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# Computer simulation study of damage and ablation of submicron particles from short-pulse laser irradiation

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**Abstract**

The dynamics of damage and ablation of individual particles of ~100 nm in size due to short-pulse laser irradiation is studied using a breathing sphere model and molecular dynamics simulations. The fluence thresholds for damage and ablation of irradiated particles have a strong pulse duration dependence. For 15 ps laser pulses, the laser induced pressure buildup and the focusing of the pressure wave in the center of irradiated particle leads to low thresholds for mechanical damage and ablation. The pressure driven particle disruption provides an effective mechanism for transfer of the laser energy into the energy of radial expansion of the ablation products. For 300 ps laser pulses, the explosive thermal decomposition of the particle is due to overheating and occurs at significantly higher laser fluences. Implications of the results of the simulations for the mass spectrometric aerosol characterization experiments and ablation of tissue in the case of inhomogeneous absorption of laser energy are discussed. © 1998 Elsevier Science B.V.

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## 1. Introduction

As laser pulses become shorter in laser ablation applications, the role of inhomogeneous absorption of laser energy in the material becomes more important. Whereas for long laser pulses thermal diffusion has time to dissipate the deposited energy over all the material, for short pulses the energy can remain localized in one component of a heterogeneous system. This spatially nonuniform absorption and hot spot formation can lead to a substantially lower ablation/damage threshold than with longer laser pulses [1,2]. An example from laser surgery is the strong absorption of visible and near infrared radiation by melanin granules, submicron pigment particles naturally occurring in many tissues including skin and eye retina [1,3–6]. In laser ablation of polymers, absorption within nanometer-sized inclusions of graphite reduces the threshold for short-pulse ablation [2]. As a basis for the analysis of mechanisms of laser ablation in these complex systems, the knowledge of the effect of laser irradiation on an individual particle is essential. The understanding of the mechanisms of laser ablation of individual particles is also critical for interpretation of data from real-time aerosol characterization experiments [7–9], as well as for experiments on vaporization and fragmentation of fog droplets [10,11] and water beams [12].

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The small size of the absorbing particles or structural compounds hampers experimental investigations and limits capabilities of analytical continuum analysis to qualitative discussions of the possible mechanisms of short-pulse laser damage and ablation. Thermal relaxation [5,6], explosive boiling [10–12], pressure generation, shock wave formation [1,3,4], and interaction with the borders of the absorbing particle [1] are the mechanisms that have been proposed to be important in different irradiation regimes. It is difficult to account for these complex and interrelated processes within a single analytical continuum description.

An alternative method of microscopic analysis of laser induced processes is the molecular dynamics (MD) computer simulation technique. The advantage of this approach is that only details of the microscopic interactions need to be specified and no assumptions are made about the character of the processes under study. Rather the physical phenomena arise naturally out of the simulations. Moreover, the MD method is capable of providing a complete microscopic description of the dynamic processes induced by the laser pulse as well as the final results of the laser irradiation. Recent application of this method to the analysis of the ablation of molecular films and matrix-assisted laser desorption (MALDI) demonstrate the ability of the method to provide insight into the microscopic mechanisms of laser ablation [13–15]. Small absorbing particles and short laser pulse widths are especially amenable to theoretical investigation using MD.

In this work, we present a microscopic simulation study of the dynamics of damage and ablation of submicron particles due to short-pulse laser irradiation at different laser fluences and pulse durations. Predictions are made about the structure of ablation products in the case of isolated particles as well as about the effects of coupling of the processes in the absorbing particles to the surrounding media in the case of inhomogeneous absorption.

## 2. Computational method

A prototypical organic cluster is used in the molecular dynamics investigation for the submicron particles. A breathing sphere model for microscopic modelling of laser ablation and the parameters used to represent an organic solid are described in detail elsewhere [13]. Briefly, the model adopts an approximate representation of internal molecular motions that permits a significant expansion of the time and length scales of the simulation. The parameters of the intermolecular potential are chosen to represent the van der Waals interaction in the molecular system. A mass of 100 Da is attributed to each particle. A two-dimensional (2D) version of the model, which offers a clear visual picture of the damage and ablation processes, is used in the present work. Simulations are performed for an isolated particle of hexagonal close-packed crystalline structure with radius of $\sim 55$ nm.

The laser irradiation is simulated by vibrational excitation of molecules that are randomly chosen during the laser pulse duration. In this case an implicit assumption is that the particle absorbs homogeneously and the effect of laser beam attenuation within the particle can be neglected. For reasonable values of the absorption length, this is a safe assumption for submicron particles. [3] The vibrational excitations are performed by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal vibration of the molecule to be excited. Laser pulses of 15 ps and 300 ps in duration at a wavelength of 337 nm are used in the simulations. The photon energy is scaled down by factor of two in order to account for the lower cohesive energies in the 2D system as compared to the three-dimensional case. A series of simulations at different laser fluences is performed for each pulse duration, starting from a fluence that does not cause any visible damage to the particle up to fluences that lead to complete disintegration of the irradiated particle.

The MD technique allows one to perform a detailed analysis of the laser induced processes in which visual observations can be correlated with microscopic dynamics. The energies and velocities of molecules are obtained directly from the MD algorithm. The concept of local atomic stresses [16] is used in calculations of the local hydrodynamic

[3] For larger particles, the absorption can be nonuniform. We are investigating the dynamics of damage and ablation under such conditions and the results are in preparation.

pressure that is defined as a first invariant of the stress tensor. The Dirichlet construction [17] has been used to define the volume per molecule and the coordination number of each molecule in the 2D model. The coordination numbers are conventionally used for characterization of the defect structure of the 2D systems [17–19]. All varieties of structural defects in 2D crystals can be identified in terms of groups of non-sixfold coordinated particles [17,18] and the melting corresponds to the rapid increase of the defect density [17,19]. Thus, calculation of the number of non-sixfold coordinated molecules can provide a quantitative description for the structural changes and phase transitions occurring in the 2D model.

## 3. Results

In this section we present the results of molecular dynamics simulations of laser irradiation of small particles for two distinct pulse widths. Snapshots from the simulations given in Fig. 1 clearly indicate that the fluence threshold values for producing minimal damage or cavitation within a particle are different for irradiation with the short, 15 ps, and the long, 300 ps, pulses. For the shorter laser pulse a substantial damage to the irradiated particle is observed at lower laser fluences and the damage has a pronounced character of mechanical disruption. For the longer laser pulse, significantly higher laser fluences are required to cause visible damage to the particle. The physical processes and mechanisms leading to this apparent pulse duration dependence of particle ablation and damage are analyzed below.

### *3.1. 15 ps laser pulses. Mechanical disruption due to pressure buildup*

For the 15 ps laser pulses, the threshold laser fluence for producing minimal visible damage to the irradiated particle is found to correspond to ~0.12 eV per molecule within the particle. Snapshots from the simulation at the threshold fluence at different times after the end of the laser pulse are shown in Fig. 2. No visible damage to the particle is observed during the first 45 ps (or 30 ps after the end of the pulse). At about 50 ps a cluster of microcracks is generated, Fig. 2a. All the microcracks originate in the central part of the particle and radiate outward from the center. The microcracks then develop into a cluster of micropores that have lower potential energy due to the reduced area of internal free surfaces, Fig. 2b,c.

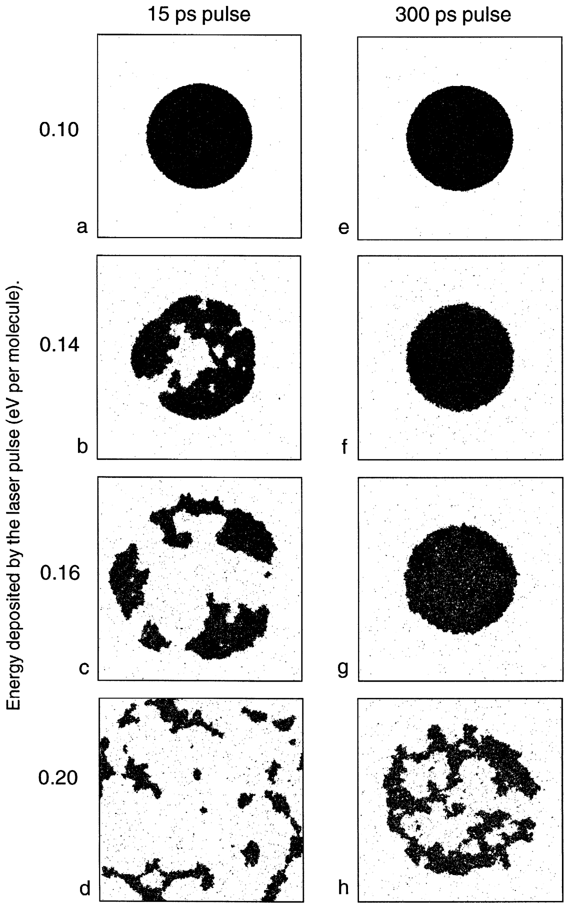


Fig. 1. Snapshots from the MD simulations of laser irradiation of individual particles vs. deposited laser energy. Results at 500 ps after the end of the laser pulses are shown for 15 ps (a–d) and 300 ps (e–h) pulse durations.

With increasing deposited energy more substantial damage is produced. Microcracks crop out to the surface of the particle, Fig. 1b, and, at energies deposited higher than ~0.15 eV per molecule, split the particle apart, Fig. 1c. The clusters resulting from the particle disintegration are moving apart in the radial direction. An additional increase of the deposited energy results in disintegration into smaller

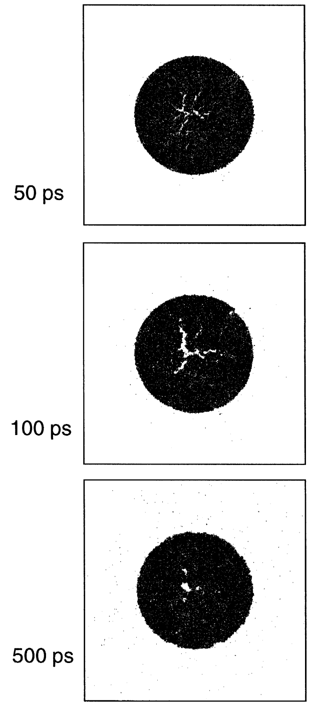



Fig. 2. Snapshots from the simulation of the particle irradiated with a 15 ps laser pulse at 50 ps, 100 ps and 500 ps. Energy deposited by the laser pulse is 0.12 eV per molecule.

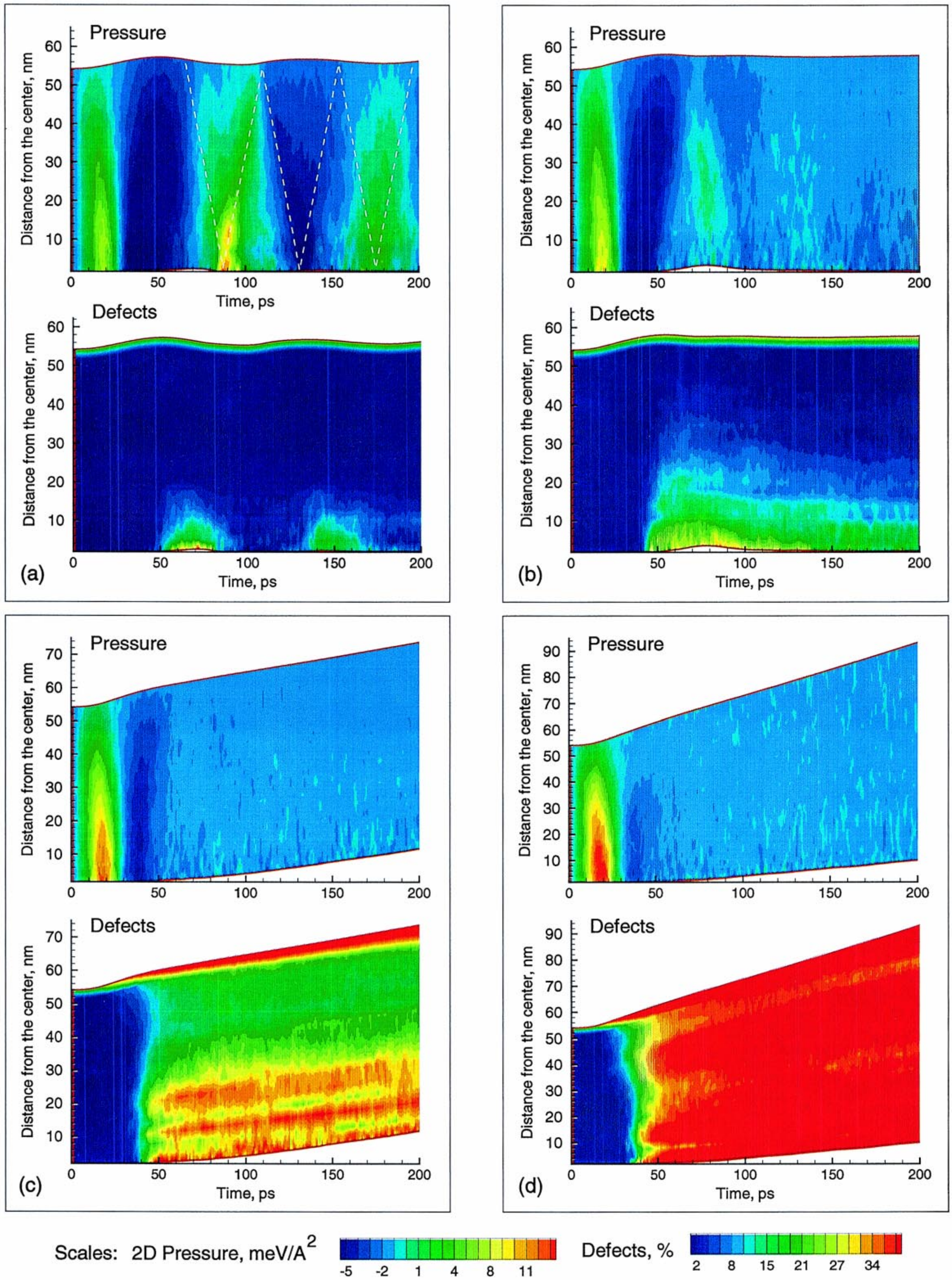
clusters that are moving apart with higher velocities, Fig. 1d.

In order to reveal the physical processes that are responsible for laser induced damage to the irradiated particles we correlate the visual pictures shown in Figs. 1 and 2 with an analysis of the temperature, pressure and defect density distributions within the system. The spatial and time development of the local hydrostatic pressure and defect density in the irradiated particles for different laser fluences is presented in Fig. 3 in the form of contour plots. The particle is divided into 20 annular (ring-shaped) zones and contour plots are drawn through the points corresponding to the average of the quantity for all the molecules in the zone. The data points are calculated at 1 ps intervals during the MD trajectories starting from the beginning of the laser pulse.

The common feature of the pressure plots for all laser fluences is that a high compressive pressure (positive pressure in Fig. 3) builds up in the central part of the particle during the laser pulse. This pressure is the result of the rapid temperature increase in the irradiated material that occurs on the time scale of the laser pulse duration [13,14]. When the heating time is shorter than a characteristic time of mechanical relaxation, the material is inertially confined [20–22]. That is, it does not have time to expand and, locally, heating takes place at nearly constant volume. This constant volume heating inevitably leads to a high pressure buildup. The minimum characteristic time of mechanical response to the heating can be estimated as the ratio of the size of the heating volume to the speed of acoustic wave propagation. For particles with a radius of $\sim 55$ nm and with a speed of sound in our model of 2760 m/s, the time of mechanical relaxation is $\sim 20$ ps. Thus, while having the conditions for inertial confinement in the central part of the particle for 15 ps laser pulses, we can expect a significant decrease of the pressure for 300 ps pulses, as shown in Section 3.2.

The analysis of the data from the simulations given below shows that for short laser pulses, the formation of a high pressure region in the center of the irradiated particle plays the decisive role in the damage processes. We start with the data from the simulation with the lowest deposited energy at which no visible damage is produced, Fig. 1a. The laser induced compressive pressure leads to expansion of the particle with tensile stresses concentrated in the center of the particle at $\sim 50$ ps, Fig. 3a. The resulting pressure wave is trapped within the particle. At each reflection at the free surface of the particle the sign of the pressure changes, that is, a compression wave changes into an expansion one and vice versa, Fig. 3a. Spherical symmetry of the particle leads to the focusing of the pressure in the center of the particle. Due to this focusing the second spike of the compressive pressure in the center of the particle at $\sim 90$ ps is more intensive than the first one at 15 ps.

Even though there are no visible damage evident in Fig. 1a, the contour plot of the defects in Fig. 3a exhibits a periodic appearance of defects in the central part of the particle. Microscopic analysis shows that the defects are vacancies, dislocations and micropores. The appearances of the defects coincide with the spikes of tensile pressure in the center of the


Pressure
Defects
Distance from the center, nm
Time, ps
(a)
(b)
(c)
(d)
Scales: 2D Pressure, meV/A$^2$
-5 -2 1 4 8 11
Defects, %
2 8 15 21 27 34

particle, 50 and 130 ps, and the annealing coincides with the spikes of compressive pressure, 90 and 170 ps, indicating that it is the pressure wave that cause these periodic changes in the defect density.

As the energy deposited increases, a cluster of microcracks appears in the central part of the particle, Figs. 2 and 3b. Similar to the case considered above, the generation of the microcracks coincides temporally and spatially with the maximum tensile stresses. At this energy, however, the microcracks develop into micropores and permanent damage is produced. A fast dissipation of the pressure wave results from its interaction with the microcracks and a fast decay of the elastic vibrations of the particle is observed, Fig. 3b.

Fig. 3c,d show the pressure and defect density plots for the cases when irradiation leads to the particle disintegration or ablation, Fig. 1c,d. The disintegration shows up in the contour plots in Fig. 3c,d where the average radial position of the particle increases linearly with time. The smaller defect density at higher distances from the center of the particle, Fig. 3c, indicates that the big chunks of material tend to originate from the outer part of the particle, whereas material in the central part is more dispersed. An additional increase of the deposited energy results in a more homogeneous explosive disintegration of the particle into small clusters and gas phase molecules, Fig. 1d and Fig. 3d. It is interesting to note that although the maximum compressive pressure is increasing with laser fluence, the maximum tensile pressure is decreasing, Fig. 3a–d. This is due to the strong temperature dependence of the critical tensile stresses that material can sustain. At the highest laser fluence simulated the material is overheated up to the limit of its stability and a homogeneous explosive disintegration occurs without formation of noticeable tensile stresses, Fig. 3d.

Analysis of the time dependence of the average kinetic energy of molecular motion in the radial and tangential directions provides information about the redistribution of the deposited energy. A common feature of the kinetic energy plots for all laser fluences is a splitting of the radial and tangential components at early times caused by the pressure relaxation. A significant part of the laser energy goes to the kinetic energy of radial expansion of the particle, Fig. 4. The subsequent kinetic energy development follows one of two ways. For lower deposited energies in which there is no particle disintegration, the dissipation of the pressure wave leads to equilibration of the radial and tangential parts of the kinetic energy as shown in Fig. 4a. For higher energies, in

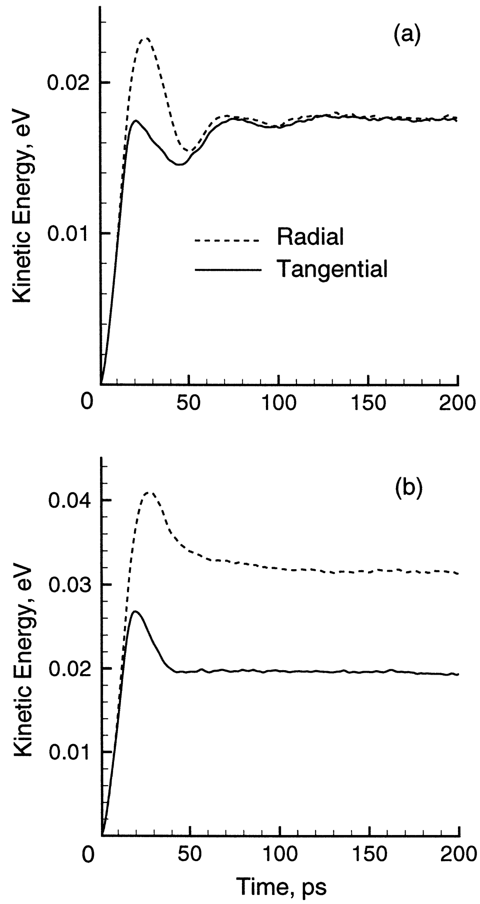



Fig. 4. Radial and tangential parts of the kinetic energy of the particle irradiated with 15 ps laser pulses. Energies deposited by the laser pulses are (a) 0.12 and (b) 0.20 eV per molecule.

Fig. 3. Spatial and time distributions of the local hydrostatic 2D pressure and defect density within the particles irradiated by 15 ps laser pulses. Energies deposited by the laser pulses are (a) 0.10, (b) 0.14, (c) 0.16, and (d) 0.20 eV per molecule. The dashed line in (a) shows schematically the path of the pressure wave.

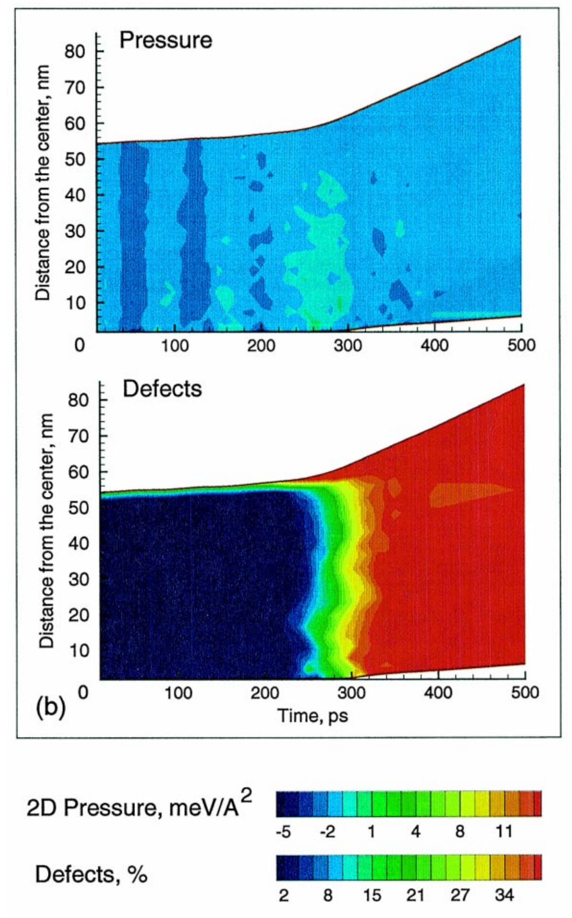



Fig. 5. Spatial and time distributions of the local hydrostatic 2D pressure and defect density within the particles irradiated by 300 ps laser pulse. Energy deposited by the laser pulse is 0.20 eV per molecule.

which the particle disintegrates, only a fraction of the excess of the radial kinetic energy is spent on disintegration of the particle, Fig. 4b, and the remaining difference between the radial and tangential parts of the kinetic energy corresponds to the energy of the radial expansion of the disintegrated particle.

### *3.2. 300 ps laser pulses. Explosive disintegration due to overheating*

The pressure contour in Fig. 5 shows that there is scarcely any pressure buildup induced by the 300 ps laser pulse even for the highest laser fluence simulated. A 300 ps laser pulse is significantly longer then the time of mechanical relaxation of the particle, as estimated in Section 3.1, and thermal expansion occurs during the energy deposition. Thus, the mechanical mechanism of particle damage and ablation that is crucial for 15 ps pulse irradiation does not play any role in the case of 300 ps pulses.

For a deposited energy of 0.16 eV per molecule, homogeneous melting occurs at the end of the laser pulse. The number of non-sixfold coordinated molecules increases up to 15–30%. An additional increase of the deposited energy leads to the overheating of the particle up to the limit of its thermodynamic stability [14,23]. When this limit is reached, the particle spontaneously decomposes into a mixture of gas phase molecules and molecular clusters with the fraction of molecules in the gas phase determined by the degree of overheating. This decomposition shows up as the sharp homogeneous rise of the defect density up to a level that far exceeds the one characteristic of the liquid state, Fig. 5.

It is interesting to note that this thermal decomposition or explosion does not lead to the transfer of a significant part of the deposited laser energy to the radial expansion of the disintegrated particle as happens in the case of 15 ps pulses. This can be seen both from the effective radii of the exploded particles in Fig. 1d and h and from the difference in the

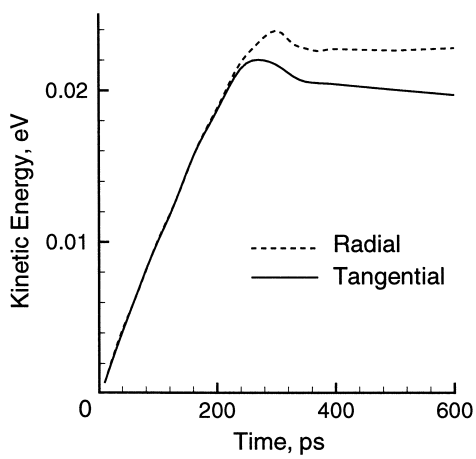



Fig. 6. Radial and tangential part of the kinetic energy of the particle irradiated with 300 ps laser pulse. Energy deposited by the laser pulse is 0.20 eV per molecule.

tangential and radial parts of the kinetic energy, Figs. 4 and 6.

## 4. Discussion and summary

Two distinct mechanisms of laser damage and ablation of small particles are clearly delineated in the present study. A high compressive pressure builds up in the irradiated particles under conditions of inertially confined photothermal (or photochemical [24]) expansion. The results from the simulation clearly demonstrate that the ablation process driven by the dynamics of the laser-induced pressure relaxation is energetically more efficient then vaporization. A relatively few interactions need to be broken in order for the particle to spall into large chunks of material and ablation can occur with energy densities significantly less then the cohesive energy, 0.31 eV for the 2D system. Moreover, the focusing of the pressure wave in the center of the particle leads to the additional reduction of the threshold energy (and the corresponding initial pressure) for the laser induced mechanical damage to the particle [4] as compared with the case of plane wave interaction with a free surface [25]. With increasing pulse duration the pressure buildup decreases and the energy density needed to initiate ablation rises to the threshold for thermal explosion. At this point the system has sufficient time to mechanically respond to the laser heating and the explosive thermal decomposition of the irradiated particle is purely due to overheating.

The difference in the ablation mechanisms leads to the difference in the final characteristics of the ablation products. With shorter laser pulses, at fluences just above the ablation threshold, the irradiated particle decomposes into a small number of large cool clusters. Increase of the laser fluence above the ablation threshold results in disintegration into smaller clusters and leads to the gradual increase of the fraction of individual molecules as shown in Fig. 1a–d. With longer pulses, when ablation is due to the thermal explosion, single molecules constitute a significant fraction of the ablation products at the threshold. This fluence and pulse width dependence of the nature of the ablation products has immediate implications for mass spectrometry experiments which characterize atmospheric aerosol particles [7,8] as well as for the analysis of the laser beam propagation in a dispersed medium such as fog or a cloud [10,11].

The results from the simulation can also help in understanding the ablation and damage processes in tissue in the case of inhomogeneous absorption of laser energy. A detailed experimental study [1,5] performed with infra-red and visible lasers points to a strong dependence on pulse duration of the threshold energy for producing a minimal visible damage in the retina. In particular, an apparent drop in the threshold energy detected for pulses shorter than 100 ps is proposed to be due to the onset of a photomechanical mechanism of damage to the absorbing submicron melanin granules [1,3–5]. The results of our microscopic computer simulations do support this hypothesis. In agreement with experimental observations, the damage to an individual submicron particle occurs at a lower energy deposition for shorter pulses. Moreover, in the case of short-pulse irradiation the deposited energy effectively transfers to the energy of radial expansion of the ablation products. The coupling of the expansion energy to the surrounding medium is likely to be responsible for the energetically efficient regime of the short-pulse laser ablation of the tissue. The irreversible damage to the particles due to the focusing of the tensile pressure reflected from the surface is found to take place in the sub-threshold irradiation regime. The damage, thus, can be accumulated in a multipulse irradiation regime. The simulation results present here lay the foundation for future work in which the effects of the media [26] and multiple particles are examined.

[4] A threshold energy of $\sim 0.15$ eV has been reported in Ref. [14] for laser-induced damage and ablation of the 2D organic solid with the same parameters of intermolecular interaction as used in the present study.

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