

Molecular-dynamics study of cluster growth by cluster-cluster collisions

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The formation of silicon clusters from cluster-cluster collisions at 2400 K is followed in time using molecular dynamics. It is found that during the first picosecond after collision, the clusters tend to agglomerate forming an intermediate complex in which the individuality of the original clusters is kept. However, during the following few picoseconds, atoms in the newly united cluster are highly mobile and agglomeration is lost. New clusters are hotter and with time they evaporate single atoms. This irreversible process by which the cluster accommodates the collision energy was studied as a function of the energy and the impact parameter. On average, the sticking coefficient is 1.

I. INTRODUCTION

Covalent low vapor pressure clusters of ceramic and semiconductor materials are found to play a critical role in a variety of industrial processes. From the prospective of microelectronic industry, the formation of particulate matter is considered to be the major limitation to reaching the goal of a 0.3- μm feature by the year 2000. By contrast, virtually all ceramic parts start from a powder precursor, the quality of the part being determined by the characteristics of the particles one starts with. In both cases clusters play an important role as the bridge between the formation of building units generated in the gas phase (generally driven by thermal or plasma chemistry) which form clusters first, and subsequently grow into particles. From the microelectronic viewpoint, it would be ideal to eliminate the cluster-to-particle step. From the ceramics-synthesis viewpoint, one would like to control the growth to obtain desired chemical and morphological specimens. *How* covalent clusters grow to reach the sub-micrometer size regime is the relevant issue.

Considerable effort has been invested in the generation¹⁻⁵ and characterization of atomic and molecular clusters, with distributions of cluster sizes displaying magic numbers observed in a variety of supersonic jet beam and gas-aggregation experiments where collision-free conditions are established.⁶⁻⁹ By contrast, manifestly nonequilibrium systems such as flames and aerosols show no evidence of ordered or structured size distributions.¹⁰⁻¹⁶ These nonequilibrium particle distributions may proceed by simple monomer addition to preformed clusters, but may be strongly influenced by the energy dissipation that follows cluster-cluster collisions.^{17,18} Modeling efforts have tried to account for both modes of growth within a kinetic scheme derived from a master-equation approach. Nucleation-kinetics models consider the small cluster size regime.¹⁵ Other models consider the large-particle regime such as coagulation.¹⁶ Attempts to model the kinetics of the full spectrum of cluster sizes

(molecules, clusters, and particles) also exist.^{12,14,19}

Since growth is essentially an irreversible process, kinetic models make the common assumption that growth rates occur at the cluster-collision rate.¹¹ That is, the sticking coefficient is unity no matter the size or composition of the species undergoing collisions. These approaches cannot account for chemical-composition changes, energy dissipation, evaporation, or molecular-level dynamics occurring on the picosecond scale. As such these models are limited to gross calculations of growth rates. Computer experiments using molecular-dynamics and Monte Carlo approaches have alleviated confusion arising in various areas of physical chemistry. In this work we point out the dramatic and irreversible energy accommodation¹⁸ that occurs in cluster-cluster collisions which determines the fate of growth during the early stages of particle formation. We were motivated to carry out this molecular-dynamics simulation by the particle-formation processes encountered in counterpropagating diffusion-flame reactors.^{12,13} The purpose of the study was to test from an atomistic approach the validity of the kinetic assumptions previously employed.^{12,14-16} Silicon was chosen because of its obvious practical importance to the microelectronics community. In Sec. II model and methods are described. Section III frames our results, and the discussion in Sec. IV concludes this paper.

II. MODEL AND METHODS

The molecular-dynamics experiment was designed to consider collisions of silicon clusters that eventually grow from an inhomogeneous two-component system composed of gaseous and nonequilibrium particulate matter as present in a flame. The temperature of the colliding clusters is assumed to be that commonly encountered in flames (about 2000 K), and the collision energy is representative of the flame temperature.

In this study we use the Stillinger-Weber (SW) model

potential²⁰ for pure silicon to model the colliding clusters. Under this potential the cluster binding energy is a sum of two- and three-body terms. Pair potentials alone are insufficient to study covalent materials and the main role of this type of three-body terms is to simulate the directional bonding and thus to allow for eventual stable cluster conformations which are less compact than the characteristic close-packed structures assumed by metals or van der Waals clusters. Very few atomistic simulations have been carried out using n -body terms in the potential model,^{21,22} although a variety of three-body classical interatomic force fields have been proposed recently to simulate structural properties of semiconductors and insulator materials.²³ The SW potential gives an appropriate thermodynamic description of the bulk solid and liquid phases,²⁰ as well as a good description at intermediate temperatures of the vapor-phase epitaxial growth into well-stacked and properly crystallized layers.²⁴ Specifically, the bulk melting temperature and the liquid inherent structure at the density of the melt are correctly predicted. This ability at fairly high temperatures, lacking in other model potentials, is very important to our simulation of clusters at temperatures high above the melting point. To date there is no universal potential function for the lighter group-IVA elements capable of describing their three phases, solid, amorphous, and liquid.²⁵ For clusters containing less than 20 atoms, SW potential does not predict^{21,23} the zero-temperature most-stable geometries of silicon clusters obtained from quantum-mechanical calculations.²⁶ However, when recalculated with the SW potential, all of the reported zero-temperature cluster geometries are bound structures or stable structures for certain cluster sizes. At about 2400 K, when the mobility of the atoms is extremely high and the cluster is liquidlike,²⁷ all of these geometries are accessible in extremely short times. At these high temperatures the entropic contribution to the stability of a cluster becomes important if not dominant.

Two clusters undergoing a collision are assumed to be immersed in a gaseous fluid formed by atoms and other clusters moving along the streamline of a laminar flow flame. For this fluid, the particle-diffusion term in the transport-of-mass equation is fairly constant in time.¹² Locally, atoms and composition-changing clusters undergo Brownian motions; therefore the overall stream velocity can be neglected as compared to the Brownian velocity which characterizes the temperature of the flame. In this simulation we have simplified the background by replacing it with an average energy of collision of 2400 K for each binary collision. No energy dissipation towards the bath is considered, mainly because the focus is to follow the early stages of the collision process.

Molecular dynamics was used throughout solving Newtonian equations of motion with a time step of 5.36×10^{-4} ps. All simulations reported in this work were started from two separated clusters each containing 15 silicon atoms, and each aged to bring it into thermodynamic equilibrium at about 1850 K. Prior to a collision, the atoms within each cluster are very mobile, and the overall shape of the cluster is continuously changing in time. The cluster temperature includes the three de-

grees of freedom of rotation—the rotational energy was not artificially set to zero prior to collision. For this cluster at 1850 K the pair-correlation function has lost all structure indicating that the colliding cluster is liquidlike.^{21,23} Furthermore, the distribution of bond angles peaks towards values lower than the characteristic 109.5° , indicating closer-packed structures than in the solid phase. The time-average coordination number at the working temperature is about 6, in agreement with the fact that liquid silicon is denser than its solid phases.

The trajectory of every pair of colliding clusters was calculated in the center-of-mass frame. A set of initial spatial coordinates and velocities for each colliding cluster was taken from an arbitrary instantaneous state of the isolated cluster equilibrated previously at 1850 K. Prior to a collision, the two hot clusters were rotated at random to yield a set of trajectories with random initial relative orientations. Only head-on collisions at various impact parameters were considered. The collision energy was set as a sudden impulse and was also used in specifying the origin of time for future observations.

The collision event commences at $t=0$ with two clusters situated far apart to ensure no interaction among them. The two clusters start moving toward one another with a uniform relative velocity of 440 m/s, consistent with a local Brownian motion at 2400 K. When the two clusters come into the interaction range of the potential, they are accelerated towards each other. At the onset of the process, when one or a few atom-atom collisions take place, the specifics of the model potential become dominant. At the onset, the two-body attractive force dominates over the initially few three-body repulsive contributions. But as the clusters get closer, many more atoms participate in the collision process, in a concerted way such that three-body repulsive and two-body compressed contributions amount to an instantaneously overall repulsion that tries to separate the colliding clusters away from each other. However, this instantaneous repulsion is not strong enough to bring about dissociation. Rather, the two clusters stick and begin a relative oscillatory motion. During this oscillatory mode the newly formed aggregate behaves as an *agglomerate*, i.e., each one of the two initial clusters keeps its individuality. As time evolves the clusters coalesce giving rise to a larger stable cluster. Similar cluster agglomeration has been reported for solid Lennard-Jones clusters.¹⁸

III. ENERGY-ACCOMMODATION MECHANISM

Collisions were almost always reactive, or completely inelastic. There was sticking in 99.7% of the trajectories analyzed up to date. The nonsticking cases, or nonreactive collisions, resulted from collisions at very large impact parameters when the clusters hit almost grazing. Let us consider the trajectory along the one typical reactive collision at zero impact parameter. Let us call the “catching” interval the time elapsed between the moment at which the first two atoms come into the range of interaction of the potential, and the moment at which the two clusters coalesce. Figure 1 illustrates the changes along the trajectory that various relevant quantities un-

dergo during the catching duration. The clusters first touch at about $t=0.1$ ps. Subsequently the clusters stick together and go into the oscillatory mode for about 1 ps. While oscillating, the new aggregate looks like an agglomerate. At later times the agglomerate fuses into one single larger specimen.

The oscillations of the relative velocity [Fig. 1(a)] during cluster-cluster approach go to zero gradually when the catching event ends and the two clusters coalesce. Figures 1(b) and 1(c) show the distribution of energy during this catching time. Note that the sharp drop in the average potential energy when the clusters first touch is mirrored by an increase in the temperature. At this point the agglomerate is formed. The agglomerate is a transient complex with a very short lifetime that lives only while the collision energy is redistributed among the degrees of freedom of the new cluster. In time, the system goes through a barrier of about 8 kcal/mole before the agglomerate starts its fusion. This presents the potential

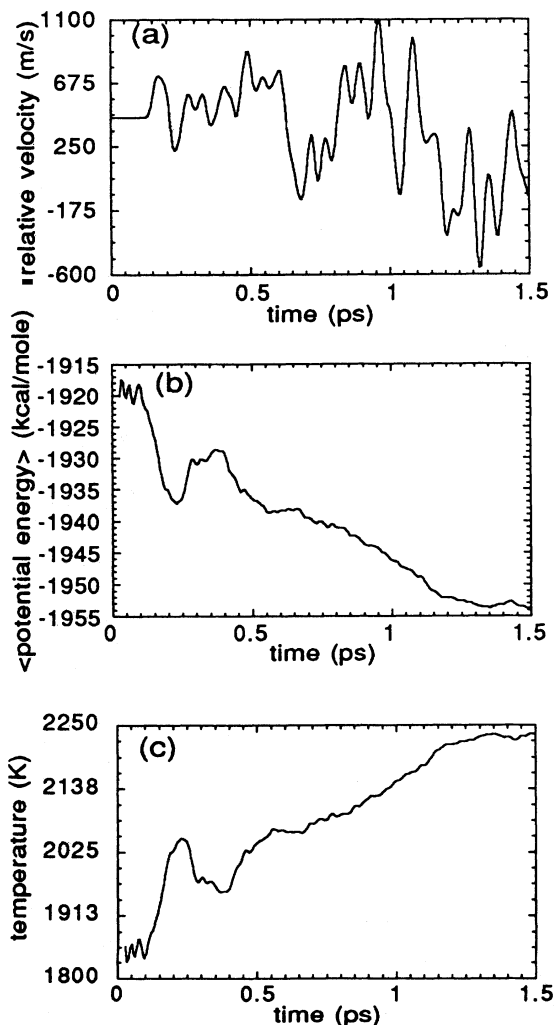


FIG. 1. The collision event during the oscillatory mode. (a) Relative velocity of the colliding clusters; (b) average potential energy of the agglomerate; (c) temperature of the agglomerate.

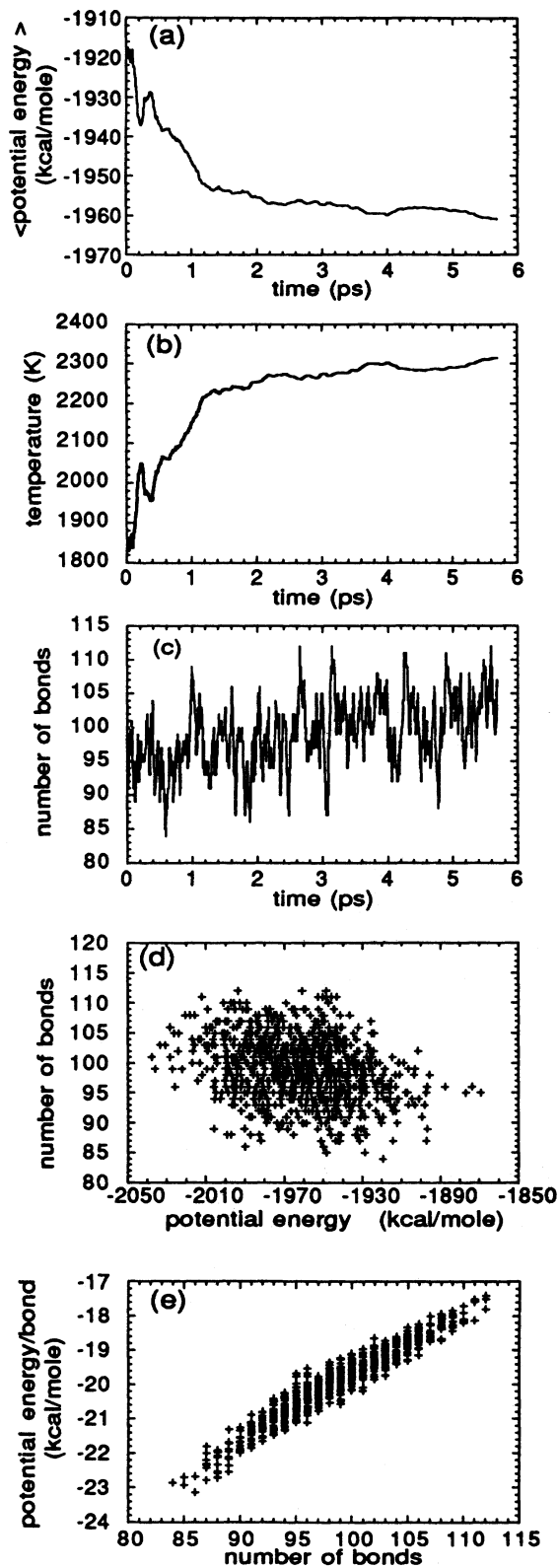


FIG. 2. The collision event. (a) Average potential energy of the unified cluster; (b) temperature of the unified cluster; (c) instantaneous values of the number of bonds in the new cluster; (d) instantaneous number of bonds as a function of the instantaneous potential energy; (e) potential energy per bond as a function of the instantaneous number of bonds.

that at sufficiently low collision energy the agglomerate could be a long-lived intermediate complex. Figure 1(b) shows how fast the potential energy reaches a maximum and declines at a slower pace when the catching time is over. Correspondingly, Fig. 1(c) shows the transient decrease of the temperature that stabilizes the agglomerate, followed by a progressive temperature increase that fuses the agglomerate.

If the clusters would have collided elastically they would have scattered after the catching time, carrying all the collision energy. Energy accommodates quite interestingly in these inelastic collisions. Figures 2(a)–2(e) illustrate relevant quantities now plotted in a longer time scale. As the cluster ages, the coalescing agglomerate gains a substantial conformational energy, it self-heats and fuses. This mechanism is responsible for the further decline in potential energy beyond $t=1$ ps and consequent rise in temperature to $T \sim 2300$ K [Figs. 2(a) and 2(b)]. On the average, the Si_{30} clusters are capable of accommodating 40 kcal/mole, a large energy for such small clusters [Fig. 2(a)]. The temperature of the unified cluster has increased by about 400 K, while the collision energy

should have contributed about 80 K only. The remaining temperature increase is attributed to the cluster going into more stable configurations, suggesting that cluster fragmentation is energetically unfavorable. Therefore, *the collision energy is totally accommodated due to the access in configuration space of energetically favorable conformations*. For clusters to scatter, it would be necessary to invent mechanisms to block those conformations. In addition, in Fig. 2(c) it is seen that the number of bonds fluctuates considerably. Despite these sharp instantaneous variations, on the average, the number of bonds presents only a slight increase. As shown in Fig. 2(d), the coalescing clusters visit a fairly localized energy region in configuration space. The approximate energy-per-bond cost to form an extra bond is about 0.2 kcal/mole, as seen from the slope of the almost linear behavior displayed in Fig. 2(e).

The snapshots in Fig. 3 begin at $t=0$ while the clusters are well separated. Subsequent photographs are spaced by about 1 ps. In these photographs the diameter of each atom equals the bond length, and two atoms are considered to be bonded if their interatomic instantaneous

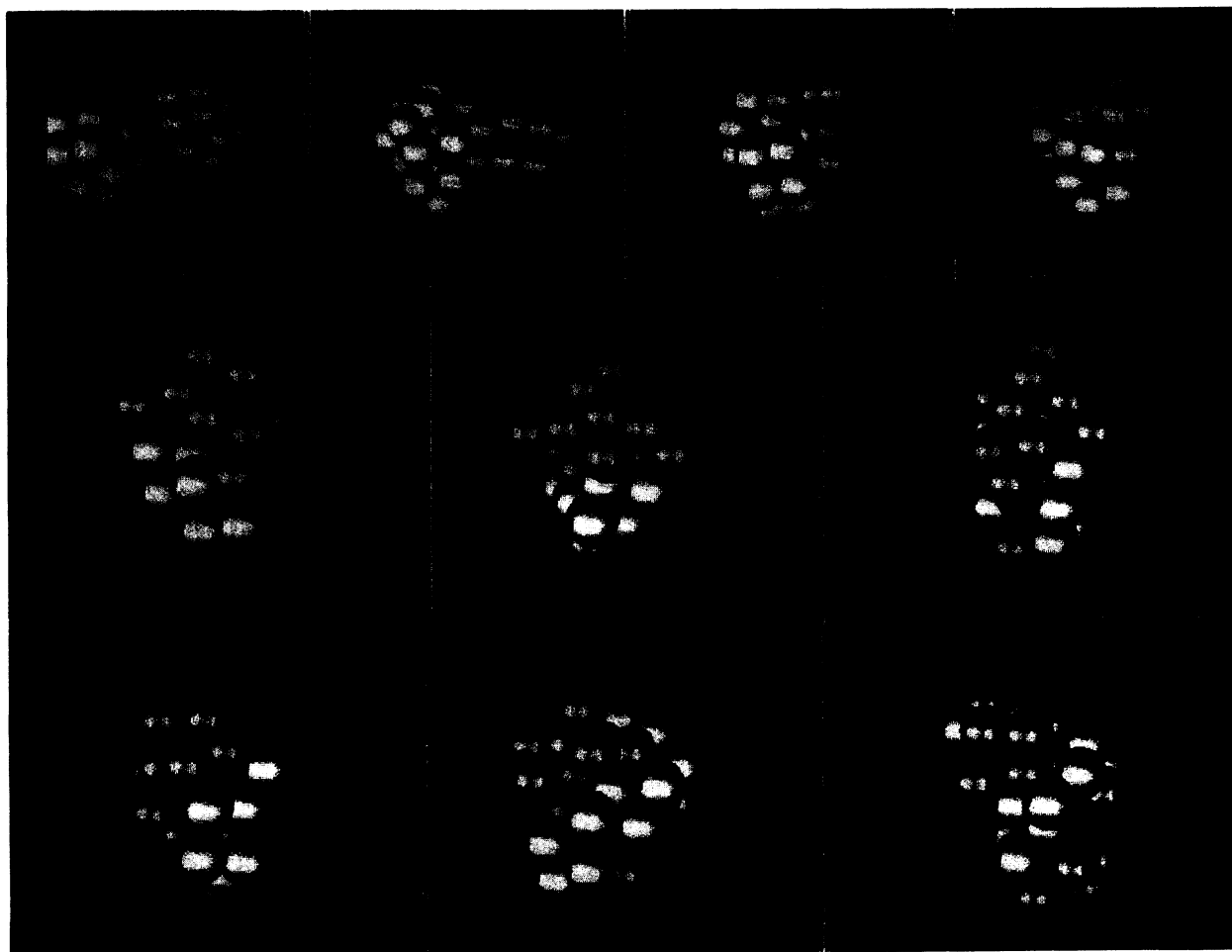


FIG. 3. Snapshots along a typical trajectory. Photographs (from left to right and top to bottom) were taken at $t=0, 0.5, 1.0, 1.5, 2, 2.75, 3.5, 4.5, 5.5, 6.75$ ps. The diameter of the spheres equals the length of a bond.

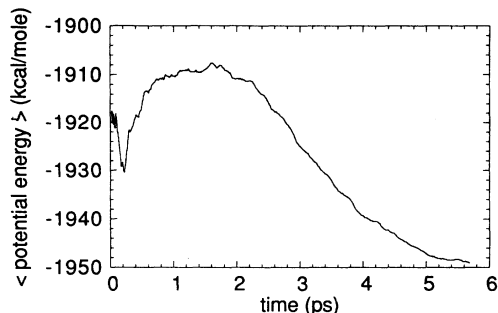


FIG. 4. Average potential energy of a united cluster produced during a cluster-cluster collision event with impact parameter of 10 Å.

distance is less than 2.94 Å (bonds are long enough to allow for vibrational amplitudes as large as 0.45 Å). The snapshots show how the clusters stick together forming the agglomerate during the catching time, and further how this entity fuses into a rather spherical cluster with fluctuating shape. Figure 4 shows the energy distribution for a typical trajectory with a large impact parameter. In this case the mechanism of the collision and energy accommodation is qualitatively the same as that for a zero impact parameter. Differences worth noticing are (i) the process of cluster coalescence is delayed, (ii) the transient energy barrier is wider allowing a longer life to the agglomerate, (iii) the angular momentum increases, giving an extra contribution to the rotational temperature.

This complete energy accommodation accompanied by overall heating of the unified cluster is an example of irreversible conversion of the collision kinetic energy. The collision energy is totally dissipated into the $3N-6$ internal degrees of freedom plus the overall rotation of the cluster. It would take an extremely long time to concentrate all the collision kinetic energy back into one degree of freedom (the relative motion).

IV. DISCUSSION

Intermolecular forces have long been acknowledged to be of importance in atomic and molecular collisions and therefore in the equations of states of real gases. The question of the energy distribution in collisions of particles^{17,18,28} is a prelude to the discussion of the enhancement in collision rates.²⁹ Let us assume that we are dealing with a gas of atoms. For gas-phase collisions the implications of the intermolecular potential can be treated qualitatively by determining the distance of separation r_{enh} between atoms (or molecules) at which the potential is equal to the thermal energy $k_B T$. This distance is to be compared with σ , the potential hard-core radius. The ratio r_{enh}/σ is a qualitative measure of the enhancement of the collision radius due to the attractive part of the potential. The corresponding enhancement of the collision cross section is $(r_{\text{enh}}/\sigma)^2$. When dealing with cluster-cluster collisions, Marlow²⁹ have extensively discussed the effect of long-range attractive cluster-cluster potentials on the collision cross section. He shows that for small van der Waals molecular clusters the calculated

enhancement factor is approximately 2. When dealing with collisions of submicrometer particles, the logistics is less clear. Okuyama, Kousaks, and Hayashi³⁰ have observed enhancement in the coagulation rate of ultrafine aerosol particles. It is a universal observation that the collision rate decreases as a function of the increasing size of the colliding particles. A qualitative explanation resulting from Marlow's theory of the effect of long-range attractive forces is in good agreement with these experimental observations for ionic aerosol particles, but is not sufficient to account for the enhancement observed in Ag aerosol particles.

In our Si_{15} clusters, when the clusters are in the range of interaction of the model potential, each of the atoms in one cluster interacts simultaneously with at least n new nearest neighbors in the other cluster. Qualitatively the enhancement ratio of thermal capture in our case is 1.9 *per pair of atoms*. From our calculations the coordination number is about 6, therefore during the catching duration there are many atom-atom interactions which contribute to the collision-enhancement process. The relevance of atom-atom interactions has previously been pointed out by Gay and Berne¹⁸ for the atomistic description of collisions of Lennard-Jones (LJ) clusters. In their work two low-temperature solidlike clusters collide at a relatively high energy of 1.35ϵ (ϵ is the LJ well depth). Under these circumstances, at the onset of the collision the repulsion among LJ clusters comes uniquely from the atomic hard core. The thermal enhancement of the cross section is 1.4 per pair of atoms, and the coordination number is approximately 8. The colliding clusters give rise to a long-lived agglomerate, not fully coalesced, because the collision energy was mainly used in exciting the normal modes of vibration of the new agglomerate. The newly formed specimen is still undergoing the catching process at the end of their simulation. This is in contrast to our results. The interactions in silicon clusters are very directional and relatively short range (3.77 Å as compared to the model bond length of 2.35 Å). This results in an overall increase of the cluster-cluster repulsion due to the orientationally unfavorable approach of any two atoms in the formation of a new bond. The catching duration in liquidlike colliding silicon clusters is clearly detected, and even overcome in the time span of the molecular-dynamics runs. Once the clusters have coalesced, the excess energy is accommodated in a gain of configurational energy. When clusters are melted the atomic mobility is very large, and the mean-square displacement is of the order of the size of the cluster.²⁷ Silicon atoms are not vibrating about fixed sites but rather moving from side to side in the volume occupied by the new cluster. Although silicon is a low-vapor-pressure material, clusters below a critical size have a finite lifetime and single-atom evaporations will eventually take place. As we have demonstrated, in the case of collisions of silicon clusters the process of energy accommodation takes place before the first evaporation event. In contrast, for LJ clusters it is very difficult to maintain a stable hot cluster above melting because of the low binding energy. LJ clusters evaporate atoms at temperatures even below melting.³¹ For this reason during a collision of melted LJ clusters

the energy disposal will favor outgoing atoms, severely limiting the lifetime of the merged cluster. Other finite systems, like simple polymers covalently bonded along the backbone, cannot support collisional energization without fragmenting and/or undergoing free-radical chain reactions.³²

Finally, in an attempt to accelerate the collision process, several trajectories were analyzed where a collision energy input of 8000 K was considered. It is seen that the clusters coalesce, do not scatter as billiards but rather start evaporating single atoms. The cluster cools by evaporating atoms, although in the real world bath thermalization will take place before two or three atoms evaporate. The results in this work show that microscopic reversibility does not apply to cluster-cluster collisions. The complete energy accommodation used efficiently in configurational stabilization, supplemented by the overall

heating proves this. These cluster-cluster collisions are, therefore, completely inelastic in contrast to the frequent hypothesis of microscopic reversibility assumed in molecular collisions of either molecules or solid surfaces. These clusters behave much as aerosols, nonequilibrium condensed-phase subsystems of two-component systems comprised of gaseous and condensed phases.¹¹ The present work points out how these condense phases, unified clusters, grow dynamically as a natural consequence of the atom-atom interactions and state variables appropriate to the system.

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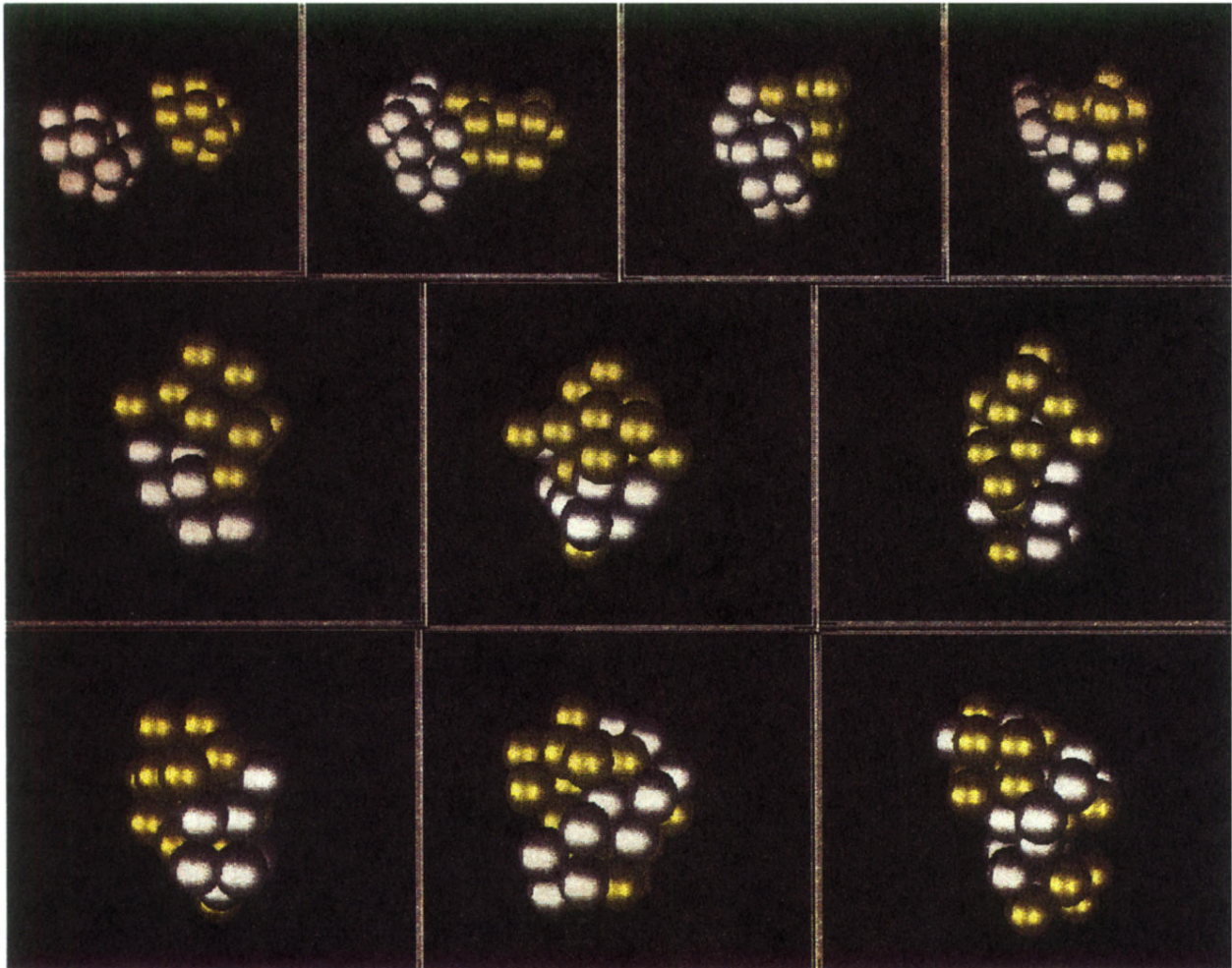


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