THE JOURNAL OF PHYSICAL CHEMISTRY C LETTERS

2007, *111,* 10135−10137
Published on Web 06/20/2007

Quadratic Friction Model for Cluster Bombardment of Molecular Solids

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Received: March 22, 2007; In Final Form: May 25, 2007

Molecular dynamics simulations of energetic cluster bombardment (C_{20}, C_{60}, C_{120}, C_{180}) are performed in the range of 5−20 keV on a solid benzene substrate. The goal is to study the trends exhibited by these bombardment events and to develop a simple analytical model that explains the general dynamics associated with cluster projectiles. These results indicate that the dynamics of these clusters can be described by a macroscale quadratic friction model and thus can provide an interpretation for the dependencies on cluster mass and size, as well as the observation that velocity of the cluster relative to its initial value decays exponentially with time with a decay constant that linearly depends on the initial velocity.

Introduction

Bombardment of a solid by energetic cluster projectiles has been shown in experimental and computational studies to have unique features from bombardment by atomic projectiles. The interest in energetic cluster bombardment has increased recently due to the stellar advancements cluster projectiles have afforded to organic/biological imaging in secondary ion mass spectrometry (SIMS). Although there have been many molecular dynamics simulations of cluster bombardment aimed at unravelling the unique properties of energetic cluster bombardment, those simulations have primarily focused on atomic, rather than molecular, solids.[1−14] The few simulations for molecular substrates[15−17] have been limited to incident energies in the range of only a few kiloelectronvolts. This restriction is due to the larger volume of reaction dynamics as a result of the much lower mass/bond strength versus atomic metal substrates, the greater computational costs due to more complex potentials, and the necessary increases in substrate size to contain these events. Thus, it is imperative to the investigation of these systems to continue to develop simple analytical models that describe the fundamental behavior of the cluster bombardment event so that full simulations are not always required.

The current analytic approach used to describe cluster bombardment is based upon a thermal spike model.[18] In this model, the authors assume a thermalized spike in the substrate and derive an expression for the yield that depends on the energy deposited in the surface region. The implementation of this model for cluster bombardment is exemplified in the study by Bouneau et al.[19] To obtain the energy deposited in the surface region due to bombardment by a cluster with n number of atoms, they assume it to be n times the energy deposited by one atom at the same velocity. Although the analytic yield expression can be fit to the experimental data, the snapshots from the simulations of cluster bombardment showing a large crater suggest a cooperative motion among the atoms, not a superposition of events by individual atoms, is playing a key role in the dynamics of this process. Thus, a need still exists for a better model which describes cluster bombardment dynamics so that the community of researchers can sort out and focus upon the important properties which govern the overall bombardment and sputtering event. The catalyst for an appropriate model can be found in a previously performed set of simulations involving C_{60} and Au_3 bombardment of water ice as a function of incident kinetic energy from 5 to ∼100 keV.[20] Figure 4 in that study gives the fraction of energy transferred to the substrate as a function of time for all of the incident particles. It is apparent from that data that the trends for each cluster projectile are nearly independent of incident energy.

The simplest model that would explain this common behavior is that of a friction applied on an object moving through a medium. In general, the friction force can be expressed as a power series in the velocity, with the linear term associated with viscosity and the quadratic term associated with drag at high velocities.[21] We tested both factors and concluded that the viscosity term is negligible for the data presented here. Newton's equation of motion is thus

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\frac{1}{2}\rho v^2 A C_{\mathrm{D}} \tag{1}$$

which integrates to

$$\frac{v}{v_0} = \frac{1}{\left(1+\frac{1}{2}\frac{\rho v_0 A C_{\mathrm{D}} t}{m}\right)} \tag{2}$$

where m is the mass of the particle, v is the velocity, t is the time, v_0 is the velocity at $t = 0$, ρ is the density of the substrate, A is a reference area of the cluster, and C_D is a drag coefficient.

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10.1021/jp072290c CCC: $37.00

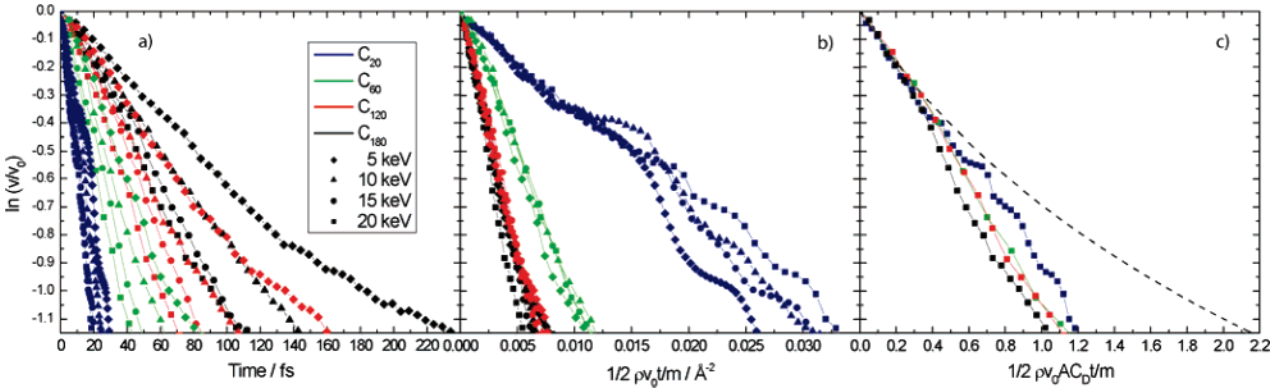

Figure 1. Ln(v/v_0) versus time. Each fullerene projectile is identified by a specific color and each energy by a specific shape as shown in the legend. (a) All four fullerene projectiles at the four energies with the time in femtoseconds. (b) Scaled time, (1/2)$\rho v_0 t/m$. (c) Scaled time, (1/2)-$\rho v_0 AC_D t/m$, using fit value of AC_D for four projectiles at 20 keV. The dashed line is from eq 2.

TABLE 1: Friction Parameters; The Product AC_D was Determined from the Slopes of the Lines in Figure 1b. The Radius, *a*, is the Initial Radius Plus an Effective Interaction Radius of 1.95 Å

	AC_D/Å^2	*a*/Å	C_D
C_{20}	45.6	3.95	0.93
C_{60}	99.5	5.49	1.05
C_{120}	165	6.94	1.09
C_{180}	187	8.07	0.91

For short times, we can use the approximation that $\ln(1 + x) \approx x$; thus, eq 2 can be transformed to

$$\ln\left(\frac{v}{v_0}\right) = -\frac{1}{2}\frac{\rho v_0 AC_D t}{m} \tag{3}$$

This model predicts that the fraction of velocity (and KE) the particles have relative to their initial values approximately follows exponential decay, but with the exponent depending on the initial velocity.

In this paper, we will explore this quadratic friction model and its applicability to fullerene bombardment of a molecular solid represented by a coarse-grained benzene substrate.[17] The choice of fullerene projectiles and the benzene substrate reflect the current interest in SIMS experiments of C_{60} beams and molecular substrates.

Description of Calculation

Molecular dynamics simulations are performed to examine the energy deposition of fullerene molecules bombarding a molecular solid, benzene. The details of the coarse-grained benzene system have been described previously.[17] The four fullerene molecules considered are C_{20}, C_{60}, C_{120}, and C_{180} with masses 240, 720, 1440, and 2160 amu. A total of four incident energies, 5, 10, 15, and 20 keV, are considered for a total of 16 simulations. The mesoscale energy deposition footprint (MEDF) model, which has been described previously, identifies that nearly all of the projectile's energy has been transferred to the substrate within the first few hundred femtoseconds of the event.[16] Therefore, only very short time simulations on relatively small targets are needed in order to assess the applicability of the friction model for cluster bombardment.

Results and Discussion

The results from the simulations are given in Figure 1a for the four fullerene projectiles at each of the four energies. For displaying the results, we use $\ln(v/v_0)$ as the quadratic friction model; eqs 2 and 3 suggest that this quantity will provide an illustrative interpretation. Following the prediction of the quadratic friction model given in eq 3, the data given in Figure 1a are plotted against the new time variable, $(1/2)\rho v_0 t/m$, as shown in Figure 1b. The data sets for each energy overlay when plotted against this new time variable. From the slopes of each projectile at short times, we can determine a value for AC_D for each fullerene cluster (Table 1). As a test of the second-order friction model, we plot $\ln(v/v_0)$ and eq 2 for each of the fullerene clusters at 20 keV against $(1/2)\rho v_0 AC_D t/m$ in Figure 1c. The curves superimpose until a value of $(1/2)\rho v_0 AC_D t/m \sim 0.3$. At this point, the curves of the four fullerene particles diverge from each other, and the short-time approximation, eq 3, produces a 14% error from eq 2. The reasons for the divergence will be discussed below.

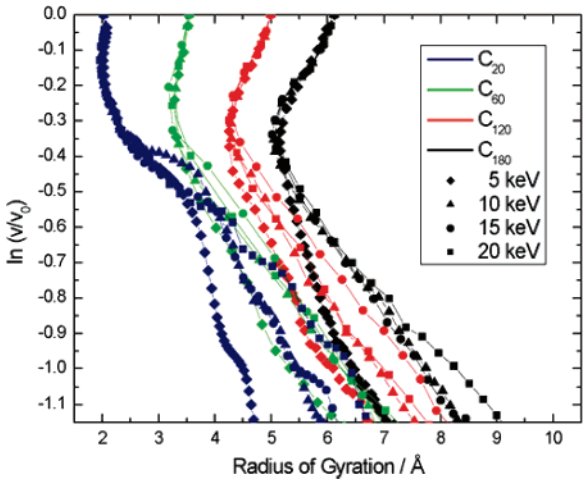

Figure 2. Ln(v/v_0) versus the radius of gyration for the four fullerene projectiles at the four energies.

The two parameters A and C_D, representing the size and shape of the cluster, cannot be unambiguously determined from our data. For illustration, we assume that $A = \pi a^2$, where a is a radius equal to the initial radius of the fullerene cluster plus an interaction radius. We fit the interaction radius so that C_D is approximately constant. The best fit is found for an interaction radius of 1.95 Å when the drag coefficient is 1 ± 0.1 for all of the projectiles. The values of a and C_D are given in Table 1. Without further information, it is not possible to determine precise values of A and C_D.

The quadratic friction model makes specific predictions about the motion of the cluster. The rate of the cluster's deceleration is proportional to the size of the cluster. This dependence is logical as there is more surface area for interacting with substrate

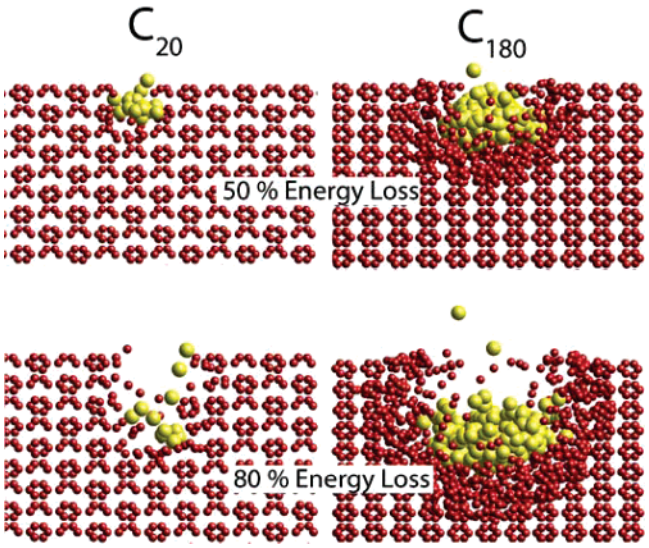

Figure 3. Snapshots of C_{20} and C_{180} at 20 keV at 50% ($\ln(v/v_0) = -0.35$) and 80% ($\ln(v/v_0) = -0.8$) energy loss. The C atoms are represented by yellow spheres and the CH coarse-grained particles by red spheres. The C_{20} snapshots are for a 6 Å slice in the sample, and the C_{180} snapshots are for a 20 Å slice in the sample. The dimensions of the sample shown are 52 Å wide by 31 Å deep.

molecules. An increase in the mass, however, has the opposite effect. The quadratic friction model explains the rates of change in the relative velocity for the four projectiles as well as explaining why they should be dependent upon the initial velocity. In addition, eqs 2 and 3 can be analytically evaluated to find the depth of energy deposition as a function of time.

The quadratic friction model implies that the fullerene molecule is acting as a unified particle. In order to determine the cohesiveness of the projectiles, we calculate their radius of gyration. Figure 2 shows $\ln(v/v_0)$ with respect to the radius of gyration calculated from the positions of the atoms in the simulation. We have chosen to put $\ln(v/v_0)$ on the ordinate so that direct comparisons can be made with Figure 1. For the first part of the motion until $\ln(v/v_0) = -0.4$ or ~55% energy loss, the radii of gyration are independent of energy and are smaller than the initial radius of each cluster except for C_{20}. Most importantly, there is a direct correlation between the time as inferred by the $\ln(v/v_0)$ value when the radius of gyration starts increasing for each cluster and the time when the cluster stops following the friction model (eq 2), Figure 1c.

Snapshots of the C_{20} and C_{180} projectiles are given in Figure 3 for 20 keV bombardment at times at which 50 and ~80% of the energy has been given up to the substrate. Even though the atoms do not form a neat fullerene particle, the atoms remain aggregated so that they can continue to work in a collaborative manner. These snapshots confirm that a single particle is an appropriate description of the fullerene motion during the time when the cluster deposits most of the energy in the solid. Because of the smaller size of the C_{20} projectile, the slice of sample shown in Figure 3 is three times thinner than the slice for the C_{180} projectile. The different amounts of perceived distortion in the substrate for the two projectiles are a visual illusion due to the three times different thickness.

The concept that a fullerene particle bombarding a molecular solid behaves as a particle moving under the influence of friction makes specific predictions, as given in eqs 2 and 3, about how the size and mass should influence the motion in the solid. Key issues to address include the general applicability of the quadratic friction model to all cluster bombardment, the a priori determination of the parameters A and C_D, the energy transfer within the substrate at short times, the factors that lead to the breakup of the cluster, and the influence of the cluster disintegration on the energy loss. For example, the quadratic friction model does not take into account the relative mass of the individual atoms with respect to the mass of the substrate particles, an effect known to influence the dynamics.[12,15,17,22]

Conclusion

We have presented a quadratic friction model to describe energetic fullerene bombardment in molecular solids. The model explains the mass, size, as well as the observation that velocity relative to its initial value decays exponentially with time, with a decay constant that linearly depends on the initial velocity. The assumption of single-particle motion correlates with the behavior of the projectile atoms in the substrate as monitored by the radius of gyration and visual images. The quadratic friction model is thus a comfortable representation for the basic description of fullerene bombardment of molecular solids.

Acknowledgment. Financial support from the Chemistry Division of NSF, Grant No. 0456514, is gratefully acknowledged. Numerous enlightening discussions have preceded this paper, including those with Arnaud Delcorte, Kristin Krantzman, John Vickerman, Roger Webb, Nick Winograd, and Andreas Wucher.

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