AB-INITIO SIMULATIONS TO STUDY THE CONFIGURATIONAL ENTROPY OF COLUMN *IV* MICROCLUSTERS

STEFAN KLEMM*, DAVID A. DRABOLD†, AND OTTO F. SANKEY††
*Department of Physics, University of Notre Dame, Notre Dame, IN 46556 and The Minnesota Supercomputer Center, Inc., 1200 Washington Ave. So., Minneapolis, MN 55415.
† Department of Physics, University of Notre Dame, Notre Dame, IN 46556
†† Department of Physics, Arizona State University, Tempe, Arizona 85287

ABSTRACT

We directly simulate the dynamics of carbon and silicon clusters to study the relevance of the probability distribution of coordinates to experimentally measured phenomena. We believe that the high temperature conformations are not necessarily related to the ground state minimum, and that care should be exercised when comparing ground state $T = 0$ calculations to experiments performed at high temperature.

INTRODUCTION

Studies of column *IV* microclusters are attractive as an area where experiment and theory can be directly compared. Elemental microclusters are accessible by theory and simulation [1][2][3][4]. There are no artificial finite size impositions on the calculations, since the systems are naturally small. The electronic structure calculation is somewhat simplified by the elemental nature of the clusters and in the ground state, the structures frequently have high symmetry. The theoretical studies of microclusters can usually be grouped into one of two broad categories: the first principles or near first principles studies of ground state energies and structures, and empirical or semi-empirical calculations which have the efficiency to explore dynamics or statistical mechanics at finite temperatures.

Experimental work on covalently bonded clusters frequently involves high temperature, where aggregation and dissociation occur. The making and breaking of chemical bonds, and the conformations that exist when this occurs are vital to the understanding of these experiments. Thus, to understand the behavior of a system undergoing cluster dissociation (and the related magic number problem) knowledge of the first few conformational states of the lowest energies is not sufficient.[1] One must have knowledge about the energies and conformations of higher stable structures, and their multiplicity, since such regions of phase space are also visited, perhaps extensively, at higher temperatures.

Ideally, one would like to be able to compute the $3N$ dimensional classical spatial distribution function that describes the probability of N particles occupying a given set of coordinates. In addition to being difficult to calculate, even for small systems, this function would be difficult to examine because of its many dimensional character. There are several alternatives to compactify or sample this information. First, there are extensive studies of the low energy geometries of these systems. These attempt to explain cluster stabilities in terms of the relative energies of the ground state clusters, and can obtain qualitative agreement to experiment.[3] Second, one can sample points on the surfaces guided by the probabilities given by statistical mechanics; the approach taken here. In the past, this technique has usually involved analytical potential functions to describe the forces acting on the ions. For example, Feuston et al. [1], did an exhaustive study of Si cluster dynamics as a function of cluster size and temperature using molecular dynamics with a Stillinger-Weber potential[5]. Also, one can study functions that succintly, although with information loss, quantify the availability of the coordinate space at given temperature. We briefly discuss two information theoretic entropies in this context.

A natural function to characterize our state of knowledge (or ignorance) of where the particles will visit during a dynamics run is a configurational entropy defined as:[6]

$$H(T) = -\int p(\Gamma,T) \quad ln\{\frac{p(\Gamma,T)}{\mu(\Gamma,T)}\}d\Gamma \qquad (1),$$

where Γ is the $3N$ dimensional coordinate space point, T is the temperature,and μ is the measure on the classical phase space. Below we use a different entropy, related to the distribution of quench states, to get a simple estimate of the behavior of of the configurational entropy. This simpler entropy is

$$H(T) = -\sum_i p_i(T) \quad ln\{p_i(T)\} \qquad (2),$$

where p_i is the probability of the quenched state designated by i occurring in one of the quenches of the dynamics run, and where we assume that we have exhausted the set of accessible minima at temperature T. We may interpret H as a measure of the randomness of the trajectory. Its relation to molecular melting and occupied phase volume is presently under study.

We attempt to provide a complementary approach to the *ab-initio* study of clusters and the dynamical studies of semi-empirical potential functions. We study high temperature clusters by dynamics, using accurate forces derived from the electronic structure at each time step. To do this, we adopt the method of Sankey and Niklewski[7] also briefly described by Drabold in this volume. The method provides accurate electronic structure results for clusters and bulk carbon and silicon[8] using the Harris Functional [9] and a local density approximation with the Hamann-Schlüter-Chiang pseudopotential scheme[10]. The pseudo-atomic orbital basis provides for accurate chemical predictions without the need for many basis functions and provides for controlled cutoffs of the overlap integrals[11].

CALCULATIONS

Using this technique, we study clusters of Si_6 and C_6. We perform molecular dynamics runs at several average temperatures (defined by $\frac{3}{2}kT = \frac{1}{2n}m\sum_i v_i^2$, where n is the number of atoms). After the dynamics runs, the simulations are analyzed for their occupation of the coordinate space. We do this by picking a set of well separated times from the simulation. We use the positions of the particles at these times as the initial state of a dynamical quench.[12] The quenching algorithm takes the system from its state during this time in the simulation to a "nearby" stable structure, a local minimum on the electronic energy surface. This is similar to the "inherent structures" discussed by Stillinger and Weber[5]. In this way, we determine the local minima on the electronic energy surface over which the particles tend to move during the dynamics run.

RESULTS

The Si_6 simulation consisted of two runs, with average temperatures of approximately 5100K and 3300K. The quenching from the 3300K run yielded the global minimum structure about 90% of the time. This structure, while having a relatively small configurational entropy, dissociated to Si_5+ Si after about 19 picoseconds. Animation of the dynamics revealed that the configuration approximated at the time of dissociation is is a capped rhombus with the sixth atom bonded to the cap.

The 5100K silicon simulation showed quite different statistics. Four stable structures were encountered in the quenches and the global minimum (Fig. 1(a)) occurred less than half the time. Structures (b)-(d) in Fig. 1 accounted for the remainder of the sample in approximately equal distributions. Thus, as expected, the higher temperature is associated with a broader distribution of quench states, and a higher configurational entropy as given by equation (2). The respective entropy values for the two runs from equation (2) were $H(3300K) = 0.3$ and $H(5100K) = 1.2$. The 5100K structure dissociated to Si_5+ Si after about 15.7 picoseconds, the dynamics from the simulation showed that the dissociation occured from a similar structure as the $T = 3300K$ run. The structure just before breaking up had the underlying structure of figure 1(d).

We performed three C_6 dynamics runs.[13] The average temperatures were 3100K, 2450K, and 1680K. The quenches from these simulations produced four distinct structures, shown in figure 2. The linear structure is the minimum of the structures we have found, consistent with quantum chemistry results [4]. The hexagon structure which both our calculation and others find to be nearly degenerate with the linear global minimum, does not appear in the quenches, presumably due to either entropic effects or insufficient sampling of the phase space.

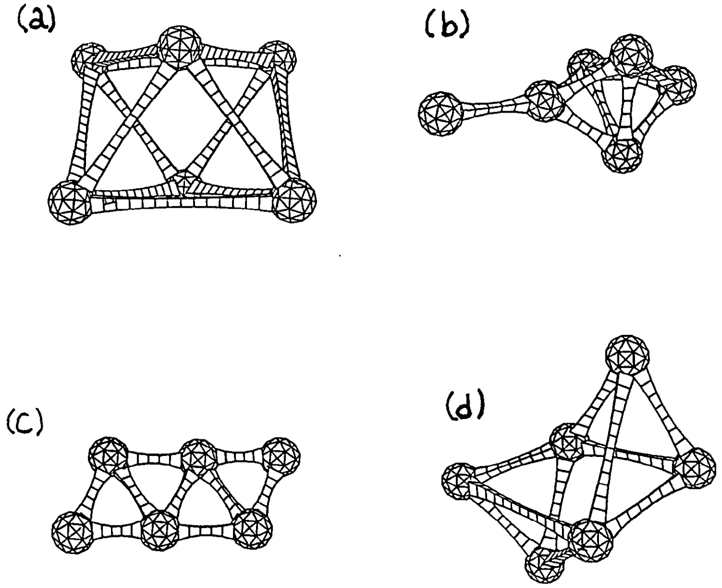

Fig. 1. The ground state of silicon (capped rhombus),(b) a tetrahedron with the end of a dimer bound to its face, (c) a pair Si_3's bound side by side and (d) the distorted capped rhombus are the structures found from quenches of Si runs.

The statistics of the C_6 runs were more evenly distributed than the Si_6. For the 1680K run, we accumulated 15.3 picoseconds of dynamics. The molecule remained bound for the entire run. The distribution of quenched conformations was 40% in the linear structure and about 20% in each of the other three structures (Fig. 2(b)-(d)). This indicates a fairly high configurational entropy of 1.3 for the dynamics run.

The 2450K and 3100K runs dissociated to $C_3 + C_3$ at 2.1 and 2.7 picoseconds respectively. Thus the quench statistics are not as good, (15 points and 12 points respectively) and not sufficient to estimate a quench configuration entropy from equation (2). The quenches are distributed over all four structures. The clusters at both temperatures broke apart from an approximately linear configuration into two C_3 molecules.

It is interesting to note than the entropy calculated from the 1680K carbon run, 1.3, is comparable to the Si runs that produced dissociation, indicating that carbon has a larger phase space available to it at relatively lower temperatures than silicon. This indicates, a more complex electronic energy surface in the sense that it has more or broader minima to occupy.

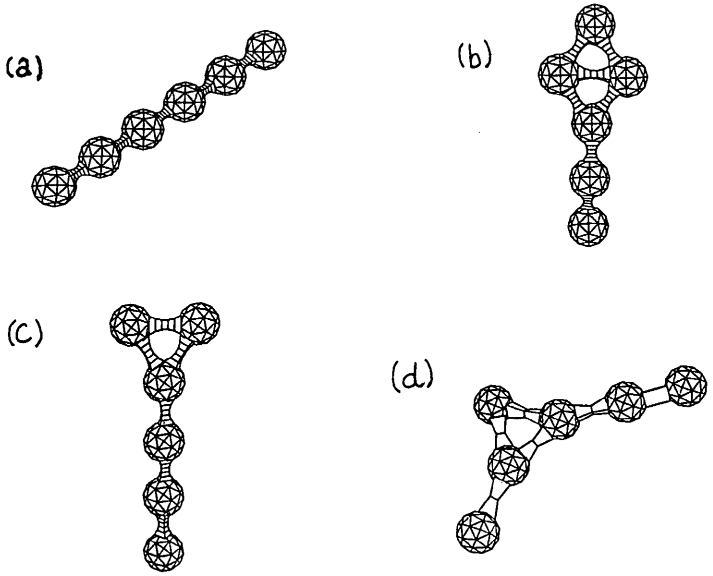

Fig. 2. The four structures of carbon found by quenching selected steps from the dynamics runs. The linear chain (a) is the global minimum, (b),(c) and (d) account for about 60% of the quenches.

CONCLUSIONS

Our calculations, although not exhaustive, support the suppostion that the ground state structure is not the only important feature in determining the dynamics of high temperature clusters, since the system spends time in other regions of coordinate space.

Similar arguments are relevant to the prediction of the vibrational states of high temperature clusters, where the calculation of the frequencies about low lying minima do not account for the geometrical breadth of motion at high temperatures. The reaction coordinates of dissociation for our simulations did not just involve the ground states. The silicon dissociations, in particular, were determined by the shape of the electronic energy surface far from ground state equilibrium.

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12. The quenching algorithm removes all kinetic energy from the system when the kinetic energy reaches a maximum. In the microcanonical ensemble, this is the point in coordinate space where the potential is a near a minimum. After the quench, the system evolves at the new constant energy until the kinetic energy again reaches a maximum and the system is again quenched. This procedure is repeated until a force criterion for convergence is reached. This criterion was typically that all forces be $\leq 10^{-5} eV/\AA$.
13. We used psuedo-atomic cutoff of $r_c = 5.0a_B$ for these calculations. See Drabold, this volume, or reference [7].

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