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Molecular dynamics simulations of laser disintegration of amorphous aerosol particles with spatially nonuniform absorption

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Abstract

A series of molecular dynamics (MD) simulations are performed in order to provide qualitative information on the mechanisms of disintegration of aerosol particles as used in aerosol mass spectrometry. Three generic types of aerosol particles are considered: strongly absorbing particles with homogeneous composition, transparent particles with absorbing inclusion, and absorbing particles with transparent inclusion. To study the effect of the mechanical properties of the aerosol material on the disintegration process, the results for crystalline (brittle) and amorphous (ductile) particles are compared. For large laser fluences, nearly complete dissociation of the absorbing material is observed, whereas the nonabsorbing portions remain fairly intact. Because large fluences can cause photofragmentation of constituent molecules, multiple pulses at low laser fluence and/or lasers with different wavelengths are recommended for the best representative sampling of multicomponent aerosol particles in laser desorption/ionization (LDI) mass spectrometry.

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1. Introduction

Due to the importance of aerosol particles to human health [1,2] and atmospheric chemistry [3], quantitative methods for aerosol characterizations are being developed. Specifically, Prather et al. have recently developed an aerosol time-of-flight mass spectrometry (ATOFMS) technique [4]. This instrument simultaneously measures real-time size and chemical composition of individual particles, and is based on the technique of laser desorption/ionization (LDI). Short pulse laser irradiation of a particle in LDI partially or completely disintegrates the particle as well as ionizes some of the

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constituents. An accurate and complete chemical fingerprint of a particle depends upon uniform disintegration with minimal fragmentation of the species. A thorough understanding of the laser-induced processes in the particle is needed to optimize the irradiation parameters and to accurately interpret the mass spectrometry data.

To investigate the dynamic laser-induced processes, the computer simulation technique of molecular dynamics (MD) can be used. Because aerosols are larger than can practically be modeled using atomistic MD techniques, groups of atoms within the particle are simulated using a coarse-grained breathing sphere model [5,6]. Using this model, as well as a two-dimensional (2D) system, we can expand the time and length scale of the simulations. To date, MD simulations have been used to investigate the dependence of the disintegration mechanism of the particle on the laser pulse width where the energy is uniformly deposited within the particle [7]. In addition, studies have been performed with spatially nonuniform energy deposition for two types of particles. One type of particle consists only of molecules that absorb the laser irradiation and the other type consists of absorbing molecules surrounding an optically transparent inclusion [8].

The purpose of this paper is to further investigate the laser-induced processes in aerosol particles in which the inclusion contains absorbing molecules and the material at the periphery of the particle is optically transparent. For these studies we must construct amorphous particles because the disintegration process of the crystalline ones used previously is strongly influenced by the symmetry of the 2D lattice. The results of the studies contained in this paper will be compared to the earlier results for crystalline particles [8] and implications to mass spectrometry will be discussed.

2. Computational model

The breathing sphere model for MD simulations as applied to aerosol particles with spatially nonuniform laser energy deposition has been detailed elsewhere [8]. The amorphous particles in the simulations presented here have a diameter of 110 nm and are comprised of 27 003 molecules. The procedure for the creation of the 2D amorphous structure is given in the next subsection. For particles that contain inclusions, the ratio of the diameter of the particle to the inclusion is 4.4 to 1 for the larger inclusion and 1.5 to 1 for the smaller one. The probability of an absorbing molecule being excited by a photon during the 15 ps laser pulse is modeled according to the Lambert–Beer law thus producing exponential attenuation of the laser light with depth into the particle or absorbing inclusion. The absorption depth of the laser is 25 nm, thus less than the diameter of the particle, but the same as the diameter of the smaller inclusion. Because the simulations are performed for a 2D system, units of eV/nm are used for fluence.

In order to generate a stable 2D amorphous structure, two differently sized molecules are required so that the closest packing arrangement of identical molecules can be broken [9]. Starting with a small crystalline sample of 90 molecules with periodic boundary conditions, the diameters of 30 molecules are increased by 1.037% and their masses are increased so that the density of the sample remains constant. The size of the computational cell is adjusted to keep the average pressure in the configuration close to zero. Following this step, the sample is quenched for 500 ps. The distribution of coordination numbers (5, 6 and 7) is examined as well as the radial distribution function of distances between molecules in order to determine when the structure is amorphous. The steps described above are repeated until the structure is determined to be amorphous. The amorphous configuration is replicated in the two directions until a circular aerosol particle with a diameter of 110 nm can be extracted. The resulting structure is quenched again. The final aerosol particle contains 8095 larger and 18 908 smaller molecules, where the equilibrium radii of the molecules for the breathing motion are 2.25 and 1.40 Å and the masses are 260 and 100 Da, respectively. The potential between the particles has an edge-to-edge equilibrium distance of 3 Å, thus the total equilibrium radii are 3.75 and 2.9 Å.

3. Results

Simulations for particles with and without inclusions at two different laser fluences are performed. Snapshots of the particles provide visual information for qualitative analysis of the laser-induced processes. The first subsection discusses amorphous particles with and without transparent inclusions. These results are compared to previous work for similar crystalline particles [8]. The second subsection presents the results of a simulation for a crystalline particle with an absorbing inclusion. Lastly, the third subsection discusses the results for amorphous particles with absorbing inclusions. For all figures, the laser irradiates the particle from the top of the page, and this defines the frontside of the particle. The color black indicates the molecules that absorb the laser light and the color red represents optically transparent molecules.

3.1. Amorphous particles with and without transparent inclusions

Four representative simulations are discussed to illustrate qualitatively the effect of laser fluence and the presence of a transparent inclusion in the aerosol particle. For the first two simulations shown in Fig. 1, the lower laser fluence (25 eV/nm) produces nearly identical results. Only material from the frontside of the particle is ejected. Similar results are observed for the same conditions for particles with crystalline structure [8]. The only difference between the amorphous results presented here and the crystalline results is that more disintegration of the amorphous particles is observed. This result is due to the amorphous material having a lower cohesive energy of 0.79 eV/nm^2 versus the crystalline value of 1.1 eV/nm^2. As the laser fluence is increased to 300 eV/nm as shown in Fig. 2, more extensive disintegration of the absorbing material occurs. The backside of the particle fractures and leaves large chunks of material. The same result occurs for the crystalline particle [8] and is attributed to the reflection of a pressure wave off the backside of the particle where the material has been weakened by absorption of the laser irradiation. The picture

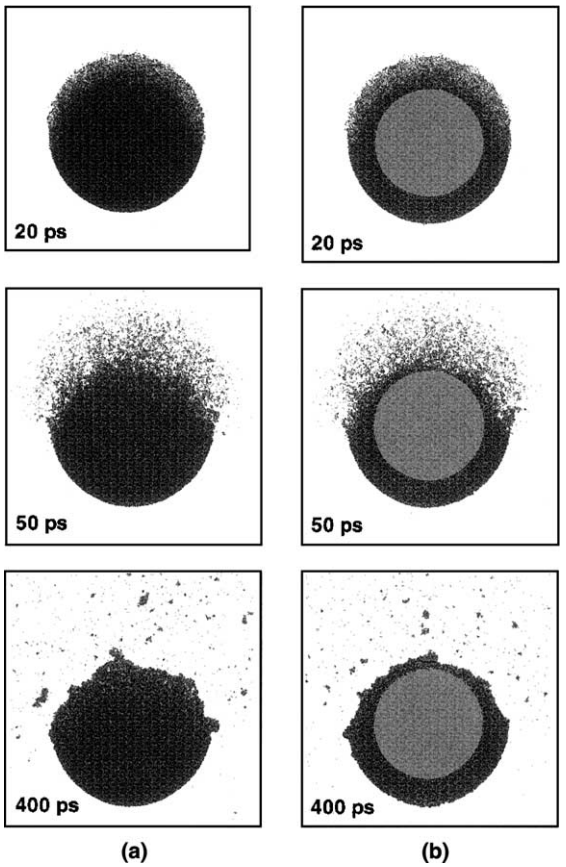

Fig. 1. Snapshots (20, 50 and 400 ps) of the amorphous particles subjected to a laser fluence of 25 eV/nm. The laser irradiation is coming from the top of the page. (a) Particle without inclusion. (b) Particle with transparent inclusion where the diameter of the particle is 1.5 times the diameter of the inclusion.

of disintegration in this case looks similar to the experimental photographs for water droplets irradiated by short laser pulses [10]. The absorbing material in the particle with the nonabsorbing inclusion, on the other hand, is nearly 100% dissociated. Very little of the inclusion material, however, is ejected. The inclusion in the amorphous particle develops voids that coalesce into a large void, whereas the crystalline material develops microcracks [8]. In both the crystalline and amorphous systems, the pressure builds up the frontside as well as in the backside of the particle. When the two pressure waves propagate in the direction toward the center of the particle, the

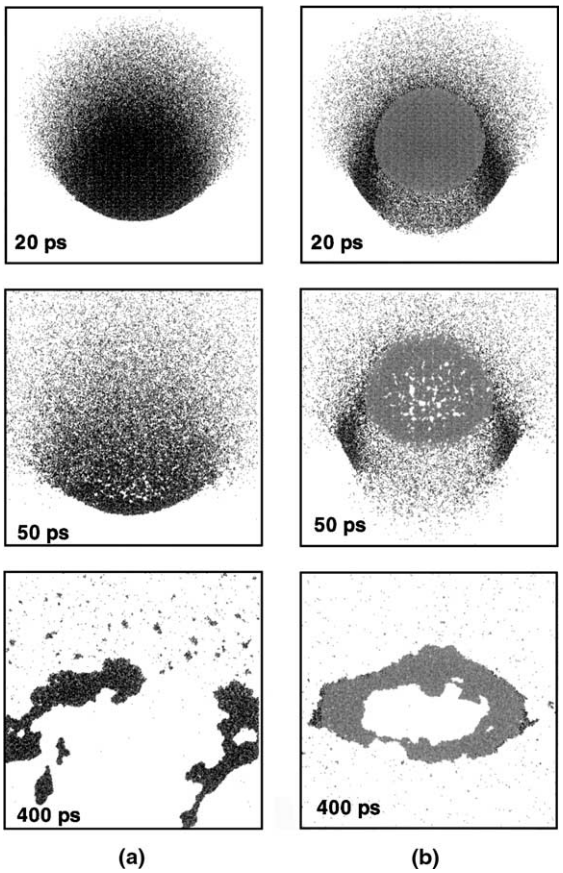

Fig. 2. Same as Fig. 1 but for a laser fluence of 300 eV/nm.

pressure waves constructively interfere in the middle of the inclusion thus creating either microcracks or voids depending on the property of the material. Brittle fracture with microcrack generation is observed for the crystalline particle and ductile fracture through void formation for amorphous particles.

3.2. Crystalline particles with absorbing inclusions

One representative simulation of a crystalline particle with an absorbing inclusion is shown in Fig. 3 to illustrate the result for this type of aerosol particle. For this simulation, the particle is twice the size of the inclusion and the laser fluence is 100 eV/nm. As the laser-induced pressure wave propagates from the inclusion to the

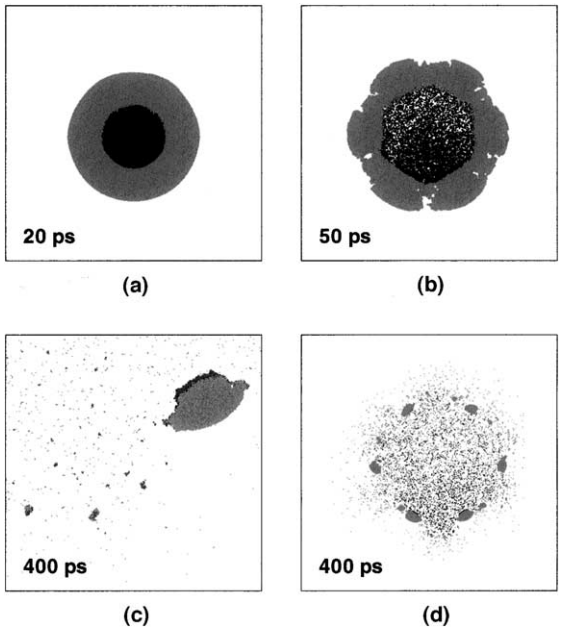

Fig. 3. Snapshots (20, 50 and 400 ps) for a crystalline particle with a diameter that is two times the diameter of the absorbing inclusion. The laser fluence is 100 eV/nm. The scale in (d) is 18.6 times larger than in (a)–(c).

surrounding material, the particle fractures according to the sixfold symmetry of a close-packed system. In fact, due to the brittle nature of the crystalline material, the fracturing occurs along the close-packed direction in the 2D triangular lattice. Although the material in a real aerosol particle is not a single crystal, the observed fast disintegration of the particle into pieces can be expected for particles composed of a brittle material.

3.3. Amorphous particles with absorbing inclusions

Four representative simulations are discussed to illustrate qualitatively the effect of laser fluence and the size of an absorbing inclusion on the mechanism of disintegration of the aerosol particles. For the lower laser fluence (25 eV/nm) shown in Fig. 4, the results are different for the two simulations. In the case of the smaller inclusion, all of the included material dissociates because the laser

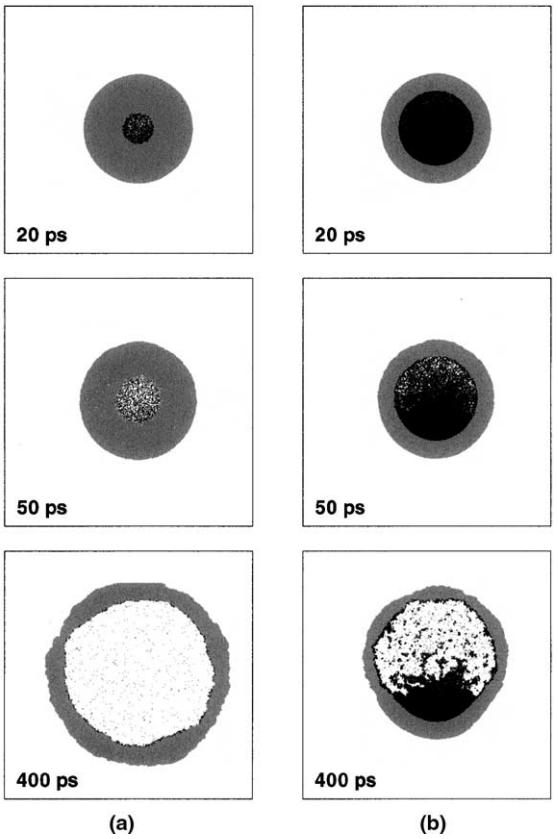

Fig. 4. Snapshots (20, 50 and 400 ps) for the amorphous particle with an inclusion that absorbs the laser fluence of 25 eV/nm. (a) The diameter of the particle is 4.4 times the diameter of the inclusion. (b) The diameter of the particle is 1.5 times the diameter of the inclusion.

absorption depth is the same as the diameter of the inclusion and the deposited energy is greater than the material's cohesive energy. The resulting laser-induced pressure causes uniform expansion of the particle, thus thinning the periphery material as it expands. The nonabsorbing periphery material, however, remains intact at 400 ps. When the simulation is run to 800 ps, the periphery material ruptures at one point, allowing the expanding included material to escape. While this behavior of the periphery appears unusual, previous MD simulations of two component 2D amorphous structures predict that the material can undergo significant plastic deformation [11] whereas crystalline materials tend to be more brittle. For the larger inclusion, Fig. 4(b), the included material is only partially dissociated, and thus the particle expands nonuniformly and the periphery is not ruptured.

As the laser fluence increases to 300 eV/nm as shown in Fig. 5, the amount of dissociation of the inclusion increases for both particles. In this case, the laser-induced pressure is larger which increases the rate of expansion of the periphery material. Because the periphery material expands more quickly, this material breaks into large clusters during the time limit of the simulation.

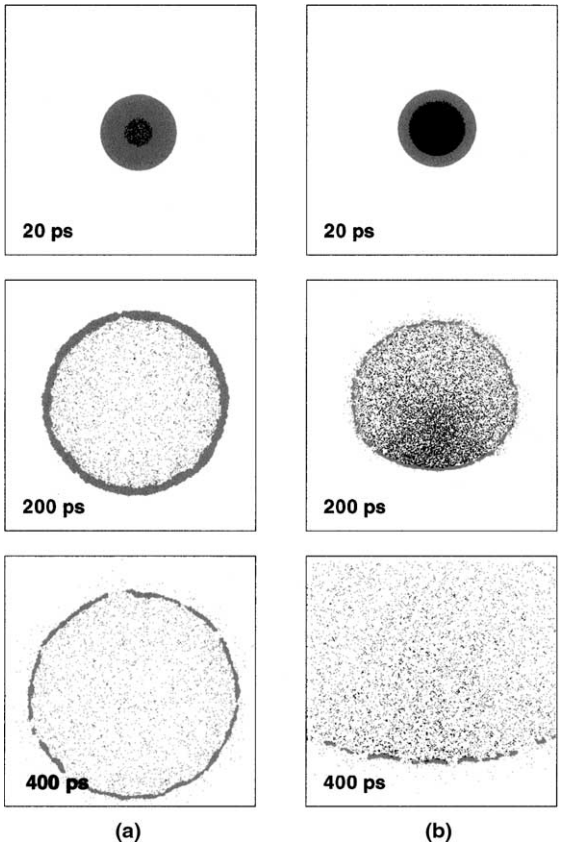

Fig. 5. Snapshots (20, 200 and 400 ps) for the particles in Fig. 4 but for a laser fluence of 300 eV/nm. The same square area is used for 20 ps for both (a) and (b) and for 200 ps for (a) and this square area is three times the area in Fig. 4. A square area that is twelve times the square area in Fig. 4 is used for both 400 and 200 ps for (b).

4. Conclusion

In an effort to examine different types of possible structural organizations of material in aerosol particles and their response to spatially nonuniform absorption, 2D MD simulations are performed on amorphous and crystalline particles with and without inclusions. The main difference between the crystalline and amorphous material is observed when the inclusion contains the absorbing material. The crystalline material breaks due to its brittle nature whereas the amorphous material exhibits extended plastic deformation, thus fragmenting when the material has been expanded beyond its cohesive capacity. In addition, the results show that the higher the laser fluence, the greater the dissociation of an aerosol particle. Dissociation, however, is not 100% for the particles whose diameters are larger than the laser adsorption depth. This conclusion applies regardless of the material's properties and the presence of a transparent or absorbing inclusion. Large laser fluences, however, increase the probability of photofragmentation of constituent molecules, thus complicating their identification in LDI mass spectrometry experiments. To alleviate the problem, multiple pulses from a low fluence laser can be used. For particles containing components with vastly different absorption properties, two different wavelengths should be used in order to achieve representative sampling of all components in the particle.

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