Mat. Res. Soc. Symp. Proc. Vol. 731 © 2002 Materials Research Society

Direct Simulation Monte Carlo Calculation: Strategies for Using Complex Initial Conditions

Michael I. Zeifman[1], Barbara J. Garrison[1] and Leonid V. Zhigilei[2]
[1]Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802, USA
[2]Department of Material Science and Engineering, 116 Engineer's Way, University of Virginia, Charlottesville, Virginia 22904, USA

ABSTRACT

Modeling of phenomena is increasingly being used to obtain an understanding of important physical events as well as to predict properties that can be directly tied to experimental data. For systems with relatively low densities of particles, the Direct Simulation Monte Carlo (DSMC) method is well suited for modeling gases with non-equilibrium distributions, coupled gas-dynamic and reaction effects, emission and absorption of radiation. On the other hand, if the density of particles is large such as in dense gases or condensed matter, the DSMC method is not appropriate and techniques such as molecular dynamics (MD) simulations are employed. There are phenomena such as laser ablation, however, in which the system evolves from a condensed state appropriate to be studied with MD to an expanding rarified gas appropriate to be studied with DSMC.

The work presented here discusses the means of transferring information from a MD simulation of laser ablation to a DSMC simulation of the plume expansion. The presence of clusters in the MD output poses the main computational challenge. When the laser fluence is above the ablation threshold, the cluster size distribution is very broad (up to 10,'000's of particles per cluster) but there are relatively few of each cluster size. We have developed a method for statistical processing of the MD results and have represented the cluster size as a random variable. Various aspects of the coupling between the MD and DSMC models are discussed and several examples are presented.

INTRODUCTION

Both molecular dynamics (MD) simulation and direct simulation Monte Carlo (DSMC) are established techniques for modeling complex phenomena. The application domains of these two methods are traditionally different. The DSMC method is well suited for modeling gaseous systems, such as rarefied gas, low-ionized plasma, emission and absorption of radiation [1]. The MD method is more suitable for modeling systems with large density of particles, e.g., condensed matter or dense gas [2]. Recently, the MD and DSMC methods have been coupled to study laser ablation phenomenon, in which the system evolves from a condensed state appropriate to be studied with MD to an expanding rarified gas appropriate to be studied with DSMC [3]. In this hybrid model, the coupling between its MD and DSMC parts is of two kinds (i) through initial conditions and (ii) via reaction cross sections.

The MD breathing sphere model, used for simulation of the initial stage of the laser ablation process [4], provides coordinates, velocities, sizes and internal energies of the ejected particles. This information in statistical form is then transformed into the initial conditions of the DSMC model, used for simulation of a long-term expansion of the ejected plume. Separate MD

calculations provide the essential cross sections of interparticle interactions for the DSMC calculations. The characterization of the reaction cross sections is beyond the scope of the presented paper and will be reported elsewhere.

The composition of the ejected particles strongly depends on the laser fluence [5]. For low fluence (desorption regime), the main ejected species is molecules, and only molecular coordinates and velocities should be statistically characterized based on the results of the MD model. For high fluences (ablation regime), clusters of sizes up to tens thousand of molecules constitute major part of the plume mass, therefore, particle coordinates, velocities, internal energies and sizes must be characterized. The available number of clusters in a typical MD model output, however, is too small to permit straightforward statistical characterization of the MD results [3].

In this work, we extend further our approach described elsewhere [6]. We explain in detail the interconnection between the MD model and the DSMC model and present procedures of statistical characterization of the MD model results for desorption regime and ablation regime.

THE MD-DSMC CONNECTION

In the DSMC method, the entire physical volume of the flow is divided into cells with dimensions of about one mean free path [1]. Each cell is filled with simulation particles that are characterized by spatial coordinates, velocities, internal energy, mass, cross-sections and weight factor. The weight factor is the number of real particles that are represented by each simulation particle. The initial and boundary conditions, including particle mass and cross sections and cell-resolution spatial coordinates and distributions of internal and kinetic energy are chosen to correspond to those of the real system.

The basic principle of DSMC is that the continuous process of particle movement and interaction is uncoupled. First, at each time step every particle is moved according to its velocity. Next, the interaction between the particles is modeled by collisions. Collision pairs are selected at random within each cell and the probability of collision acceptance is calculated with regard to the relative velocity and the reaction cross section. Once accepted, the collision alters the particle velocities in elastic collisions and the internal energies in inelastic collisions. Reactions, other than two-particle interactions (e.g., three-body collisions and cluster decomposition [7]) can be incorporated in the interaction stage.

The typical area of a surface region simulated by the breathing sphere MD model is about 40x40 nm, while the range of particle heights above the target surface at the end of the MD calculation is on the order of 3,000 nm [8]. Figure 1 represents a typical snapshot from the MD model. Also shown is the typical size in the Z direction (the plume axis direction) of the initial cells in the following DSMC calculations. In this paper we will refer to the regions of the MD computational cell that match the corresponding DSMC cells, as “would-be cells.” The periodic boundary conditions used in the breathing sphere model imply uniform distributions of X and Y particle coordinates. If the laser fluence is uniform throughout the spot, the results of the single run of the MD model can be used as the initial conditions for the following DSMC calculations [3].

In our DSMC simulation the cylindrical volume surrounding the plume above the laser-ablated surface is divided into cells and filled with simulation particles, representing the real molecules or molecular clusters (see Figure 2). The characteristics of the simulation particles in a given DSMC cell at the beginning of the DSMC simulation are defined by the parameters of

molecules and clusters located in the corresponding region of the ablation plume obtained by the end of the MD simulation, as schematically shown in Figure 1. Below we describe two different

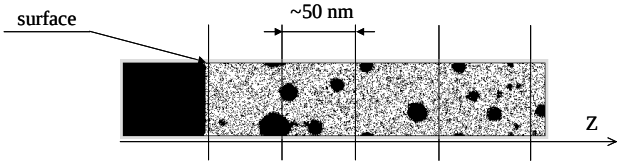

Figure 1. Typical snapshot from a MD simulation in the ablation regime. Vertical lines correspond to the cells in the following DSMC procedure.

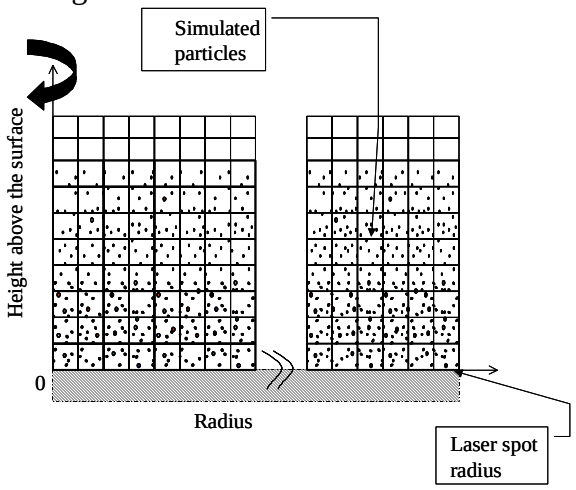

Figure 2. Initial cylindrical volume filled with the simulation particles. The grid lines correspond to the cell structure.

statistical procedures that we developed for making connection between the MD and DSMC simulations for two distinct regimes of laser-induced molecular ejection, desorption and ablation.

DESORPTION REGIME – RESAMPLING

The only ejected species in the desorption regime is molecules and there are about 75 molecules in a would-be cell at the end of the breathing sphere model calculations.[1] Therefore, if the analytical forms of distribution functions of velocities and coordinates are known, it is possible to estimate the corresponding parameters with good accuracy. For example, assuming a Boltzmann velocity distribution and uniform distribution of each coordinate in a cell, one has to estimate just two local parameters, flow velocity and temperature. The procedure of representing of simulation particles in the DSMC cells, therefore, would take the following form:

MD data in a cell → Analytical distribution models → Parameter estimations → Sampling from the reconstructed distributions (1)

It is possible, however, to do without analytical distribution functions by sampling variables directly from the MD data. Such resamplings, known as the Bootstrap procedure [9], is an established technique in statistics. The obvious advantage of this procedure is that no assumptions about specific analytical forms of the distribution functions need to be made. Another advantage is that the procedure will keep possible correlations between different parameters of the particles, e.g., molecular location and velocity.

[1] The size of each cell is defined by the local mean free path, which is inversely proportional to the local molecule concentration, therefore, proper cell structure involves the same number of molecules for cells.

To fill a DSMC cell with simulation particles, the number of simulation particles in each cell is calculated based on the number of particles in the corresponding would-be cell in the MD output, the cell volumes and the weight factor. Then a molecule from the would-be cell is chosen at random and its coordinates and velocities are assigned to the first simulation particle. The procedure is repeated until the calculated number of the simulation particles in the DSMC cell is reached. The limitation of such Bootstrap procedure is the minimum number of ten molecules in a would-be cell [9].

ABLATION REGIME – ANALYTICAL MODELS

However simple the Bootstrap procedure is, it cannot be applied to resample particles in the ablation regime. The main challenge of MD data processing in the ablation regime is that the available number of large clusters in would-be cells is too small to permit either the Bootstrap procedure or analytical estimations on the cell level. For example, in a typical output of the breathing sphere model there are on average only about two clusters in the size range from decamers to clusters of 14,000 molecules per a would-be cell [3] (see also Figure 1). In the following, we will concentrate on statistical characteristics of clusters in this size range, because smaller clusters are better represented in the MD data [6,8].

Since estimations on the cell level would be ineffective, the proposed estimation procedure uses the overall MD data. To derive cluster statistical properties in a cell, the spatial dependence of the properties must be characterized. Cluster properties to be statistically characterized include cluster size in molecules (N), internal energy (E), and velocity (V). As it was mentioned above, the periodic boundary conditions implemented in the breathing sphere model reduce the spatial dependence of particle properties to the dependence on height above the surface (coordinate z).

The first step in the estimation procedure is to check if there is statistical dependence among cluster properties, and between cluster properties and spatial location. Correlation analysis shows that the following groups of properties are mutually correlated: (i) cluster size – height above the surface, (ii) cluster internal energy – cluster size, and (iii) cluster velocity – height above the surface and cluster size. All other pairs of properties are found to be mutually independent.

The second step is to seek for a proper model of the dependence in question. One way to model the statistical dependence is to seek first for a functional dependence and then to characterize statistical variability around the functional dependence. Below we outline the proposed models.

Cluster size – height dependence

The dependence between cluster size and height is close to a linear regression in semilogarithmic coordinates [7]. Therefore,

$$\log(N) = a + b \cdot Z + \varepsilon \,. \tag{2}$$

Here, a and b are constants and ε is a random variable with zero expectation. Statistical analysis shows that ε can be characterized by a normal distribution with zero mean value and standard deviation σ. The three parameters of the cluster size distribution a, b, and σ can be accurately estimated by the available MD data (a typical total number of large clusters in MD output is about 60 [3]).

Cluster internal energy – size dependence

The actual dependence of cluster internal energy on cluster size significantly deviates from linear dependence [8], which could be expected in the case of thermal equilibrium in the initial plume. The functional dependence between *E* and *N* can be fitted, i.e., to a polynomial one. The statistical scatter of internal energy for a given cluster size can be characterized by a Gamma distribution [7]

$$f(E) = \frac{1}{\Gamma\left(\frac{6N-9}{2}\right) \cdot k_B T_{\text{int}}(N)} \left(\frac{E}{k_B T_{\text{int}}(N)} \right)^{\frac{6N-9}{2}-1} \exp\left(-\frac{E}{k_B T_{\text{int}}(N)} \right). \quad (3)$$

Here, *f* is the distribution function, Γ is the gamma function, k_B is the Boltzmann constant, and T_{int} is a size-dependent constant (typical internal temperature of a cluster of size *N*).

Cluster velocity dependence of height above the surface and size

This dependence is described theoretically with the aid of flow velocity and local translational temperatures [6,7,8]. The flow forms in the axial direction and at the end of the breathing sphere model calculations the flow velocity *u* is linearly proportional to the height above the surface

$$u(z) = \alpha \cdot z\,. \quad (4)$$

Here, α is a constant. The dependence of cluster translational temperature on the height above the surface is assumed to follow similar dependence of monomers [7,8]. The velocity distribution of clusters is then characterized by the Boltzmann-type distribution

$$f(v_x, v_y, v_z) \propto \exp\left(-\frac{mN[v_z - u(z)]^2}{2k_B T(z)} - \frac{mN[v_x^2 + v_y^2]}{2k_B T(z)} \right), \quad (5)$$

where *f* is the distribution function of velocity components, *T* is the translational temperature, *m* is the molecular mass, and *u* is the flow velocity, equation 4.

To fill a DSMC cell with simulation particles representing large clusters, the number of simulation particles in each cell is calculated based on the number of large clusters in the corresponding would-be cell in the MD output, the cell volumes and the weight factor. Then, a random cluster size is sampled from the distribution, equation 2, and is assigned to the first simulation large cluster in the cell. The internal energy and velocity for this simulation cluster are assigned by sampling from the corresponding distributions, equations 3-5, and the cluster position is chosen at random within the cell. The procedure is repeated until the calculated number of the simulation large clusters in the DSMC cell is reached. Note, that to fill the DSMC cells by simulation clusters, it is sufficient to define functions $T_{\text{int}}(N)$, equation 3, and $T(z)$, equation 5, numerically.

CONCLUSIONS

We have presented the methodology for statistical interconnection between MD breathing sphere model of the initial formation of a plume in laser ablation and DSMC model of the following plume expansion. When the laser fluence is below the ablation threshold, the main

ejected species is molecules and the proposed non-parametric scheme is suitable. When the laser fluence is above the ablation threshold, the main ejected species is molecular clusters in a broad size range. In this case a parametric scheme is proposed for estimation of the MD results and the following initiation of the DSMC calculations. The proposed methodology is applicable to systems, which evolve from a condensed state to an expanding gas, as in the laser ablation process and in explosion.

ACKNOWLEDGMENTS

This work was supported through the Medical Free Electron Laser Program of the Air Force Office of Scientific Research. The computational support was provided by IBM through the Selected University Research Program, and the Center for Academic Computing at Penn State University.

REFERENCES

1. G. A. Bird, "Molecular gas dynamics and the direct simulation of gas flows" (Clarendon Press, Oxford, 1994); J. Struckmeier, K. Steiner, *Phys. Fluids* **7**, 2876 (1995); S. Dietrich, I.D. Boyd, *J. Comput. Phys.* **126**, 328 (1996); S. Dunn, J.B. Anderson, *J. Chem. Phys.* **99**, 6607 (1993).
2. J. A. Poulsen and P. J. Rossky, *J. Chem. Phys*. **115**, 8024 (2001); M. P. Surh, T. W. Barbee, L. H. Yang, *Phys. Rev. Lett*. **86**, 5958 (2001).
3. M.I. Zeifman, B.J. Garrison, and L.V. Zhigilei, *Appl. Surf. Sci*., in press (2002).
4. L. V. Zhigilei, P. B. S. Kodali, and B. J. Garrison, *J. Phys. Chem.* B **101**, 2028 (1997); ibid., **102**, 2845 (1998).
5. L. V. Zhigilei and B. J. Garrison, *J. Appl. Phys*. **88**, 1281 (2000).
6. L.V. Zhigilei, *Mat. Res. Soc. Symp. Proc*. **677**, AA2.1.1 (2001).
7. M.I. Zeifman, B.J. Garrison, and L.V. Zhigilei, submitted to *J. Appl. Phys.*
8. L. V. Zhigilei, *Appl. Phys. A*, in press (2002).
9. B. Efron, *J. Am. Stat. Assoc*. **85**, 79 (1990).