Molecular Dynamics with Molecular Temperature

Denis J. Phares* and Arun R. Srinivasa

Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843-3123

Received: December 17, 2003; In Final Form: May 18, 2004

The difficulty in simulating a large number of large molecules lies in the enormous difference in time scale between translational and intramolecular motions. If a molecular dynamics simulation is to model an event of microsecond duration, a computation time step on the order of a femtosecond is still required, making the simulation virtually impossible. One approach is to ignore intramolecular interactions (i.e., a hard spheres or rigid molecule model; see, for example, Chushak, Y. G.; Bartell, L. S. *J. Phys. Chem. B* **1999**, *103*, 11196), which may be adequate if the energy stored inside a molecule is unaltered. This excludes a number of important applications, such as MALDI and laser desorption/ionization of organic particles, which are based on the ability of molecules to absorb energy. Another approach is to combine all molecular motions into a single degree of freedom with a time scale that is chosen based on the phonon spectrum of the particle (Zhigilei, L. V.; Kodali, P. B. S.; Garrison, B. J. *J. Phys. Chem. B* **1997**, *101*, 2028). This approach has been used to model MALDI (Zhigilei, L. V.; Yingling, Y. G.; Itina, T. E.; Schoolcraft, T. A.; Garrison, B. J. *Int. J. Mass Spectrom.* **2003**, *226*, 85) and laser ablation of nanosized (Zhigilei, L. V.; Garrison, B. J. *Appl. Surf. Sci.* **1998**, *129*, 142) and micrometer-sized (Schoolcraft, T. A.; Constable, G. S.; Zhigilei, L. V.; Garrison, B. J. *Anal. Chem.* **2000**, *72*, 5143) particles, although the incorporation of chemical reactions is quite challenging in this approach due to the difficulty in enforcing energy conservation. We propose an alternative molecular dynamics model (based on the notion of dissipative particle dynamics with energy conservation, developed by Avalos and Mackie; see, Avalos, J. B.; Mackie, A. D. *J. Chem. Phys.* **1999**, *111*, 5267; Avalos, J. B.; Mackie, A. D *Europhys. Lett.* **1997**, *40*, 141) that uses concepts of statistical mechanics and thermodynamics of irreversible processes to describe the intramolecular energy. This is manifested in the definition of an internal molecular temperature, which describes the stored energy and governs the energy transfer into and out of the molecule. This model allows for the incorporation of some quantum statistical phenomena of the internal interactions and satisfies irreversibility of collision processes, while remaining computationally inexpensive. In this approach, criteria for chemical reactions to take place can be easily stated in terms of internal molecular temperatures and proximity of approach. Also energy conservation can be implemented in a computationally efficient manner. We apply the model to the laser ablation of chlorobenzene nanoparticles, a system similar to that studied by Yingling et al. (Yingling, Y. G.; Zhigilei, L. V.; Garrison, B. J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *180*, 171).

I. Introduction

Consider a particle comprised of N molecules of a condensed organic compound subjected to a laser pulse of known frequency, intensity, and duration. The interaction of the photons with the molecules may cause ablation, disintegration of the individual molecules, and recombination to create new compounds. One of the standard techniques for dealing with the simulation of such events is molecular dynamics, wherein the entire set of atoms composing all the molecules is treated as a set of points (or spheres) that interact with each other. If we assume that these atoms obey the laws of classical mechanics, the equations of motion can be derived via Lagrangian mechanics, wherein the coordinates of the particles are treated as generalized coordinates.

For particles made up of large molecules (with a number of constituent atoms), simulation of each individual atom is almost impossible because the interactions between the atoms that make up the molecule are substantially different from those between the molecules. Typically, the latter are very weak for nonpolar organic molecules, whereas the intramolecular forces are very strong. Thus, even if it were possible, the fastest time scale of interest (which controls the time-stepping scheme in the simulations) is associated with the natural frequency of the intramolecular interactions and is typically on the order of a few femtoseconds, whereas the simulation time is on the order of microseconds. This means that the computation time would become prohibitively large. Moreover, the intramolecular interactions cannot be fully described by classical mechanics. One must instead use a quantum mechanical formulation to deal with them. Apart from the near impossibility of solving the Schrödinger equation for a large organic molecule, a single particle may contain as many as 10^6 molecules making the task virtually impossible. Molecular dynamics simulation of the individual atoms is also complicated by the interaction with the photons and subsequent fragmentation.

Because of all these difficulties and the fact that we are primarily interested in a statistical description of the properties of the fragments (such as the yield of the different species as a function of time, the velocity distributions, etc.), it is sufficient to develop an *approximate* method to simulate the photofragmentation of such particles, ignoring the details of molecular structure.

10.1021/jp037910y CCC: $27.50

Garrison and co-workers in a series of papers[2−5,8−10] have pioneered this approach, using a "breathing spheres" molecular dynamics model to account for the internal degrees of freedom of a molecule. In this model, the internal degrees of freedom of the molecules are modeled by attributing a single vibrational degree of freedom to each molecule so that the molecule expands and contracts. In this model, the incoming laser pulse simply increases the amplitude of the oscillations. The interaction between the internal degrees of freedom and the translational modes of the molecule is treated by assuming that the interaction potentials explicitly depend on the internal degree of freedom. The model was used to gain a great deal of qualitative insight into such processes as MALDI[3] and particle laser ablation.[4,5] Some comparison with experiment was also presented concerning stress distributions in a solid upon laser irradiation and the threshold laser fluence for ablation of solid surfaces. An important drawback to the model, which may make further quantitative comparison tenuous, is that the vibrational and rotational modes of the molecule are "lumped" into a single degree of freedom that is treated within the context of classical mechanics. Quantum effects are thus completely ignored.

In this paper, we propose an alternative approach that allows for treatment of intramolecular quantum effects, while still preserving computational feasibility. This approach shares a number of features in common with the breathing spheres model such as (1) the intramolecular degrees of freedom are accounted for in an approximate way by means of a single scalar variable, (2) the governing equations are modified to account for the interaction between the intramolecular and translational degrees of freedom, and (3) the absorption of photons and subsequent splitting are treated as chemical reactions or "collision processes" so that the details of the interaction are not modeled. Rather, a simple "before and after" description is used. However, the manner in which the intramolecular degrees of freedom are accounted for and the nature of the interactions are quite different in the present approach. Instead of using a single intramolecular degree of freedom and a suitably modified Lagrangian to account for the interactions between the various degrees of freedom, we utilize the notion of a "molecular temperature" to characterize the energy distribution due to the intramolecular degrees of freedom (see Avalos and Mackie[6,7]). However, the quantization of the internal modes is not ignored since it is crucial to the ability of the molecule to absorb the incident photons. The procedure to be adopted for the analysis is based on the notion of *collective motion* of dynamical systems. In other words *we find equations that represent the evolution of quantities that represent meaningful averages of internal states of the system.* We shall present here a physical argument based on the idea that the motion of a large collection of interacting molecules (such as that considered in a typical molecular dynamics simulation) can be considered as a superposition of two motions, one that occurs on a time scale that is much larger than that associated with the intramolecular motions, and another on much a faster time scale representing the internal motions of the individual molecules.

Consider the Hamiltonian dynamics of a particle consisting of N molecules (where N is a very large number) each of which contains n atoms. Due to the vast differences in the strength of the intra- and intermolecular forces, the Hamiltonian is highly oscillatory in nature so that it is impossible to simulate the actual dynamics of the $N\times n$ atoms for durations larger than a few nanoseconds (see, for example, Reich[11]). However, since the primary quantities of interest are related to the correlated motion of the molecules that occurs over time scales on the order of microseconds, additional variables are introduced that represent the collective motion. These variables represent a small submanifold in phase space of lower dimensionality (N) corresponding to the predominant, observable degrees of freedom of the body. The generalized coordinates and momenta associated with this subset are given as q_i ($i = 1,N$). These represent the "macrostates of the system". For the case of the organic particle in question, the collective motion is represented by the positions and momenta of the center of mass of the molecules. Now, we consider the set of all possible configurations of the system and classify them into cells, according to the value of these generalized coordinates. The configurations inside the cell represent the "microstates" of the system. For each macrostate, a partition function is calculated, according to the probability distribution of these states. Several precise results regarding the nature of the average response can be obtained based on certain assumptions regarding the ergodicity of the "fast" internal variables,[12,13] i.e., the variables describing the "microstates" of the body.

Variations of such state space reduction techniques, usually referred to as "collective variable theory",[14] have been successfully adopted to deal with a wide range of phenomena, including the transmission of pulses in nonlinear optics and lasers,[15] the study of solitons,[16] and the study of vortices and domain walls in condensed matter systems.[17] The connection with statistical mechanics is obvious. Hence, we can utilize the ideas of statistical mechanics to describe the energy distribution associated with the intramolecular motions by means of a single "molecular temperature" θ_i. Thus, in this model, there are two temperatures. The first is the bulk temperature, θ_T, which represents the mean translational kinetic energy of the molecules

$$\theta_T = \frac{1}{3Nk}\sum_{i=1}^{N} m_i(\mathbf{v}_i - \bar{\mathbf{v}})\cdot(\mathbf{v}_i - \bar{\mathbf{v}}) \qquad (1)$$

where N is the total number of molecules in the particle, k is Boltzmann's constant, $\mathbf{v}_i$ is the velocity of the center of mass of the ith molecule and $\bar{\mathbf{v}}$ ($=1/m_{\text{total}} \sum_{i=1}^{N} m_i\mathbf{v}_i$) is the velocity of the center of mass of the particle. The second is the molecular temperature, θ_i, which represents the energy distribution of the intramolecular degrees of freedom.

II. The Molecular Temperature Model

The basic idea behind this scheme is that, unlike the translation degrees of freedom r_i of the molecules, the internal degrees of freedom are treated in a statistical sense based on the ergodicity of the motion of the fast variables. Thus, when calculating the internal vibrational and rotational modes of a molecule, we assume that the molecule is isolated and that the center of mass of the molecule is stationary. This is a reasonable approximation since the internal modes undergo many cycles of oscillation on the time scale associated with the simulation. Such quantum mechanical calculations of the energy levels associated with a molecule are readily available. For example if one considers a simple diatomic molecule such as HCl in contact with a thermal reservoir, the energy of the molecule in its normal electronic state is given in terms of the vibrational and rotational quantum numbers as[18]

$$W(\upsilon,K) = (\upsilon + 1/2)h\nu + K(K+1)\frac{h^2}{8\pi^2 I} \qquad (2)$$

where υ is the vibrational quantum number, K is the rotational quantum number, ν is the vibrational frequency, I is the moment of inertia of the molecule (both of which depend on the nature of molecule and the interaction forces), and h is Planck's constant. Now, over a time scale that is much larger than the time scale associated with the vibrational modes of HCl, we assume that the molecule occupies all the quantum states that are available due to its interaction with the thermal reservoir. Thus, the probability of finding the molecule in any particular quantum state is given by Boltzmann statistics as

$$P(\upsilon,K,\theta) = P(\upsilon,\theta)P(K,\theta) = (B\,\mathrm{e}^{-((\upsilon+1/2)h\nu)/(k\theta)})(C\,\mathrm{e}^{-(K(K+1)h^2)/(8\pi^2 Ik\theta)}) \quad (3)$$

where B and C are normalization constants and θ is the molecular temperature. The average energy of the internal modes of the molecule is then simply a function of the molecular temperature and is given by

$$f(\theta) = \sum_{\upsilon=0}^{\infty}\sum_{K=0}^{\infty} W(\upsilon,K)P(\upsilon,K,\theta) \quad (4)$$

For complex molecules, we can simplify eq 4 using Boltzmann statistics to give

$$\langle\epsilon\rangle = \int \rho(\epsilon)\,\mathrm{e}^{-\epsilon}/k\theta\,\mathrm{d}\epsilon = f(\theta) \quad (5)$$

assuming that the energy density of states, $\rho(\epsilon)$, is known.[19] Using this process, we can define the internal temperature, θ_i, of the ith molecule. If the temperatures are high, then eq 3 can be replaced with its high-temperature equipartition value, i.e.,

$$f(\theta_i) = \left(3n_i - \frac{9}{2}\right)k\theta_i = C_i\theta_i \quad (6)$$

where n_i is the total number of atoms in the ith molecule, $C_i = (3n_i - 4.5)k$ is the *heat capacity* of the molecule, and k is the Boltzmann constant. Equation 6 comes from a simple counting procedure assuming that each rotation degree of freedom contributes $^1/_2(k\theta_i)$ and that each vibrational degree of freedom contributes $k\theta_i$ to the total internal energy. Of course, the equipartition assumption is not accurate for the vibration of very stiff bonds unless the temperature is high enough. In this case, either one needs to calculate the internal energy−temperature relation from statistical mechanics for the energy levels or one can assume that the higher frequencies are "frozen" (so that the heat capacity is lower) until a critical temperature is reached (similar to the approach used for low-temperature heat capacity calculations for polyatomic molecules[20]). Thus, for HCl, we could count only the rotational degrees of freedom in the calculation for the heat capacity, adding the extra term due to the vibrational degrees of freedom at a higher temperature.

II.1. Interaction Forces between the Molecules and the Evolution of the State of the Particle. We now turn our attention to the evolution of the state of the system, i.e., the equations that govern the way in which the positions and momenta of the individual particles, as well as the molecular temperature, evolve with time. In order to derive these equations, we identify four types of interactions: (1) interactions between the center of masses of the individual molecules, (2) interactions between the molecules and external fields, such as applied electromagnetic fields, (3) interactions between the internal degrees of freedom of the molecules, and (4) interactions between the internal degrees of freedom of a molecule with the translational modes of another molecule. These interactions take place over the space and time scales of the translational motion. In addition to these are the various photon absorption and fragmentation processes that occur on time scales that are much smaller than that associated with the translational motions of the molecules. We will now discuss each of these in turn.

II.1.a. Interactions between the Centers of Mass of the Molecules. We model these interactions by a standard Lennard-Jones interaction potential between the ith and the jth particle of the form

$$V_{ij}(\boldsymbol{r}_{ij}) = \epsilon_0\left(\frac{r_0^{\ 12}}{||\boldsymbol{r}_{ij}||^{12}} - \frac{r_0^{\ 6}}{||\boldsymbol{r}_{ij}||^{6}}\right) \quad (7)$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, and ϵ_0 and r_0 are the Lennard-Jones energy and radius, respectively. Since several different types of molecules are created, the interaction potentials for these different species are required. Lennard-Jones parameters are listed for several common organic compounds (see ref 21). It has been observed that these parameters depend on the number of electrons in the outer shells which in turn depend on the molecular weight, M_w, of the compounds (see Pauling[22]). Thus simple regression relations ($r_0 = 366.84 - 343.31\exp(-0.0299M_w)$ (in angstroms) and $\epsilon_0 = (3.409 + 0.0322M_w)k\theta_0$) are used to estimate the Lennard-Jones parameters for the various products of photofragmentation. For interactions between two dissimilar molecules, the Lennard-Jones parameters are taken as the average of those for each molecule. No external electrostatic field was considered for the cases simulated here.

II.1.b. Evolution of the Translational Modes of One Molecule Due to Internal Modes of Molecules in the Vicinity. We model the energy transfer between the internal modes of one molecule and the translational modes of those in the vicinity in such a way as to drive the molecular temperature to become equal to the translational temperature so that the body achieves thermal equilibrium. In order to accomplish this, we introduce a *velocity-dependent interaction force*. The introduction of such a force is motivated by the use of a *thermostat control*[23] for modeling isothermal systems that interact with a heat bath (see eqs 5−9 in ref 24 for a comparison between two different thermostat controls). In such molecular dynamics algorithms, the interaction with a heat bath is modeled by a velocity-dependent force that depends on the history of the temperature. This may be viewed as a nonlocal control algorithm to maintain a constant temperature. For example, consider a system of N molecules that is maintained at a constant temperature with a Gaussian thermostatic control. The equations of motion for such a system are given by

$$\frac{\mathrm{d}}{\mathrm{d}t}(m_i\mathbf{v}_i) = -\frac{\partial V}{\partial \mathbf{r}_i} - \left(\frac{-\sum_{j=1}^{N}\frac{\partial V}{\partial \mathbf{r}_j}\cdot\mathbf{v}_j}{3k\theta}\right)(m_i\mathbf{v}_i), \quad i = 1, ..., N \quad (8)$$

where V is the total potential energy of the system. Such a system maintains the total kinetic energy at a constant value of $3Nk\theta$.

Here, following the procedure outlined in refs 6 and 7, we consider the molecule to be in a thermal bath provided by the surrounding molecules so that the interaction force (1) is appreciable only when then molecules approach within a certain interaction distance, (2) leaves invariant the linear and angular momentum of the particle and is in the form of a pairwise central force, and (3) results in a net energy transfer *to* the translational modes when the internal temperatures of the interacting molecules is higher than the translational temperature and vice versa. To satisfy these conditions, and motivated by the form of eq 8 for the Gaussian thermostat and by the form of eq 7 for the interaction potential, we stipulate that this interaction force is given by

$$\mathbf{F}_{ij} = -\eta(2\theta_{\mathrm{T}} - \theta_i - \theta_j)(\mathbf{r}_{ij})\cdot(\mathbf{v}_i - \mathbf{v}_j)\frac{\mathbf{r}_{ij}}{||\mathbf{r}_{ij}||^6} \tag{9}$$

The above pairwise central force is Galilean invariant, and it can be shown that (1) there is no change in the total linear and angular momentum of the particle, (2) the force vanishes whenever the temperature of the particle is equal to the molecular temperatures of the interacting molecules, (3) there is a net loss of energy of the translational modes if the translational temperature is higher than that of the interacting molecules, and (4) there is a net gain of energy of the translational modes if the translational temperature is lower than that of the interacting molecules.

Here, the control depends on the instantaneous internal temperature of the molecules, and hence it is nonlocal in space. Also the force constantly fluctuates due to the fluctuating velocity and temperatures of the particles. The approach is analogous to that considered in dissipative particle dynamics (DPD) for the simulation of suspensions, wherein the particles are assumed to move through a fluid that exerts a velocity-dependent stochastic force on them.[25] Since there is no fluid in this case, we depart from the use of a stochastic forcing function used in DPD but obtain a similar effect from the fluctuating states of the neighboring molecules. This is fully in keeping with the notion that each molecule is like a thermodynamic system that is interacting with the “heat bath” provided by the surrounding molecules (i.e., a grand canonical ensemble) (see ref 7).

With these assumptions, Newton’s laws for the translational degrees of freedom become

$$\overbrace{m_i\ddot{\mathbf{r}}_i}^{\text{Rate of change of momentum}} = -\overbrace{\sum_{j=1,j\neq i}^{N}\frac{\partial V_{ij}}{\partial \mathbf{r}_i}}^{\text{Lennard-Jones}} + \overbrace{\sum_{j=1,j\neq i}^{N}\mathbf{F}_{ij}}^{\text{Interaction force due to internal motion of other molecules}} \tag{10}$$

where F_{ij} is the velocity- and temperature-dependent dissipative force defined by eq 9.

This velocity-dependent force only comes into play between molecules that are close together (since it decays with distance), and its direction depends on the sign of

$$\eta(2\theta_{\mathrm{T}} - \theta_i - \theta_j)(\mathbf{r}_{ij})\cdot(\mathbf{v}_i - \mathbf{v}_j) = \frac{\eta}{2}(2\theta_{\mathrm{T}} - \theta_i - \theta_j)\frac{\mathrm{d}||\mathbf{r}_{ij}||^2}{\mathrm{d}t} \tag{11}$$

For example, if the average internal temperature of the two interacting molecules is *less* than the macroscopic particle temperature and the distance between the molecules is *increasing*, then the force between the molecules is *attractive*. This will tend to reduce the relative velocity between the molecules and hence decrease the particle temperature defined by eq 1. The loss of kinetic energy in turn will cause the internal energy of the molecule to increase thus increasing the internal temperatures. Thus there will be a net transfer of energy from the translational mode to the internal modes of the molecules.

II.1.c. Evolution of the Internal Modes of One Molecule Due to the Translational and Internal Modes of Molecules in the Vicinity. It is here that we depart from the approach of dissipative particle dynamics with energy conservation, as presented by Avalos and Mackie.[6,7] In those studies, the fluctuating force for the translational degrees of freedom arises from the surrounding fluid bath. Here, there is no fluid bath, so the fluctuating force must be supplied by the internal modes in such a way that the total energy is conserved. To conserve energy, the rate at which energy is lost by the translational modes must equal the rate at which energy is transferred to the internal modes. There will also be energy exchange between the internal modes of the molecules. The driving force for this latter exchange is the difference between the internal temperatures of the interacting molecules. We assume that the rate of change of the internal energy of one molecule due to its interaction with the internal degrees of freedom of the other molecules is proportional to all of the differences in molecular temperature taken pairwise, i.e.,

$$\text{Rate of energy increase due to interaction} = \sum_{j=1}^{N}\frac{\mu(\theta_j - \theta_i)}{||\mathbf{r}_{ij}||^{\alpha}} \tag{12}$$

where μ is a coefficient analogous to a heat conduction coefficient and $\alpha = 6$. The value of α is chosen since we expect the interaction between the internal degrees of freedom to decrease at the same rate as that due to the Lennard-Jones potentials. Note that, due to the form of this interaction term, there is no net gain or loss of internal energy due to these interactions but merely an irreversible redistribution. This irreversibility is the counterpart of the irreversibility associated with the heat conduction across a temperature difference. The rate of change of molecular temperature is thus given by

$$\frac{df}{d\theta_i}\dot{\theta}_i = \sum_{j=1,j\neq i}^{N}\left\{\frac{\overbrace{\mu(\theta_j-\theta_i)}^{\text{"heat" transfer between internal modes}}}{\|\mathbf{r}_{ij}\|^6} - \overbrace{\mathbf{F}_{ij}\bullet(\mathbf{v}_i-\mathbf{v}_j)}^{\text{rate of energy loss from translational modes}}\right\} \tag{13}$$

The first term inside the summation on the right-hand side of the above equation is the counterpart of the classical heat conduction equation and represents the direct energy transfer between the internal degrees of freedom of the molecules due to the difference in temperature. The constant μ is the counterpart of the conductivity. The second term on the right-hand side represents the energy transfer from the translational degrees of freedom due to the difference between the molecular and translational temperatures. The term $\mathrm{d}f_i/\mathrm{d}\theta_i$ is the “heat capacity” of the ith molecule.

Equations 10 and 13 are the governing differential equations for the evolution of the state of the particle when no photofragmentation processes occur. It can be demonstrated that the above set of equations conserves the total linear and angular momentum of the particle as well as the total energy of the particle.

II.2. Photofragmentation Processes. So far, we have only considered processes that conserve the total energy of the system. We now consider processes where energy may be absorbed or released,[28] as required for modeling photofragmentation and chemical reaction. We consider three fundamental types of processes: (a) absorption of a photon by a molecule,

(b) fragmentation of a molecule, and (c) recombination of two molecules to form a new molecule. Every chemical reaction between molecules will be considered as a suitable combination of (b) and (c).

II.2.a. Absorption of Photons. Let us assume that the system is exposed to a laser pulse with frequency ν, uniform fluence, and of finite duration. When the photons pass though the particle a certain number of them are absorbed by the molecules. Whether or not a photon is absorbed by a molecule depends on the current quantum state of the molecule and its relationship to the energy of the photon. To elaborate, a photon can be absorbed if and only if the absorption will allow molecule to jump to a different quantum state, i.e., if and only if

$$h\nu = \Delta E \tag{14}$$

where ΔE is an allowable jump in the energy level. The above condition implies that only certain frequencies can be absorbed by a given type of molecule.

Following Yingling et al.,[9] we model the absorption of a photon by depositing a quantum $h\nu$ of energy to the internal modes of the absorbing molecule, i.e,

$$A + h\nu \rightarrow A^*$$

In our model, this results in a rise in its internal temperature. If the absorption is very rapid, then we can assume "adiabatic" conditions and we calculate the jump in the molecular temperature as

$$\left(\frac{\partial f_i}{\partial \theta_i}\right)\Delta\theta_i = h\nu \tag{15}$$

This energy will be gradually distributed to the other molecules through the "thermal" and mechanical interactions between the molecules.

II.2.b. Fragmentation. The fragmentation process is modeled as a chemical reaction of the form

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} + \Delta E \tag{16}$$

where ΔE is the internal energy released due to the breaking of the bonds. In order to model this event, we need to consider two issues. First, when does such an event occur? And second, what are the positions, velocities, and internal temperatures of the product molecules, given those of the parent molecules and the bond energies?

Considering the first issue, we assume that a reaction of the type 16 occurs only if the parent molecule A has sufficient internal energy to overcome the energy barrier to splitting. We stipulate that such an event can occur if its internal temperature, θ_i, is greater than a critical value, θ^*, for a sufficiently long time. This latter condition implies that fragmentation can occur only if other molecules are sufficiently far away (at least one Lennard-Jones radius) so that the molecule is isolated and the high temperatures can be maintained. We assume that when these two conditions are met, fragmentation can occur.

Once fragmentation occurs, the states of the products are assigned as follows: (1) the products are separated by a distance of one Lennard-Jones radius (of the parent) of each other in a random direction, (2) the distance between the location of a product and that of the parent molecule is inversely proportional to the mass of the product, (3) the velocity of the products is the same as that of the parent (so that linear and angular momenta and kinetic energy are conserved by the reaction), and (4) the final temperatures of the products are equal and given by

$$\theta_{\mathrm{B}} = \theta_{\mathrm{C}} = \frac{C_{\mathrm{A}}\theta_{\mathrm{A}} + \Delta E - \Delta U}{C_{\mathrm{B}} + C_{\mathrm{C}}} \tag{17}$$

where $\theta_{\mathrm{A,B,C}}$ are the internal temperatures of the reactants, $C_{\mathrm{A,B,C}}$ are the heat capacities of the molecules, and ΔU is the increase in the interaction energy due to the disappearance of the molecule A and the appearance of the molecules B and C at new locations. This last correction is essential to maintain energy conservation in the sense that the increase in total energy due to this reaction must exactly equal the release of bond energy.

II.2.c. Recombination. For a recombination reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \Delta E \tag{18}$$

to occur, we require that (1) the reactants A and B are sufficiently close to one another, (2) the particles have sufficient internal energy for the bond formation, and (3) they are in the right orientation for the reaction to occur. We model the first two conditions by stipulating that a recombination occurs if the distance between the reactants is less than their Lennard-Jones radius and that their internal temperatures are higher than a critical value. For simplicity, we do not enforce condition 3 in the present study. In future work, condition 3 may be implemented by using Boltzmann statistics and an accurate description of the energy levels associated with the rotational degrees of freedom of the system.

For this case, we assume that the product is located along the line joining the reactant molecules and its velocity is given by momentum conservation as

$$\dot{\mathbf{r}}_{\mathrm{C}} = \frac{m_{\mathrm{A}}\dot{\mathbf{r}}_{\mathrm{A}} + m_{\mathrm{B}}\dot{\mathbf{r}}_{\mathrm{B}}}{m_{\mathrm{C}}} \tag{19}$$

Again the temperature of the product is given by energy conservation as

$$\theta_{\mathrm{C}} = \frac{C_{\mathrm{A}}\theta_{\mathrm{A}} + C_{\mathrm{B}}\theta_{\mathrm{B}} + \Delta E - (\Delta U + \Delta \mathrm{KE})}{C_{\mathrm{C}}} \tag{20}$$

Unlike eq 17, there is also a change in the kinetic energy of the system due to "inelastic" impact of the two reactants.

III. Example System and Computational Techniques

To illustrate the procedure, a particle initially composed of 20 000 chorobenzene (C_6H_5Cl) molecules irradiated by a 193 nm laser pulse was chosen. Yingling et al.[9] also used a chlorobenzene system, and so some qualitative comparisons can be made. The particle is placed in a large square box with perfectly reflecting sides. When the particle is irradiated by a laser, the following reactions are considered:[9]

$$\begin{gathered}
\mathrm{C_6H_5Cl} + h\nu \rightarrow \mathrm{C_6H_5Cl^*} \\
\mathrm{C_6H_5Cl} \rightarrow \mathrm{C_6H_5\cdot} + \mathrm{\cdot Cl} \quad \left(\frac{\Delta E}{3k\theta_0} = -47.9\right) \\
\mathrm{C_6H_5Cl} + \mathrm{\cdot Cl} \rightarrow \mathrm{C_6H_4Cl\cdot} + \mathrm{HCl} \quad \left(\frac{\Delta E}{3k\theta_0} = 2.6\right) \\
\mathrm{C_6H_4Cl\cdot} + \mathrm{C_6H_4Cl\cdot} \rightarrow \mathrm{C_{12}H_8Cl_2} \quad \left(\frac{\Delta E}{3k\theta_0} = 50.8\right) \\
\mathrm{C_6H_4Cl\cdot} + \mathrm{C_6H_5\cdot} \rightarrow \mathrm{C_{12}H_9Cl} \quad \left(\frac{\Delta E}{3k\theta_0} = 50.8\right)
\end{gathered} \tag{21}$$

TABLE 1: Algorithm for Simulation

```
Start
    1. Initialize positions and velocities of $C_6H_5Cl$ molecules to match specified temperature.
    2. Choose $P$ molecules to each absorb a photon.
    3. Calculate total energy of system and estimate time step $dt$.
At each time $t$:
    3. Check for chemical reactions and find all the molecules that react with each other. Mark those molecules that combine.
       Create new molecules as necessary. Update the total energy to account for energy released/absorbed by chemical reactions.
    4. If no reactions occur at this time update positions and velocities using the estimated time step.
Go to 7
    5. If reactions occur at this time, set time step to zero and update internal temperatures ignoring interaction energy.
    6. Calculate total energy (internal + interaction + KE), set $t = t + dt$, and estimate new time step $dt$.
    7. Adjust the internal temperatures to conserve energy.
Go to 4
```

The given reaction energies were calculated from the bond enthalpies and normalized using $\theta_0 = 300$ K. We seek to simulate this process and calculate the number of molecules of different species (there are a total of six species) as functions of time, the trajectories of the molecules, the temperature of the particle, and the molecular temperatures. The heat capacity, C, was calculated from the number, n, of atoms per molecule using $C_i = (3n_i - 4.5)k$. All distances and masses were nondimensionalized with the Lennard-Jones radius, r_b, and mass, m_b, of the benzene molecule, respectively. Velocities were nondimensionalized with the rms velocity of a benzene molecule at 300 K, i.e.,

$$v_0 = \sqrt{\frac{3k\theta_0}{m_b}} \tag{22}$$

We combine this characteristic velocity with the characteristic distance, r_b, to define a characteristic time:

$$t_0 = \frac{r_b}{v_0} = \sqrt{\frac{m_b r_b^{\,2}}{3k\theta_0}} \tag{23}$$

It can be shown that $\eta/(3kr_b^{\,2})$ is a characteristic time associated with the exchange of energy between the internal and translational degrees of freedom, and it is set to $0.1t_0$. Similarly, it can be shown that $3kr_b^{\,6}/\mu$ is a characteristic time associated with the exchange of energy between the internal degrees of freedom of two interacting molecules; and it has also been set to $0.1t_0$. Both of these parameters were selected so that the redistribution of intramolecular energy of an excited molecule within a particle and subsequent vibrational cooling[2] occurs on the order of ~10 ps. The critical internal temperature for fragmentation was taken to be $10\theta_0$, and the minimum separation was taken to be one Lennard-Jones radius of the fragmenting molecule.

The entire computer program was implemented in C with a LabView front end using the CINRun facility provided by LabView and was run on a laptop with a Pentium 4 processor. The use of a LabView front end allows for real-time display of the positions of all the particles, as well as a variety of statistics that were used to monitor the program. The dataflow concept utilized by LabView (as opposed to the control flow concept used by usual programming languages) allows for changing the system parameters as the program runs to investigate a variety of "what if" scenarios. It also provides early warning of catastrophic instabilities (due to programming errors, etc.), and it is easy to see the precise nature of the instability.

The state variables of the system are $S = \{r_i, v_i, \theta_i\}$. The basic algorithm for carrying out the simulation is shown in Table 1: We shall discuss each step in this algorithm in turn

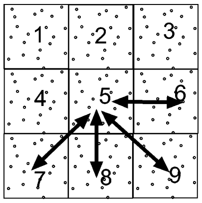

Figure 1. Schematic of the cell structure used in the algorithm. The domain is broken up into the numbered cells as shown. The calculation proceeds from cell to cell. For each cell, the interaction forces are calculated between all the particles in the current cell as well as those in the adjoining cells whose number is greater than the current cell as shown by the double arrows. This allows for an efficient search through the particle list.

III.1. Initialization. The molecules are initially placed at random inside a circular region whose radius is determined by the density of chlorobenzene and its atomic mass. The velocities are assigned at random from a Maxwell distribution at a temperature of 300 K. The internal temperatures are also set to 300 K. Of course, due the interactions between the molecules, the particle will not remain at 300 K but will change its temperature substantially (since this is a constant energy simulation rather than a constant temperature simulation). When the temperature is substantially different from 300 K, the particle is "quenched", i.e., its velocity distribution is reassigned from a Maxwell distribution and its internal temperature is reset to 300 K. This process is repeated until a stable temperature is reached.

III.2. Calculation of the Total Energy and the Estimation of a Time Step. A cell structure scheme is used to carry out the calculation of the interaction energy which involves a many to many interaction. The entire domain is broken up into numbered cells with the cell size being at least 3 to 5 times the largest Lennard-Jones radius of the molecules. The particles in each cell and the cell number associated with each particle are stored. For each cell, only the interactions between the particles within itself and with other particles that are in its lower near neighbors are found (see Figure 1). This enables an efficient search through all the cells that scales very well with the number of particles.

The allowable time step is based on two fundamental dynamical time scales involved in the calculation. If the particles are far apart, a characteristic time can be calculated by dividing the separation distance between the particles by the relative speed of the particles toward each other (shortest time between collisions for point particles). When they come near each other, then the interaction force comes into play and we can calculate a characteristic time by dividing the reduced mass ($\bar{m} = m_1 m_2/(m_1 + m_2)$) by the curvature k of the Lennard-Jones potential well and taking the square root of the result. The time step is

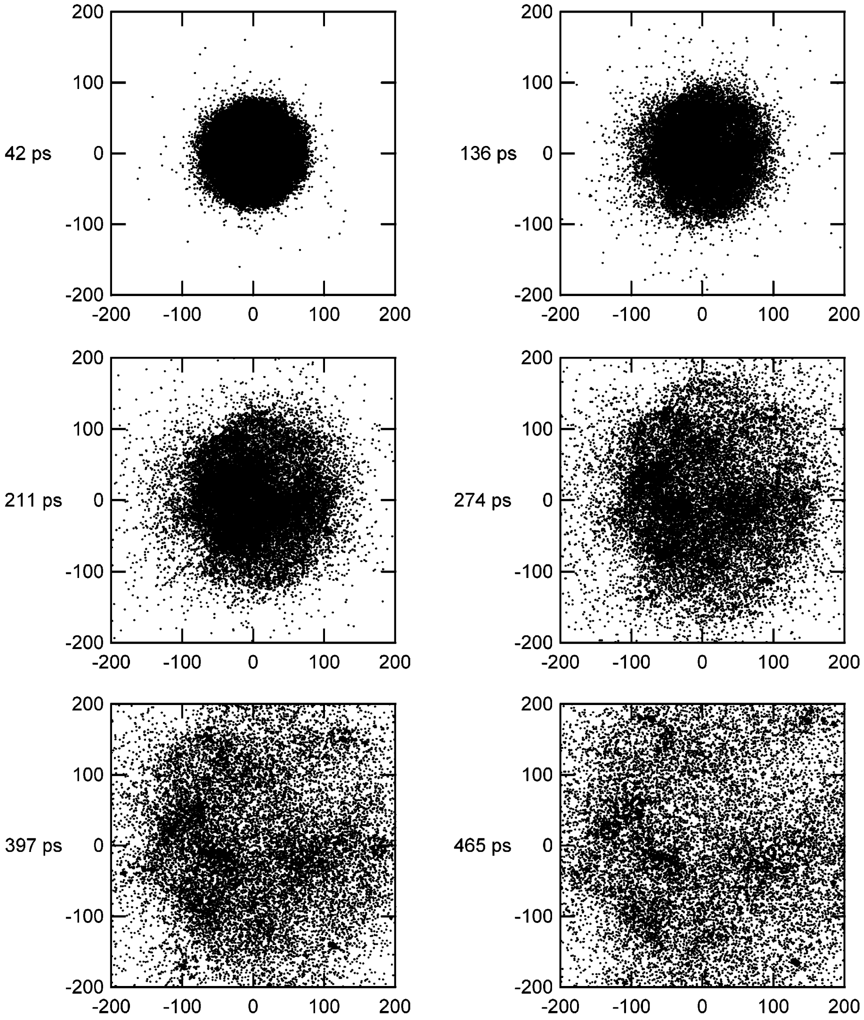

Figure 2. Ablation of a two-dimensional chlorobenzene nanoparticle, initially composed of 20 000 molecules, after 10% of the molecules absorbed a photon (193 nm). Both axes in the plots are labeled in nanometers.

then taken to be a fraction (typically a tenth) of the minimum of these two characteristic times.

III.3. Calculation of the Change of State When There Is No Chemical Reaction. The position and velocity of a molecule is determined by eq 10, and its temperature is computed by eq 13. Due to the presence of velocity-dependent terms, standard techniques such as Verlet, Leapfrog, Velocity Verlet, and Beeman's algorithms are not directly applicable. We used an extremely simple Euler scheme, wherein the particle positions and temperatures are computed at discrete times, $t_n = n\Delta t$.

Such a scheme is expected to be only conditionally stable at best. Nevertheless, it was found that, in conjunction with the stabilizing influence of the dissipative forces and the use of a variable time step as described, fairly large time steps (of the order of nanoseconds or larger) can be taken, except during the early stages when there are a large number of particles in close proximity and when chemical reactions are taking place. The use of the internal temperature also allowed for a simple scheme to ensure energy conservation and thus prevent catastrophic build up of energy that could occur due to the drift that occurs in explicit schemes.

III.4. Calculation of the Change in State When Chemical Reactions Take Place. It is straightforward to implement the change in the internal temperature and locations as described earlier. The most challenging part of the procedure is to find the particles that take part in the reaction. We implement the following procedure:

1. At each time step, the closest particle to any given particle is identified (this is done during the calculation of the total energy and the time step, since the distance between the particles is calculated here).
2. If the particle is capable of fragmenting and if there is no particle within one Lennard-Jones radius of the particle, then fragmentation occurs.
3. If a chemical reaction can occur between the closest particles, then that reaction occurs.
4. If a particle has been created by a recent reaction, i.e, within this time step, it is not considered to be capable of reacting again in that time step.
5. An initial *approximate* temperature for the reacting molecules is calculated from eq 17 for fragmentation reactions and from eq 20 for recombination reactions by ignoring the interaction and kinetic energy terms.
6. The total initial energy is incremented by the amount of energy released or absorbed by the reactions.

III.5. Updating the State and Implementing Energy Conservation. Finally the current state of the particle is updated to a new state, the actual energy of the system and the new time step are calculated. Due to the fully explicit nature of the calculations, the energy will not be conserved. Although the error in the total energy is very small in each time step, these errors accumulate and can lead to catastrophic instabilities in the system. Conservation of energy is achieved by scaling the internal temperatures of the molecules by the error in energy

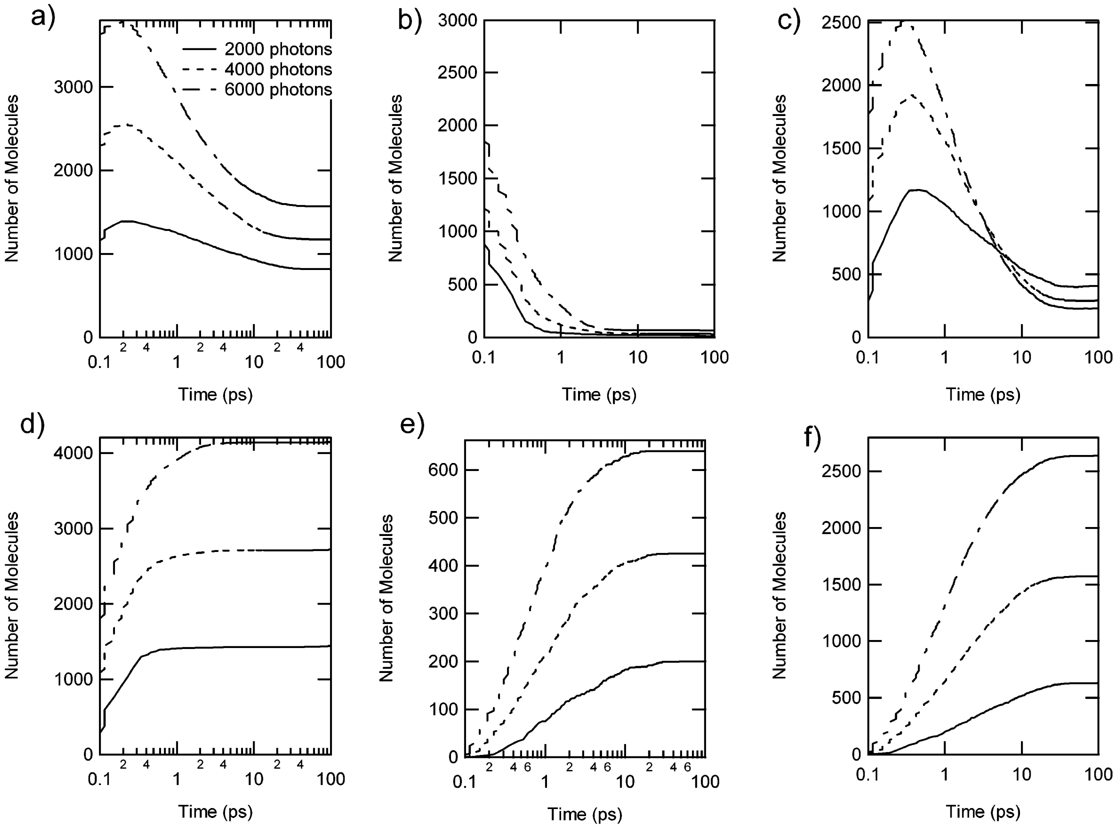

Figure 3. Evolution of photochemical products, including (a) $C_6H_6\cdot$, (b) $Cl\cdot$, (c) $C_6H_4Cl\cdot$, (d) HCl, (e) $C_{12}H_8Cl_2$, and (f) $C_{12}H_9Cl$.

divided by the total heat capacity. Geometrically, this is analogous to a projection operation where the state of the system is projected onto the constant energy surface.

IV. Results and Discussion

Figure 2 displays a two-dimensional chlorobenzene nanoparticle undergoing ablation and chemical reaction upon absorption of 2000 photons with a wavelength of 193 nm. These images correspond roughly to those presented by Zhigilei & Garrison.[4] In that study, a 55 nm two-dimensional particle composed of a sample organic molecule and exposed to laser pulses with varying duration was simulated using the breathing spheres model. They observed microcrack initiation in the interior of the particle and subsequent propagation to the edge resulting in large clumps of molecules. A direct comparison is difficult, not only because of the differences in modeling approach, but also because we have allowed for molecular fragmentation. In general, large clumps are missing in Figure 2, because molecular fragmentation releases energy that is eventually redistributed in the translational motion of the molecules. We have also deposited more energetic photons into the particle, which would lead to higher translational energy.

The evolution of the various chemical species considered is presented in Figure 3. These figures may be qualitatively compared to those presented by Yingling et al.,[8,9] using the breathing spheres model, although any quantitative comparison is beyond the scope of this manuscript. Some common trends include the rapid production and ejection of HCl, the formation and subsequent recombination of the $C_6H_6\cdot$ and $C_6H_4Cl\cdot$ radicals, and the increase in photochemical products with laser fluence. One notable difference between the two models is that the present model does not impose any time constraints on the lifetime of radicals, such as $Cl\cdot$. Rather, they are permitted to react whenever they encounter another potential reactant. Nevertheless, all of the $Cl\cdot$ radical is quickly used up within the first few picoseconds of the simulation, as shown in Figure 3b. Figure 4 shows the distribution of speeds that are obtained from the calculation presented here. It is clearly Maxwellian and can be shown to correspond to the particle temperature. The evolution of the particle temperature, calculated from the molecular velocities, is shown in Figure 5. The temperature appears to stabilize within the first 10 ps of simulation for each case.

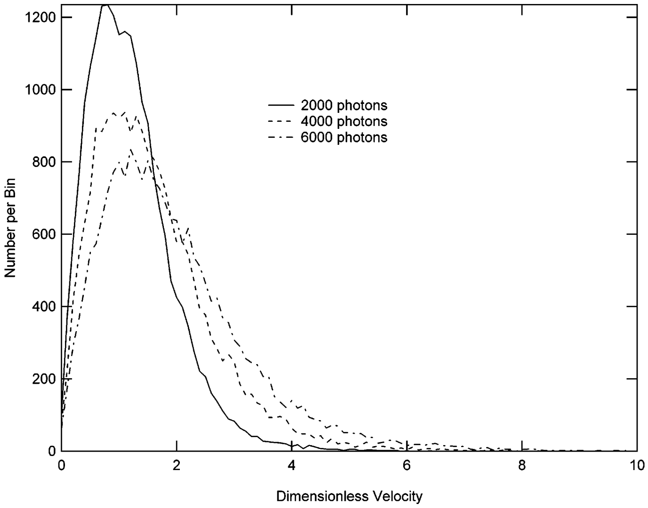

Figure 4. Calculated velocity distributions.

Presently, comparison of the model to experimental results is nontrivial because, similar to the breathing spheres model, the rate of energy dissipation is dictated by several free variables (such as the conduction parameter, μ, and the interaction parameter, η) that require experimental verification. This would entail determining the internal energy as well as the translational

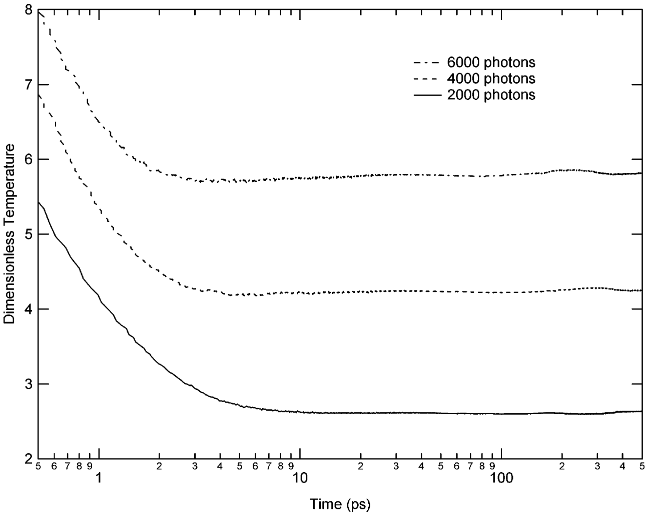

Figure 5. Evolution of particle temperature.

energy during a laser ablation experiment. Recently, Woods et al.[19] reported a promising technique for such measurements using soft UV ionization coupled with mass spectrometry. In that study, the internal energies of ethylene glycol molecules, vaporized using a CO_2 laser, were determined from the ratio of the fragments produced after UV irradiation. This ratio is sensitive to the internal energy of the parent ion, as determined from photoelectron−photoion coincidence measurements. The internal energy of the neutral parent is then recovered from energy conservation. The authors of the study report average internal energies varying from 1300 to 10 250 cm^{-1} for CO_2 laser powers between 25 and 112 mJ/pulse. They even define an “equivalent temperature” by equating the measured average internal energy to the average calculated from a Boltzmann distribution. With this definition, the equivalent temperature was shown to vary between 400 and 1200 K.

Ultimately, the present model may be used to quantitatively determine the ion fragments produced when a submicrometer particle is exposed to a high-power UV laser pulse. The lack of quantification of this phenomenon remains the Achilles heel of single-particle mass spectrometers,[26,27] which typically ablate and ionize individual particles using a single UV laser pulse. These instruments, which are capable of analyzing the composition of an aerosol population one particle at a time, lack an inversion scheme that would allow determination of the number of parent molecules in the target particle and, in the case of organic molecules, identification of the parent molecules.

V. Conclusion

We have presented a modeling and computation technique to facilitate the molecular dynamics simulations of complex systems. The notion of an internal molecular temperature was introduced to describe the storage of energy within individual molecules. The model was applied to the laser ablation of a two-dimensional submicrometer chlorobenzene particle, allowing for chemical reaction. Although quantitative comparisons are beyond the scope of the present work, the results exhibit qualitative agreement with previous studies. Follow-up work will extend the computation to three dimensions, in order to begin comparison with experiments and further develop the concept of energy transfer driven by differences in molecular temperature.

Acknowledgment. The authors would like to acknowledge one of the reviewers for suggestions that improved the presentation of the model.

References and Notes

(1) Chushak, Y. G.; Bartell, L. S. *J. Phys. Chem. B* **1999**, *103*, 11196.

(2) Zhigilei, L. V.; Kodali, P. B. S.; Garrison, B. J. *J. Phys. Chem. B* **1997**, *101*, 2028.

(3) Zhigilei, L. V.; Yingling, Y. G.; Itina, T. E.; Schoolcraft, T. A.; Garrison, B. J. *Int. J. Mass Spectrom.* **2003**, *226*, 85.

(4) Zhigilei, L. V.; Garrison, B. J. *Appl. Surf. Sci.* **1998**, *129*, 142.

(5) Schoolcraft, T. A.; Constable, G. S.; Zhigilei, L. V.; Garrison, B. J. *Anal. Chem.* **2000**, *72*, 5143.

(6) Avalos, J. B.; Mackie, A. D. *J. Chem. Phys.* **1999**, *111*, 5267.

(7) Avalos, J. B.; Mackie, A. D *Europhys. Lett.* **1997**, *40*, 141.

(8) Yingling, Y. G.; Zhigilei, L. V.; Garrison, B. J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *180*, 171.

(9) Yingling, Y. G.; Zhigilei, L. V.; Garrison, B. J. *J. Photochem. Photobiol.* **2001**, *145*, 173.

(10) Yingling, Y. G.; Garrison, B. J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *202*, 188.

(11) Reich, S. *Physica D* **1995**, *89*, 28.

(12) Reich, S. *J. Comput. Phys.* **1999**, *151*, 49.

(13) Reich, S. *Physica D* **2000**, *138*, 230.

(14) Schnitzer, H. J.; Mertens, F. G.; Bishop, A. R. *Physica D* **2000**, *141*, 261.

(15) Dinda, P. T.; Moubissi, A. B.; Nakkeran, K. *Phys. Rev. E* **2001**, *64*, No. 01608, part 2.

(16) Moubissi, A. B.; Nakkeran, K.; Dinda, P. T.; Kofane, T. C. *J. Phys. A: Math. Gen.* **2001**, *34*, 129.

(17) Boesch, R.; Willis, C. R. *Phys. Rev. B* **1990**, *42*, 6371.

(18) Pauling, L.; Wilson, E. B., Jr. *Introduction to Quantum Mechanics with Applications to Chemistry*; McGraw-Hill Book Company: New York, 1935.

(19) Woods, E.; Miller, R. E.; Baer, T. *J. Phys. Chem. A* **2003**, *107*, 2119.

(20) Callen, H. B., *Thermodynamics and an Introduction to Thermostatics*; Wiley: New York, 1985.

(21) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Notes on Transport Phenomena*; Wiley: New York, 1960.

(22) Pauling, L. *General Chemistry*; Dover: San Francisco, 1988.

(23) Branka, A. C.; Wojciechowski, K. W. *Phys. Rev. E* **2002**, *62*, 3281.

(24) Dettmann, C. P.; Morriss, G. P. *Phys. Rev. E* **1996**, *54* (3), 2495.

(25) HoogerBrugge, P. J.; Koelman, J. M. V. A. *Europhys. Lett.* **1992**, *19*, 155.

(26) Phares, D. J.; Rhoads, K. P.; Wexler, A. S. *Aerosol Sci. Technol.* **2002**, *36*, 583.

(27) Phares, D. J.; Rhoads, K. P.; Wexler, A. S.; Kane, D. B.; Johnston, M. V. *Anal. Chem.* **2001**, *73*, 2338.

(28) If we include the bond and electronic energies of all the molecules then there will be no net energy change due to fragmentation processes. We emphasize that the internal energy of the molecules considered here is associated only with the *change* in the energy due to internal motion.