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Molecular Dynamics Studies of Properties of Supercritical Fluids

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This work involves the determination of transport coefficients and equation of state of supercritical fluids by equilibrium molecular dynamics (MD) simulations on parallel computers using the Green–Kubo formulas and the virial equation of state, respectively. The MD program uses the effective Lennard–Jones potential, linked-cell lists for efficient sorting of molecules, periodic boundary conditions, and a modified velocity Verlet algorithm for particle displacement. Simulations have been carried out on pure oxygen at various supercritical conditions, with shear viscosity and thermal conductivity coefficients, and pressures computed for most of the conditions. Preliminary results compare well with experimental and the National Institute of Standards and Technology (experimental) results. Results show that the number of molecules and the potential cutoff radius have no significant effect on the computed coefficients, while long-time integrations are necessary for accurate determination of the coefficients.

Nomenclature

A = equation constant
$\boldsymbol{a}$ = acceleration vector
d_α^{ij} = desired separation distance between two atoms in a molecule
$\boldsymbol{i}$ = unit tensor
$\boldsymbol{J}_p$ = stress tensor
$\boldsymbol{J}_q$ = heat tensor
k_B = Boltzmann constant
m = molecular mass
N = number of molecules in the system
n = number of atoms per molecule
P = pressure
$\dot{\boldsymbol{R}}_\alpha$ = c.m. velocity of a given molecule
$\boldsymbol{R}_{\alpha\beta}$ = c.m. position vector between two molecules
$\boldsymbol{r}$ = position vector
$\boldsymbol{r}_\alpha^i$ = position vector of a given atom
$\boldsymbol{r}_{\alpha\beta}^{ij}$ = position vector between two atoms i, j
T = temperature
t = time
t_d = time delay
t_0 = time origin
V = volume
$\boldsymbol{v}$ = velocity vector
$\boldsymbol{v}_\alpha^i$ = velocity vector of a given atom
α, β = given molecules
γ_B = constraint between atoms
δt = time-step size
ε = Lennard–Jones energy parameter
λ = thermal conductivity
μ = shear viscosity
ρ = density
$\Phi_{\alpha\beta}^{ij}$ = potential between two atoms i and j

I. Introduction

CURRENT rocket motors, gas turbines, and many projected advanced combustor designs operate supercritically or near critical conditions.[1] Computational fluid dynamics (CFD) has been used to model droplet evaporation and combustion in supercritical and near critical environments by several researchers including Yang et al.[2] and Delplanque and Sirignano.[3] Quantitative information on the coefficients of mass, momentum, and energy transport, and the equation of state are very important in these studies. However, in many complex systems such as rarefied flows, supercritical environments, shock regions, and highly energized plasmas, these coefficients are not known accurately and the experiments to measure them are difficult and costly. As a result the necessary information is lacking in the use of the CFD methods for simulating supercritical evaporation and combustion. Moreover, these techniques make use of such limiting approximations as spherical droplet shape and constant density that are not necessarily valid under these supercritical conditions. Hence, alternative methods for modeling the evaporation of supercritical droplets have to be considered.

Molecular dynamics (MD), the technique used in the present study, involves the solution of the equations of motion of a system of molecules that interact with each other through an intermolecular potential.[4] Provided that an accurate potential can be found for the system of interest, MD can be used regardless of the phase and thermodynamic conditions of the substances involved. Although computationally intensive, this method requires no a priori assumptions regarding geometrical symmetry, transport properties, or thermodynamic behavior. All calculations are performed from first principles based on intermolecular potentials, and thermodynamic and transport properties are results instead of assumptions. MD has been used to support research in such fields as chemistry, biology, physics, and material science. It is also currently being used to model the evaporation of a submicron droplet in supercritical environments.[5–8]

MD simulations are computationally intensive because the interaction between each particle and all its neighbors must be taken into account. The speed of these simulations can be greatly increased by running on parallel computers. The natural parallelism in MD comes from the fact that the force calculations and position/velocity updates can be done simultaneously for all of the molecules.

The method of parallelization currently being used is the particle decomposition method. This technique is implemented by distributing the particles evenly among the different processors. Each processor calculates the forces and displacements for the particles for which it is responsible. Then the

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new positions and velocities from each processor are broadcast to all other processors with which the next time step begins. Using the particle decomposition method, almost perfect load balancing has been achieved.[5]

Transport coefficients can be computed either by the use of Green–Kubo formulas or Einstein relations during equilibrium molecular dynamics (EMD) simulations,[4,9,10] or by conducting suitable nonequilibrium molecular dynamics (NEMD) simulations.[11,12] The Green–Kubo formulas have been used successfully to compute the transport coefficients of atomic fluids, while only limited success has been achieved for molecular fluids that are essential for supercritical droplet studies.[13–18] At various times this might be because of the inadequate modeling of the long-time tail behavior of the relevant autocorrelation functions, the use of small system sizes because of the limited computer resources available, or because of the incorrect use of potential model parameters. The NEMD emerged as a suitable simulation technique for computing the transport coefficients of fluids caused by the preceding drawbacks. Normally, to compute shear viscosities or thermal conductivities, separate computer experiments have to be computed and these cannot be incorporated easily into an MD droplet evaporation computer program to compute the relevant properties as the droplet vaporizes. Hence, this method is not utilized in the following study.

Although MD has been used to compute the equation of state of some fluids by several researchers,[19–24] the pressures have been computed for only a few state points. No comprehensive study has been done to calculate the pressures of oxygen and other fluids over the entire range of states.

An attempt is made herein to compute the transport properties and pressures of supercritical fluids that are relevant for droplet evaporation studies using the Green–Kubo formulas and the virial equation of state, respectively. The effects of the number of molecules, the potential cutoff radius, and the delay time on the computed transport coefficients were investigated. Successful implementation of the code will impact the understanding and modeling of the processes occurring in current and future aerospace propulsion systems.

II. Molecular Dynamics

A. Molecular Potentials

The cornerstone of all molecular dynamics simulations is the intermolecular potential. To calculate the positions, velocities, and accelerations of each molecule in the system, the forces acting on each of the molecules are required. These forces are derived from the intermolecular potentials. All results and properties determined with MD simulations also follow directly from the potential.

The potential used for the simulations of systems of oxygen molecules is the two-center Lennard–Jones (LJ) 12–6 potential[4]:

$$\Phi^{ij}_{\alpha\beta} = 4\varepsilon \sum_{i=1}^{2} \sum_{j=1}^{2} \left[\left(\frac{\sigma}{r^{ij}_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma}{r^{ij}_{\alpha\beta}} \right)^{6} \right] \tag{1}$$

Here each oxygen molecule is treated as two atomic sites subject to the constraint of fixed bond length.[4,25] The intermolecular force is obtained from the spatial gradient of the potential and the resultant force on each particle is simply the sum of all the pairwise forces resulting from the surrounding particles. The equations of motion are integrated once the resultant forces are known.

B. Finite Difference Method

The algorithm used for solving the equations of motion is the RATTLE algorithm that uses the modified velocity Verlet finite differencing scheme.[4,5] This is given by the following equations:

$$\boldsymbol{r}(t + \delta t) = \boldsymbol{r}(t) + \delta t \boldsymbol{v}(t) + \tfrac{1}{2}\delta t^2 \boldsymbol{a}(t) \tag{2}$$

$$\boldsymbol{v}(t + \tfrac{1}{2}\delta t) = \boldsymbol{v}(t) + \tfrac{1}{2}\delta t \boldsymbol{a}(t) \tag{3}$$

$$\boldsymbol{v}(t + \delta t) = \boldsymbol{v}(t + \tfrac{1}{2}\delta t) + \tfrac{1}{2}\delta t \boldsymbol{a}(t + \delta t) \tag{4}$$

The algorithm is applied to oxygen molecules by means of constraint dynamics that involves writing the equations of motion to include a constraint force as a result of fixing of the bond length between the two atoms of each molecule. The constraint is given by the following equation:

$$\gamma_B = |\boldsymbol{r}^i_\alpha - \boldsymbol{r}^j_\alpha|^2 - (d^{ij}_\alpha)^2 = 0 \tag{5}$$

To solve the equations of motion under constraints, the positions and the velocities of all the atoms in the system are first determined without the constraints. Then these values are corrected with the incorporation of the constraints that are solved iteratively using undetermined multipliers.

C. Molecular Dynamics Techniques

The simulations were done using cubical geometries with periodic boundaries. These boundary conditions were used in the simulations to minimize surface effects as a result of the relatively small size of the systems.[4] Periodic boundaries refer to the method of assuming the central simulation cell to be replicated throughout space to form an infinite lattice. This lattice forms a macroscopic sample of the substance of interest. The image cells are each the same size and shape as the primary cell, and each of them contains N particles that are images of the particles in the primary cell. The periodicity extends to the position and velocities of the images in the image cell.[26] In the course of the simulation, as a molecule moves in the original cell, its periodic image in each of the neighboring cells moves in exactly the same way. As a molecule leaves the central simulation geometry, an image of the molecule will enter the central geometry through the opposite face.

Several other techniques were also used to increase the speed and efficiency of the code.[4,25] A minimum image convention was used to reduce the number of force calculations, and a linked list method was used for fast sorting of molecules.

D. Green–Kubo Formulas

The use of the Green–Kubo formulas for the determination of transport coefficients depends on the evaluation of a microscopic current at a given time t, subsequent to an initial time t_0 by the application of an MD simulation. For molecular fluids the coefficients can be calculated based on two different formalisms that essentially give the same results: atomic and molecular.[27–29] In the atomic formalism, the coefficients are calculated based on the motion of the individual atoms comprising the molecules in the system, while they are based on the motion of the molecules in the molecular formalism. The atomic formalism is used in the present study and the two coefficients considered are those of shear viscosity and thermal conductivity.

The shear-viscosity coefficient is a measure of the internal fluid friction that tends to oppose any dynamic change in the fluid motion. The corresponding autocorrelation function (ACF) contains the nondiagonal elements of the stress tensor, and the Green–Kubo formula is given by[10]

$$\mu = \frac{1}{3Vk_BT} \int_0^\infty \langle \boldsymbol{J}_p(t_0)\boldsymbol{J}_p(t_0 + t_d)\rangle \,\mathrm{d}t_d \tag{6}$$

where $\boldsymbol{J}_p$ is given by

$$\boldsymbol{J}_p = m\sum_{\alpha=1}^{N}\dot{\boldsymbol{R}}_\alpha\dot{\boldsymbol{R}}_\alpha - \frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{i=1}^{n}\sum_{j=1}^{n}\boldsymbol{R}_{\alpha\beta}\nabla\Phi^{ij}_{\alpha\beta}(\boldsymbol{r}^{ij}_{\alpha\beta}) \qquad (7)$$

The shear stress ACF is composed of kinetic, potential, and cross (kinetic-potential) terms.

The thermal conductivity coefficient measures the transport of heat in a system. The correlation function is obtained from the heat current and the Green–Kubo formula is given by[10]

$$\lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \boldsymbol{J}_q(t_0)\boldsymbol{J}_q(t_0 + t_d)\rangle \, \mathrm{d}t_d \qquad (8)$$

where $\boldsymbol{J}_q$ is given by

$$\boldsymbol{J}_q = \frac{m}{2}\sum_{\alpha=1}^{N}|\dot{\boldsymbol{R}}_\alpha|^2\dot{\boldsymbol{R}}_\alpha$$

$$-\frac{1}{2}\sum_{\alpha=1}^{N}\sum_{i=1}^{n}\boldsymbol{v}^i_\alpha\sum_{\beta=1}^{N}\sum_{j=1}^{n}\left[\left(\boldsymbol{R}_{\alpha\beta}\nabla\Phi^{ij}_{\alpha\beta}(\boldsymbol{r}^{ij}_{\alpha\beta}) - \Phi^{ij}_{\alpha\beta}(\boldsymbol{r}^{ij}_{\alpha\beta})\boldsymbol{i}\right)\right] \qquad (9)$$

The ACF is also composed of kinetic, potential, and cross (kinetic-potential) terms.

E. Pressure Calculation

The pressure of the system may be calculated during MD simulation by means of the virial equation of state[4,26]:

$$\frac{P}{\rho k_BT} = 1 - \frac{1}{3Nk_BT}\left\langle\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{i=1}^{n}\sum_{j=1}^{n}\boldsymbol{R}_{\alpha\beta}\nabla\Phi^{ij}_{\alpha\beta}(\boldsymbol{r}^{ij}_{\alpha\beta})\right\rangle \qquad (10)$$

This may be rewritten as

$$PV = Nk_BT - \frac{1}{3}\left\langle\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{i=1}^{n}\sum_{j=1}^{n}\boldsymbol{R}_{\alpha\beta}\nabla\Phi^{ij}_{\alpha\beta}(\boldsymbol{r}^{ij}_{\alpha\beta})\right\rangle \qquad (11)$$

The first term on the right-hand side is the ideal-gas contribution, and the second term accounts for intermolecular forces, assuming a pairwise additive potential.

III. Molecular Dynamics Simulations

The MD computer code is written in Fortran-77 and uses the message-passing interface (MPI). All of the runs were made on an IBM SP2 computer using 8, 16, or 32 processors. The simulations were carried out in the conventional constant number of molecules-energy-volume (NEV) ensemble. The equations of motion were solved using the modified velocity Verlet algorithm with a time step of 2×10^{-15} s, periodic boundary conditions, and a potential cutoff radius of 2.5σ. The simulations were done using cubical geometries, with the length of each side about 12–45σ, depending on the density and the number of molecules in the system. These lengths are much larger than the critical-point correlation length.[15] The system sizes ranged between 1000 and 1200 molecules. The LJ 12–6 potential was used for the pair interactions. The LJ parameters of oxygen used in the simulations as well as the critical temperature and pressure of oxygen are as follows[30]: $P_c = 5.04$ MPa, $T_c = 154.6$ K, $\sigma = 3.09$ Å, $\varepsilon/K_B = 44.6$ K, and $d = 1.017$ Å.

Starting from an initial configuration with the molecules placed on the positions of a face-centered-cubic lattice, the first 5×10^4 time steps were used for equilibrating the system to the chosen thermodynamic state. During the equilibration run the velocities of the molecules are frequently rescaled to obtain the desired temperature. Normally, at the end of this period the final temperature of the system differs by less than 1% of the desired value, whereas the total energy of the system would have stabilized with a fluctuation of less than 0.2% from the mean value. The data runs were about 2×10^6 time steps for the transport coefficients and 2×10^5 for pressures. Statistical uncertainties in these calculations were estimated by evaluating independent averages over blocks of 1×10^5 and 1×10^4 time steps, respectively, for the transport coefficients and pressures.[31]

Most of the calculated results are compared to values obtained from the National Institute of Standards and Technology (NIST) software that uses equations to determine the transport coefficients and pressures of substances.[32] The parameters of these equations for the transport coefficients were determined by experiments.[33,34] The average uncertainties for these values are 2 and 4% for shear viscosity and thermal conductivity, respectively. The NIST results can only be obtained for temperatures up to 400 K, whereas the MD results have no temperature restrictions. Hence, only results for temperatures below 400 K have been presented in this study.

IV. Results and Discussion

The main objective of this research is to develop tools for predicting the transport properties and pressures of pure fluids and fluid mixtures that are relevant for modeling supercritical droplet evaporation. Simulations have been performed using pure oxygen at various subcritical, supercritical, and near critical conditions.[35] Pressures, shear viscosity, and thermal conductivities have been computed.

Preliminary MD runs were carried out to study the effect of the delay time, number of particles, and cutoff radius on the transport coefficients. Figure 1 shows plots of the normalized ACFs for shear viscosity and thermal conductivity as functions of delay time. These plots indicate a remarkably long-time behavior of the correlation functions. For the state shown, the functions do not decay to zero even at delay times of up to 15

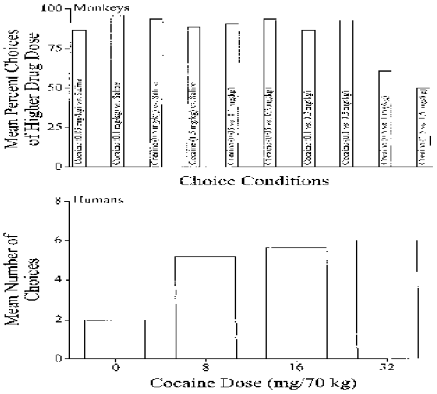

Fig. 1 Normalized ACFs vs delay time. The fluid conditions are $P = 3$ MPa and $T = 160$ K.

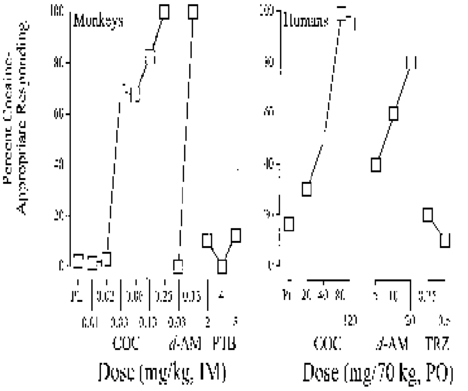

Fig. 2 Effect of the number of molecules on shear viscosity.

ps. Hence, precise computation of transport coefficients depends on the accurate determination of this long-time behavior. However, for some state points the ACFs decay to zero within 4 ps. In the present study the long-time tails were fitted to polynomials of the form $f(t) = At^{-3/2}$.

The effect of the number of particles in the system on the computed transport properties were investigated for two different states and are presented in Figs. 2 and 3. The plots show results for system sizes of about 300–3200, and they demonstrate clearly the independence of the shear viscosity and thermal conductivity values on the number of particles for the range studied. Most of the simulations in this study were done with about 1000–1200 molecules.

Figures 4 and 5 show the effect of the radius of sphere used for truncating the potential on the computed transport coefficients. For the range studied, 2.0–3.0σ, the cutoff radius can be seen to have no significant effect on the calculated results. A value of 2.5σ was used for most of the simulations made in this study.

Figures 6 and 7 show plots of the shear viscosity and thermal conductivity coefficients, with the corresponding error bars, as functions of temperature and pressure for oxygen. Plots have

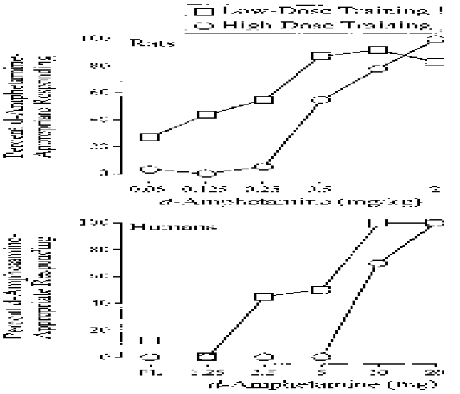

Fig. 3 Effect of the number of molecules on thermal conductivity.

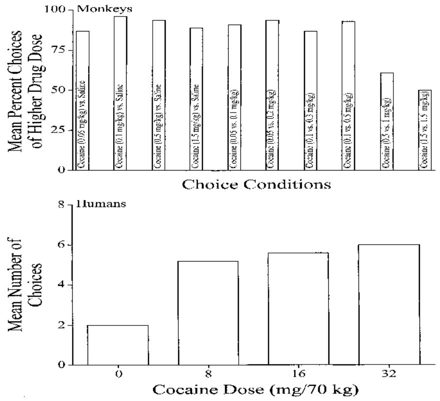

Fig. 4 Effect of potential cutoff radius on shear viscosity. The fluid conditions are P = 3 MPa and T = 160 K.

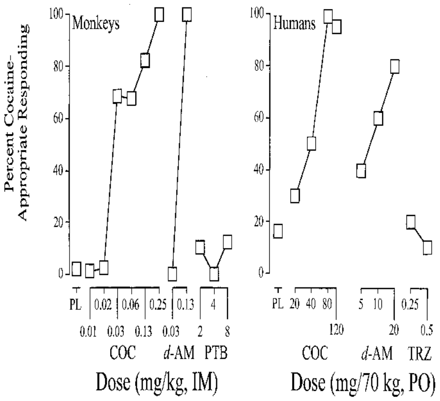

Fig. 5 Effect of potential cutoff radius on thermal conductivity. The fluid conditions are P = 3 MPa and T = 160 K.

Fig. 6 Shear viscosity values from MD and NIST for oxygen: a) 3, b) 5, c) 10, and d) 15 MPa.

Fig. 7 **Thermal conductivity values from MD and NIST for oxygen: a) 3, b) 5, c) 10, and d) 15 MPa.**

been shown for pressures of 3, 5, 10, and 15 MPa with temperatures ranging between 120 and 400 K. These are typical conditions experienced during droplet evaporation. The critical pressure and temperature of oxygen are 5.04 MPa and 154.6 K, respectively. The MD results compare well with the NIST values. Both transport coefficients can be observed to increase abruptly for temperatures below the critical value of 154 K.

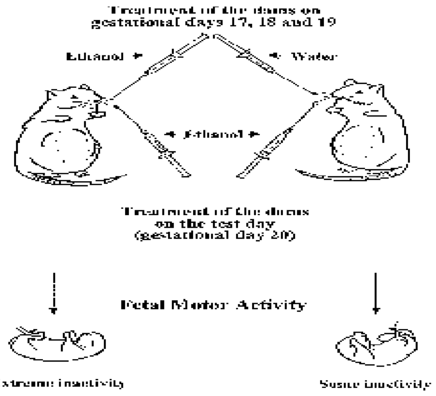

Fig. 8 Pressure calculations from MD and NIST for oxygen.

Figure 8 shows plots of calculated pressures against temperature for various densities for oxygen. Simulations have been done under various conditions between densities of 200–1000 kg/m^3 and temperatures of 100–400 K. For most of the cases, there is excellent agreement between the MD and NIST results.

V. Conclusions

The transport properties and pressures of fluids are being computed via MD simulations using the Green–Kubo formulas and the virial equation of state, respectively. Results show that the number of molecules in the system and the potential cutoff radius have no significant effect on the computed coefficients, while long-time integration of the ACFs are necessary to obtain accurate results. Computed shear viscosity and thermal conductivity coefficients compare well with NIST results. Future studies will include the computation of the transport properties for liquid mixtures and the properties at the surface of evaporating droplets in supercritical environments.[36] A successful implementation of the code should have a great impact on the understanding of the processes occurring in current and future aerospace propulsion systems.

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