AB INITIO MOLECULAR DYNAMICS OF COLUMN IV MICROCLUSTERS

by

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ABSTRACT

We report the results of *ab-initio* molecular dynamics simulations for small clusters of Si and C atoms. Ground-state geometries and vibrational spectra are presented. We also describe a Bayesian spectral estimation technique which we have found to be useful in analyzing molecular dynamics trajectories.

INTRODUCTION

Microcluster geometry and dynamics have long been of interest to chemists. In the last few years, there has also been considerable interest in the condensed matter physics community. Beside an intrinsic interest in such molecules, calculations of cluster properties lend insight into how well the various approaches to electronic structure are working. In particular, the molecular environment is very different than the bulk, and successes (and failures!) there can motivate improved approaches to the electronic structure problem.

In this paper we will discuss the application of the first principles molecular dynamics (MD) scheme of Sankey and Niklewski [1] to microclusters. This methodology is particularly well suited to cluster studies, as the entire calculation is carried out in *real space*. The MD method is founded upon four major approximations. (1) Non-local norm-conserving pseudopotentials of the Hamann-Schlüter-Chiang type[2]. We treat the non-local pseudopotential exactly. No local approximations are made. (2) A local orbital basis set with slightly excited free atom sp^3 orbitals on each atomic site.[1] "Slightly excited" means that in addition to satisfying the free atom Schrödinger equation, the basis orbitals satisfy a boundary condition that imposes a finite range – the orbitals have support only in a sphere of radius r_c. We choose r_c to give a third neighbor model in the diamond structure. This gives an interaction range of $10a_B$ and $6.6a_B$ for Si and C, respectively. (3) The Harris implementation[3] of the Local Density Approximation (LDA) is used. This approximation is accurate in Si and C with a superposition of free slightly excited atomic densities as the "input density" in the language of Foulkes and Haydock[4]. As the calculation is non-self-consistent, it is considerably more efficient than fully self-consistent methods. The Harris approximation yields an electronic charge density exact to first order in the difference between the starting and self-consistent densities. (4) Matrix elements are calculated from lookup tables which are computed once for each atomic species. Some three center integrals associated with the pseudopotential, neutral atom and exchange-correlation matrix elements are computed with the aid of an angular momentum expansion. These approximations are collectively and separately quite accurate. The MD scheme has been applied with success to surfaces[5], clusters[6], amorphous Si[7], and crystalline phases[1] of Si and C, with accuracy close the *ab-initio* simulations of Car-Parrinello[8] type.

The method is very convenient to use. To simulate a new material, one simply calculates the lookup tables for the various matrix elements. This (one time) investment takes several Cray hours. Simulation of a small molecule (Si_6 for example), takes about 1 sec per time step on a Cray X/MP. The time step length is set by a purely *nuclear* (not electronic) time scale. Additionally, our compact basis set allows us to store information from previous time steps which enables the use of quadrature schemes more sophisticated than the commonly used Verlet method, which helps to accurately extend the time step even further.

APPLICATION TO MICROCLUSTERS

To find ground state geometries of small clusters, we have applied both the simulated annealing and dynamical quenching methods. [1,6] The former is less efficient, but more likely to find a global minimum in the total energy. For the small clusters discussed here, dynamical quenching is adequate. For both Si and C our results are in good agreement with quantum chemistry calculations[9] and self-consistent LDA calculations[8]. Results for Si structures have been reported elsewhere[6]. In Table 1, we display geometrical parameters for selected C clusters. The results are quite satisfactory.

We have found that within our approximations, carbon is more difficult to accurately simulate than silicon. For $r_c = 3.3a_B$, we find an unexpected global minimum in the potential energy for an isosceles triangle structure for C_3, which is inconsistent with more sophisticated calculations. Note however, that the bondlength predicted for the metastable linear C_3 structure is in excellent agreement with the state-of-the-art calculations of Almlöf and coworkers[9]. This is the only case for which we have encountered a sensitivity to r_c. For a larger r_c ($r_c = 5.0a_B$) we find a linear ground state (global minimum in the potential energy), though the bondlengths are not so satisfactory as our "preferred" $r_c = 3.3a_B$ calculation. Parasuk and Almlöf[9] also detected a sensitivity to the choice of basis sets for C_6.

molecule	structure	bondlengths (A)	energy difference (eV/atom)
C_2	linear	1.235	0.0
C_3	triangle	1.3244,1.691	-2.2
C_3	linear	1.303 (1.302)*	-2.1
C_6	linear	1.281,1.301,1.291	-3.2
C_6	hexagon	1.311 (1.31)*	-3.4

linear C_6 bondlengths from molecular end to center

TABLE 1. Geometry of Selected Carbon Molecules ($r_c = 3.3a_B$)
* Reference 9

The efficient execution of dynamics for microclusters has enabled us to study finite temperature entropic effects, and some of the "phase space" properties of small clusters. Most of these results will be presented in another paper (Klemm et. al. – this volume). In a preliminary way, we have also successfully simulated molecular collisions/scattering and unimolecular dissociation. In this paper we will describe some elementary dynamical properties and discuss a novel approach to analyzing time series data to extract spectral information.

In Fig. 1a we show traces of the (planar) motion of Si_3 at kinetic temperature $T = 500K$, where T is defined by:

$$3/2k_BT =< p^2/2M_{Si} >, \tag{1}$$

where the right hand side is the average kinetic energy of the molecule after many oscillations. For $T = 50K$ and $500K$ the molecule essentially executes small oscillations about its equilibrium (isosceles triangle) configuration. For the considerably higher temperature of $2500K$ (Fig. 2), the motion is more complex, and exhibits a six-fold pattern. Animation of this trajectory reveals that the six-fold structure is a consequence of a repeated exchange of the role of "vertex atom" (vertex of the isosceles triangle). For these simulations the velocity of the center of mass and the total angular momentum vanish; this was accomplised with a judicious choice of initial conditions[6].

In Fig. 1b,2b we show spectral densities calculated by Fourier transforming the velocity-velocity autocorrelation function, obtained from the trajectories. At 50K and

500K there are three dominant peaks corresponding to the normal modes expected for the Si_3 system. Even at 500K there are indications of anharmonic effects in the spectra. The spectrum for the 2500K molecule (Fig. 2b) is very much more complex; it may be quasi-continuous. For the $50K$ and $500K$ case we have identified the dominant frequencies with a Bayesian spectral estimation procedure due to G. L. Bretthorst[10], which we discuss in the next section. The Bayesian frequency estimates are from a direct analysis of the raw atomic velocities, not from the discrete Fourier transform (DFT) plotted in the Figure.

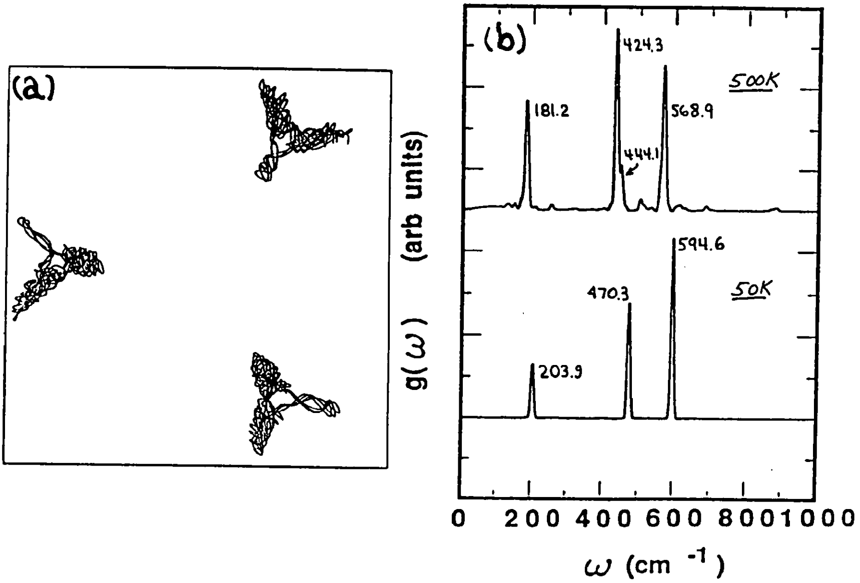

FIGURE 1. (a) Trajectory of Si_3 molecule at T=500K. (b) Vibrational spectra of Si_3 for 500K and 50K. Frequencies labeling peaks are Bayesian estimates (see text). Frequencies are from five and three frequency models, respectively. Uncertainty in frequencies is $\approx 0.2cm^{-1}$.

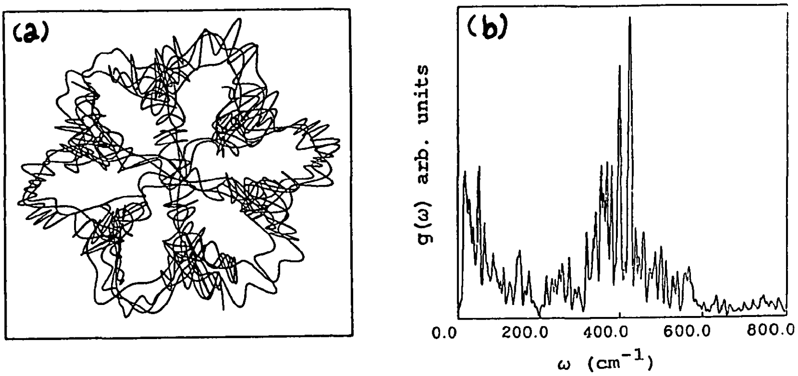

FIGURE 2. (a) Trajectory of Si_3 at $T \approx 2500K$. (b) Vibrational spectrum for Si_3 at $T \approx 2500K$.

BAYESIAN SPECTRAL ESTIMATION

The standard way to obtain a vibrational density of states from MD data is to calculate a velocity autocorrelation function $g(t)$ whose Fourier transform is the spectral density $g(\omega)$. A practical difficulty with this relation is that the function $g(t)$ is known only for finite range of t – which depends upon how long the MD simulation was performed, and $g(t)$ is only sampled at discrete points (because of the discreteness of the MD time step). For a $g(t)$ with these limitations, the most general and accurate way to spectrally decompose the time-dependent function is to employ Bayesian spectral estimation techniques. One purpose of this section is to provide a brief commentary on this method, and suggest a reference which we hope will be useful to readers.

In Bayesian spectral estimation, one uses the principles of probability theory to ascertain the *optimal* procedure to find the frequencies present in a stationary time series. It has been rigorously demonstrated[10] that the standard DFT is an optimal frequency estimator only for time series with one frequency present (a rare case in MD simulations). There are several advantages to the Bayesian method. (1) The spectral resolution is *very* much improved over the DFT with window. (2) If the problem has noise (either experimental or statistical) the estimation algorithim can handle it naturally, unlike some other successful spectral estimation techniques. Accurate estimates of the noise in the "data" and errors in estimated spectral parameters are useful byproducts of the method. (3) The Bayesian scheme gives a very elementary representation of both $g(t)$ and $g(\omega)$ in terms of finite Fourier sums. (4) The method is efficient, in part because of the ability to integrate out nuisance parameters (Fourier amplitudes, for example). The central point is that the Bayesian method allows one to "make the most" of spectral information in a time series which may be very difficult to extend to longer times. A complete introduction to this subject is given in Ref. 10.

CONCLUSION

We have illustrated the application of a new, efficient MD scheme to elemental microclusters. The method accurately describes bulk, amorphous, surface and molecular bonding. A recently develped probability-theoretic method for time series analysis is presented in the context of spectrally decomposing MD trajectories.

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