

# Experiments and Molecular Dynamics Simulations of Supercritical Nitrogen Injection

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The state-of-the-art for modeling supercritical combustion chamber injection is still unable to accurately predict the mixing between the fuel and the oxidizer without initial parameters provided from experimental correlations. This greatly limits the ability to predict high-pressure liquid propellant rocket engine performance as a function of injector design changes. The objective of this program is to develop an accurate and fast simulation methodology for supercritical injection in liquid rocket engines. The approach is to use molecular dynamics, in both unscaled and scaled implementations, to model and predict supercritical injection and mixing. The use of molecular dynamics allows the supercritical mixing to occur ‘naturally’ without the need for tracking phase boundaries and intrinsically includes all physical processes, material properties and equations of state in both subcritical and supercritical environments. Current molecular dynamics simulations of subcritical liquid nitrogen injection and atomization result in droplet sizes that match Rayleigh theory and are being extended to supercritical conditions to be compared to experimental Raman measurements of jet spreading and mixing conducted at DLR Lampoldshausen. In order to increase simulation Reynolds numbers, scaling of the interatomic potential parameters and particle mass according to the method proposed by Greenspan is being investigated, which has resulted in the simulation of turbulent tube flow at a Reynolds number of 11,000.

## **1. Introduction**

Traditional supercritical spray models have several limitations. Since few simulations are three-dimensional, geometries such as planar or axisymmetric must be assumed. Due to the multiphase nature of atomization and spray phenomena, a means for tracking the phase boundaries must be included when conditions are subcritical. And since all traditional methods for modeling such processes are based on the solution of the Navier-Stokes equations, an accurate knowledge of the constituent transport and material properties along with an accurate equation of state are required. This can be particularly difficult as one approaches the critical pressures and temperatures of one or more of the constituents.

The current state-of-the-art for models of supercritical injection and mixing is represented by the work conducted at DLR Lampoldshausen [1], [2] and by Oefelein and Yang [3]. The DLR work has involved both single-phase turbulent reacting models for pure supercritical systems and two-phase sub and transcritical models involving droplets, droplets with a fixed liquid core or droplets with a variable liquid core. The work by Oefelein and Yang looked at mixing and reactions in a two-dimensional planar gaseous hydrogen/liquid oxygen shear layer.

## 2. Molecular Dynamics

Molecular dynamics (MD) is a particle-based method wherein only Newton's Law,  $F = ma$ , is required to be solved to obtain the particle positions and velocities. These particles can be individual atoms or molecules or quasiparticles that represent a large number of atoms or molecules. The force in Newton's Law is obtained from an interatomic potential, which can take one of a number of forms. 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. The simulation then proceeds naturally with no a priori assumptions regarding transport or material properties or phase boundaries. Since most molecular dynamics simulations are three-dimensional, no assumptions regarding geometric symmetry are required. Transport and material properties are results of molecular dynamics simulations, not input parameters or assumptions.

The most significant part of a molecular dynamics simulation is the interatomic potential. Although many possible potentials exist, such as the hard sphere, soft sphere, square well and Sutherland [4], the most commonly used one is the Lennard-Jones 12-6 potential given by:

$$u_{ij}(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

where  $r_{ij}$  is the distance between particles  $i$  and  $j$ ,  $\varepsilon$  is the depth of the interatomic potential well and  $\sigma$  is the interatomic separation where the potential is zero. The force experienced by the two atoms is given by the negative of the gradient of the potential,  $\vec{F}_{ij} = -\nabla u_{ij}$ . The potential is characterized by a strong repulsive force at very short range and a weak attractive force at intermediate range. The total force experienced by an atom is simply the sum of the forces due to all neighboring atoms. Since the potential quickly decays with the interatomic separation, a cutoff distance, usually set equal to  $2.5\sigma$  where the value of the Lennard-Jones 12-6 potential is only 1.6% of the minimum energy, is used beyond which the interatomic force is neglected, reducing the amount of computation.

Molecules are simulated by assuming a Lennard-Jones potential for each atom or groups of atoms, such as methyl radicals, and applying constraints such as fixed bond lengths between them. In this manner large molecules can be simulated.

The equation of motion,  $F = ma$ , can be numerically integrated using any algorithm one desires, but is most commonly done using the 'velocity Verlet' algorithm [5]. In this algorithm the particle positions are advanced every time step while the velocities are advanced every half time step. This results in an algorithm that is computationally efficient but accurate to order  $\Delta t^2$ .

Periodic boundary conditions are often used, however solid boundaries can be simulated by several means. One method uses a layer of fixed atoms that mimic the effect of a wall and a thermostat is applied to the wall atoms to specify the wall temperature or heat flux [6]. A second method uses a stochastic wall, where particles are reflected, either specularly or diffusely, when they cross the wall boundary [7]. A diffuse reflection results in a no-slip boundary condition. The wall temperature or heat flux is specified by adjusting the velocity of the reflected particles. A third method simply uses a potential field for the wall.

Various phenomena relevant to injection, atomization and mixing have been previously simulated using molecular dynamics. Droplet formation from liquid cylinders has been

simulated and the results have been found to agree with Rayleigh breakup theory [8-10]. For cases where the initial cylinder length to diameter ratio is long enough, multiple droplets are formed as predicted by the Rayleigh theory. Droplet formation from the isentropic expansion of a liquid [11] and liquid oxygen droplet vaporization under both subcritical and supercritical conditions into a variety of gaseous environments have been simulated [12]. Droplet interactions such as collisions and coalescence that cannot be simulated at all by the use of the Navier-Stokes equations without the inclusion of ad hoc assumptions are simulated naturally by molecular dynamics [13-15]. Finally, liquid flows, such as those that would be found within injectors, can be simulated using MD and in all cases results match those given by the solution of the Navier-Stokes equations [16]. Poiseuille flow, Couette flow and flow around a solid body have been simulated.

### 3. Results

Initially, a previous liquid argon/gaseous argon molecular dynamics code was modified to simulate liquid and gaseous diatomic nitrogen. This was done by the addition of a constraint dynamics algorithm for the nitrogen molecules [4], [5]. Each nitrogen atom in the molecule is simulated separately with its own interatomic potential. A constraint force is added to the sum of the interatomic forces acting on each atom and iteratively adjusted using the RATTLE algorithm to satisfy the specified constraint, which in the case of molecular nitrogen is the fixed bond length [17].

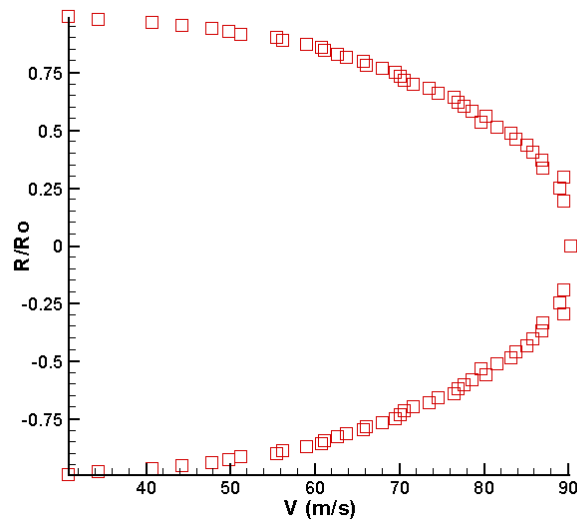
The code is a parallel processor domain decomposition simulation developed using the MPI parallel library. The domain decomposition algorithm divides the computational region along the longitudinal axis into disk-shaped geometric domains, with each domain assigned to a separate processor. Particles are exchanged between processors when they travel between domains. A Verlet nearest neighbor list was used to reduce the needed force calculations to those atoms within a cutoff radius of  $2.5\sigma$  [5].

Approximately 5000 nitrogen molecules were used in the initial simulation region that was 4 nm in diameter and 40 nm long. The atoms were initialized at a liquid density in a cubic lattice with a Maxwellian velocity distribution representative of a given initial temperature. A stochastic boundary condition was applied on the sidewalls using diffuse reflections to obtain a no-slip boundary at a constant temperature. Periodic boundary conditions were used on the ends of the tube, if an atom exited from one end of the tube it re-entered at the other end. The time step used was 2.5 femtoseconds (fs). 10,000 time steps were used to allow the liquid argon to equilibrate, then a body force was applied to the atoms to induce a mean flow in the tube. The simulation was continued for another 350,000 time steps to allow the fully developed pipe flow to reach equilibrium.

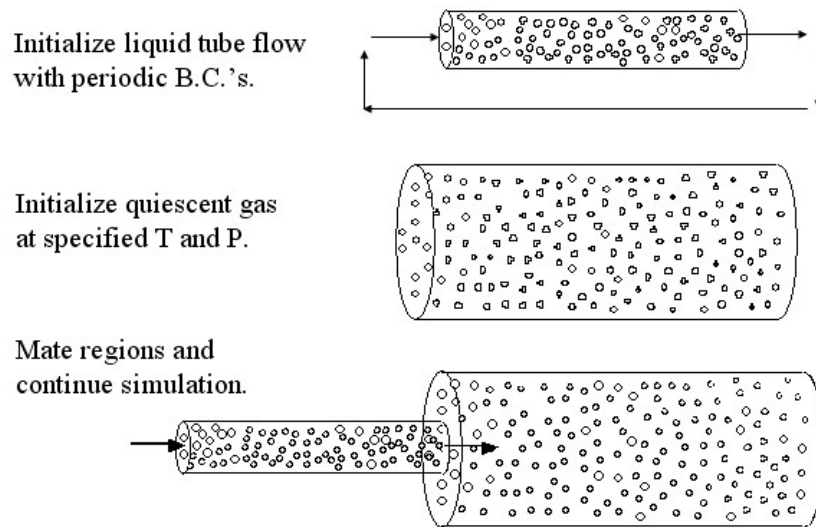
Figure 1 shows the radial velocity profile of the computed fully developed pipe flow. The analytically predicted parabolic velocity profile for the Poiseuille flow is obtained. The Reynolds number of the flow is approximately 5. The simulation requires approximately twelve hours to run on sixteen processors of our Beowulf PC cluster.

After the liquid argon pipe flow reached equilibrium, the initial simulation region was mated to a larger diameter (20 nm) cylindrical region 40 nm long containing quiescent gaseous nitrogen at a specified pressure and temperature. The liquid nitrogen was then allowed to flow under the influence of the body force into the gaseous region. The periodic boundary

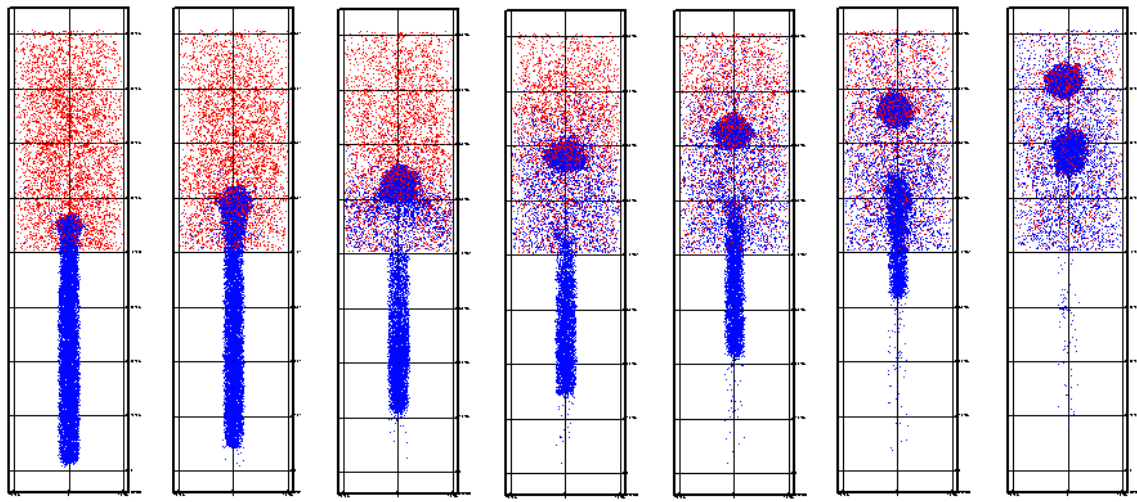
conditions were removed from the upstream end of the liquid region and the downstream end of the gaseous region. The gaseous region had the same sidewall boundary condition as the liquid region, i.e., no-slip and a specified temperature. An additional eight processors were used for the gaseous region utilizing the same domain decomposition scheme as for the liquid region. Figure 2 shows a schematic of the initialization of the jet injection simulation. In order to validate the accuracy of the molecular dynamics simulation to model supercritical injection and mixing, simulations were initiated to model subcritical liquid nitrogen injection for comparison to classical analytical theories. Figure 3 shows the simulation of subcritical liquid nitrogen at 84 K and 0.5 MPa injected into gaseous nitrogen at the same conditions. The blue molecules are initially liquid and the red molecules are initially gas. The injection velocity was 44 m/s, corresponding to a Reynolds number  $Re=1.14$ . The pinch-off and formation of two liquid nitrogen droplets can be seen. The



**Fig. 1** Radial velocity profile for fully developed liquid nitrogen pipe flow.  $Re = 5$ .



**Fig. 2** Schematic of initialization of molecular dynamics jet injection simulation.

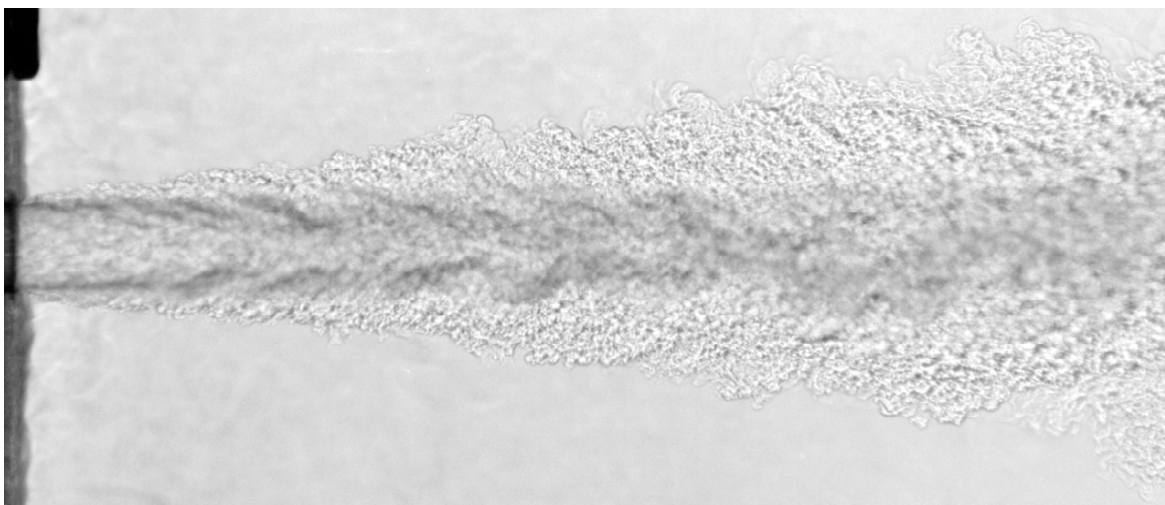


**Fig. 3** Molecular dynamics simulation of subcritical liquid nitrogen injection at 0.5 MPa and 84 K demonstrating Rayleigh break-up.

diameter of the drops matches the Rayleigh predicted size for low Reynolds number flow of 1.89 times the diameter of the liquid jet [18]. Clearly the instability of the liquid jet due to the surface tension is reproduced.

Simulations have also been conducted at 1 and 2 MPa liquid and gas pressures (critical pressure for nitrogen is 3.38 MPa). The Rayleigh atomization is still reproduced at these higher pressures, although the droplets are more difficult to visualize due to the increased gas density.

Initial simulations have been conducted of liquid nitrogen injection into a supercritical nitrogen environment. These will be compared to measurements of jet spreading angle and radial and axial density profiles taken from Raman measurements at DLR [19]. Figure 4 shows a shadowgraph image of a supercritical nitrogen jet at 4 MPa and 130 K taken at DLR



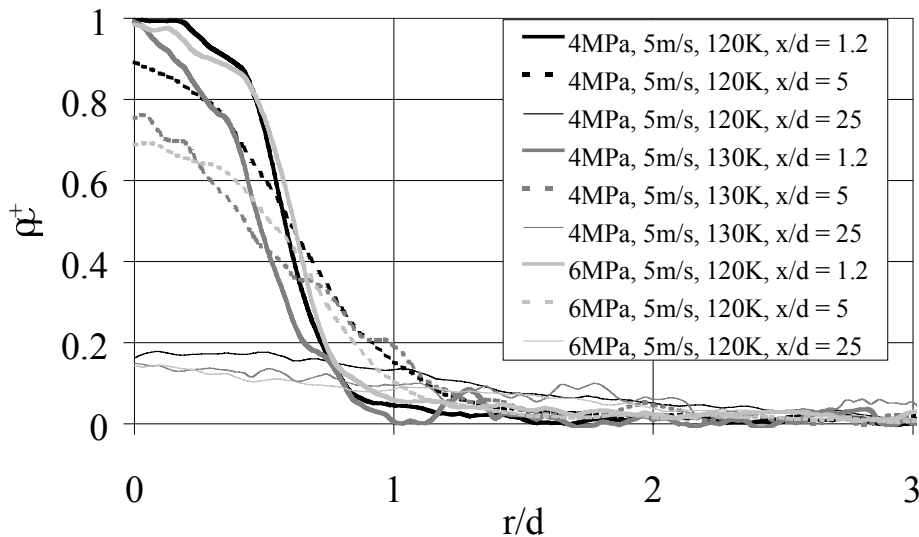
**Fig. 4** Shadowgraph image of supercritical liquid nitrogen jet at 4 MPa and 130 K [19].



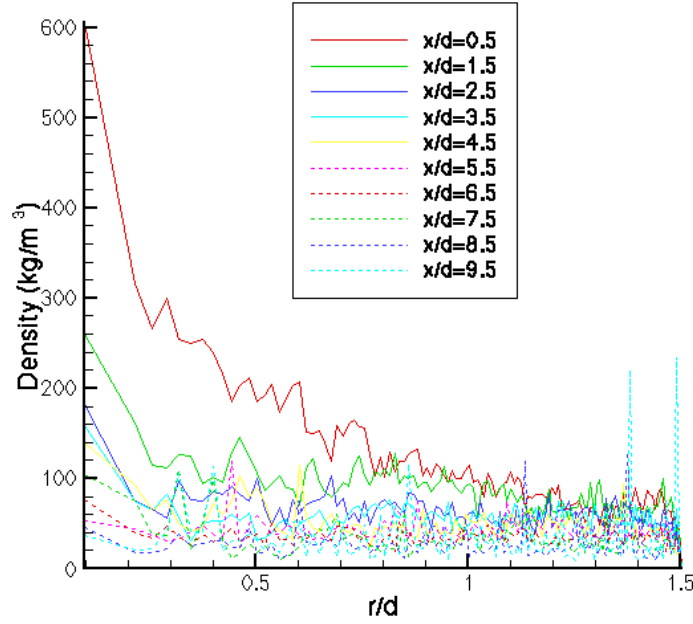
**Fig. 5** MD simulation of liquid nitrogen before and after injection at 3.96 MPa and 126 K.

[19]. Figure 5 shows an initial molecular dynamics simulation for nitrogen injection at 3.96 MPa and 126 K. The liquid nitrogen before and after injection can be seen. In order to quantitatively compare results from the molecular dynamics simulations to the experimental measurements, means for calculating the radial and axial density profiles produced by the MD simulations are being developed. Figure 6 shows radial density profiles taken from Raman measurements for a variety of pressures and temperatures from the experiments at DLR [19]. Figure 7 shows initial radial density profiles at various axial locations downstream of the injector obtained from a molecular dynamics simulation of nitrogen injection at 4 MPa. The curve roughness is due to insufficient averaging of the molecular dynamics results and will decrease as the computational system size is increased. Axial density profiles are also being obtained.

Current computer technology does not allow a sufficient increase in the simulation size to higher (turbulent) Reynolds numbers since the number of molecules scales with the cube of the system characteristic length. In order to increase the size scale and therefore the Reynolds and Weber numbers of the simulations, scaling of the interatomic potential parameters  $\epsilon$  and  $\sigma$  as well as the particle mass is being examined. This is similar to the Direct Simulation Monte Carlo (DSMC) method where a computational particle can simulate a vastly greater number (millions) of real particles [20]. A method proposed by



**Fig. 6** Raman measured nondimensionalized radial density profiles for liquid nitrogen injection [19].



**Fig. 7** Initial radial density profiles obtained from molecular dynamics simulation.

Greenspan [13], [14] is initially being examined. Greenspan's method scales the potential parameters and particle mass to match total system mass (and therefore density) and energy, resulting in the scaling relationships:

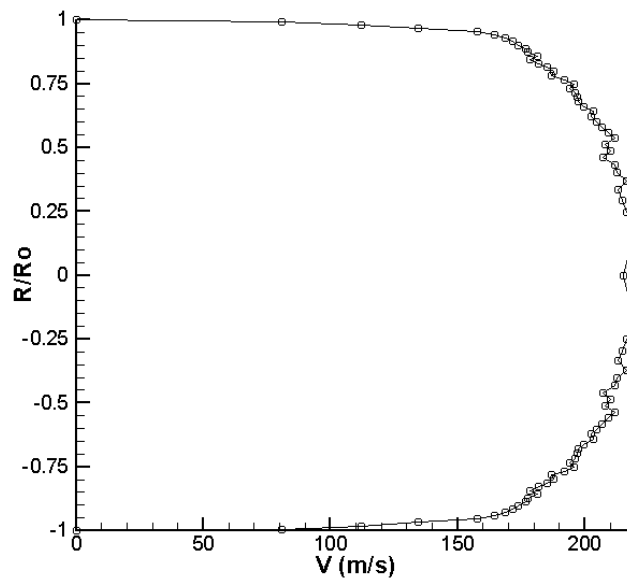
$$\varepsilon_s = \frac{N}{N_s} \varepsilon \quad \sigma_s = \sqrt[3]{\frac{N}{N_s}} \sigma \quad m_s = \frac{N}{N_s} m \quad (2)$$

where the subscript s indicates the scaled quantities and N is the number of particles. This scaling also matches nondimensional temperature and pressure.

Greenspan scaling was implemented in the molecular dynamics simulation of the liquid nitrogen tube flow. Ratios of  $N/N_s$  up to  $10^{10}$  were implemented, resulting in a Reynolds number of approximately 11,000. This increases the tube diameter from the previous 4 nm to 9 microns. Figure 8 shows a turbulent velocity profile for the Reynolds number of 11,000 in a 9 micron diameter flow. Figure 8 can be compared to the unscaled low Reynolds number laminar velocity profile shown in Figure 1. The simulations in Figures 1 and 8 use the same number of molecules, approximately 10,000.

#### 4. Conclusions

A molecular dynamics simulation of liquid nitrogen injection into a gaseous nitrogen environment under both subcritical and supercritical conditions has been developed. Liquid nitrogen injection under subcritical conditions results in droplet formation in agreement with Rayleigh theory. For supercritical nitrogen injection adial and axial density profiles and jet spreading angles can be computed. In order to increase simulation Reynolds numbers, scaling of the interatomic potential parameters and particle mass according to the method proposed by Greenspan has produced the simulation of turbulent pipe flow at a Reynolds number of 11,000.



**Fig. 8** Turbulent velocity profile for liquid nitrogen tube flow at a Reynolds number of 11,000 obtained by the application of Greenspan scaling.

## 5. References

- [1] Schley CA., Schik A and Krulle G 1995 AIAA Paper 95-2556.
- [2] Mayer W, Schik A, Schweitzer C and Schaffler M 1996 AIAA Paper 96-2620.
- [3] Oefelein JC and Yang V 1998 *Journal of Propulsion and Power* **14** 843-857
- [4] Sadus R J 1999 *Molecular Simulation of Fluids* (Amsterdam, Elsevier)
- [5] Allan M P and Tildesley D J 1984 *Computer Simulation of Liquids* (New York, Oxford University Press)
- [6] Ashurst W T and Hoover W G 1975 *Phys. Rev. A* **11** 658
- [7] Trozzi C and Ciccotti G 1984 *Phys. Rev. A* **29** 916-925
- [8] Koplik J and Banavar J R 1993 *Phys. Fluids A*, **5** 521-536
- [9] Koplik J and Banavar J R 1995 *Annu. Rev. Fluid Mech.* **27** 257-292
- [10] Kawano S 1998 *Phys. Rev. E* **58** 4468-4472
- [11] Ashurst W T and Holian B L 1999 *Phys. Rev. E* **59** 6742-6752
- [12] Kaltz T L, Long L N, Micci M M and Little J K 1998 *Combustion Science and Technology* **136** 279-301
- [13] Greenspan D 1997 *Particle Modeling* (Boston, Birkhauser)
- [14] Greenspan D 1991 *Quasimolecular Modeling* (Singapore, World Scientific Publishing Company)
- [15] Svanberg, M, Ming, L, Markovic N and Pettersson J B C 1998 *J. Chem. Phys.*, Vol. **108** 5888-5897
- [16] Rapaport D C 1995 *The Art of Molecular Dynamics Simulation* (Cambridge, Cambridge University Press)
- [17] Andersen H C 1983 *J. Comp. Phys.* **52** 24-34
- [18] Rayleigh Lord 1878 *Proc. Lond. Math. Soc.* **10** 4-13
- [19] Mayer W, Telaar J, Branam R, Schneider G and Hussong J 2003 Scheduled for publication in *Int. J. of Heat and Mass Transfer*
- [20] Bird G A 1994 *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*, (Oxford, Clarendon Press)