

Larger Cluster Ion Impact Phenomena

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I. Introduction

This review will be concerned primarily with larger clusters that have been used in surface-impact studies and with energy-transfer processes in cluster ion impacts. The term larger clusters is used to distinguish the species of interest from dimers, trimers, and similar species with properties that are more closely identified with smaller molecular systems rather than microparticulates. There are however upper limits to the size of the larger clusters considered in this review. Particulates such as aerosol beams detectable with conventional light scattering techniques will not be reviewed except in a few cases in which they were used as hypervelocity projectiles. A brief review of techniques of generation, separation, identification, and detection of cluster ions will also be included. Relevant experiments dealing with the formation of smaller cluster ions and studies of their properties will not be examined because they will be covered in more detail in separate reports in this collection of articles on clusters. Inasmuch as experimental studies with larger clusters is a relatively new area of research, some attempt will be made in this review to look forward to possible applications and future work.

II. Impact Processes

The problem of understanding of impact processes attracted the attention of Galileo¹ and Newton.² An historical account of the scientific study of impact phenomena can be found in the *Handbuch der Physik*.³ The initial concept of impact as a process based on the interaction of rigid bodies was presented by Galileo with some confusion between the ideas of momentum and energy. This is not surprising because the difference between momentum and energy was defined after Galileo's death. Impact processes can take place on a microscopic molecular scale or with macroscopic objects. The classical theory of the impact of macroscopic rigid bodies assumes negligible amounts of translational energy of the colliding bodies converted into vibrational energy and does not account for local deformations at the contact point. This is an adequate treatment for the collisions of spheres or of a sphere with a large rigid



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mass.⁴ With high velocity impact processes deformation at contact points and energy conversion to internal degrees of freedom can not be neglected.

Impacts are generally characterized as dynamic processes as opposed to static loading of systems with

sufficient time for the establishment of equilibrium between objects in contact. The process of energy transfer under impact conditions has been successfully treated in the case of atom-ion collision processes when boundary conditions of force and or velocity are prescribed. The interaction between atomic projectiles and solid surfaces has been successfully described in terms of models that idealize interactions as a sequence of two-body collisions.⁵ The problem of macroscopic impact processes on solid targets, particularly processes that involve penetration or perforation of targets, has long been a subject of very practical interest. A large body of empirical knowledge has been collected⁶ but the complicated mechanisms encountered in these processes have not yet been completely explained. With impact velocities in excess of normal ordinance velocities or in the hypervelocity region of more than a few km/s, fusion or vaporization of target and projectile materials takes place with crater or hole formation. The energy-transfer process under these circumstances can be interpreted with the aid of a hydrodynamic model.⁷ Cluster ion projectiles are of potential value in the study of impact processes because they provide a means of investigating the transition between energy transfer from atomic and molecular species and bulk particulates or even ballistic projectiles. It is possible with smaller clusters, measured on the scale of dust particles and micrometeorites, to generate projectiles with higher velocities than the fastest bulk projectiles. In so doing, extremely high-energy densities can be generated in assemblies of more than thousands of atoms. Consequently cluster ions can be used to investigate the properties of assemblies of atoms that have been subjected to transient pressure measured in units of megabars or tens of megabars and with transient "translational temperatures" that are in excess of millions of degrees.

III. Generation of Cluster Ions

Cluster ions and neutral clusters can be generated in jet or nozzle expansions. The physics of neutral gas expansion processes has been examined in some detail by Hagena and Obert⁸ and reviewed more recently by Hagena.⁹ Hagena and Obert experimentally investigated the preparation of neutral clusters of Ne, Ar, Kr, Xe, N₂, and CO₂ containing between 100 and 10⁴ molecules/cluster.

They found that cluster sizes with inert gas expansions were determined to a large extent by collision frequencies in the expanding jet and sticking probabilities of monomers on growing clusters. Details of gas dynamics of expanding nozzle flows are presented concisely and completely in Hagena's 1981 *Surface Science* paper. In addition condensation theory is briefly reviewed along with scaling laws for cluster formation which deal with the kinetics of cluster growth as a function of source geometry and source conditions.

Large cluster ions can be generated either by the ionization of neutral clusters produced by free jet or nozzle expansion, by the direct expansion of ionized gases with the growth of cluster ions in ion-molecule condensation reactions, or by electrospray mass spectroscopy. Large clusters containing up to roughly 100 molecules have been produced by the ion or atom surface bombardment techniques.¹⁰ The growth of

cluster ions in expanding gases has been used for many years as a means of identification of mass, charge, and velocity of nuclear particles in cloud chambers.¹¹

An example of the technique of generation of cluster ion beams by electron impact on neutral beams generated by nozzle expansion techniques is found in the work of Henkes et al.¹² Ionization of neutral cluster beams was brought about by a multiple electron emission filament ion source which gave electron currents up to 600 mA. Hydrogen particle flux into the ionizer was determined by measurement of the mass flux into an ionization gauge. Up to 80% of the clusters containing a flux of about 6×10^{16} particles s⁻¹ were ionized and extracted with voltages up to 15 keV. The resultant ion clusters had a mass distribution which peaked around 1500. Henkes and co-workers concluded that multiply charged ions could be formed in the electron impact ionization process. Mutual repulsion of charges was sufficient to fragment the very weakly bound hydrogen cluster ions. The total extracted ion current of roughly 10 μ A was divided over a mass range which extended from about 450 to 2500. The use of electron impact ionization for neutral beam diagnostics has raised questions on the validity of correlations of ion mass distributions with precursor neutral mass distributions. With very weakly bound cluster systems such as hydrogen or inert gas neutral clusters, Franck-Condon ionization mechanisms could give rise to broad and degraded mass distributions. With strongly bonded systems such as neutral metal clusters, electron impact excitation may be distributed over many internal degrees of freedom with much slower decomposition rates or longer cluster ion lifetimes. Many cluster applications do not require lifetimes of excited cluster ions longer than milliseconds. Mass analysis and detection and cluster impact studies are easily carried out during these time periods.

An alternative approach to the generation of larger cluster ions is the direct expansion of ionized gas from a high-pressure ion source. This technique was used by Searcy and Fenn¹³ for the generation of water cluster ions containing up to 28 water molecules. Weakly ionized mixtures of water and inert carrier gases were expanded into a high vacuum through an aperture and skimmer with the condensation of protonated water cluster ions. Cluster formation around seed ions takes place in a "bath" of carrier gas in local thermodynamic equilibrium corresponding to the state predicted for expansion from a specified set of initial conditions, stagnation temperature, pressure, and nozzle geometry. Searcy and Fenn correctly concluded that cluster ions were not in equilibrium with the bath gas because of a time lag in the collisional deactivation of excited clusters formed by condensation reactions. They found mass distributions shifted significantly to large cluster sizes from initial equilibrium distributions expected inside the ion source. Distinction must be made between free jet expansion of gases emerging from a high-pressure mass spectrometer ion source in which pressure gradients are maintained which minimize clustering in the low-pressure regions of the mass spectrometer, and supersonic experiments designed to produce clusters around seeds generated in an ion source. Small clusters generated in mass spectrometer ion sources under carefully controlled conditions can

be prepared with mass distributions that closely approximate equilibrium conditions if sufficient care is taken to reduce the probability of condensation or collisional dissociation in the steep pressure gradient beyond or in the source aperture. The use of high-pressure mass spectrometer ion source techniques for small cluster preparation will be discussed in a separate review by Castleman.¹⁴ During the early stages of cluster ion growth in the jet or nozzle expansion process, collision frequencies will be determined by factors similar to those operative in neutral gas cluster growth. Number densities of neutral gas molecules available for clustering and for collisional deactivation are determined by nozzle geometry and source stagnation conditions. Cross sections for associative collisions are larger than for neutral cluster growth because of the long range ion-dipole or ion-induced dipole interactions of the cluster ion and monomer gas in the expanding jet. A linear dependence of median cluster ion distribution on concentration of water vapor in nitrogen carrier gas was observed in the authors' laboratory. The formation of protonated water clusters¹⁵ with mass up to 11 000 was found with water concentrations ranging from 1 to 3% in nitrogen carrier gas. The linear dependence of cluster size on reagent concentration was explained by noting that the ion-molecule collision cross section for cluster growth eclipsed "hard sphere" cross sections for protonated clusters with the relatively low velocity cold protonated ions and water molecules in the expanding gas. The rate controlling process for cluster ion growth in carrier gases becomes the associative collision rate of monomers with clusters above a critical size in an expanding carrier gas cooled below a critical temperature. Lifetimes of excited clusters can be calculated using classical unimolecular rate theory.¹⁶ If one takes the threshold energy for decomposition of an excited cluster as equal to the heat of monomer condensation, clusters containing in excess of about 6-10 atoms will have sufficient numbers of internal degrees of freedom to distribute the energy of excitation associated with the condensation of a monomer and survive for ample time periods for collisional deactivation. A problem in the estimation of cluster size produced in expansion process involving weakly ionized gases is the distinction between the unimolecular decomposition of excited cluster ions and inefficient associative collisions. Experimental studies on water¹⁵ cluster formation in weakly ionized mixtures of water and carrier gas support the conclusion that protonated water ion-molecule collisions are efficient with sticking probabilities close to unity. Cluster sizes produced by nozzle expansion of ionized water in carrier gases can be quantitatively correlated with the mass of the inert carrier gases. Under identical ion source conditions protonated water clusters produced with He carrier were found to be about $1/4$ the size of those made with Ne and the latter were roughly $1/2$ the size of those made with Ar. Thus one can predict size distributions of cluster ions if one knows the geometry, stagnation conditions, and concentration of reagent gases in the ion source. Careful examination of the effect of the relative velocities of the carrier gases on the residence time of the reactive species in the expanding jet and on the ion molecule associative collision cross sections gives a remarkably good correlation between observed and

predicted cluster size distributions.

Electrospray mass spectroscopy^{17,18} and the technique of charging of dust particles by bringing them into contact with an ionizing electrode¹⁹ are techniques for the generation of charged particulates from the condensed phase and may be viewed as methods for generation of much larger seed ions for either direct injection into high vacuum or additional growth in gas expansion processes. These techniques have interesting potential for generation of high molecular weight ionic species but offer somewhat less opportunity for control of the product cluster ion distribution in the preparation of beams of cluster ions.

Some mention of the intensities of cluster ion beams that can be generated by expansion of ionized gases should be made. As noted above Henkes, Hoffman, and Mikosch developed an ionizer which generated positive ions from hydrogen neutral clusters with an efficiency of up to 80% and generated ion currents as high as 45 μA with particle currents for clusters containing 4000 atoms as high as 150 mA. These ion beams were made up of ions with very broad mass distributions with widths at half height of the order of 2000 mass units. Much narrower beam mass distributions are obtained with weakly ionized plasma expansion techniques. The limiting factor in beam intensity under these conditions is determined by space charge considerations. Child's law giving the space charge limit of current, I , as a function of ion accelerating voltage, V , and mass to charge ratio, m/e , can be recast in the following form,²⁰

$$I = 1.7 \cdot 10^{-8} \frac{V^{3/2}}{(m/e)^{1/2}} \quad (1)$$

For a beam of $m/e = 10\,000$ with 30 V kinetic energy, $I = 2.8 \times 10^{-8}$ A, the particle beam current with a cluster of mass 10,000 made up of water molecules is 15.5 μA . The practical problem with cluster beam intensity is that increasing extraction voltages to achieve higher beam intensities tends to increase the number of dissociative collisions by providing more kinetic energy to the emerging gaseous ions. The higher velocity emerging ions have smaller associative collision cross sections and less time for growth in the expanding gas. Thus higher extraction voltages tend to produce smaller clusters. If larger nozzles are used for expansion to obtain longer effective path lengths for associative collision reactions, then the limits on extraction voltage are determined by breakdown between extraction electrodes and the nozzle or lens elements over which the extraction voltage is applied. The problems encountered in extraction of high-intensity cluster beams are similar to those encountered in high-intensity atomic ion sources. The basic difference between the cluster and atomic systems is in the effect of high-temperature plasmas and high-velocity extraction techniques on the formation and survival of the cluster ions. Nevertheless cluster ion currents of the order of microamperes in intensity with relatively narrow mass distribution containing many hundreds of atoms can be generated with protonated water molecules or negatively charged assemblies of water molecules from relatively simple ion sources. Lower intensity beams of clusters of hydrogen ions have been generated from sources operated at temperatures of the order of 20 K.

IV. Mass Analysis of Cluster Ions

The problems encountered in the mass analysis and detection of cluster ions are essentially those of high molecular weight mass spectrometry with the possible added complication of dealing with ions that are in some cases generated with rather large kinetic energy distributions. Dole^{17,21} and his co-workers in their pioneering studies on the mass spectra of polymers generated in an electrospray ion source used retarding potentials to establish the kinetic energy of ions generated in seeded molecular beams. They could not use time of flight techniques because they found that secondary electron multipliers, with the time response required for TOF mass analysis, were not sensitive macroion detectors. Dilute solutions of polystyrene, (approximately 50 000 molecular weight), in benzene-acetone solvent were electrosprayed into a chamber of dry nitrogen at atmospheric pressure. This chamber was designed to facilitate evaporation of solvent from polystyrene ions which were introduced into a high vacuum system in the nitrogen carrier gas by expansion through a differentially pumped nozzle and skimmer. Ions were detected using a vibrating reed electrometer capable of measuring the ion currents, of the order of 10^{-14} A. The more sensitive and rapid detection techniques of electron multiplication were unsuccessful because of the very low velocity of these high molecular weight ions.

The technique that would appear to be most suitable for determination of masses of high molecular weight cluster ions, if ion detection problems were solved, is time of flight mass analysis. Time of flight techniques designed to identify metal cluster ions with mass up to 20 000 with a resolution of about 1% have been studied by Recknagel and co-workers in Konstanz.²² Investigation of the mass spectra of clusters of N_2O with their TOF technique showed unit resolution between clusters containing 36 and 37 molecules of nitrous oxide but no evidence of resolution in the vicinity of clusters containing about 100 molecules at the low end of distributions peaking between 300 and 400 molecules.²³ Moser²⁴ developed a pulsed deflection, time of flight technique used for the mass analysis of clusters, containing up to 10^6 atoms of hydrogen/cluster, accelerated to up to 650 keV kinetic energy. Moser noted that analysis of these extremely energetic cluster ions having energies of hundreds of keV excludes the use of magnetic analyzers, quadrupole rf-dc resonant systems, or gated grids that intercept ion beams and chop them into bunches. Formation of ion bunches of energetic beams with gated grids is difficult because the generation of high voltage pulses with rise times on the order of 50 ns is not possible. Ion deflection TOF can be achieved with voltages much lower than beam energies applied to a deflecting field. The technique described by Moser has been used at Lyon and Karlsruhe for mass analysis of energetic cluster ions with m/e values between 3×10^4 to 5×10^5 atoms/charge. Timing pulses consisted of turning off the deflection voltage of 1–10 keV for 50 ns; resolution was about 1 part in 5. Moser's interesting observation that with these larger cluster ions an increase in ionizing electron current from 15 to 29 mA produced a decrease in mean value of atoms/charge from 1.3×10^5 to 8×10^4 led to the conclusion that multiple charging of these ions was possible without

appreciable fragmentation. Fragmentation was observed with electron impact on smaller cluster ions by Henkes and co-workers but in the case of Moser's observations the mass decrease was more reasonably ascribed to sequential electron impact interactions increasing the cluster ion charge. The investigation of multiple charging and charge changing processes with large cluster ions is an area of interesting potential for future work. Time of flight mass spectrometry of high molecular weight species that are relatively strongly bonded chemically has been pioneered by MacFarlane and co-workers.²⁵ The development of fission fragment mass spectroscopy for structural analysis of high molecular weight fragile molecules, while not a technique directly related to cluster ion mass analysis, demonstrates that TOF measurements with $m/\Delta m$ of up to 2000 can be achieved when ions from well-defined volume elements can be generated with distributions of kinetic energy less than 10 V within time periods of less than 5 ns.

High molecular weight mass analysis using large magnetic analyzers have been the subject of some considerable effort. Derrick²⁶ has constructed a large magnetic analyzer capable of mass analysis up to m/e values of 20 000. A very high field, 2.3 tesla, magnetic system has been used by Campana and co-workers¹⁰ to obtain resolved mass spectra of alkali iodide clusters with m/e greater than 25 000. These ions were produced by ion bombardment of solids, a technique that has been used for the production of smaller clusters. The double focusing mass analytical technique used by Campana and co-workers has the advantage of providing high resolution for ion beams with broad kinetic energy distributions with some sacrifice of ion transmission. Fourier transform ICR techniques show promise of extremely high resolution^{27,28,29} of high molecular weight ions. The practical upper limits of mass range in both the magnetic analysis and FTICR techniques have so far not been demonstrated equal to what appears to be achievable with time of flight or quadrupole mass spectrometer. The mass range of a quadrupole analyzer is determined by the resonant conditions for ion transmission that must be established by the radio frequency and dc fields applied to the quadrupole rods. The use of a low-frequency 292-kHz power supply with $1/4$ inch diameter rods provides a quadrupole system that will transmit ions with m/e values close to 200 000. Thus a device approximately 20 cm in path length can be used to transmit and mass analyze large cluster ions with a resolution of better than 1% in mass with relatively high transmission efficiency. Electrosprayed ions of bismuth and lead were analyzed over a decade ago using a quadrupole mass analyzer.³⁰ This work was motivated by an interest in the development of electrostatic thrusters for space vehicles. Quadrupole analyzers are not particularly useful for the preparation of high current density resolved ion beams because they require relatively low-velocity ions. Beams accelerated to minimize space charge limitations on current density can pass through the analyzer without resolution.

V. Identification and Detection of Cluster Ions

The problem of large cluster ion detection arises from the relatively low velocity of heavy species accelerated

with usually less than 10 or 20 keV. Dole and co-workers found secondary electron multipliers insensitive to 50 000 molecular weight polymer ions with kinetic energy of the order of a few hundred eV or less. Much larger particles with higher charge can be detected by measurement of the voltage induced on coaxial cylinders in a drift tube. Induced voltage is directly proportional to particle charge and inversely proportional to the capacity of the system. Shelton et al.³¹ used the technique of measuring the velocity of heavy, highly charged particles passing through a pair of coaxial cylinders along with a measurement of induced charge on these cylinders to determine m/e of species accelerated with known voltages. Mass distributions of micrometer-sized particles used in simulated micrometeorite impact studies were assayed.

Particles too large to be accelerated conveniently to energies suitable for efficient secondary electron detection can be detected by decomposition into smaller species which are analyzed by standard techniques. Stoffel and Lagergren³² showed that ion current produced by impact of alkali metal containing particulates can be correlated with the cube of particle size. Particulates ranging from .076 to .114 μm were introduced into a high-vacuum system and collided with a hot rhenium filament. The resulting positive ion current was calibrated with particulates of known size and used to identify airborne materials of the same composition. Myers and Fite³³ had previously demonstrated the more efficient detection of high molecular weight species by use of grids on which degradative impact took place prior to electron multiplier detection. Haberland and Winterer³⁴ have used the Cu-Be converter surface of a secondary electron multiplier to collisionally dissociate large Van der Waals neon and argon cluster ions to facilitate multiplier detection of smaller ionic species on the second dynode of the multiplier.

The poor efficiency of secondary electron ejection by slow massive ions is primarily the result of inefficient energy transfer between atoms and electrons in impacts on and penetrations of surfaces. Kinetic emission of secondary electrons by atomic ion impact on solid surfaces takes place with threshold velocities of roughly 5×10^6 cm/s.³⁵ Sternglass³⁶ developed a theoretical model for secondary electron emission from surfaces bombarded by atomic ions at velocities of order 10^8 cm/s which gave the electron yield proportional to the rate of energy loss of the incident particle. The rate of energy loss must be qualified as the rate of energy loss to electronic degrees of freedom in the target surface or the velocity dependent electronic stopping power. The relationship between the average secondary electron yield on particle impact and electronic stopping power, $(dE/dx)_e$, for ions with velocity of order 10^7 cm/s has been pointed out by Schram et al.³⁷ and by Dietz and Sheffield.³⁸ Thus one can calculate the average number of secondary electrons per impact on a specific target surface for the number and kind of atoms in a projectile of known velocity from estimates of low-velocity stopping power. Representative examples of calculating secondary electron yields would be ref 35, work from our laboratory,^{39a} and the work of Holmen et al.^{39b} Attempts, with no success, to look for energy conversion in thermal spikes that would give enhanced electron yields with low velocity cluster ions were made

by Hofer and Thum⁴⁰ with vanadium clusters containing up to nine atoms. Investigations in the author's laboratory with much larger water cluster ions⁴¹ also showed no evidence for secondary electron emission above values calculated from a simple theoretical model based on additivity of contributions from electronic stopping of the respective constituent cluster atoms. Experimental methods for determining the distribution of electrons produced by ion impact using solid state detectors were developed by Dietz and Sheffield.³⁸ Delaney and Walton⁴² recognized the advantage of amplification of the energy of electrons rather than their number in the determination of secondary electron yields. The detection system developed by Dietz and Sheffield differs from the one developed by Daly⁴³ in that secondary electrons produced by projectile impact on a converter electrode are taken into a solid-state detector after acceleration to a suitable energy. The solid-state detector measures the total energy in the initial electron pulse produced at the converter. With the Daly detector, electrons are eventually subjected to numerical rather than energy amplification in a photo or secondary electron amplifier. The statistics of this process tends to smear out the initial distribution produced on the converter electrode. The effective loss of information in the multistage device makes a less precise and more difficult quantitative correlation between the charge, composition, and velocity of the projectile with the secondary electron pulse distribution. With larger relatively weakly bound cluster ions, secondary electron pulse distributions can serve to identify collision-induced dissociations in the gas phase or by ions grazing on lenses in flight between mass analysis and targets or detectors. A final nontrivial advantage of the Dietz detector is the ability to discriminate against one or two electron noise pulses from signals that can range upwards from several to several hundred electrons per impact for polyatomic cluster ions of modest size.

VI. Macroion Impact Processes

Interest in impact of hypervelocity macroions was stimulated nearly 2 decades ago by space research and questions dealing with the impact of micrometeorites on space vehicles. The techniques of hypervelocity accelerators have been reviewed by Cable.⁴⁴ Gas gun accelerators and electromagnetic gun accelerators are described which are capable of accelerating particles with velocities up to roughly 10 km/s. Particles with masses as large as 0.08 gms were accelerated to velocities as high as 16.5 km/s using an inhibited shaped charge explosive accelerator. The highest velocities reported were achieved with much smaller particles, glass spheres, with plasma drag accelerators. With plasmas generated by exploding lithium wires, glass spheres weighing 1.46×10^{-7} gms were accelerated to 20 km/s and with hydrogen plasmas generated by the discharge of a capacitor bank into an arc chamber filled with hydrogen, glass spheres weighing 5.9×10^{-8} gms were accelerated to a velocity of 30 km/s. Somewhat smaller particles can be accelerated to velocities of the same order of magnitude using electrostatic acceleration in a high-vacuum system. With both plasma drag acceleration and electrostatic acceleration, macroions are generated and accelerated to hypervelocities.

The inverse relation between particle size and maximum acceleration velocity in practical single stage acceleration and the limit set on maximum particle velocity determined by forces binding atoms within the particle to lattice sites was pointed out by Shelton et al.³¹ Particle velocity in single stage electrostatic acceleration is given by the relation

$$v = [6VE\epsilon_0/r\rho]^{1/2}$$

where V is the potential drop, E is the electrostatic field at the surface of the spherical particle of radius r and density ρ and ϵ_0 the permittivity of free space, $(1/36\pi) \times 10^{-9}$ F/m. For iron particles the maximum value of E is about 2×10^{10} V/m. Consequently a particle with a radius of 0.25μ can be accelerated through a potential drop of 1 meV to a velocity of 2.3×10^4 m/s. Very much higher velocities are in principle possible if multistage acceleration techniques are used. Even with very weakly bonded Van der Waals cluster ions there is no mechanism for the conversion of translational energy to internal degrees of freedom in the cluster if the cluster ion trajectory is free of collisions. Shelton and co-workers concluded that electrostatic acceleration had significant advantages over ballistic acceleration. These workers used a 100-keV potential to accelerate small iron particles to velocities of between 1 and 2 km/s. Friichtenicht¹⁹ extended this technique to much higher velocities using a 2-meV Van de Graaf accelerator. Dietzel, Neukum, and Rauser⁴⁵ used the technique of Van de Graaf acceleration of iron particles to investigate simulated micrometeorite impacts on metal targets. Their goal was to obtain information useful in understanding the process of crater formation and to develop techniques for the detection and analysis of dust particles using charge sensitive detectors on satellites and rockets. Particles ranging in mass from 10^{-15} gms to 5×10^{-10} gms were accelerated to velocities between 0.2 and 40 km/s. Targets for impact were polished plates of Al, Cu, Cd, Ag, Ta, and W metals. Masses were determined by measurement of particle charge and velocity after acceleration through a known potential drop. Particle masses could be selected using a velocity window which served as a mass or velocity filter. With velocities less than 0.5 km/s semielastic reflection of particles was observed. Crater formation was detected at velocities above 0.8 km/s. Electron microprobe techniques were used to examine the distribution of projectile matter in the craters. Between 1 and 1.5 km/s the crater is formed with the projectile lying in it, for the most part intact. At higher velocities, projectiles deform plastically into an "approximately coherent layer" inside the crater. Between 1 and 8 km/s incident velocity, a good proportionality was found between the charge released on impact and particle mass and velocity. Dietzel et al. discussed impact cratering and ionization in terms of shock effects by applying a hydrodynamic model using Rankine-Hugoniot theory. Their treatment followed models developed by Opik⁴⁶ and Zeldovich et al.⁴⁷ The one-dimensional Rankine-Hugoniot theory is best described in terms of a P - V plot of material undergoing a shock on impact, Figure 1. The material starts at an initial density or volume ρ_0 or V_0 and is compressed to a pressure P_H by a shock wave. This initial compression is nonisentropic but the release process is isentropic.

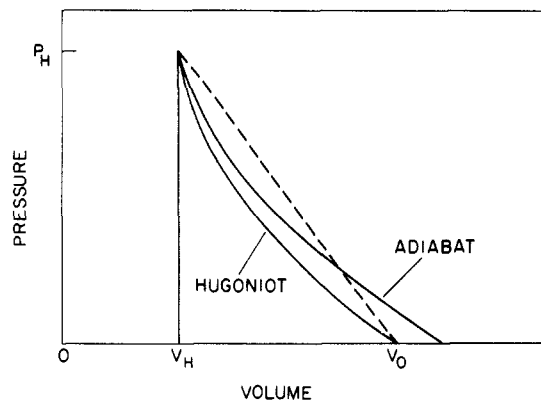


Figure 1. Rankine-Hugoniot pressure-volume plot. A target material is shocked by projectile impact from initial volume V_0 to shocked volume V_H and pressure P_H . The initial shocking process takes place along the Hugoniot, while the cooling takes place along the adiabat.

The entropy of the impacted material is initially increased, and the material in its final state is heated. The specific internal energy of the shock compressed material is equal to the area of the dashed triangle $P_H(V_0 - V_H)/2$, while the energy that is returned to the material in the P - V work on expansion is under the adiabat. This area is less than the area under the triangle and the difference is proportional to the residual heat left in the impacted element. As the shock strength increases the excess entropy increases rapidly and melting or vaporization can occur. McQueen and Marsh⁴⁸ have calculated values of shock pressure sufficient to cause melting for a variety of materials. Deitzel et al. found that with iron projectiles and heavy metal targets, W or Au, a relatively high amount of projectile energy (up to 40%) can be trapped by the projectile as an internal energy but a much smaller amount is trapped with targets such as basalt or Al. The relative masses of target and projectile atoms play a significant role in the partition of energy predicted by the Rankine-Hugoniot theory. The theoretical treatment requires equation of state data that is applicable to the transient conditions of high temperature and pressure of the shock process. With a known mass and velocity projectile, the shock and flow velocities of the respective target and projectile systems are determined from conservation laws, and the respective material constants from equation of state data. The partition of energy between the projectile and target can be calculated in the form of kinetic and internal energy. The problems encountered in the application of a hydrodynamic model for calculation of energy transfer on cluster impact on the hypervelocity region go beyond uncertainties with respect to very high-temperature equation of state data. The assumption of thermodynamic equilibrium for processes which occur on time scales of picoseconds or less may be a reasonable approximation if the contributions of electronic degrees of freedom to the thermodynamic properties of the system are considered small or can be neglected. A zeroth order test of equilibration of projectile and target translational energy and electronic energy can be made by considering the "temperature" of the iron projectile when it is plastically deformed in the crater after impact at about 5 km/s, and the observed yield of charge produced in impacts at this velocity on W targets. For iron projectiles with mass of about 10^{-11} gms, particles

were deformed on impact to a thickness that was roughly 0.1 of the original particle diameter and the charge per particle released on impact was determined to be about 2×10^{-13} C. Roughly 10^6 electrons were emitted from a surface area of approximately 10^{-7} cm². With projectile internal energy after impact the order of 10^{11} ergs/g, the temperature of the plastically deformed iron deposit is estimated at 20 000 K. One then assumes that this temperature is maintained for no longer than 10^{-12} seconds in the iron disc flattened to an area of 10^{-7} cm² and uses the Richardson equation⁴⁹

$$I = AT^2 e^{-\chi/kT}$$

where I is the thermionic current, A , a constant, and χ , the work function of the emitting surface, to calculate the number of electrons evaporated from this area at this temperature during this time. With a value of 4.75 eV for the work function of iron, and the constant in the Richardson equation taken at 60 A/cm²/deg², the number of electrons emitted is estimated at about 4×10^9 or about 1000 times that observed coming from the impact area.

The electron emission from the heated W surface has not been considered nor has the electron emission from the surface during the time period more than 10^{-12} seconds after impact. The electron emission expected from a surface element heated to the estimated temperature generated by particle impact is clearly orders of magnitude larger than the observed charge emission. Questions may be raised concerning the validity of using a value of the thermionic work function of iron, measured at much lower temperatures, for a calculation of emission at 20 000 K. At high temperatures the rate of thermionic electron emission is determined for the most part by the preexponential term in the rate equation. The result is consistent with the concept that many collisions are required before the projectile translational energy can be equilibrated with electrons. The term temperature in these systems is interpreted as primarily translational energy density. More extensive studies of plasma yields, ion and electron emission with hypervelocity iron particles, have been made by Smith and Adams.⁵⁰ Here again iron micro particles were accelerated with a 2 MeV Van de Graaf to velocities of between .05 and 10 km/s. A time of flight mass spectrometer was used to investigate the mass distribution of ions produced by particle impact. The total charge released was described empirically by the relation

$$Q \sim m^\alpha v^\beta$$

with α for velocities greater than 1 km/s, 0.85, and β , 3.2, over the whole velocity range investigated. Smith and Adams concluded that the rates of positive charge collection from the impact generated plasmas reached their maxima a few microseconds after impact and then decayed exponentially, and this decay rate increased with increasing field strength at the target. The temperature of the impact produced plasma was estimated at roughly 3000 K for projectiles with velocities between 2–4 km/s. Smith and Adams assumed that the high density plasmas generated by ion impact were in thermodynamic equilibrium. They based this assumption on the conclusion that they had carried out valid measurements of plasma lifetimes with observation of rates of charge collection from plasmas in their

experiments. Unfortunately in 2 or 3 sets of observations reported there is only evidence of the decay in the collection rate of positive ions and no solid evidence for the time dependence for the onset of positive charge collection. The quantitative measurement in a few microseconds of the approximately 10^5 to 10^6 charged species formed after an impact taking place over a time period of less than a picosecond is difficult and must be viewed with caution in view of the possibility of artifact in the instrumentation used in this pioneering study. Indeed in examination of the data presented for projectiles with 2 km/s particle velocity and negative 300 eV extraction potential from the impact surface there is no indication of a measurable time delay for detection of positive ions from the impact surface. Smith and Adams concluded their study with remarks to the effect that many of the problems examined have only been partially resolved and that some of the problems "so far encountered have been discussed in the light of the limited amount of experimental evidence available".

If the negative charge released in the experiments of Smith and Adams is taken as electron current, according to the Richardson equation and with surface temperature determined by projectile kinetic energy, the electron yield should vary with the fourth power of the projectile velocity and the square of the projectile mass. The power law observed by Smith and Adams shows a proportionality to the 3.2 power of v , which may be considered good agreement with a T^2 dependence predicted by the Richardson equation for high-temperature electron emission. The dependence on the 0.85 power of the mass at higher velocities does not, however, fit the conclusion that the charge emission is proportional to the square of the kinetic energy deposited in the target. The secondary electron emission or charged particle yields observed by both Smith and Adams and by Dietzel, Neukum, and Rauser do not approach a linear dependence on projectile velocity predicted for higher velocity atomic and smaller cluster ion projectiles. This linear velocity dependence on small cluster ion velocity predicted by stopping power theory is observed with ions moving with velocities in excess of 100 km/s.⁵¹

The correlation between the charge released on impact per unit mass of projectile and projectile velocity over a range of velocities from 0.1 to 100 km/s is given in Figure 2 which contains the data of Smith and Adams as well as results of secondary electron yields from cluster impact with higher velocity smaller clusters obtained in the author's laboratory. The lines in Figure 2 showing the respective slopes of a linear and fourth power dependence of electron emission with projectile velocity are schematic with respect to the quantity of electrons released on impact. The actual electron yields on kinetic ejection with linear dependence on v , would fall well below the values predicted by the Richardson equation, the fourth power dependence. The results presented in Figure 2 must be considered in terms of mechanisms of electron emission. The data obtained with the highest velocity projectiles, which show a linear dependence on v , are obtained with projectiles moving with velocities close to or greater than threshold velocities for kinetic ejection of secondary electrons.³⁵ There is a closer correlation with a fourth power de-

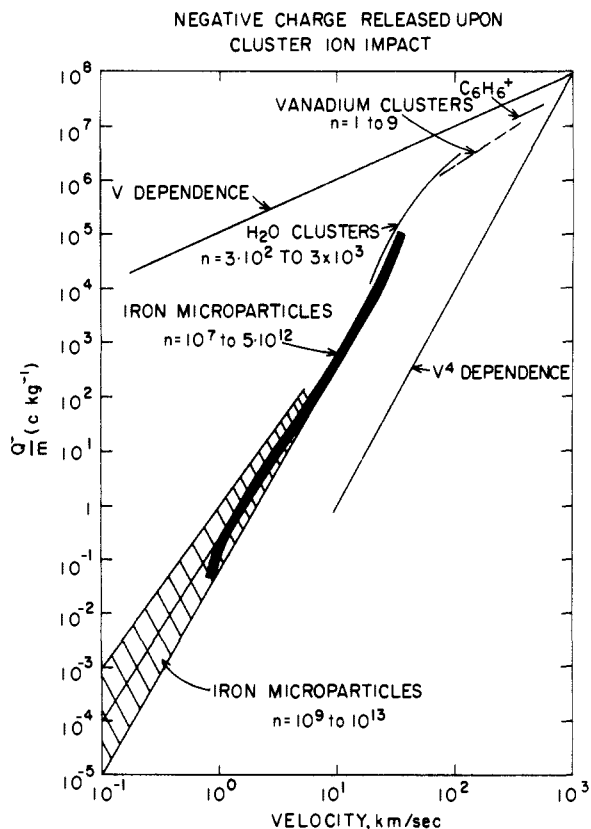


Figure 2. Total negative charge collected per unit mass is plotted as a function of velocity for a wide variety of different cluster ions striking different targets. n indicates the number of atoms in the cluster. At the lowest velocities, the cross-hatched area brackets the results from Smith and Adams for iron projectiles on a molybdenum target (ref 50). Results from Dietzel, Neukum, and Rauser (ref 45) for iron microparticles impacting tungsten bridge the gap between the larger iron particles and clusters containing under a thousand atoms. Results from water cluster and $C_6H_6^+$ impacts on a copper target were taken in our laboratory (ref 43 and 51) and results for vanadium clusters striking stainless steel from Hofer and Thum (ref 42). The lines indicating a linear velocity dependence and a v^4 dependence are shown only for comparison of the slopes with the experimental points. At high velocity the release of secondary electrons approaches a linear velocity dependence, (top line) while at lower velocities the yield drops to a 3.2 power dependence on the projectile velocity.

pendence on v with lower velocity projectiles suggesting a closer approach to equilibrium ejection of electrons. This correlation is attributed in part to the inefficiency of kinetic ejection at low velocities and in part to the fact that the lower velocity projectiles were much larger, generating much larger thermal spikes. Larger thermal spikes cool more slowly by thermal conduction and provide more time for energy equilibration. We note that in the study of Smith and Adams, the lowest velocity large projectiles produced thermal spikes which consisted of assemblies of atoms made up primarily from projectile rather than target atoms. In either case the results show that the "temperature" dependence of secondary electron emission as well as the quantity of charge released reflect incomplete equilibration of energy in the hot atom assemblies generated by cluster impacts even with relatively low-velocity projectiles. The failure to reach equilibrium during secondary electron emission minimizes the value of this process as a thermometer for the determination of temperatures in the impacted volume elements. Nevertheless secondary electron yields provide insight into the phenomena with clear experimental evidence for the kinetic

nature of processes occurring with higher velocity cluster ion impacts.

Theoretical calculations designed to obtain the empirical parameters required for use with Rankine-Hugoniot equations must take into consideration the relatively slow process of electron-atom equilibration if applied to the energy-transfer problem of cluster impact phenomena. In addition to the problem of thermodynamic equilibrium the hydrodynamic model has no simple or direct means of dealing with problem of penetration of high-velocity projectile atoms into the target. If a hydrodynamic model of energy transfer is used, the compression associated with the impact process should not be accompanied by penetration of the projectile into the target. If penetration occurs with a gradual attenuation of projectile velocity, the calculation of the force on surface layers and the pressure on the surface layers is complicated. With velocities of the order of 10 km/s the kinetic energy per atom is for light atoms, carbon or oxygen, roughly 10 eV and the penetration problem is minimal. At the upper limit of velocities achieved so far by electrostatic cluster ion acceleration, 30–40 km/s, light projectile atoms have kinetic energies in excess of 100 eV and penetration of several layers of target surface is probable. With cluster ions with kinetic energy in the keV/atom range the penetration problem is serious and hydrodynamic models appear to be of less practical value. One nevertheless can use a hydrodynamic model, qualitatively, to gain insight into the rough magnitude of the transient pressure and temperature induced by cluster impact processes. Calculation of the transient temperature, pressure, and density within a deuterium droplet with velocities ranging from 30–60 km/s striking a gold target, were made at Brookhaven⁵² using data from the Equation of State Library at Los Alamos. For droplets with velocity of 60 km/s the penetration of deuterium into gold is estimated at less than 10 Å and pressures of 7 Mbars, and temperatures of 120 000 degrees result from the equilibrium calculation (Figure 3).

Kitazoe and Yamamura⁵³ attempted to develop a hydrodynamical approach or shock wave model to account for the nonlinear effect of heavy ion bombardment on sputtering. Nonlinear means that sputtering yields on a per atom basis are larger for a diatomic ion compared to the atomic ion at the same velocity. In this work the goal was to devise a model which accounts for higher energy densities in the target than those generated by the two body interaction stopping power mode. Kitazoe and Yamamura assumed that energy was initially deposited at a rate predicted by stopping power theory but that recoiling struck target atoms produced by the very dense beam, generated a plasma which they referred to as a local region in a state of "gas in fire". The "fire gas" is assumed to generate a shock wave which compresses the surrounding volume element and is then reflected in an unloading process. This reflection of energetic atoms creates a higher energy density in a hemispherical or possibly a cylindrical volume element which is responsible for "nonlinear" sputtering effects and related phenomena observed with high density beams. The Kitazoe-Yamamura model uses the Rankine-Hugoniot relations to calculate the internal energy and pressure of the compressed target with energy initially deposited at a rate determined by

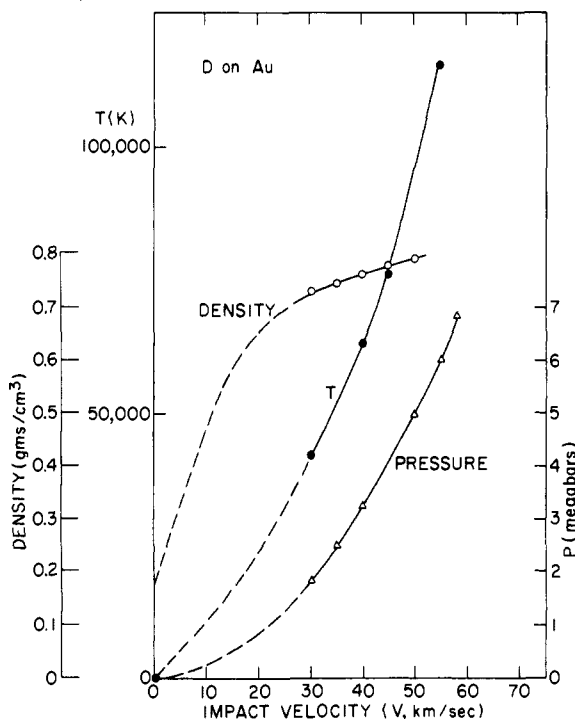


Figure 3. Calculated values of density, temperature, and pressure as a function of projectile velocity based on the Hugoniot calculation for a droplet of deuterium striking a metallic gold surface as a function of the droplet velocity. The model assumes the interaction of a plane, semiinfinite slab of deuterium colliding with a planar target surface.

atomic stopping power theory. The energy density that is achieved is regarded as a function of the compressibility of the target material, not of the incident energy of the projectile. This model is in some respects an outgrowth of ideas put forth by Carter.^{54,55} In his more recent report Carter concludes that development of surface discontinuities, points, edges etc. in the course of high beam density impacts provides irrefutable evidence of shocks which indicate the need for including hydrodynamic effects in improved descriptions of high-density cascades. Computer simulations of argon ion bombardment of copper carried out by Webb and Harrison,⁵⁶ showed an "ejection wave" for sputtering that propagated outward on a roughly circular front at hypersonic speed, supporting the concept of shock phenomena in dense beam sputtering. An alternative to the approaches cited above to estimate the magnitude of the energy transferred from projectile to target and to determine the extent of the conversion of kinetic to internal energy on particle impact is to consider the energy transfer process in cluster impacts in terms of enhanced stopping power. The energy density deposited in the target by a projectile then becomes a stopping power problem with no particular difficulty arising from particle penetration into the target. With projectile velocities much less than 100 km/s the electronic stopping power accounts for a relatively small fraction of the energy deposited in the solid and can be neglected. This assumption identifies the loss of energy of projectile atoms in the target taking place via screened coulomb interactions between the respective projectile atoms and target atoms. A comprehensive unified theory of atomic stopping has been developed by Lindhard and Scharff⁵⁷ for isolated two body interaction processes. With differential scattering cross

sections based on Fermi-Thomas atomic potentials, values of dE/dx for atomic stopping were derived which were found to be in relatively good agreement with experimental results. Above a critical velocity, dE/dx decreases very gradually with increasing projectile velocity. For example with oxygen atoms striking a carbon target, with projectile atom velocity between 50 and 500 km/s, the calculated atomic stopping power energy loss ranges between 20 and 40 eV/A with values limited to about $32 \pm$ a few eV/A between 100 and 400 km/s. This relative insensitivity of the specific energy deposited in the solid to the velocity of projectile atoms is different from predictions of energy deposited in the hydrodynamic shock process. In the latter case higher velocity projectiles produce higher specific energies while with atomic stopping larger volumes of target are heated to nearly the same "temperature" initially. With cluster ion impacts the treatment of screened coulomb collision processes between n projectile atoms and n target atoms interacting nearly simultaneously and in very close proximity presents a rather complex computational problem. The solution of this problem is preferable to the use of models that require thermodynamic equilibrium for energy-transfer processes taking place on time scales that are fractions of a picosecond. A crude approach to the solution of this problem is to make the assumption that the atoms in the cluster interact with target atoms with smaller impact parameters because of the greater rigidity of the "internal" atoms of the interacting system. Thus projectile atoms would experience stronger repulsive interactions than isolated two body collisions between projectile and target atoms with the same relative velocities. Energy transferred per unit length of target would be greater, accounting for enhanced stopping power of the cluster compared to the same number of isolated atoms at the same velocity. One would expect energy transfer to approach that of isolated two body processes with decreasing cluster size when clusters approach the size of atoms and small polyatomic systems. The hope is that experimental information will provide insight that will serve as a basis for the simplification of this complex problem. Until models have been developed, the option that can be pursued is experiment directed to testing the extent to which information from atomic stopping power can be used to account for phenomena observable with energetic cluster impacts.

Consideration of the use of stopping power rather than hydrodynamic models for analysis of experimental data from cluster impacts raises the question of whether beam density effects can be accounted for by the formation of larger and longer lived thermal spikes or whether beam density effects can actually perturb rates of energy loss of projectiles penetrating targets. Thus energy deposited by cluster ions in a target must be compared with energy deposited by very high density atomic ion beams rather than isolated atom impacts. A clue to the effect of beam density on the rate of energy deposition can be found in studies on sputtering with intense ion beams. Nonlinear sputtering of gold by heavy atomic and diatomic projectiles was observed by Andersen and Bay.^{58a,b} Enhanced yields of sputtered Ag, Au, and Pt were measured by Johar and Thompson^{58c} in very heavy ion bombardments. These en-

hancements become much larger for polyatomic ion bombardment and were strongly nonlinear with the number of atoms comprising the ion. The explanation given in ref 58c for the observed phenomena was that the enhanced sputtering was the result of a highly disrupted surface region and an associated reduction in the local surface binding energy. Johar and Thompson concluded that the high sputtering yields could not be explained by a thermal spike model and a local evaporation process. Their argument against local evaporation is essentially an argument against evaporation subsequent to thermal equilibrium in time periods of the order of 10^{-10} or 10^{-11} seconds after impact. The focus of attention in the study cited, and earlier studies on the breakdown of linear cascade theory in predicting damage to semiconductors subjected to intense ion bombardment, was on the effect of increasing energy density within a target volume element. The question of whether or not the rate of energy deposition was affected by the interaction of a dense beam with the target was not discussed. Arguments were pointed to the question of whether a thermal evaporation model could legitimately be used to account for the extent of sputtering observed. With cluster projectiles above a critical size the "effective" beam density is tremendously increased because of the "chemical bunching" of the cluster atoms. To illustrate this point, a cluster consisting of only 20 atoms will strike an element of area on the target surface no larger than about 200 \AA^2 within a time period of less than 10^{-13} seconds. This time estimate is based on a cluster velocity of greater than 10 km/s . The equivalent atomic ion current density is about 10^9 A/cm^2 .

In the illustration cited a cluster of 20 atoms was arbitrarily selected. The question of the minimum number of atoms that constitute a cluster is worthy of comment. One might argue that the current carried by one or two atomic ions could be presented in terms of very high amperage/cm²/s. The point is that a significant beam density is achieved only with polyatomic clusters that deposit their energy within the same or very closely spaced thermal spikes. The geometry of the thermal spike, its surface to volume ratio, will, in part, determine the relative amounts of energy dissipated in conduction and evaporation. Spikes produced by isolated atom impact and penetration processes will cool much more rapidly by conduction than larger volume spikes produced by clusters which give beam density effects on sputtering. Quantitative discussion of rates of conductive cooling of thermal spikes having different initial radii will be discussed below, within the framework of the model developed by Seitz and Kohler⁵⁹ in connection with studies reported below on cluster impacts on thin carbon films.

Experimental studies of atomic stopping power are usually carried out by measurements of ranges of projectiles or energy losses in films which transmit species with sufficient energy for their subsequent detection. With cluster impacts, thermal spikes are created which produce damage well beyond the penetration range of the projectile so that range measurements that identify the depth of penetration of the projectile or trajectory of the projectile atoms in the target becomes very difficult. With accelerated cluster ions the energy available per constituent atom is the total kinetic energy

divided by the number of atoms in the cluster. This limits the energy per atom with large cluster ions so that transmission experiments designed for measurement of dE/dx require very thin absorbers or higher energy accelerators than normally used in atomic stopping power studies. Reliable measurements of dE/dx of particles in larger cluster ions is a more difficult task than with atomic species.

VII. Cluster Crater Morphology

An experimental approach that does not require MeV cluster ion acceleration is the investigation of cratering and the attempt to relate crater morphology to the energy deposited in the target. Target morphology, the diameter and depth of craters formed by cluster impact, is determined by the kinetics of energy transfer from the projectile to the target, the flow of energy by thermal conduction from the initial volume element of target impacted by the projectile, and rates and mechanisms of evaporation of target atoms or molecules from the thermal spike produced by impact.

The formation of craters with diameters of 30 to 90 Å on 600 to 800 Å thick gold films by bombardment with accelerated beams of Bi^+ and Bi_2^+ was observed by Merkle and Jäger.⁶⁰ The formation of a crater was a low probability event, not representative of the "usual" ion impact. The probability of crater formation rose from .1% to 1% as the incident Bi^+ beam was raised in energy from 50 to 125 keV. An increased probability of crater formation was observed for Bi_2^+ compared to the atomic ion, and the threshold probability of .1% was observed at 12 keV/Bi atom and rose to 1.3% at 125 keV/atom. Their proposed explanation for the formation of these craters was the occurrence of extra-high-energy density surface spikes, and this was supported by estimating the probability of forming an energetic subcascade with energy between 100 and 1000 volts and a radius of 25 Å. The difficulty of explaining their results with existing "thermal-spike" models (to be outlined later in this section) was pointed out, and the occurrence of other complex phenomena such as the collective emission of material as a microparticle and the formation of a crater with a lid sticking out was demonstrated.

A cautionary note to the interpretation of experiments which investigate cratering in targets must be added: one must not overlook the possibility of overlapping hits. For example, if a disrupted area of 50-Å diameter is created with each ion impact, then after 10^{11} hits per cm², the probability of further hits striking an already disrupted area is about 2%. These second strikes on an impacted area could cause very different phenomena compared to the area struck with a single ion. Merkle and Jäger concluded that craters are formed in individual displacement cascades by inspecting targets bombarded with low-dose bombardments of less than 10^{10} ions/cm². Therefore, double strikes should not have been a problem in their work, though almost all the transmission electron micrographs shown in their article had doses much higher than 10^{10} ions/cm².

Investigation of the morphology of craters of holes made by larger cluster ion impact provides a crude basis for the estimation of sputtering yields which can be used to test models of the energy transfer processes.

Analysis of transmission electron microscope studies of thin carbon films bombarded with protonated water cluster ions requires estimates of the rate of energy deposition and the geometry of the initially generated assembly of energetic target atoms.⁶¹ Hypervelocity cluster ions were assumed to plastically deform on impact with the target surface taking the geometry of thin disks which would interact with the maximum area surface element. This assumption gives a lower limit of energy density deposited in the target compared with values derived from projectiles which have successive layers of atoms striking the same target area. The initial radius of thermal spike generated by disk cluster impact is the radius of the disk. Cylindrical or hemispherical geometry can be assumed for the spike generated by penetration of cluster atoms in the target. Craters or holes created by these impact processes will have dimensions that are determined by volume elements that are heated by projectile-target atom and target-target atom energy-transfer processes and which retain a sufficient density of energy to permit evaporation before conductive cooling takes place. A minimum critical diameter crater or hole observable with transmission electron microscopy depends on the resolution of the microscope which in the case of the study cited was roughly 10 Å. A necessary condition required for crater observation was a minimum ratio of crater depth to film thickness. Craters with depths less than 15 Å were marginally observable in 60-Å carbon films with the techniques used. The minimum number of carbon atoms sputtered from a crater, visible to the technique used in this study was then somewhere in excess of 100. This estimate accounts for the difficulty in observation of craters from isolated atom impacts using transmission electron microscopy. Sputtering yields are generally somewhat lower than this although yields as high as nearly 1000 were reported by Thompson and Johar⁵⁸ when Sb_3 projectiles with 30 keV/atom were used to bombard Ag and Au targets. Sputtering with larger cluster ions proceeds with yields equal to or greater than those reported by Thompson and Johar but with much higher energy efficiency.⁶¹ If targets thin enough to study with TEM gave sputtering yields of this magnitude visible craters or holes should be observed and would be of interest.

We have emphasized the idea that on the time scale of evaporative processes which lead to sputtering and cooling of thermal spikes by thermal conduction there is insufficient time for electrons and hot atoms to reach thermal equilibrium. In the cases of sputtering of metals and semiconductors by laser or electron bombardment⁶² or atomic ion sputtering with particles with velocities in excess of 100 km/s, large fractions of energy are deposited initially in electronic degrees of freedom in the target. Electronic energy must be converted into translational energy for evaporative or sputtering processes. The relative inefficiencies of laser sputtering or atomic ion sputtering particularly in terms of total energy deposited, compared to cluster ion sputtering, is a result of the relatively slow rate of energy transfer in thermal spikes generated by the electronic energy deposition process.

The results obtained with water cluster projectiles accelerated to energies up to 300 keV⁶¹ and impacted on thin carbon targets showed that both critical con-

ditions of cluster size and energy had to be satisfied for the production of a visible crater or hole. The model selected for the analysis of the results of cluster impact on carbon films was that of Sigmund and Claussen.⁶³ Sigmund and Claussen developed a model for the calculation of the sputtering yield from a thermal spike in which sputtering takes place by evaporation from a high "temperature" assembly of atoms in the spike. The rate of quenching of the spike was calculated using heat conduction theory with a thermal conductivity based on kinetic gas theory. Similarly evaporation was treated as a kinetic process for an ideal gas confined by a planar surface potential. With this model Sigmund and Claussen showed that while sputtering yields calculated from linear cascades will be proportional to the energy deposited, thermal sputtering will vary more rapidly than proportional to the square of the energy deposited because of the effect of increased temperature on the rate of evaporation of molecules from the thermal spike. Sigmund and Claussen recognized the weakness in the description of thermal spikes as systems having temperatures and used values of heat conductivity appropriate to insulators for calculating the integrated evaporation yield over the spike lifetime. The legacy of the term "thermal spike" and the use of the term temperature for systems undergoing change on time scales measured in picoseconds has probably created unnecessary confusion. Clearly electronic degrees of freedom are not equilibrated with the translational energy in the "thermal spike" on this time scale. This however does not seriously damage the Sigmund model for thermal evaporation from the spike when "temperatures" are used in place of energy densities in calculation of rates of evaporation. We note that discussion of the Sigmund model for sputtering is not presented as part of a comprehensive review of sputtering theory. Alternative approaches to sputtering theory, the work of Kelly for example,⁶² could have been used as a basis for examination of sputtering by cluster impact.

One wishes to gain insight into the question of whether clusters above a critical size will deposit energy into targets at rates more rapid than theoretical atomic stopping power values. The problem of calculating the volume of material evaporated by atomic projectile impact is more tractable because stopping power theory provides more reliable estimates of initial energy densities resulting from the projectile-target energy transfer. A problem in the use of models to calculate the extent of sputtering by cluster ions is to obtain a value of initial temperatures or energy densities determined by the rate of energy transfer during the penetration process. This temperature must account for the extent of evaporation that takes place in competition with cooling by thermal conduction. We note that a lack of information on the composition of the carbon species produced by cluster impact is a major weakness in attempts to examine the experimental data within the framework of any model. In the thermal evaporation of carbon, species containing one, two, or three carbon atoms are observed experimentally with activation energies for evaporation of approximately 8 eV respectively.⁶⁴ With the much higher temperatures or energy densities it is reasonable to conclude that the very rapid heating of the target surface will generate

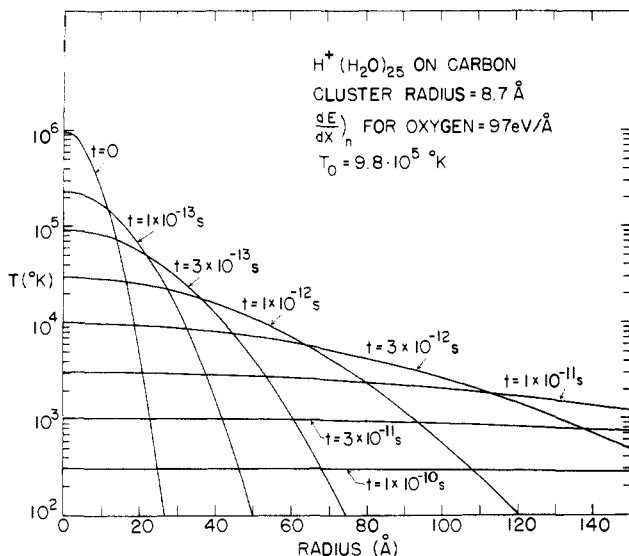


Figure 4. The temperature of the thermal spike generated by a 25 water molecule cluster striking a carbon target is plotted as a function of spike radius at different times after cluster ion impact. The value of the nuclear stopping power was assumed independent on the cluster size. After one picosecond thermal conductivity has decreased the calculated temperatures below 30 000 K and evaporation of carbon effectively stops.

higher molecular weight carbon fragments.⁶⁵ Some features of the observations made on craters in the carbon films can be explained with very crude estimates of competitive rates of target evaporation and conductive cooling. For example neither craters or holes were observed in thin carbon films with clusters containing 25 or fewer water molecules. Clusters containing 25 water molecules and a proton with a "two-dimensional" disk structure will have a maximum radius of about 9 Å if the density of the cluster is taken as the same as that of liquid water. If one assumes an initial energy density corresponding to a temperature of 10^6 °K deposited by the penetrating cluster and a thermal conductivity to heat capacity ratio of carbon of $0.061 \text{ cm}^2/\text{s}$, and inserts these values into the Seitz-Kohler relation⁵⁹

$$T = T_0(1 + y)^{-\eta} e^{-r^2/\sigma^2(1+y)}$$

for T as a function of radial distance from the center of impact at different times after impacts the results plotted in Figure 4 are obtained. T and T_0 are the respective temperatures and initial temperature, r is the radial distance from the center of impact, and σ , the radius of the projectile. η is $3/2$ and 1, respectively, for spherical and cylindrical spike geometry. y is defined by the relation

$$y = 4Kt/\sigma^2c$$

with t the time after impact, K , the thermal conductivity coefficient, and c , the heat capacity per unit volume of the target. The temperature in the spike created by impact of the 25 water molecule cluster drops after 10^{-12} seconds to a maximum value of 20 000 K. Evaporation rates for carbon atoms at this temperature given by the relation

$$k = \nu_0 e^{-E/RT}$$

where ν_0 is the frequency factor and E , the activation

energy, are insufficient to generate a crater visible to the EM technique used in the experiments.

There will be sputtering and evaporation when a cluster containing 25 molecules of water moving with velocities in excess of 10^7 cm/s strikes a carbon target but with rapid cooling of thermal spikes the extent of sputtering will be such that the critical number of hundreds of carbon atoms per impact will not be reached. If the same assumptions of initial energy density, thermal conductivity, etc. made for the 25 molecule cluster are applied to 100 and 150 molecule water clusters with maximum radii of 17.5 and 21.4 Å respectively, the larger thermal spikes cool from initial temperatures of 10^6 to approximately 20 000 K in times increased by more than a factor of 3 with the possibility of visible crater formation.

The question of rates of evaporation at thermal spike temperatures was considered by Sigmund et al. taking the hot atom assembly in the thermal spike as an ideal gas confined by a planar surface potential with the rate coefficient expressed as the product of a frequency factor and an exponential energy dependent term given above. The frequency factor was calculated from the relation

$$\nu_0 = \frac{N_v}{N_s} \left[\frac{kT}{2\pi m} \right]^{1/2}$$

where N_v is the number density of target atoms/unit volume and N_s is the surface number density of target atoms. Thus frequency factors for evaporation are proportional to the velocity of atoms in the thermal spike. An interesting feature of the Sigmund model is the lower predicted rate of evaporation of larger molecular fragments, compared with atomic species, at temperatures sufficiently high for rates to be determined exclusively by the frequency factors. In the case of carbon evaporation at energy densities corresponding to temperatures above 30 000 K the Sigmund model would favor evaporation of atomic rather than polyatomic fragments given similar activation energies for evaporation. The energy deposition process may produce an assembly of molecular fragments with number densities that favor evaporation of the latter over atomic evaporation in spite of the fact that atoms may evaporate at a much faster rate. Unfortunately there is relatively little data available on the distribution of molecular versus atomic products in cluster sputtering. If studies of sputtering with atomic projectiles can be used as a basis for estimation of the distribution of molecular products with cluster sputtering, then extensive contributions of molecular species must be expected. A question that is opened by consideration of cluster sputtering as compared to atomic projectile sputtering is whether the generation of thermal spikes by cluster impact indeed produces an assembly of hot atoms or hot molecular fragments which evaporate from the solid surface.

The Sigmund model value of frequency factor for evaporation of carbon atoms from carbon target surfaces at temperatures in excess of 30 000 K is of the order of $5 \times 10^{13}/\text{s}$ and this value is effectively a measure of the rate coefficient for carbon evaporation from the freshly formed thermal spike. This value of rate coefficient accounts for rapid evaporation of carbon atoms heated to temperatures between 30 000 and

100 000 K in times of roughly a picosecond. If spike temperatures drop below values that permit neglect of the exponential term in the rate equation then much less evaporation can take place. The Sigmund model for calculation of sputtering commences with an assumed Gaussian temperature distribution

$$T = T_0 e^{-r^2/\sigma^2}$$

with the maximum temperature T_0 , found by normalizing the energy in the spike. T_0 is for cylindrical geometry spikes, proportional to dE/dx and the reciprocal of the heat capacity of the target. Temperature distributions as a function of time and distance can be calculated using equations of the form developed by Seitz and Kohler and these temperatures can be substituted into the evaporation rate equation. Integration of the rate equation over time and target surface area then gives the number of evaporated atoms, N_e

$$N_e = \int_0^\infty 2\pi r dr \int_{t_0}^\infty dt N_s \nu_0 e^{-E/kT}$$

N_s is the number density of target surface atoms. As each layer evaporates, the layer below is exposed and in turn starts to evaporate; the number density of atoms available for evaporation is always N_s , since the surface is assumed to remain undeformed for purposes of calculation of evaporation flux. If the initial rate of deposition of energy in the target, the geometry of the thermal spike, the thermal conductivity of the target, and the activation energy for evaporation of target atoms are all known, then the Sigmund model can be used for calculation of the number of atoms that evaporate or the sputtering ratio on cluster ion impact. If molecular species evaporate then activation energies for evaporation of these species are required and average values of translational energies are required for calculation of frequency factors. It is clear that experimental data of cluster ion sputtering are required to establish mechanisms before the crudest of calculations can be trusted. Measurements of kinetic energy distributions of gaseous products of cluster impact should provide valuable information on the nature of energy densities, of "temperatures" in the thermal spike at the time of evaporation and these results will provide lower limits of values of initial energy densities, shedding light on cluster projectile stopping powers.

The Sigmund model was used by the Brookhaven group to calculate the extent of evaporation from thermal spikes produced by different sized cluster projectiles as a function of initial energy densities or temperature. Comparison of experimental values of the numbers of atoms evaporated with the calculated number of evaporated atoms showed that with larger cluster (150 H_2O) ions, initial energy densities approximately twice that predicted from classical stopping power theory were required to account for the extent of evaporation, Figure 5. Smaller 50 molecule cluster ions gave calculated evaporation yields close to values estimated from the sizes of holes observed microscopically with energy densities much closer to those predicted by theory.

Singly charged clusters containing 25 water molecules or less with 300-keV energy showed no signs of holes or craters in carbon films of roughly 100 Å in thickness.

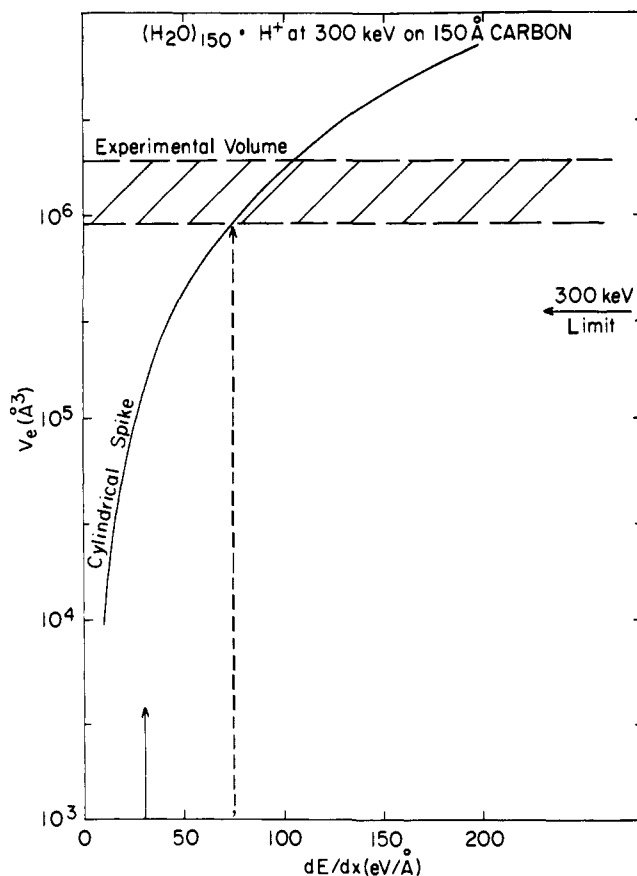


Figure 5. The volume of carbon target evaporated is calculated using the Sigmund model as a function of stopping power for a cylindrical spike created by the impact of a 150 water molecule cluster striking a 150-Å-thick carbon foil at 300 keV. Cross hatching indicates the experimental volume evaporated which reflects an uncertainty in hole volume of a factor of two. The arrow at the 300-keV limit indicates the volume that would have been excavated by the evaporation of single carbon atoms with 8 volts as the heat of vaporization. The vertical arrow on the dE/dx scale indicates the value of nuclear stopping power for oxygen on carbon from two-body stopping power theory. For this experiment to fit these calculations, one has to assume that the evaporation of small carbon aggregates containing at least 2-3 carbon atoms has taken place. The value of the stopping power for oxygen on carbon has to be almost doubled to make the model calculation fit the experimental observation.

Fifty water molecule cluster ions with the same kinetic energy gave fairly sharply defined round holes with diameters ranging from 15 to 25 Å in similar carbon films. Figure 6 is presented to show holes made in a 95-Å platinum-carbon film (50-50 Pt,C) by 300 keV, 50 water molecule cluster ions. The holes are roughly 60 Å in diameter approximately 3 times the diameter of holes made by similar projectiles on pure carbon films of the same thickness. Rings of denser platinum can be seen around the edges of the holes. The difference between the carbon and Pt-C target films are attributed in part to the higher volatility of Pt in the thermal spike and to wide-angle scattering of light projectile atoms by the much heavier Pt target atoms.

Stopping power of projectile atoms has been considered above with comparison of experimental hole or crater morphology and results of model calculations of evaporation or sputtering as a function of initial energy densities. Crude values of projectile atom ranges or penetration depths in thin carbon films can be obtained if one assumes that the ratio of the diameter of the observed crater to the diameter of the cluster projectile

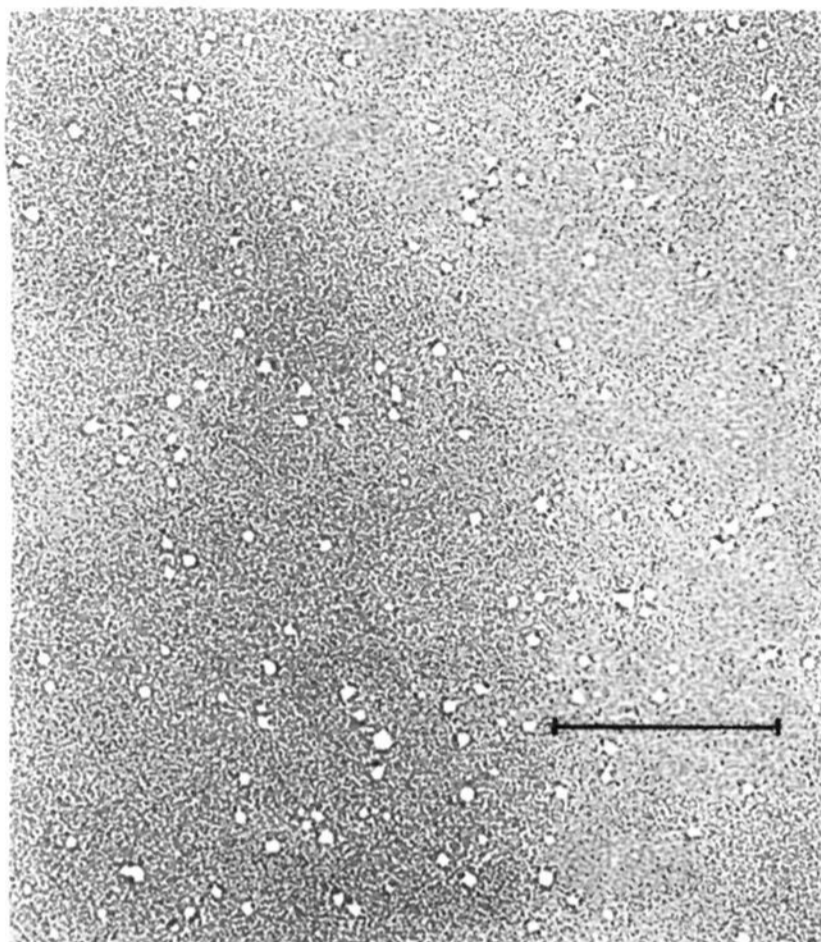


Figure 6. Bright-field micrograph of the holes formed in a 95-Å-thick platinum-carbon foil bombarded with 50 water molecule cluster ions at 250 keV. Magnification is indicated by the 1000-Å bar. Diameter of the impacting clusters is a maximum of 25 Å and the average diameter of the holes is ~60 Å. (Electron micrograph provided by Dr. Myron Ledbetter of BNL, Biology Department.)

provides a measure of the ratio of the depth of the crater to the range of the projectile. This assumption implies that energy flow radially outward from the center of a thermal spike is equivalent to energy flow from the limit of projectile penetration depth into the target along the axis of penetration. There is also the assumption of little or no straggling of projectile atoms. With oxygen atom projectiles carrying most of the energy the latter assumption is a fair approximation for carbon targets. In view of the gradual loss of velocity of projectile atoms in penetration of the target, a higher energy density is expected near the surface so that evaporation enlarging craters or holes near the surface would be expected to be more probable than from greater depths in the target. Thus one would expect a smaller ratio of range to crater depth than cluster size to crater diameter. The original assumption of the Brookhaven group would then give a lower limit of stopping power or upper limit of projectile range.

With thin 65-Å carbon films, 100 water molecule clusters with 300-keV energy generated holes that were roughly twice the maximum diameter of the projectile deformed into a disk consisting of a single layer of water molecules. Reduction of cluster energy from 3 keV/water molecule to 2 keV/water molecule gave no visible crater with in-focus electron microscopy. Out of focus studies revealed shallow craters estimated to be roughly twice the diameter of the maximum projectile diameter. These results indicate a range of water molecules of less than 33 Å for 2 keV molecules if the assumption above is used. This corresponds to a stopping power greater than 60 eV/Å which must be compared with a stopping power of approximately half this for oxygen atoms obtained from classical stopping power theory. If the

failure to observe craters with in-focus microscopy is taken as evidence for the failure to evaporate carbon atoms to a depth of approximately $1/2$ the 65-Å carbon film thickness and the range is then estimated using the assumption given above, the stopping power for water molecules is increased by another factor of 2.

The evidence obtained for enhanced stopping power in the study of the morphology of craters or holes in thin carbon films should be considered as preliminary support for the argument that clusters can generate much higher translational energy densities in solid targets than isolated atom impacts. This conclusion is consistent with observed beam density effects on sputtering.

The results obtained from the morphology of craters and holes generated by water cluster bombardment of carbon films are conclusive in that they demonstrate a high efficiency of energy conversion into evaporative or sputtering processes. The use of atomic stopping power as an approximation for estimates for energy densities appears to be a reasonable lower limit approximation. Conclusions on enhanced stopping power were also drawn from studies of impact processes on targets made up of thin gold and tantalum deposits on carbon support films.⁶⁶ A major difference in holes or craters generated by water cluster impact on heavy metal film targets in contrast to results with carbon was the much shallower penetration and larger cross sectional areas of craters generated by wide angle scattering processes of relatively light oxygen projectile atoms by the heavier target atoms. Fifty water molecule cluster ions produced holes 15–25 Å in diameter in pure thin carbon films. With tantalum targets between approximately 10 and 30 Å in thickness holes or craters ranging from 50 to 150 Å in diameter were made. Tantalum and carbon films were similar in that both were very fine grained structures. Gold evaporated on carbon films in thin layers presented a grainy appearance with grain size varying from particles ranging from 10–50 Å in diameter in deposits 1 or 2 $\mu\text{g}/\text{cm}^2$ in thickness to what appeared to be nearly continuous films in deposits in excess of 40 $\mu\text{g}/\text{cm}^2$. Craters made in thin gold films were generally insensitive to cluster size with clusters that were usually smaller in diameter to the majority of the gold grains. With both the gold and tantalum deposits the evidence that a major fraction of the cluster energy was absorbed in evaporative or sputtering processes was additional evidence for enhanced stopping power.

VIII. Applications of Larger Cluster Impacts

The utility of cluster ion impact processes in altering surface architecture has been recognized by Takagi and co-workers in studies of the use of ionized metal clusters for the growth of epitaxial, preferentially oriented and amorphous films.⁶⁷ Takagi and co-workers recognized the advantage in beam transport of cluster ions compared to atomic ion beams which are more seriously limited in intensity because of space charge effects. This limitation was of particular importance to these workers because they were primarily interested in thin film formation by ion deposition with relatively low-energy ion beams, i.e. less than 8 keV. With displacement energies of atoms in solids of the order of 20 eV, thin film fabrication without accompanying radiation

damage requires beam energies ranging from thermal beams to maxima of a few hundred volts/projectile atom. Takagi and co-workers noted that with much higher energy ion bombardment, cross sections for surface atom displacement decrease, and buried insulating and conducting layers can be produced by this technique. For the preparation of thin films on surfaces the fine control of kinetic energy with cluster ion beams can be used to minimize self sputtering or maximize sticking probabilities. Thus conductive films of Pd, 20–40 Å in thickness, were prepared with much finer grain size than produced by vacuum evaporation techniques.⁶⁸ These films deposited on silicon substrates with ion cluster beam bombardment provided evidence of higher densities of nucleation centers on the surface. The crystalline structure of silicon films was demonstrated to be controllable by changing the ion cluster kinetic energy. Epitaxial silicon films were formed with 3–8 keV acceleration energies of ion clusters ranging in mass from 500 to 2000 Si atoms. Lower kinetic energy/atom (1–4 keV/cluster) gave thermally stable amorphous films. Hydride, oxide, nitride, or carbide films were generated by chemical reaction of cluster ion beams and appropriate substrate gases when surface bombardments were carried out at gas pressures of 10^{-4} to 10^{-5} torr.

The techniques described by Takagi and co-workers demonstrate the utility of cluster ions as materials which are for all practical purposes slightly "impure" neutral species which can be accelerated and reacted with controlled kinetic energy on solid surfaces. The application to surface studies has been demonstrated as being very powerful. Higher energy clusters show promise as a means for the permanent alteration of surface structures by sputtering, cratering, or drilling very small holes. The depositions of extremely high energy densities by laser irradiation has also been demonstrated as a valuable tool in electronic device fabrication.⁶⁹ Lasers have been used to photochemically write submicrometer wide metal lines on a solid surface immersed in a gaseous atmosphere. The energy deposition mechanism with lasers is significantly different from that of cluster impacts. Lasers, electron beams, and X-rays used for lithography all deposit energy by exciting electrons with subsequent energy transfer to produce the desired effects of chemical reactions or very localized evaporation or sputtering. The very powerful technique exploiting nuclear tracks made by penetration of heavy ions generated with spontaneous fission sources, heavy ion accelerators, or nuclear reactors also relies on energy transfer processes in which most of the energy deposited in the target is deposited as electronic excitation.⁷⁰

Energetic cluster ions can be used to generate holes in thin films that are as small or perhaps smaller in diameter than those produced by track etching in a wider variety of materials than the refractory insulating materials used in track etching. Film thicknesses in which holes can be made are limited mainly by the available energy in the cluster ion acceleration system. With energy of the order of a few hundred kilovolts, carbon films of more than 150-Å thickness are difficult to perforate. Results are not yet available on thickness of plastic films that can be punctured by cluster ion impact. Small water clusters have been used to produce

holes of the order of 150–200 Å in diameter in thin procelloiden films in the authors' laboratory.

The possibility of generating intense beams of high molecular weight clusters and their acceleration to energies that provide reactant materials with translational energies going up to tens of volts/atom opens new areas of investigation in "hot atom" or hot molecule chemistry. The advantage recognized by Takagi and co-workers that the very high mass to charge ratio in cluster ion beams can overcome space charge limitations in ion beam transport makes possible the acceleration of clusters of thousands of molecules/clusters, with the result of effectively generating an accelerated neutral beam. The neutral beam is only slightly impure with a single charge but the reactant molecules with kinetic energies of, for example, 5–10 volts per constituent differ from accelerated species in a seeded molecular beam in that third or *n*th bodies to carry off excess energy of reaction are found in close proximity with the local high reagent density of the cluster system. Thus chemical interactions of assemblies of translationally hot molecules can be investigated by the introduction of cluster beams into collision chambers containing gaseous reactants. This area of investigation is similar to reaction studies on surfaces exploited by Takagi and co-workers but applied to homogeneous gas phase reactions.

Interest in the exploitation of cluster ion beams for fueling thermonuclear fusion reactions was a major driving force behind the work of the group at Karlsruhe in West Germany.^{71–75} Neutral hydrogen clusters were generated containing as many as millions of hydrogen atoms by nozzle expansion techniques and these neutral cluster beam were subsequently ionized and accelerated to potentials as high as 650 keV. Techniques developed at Karlsruhe demonstrated the possibility of generating relatively intense cluster beams useful for fueling fusion devices but because of very broad mass distributions, maximum beam energies were limited to single stage electrostatic acceleration with upper limits estimated at roughly 10 MeV. Efficient thermonuclear reactions require energies in excess of keV/atom so that fueling and heating plasmas with clusters consisting of thousands or more desirably tens of thousands of fuel atoms indicate the need for multistage acceleration systems capable of maintaining conditions of phase stability with broad mass distribution ion beams. Relativistic electron rings were proposed by Bottigioni et al.^{76,77} as a potential solution for this problem. An alternative approach to the solution of the problem of fueling and heating thermonuclear reaction devices with cluster ions is the generation of intense beams of ions with relatively narrow mass distributions suitable for linac acceleration. Singly charged cluster ion beams with mass to charge ratios as high as 15 000 and much narrower mass distributions have been made by nozzle or free jet expansion of weakly ionized plasmas of hydrogen gas at temperatures close to 20 K.⁷⁸ The hydrogen cluster beams made by expansion of ionized gases at very low temperatures were not of sufficient intensity to be seriously considered for fusion applications.

Perhaps the most exciting and speculative area of investigation open to accelerated cluster ions is that of the creation of transient assemblies of energetic species at stellar temperatures and pressures. The time re-

quired to equilibrate the high translational energy densities achievable with accelerated cluster ions with electronic degrees of freedom in a thermal spike serves to minimize the importance of one of the most effective channels of cooling of assemblies of hot atoms or molecules, cooling by electron emission. The energy densities achievable are in part limited by techniques of cluster ion acceleration and by the intensities available with bright cluster ions reduce space charge limitations in beam transport so that in principle the conditions required for the generation of assemblies of atoms at sufficient density and energy to produce a thermonuclear chain reaction may be satisfied by acceleration, bunching and focusing of intense cluster ion beams into very small target volumes. Calculations by Maschke⁷⁹ have shown that the particle density achievable by focusing and bunching a number of beams into a target volume is proportional to $N^{5/2}$ where N is the number of atoms in a cluster. Thus with clusters containing 10 000 fuel atoms, a density gain of 10^{10} is expected over the acceleration of deuterons. The practical problems of development of very bright cluster ion sources are primarily associated with the incompatibility of a dense ion plasma with the growth of cluster ions of any appreciable size.

The problem of satisfying the conditions required for an economical controlled thermonuclear reaction in an inertially confined system is essentially a problem of achieving both high energy density and high particle density in a system of fuel atoms. The preliminary evidence that cluster ion impacts deposit energy in target materials at rates faster than predicted for atomic projectile impact and penetration processes taken with the potential that clusters have for overcoming limitations of space charge in ion beam transport should encourage investigation of the possibility that cluster beams can compress and heat systems of fuel atoms to initiate controlled thermonuclear reactions. The competitive processes of heavy ion fusion using atomic projectiles and rail gun fusion schemes of heavy ion fusion using atomic projectiles and rail gun fusion schemes using much larger particles have been seriously considered. The advantage of cluster techniques will become clearer with the development of improved ion sources and a larger body of knowledge on clusters and cluster impact phenomena.

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