JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 13, No. 3, July–September 1999

# Molecular Dynamics Studies of Thermophysical Properties of Supercritical Ethylene

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**This work involves the determination of transport coefficients and equation of state of supercritical ethylene 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 an effective Lennard–Jones potential, linked cell lists for efficient sorting of molecules, periodic boundary conditions, and a modified velocity Verlet algorithm for particle displacement. Previously, simulations had been carried out on pure argon, nitrogen, and oxygen, and this has now been extended to ethylene, $C_2H_4$, at various supercritical conditions. Shear viscosity and thermal conductivity coefficients, and pressures, have been computed for most of the conditions. The results compare well with experimental and National Institute of Standards and Technology values.**

## Nomenclature

$d$ = molecular bond length
$i$ = unit tensor
$J_p$ = stress tensor
$J_q$ = heat tensor
$k_B$ = Boltzmann constant
$m$ = atomic mass
$N$ = number of molecules in the system
$n$ = number of atoms per molecule
$P$ = pressure
$\boldsymbol{R}_{\alpha\beta}$ = c.m. position vector between two molecules
$\dot{\boldsymbol{R}}_{\alpha}$ = c.m. velocity of a given molecule
$\boldsymbol{r}^{ij}_{\alpha\beta}$ = position vector between two atoms $i$, $j$
$T$ = temperature
$t$ = time delay
$V$ = volume
$\boldsymbol{v}^{i}_{\alpha}$ = velocity vector of a given atom
$\alpha, \beta$ = given molecules
$\varepsilon$ = Lennard–Jones energy parameter
$\lambda$ = thermal conductivity
$\mu$ = shear viscosity
$\Phi$ = intermolecular potential

## I. Introduction

BECAUSE many chemical propulsion systems operate with one or more of the reactants above the critical points, there is interest in studying the properties and droplet evaporation at these supercritical conditions.[1] The traditional techniques of modeling droplet evaporation, such as computational fluid dynamics (CFD), require accurate information on the transport properties and equations of state.[2,3] However, under these supercritical conditions, the properties are not known accurately and experiments to measure them are difficult and costly. Hence, alternative methods of obtaining these properties must 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. MD has been used to support research in such fields as chemistry, biology, physics, and material science.[5–10] It is also currently being used to model the evaporation of a submicron droplet in the supercritical environments.[11,12]

MD simulations are computationally intensive because the interaction between each particle and all of its neighbors must be taken into account. The speed of these simulations can be greatly increased by using 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.[13]

Transport coefficients can be computed either by the use of Green–Kubo formulas or Einstein relations during equilibrium molecular dynamics simulations[4,14,15] or by conducting suitable nonequilibrium molecular dynamics simulations.[16,17] The Green–Kubo formulas have been used successfully to compute the transport coefficients of atomic fluids, whereas only limited success has been achieved for molecular fluids that are essential for supercritical droplet studies.[18–20] However, when the Green–Kubo formulation is applied properly for molecular fluids, more accurate results that match experimental values more accurately can be obtained.[21]

MD has been used to compute the equation of state of some fluids by several researchers including Barker et al.,[22] Singer et al.,[23] and Vogelsang and Hoheisel,[24] for only a few state points. No comprehensive study has been done to calculate the pressures of ethylene and other fluids over a wide 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. Previous studies have been done on argon, nitrogen, and oxygen, and work has now been extended to ethylene in this paper.[25,26] 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

MD has become a widely used direct simulation technique. The advantage of this technique for the solution of complex flow problems is that all attendant physical phenomena—shear viscosity, thermal conductivities, and surface tension—come from the force potential between the particles. MD does not require the use of empirical submodels for each physical process or temperature-dependent physical properties. It is an extremely powerful and simple method of simulation. The accuracy of a given MD model depends mainly on the chosen intermolecular potential and the finite difference scheme.

Received 29 July 1998; revision received 4 December 1998; accepted for publication 5 December 1998. 

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The potential used for the simulation of the system of ethylene molecules in this study is the Lennard–Jones (L–J) 12-6 potential[4]:

$$\Phi = 4\varepsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right] \tag{1}$$

where $\Phi$ is the energy of interaction between the centers of two atoms $i$ and $j$, which are a distance $r_{ij}$ apart. $\sigma$ represents the zero-energy separation distance and has units of length, whereas $\varepsilon$ represents the depth of the potential well and has units of energy. The velocity–Verlet algorithm is used for advancing the displacements and velocities of the molecules in time.[4]

Ethylene ($C_2H_4$) is modeled in this study using the site–site method, which consists of the solution of the ordinary equations of motion for each atomic site subject to a constraint that is the fixed bond length.[4,27] The sites are located at the positions of the nuclei of the constituent atoms. Because of the fact that each carbon atom is much heavier than a hydrogen atom, each group of $CH_2$ atoms in ethylene can be treated as a single site (composed of just the carbon atom) with the effects of the hydrogen atoms accounted for by the use of an effective L–J potential.

## III. Property Calculation

In the present study, the transport coefficients are computed using Green–Kubo formulas in which an autocorrelation function is integrated over time during an equilibrium molecular dynamic simulation.[4,14,15] The Green–Kubo formula for the shear viscosity coefficient is given by

$$\mu = \frac{1}{3Vk_BT}\int_0^\infty \langle J_p(0)J_p(t)\rangle \,\mathrm{d}t \tag{2}$$

where $J_p$ is the stress tensor that depends on the velocities, displacements, and potentials of the particles of the system. In this study, the stress tensor is given by

$$J_p = m\sum_{\alpha=1}^{N}\dot{\boldsymbol{R}}_\alpha\dot{\boldsymbol{R}}_\alpha - \frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{i=1}^{2}\sum_{j=1}^{2}\boldsymbol{R}_{\alpha\beta}\nabla\Phi\left(\boldsymbol{r}_{\alpha\beta}^{ij}\right) \tag{3}$$

The Green–Kubo formula for the thermal conductivity coefficient is given by

$$\lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle J_q(0)J_q(t)\rangle \,\mathrm{d}t \tag{4}$$

where $J_q$ is the heat current. The heat current for ethylene is given by

$$J_q = \frac{m}{2}\sum_{\alpha=1}^{N}|\dot{\boldsymbol{R}}_\alpha|^2\dot{\boldsymbol{R}}_\alpha - \frac{1}{2}\sum_{\alpha=1}^{N}\sum_{i=1}^{2}\boldsymbol{v}_\alpha^i\sum_{\beta=1}^{N}\sum_{j=1}^{2}\left\{\left[\boldsymbol{R}_{\alpha\beta}\nabla\Phi\left(\boldsymbol{r}_{\alpha\beta}^{ij}\right) - \Phi\left(\boldsymbol{r}_{\alpha\beta}^{ij}\right)i\right]\right\} \tag{5}$$

The pressure of a system of molecules may be calculated during an MD simulation by means of the virial equation of state.[4,21] This is given by the following equation:

$$PV = Nk_BT - \frac{1}{3}\left\langle\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{i=1}^{2}\sum_{j=1}^{2}R_{\alpha\beta}\nabla\Phi\left(\boldsymbol{r}_{\alpha\beta}^{ij}\right)\right\rangle \tag{6}$$

The first term on the right-hand side of Eq. (6) denotes the ideal-gas contributions. It arises because of the motion of the particles, whereas the second term accounts for intermolecular forces, assuming a pairwise additive potential.

## IV. Molecular Dynamics Simulations

The MD computer program is written in FORTRAN-77 and it uses the message passing interface. All of the runs were made on an IBM SP2 computer using 8, 16, or 32 processors. The simulations were performed in cubical geometries using periodic boundary conditions. The system sizes of the simulations carried out ranged between 1000 and 1200 molecules. The L–J potential parameters for ethylene used in the simulations are given as follows: $\sigma = 3.33$ Å, $\varepsilon/k_B = 137.7$ K, and $d = 2.46$ Å.

Starting from an initial configuration with the molecules placed on the positions of a face-centered cubic lattice, the first $5 \times 10^4$ time steps were used for equilibrating the system to the chosen thermodynamic state. The data runs were about $2 \times 10^6$ time steps for the transport coefficients and $2 \times 10^5$ for pressures. Statistical uncertainties in these calculations were estimated by evaluating independent averages over blocks of $1 \times 10^5$, and $1 \times 10^4$ time steps for the transport coefficients and pressures, respectively.[9]

The number of molecules used in the simulations, the time step size, and the length of the runs were chosen to allow for accurate evaluation of the Green–Kubo time correlation functions and the computation of pressures. The calculated transport coefficient results are compared with values obtained from the National Institute of Standards and Technology (NIST) software, which uses equations to determine the transport coefficients and pressures of substances.[28] The parameters of these equations for the transport coefficients were determined by experiments.[29,30] The pressure results are compared to experimental values determined by Sychev et al.[31]

## V. 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 ethylene at various thermodynamic conditions.[25] Pressures, shear viscosity, and thermal conductivity coefficients have been computed.

Figures 1 and 2 show plots of the shear viscosity and thermal conductivity coefficients, with the corresponding error bars, as functions of temperature and pressure for ethylene. Plots are shown for pressures of 3, 5, 10, and 15 MPa, with temperatures ranging between 270 and 600 K. These are typical conditions experienced during droplet evaporation. The critical pressure and temperature of ethylene are 5.04 MPa and 282.0 K, respectively.[32]

For the low-pressure cases, the increase in the shear viscosity coefficient with temperature is greater than the increase for the high-pressure cases. At low pressures, the viscosity increases with temperature because of purely kinetic effects, whereas at high pressures, the kinetic effects are counterbalanced by collisional effects that tend to reduce viscosity as the temperature is increased.[17] The plots also show that the transport coefficients have the lowest values around the critical temperatures. This is primarily a result of the long wavelength fluctuations that become very predominant around the critical point, and hence, cause anomalies in the transport and thermodynamic properties.[17]

The MD results compare well with the NIST values for most of the cases.[33] Generally, at lower temperatures and pressures, the agreement between the computed and NIST values is excellent, whereas the agreement is not as good at higher temperatures and pressures. This is particularly true for the thermal conductivity coefficient. All of the results presented in this paper were obtained using only one set of L–J parameters, which had been optimized for calculating transport properties at lower temperatures and pressures. More accurate results at higher pressure and temperature values can be obtained by making use of parameters that have been optimized for those conditions. In other words, different parameters will have to be used for modeling systems at different thermodynamic conditions, and this could be very cumbersome if several different states are being simulated. Ethylene has been modeled as just a two-site molecule instead of a six-site molecule to reduce the amount of computations. Here, each group of $CH_2$ atoms in ethylene is treated as a single site (composed of just the carbon atom) with the effects of the hydrogen atoms accounted for by the use of an effective L–J

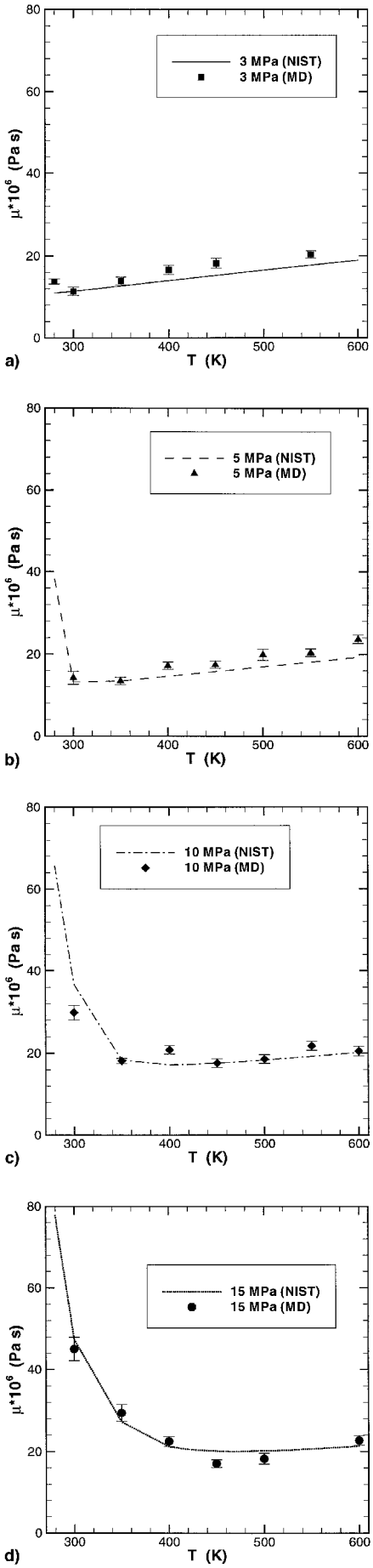


Fig. 1 Shear viscosity values from MD and NIST for ethylene: a) 3, b) 5, c) 10, and d) 15 MPa.

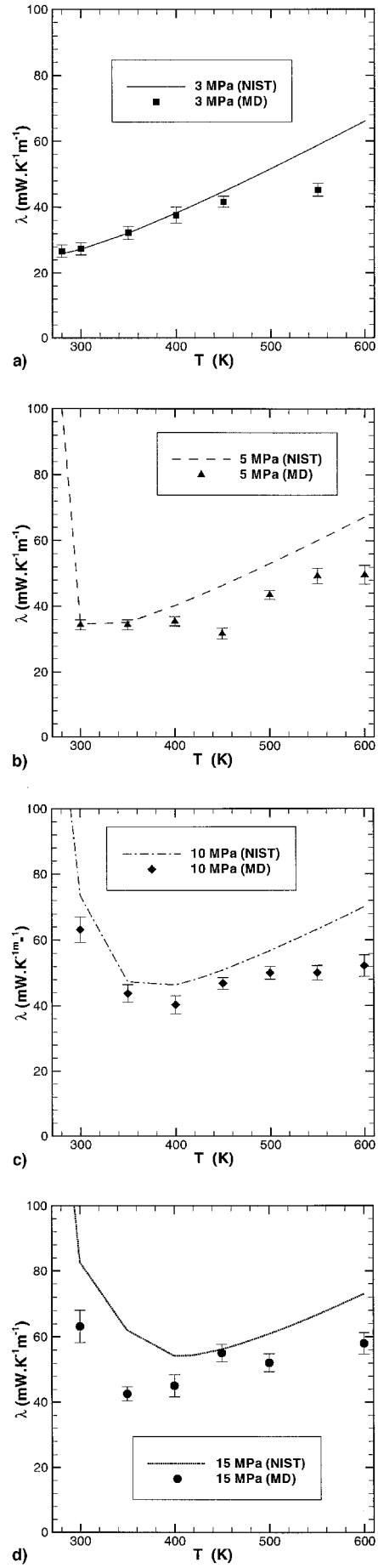


Fig. 2 Thermal conductivity values from MD and NIST for ethylene: a) 3, b) 5, c) 10, and d) 15 MPa.

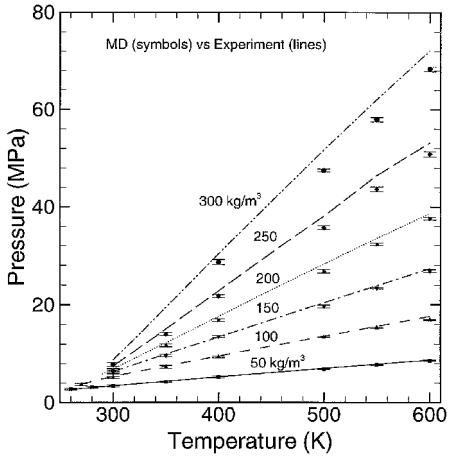


**Fig. 3 Pressure calculations from MD and experiment for ethylene.**

potential. This could also be a possible source of error in the computed results.

Figure 3 shows plots of the calculated pressures against temperature for various densities for ethylene. Simulations have been done under various conditions between densities of 50 and 300 kg/m$^3$ and temperatures of 100 and 600 K. For most of the cases, particularly the lower density states, there is excellent agreement between the MD and experimental results.[31] The larger discrepancy at higher densities is probably because the L–J potential parameters have been optimized for the lower density cases. Like the transport coefficients, more accurate results can be obtained at higher densities by using the potential parameters that are optimized for those thermodynamic states. Also, the fact that a two-site instead of a six-site model was used could also be a possible source of error.

## VI. Conclusions

The transport properties and pressures of ethylene are being computed via MD simulations using the Green–Kubo formulas and the virial equation of state, respectively. Simulations have been carried out for a large number of subcritical, near critical, and supercritical conditions. The computed shear viscosity and thermal conductivity coefficients compare well with NIST results, whereas the pressure results compare well with experimental values. Future studies will include the computation of the transport properties of other hydrocarbons typically found in propulsion systems, and the properties at the surface of evaporating droplets in supercritical environments. 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.

## Acknowledgments

This work was supported by the U.S. Air Force Office of Scientific Research Grant F49620-94-1-0133,and NASA Grants NAGW-1356 Supplement 10, and NGT-10034.

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