ion pair (SSHIP), and solvent-separated ion pair (SSIP) states respectively, as depicted in Fig. 2. Experimental evidence indicates that these ion-paired states might act as reaction intermediates [17–21]. We determine the anion–cation potential of mean force by molecular simulation [22] complementing other results at higher temperature [23,24] and ambient conditions [25].

Technical details of the simulation are provided elsewhere [26]. 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. [27], the ion–water interactions were modeled using the Pettitt–Rossky model [28] while for the ion–ion interaction we used the Fumi–Tosi model for alkali–halide interactions [29,30]. 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 Ciccotti et al. [31]. At each state point, a series of 40 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, \(\vec{F}_{w1}\), for I = Na, Cl corresponding to sodium and chloride respectively according to:

\[
\Delta F(r) = 0.5 \langle \hat{r}_{NaCl} \cdot (\vec{F}_{wCl} - \vec{F}_{wNa}) \rangle
\]

(4)

where \(\hat{r}_{NaCl}\) 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 \(F_{NaCl}(r)\) and integrated from a large distance \(r_0\) to \(r\) to calculate the potential of mean force, \(W_{NaCl}(r)\), via:

\[
W_{NaCl}(r) = W_{NaCl}(r_0) - \int_{r_0}^{r} F_{NaCl}(r') \, dr'
\]

(5)

From this, the NaCl radial distribution function at infinite dilution is calculated by \(g_{NaCl}(r) = \exp[-W_{NaCl}(r)/k_B T]\) where \(k_B\) is Boltzmann’s constant and \(T\) is the absolute temperature. The simulations were performed at state conditions corresponding to \((\rho, T) = (\rho/\rho_c, T/T_c) = (1.0,\)
Fig. 3. Potential of mean force (left) and radial distribution function (right) between sodium and chloride ions at infinite dilution in supercritical water ($T_s = 1.05$, $\rho_s = 1.0$) calculated by simulation (solid line) and using the continuum theory given by Eq. (6).

1.05), (1.0, 1.2), (1.0, 1.4), (1.5, 1.05) and (2.0, 1.05) based on the critical conditions for the SPC water model [32]. 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 [22]. System size effects were evaluated by performing domain decomposition simulations on systems containing between 10,000 and 43,000 molecules. The production runs for thermodynamic and structural properties comprised $3 \times 10^4$ time steps (30 ps) while those for mean-force calculations were extended to $10^5$ time-steps for each constrained ion-pair distance. State points are described in dimensionless units (reduced density $\rho_r = \rho/\rho_c$ and reduced temperature $T_r = T/T_c$) reduced by the critical constants of SPC water ($T_c = 587$ K and $\rho_c = 0.27$ g cc$^{-1}$) [32]. The thermodynamic properties of the SPC model in supercritical states are predicted quite accurately at corresponding states (same reduced state conditions) as shown by Cummings et al. [33].

The potential of mean force and NaCl radial distribution function at infinite dilution at $T_s = 1.05$, $\rho_s = 1.0$ are shown in Fig. 3. 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, $u_{\text{NaCl}}(r)$, with the Coulombic part screened by the dielectric constant of the solvent, $\varepsilon$,

$$W_{\text{NaCl}}^{\text{continuum}}(r) = u_{\text{NaCl}}^{\text{Coulombic}}(r) + \frac{u_{\text{Coulombic}}^{\text{NaCl}}(r)}{\varepsilon}$$  \hspace{1cm} (6)

The equilibrium constant for association is given by:

$$K_a^M = \frac{\rho_{\text{SSIP}} + \rho_{\text{SSIP}} + \rho_{\text{SSIP}}}{\rho_{\text{Na}} \cdot \rho_{\text{Cl}}} = K_1 (1 + K_2 + K_2 K_3)$$  \hspace{1cm} (7)
where the superscript $M$ denotes units of liter/mole and $\rho_{SSIP}$, $\rho_{SSIP}$, $\rho_{CIP}$, $\rho_{Na^+}$ and $\rho_{Cl^-}$ are the density of solvent-separated ion pairs, solvent-shared ion pairs, contact ion pairs, unassociated $Na^+$ ions and unassociated $Cl^-$ ions respectively while the equilibrium between CIP ion pairs and SSIP/SSIP ion pairs is given by:

$$K_e = \frac{\rho_{SSIP} + \rho_{SSIP}}{\rho_{CIP}} = K_2(1 + K_3) \quad (8)$$

As described in detail elsewhere [26], the equilibrium constants for association and for intraconversion between CIP ion pairs and SSIP/SSIP ion pairs can be written [26]:

$$K_a = 4\pi \int_{0 < r < r_2} g_{AC}(r) r^2 dr, \quad K_e = \int_{r_1 < r < r_2} g_{AC}(r) r^2 dr / \int_{0 < r < r_1} g_{AC}(r) r^2 dr \quad (9)$$

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 $I_a = K_a^M \exp(q_{Na^+}q_{Cl^-}/e \epsilon_0 k_B T)$ 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 $\log I_a \approx 4.3$ at $\rho = 0.1252$ g cc$^{-1}$ and $T = 800$ K [23], $\log I_a \approx 5.6$ at $\rho = 0.0832$ g cc$^{-1}$ and $T = 800$ K [23], and $\log I_a \approx -1.38$ at ambient conditions [25]. For the state points under consideration here, the simulation predictions are shown in Fig. 4 along with experimental results. As previously shown [26], at $(\rho, T) = (1.0, 1.05)$ 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. As is clear from Fig. 4, this agreement does not persist to higher densities or temperatures, although given the range of values of $I_a$, the agreement is still quite impressive given
4. Molecular dynamics simulations of model polymer blends

The most widely used theory in describing the mixing property of polymer blends is the Flory–Huggins theory [36]. The theory predicts that the free energy of mixing for a two component polymer blend is given by

$$\frac{\Delta G}{k_B T} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + 2 \chi \phi_1 \phi_2$$

(10)

where $\Delta G$ is the free energy of mixing, $N_1$ and $N_2$ are the numbers of repeat units of the polymer chains, $\phi_1$ and $\phi_2$ are the compositions (volume fractions) of the two species, and $\chi$ is a constant parameter characterizing the interaction between the two species. The $\chi$-parameter can be measured from small angle neutron scattering (SANS) experiments using the random phase approximation (RPA) scattering theory [37] due to de Gennes. The RPA is a mean-field theory assuming that the chains are Gaussian, from which $\chi$ can be determined through:

$$\chi = \frac{1}{2} \left( \frac{1}{N_1 \phi_1 P_1(qR_g^1)} + \frac{1}{N_2 \phi_2 P_2(qR_g^2)} - \frac{1}{S(q)} \right)$$

(11)

where $S(q)$ is the structure factor, $P_1(qR_g^1)$ and $P_2(qR_g^2)$ are the single chain structure factors for the two components, $q$ is the wave vector, $R_g^1$ and $R_g^2$ are the radii of gyration of a polymer chain of components 1 and 2. Recent experiments have found that the miscibility of binary polymer blends deviates significantly from the prediction of Flory–Huggins mean field theory and de Gennes’ random phase approximation [38–40]. In particular, the SANS-determined Flory $\chi$-parameter for a number of polymer blends has been found to be composition-dependent.

We have used domain-composition molecular dynamics simulation to study two model binary symmetric polymer blends of chain lengths of 25 and 50 monomers [10]. All monomers interact with a shifted force Lennard–Jones potential characterized by an energy parameter $\varepsilon_{ab}$ and a length parameter $\sigma$, where $a$ and $b$ denote the two species of polymer molecules. Note that we consider the systems with the same length parameter but different energy parameter. For convenience all energies are expressed in terms of the single energy parameter and all lengths in terms of $\sigma$. A cutoff distance of 2.5$\sigma$ is used for calculating the Lennard–Jones interactions. The systems consisted of 13,500 monomers, i.e., 540 and 270 molecules for the $N = 25$ and $N = 50$ chain length respectively, at a monomer number density of $\rho = 0.7/\sigma^3$. A relatively large system is required for this simulation since the structure factors at small wave vector need to be determined accurately to obtain the $\chi$-parameter at zero wave vector. The monomers on a chain are connected by the finite extensible nonlinear elastic spring potential with parameters chosen to insure that the chains do not cross each other at the higher temperature states have studied.
The mixing properties of the model blends may be controlled by the energy parameter as well as the length parameter. As an illustration of our work, we present results for an attractive blend, in which \( e_{ab} = 1.2 \varepsilon \), \( k_B T = 2.0 \varepsilon \) and \( N = 25 \), and for a repulsive blend with \( e_{ab} = 0.99 \varepsilon \), \( k_B T = 1.5 \varepsilon \) and \( N = 50 \). The \( \chi(q) \), which is found to be linear in \( q^2 \) at low \( q \) is extrapolated to \( q = 0 \) to obtain the corresponding \( \chi \)-parameter in the Flory–Huggins. Simulations were carried out for different compositions of the two components of the polymer blend. Fig. 5 shows the zero wave-vector \( \chi \)-parameter determined from the above procedure as a function of the volume fraction of component 1 in the polymer blend. Similar to experiments, we see the usually observed composition dependence of the \( \chi \)-parameter for the \( N = 25 \) system. At equal composition of the two components, the \( \chi \)-parameter is smaller, and it increases at the composition extremes. Although this behavior is similar to the result of neutron scattering experiments, the \( N = 25 \) systems studied here are attractive mixtures, while most of the neutron scattering experiments were performed for repulsive mixtures. Also plotted in the figure is the zero wave-vector \( \chi \)-parameter for the \( N = 50 \) system. Because of large statistical uncertainty in the data, the simulation results cannot distinguish whether or not there is composition dependence in the \( \chi \)-parameter, which is small and positive. These results suggest that the classical theories of polymer mixing may not provide a fully satisfactory description for the phenomena of polymer mixing.

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