

Molecular Dynamics Studies to Understand the Mechanism of Heat Accommodation in Homogeneous Condensing Flow of CO₂

Rakesh Kumar, Zheng Li, A.C.T. van Duin, D.A. Levin

Pennsylvania State University, University Park, PA 16802

Abstract. In the present work, we investigate the accuracy of the heat accommodation model, used in a meso-scale discrete particle BGK based condensation model for studying the homogeneous condensing flow of CO₂. It was found in those studies that the heat accommodation model played a key role in the numerical reproduction of the experiments. The major assumption made in such a heat accommodation model was the instantaneous release of heat of condensation to the gas particles in a cell. In the present work, we examine the veracity of the assumption used in the heat accommodation model, and understand the heat accommodation mechanism in general. To this end, we have used the atomistic molecular dynamics method to study the gas-cluster interactions from a fundamental standpoint. It is found that the time taken by gas-cluster interactions to establish an equilibrium from an initial state of non-equilibrium is less than the time step used in meso-scale analysis [1]. We also find that a dynamic equilibrium is established by the gas-cluster interactions in which condensation and evaporation constantly takes place to and from a cluster.

Keywords: Heat accommodation mechanism in condensation, Molecular dynamics, BGK condensation model

PACS: 05.20.Jj

INTRODUCTION

Condensation is an active area of research in many fields of science and engineering, such as meteorology, metallurgy, chemistry, mechanical and aerospace engineering. Even though the history of condensation studies can be traced back to the eighteenth century, a complete understanding of the phase change process is still missing from the molecular perspective [2]. Condensation is primarily of two kinds, viz., homogeneous and heterogeneous condensation. The conditions that lead to these two kinds of condensation are quite different. Heterogeneous condensation takes place when the gas particles find active condensation sites such as aerosols, dust etc. On the other hand, in homogeneous condensation, initial nuclei are created in a supersaturated state of the condensible gas, where the condensible gas pressure exceeds its saturated vapor pressure. In any case, whenever gas particles condense on a surface, a finite amount of heat of condensation is released, affecting the flow-field and plume radiation signatures of supersonic expansions to vacuum. Therefore an accurate model for the accommodation of the heat released is important in the numerical prediction of expanding condensing flows, which are widely encountered in the aerospace sciences.

In our recent work, we developed a condensation model in the statistical BGK framework [1]. The work involved the development of a comprehensive BGK based condensation model taking into account the processes of nucleation, cluster-monomer sticking and non-sticking collisions, cluster-cluster coalescence, and evaporation. We verified the accuracy of the condensation model against the experimental data of Ramos *et al.* [3] for a freely expanding homogeneous condensation flow of CO₂ at stagnation pressures in the range of 1-5 bar and at a stagnation temperature of 294 K. The BGK condensation model was found to be in good agreement with the experimental data, but, it was observed that the simulation results were highly sensitive to the mechanism of heat accommodation, particularly in the region of the flow close to the nozzle exit. Since condensing flows essentially involve heat addition (nucleation, cluster growth) or heat removal (evaporation) processes, this observation is not surprising and warrants the development of an accurate physical model. In our previous work [1], the heat accommodation model (described briefly in the next section) was validated for a non-condensing flow of nitrogen through a nozzle with heat addition at a station half way through the nozzle. However, when it comes to modeling of condensing flows, the heat accommodation mechanism is more complicated due to the interaction of cluster particles and the gas monomers. When the gas condenses onto a cluster in a cell, the heat of condensation is released, but, there lies an uncertainty as to how the released heat should be distributed into the two phases, gas and cluster. The heat accommodation model assumed that the release of heat to the gas particles in a cell, upon cluster formation was instantaneous, i.e., within a single time step (1 nanosec) used in the simulation. We carry out a more fundamental level investigation of the heat-accommodation mechanism in the present work in order to check the assumptions made in the heat accommodation model.

HEAT ACCOMMODATION MODEL

The heat accommodation model is primarily based on the fact that the addition of heat to a simple gas, i.e., a monoatomic gas, results in an increased thermal motion, as known from elementary gas dynamics [4]. If q is the amount of heat added to the gas particles per cell per time step, the thermal velocity of each gas particle in the cell is scaled up by a factor ϕ such that the final velocity component, u'_j , is given by

$$u'_j = \phi (u_j - U_j) + U_j \quad (1)$$

where j refers to the x, y or z component of velocity, U_j is the local flow velocity component in the j direction and ϕ is the heat accommodation factor [5] given by

$$\phi = \left[\left(\sum_{p=1}^N e_{tr,p} + q \right) / e_{tr,p} \right]^{0.5} \quad (2)$$

where $e_{tr,p}$ is the translational energy associated with the random thermal motion of a particle p .

Thus the effect of heat addition to a gas is to scale up the random velocities of gas particles by a factor that is determined by the ratio of heat added per cell per time step and the total random translational energy of all the particles belonging to the cell. In the case of a polyatomic gas, rotational and vibrational energies will also be agitated automatically due to the molecular interactions resulting in the transformation of translational energy to rotational and vibrational energies according to the respective relaxation rates. The heat accommodation model in the BGK framework was validated against an analytical solution for the supersonic expanding flow of a diatomic gas, nitrogen, through a nozzle with heat addition at the middle of the diverging part [1]. Remarkably good agreement was obtained between the results obtained by the heat accommodation model and the analytical solution.

The heat accommodation model shown above is applicable for non-condensing gas flows when a finite amount of heat is added to the gas by some source. However, our current subject of interest is to understand the mechanism of accommodation of the heat of condensation released when a gas monomer condenses onto a cluster particle. Here the heat accommodation mechanism gets more complicated due to the interaction of cluster particles with the gas monomers. Uncertainty lies in distributing the heat of condensation into the two phases, gas and cluster. In our previous work on the study of homogeneous condensing flow of CO₂ [1], we assumed that the released heat is adjusted among the gas particles in a cell in a single time step, 1 nanosec. It is worth noting that with this assumption, the equations shown above for the heat accommodation model are still valid for gas-cluster interactions with q as the cumulative amount of heat of condensation or evaporation in a cell per time step. We will examine this assumption using the MD method explained in the next section.

COMPUTATIONAL METHOD AND NUMERICAL PARAMETERS

Since we want to understand the heat accommodation mechanism from a microscopic standpoint, we choose to use an atomistic method such as molecular dynamics (MD) for the present work. MD method is a means of simulating molecular models of matter. The method was originated in 1950s, but started to get widespread attention in the mid 1970s with the advent of a dramatic increase in computational resources [6, 7]. It is a particle simulation method, in which a particle moves in a force-field exerted by the surrounding particles. The method is deterministic from the point of view of both particle movement and collisions, where a collision is defined as a change in the straight-line trajectory due to the influence of other particles. In contrast to MD, the DSMC and BGK methods are deterministic only in particle movement while probabilistic in calculating the collisions. However, MD is a very expensive method, and is therefore only amenable for use in limited cases. Currently MD is being used in several areas of science and engineering such as the study of liquids, clusters, surface chemistry, crystal defects, biomolecules and drug design.

In essence, the molecular dynamics method is a numerical way of solving the classical equations of motion for a system of N molecules interacting with each other through an intermolecular potential, V . In a simple form, the equations of motion for a system of atoms can be written as follows,

$$m_i \cdot \ddot{r}_i = f_i \quad (3)$$

where m_i is the mass of an atom i and the force $f_i = -\nabla_{r_i} V$

Here, V represents the intermolecular potential between the molecules, modeling of which bears immense importance in a realistic MD analysis. In the present work, the working fluid is CO₂, which is a linear quadrupolar molecule. The model potential for CO₂ is taken from the work of Harris *et al.* [8], who proposed a simple site-based intermolecular potential model for CO₂, referred to as the elementary physical model (EPM2). The model is a summation of a

Lennard-Jones potential and a Coulomb potential with point charges centered at atom sites and has a quadrupolar moment of 4.3×10^{-26} esu that is quite close to the experimental value of 4.1×10^{-26} esu [8]. Harris *et al.* also validated the model potential for the liquid-vapor coexistence curve. Table-1 shows the atom-atom interaction parameters for the model potential with the $C - O$ bond length of 1.149 \AA [8], for a completely rigid molecule. In this table, ϵ and σ are the Lennard-Jones well depth and core diameter in the intermolecular potential, $V(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$, and q_c and q_o are the charges on the centers of the carbon and oxygen atoms respectively.

In general, the finite difference methods are used to solve the ordinary differential equations represented by Eq. 3. The key idea is to update the positions and velocities of particles using the current state of positions and velocities. In general the time step used in such methods is much smaller than the time taken by a molecule to traverse its own length [6]. A good algorithm is expected to allow a large time step while honoring the energy conservation law in an acceptable limit. Among all finite difference methods used in MD simulations, the Verlet algorithm is perhaps the most widely used integration algorithm mainly because it is simple in form and easy to program. The Verlet algorithm or method provides a solution of the Eq. 3 in the following simple form, as a function of positions $r(t)$, accelerations $a(t)$ and positions $r(t - \delta t)$ from the previous step.

$$r(t + \delta t) = 2r(t) - r(t - \delta t) + \delta t^2 a(t) \quad (4)$$

The Verlet algorithm is accurate to the order δt^4 and is known to have good energy conserving properties even with long time steps [6]. However it is easy to introduce some numerical imprecision, as quantities of very different magnitude are added in the algorithm. Also, worth mentioning is the fact that velocity is not among the variables in the method, and it is because of this reason that it is difficult to implement some of the recently developed molecular dynamics methods using the Verlet algorithm [6, 9]. For example, in the constant pressure MD method, the governing equations of motion essentially involve the velocities, and the Verlet method cannot handle such equations. Another example is the use of the velocity rescaling techniques employed in non-equilibrium MD calculations, also used in the present work, which is difficult to be implemented using the Verlet algorithm. It is because of these reasons that we employ the velocity Verlet algorithm to solve the equations of motion in the present work.

The velocity Verlet algorithm makes use of positions, velocities and accelerations at the same time t , and is given as follows:

$$r(t + \delta t) = r(t) + \delta t \cdot v(t) + \frac{1}{2} \delta t^2 a(t) \quad (5)$$

$$v(t + \delta t) = v(t) + \frac{1}{2} \delta t [a(t) + a(t + \delta t)] \quad (6)$$

The velocity Verlet algorithm is a simple, accurate and easy to implement algorithm that minimizes the round-off error. On top of that it allows the velocity rescaling technique to be used in the present work [9]. Next we discuss constraint mechanisms used to constrain some degrees of freedom in a polyatomic molecule.

As mentioned above, CO_2 is a linear molecule with stretchable interatomic bonds and bending motions. It has three vibrational frequencies, 667.3 cm^{-1} , 1340 cm^{-1} and 2350 cm^{-1} corresponding to the characteristic vibrational temperatures of 967.2 K , 1942.1 K and 3405.9 K respectively. As the operating temperature range in the present MD analysis is less than 200 K , it can be assumed that the bond stretching and bending modes are not activated in CO_2 molecules in the present work. Therefore, CO_2 bond lengths and bending are constrained in the present work. Initially we used a widely used method of undetermined multipliers [10] to constrain the bond lengths and bond bending. It was however found that for a linear molecule like CO_2 , the constraint matrix was singular with a zero determinant, thus disallowing this method to be used for governing the constraint dynamics of CO_2 .

Subsequently, we implemented an iterative technique of imposing the constraints, following the work of Andersen [9]. The constraint algorithm proposed by Andersen [9] is called as the RATTLE algorithm. It is a modified version of the SHAKE algorithm [10] and is compatible with the velocity Verlet time integration algorithm. Apart from the positional constraints, as done for the SHAKE algorithm, velocity constraints are also imposed in the RATTLE algorithm. It guarantees that at each time step, positions and velocities of the atoms in a molecule satisfy the internal constraints, i.e., atoms remain a fixed distance apart and there is no relative velocity between the atoms in a molecule. In the present work, we assumed a positional tolerance of 2×10^{-3} of the fixed bond length and a velocity tolerance defined by $\Delta r \cdot \Delta v \leq 2 \times 10^{-6}$. One advantage of using the Rattle constraint algorithm is that along with the velocity Verlet integration algorithm, it allows the use of the velocity rescaling technique described below.

The velocity rescaling technique is a simple way of constraining the kinetic temperature of a system. It works by scaling the velocities by the following factor [6] at every time step or after every fixed number of time steps.

$$\xi = \left[1 + \frac{\delta t}{t_T} \left(\frac{T}{\tau} - 1 \right) \right]^{1/2} \quad (7)$$

where T is the desired temperature, τ is the current temperature calculated from the current state of velocities of particles and t_T is a predefined time constant. The method is used extensively in the equilibration phase of MD

simulations and is also suggested to be the means of performing constant temperature molecular dynamics. In the present work, this method is used for carrying out the canonical NVT analysis by rescaling the velocities after every 25 time steps.

VALIDATION RESULTS FOR THE CONDENSATION MODEL IN STATISTICAL BGK FRAMEWORK

Before carrying out the MD analysis, we checked if the model potential reproduces the reported pair potential for CO₂ molecules. Figure 1 compares the CO₂ pair potential obtained by us using the EPM2 model [8] with EXP-6 spherical model potential obtained by Johnson *et al.* [11]. It is evident that the EPM2 model potential shows a reasonably good agreement with the Johnson's potential [11]. We carried out another verification test for the EPM2 model, as described later.

We now present and discuss the results obtained in the present MD analysis. It is intended in the analysis that the system mimics a volume element in the real fluid, i.e., the simulation box used in the MD method represents a cell used in the meso-scale BGK based analysis of the condensing flow of CO₂. The size of the cubical simulation box used is 70 Å and the number of particles chosen roughly correspond to the typical number density found in CO₂ condensation studies close to the nozzle exit [1]. To overcome the surface effects, periodic boundary conditions are used in which the cubic box is replicated throughout space to form an infinite lattice. Noteworthy is the fact that in the present work, temperature is derived from kinetic energy by following the kinetic theory assuming 5 degrees of freedom for a CO₂ molecule, i.e., 3 translational and 2 rotational.

The MD studies are carried out in three stages; in the first stage, we form a cluster from a number of CO₂ gas molecules positioned randomly in phase space. Velocities are randomly sampled for these molecules from Maxwellian distribution at the initial temperature varying from 175 K to 225 K. Non-equilibrium MD is then performed by scaling down the velocities of atoms so as to reduce their thermal motion so that cluster could be formed. The final temperature at which clusters are formed was chosen as 40 K. The time step used in this stage and in rest of the stages is chosen as 1 fs, and it was found that further reducing the time step did not alter the results. Figure 2(a) shows a snapshot taken at a time 200000 fs. It is clear that a cluster is formed out of the 16 gas molecules. Figure 2(b) shows the temperature and energy conservation profiles, which show that the system is equilibrated at the final temperature of 40 K.

In the second stage of the MD analysis, cluster temperature is raised to 145 K, and it is found that although at this temperature the molecules have more agitated motion, the cluster is still intact. Figure 3(a) shows the temperature and energy conservation profiles for the cluster at a temperature of 145 K. As part of the second stage analysis, another test was performed to check the accuracy of the chosen model potential [8] by rescaling the velocities of atoms belonging to the cluster to different levels of final temperature. It is found that if we keep increasing the velocities of the cluster particles, by enhanced velocity rescaling, the cluster eventually evaporates at a temperature of ~190 K. Figure 3(b) shows the total energy (summation of kinetic and potential energies for the set of monomers belonging to the cluster) profiles at different target temperatures of the cluster. It is found that the total energy increases to a value more than zero for 190 K target temperature, at which it is also seen that the cluster disintegrates into the gaseous state. It is worth mentioning that the numerically obtained value of 190 K agrees fairly well with the known value of sublimation temperature found in the literature, ~195 K.

In the third stage of the MD analysis, we carry out gas-cluster interaction studies. To this end, 4 gas molecules are chosen to interact with a cluster formed by 16 monomers. The initial cluster temperature is ~145 K as obtained in the second stage of the MD analysis. Four gas molecules are introduced into the simulation box positioned randomly in the phase space, with velocity sampled from the Maxwellian distribution at a temperature of 115 K. We attempt to find the time taken by the system to reach equilibrium from an initial state of disequilibrium, characterized by the difference in temperatures of gas and cluster phase. In order to show the process of equilibration, we determine the cluster and gas temperatures separately that required us to implement an algorithm to demarcate cluster from the other gas monomers. The algorithm is based on finding the number of neighbors within a sphere of pre-defined radius around a molecule, and choosing the maximum neighborhood value. The algorithm bears special importance since the system is in a dynamic equilibrium. Figure 4(a) shows how the cluster and gas temperatures reach equilibrium in a time of ~500000 fs. Figure shows averaged data over six numerical experiments on gas-cluster interaction. We can also calculate the half-life time associated with this equilibration process when the difference between the cluster and gas temperature is roughly half of the original one. From six of such numerical experiments, the half-life time is found to be ~225000 fs with an error bar of ±25000 fs. The same study was repeated for a cluster of size 24 interacting with 6 gas monomers at temperatures of 145 K and 115 K respectively. Figure 4(b) shows the gas and cluster temperature profiles for the interaction between 6 gas monomers and a cluster formed by 24 monomers. Again it is found that the half-life time of equilibration process is of the same order, i.e., ~225000 fs. Overall it can be observed that it takes ~0.5 ns for a cluster-gas system to get dynamically equilibrated. It is found that the system reaches a state of dynamic

equilibrium in which the condensation and evaporation processes occur simultaneously at the cluster surface.

CONCLUSIONS

Molecular dynamics method was used to study the heat accommodation mechanism from a fundamental standpoint. A particular objective of this study was to check the assumptions made in the heat accommodation model, which was used earlier in the statistical BGK based condensation studies of CO_2 [1]. It was found that the time constant associated with the gas-cluster equilibrium process from an initial state of non-equilibrium was roughly half of a nano second that is smaller than the time step (1 nanosec) used in the statistical BGK based analysis of condensing flow. It was also observed that there existed a dynamic equilibrium in which condensation and evaporation processes take place simultaneously to or from a cluster surface.

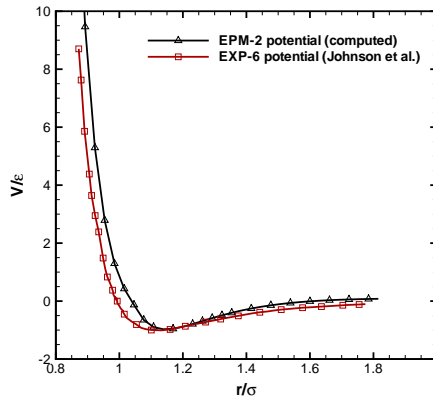


FIGURE 1. Normalized pair potential between two molecules, obtained by us using the EPM2 model, compared with the EXP-6 model potential of Ref. [11].

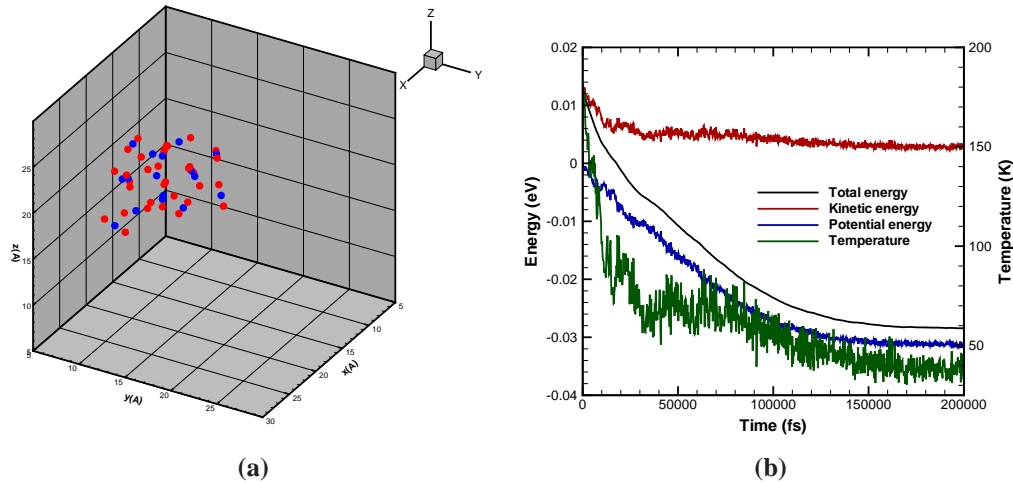


FIGURE 2. (a): Cluster formed at 40 K by velocity rescaling of the gas molecules; (b): Energy conservation and temperature profiles shown during the cluster formation process.

TABLE 1. Model Potential Parameters [8]

Parameter	Value (K)	Parameter	Value (\AA)	Parameter	Value (e)
ϵ_{c-c}	28.999	σ_{c-c}	2.757	q_c	0.6512
ϵ_{o-o}	80.507	σ_{o-o}	3.033	q_o	-0.3256
ϵ_{c-o}	47.588	σ_{c-o}	2.892	---	---

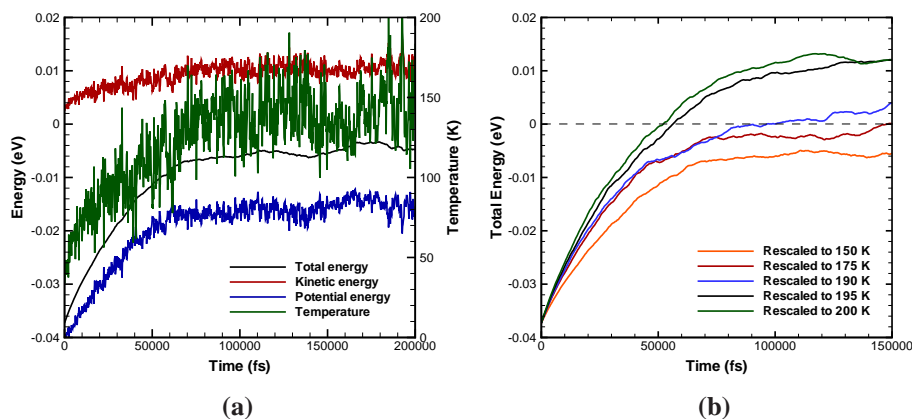


FIGURE 3. (a): Energy conservation and temperature profiles when cluster temperature is increased by scaling the velocities up to a temperature of 145 K; (b): Comparison of total energy profiles for a number of cases corresponding to the final target cluster temperature achieved by velocity rescaling.

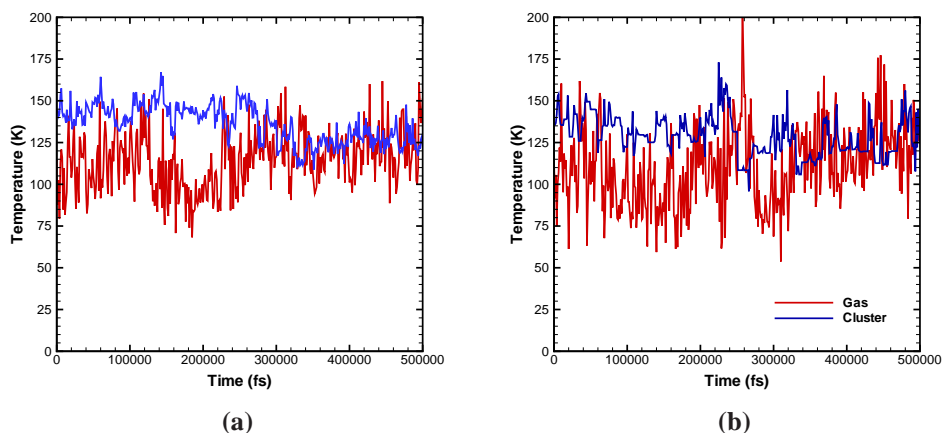


FIGURE 4. Temperature profiles for gas and cluster during equilibration process from an initial state of disequilibrium; (a): cluster of 16 monomers at 145 K interacting with 4 gas molecules at 115 K; (b): cluster of 24 monomers at 145 K interacting with 6 gas molecules at 115 K.

ACKNOWLEDGMENTS

The research performed at the Pennsylvania State University was supported by the Air Force Office of Scientific Research Grant No. F49620-02-1-0104 whose support is gratefully acknowledged. We thank Professor M. Ivanov of the Institute of Theoretical and Applied Mechanics, Russia for the use of the original SMILE code.

REFERENCES

1. R. Kumar, Z. Li, and D. Levin, *AIAA Paper 2010-818* (2010).
2. P. Wegener, and J. Parlange, *Naturwissenschaften* **57**, 525–533 (1970).
3. A. Ramos, J. M. Fernández, G. Tejeda, and S. Montero, *Physical Review A* **72**, 3204–3210 (2005).
4. W. Vincenty, and C. K. Jr., *Physical Gas Dynamics*, John Wiley and Sons, Inc., 1967.
5. C. R. Lilley, and M. N. Macrossan, *Physics of Fluids* **16**, 2054–2066 (2004), ISSN 1070-6631.
6. M. Allen, and D. Tildesley, *Computer Simulation of Liquids*, Ocford University Press Inc., New York, 1992.
7. J. Haile, *Molecular Dynamics Simulation : Elementary Methods*, Wiley Inc., New York, 1992.
8. J. Harris, and K. Yung, *Journal of Physical Chemistry* **99**, 12021–12024 (1995).
9. H. Andersen, *Journal of Computational Physics* **52**, 24–34 (1983).
10. J. Ryckaert, G. Ciccotti, and H. Berendsen, *Journal of Computational Physics* **23**, 327–341 (1977).
11. J. Johnson, and M. Shaw, *Journal of Chemical Physics* **83**, 1185 (1980).