

## Impact disintegration of submicron cluster – molecular dynamics simulation

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**Introduction.** The widely diverse world of clusters is populated by species of a wide range of sizes – from several atoms to millions of molecules. Here we consider the largest ones – micron/sub-micron size clusters. Such clusters have found an analytical application in a novel ionization method – Impact Desolvation of Electrosprayed Clusters (IDEC) [1]. The charged clusters are produced by electrospray of an analyte solution in vacuum. They are subsequently accelerated through a potential drop of several kV and directed towards a solid target. The collision with the target surface is believed to lead to explosion of the cluster and release of analyte ions, which can be subsequently extracted and analyzed.

The advancement and optimization of this promising ionization method could be facilitated by a better understanding of the impact phenomenon and the conditions that analyte molecules experience during the cluster disintegration. In the present study the molecular dynamics simulation technique is used to obtain a molecular-level picture of the cluster impact phenomenon. The conclusions from the simulations are related to the experimental data [1] and to the predictions from an analytical shock wave model [2].

**Computational method.** A molecular dynamics (MD) simulation technique is used in this work to obtain detailed information on the processes involved in cluster impact desolvation under experimental conditions realized in IDEC. In order to expand the length- and time- scales of the simulations up to the ones comparable to the experimental conditions, we apply the breathing sphere model [3,4], which describes the cluster material with molecular rather than atomic resolution. The parameters of inter-particle interaction in the breathing sphere model are chosen to reproduce the properties of water and glycerol clusters used in the IDEC experiments, in particular the velocity of sound. The first simulations were performed for clusters of up to 300,000 constituent particles, impacting a rigid target with an incident velocity of 500-2000 m/s, below and above the sound velocity, respectively. A visual picture of the cluster impact can be correlated with the evolution of the physical parameters of the involved processes (the energy and pressure evolution during the impact) and final characteristics of the ejected species (velocity and angular distributions).

**Results and Discussion.** Simulations performed for 2000 m/s impact velocity (super-sonic in water environment) clearly demonstrate that the formation and propagation of an intra-cluster shock wave is the dominant process that defines the character of the initial cluster energy redistribution, Fig.1. As the shock wave propagates from the impact area through the cluster, the shock-compressed region near the surface relaxes by expansion in the lateral directions. The expansion provides an efficient channel of energy transfer from the kinetic energy in the impact direction (red line in Fig. 2) to the energy of expansion parallel to the surface plane (blue line in fig. 2). By the end of the simulation, the energy of the lateral expansion corresponds to ~80% of the total impact energy.

Although the system is far from thermal equilibrium at any time, we can use the tangential component of the molecular velocities to estimate the “thermal contribution” to the total kinetic energy of the system. The maximum “thermal K.E.” reaches ~ 11% of the total impact energy during the impact, but quickly drops to ~ 1.2% as a result of cooling due to the expansion of the cluster material, Fig. 3. Nevertheless, the temperature increase is sufficient for nearly complete vaporization of a layer of cluster material adjacent to the surface. The expansion of the

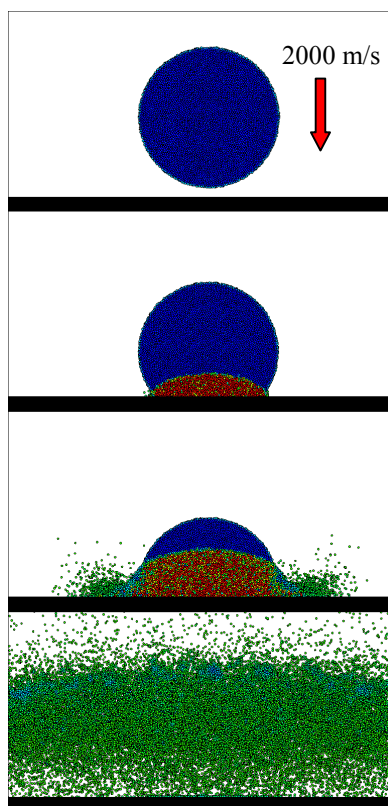


Fig. 1. Snapshots from MD simulations of impact disintegration of sub-micron clusters for impact velocity of 2000 m/s. The color shows the changing potential energy of molecules (red color corresponds to the molecules compressed by the shock wave).

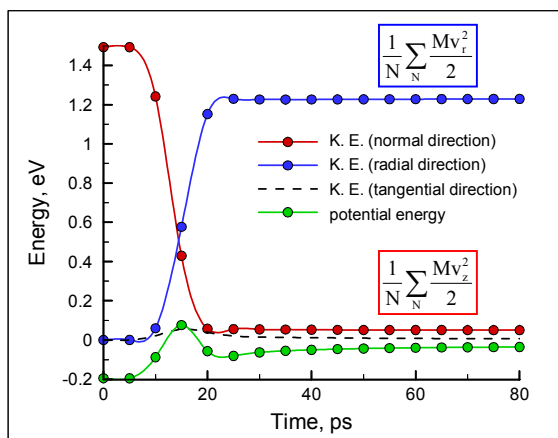


Fig. 2. Impact energy redistribution.

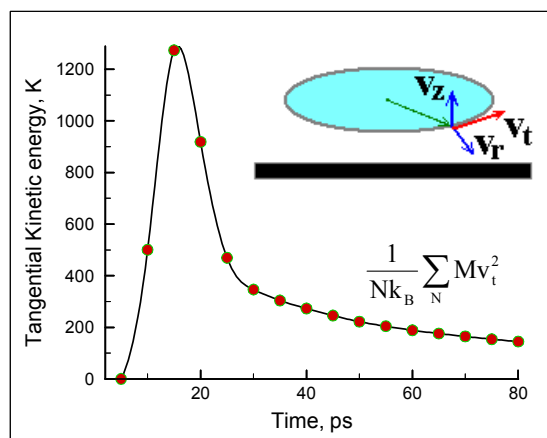


Fig. 3. Average "temperature" of the cluster material

vapor propels the rest of the cluster material away from the target surface. The region of the cluster that is more distant from the impact area remains significantly colder, does not undergo complete vaporization, and produces relatively large secondary molecular clusters. One can speculate that large analyte molecules (e.g. oligonucleotides) located in this part of the cluster are likely to survive the impact and contribute to the mass spectrometry signal. High, up to 3000 m/s, maximum velocities of the lateral expansion and moderate, hundreds of m/s, velocities in the direction normal to the surface result in a broad angular distribution of the ejected species.

The results for the 500 m/s impact (sub-sonic in water environment) reveal a rather different picture, Fig. 4. The cluster compression at the impact does not lead to shock wave formation. Rather, the pressure is released by an acoustic wave propagating back and forth within the cluster and by spreading out the cluster material on the surface. The cluster does not lose its integrity and a relatively small number of single molecules and small clusters is ejected. The analytes are unlikely to be ejected and desolvated in this regime. The existence of a threshold acceleration voltage for detection of the analyte ion signal in IDEC can be related to the strong dependence of the impact-induced processes on the cluster velocity.

**Summary and Future Work.** Initial results of the presented molecular-level computer simulation study demonstrate the ability of the technique to provide insight into microscopic mechanisms of the cluster impact desolvation phenomenon. For supersonic impact velocities, simulations predict the formation of an intra-cluster shock wave leading to the cluster disintegration and efficient transfer of the impact energy into the energy of the lateral expansion of cluster material. Only a small fraction of the impact energy transfers into heat, allowing for survival of relatively large molecular clusters. We can speculate that fragile biomolecules can also survive the impact desolvation.

Realistic representation of metal or glycerol target, incorporation of large bioorganic molecules into clusters, a more detailed investigation of the velocity and angular distributions of the secondary clusters and molecules are among the directions for further mechanistic investigation of IDEC ionization technique.

## References

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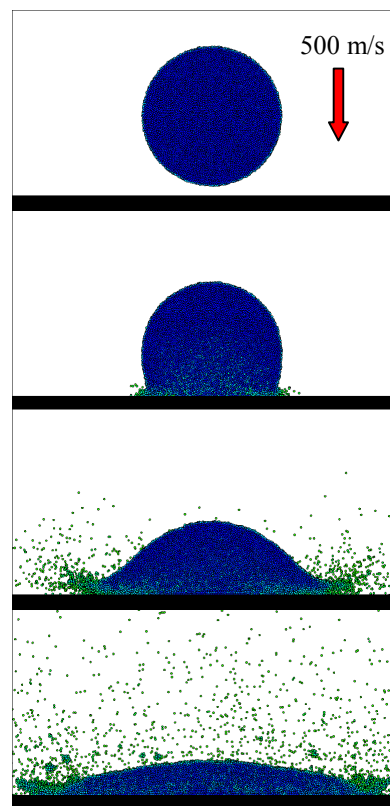


Fig. 4. Snapshots from MD simulations for impact velocity of 500 m/s. The color scheme is the same as in Fig. 1.