

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual Physical Review standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Efficient *ab initio* molecular-dynamics simulations of carbon

D. A. Drabold, Ruoping Wang, and Stefan Klemm*

Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

Otto F. Sankey and J. D. Dow

Department of Physics, Arizona State University, Tempe, Arizona 85287

(Received 4 September 1990)

We evaluate an *ab initio* scheme for performing molecular-dynamics simulations of elemental carbon. The method involves no free parameters and has been rigorously tested in a wide range of bonding environments. For elemental covalent systems this approach has an accuracy comparable to other density-functional schemes, and is more efficient. Carbon microclusters, bulk diamond, and graphite are discussed. The vibrational spectrum of C_4 is examined in detail with a Bayesian probability theoretic analysis of the vibrational modes of the molecule at a variety of kinetic temperatures.

An ideal simulation of a condensed-matter system should provide more than replication of selected experimental data. General predictive capabilities are available only if the simulation is not heavily dependent upon experimental input. In addition, the method should be efficient enough that dynamical properties or ensemble averages of realistic systems can be calculated. Typically, analytic interatomic potentials do not satisfy the former, and *ab initio* calculations fail in the latter.

In this Brief Report we report *ab initio* molecular-dynamics (MD) simulations of carbon that represent an important step toward meeting both of these needs. The calculations presented in this paper are a direct outgrowth of the work of Sankey and Niklewski on silicon.¹ The approach does not involve the input of experimental data, and does not suffer from the transferability problems associated with empirical interatomic potentials²—the method is equally applicable to small clusters, surfaces, or bulk problems. The earlier work of Sankey and Niklewski with Si demonstrated excellent quantitative agreement between this method and other *ab initio* techniques, as well as with experimental data where available. In particular, the method produced accurate ground-state geometries and vibrational spectra for Si microclusters and outstanding agreement with the phase diagram of Yin and Cohen.³

We are motivated to study carbon because of the large number of potential applications of an accurate MD scheme. An incomplete list of current research on carbon would include the study of clusters (of interest to stellar-atmosphere research, catalysis and combustion,

and laser-evaporation experiments), surface properties (of great interest in the growth of thin diamond films, for example), and the bulk properties; both static and dynamic. Additionally, the simulation of carbon provides a rigorous test of a MD method because of carbon's unusually rich chemical bonding properties.

Galli *et al.* have presented important work on *a*-C (Ref. 4) and *l*-C (Ref. 5) using the Car-Parinello (CP) method.⁶ This approach provides a rigorous *ab initio* framework for the simulation of covalent systems. For systems where a linearized-density-functional method is valid, however, our approach is more efficient and essentially as accurate. This accuracy is indicated here and in Ref. 1. The efficiency is a consequence of the small basis set that we employ. High accuracy is obtained because the chemistry of the atoms is taken naturally into account by our choice of basis. We have performed MD simulations for picosecond durations with more than 100 atoms per unit cell.⁷ We will present these results elsewhere.

The theory is based upon three approximations. (i) For each site there is a minimal tight-binding-like basis of pseudo-atomic-*sp*³-orbitals calculated from nonlocal pseudopotentials of the Hamann-Schlüter-Chiang type.⁸ (ii) We employ the Harris-Foulkes linearization⁹ of the density-functional method.¹⁰ (iii) The pseudo-atomic-orbitals (PAO's) have compact support: following the same scheme employed in Si,^{1,11} we require the PAO's to vanish beyond the third-neighbor distance of the bulk (diamond)—thus we use a cutoff radius $r_c = 3.3$ Bohr radii. These approximations have been well justified in ear-

TABLE I. Geometry of carbon microclusters. Results of experiment and recent quantum-chemical calculations are included in parentheses. ΔE is the difference in binding energy per atom above the dimer.

Cluster	Structure	Bond lengths (\AA)	ΔE (eV/atom)
C_2	linear	1.235 (1.24) ^c	0.00
C_3	linear	1.303 (1.302) ^a (1.297) ^c	2.13
C_3	triangle	1.324,1.691	2.26
C_4	rhombus	1.445,1.486 (1.448)(1.50) ^b	3.20
C_6	linear	1.281,1.301,1.291	3.21
C_6	hexagon	1.311 (1.31) ^a	3.41

^a *Ab initio* CASSCF (Refs. 14 and 15).

^b *Ab initio* (Ref. 20).

^cExperimental data quoted from Refs. 9 and 14.

lier work and references therein,¹ and the analysis presented there for Si is immediately applicable to C. Molecular-dynamics simulations are performed by using a variation of the Hellmann-Feynman¹² theorem to calculate the interatomic forces; Newton's equation is then integrated using a standard predictor-corrector technique¹³ to obtain particle trajectories. For bulk simulations, we carry out these calculations in a supercell to simulate an infinite system and we always use several special points in the Brillouin zone to calculate the total energy and interatomic forces.

We illustrate this method by studying microclusters and bulk phases. Throughout this paper we report results for $r_c = 3.3a_B$. To find minima in the total energy, we have used dynamical quenching¹ (DQ). For C (unlike Si) we have found some sensitivity to the value of r_c chosen. Normally this sensitivity is manifested as a moderate ($\approx 7\%$) shift in bond lengths (smaller r_c yields a smaller bond length). In C_3 , however, $r_c = 3.3a_B$ leads to an isosceles-triangle ground state instead of the correct linear structure that is obtained for a larger $r_c = 5a_B$, which is essentially identical to the free-space PAO. We therefore view the effects of varying r_c as being a sensitivity to the basis set. More sophisticated calculations^{14,15} have also displayed a basis-set dependence. For C_6 , we find two energetically comparable minima: a linear chain and a regular hexagon with geometry as indicated in Table I. For $r_c = 3.3a_B$, our bond lengths differ by a maximum of 2% from CASSCF (quantum-chemical "complete-active-space self-consistent-field") calculations.^{14,15} The linear chain has a "cumulene-like" structure¹⁵ (with double bonds between all carbon atoms).

The quenched bond lengths and energies relative to the dimer are given in Table I. In each case, the agreement between the present method and state-of-the-art quantum-chemistry calculations^{14,15} is gratifying. One might naively expect that our minimal basis set should be incapable of such accuracy. We note, however, that approximation (iii) above may be physically interpreted as supplementing the basis with additional excited s and p

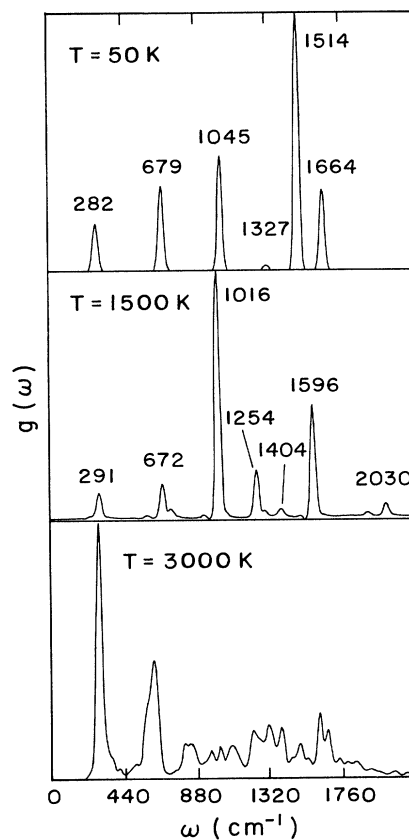


FIG 1. Vibrational spectral densities for the rhombus C_4 molecule (see text). Kinetic temperatures of 50, 1500, and 3000 K are illustrated. A 14-frequency harmonic model is analyzed using the techniques of Ref. 16, and Bayesian frequency estimates from the velocity time series are displayed adjacent to prominent features in the spectra. The error in these estimates is less than 2 cm^{-1} . The widths of the peaks shown are an artifact of the Fourier transform.

orbitals.^{1,11} It should not be forgotten that MD simulations have advantages over static total-energy calculations. DQ via MD allows the investigation of structures of low symmetry, which would be difficult to anticipate *a priori* for gradient searches near an assumed structure within a total-energy calculation.

To lend further insight into the dynamics of the C₄ molecule, we have also calculated vibrational densities of states (VDOS) at three temperatures: 50, 1500, and 3000 K. We have analyzed these spectra using both conventional velocity-velocity autocorrelation function (ACF) techniques, and a direct spectral analysis of the raw velocities using a Bayesian probability-theoretic method due to Bretthorst.¹⁶ The frequency-dependent ACF is depicted in Fig. 1 along with the Bayesian frequency estimates, which are vastly more accurate than an examination of the discrete Fourier transform of the ACF (typical errors are less than 2 cm⁻¹). The Bretthorst method makes anharmonic effects very explicit: second and higher harmonics of some of the principals are evident, as are the expected shifts in the centers of the main peaks and mode softening at the higher temperatures. For 3000 K we observe a very complicated VDOS with considerable structure. Here, anharmonic effects are dominant, as the large number of spectral features reveals. For 1500 K we have observed a slight sensitivity of the peak positions to the initial conditions. This effect is of order 1 cm⁻¹.

We now discuss tests of this scheme in bulk systems. By minimizing the total energy as a function of lattice constant we have determined a cubic lattice constant for

the diamond structure of $a=3.535$ Å (3.556 Å expt.) and for graphite we obtain a nearest-neighbor distance of $d=1.416$ Å (1.420 Å expt.).¹⁷ It is interesting that the FLAPW calculations of Wimmer *et al.*¹⁸ also yield a graphite monolayer nearest-neighbor distance of 1.416 Å. We have also calculated the diamond bulk modulus to be 5.70 GPa (5.45 GPa expt.). For these computations we used the special points following the prescription of Chadi and Cohen.¹⁹

In conclusion, we have demonstrated the efficacy of this linearized-density-functional technique for simulating the dynamics of the important element carbon. The computational efficiency of the method allows the study of dynamical and statistical-mechanical properties from an accurate first-principles foundation. For every bonding environment for which we have experimental data (from the C dimer to bulk crystalline structures), the predicted and experimental bond lengths differ by $\leq 0.5\%$. Having established the method's accuracy in many bonding environments, we may now proceed to consider a number of applications with confidence.

We are indebted to Dr. Larry Bretthorst for generously providing us with a copy of his Bayesian Spectral Analysis code, and for helpful conversations. We have also benefited from discussions with Professor Peter Fedders and D.J. Niklewski. This work was supported in part by the Office of Naval Research, under Contracts No. ONR N00014-85-K-0442 and No. ONR N00014-84-K-0352.

*Permanent address: Minnesota Supercomputer Center, Inc., 1200 Washington Avenue So., Minneapolis, MN 55145.

¹O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989); for Si clusters, see O. F. Sankey, D. J. Niklewski, D. A. Drabold, and J. D. Dow, *ibid.* **41**, 12 750 (1990).

²A comprehensive review of interatomic potentials and their applications is given by Anders Carlsson, in *Solid State Physics, Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1990), Vol. 43, p. 1.

³M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

⁴G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **62**, 555 (1989).

⁵G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 988 (1989).

⁶R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

⁷D. A. Drabold, P. A. Fedders, O. F. Sankey, and S. Klemm (unpublished).

⁸D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

⁹J. Harris, Phys. Rev. B **31**, 1770 (1985). A particularly lucid exposition on the method, and its relation to the tight-binding method, is given by W. M. C. Foulkes and R. Haydock, *ibid.* **39**, 12 520 (1989).

¹⁰W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

¹¹R. W. Jansen and O. F. Sankey, Phys. Rev. B **36**, 6520 (1987).

¹²H. Hellmann, *Einführung in die Quantumchemie* (Franz Deutsche, Leipzig, 1937); R. P. Feynman, Phys. Rev. **56**, 340 (1937).

¹³See, for example, R. L. Burden, J. D. Faires, and A. C. Reynolds, *Numerical Analysis* (Prindle, Weber and Schmidt, Boston, 1981) p. 222.

¹⁴For C₃, U. G. Jørgensen, J. E. Almlöf, and Per E. M. Siegbahn, *Astrophys. J.* (to be published).

¹⁵For C₆, see V. Parasuk and J. Almlöf, J. Chem. Phys. **91**, 1137 (1989).

¹⁶For a clear discussion of the general parameter-estimation problem from a Bayesian point of view, see G. L. Bretthorst, *Bayesian Spectral Analysis and Parameter Estimation* (Springer-Verlag, New York, 1988). For the special case of Gaussian noise and one frequency, see E. T. Jaynes, in *Maximum Entropy and Bayesian Spectral Analysis and Estimation Problems*, edited by C. Ray Smith and G. J. Erickson (Reidel, Dordrecht, 1987), pp. 1–37.

¹⁷The experimental numbers cited here are from *CRC Handbook of Chemistry and Physics*, 67th ed., edited by R. C. Weast, M. J. Astle, and W. H. Beyer (CRC, Boca Raton, 1987).

¹⁸E. Wimmer, A. J. Freeman, C-L. Fu, P-L. Cao, S-H. Chou, and B. Dely, in *Supercomputer Research in Chemistry and Chemical Engineering*, edited by Klavs F. Jensen and Donald G. Truhlar (American Chemical Society, Washington, D.C., 1987).

¹⁹D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973); see also H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5188 (1976).

²⁰J. P. Ritchie, H. F. King, and W. S. Young, J. Chem. Phys. **85**, 5175 (1986).