AFRL-SR-BL-TR-98-

0063

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	10/24/97	Final Technical Report 1/15/94-5/31/97

4. TITLE AND SUBTITLE
(U) Application of Parallel Processing to the Investigation of Supercritical Droplet Evaporation and Combustion Using Molecular Dynamics

5. FUNDING NUMBERS
PE - 61102F
PR - 2308
SA - BS
G - F49620-94-1-0133

6. AUTHOR(S)
Michael M. Micci and Lyle N. Long

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Aerospace Engineering
The Pennsylvania State University
233 Hammond Bldg.
University Park, PA 16802

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NA
110 Duncan Avenue, Suite B115
Bolling AFB DC 20332-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Molecular dynamics (MD) implemented on parallel processors was used to model supercritical droplet phenomena occurring in combustion devices. The use of molecular dynamics allows the modeling of supercritical phenomena without an a priori knowledge of the equation of state or transport properties of the individual components or the mixture. Three-dimensional supercritical oxygen vaporization into gaseous oxygen and helium using two-site Lennard-Jones potentials for the oxygen has been modeled and both the disappearance of surface tension above the critical point and the modification of the critical point for a binary mixture have been observed. A distinct change in droplet morphology was observed when passing through its critical point. The droplet remains spherical as it vaporizes under subcritical conditions but becomes broken and cloud-like when supercritical. Equations of state and transport coefficients for mass, momentum and energy have been calculated for supercritical argon, nitrogen and oxygen which agree with NIST values.

14. SUBJECT TERMS	15. NUMBER OF PAGES
supercritical, molecular dynamics, droplet vaporization	12
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

APPLICATION OF PARALLEL PROCESSING TO THE INVESTIGATION OF SUPERCRITICAL DROPLET EVAPORATION AND COMBUSTION USING MOLECULAR DYNAMICS

Final Report
1/15/94-5/31/97

AFOSR Grant No. F49620-94-1-0133

M. M. Micci and L. N. Long

Department of Aerospace Engineering
The Pennsylvania State University
University Park, PA 16802

ABSTRACT

Molecular dynamics (MD) implemented on parallel processors was used to model supercritical droplet phenomena occurring in combustion devices. The use of molecular dynamics allows the modeling of supercritical phenomena without an a priori knowledge of the equation of state or transport properties of the individual components or the mixture. Three-dimensional supercritical oxygen vaporization into gaseous oxygen and helium using two-site Lennard-Jones potentials for the oxygen has been modeled and both the disappearance of surface tension above the critical point and the modification of the critical point for a binary mixture have been observed. A distinct change in droplet morphology was observed when passing through its critical point. The droplet remains spherical as it vaporizes under subcritical conditions but becomes broken and cloud-like when supercritical. Equations of state and transport coefficients for mass, momentum and energy have been calculated for supercritical argon, nitrogen and oxygen which agree with NIST values.

RESULTS

Argon and LOX Evaporation. The results were obtained on either 8 or 32 nodes of IBM's Scaleable Powerparallel 2 (SP-2) using the Message Passing Interface subroutine library for parallel communication. In order to parallelize the problem, the molecules were distributed evenly over all of the processors, regardless of their location in the computational domain. This technique, called 'atom decomposition' [1], allowed almost perfect load-balancing to be achieved. The results presented here use a common pair-wise additive intermolecular potential called the Lennard-Jones 12-6 potential (Fig. 1) [2]. This potential contains two parameters that determine the molecular type: σ, the zero energy separation distance, and ε, the minimum energy. The gradient of this potential is used to determine the force, which is then summed over all pairs to determine the net force on a given atom. This is applied to each atom of an oxygen molecule, which is called the Lennard-Jones site-site approximation.

5,500, 27,000 and 100,500 (366,800 system total) atom liquid argon droplets have been evaporated under both subcritical and supercritical conditions [3-5]. Evaporation is carried out by placing an equilibrated droplet within a warm gaseous environment. For the subcritical simulations, the d^2 versus time law was obtained. Figure 2 shows the change in surface area with time for two subcritical conditions and one supercritical condition with two initial droplet sizes. As expected, as the environment pressure and temperature increase, so does the droplet evaporation rate. For the supercritical simulations, both the 5,500, 27,000 and 100,500 atom drops reached the same surface regression rate after an initial heat-up period. Figure 3 shows the supercritical

surface regression rates for three different size droplets scaled by the initial surface area. The 27,109 and 100,570 atom droplets show identical behavior when scaled, with the 5,587 atom drop following the same curve but with slightly greater statistical variation. This leads us to believe that extremely large systems are not required to accurately model phase change phenomena. Also significant is the result that the surface tension disappeared after the same time interval for the differently sized supercritical drops. Subcritical droplets retain a spherical geometry while supercritical droplets quickly lose their spherical shape and become more cloud-like in form.

Although Lennard-Jones is sufficient to describe intermolecular interactions, some other method must account for constraining two oxygen atoms to be in the same molecule. Ideally, one would like to treat chemical bonds as additional terms in the potential energy equation, but this proves to be both intractable and unnecessary. Because bond vibrations tend to be both high frequency and low amplitude, one can simply fix the interatomic distance to a prescribed value with little consequence to the results of the simulation. This approach, of course, would not be valid for large molecules where torsional motion about the bonds may have to be included. Another difficulty encountered when simulating multiple chemical species is determining the appropriate Lennard-Jones parameters for interactions between unlike molecules. The results presented here use the Lorentz-Berthelot mixing rules [2]. Finite-differencing of the equations of motion was accomplished using a modification of the 'velocity Verlet' algorithm called RATTLE [6]. This algorithm constrains the bond length of the oxygen molecules to a given value within a specified tolerance through an iterative process. Both the positions and the velocities are determined at the current time step to order dt^2, and the round-off error is minimized.

Two representative cases of an oxygen droplet evaporating into a helium environment are summarized in Table 1. The systems consisted of roughly 20,000 moleculaes and the initial LOX droplet diameter was 7.7 nm. As a reference, the critical temperature and pressure of oxygen is 154.77 K and 5.087 MPa, respectively. The initial condition for both simulations consisted of placing a saturated droplet at 100 K into an equilibrated environment at the various conditions listed in the table. The method of the placing the droplet into the environment assured that the initial

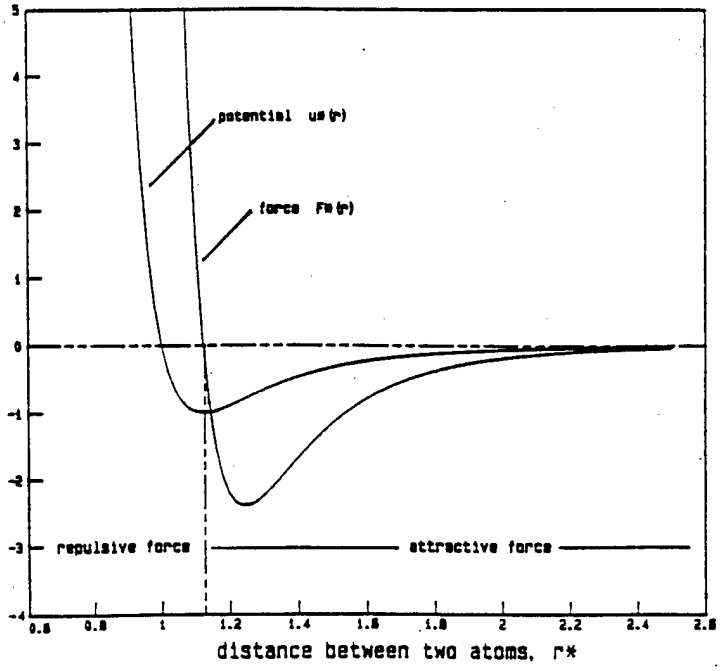

Figure 1. Lennard-Jones 12-6 interatomic potential and force.

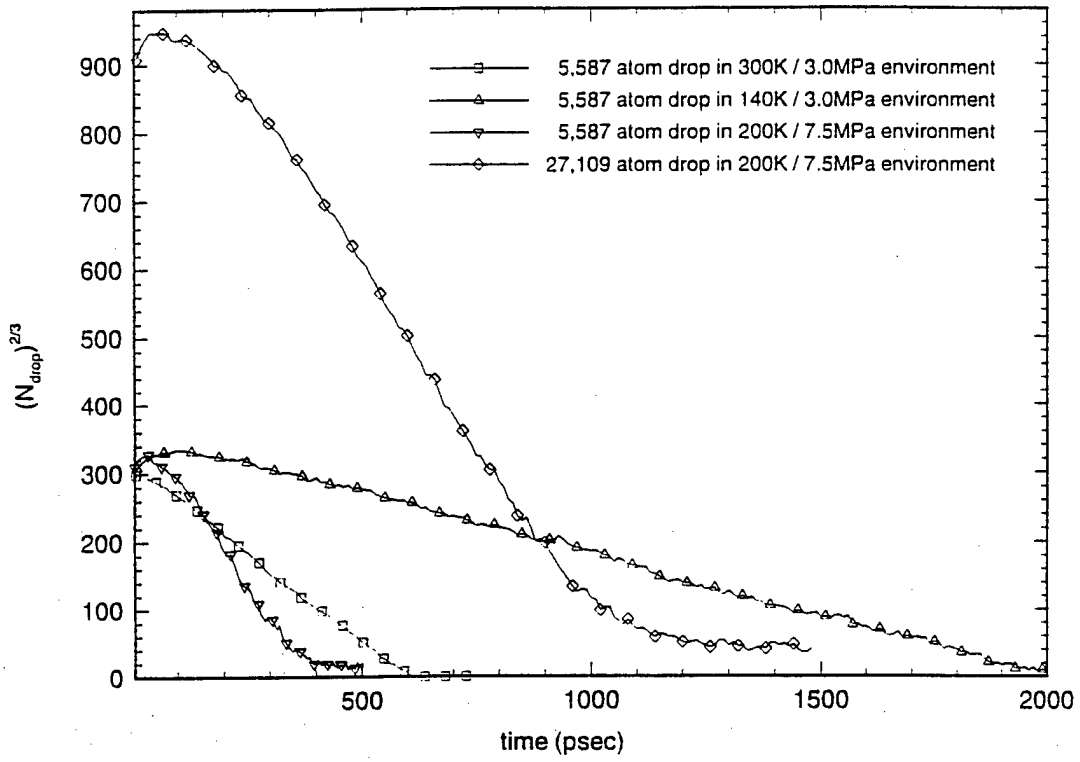

Figure 2. Argon droplet surface area as a function of time for three environmental conditions and two drop sizes showing linear d^2 versus time behavior.

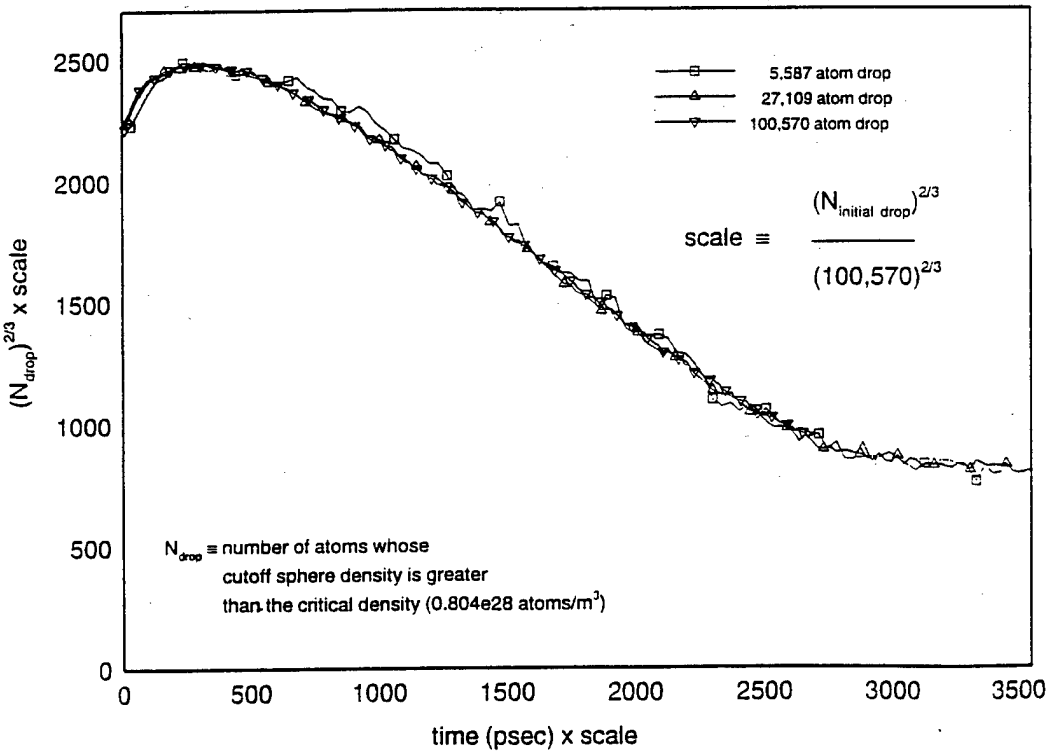

Figure 3. Supercritical argon droplet scaled surface area as a function of time for three initial drop sizes showing no dependance on initial droplet size.

surface tension of the droplet was retained for the start of the simulation. The simulation geometry was a cube with periodic boundaries and the time step was 2.5 femtoseconds. The potential cut-off was 2.5 σ, which refers to the intermolecular distance at which the potential between two atoms is so small as to be neglected. Energy was added to the system in order to induce evaporation by 'heating the boundaries', which amounts to scaling the velocities of the molecules in the boundary region of the cube to a value corresponding to a prescribed temperature.

A droplet in its own vapor under supercritical conditions shows significant differences in evaporation behavior, such as immediately vanishing surface tension and cloud-like density profiles [4]. The results of extending the modeling to mixtures is shown in Figures 4 and 5. These figures contain contour plots of oxygen mass fraction, density, temperature, and the average force in a cubic volume for two different helium environments at times of 250 psec and 110 psec, respectively. Because surface tension is the macroscopic manifestation of the unequal forces exerted on surface molecules in a liquid, the average force should provide an approximation of the surface tension present in the system. Hence a large surface tension would be indicated by a bright ring. The environment conditions of 300 K and 4 MPa in Figure 4 are below the critical pressure of oxygen, so subcritical behavior is expected. This is observed in the figure by a spherical droplet profile and strong surface tension. In contrast, Figure 5 contains results when the environment pressure and temperature are at 300 K and 20 MPa, which are both well above the critical point of oxygen. Although one might expect supercritical behavior, this is not observed. The droplet profile remains spherical and surface tension is retained throughout the droplet lifetime. But experiments have shown that binary mixtures containing helium can easily have critical pressures over 100 MPa [7].

Case	Temperature	Pressure
1	300 K	4.0 MPa
2	300 K	20.0 MPa

Table 1: Summary of thermodynamic conditions for two different helium environments used in the LOX droplet evaporation simulations. The critical temperature and pressure of oxygen is 154.77 K and 5.087 MPa, respectively.

Equation of state and transport properties. This work involved the determination of transport coefficients and pressures of supercritical fluids by molecular dynamics (MD) simulations using the Green-Kubo formulae [8] and the virial equation of state [2], respectively. The transport coefficients that are of interest include self-diffusion, shear viscosity, and thermal conductivity. The coefficients are computed using Green-Kubo formulae in which a correlation function is integrated over time. A time autocorrelation function measures the relation between the values of some dynamic quantity at two different times.

$$C(t) = \lim_{\tau \to 0} \frac{1}{\tau} \int_{t_0}^{\tau} A(t_0) A(t_0 + t) dt_0 \qquad (1)$$

This can be written in the form

$$C(t) = \langle A(t_0) A(t_0 + t) \rangle \qquad (2)$$

where t_0 and t denote an arbitrary time and the time difference, respectively, and the brackets denote an autocorrelation.

The self diffusion process is the mass transport associated with the motion of a single particle in a fluid, and hence characterizes a one-particle property of the system. Self diffusion may be described by the mass and velocity of a marked particle of the fluid. For the self-diffusion, the Green-Kubo formula contains the velocity autocorrelation function,

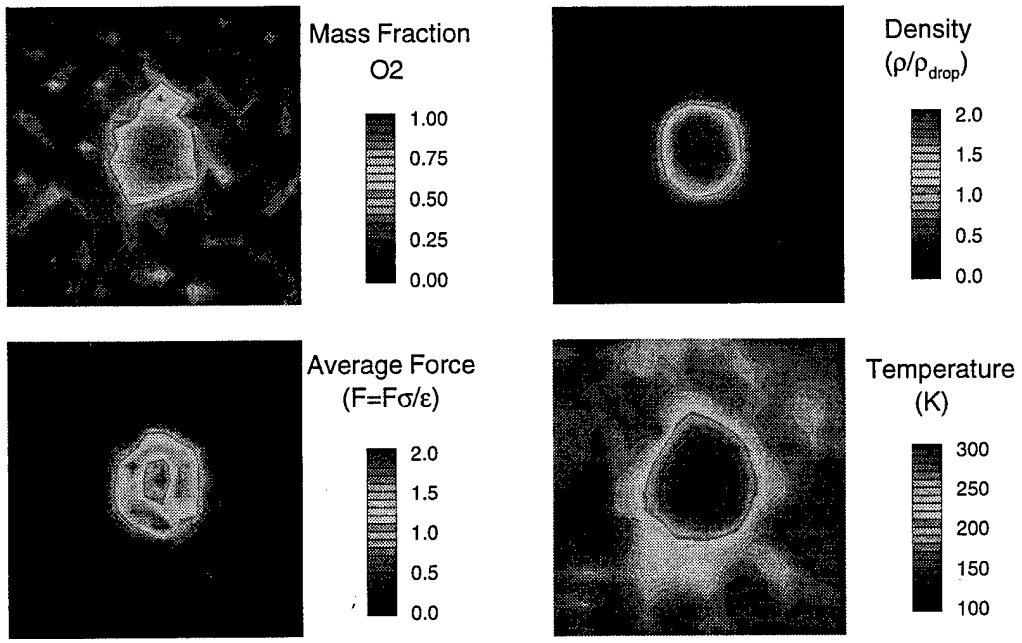

Figure 4: Contour plots of oxygen mass fraction, density, temperature, and the average force after 250 picoseconds of simulation time. The helium environment is at 300 K and 4.0 MPa, and the droplet is exhibiting subcritical evaporation behavior.

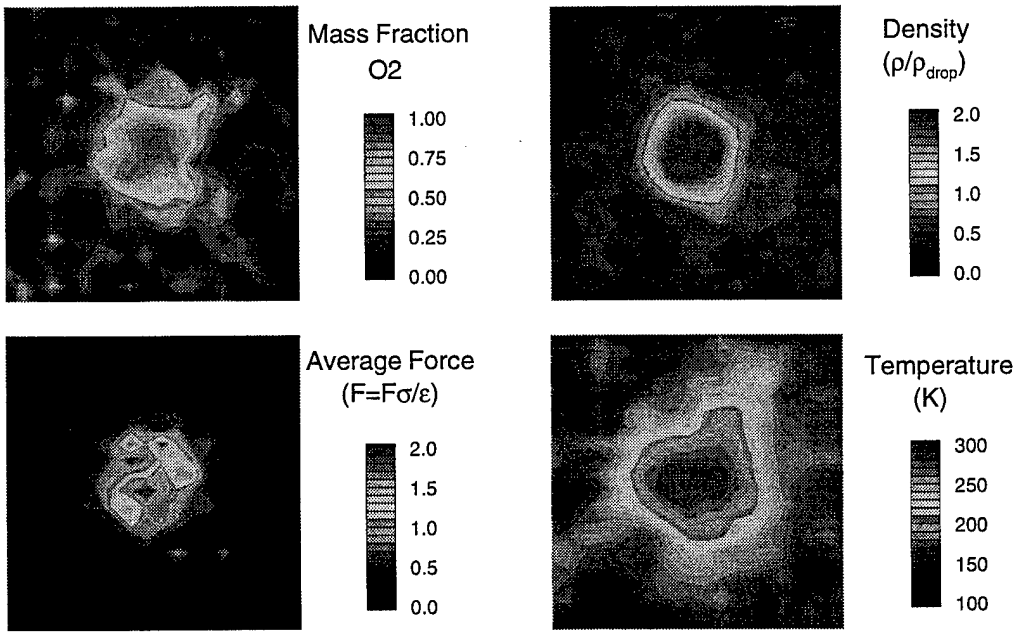

Figure 5: Contour plots of oxygen mass fraction, density, temperature, and the average force after 110 picoseconds of simulation time. The helium environment is at 300 K and 20.0 MPa, which is well above the critical point of both helium and oxygen. The droplet is still exhibiting subcritical evaporation behavior.

$$D = \frac{1}{3N}\int_0^\infty \sum_{i=1}^{N} \left\langle \vec{v}_i(t_0) \cdot \vec{v}_i(t_0 + t) \right\rangle dt \tag{3}$$

where D denotes the mean self diffusion of the system and $\vec{v}_i$ is the velocity of the i^{th} particle. This mean value is obtained by summing the velocity autocorrelation function of each of the particles over the total number N.

The shear viscosity coefficient measures the resistance of the fluid to a shearing force. For the shear viscosity the integration is over the non-diagonal terms of the stress tensor and it is a collective property of the fluid. The Green-Kubo formula is given by,

$$\mu_{XY} = \frac{1}{Vk_bT}\int_0^\infty \left\langle J^{xy}(t_0) J^{xy}(t_0 + t) \right\rangle dt \tag{4}$$

where J^{XY}, an off-diagonal term of the stress tensor is given by

$$J^{xy} = m\sum_{i=1}^{N} v_i^x v_i^y - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} r_{ij}^x \nabla_y \Phi(r_{ij}) \tag{5}$$

Here T and V denote the temperature and volume of the system, respectively, and m denotes the mass of each particle. v^X, r_{ij} and $F(r_{ij})$ denote the x-direction velocity, position vector and the potential, respectively, between particles i and j. Statistical precision is improved by averaging over all six terms that result from the stress tensor:

$$\mu = \frac{1}{6}\left(\mu_{xy} + \mu_{yx} + \mu_{xz} + \mu_{zx} + \mu_{yz} + \mu_{zy}\right) \tag{6}$$

The thermal conductivity coefficient measures the transport of heat in a system. The correlation function is obtained from the heat current and it is also a collective property of the entire fluid. The Green-Kubo formula is given by:

$$\lambda_x = \frac{1}{Vk_bT^2}\int_0^\infty \left\langle T_q^x(t_0) T_q^x(t_0 + t) \right\rangle dt \tag{7}$$

where T_q^x denotes an arbitrary component of the heat current and is given by

$$T_q^x = \frac{m}{2}\sum_{i=1}^{N} |v_i|^2 v_i^x - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\left(r_{ij}^x \nabla_x \Phi(r_{ij}) - \Phi(r_{ij})\right) i\right] v_i \tag{8}$$

where i denotes a unit tensor. Again, statistical precision is improved by averaging over all three components:

$$\lambda = \frac{1}{3}\left(\lambda_x + \lambda_y + \lambda_z\right) \tag{9}$$

These functions are computed during the simulation. The velocity autocorrelation is computed outside the force subroutine, while the other components of the other autocorrelation functions are calculated within it. Once the correlation functions have been obtained, standard numerical integration techniques are used to obtain the transport coefficients. The statistical precision of the self-diffusion coefficient is improved by averaging over all the particles in the system. The viscosity and thermal conductivity values are improved by averaging over all the six terms from the stress tensor, and the three terms of the heat current, respectively.

The MD program uses the effective Lennard-Jones potential, with system sizes of 256 molecules, and simulations of 500,000 timesteps for the transport coefficients computation and 50,000 timesteps for pressures. A typical timestep size of 2 fs is used for most of the simulations. The code also uses 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 argon, nitrogen, and oxygen at various supercritical conditions, with self-diffusion coefficients, shear viscosity coefficients, thermal conductivity coefficients, and pressures computed for most of the conditions. Results have been compared to the National Institute of Standards and Technology (NIST) [9] values. Figure 6 shows diffusion coefficients for oxygen. It can be observed that the coefficient decreases with temperature at 3 MPa, but increases at supercritical pressures. Figures 7 and 8 show shear viscosity and thermal conductivity. The MD results compare well with the NIST values, especially at the higher temperatures. The poorer match at 160 K for the 10 and 15 MPa cases may be due to the use of an insufficient sample size as the critical temperature is approached. Figure 9 shows calculated pressures as a function of temperature for various densities. For most of the cases there is excellent agreement between the MD and NIST values.

Three-Body Forces. MD simulations normally use two-body (pair-wise additive) potentials such as the Lennard-Jones 12-6 potential to calculate interatomic forces. This is done because good agreement with experimental results can be achieved with two-body potentials and because calculations using three-body potentials become extremely computationally intensive. However concern has been expressed that the high densities associated with supercritical conditions could lead to errors when using only two-body potentials. Thus an argon evaporation model using the classical three-body Axilrod-Teller potential [10] has been constructed in order to examine any difference in evaporation behavior under supercritical conditions between two- and three-body potentials [11]. Little difference was detected between the two-body and three-body simulations.

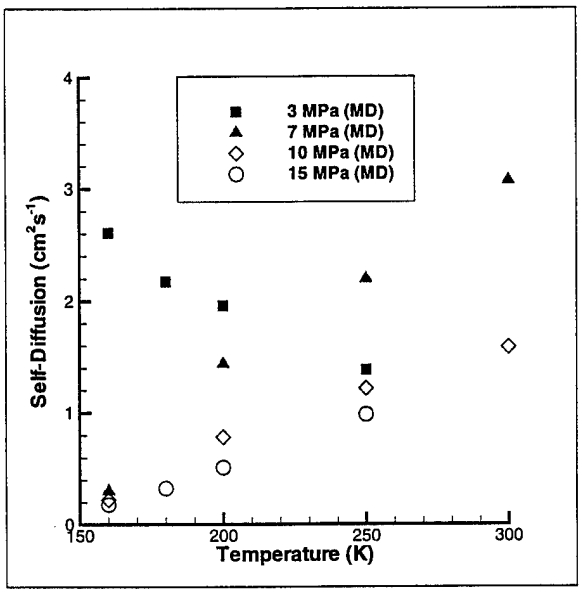

Fig. 6 Oxygen self-diffusion coefficients as a function of temperature for various pressures calculated via MD

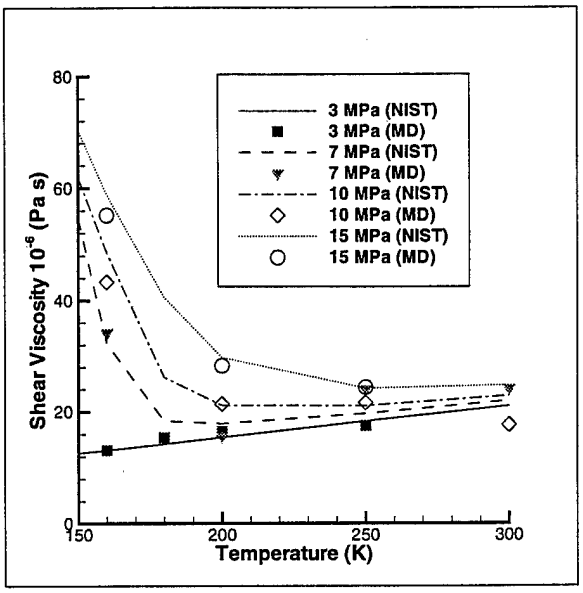

Fig. 7 Oxygen shear viscosity as a function of temperature for various pressures comparing MD and NIST calculated values

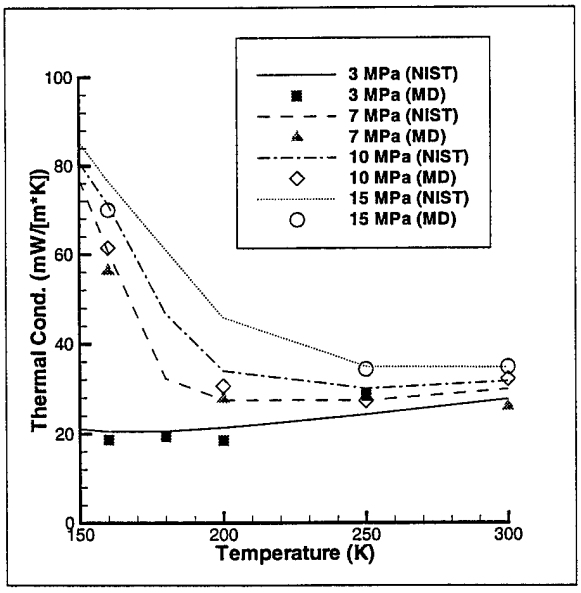

Fig. 8 Oxygen thermal conductivity as a function of temperature for various pressures comparing MD and NIST calculated values

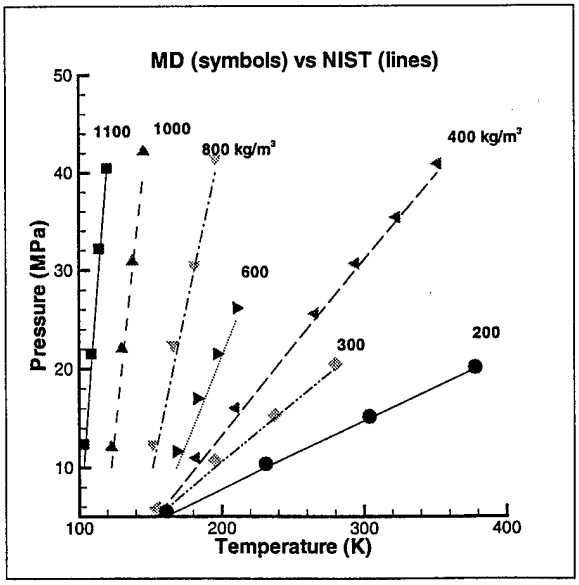

Fig. 9 Oxygen pressure as a function of temperature for various densities comparing MD and NIST calculated values

REFERENCES

1. Plimpton, S., "Fast Parallel Algorithms for Short-Range Molecular Dynamics," *J. Comp. Phys.*, **117**, pp. 1-19, 1995.

2. Allen, M. P. and Tildesly, D. J., *Computer Simulation of Liquids*, Oxford University Press, New York, NY, 1984.

3. Long, L. N., Micci, M. M. and Wong, B. C., "Molecular Dynamics Simulations of Droplet Evaporation," *Computer Physics Communications*, Vol. 96, Aug. 1996, pp. 167-172.

4. Little, J. K., *Simulation of Droplet Evaporation in Supercritical Environments using Parallel Molecular Dynamics*, Ph.D. thesis, The Pennsylvania State University, August 1996.

5. Micci, M. M., Long, L. N. and Little, J. K., "Parallel Molecular Dynamics Code for Supercritical Droplet Evaporation," *Parallel Computational Fluid Dynamics: Algorithms and Results Using Advanced Computers*, Elsevier, Amsterdam, 1997, pp. 312-319.

6. Andersen, H. C., "RATTLE: A 'Velocity' Version of the Shake Algorithm for Molecular Dynamics Calculations," *J. Chem. Phys.*, **52**, pp. 24-34, 1983.

7. Sadus, R. J., *High Pressure Phase Behavior of Multicomponent Fluid Mixtures*, Elsevier Science Publishers, New York, NY, 1992.

8. Hoheisel, C. and Vogelsang, R., "Thermal Transport Coefficients for One-Component and Two-Component Liquids from Time Correlation Functions Computed by Molecular Dynamics," *Computer Physics Report*, **18**, pp. 1-69, 1988.

9. National Institute of Standards and Technology, NIST, Thermophysical Properties of Pure Fluids Database: Version 3.0, *http://www.nist.gov/srd/nist12.htm*, Gaithersburg, MD, 1996.

10. Axilrod, B. M. and Teller, E., "Interaction of the Van Der Waals' Type Between Three Atoms," *J. Chem. Phys.*, Vol. 11, 1943, pp. 299-300.

11. Ohlandt, C., *Molecular Dynamics Simulation of Argon Droplet Evaporation with Three Body Force Potentials*, M.S. thesis, The Pennsylvania State University, August 1996.

PERSONNEL

Professional Staff

Michael M. Micci, Associate Professor, Aerospace Engineering
Lyle N. Long, Associate Professor, Aerospace Engineering

Graduate Students

Brian Wong, 1994-1996
Teresa Kaltz, 1994-present
Jeffrey Little, 1994-1996
Obika Nwobi, 1994-present
Chad Ohlandt, 1994-1996

PUBLICATIONS

"Molecular Dynamics Simulations of Droplet Evaporation," Long, L. N., Micci, M. M. and Wong, B. C., *Computer Physics Communications*, Vol. 96, Aug. 1996, pp. 167-172.

"Parallel Molecular Dynamics Code for Supercritical Droplet Evaporation," Micci, M. M., Long, L. N. and Little, J. K., *Parallel Computational Fluid Dynamics: Algorithms and Results Using Advanced Computers*, Elsevier, Amsterdam, 1997, pp. 312-319.

THESES

Jeffery K. Little, *Simulation of Droplet Evaporation in Supercritical Environments using Parallel Molecular Dynamics*, Ph.D. thesis, The Pennsylvania State University, August 1996.

Chad Ohlandt, *Molecular Dynamics Simulation of Argon Droplet Evaporation with Three Body Force Potentials*, M.S. thesis, The Pennsylvania State University, August 1996.

PRESENTATIONS and INTERACTIONS

"Supercritical Droplet Evaporation Modeled Using Molecular Dynamics on Parallel Processors," Micci, M. M. and Long, L. N. Presented at the AFOSR Supercritical Fuels/Combustion Workshop, Wright Laboratory, Wright-Patterson AFB, OH, Feb. 7-9, 1994.

"Application of Parallel Processing to the Investigation of Supercritical Droplet Evaporation and Combustion Using Molecular Dynamics," Micci. M. M. and Long, L. N. Presented at the AFOSR Contractors Meeting on Propulsion Research, June 5-10, 1994, Lake Tahoe, NV.

"Molecular Dynamics Simulations of Droplet Evaporation," Long, L. N., Micci, M. M. and Wong, B. C., AIAA Paper 94-2907. Presented at the 30th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, June 27-29, 1994, Indianapolis, IN.

"Supercritical Droplet Evaporation Modeled Using Molecular Dynamics on Parallel Processors," Kaltz, T., Little, J., Wong, B., Micci, M. and Long, L. Presented at the Euromech Colloquium 324, The Combustion of Drops, Sprays and Aerosols, July 25-27, 1994, Marseilles, France.

"Submicron Droplet Modeling Using Molecular Dynamics", Long, L. N., Micci, M. M. Kaltz, T. L., Little, J. K. and Wong, B. C. AIAA Paper 95-0412. Presented at the 33rd Aerospace Sciences Meeting and Exhibit, January 9-12, 1995, Reno, NV.

"Supercritical Droplet Evaporation Modeled Using Molecular Dynamics on Parallel Processors," Long, L. N. and Micci, M. M. Presented at the AFOSR Supercritical Fuels/Combustion Workshop, Ann Arbor, MI, June 15, 1995.

"Submicron Droplet Modeling Using Molecular Dynamics," Micci, M. M., Long, L. N., Little, J. K. and Kaltz, T. L. Presented at the 32nd JANNAF Combustion Meeting, Oct. 23-27, 1995, Huntsville, AL.

"Parallel Molecular Dynamics Code for Supercritical Evaporation," Micci, M. M., Long, L. N. and Little, J. K. Presented at Parallel CFD '96, May 20-24, 1996, Capri, Italy.

"Application of Parallel Processing to the Investigation of Supercritical Droplet Evaporation and Combustion Using Molecular Dynamics," Micci, M. M. and Long, L. N. Presented at the AFOSR/ARO Contractors Meeting in Chemical Propulsion, June 3-6, 1996, Virginia Beach, VA.

"Molecular Dynamics Studies of Transport Properties of Supercritical Fluids," Presented at the 35th Aerospace Sciences Meeting, January 6-10, 1997, Reno, NV.