

Incorporation of chemical reactions into UV photochemical ablation of coarse-grained material

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Abstract

A coarse-grained representation of material can significantly speed up molecular dynamics simulations. The difficulty arises when the simulations need to include chemical reactions. We have developed a methodology for including the effects of chemical reactions in coarse-grained molecular dynamics simulations, namely the Coarse-Grained Chemical Reactions Model (CGCRM). The model adopts physically and experimentally based parameters of a specific material, such as photochemical pathways, the probabilities, and the exothermicities of chemical reactions. We have applied this approach to elucidate the effects of photochemical reactions on laser ablation of organic and polymeric materials. We find that the model provides a plausible description of the essential processes.

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1. Introduction

Laser ablation is a process with many important applications and involves a massive material removal from a target material due to pulsed laser irradiation. The detailed understanding of the mechanistic aspects of laser ablation will lead to the improvement of current applications and the development of novel ones. Computer modeling is capable of providing a credible description of ablation processes and can offer practical insights into this complex multiscale phenomenon [1–12].

Laser ablation is a process that requires thousands of atoms to be modeled and relatively long time scales for the plume development. Coarse-grained approaches can overcome time and length limitations of atomistic simulations by replacing parts of the system with a larger scale models and by approximating the non-essential parts. One very successful approach is to reduce the number of atoms via the united atom approximation (as in the case of molecular compounds, Fig. 1a) and bead-and-spring approximations [13] (as in the case of

polymeric materials, Fig. 1c). In the breathing sphere model [8], each organic molecule containing a light absorbing chromophore is replaced by a spherical particle. The internal movement of the organic particle is represented by an additional degree of freedom. In polymeric materials, each bead can be either a poly-monomer or a group of atoms interconnected via springs [4,14]. We have successfully used our Coarse-Grained Chemical Reactions Model (CGCRM) to account for the photochemical reactions in both molecular solids and polymeric materials [3]. In this publication, we will discuss the setup and results of simulations containing chemical reactions in organic (on the example of chlorobenzene) and polymeric materials (on the example of polymethyl methacrylate (PMMA)).

2. Method

A coarse-grained model has been developed for molecular dynamics simulations of laser ablation. The photon energy can result in a vibrational excitation (photothermal processes) or disruption of a chemical bond (photochemical processes). In the latter case, the formation of active radical sites and the occurrence of chemical reactions have to be taken into consideration. The novel feature of our model is the incorporation of chemical reactions into the united atom

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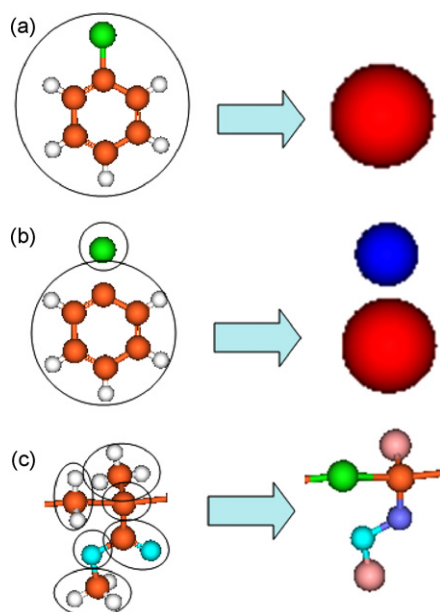


Fig. 1. Representation of the coarse-grained scheme for (a) chlorobenzene molecule; (b) photochemical cleavage of chlorobenzene molecule; (c) PMMA. Carbon atoms are orange; chlorine atoms are green; oxygen atoms are cyan; and hydrogen atoms are white. The ellipses represent approximations used for the coarse-grained representation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

representation of the organic and polymeric materials, which permits the study of laser ablation, degradation, or the effect of various chemical reactions on a large time and length scale.

2.1. Coarse-Grained Chemical Reaction Model (CGCRM)

In united atom approximation each molecule or group of atoms is considered as a spherical particle, thus, quantum mechanical descriptions of reactions cannot be defined. Our methodology adopts the philosophy of kinetic Monte Carlo method, where the reaction events can be described by the rates, probabilities, and reaction energies. Monte Carlo simulation was found to be a successful technique for simulation of the laser ablation processes. For example, this method was used to investigate the influence of elastic collisions and chemical reactions in the ablated plume [15,16].

To describe the chemical reaction events, we need to choose a specific compound with known photochemistry. The CGCRM model uses as input, the known chemistry of the specific material and adopts physically and experimentally known parameters such as enthalpies and probabilities of reactions. Moreover, no chemically correct interaction potential is required in order to incorporate the effects of chemical reactions on dynamics of the system. The particles participating in a chemical reaction can change their state via changes in the interaction potential, mass, and size changes. The possibility of chemical reaction is controlled by the computational parameter, “reaction time”, which is assigned to each radical and reflects the combination of the lifetime, the relative reactivity of the radical, and the particular reaction’s activation energy. This parameter is used along with the proximity of reaction partners

to determine the possibility of reaction. The activation energy for radical–radical recombination reactions is zero, thus, the possibility of reactions in this case will depend only on the proximity of reactants. For the abstraction reactions, the reaction time will largely depend on reactivity of the participating radical. The amount of energy deposited by the reactions depends on the local phase of surroundings. More details of relative lifetimes were given previously [3]. The deposition of the experimentally correct energy of reaction is maintained by adjusting the interaction potential and kinetic energy of the products when a reaction occurs.

2.2. Molecular solids model

The laser ablation processes are modeled using the breathing sphere model [8] with properties of chlorobenzene, which is described elsewhere [5]. Chlorobenzene was chosen due to the simplicity of its fragmentation, entailing exclusively scission of C–Cl bond to yield C_6H_5 and Cl radicals, and available experimental data. The photon absorption event can cause photothermal processes, which are simulated by depositing the photon energy into an internal mode of vibration of breathing sphere, or photochemical processes, which are simulated by using CGCRM, where a molecule can split into two reactive radicals with subsequent change in a number of particles, potential, and kinetic energies (Fig. 2b). The probability of photochemical absorption can be set to a desired value or can be taken from known experimental data [17,18]. These radicals can react with the parent molecule or other radicals via various abstraction and recombination reaction, yielding such products as HCl, Cl_2 , C_6H_6 , $C_6H_4Cl_2$, $C_{12}H_{10}$, $C_{12}H_8Cl_2$, and $C_{12}H_9Cl$.

A computational cell of $10\text{ nm} \times 10\text{ nm} \times 191\text{ nm}$ ($\sim 130,000$ molecules) is used with periodic boundary condition on the sides and non-reflecting boundary conditions at the bottom of the sample. In this publication we discuss laser irradiation at a wavelength of 248 nm, which is simulated by a random excitation of molecules with absorption probability following the Beer’s Law and a 50 nm penetration depth. The laser pulse width is 150 ps.

2.3. Polymeric solids model

To apply the CGCRM for ablation of polymers we have chosen PMMA due to its extensive use in industry, available experimental and theoretical data, and straightforward photochemistry. The interaction of a high-energy photon with PMMA results in one of the three outcomes, main chain scission (Norrish Type II), side chain scission (Norrish Type I), or blocking group deprotection (Ester Elimination). Norrish Type II reaction leads to the decomposition of the polymer into chains with lower molecular weight or monomers. Norrish Type I and Ester Elimination reaction can result in formation of carbon radicals on the main chain, which can lead to cross-linking of polymers, or can be followed by the loss of carbon dioxide or carbon monoxide. The relative probabilities of these reactions largely depend on the laser wavelength. Thus, the particular coarse-grained representation of PMMA was chosen

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