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A method and results for realistic molecular dynamic simulation of hydrogenated amorphous carbon structures using a scheme consisting of a linear combination of atomic orbitals with the local-density approximation

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Abstract. A method for realistic molecular dynamic (MD) simulations of the chemical bonding formation in extended hydrogenated amorphous carbon (a-C:H) structures of varying density and incorporated hydrogen content is presented. Applying the Born–Oppenheimer approximation, the forces moving the atoms via MD on the potential energy surface are calculated within an approximated MD-density functional theory which uses localized basis functions. The method is shown to describe correctly the ground state configurations of C_n microclusters, C_nH_m hydrocarbon molecules and radicals, as well as bulk crystalline carbon. Application to dynamical structure simulation of a-C and a-C:H results in realistic metastable configurations which are characterized electronically by a well defined gap in the electronic density of states around the Fermi energy. A reasonable structure statistics is obtained and compared with fully *ab initio* calculations and experiments.

1. Introduction

There has been much recent progress in understanding the structural and physical properties of amorphous carbon (a-C) (Robertson 1986, Robertson and O'Reilly 1987, Tersoff 1988, Galli *et al* 1989, 1990). In most of the metastable carbon modifications a large amount of hydrocarbon (up to about 50 at. %) is incorporated in the material, which strongly influences the structural stability during thin-film deposition (Angus and Jansen 1988). Besides the possible twofold, threefold and fourfold coordination in sp -, sp^2 - and sp^3 -bonding configurations, it is the influence of hydrogen on the structural stability which is responsible for the broad structural variability of hydrogenated amorphous carbon (a-C:H) modifications having a great diversity in their physical properties. To produce thin a-C:H films with well defined physical characteristics, one crucial problem is the control of the dynamical influence of the hydrogen on clustering and on the structure formation of metastable a-C:H modifications, which will differ in their medium-range characteristics. The ability of theoretical carbon structure simulation, including hydrogen, to clarify such issues has been limited owing to difficulties in

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the construction of empirical potentials; also, the hydrogen influence on dynamical structure relaxation is not understood at all.

There have been only a few attempts at the computer simulation of a-C:H structures in the past. One such was performed by our group, extending the work of Wooten and Weaire (1987); their method was based on Monte Carlo simulated annealing on the basis of the empirical strain energy concept of Keating (1966) to mix sp^2 and sp^3 structures, also allowing for hydrogen insertion by saturation of dangling bonds (Jungnickel *et al* 1991). A second attempt has been made by Brenner (1990), generalizing the empirical binding energy of Tersoff (1988) for Monte Carlo or molecular dynamics (MD) simulations of a-C (see also Haase *et al* (1991)) to include hydrogenated structures. This procedure, however, seems questionable because of the large increase in the number of empirical potential parameters, for which a unique fitting to well known C_nH_m clusters, molecules and radicals as well as to bulk structures is very difficult or, more probably, not possible at all. Fitting all parameters well requires a great amount of physical intuition; even then doubts remain if one uses bulk potentials within atomic environments that are very different from where they were developed, e.g. small clusters, surface problems (non-bulk materials) and inhomogeneous heteronuclear amorphous structures with a high degree of medium-range order.

To treat the problem of the hydrogen influence on dynamical structure formation in a-C:H with correct binding configurations, quantum mechanically based methods have to be applied. Combining the density functional (DF) calculation of the energy surfaces and forces with finite-temperature MD (Car and Parinello 1985); Galli *et al* (1989, 1990) obtained remarkable first-principle results concerning the structural and electronic properties of liquid and amorphous pure carbon. In their calculation they used a large basis of (delocalized) plane waves to expand the electronic Kohn-Sham orbitals at the Γ point of the supercell Brillouin zone. Owing to the great demands on computer time this procedure allows for practical structure simulations of only small supercells (54 atoms) embedded in a periodic structure. Such a 54-atom supercell obviously is too small to account well for the rich spectrum of clustering and medium-range order effects, perhaps extending over three or more atomic distances in a-C:H and in analogous multicomponent amorphous semiconductor materials. While the plane-wave basis has advantages for the calculation of forces in MD simulations of atomic structures, it must be rather large to obtain accurate total energies and forces and must involve time-consuming computer calculations, especially for systems containing hydrogen or transition elements that cannot be characterized by weak pseudopotentials.

As discussed by Laasonen and Nieminen (1990) it is worthwhile to develop new approaches which are computationally faster. They use as an alternative the empirical tight-binding (or Hückel) approximation for solving the electronic problem in one-component amorphous materials in combination with MD; we apply in this paper an approximate MD-DF method which uses the localized basis functions suggested by Seifert *et al* (1989). This procedure serves as the foundation for a realistic theoretical study of dynamical structure forming processes in real heteronuclear amorphous semiconductors, including a-C:H.

This method is tested to describe the chemical bonding in the ground-state structure configurations of C_nH_m hydrocarbon molecules and bulk crystalline carbon modifications as well. To develop and establish the method all dynamical simulations of periodic a-C and a-C:H supercell structures of varying density and hydrogen content (C_{54} and $C_{55}H_{45}$) are performed on a RISC workstation DEC-5000 and results in realistic structures and electronic densities of states. The now well tested software package will

be used in future to allow for realistic dynamical structure formation in heteronuclear systems including hydrogen up to a few hundred atoms.

2. Method

To apply the linear combination of atomic orbitals (LCAO) scheme to systems with a great variety in structure including different types of atom, as for example in a-C:H and real mixed amorphous semiconductors, the empirical tight-binding LCAO parameters obtained from fitting to crystalline situations cannot provide a good approximation. For this purpose it is desirable to calculate LCAO data from first principles, assuming a continuous spectrum of interatomic distances and bond angles in the amorphous material. As an important requirement the method should allow one to build any kind of atom into the structure.

Car and Parinello (1985) combined the DF theory with MD. However, a large basis of (delocalized) plane waves is used in their method. Such a basis is not easily applicable to many cases of interest, such as transition elements or perhaps also systems containing elements of the second row of the periodic table (C, N, O and F) where localized basis functions should have significant advantages. In this paper we apply a simplified variant of the MD-DF technique, which was originally developed for molecules and clusters (Seifert *et al* 1989, Seifert and Jones, 1991).

We use the LCAO for expanding the Kohn-Sham orbitals:

$$\psi(r) = \sum_{\mu} C_{\mu} \varphi_{\mu}(r - R_{\mu}). \quad (1)$$

In this way the Kohn-Sham equations are transformed into a set of algebraic equations (secular equations):

$$\sum_{\mu} C_{\mu} (h_{\mu\nu} - \epsilon S_{\mu\nu}) = 0. \quad (2)$$

These equations can be solved by diagonalization of the secular matrix. (In a previous paper, Seifert *et al* (1989) have presented a variant of this method, which applies orbital dynamics—as proposed by Car and Parinello (1985)—instead of diagonalization of the secular matrix.) The $h_{\mu\nu}$ are the Hamiltonian matrix elements of the basis functions with the Kohn-Sham Hamiltonian \hat{h} :

$$\hat{h} = \hat{t} + V_{\text{eff}}(r) \quad (3)$$

where \hat{t} is the operator of kinetic energy, and V_{eff} is the effective one-particle potential, consisting of the electron-nuclear part V_{ext} , the mean-field electron-electron interaction contribution (Hartree potential V_{H}) and the exchange-correlation part V_{xc} in the local-density approximation (LDA):

$$V_{\text{eff}} = V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}}. \quad (4)$$

The overlap matrix elements $S_{\mu\nu}$ are due to the non-orthogonality of the basis functions at different sites in the system. As an approximation we write V_{eff} as a sum of potentials V_j^0 of neutral atoms:

$$V_{\text{eff}} = \sum_j V_j^0. \quad (5)$$

Consistent with this approximation, one has to neglect several contributions to the Hamiltonian matrix elements $h_{\mu\nu}$ (Seifert and Eschrig 1985, Seifert *et al* 1986):

$$h_{\mu\nu} = \begin{cases} \langle \varphi_{\mu} | \hat{t} + V_j + V_k | \varphi_{\nu} \rangle & \text{if } \mu \cap \nu \in \{j, k\} \\ 0 & \text{otherwise.} \end{cases} \quad (6)$$

This treatment may be viewed as the LCAO variant of a cellular Wigner-Seitz method, as applied to molecules by Inglesfield (1979).

The forces F^k on the ions can be divided into a nuclear part F_n^k and an electronic part F_e^k (R_k is the position vector of atom k):

$$F^k = -\partial E / \partial R_k = F_e^k + F_n^k$$

$$F_n^k = \sum_{j \neq k} \frac{\partial}{\partial R_k} \left(\frac{Z_k Z_j}{|R_k - R_j|} \right). \quad (7)$$

It is possible to write the electronic part of the force as a sum of orbital contributions:

$$F_e^k = \sum_i n_i F_i^k = -\frac{\partial}{\partial R_k} \left(\sum_i (\Psi_i | \hat{h} | \Psi_i) \right) \quad (8)$$

where n_i is the occupation number of orbital i . Finally, F_i^k may be written in the following form:

$$F_i^k = \sum_{\mu} \sum_{\nu} C_{\mu}^i C_{\nu}^i \left(-\frac{\partial h_{\mu\nu}}{\partial R_k} + \varepsilon_i \frac{\partial S_{\mu\nu}}{\partial R_k} + \frac{\partial V_{\mu\nu}^{cc}}{\partial R_k} \right). \quad (9)$$

$V_{\mu\nu}^{cc}$ are the matrix elements of the electron–electron interaction potential: $V^{cc} = V_H + V_{xc}$. The nuclear repulsion force F_n^k and the contribution, arising from $\partial V_{\mu\nu}^{cc} / \partial R_k$, compensate strongly, so that rather large LCAO basis sets are needed to calculate the force accurately.

For this reason we combine that term and F_n^k together as an empirical repulsive force, for which we have chosen the force related to the energy:

$$U(R) = a(R - R_1)^2 \quad (10)$$

for $R < R_1$ and zero for $R \geq R_1$. The parameters a and R_1 are obtained by fitting the calculated equilibrium distance and vibration frequency in a diatomic molecule to their experimental values. Such a description of the forces is comparable with a similar partitioning of the cohesive energy used in calculations of the structural properties of clusters by Tomanek and Schlüter (1987). The scheme proposed here may be viewed as a 'hybrid' between an *ab-initio* MD method based on DF theory and the use of purely empirical potentials. We thereby overcome the transferability problem, where parametrized potentials based on experimental data cannot be transferred from one system to another. We also require much less computational effort than the *ab-initio* MD route because of the significantly smaller number of basic states. The method described here has already been applied by Seifert and Jones (1991) to describe the structural properties of phosphorus clusters, using MD and the technique of simulated annealing.

There is also a relatively simple way to apply the scheme to a supercell in a periodic infinite structure. If the supercell contains many atoms (compared with a typical unit cell of a crystal) the eigenvalue spectrum at the Γ point of the Brillouin zone is a good approximation to the whole density of states (DOS). The applicability of the localized base has been tested by computing the DOS per atom for crystalline carbon using a C_{48} and C_{64} supercell for graphite and diamond, respectively. It turns out that the DOS matches quite well to the LDA–band-structure results (Painter *et al* 1971, Holzwarth *et al* 1982) from the bottom of the valence band up to the Fermi energy. Obviously, the LCAO base, consisting only of the valence electron states, is unable to form states in the conducting band sufficiently well. However, this does not matter if we are only interested in the occupied states as in the Hellmann–Feynman theory approach used in this paper.

Furthermore, Blaudeck (1991) has pointed out a simple and practicable approach to complete the LCAO base using the energetically lowest plane waves in the supercell. With only a few additional plane waves per atom the resulting expanded mixed base can be

Table 1. Equilibrium distances, vibrational frequencies and fitted values of empirical parameters for diatomic molecules using (a) $V(r) = V_{\text{LDA}}$ vacuum atoms and (b) the modified atomic LDA potential in (11).

Molecule	r_0 (units of a_B)	ν (cm ⁻¹)	a (Hartree/ a_B^2)		R_1 (units of a_B)	
			(a)	(b)	(a)	(b)
C-C	2.30	1855	0.568	0.861	3.000	3.147
C-H	2.08	2861	0.174	0.162	2.658	3.327
H-H	1.40	4400	0.207	0.189	1.854	2.336

used to compute the electronic DOS up to the lowest part of the conduction band. This will be important for interpreting electronic and optical properties, associated with the band-gap width, etc. The densities of states introduced in this paper for the modelled continuous a-C and a-C:H structures are calculated in this way.

As shown by Eschrig and Bergert (1978), one can avoid large lattice sums in the calculation of the Hamiltonian and overlap matrices and improve the approximation (5) and (6) by using modified and more localized atomic orbitals. Following Eschrig and basis functions are determined in a modified atomic LDA potential:

$$V(r) = V_{\text{LDA}} + \left(\frac{r}{r_0}\right)^R - \sum_k a_k (1 + \alpha_k r) \exp(-\alpha_k r). \quad (11)$$

Apart from Eschrig's parabolic term ($n = 4$; $r_0 \approx r_{\text{Wigner-Seitz}}$), our potential includes some additional Slater summands which form a flat and slightly negative potential. The coefficients a_k ($k = 1, 2$) are chosen in such a way that the s and p valence states of the atomic Hamiltonian are exactly the same as they would be without any additional potential to V_{LDA} . In other words, the additional potential does not shift the energy of the valence states in a single atom. Hence, the correct DOS on the energy scale will be obtained in the whole range of atomic densities, going from densely packed structures to low-density systems, e.g. porous amorphous materials.

The Verlet (1967) algorithm was applied for the integration of the Newton equations for the atoms:

$$M_k \ddot{\mathbf{R}} = -\partial E / \partial \mathbf{R}_k. \quad (12)$$

A time step of 100 atu (1 atu = 2.4×10^{-17} s) has been found to be sufficient for handling these equations.

The calculation starts with a non-relativistic and self-consistent determination of the effective one-electron potential in (4) and the corresponding wavefunctions of a single atom in LDA with the local exchange-correlation potential of Hedin and Lundquist (1971). The single atom s- and p-valence electron wavefunctions form the basis for the LCAO *ansatz* for expanding the Kohn-Sham orbitals in (1), from which the Hamiltonian, and overlap matrices in (2) and (9), may be obtained. We have to determine the parameters a and R_1 by fitting the calculated equilibrium distances and vibrational frequencies in the diatomic molecules to the corresponding experimental values listed in table 1.

3. Tests and results

The MD simulation has been shown to yield the correct stable and isomer ground-state (minimal-energy) structure and chemical bonding of carbon microclusters C_n ($n =$

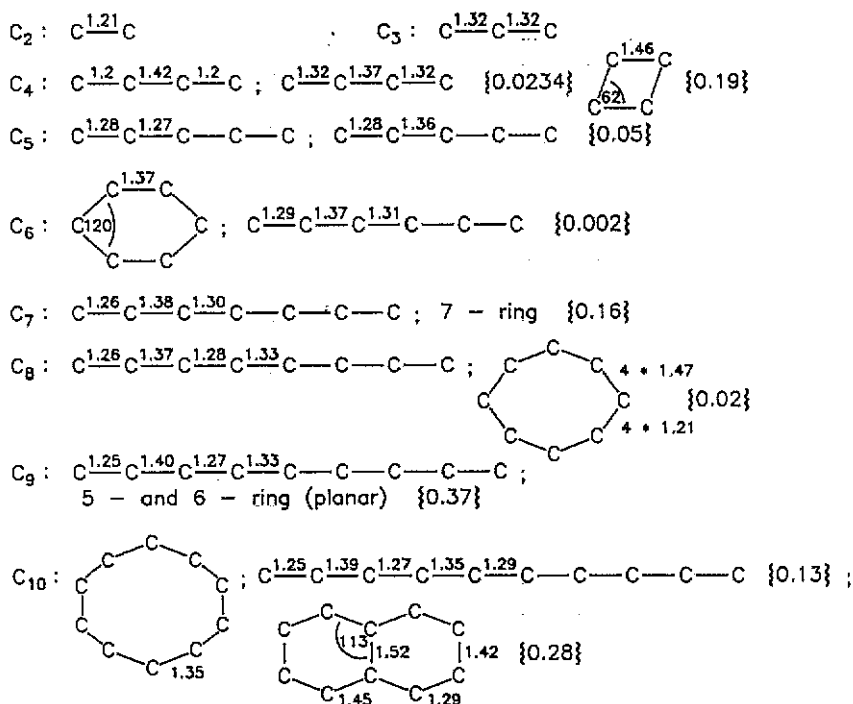


Figure 1. Calculated ground-state and isomer state geometries of C_2 to C_{10} molecules. The bond lengths are shown in ångströms and the bond angles in degrees. The structures are arranged in order of increasing energy (E is the energy difference in hartrees to the ground-state energy) {...}.

3–10) (Weltner and van Zee 1989), hydrocarbon molecules (the most prominent are CH_4 , C_6H_6 , C_6H_{12} , $C_{10}H_8$, C_2H_2 , C_2H_4 , C_2H_6 and C_4H_{10}) and corresponding radicals.

The equilibrium bond lengths and bond angles in all configurations, as well as in the crystalline modifications (graphite and diamond) are reproduced very well within an error of less than 3%; the correct tendency of single, double and triple bonds is also yielded. Figure 1 shows the calculated ground-state and isomer state geometries of C_2 to C_{10} molecules, which correspond to quantum chemical results from Jena *et al* (1987).

In table 2 the calculated bond lengths r and angles are summarized for some hydrocarbon species. The numbers in parentheses are the experimental values quoted by Hehre *et al* (1986). These results show that in the case of small and stable molecules the rough approximation (10) is sufficient. In calculating these structures the energy minimum is obtained simply by relaxation of the atomic positions without topological changes and the correct description of the interatomic forces at larger distances is not very important. In the case of amorphous structures, however, the dynamics of changing the neighbourhood of each atom will become the most important process in the MD simulation. The main problem is to model sufficiently well the attractive forces for capturing an additional neighbour and the repulsive forces for pushing away a superfluous atom.

We have found by comparison with correct interatomic potentials, e.g. C_2 , from *Selected Constants* (1970), that (10) will overestimate the attractive forces in such

Table 2. Calculated bond lengths r and angles θ for some hydrocarbon molecules and radicals (the numbers in parentheses the experimental values quoted by Hehre *et al* (1986)).

Molecule	r (Å)		θ (deg)	
	C-H	C-C	H-C-H	H-C-C
CH	1.07 (1.12)	—	—	—
CH ₂	1.07 (1.078)	—	136 (136)	—
CH ₃	1.06 (1.079)	—	120 (120)	—
CH ₄	1.09 (1.092)	—	109 (109)	—
C ₂ H	1.05 (1.06)	1.22 (1.18)	—	Linear
C ₂ H ₂	1.034 (1.061)	1.21 (1.203)	—	Linear
C ₂ H ₄	1.08 (1.085)	1.38 (1.34)	120 (117.8)	120 (121.1)
C ₂ H ₆	1.07 (1.08)	1.535 (1.54)	109	109
C ₄ H ₁₀	1.06 (CH ₃) 1.11 (CH ₂)	1.506, 1.503 1.506	109	109
C ₆ H ₆	1.07 (1.084) ^a	1.43 (1.40) ^a	—	120
C ₆ H ₁₂	1.07 (1.08)	1.535 (1.54)	109	109

^a From Anderson *et al* (1987).

processes. Therefore the forces and potentials at distances between next neighbours and more distant ones (about 1.5–3.0 au) must be handled more carefully. For this purpose we have extended equation (10) to

$$U(R) = \sum_{n=2}^5 c_n (R_1 - R)^n \quad (13)$$

in order to fit the additional parameters in such a way that the position and shape of the potential minimum remain unchanged but the shape at larger distances is as close as possible to the correct interatomic potential of C₂.

Taking the improved potential model we have carried out MD calculations for firstly pure carbon (54 atoms) and secondly hydrogenated carbon (55 C and 45 H atoms) with different mass densities. The mass densities are determined by the fixed sizes of the cubic periodic supercells in which all atoms are initially and randomly arranged. After equilibrium of a random starting configuration 4×10^{-13} s at 8000 K, all systems have been cooled at a rate of 2.5×10^{16} K s⁻¹ and finally relaxed 4×10^{-13} s within an equilibrium run at 300 K. To save computation time during the formation of a sensible initial liquid structure it is advantageous to start at a higher temperature of 8000 K compared with 5000 K in the Car-Parinello simulation. A test with a lower cooling rate did not yield a significant improvement in the relaxation process.

Two structures for a-C (2.0 and 3.0 g cm⁻³) and a-C:H (1.6 and 2.4 g cm⁻³) are shown in figures 2(a) and 2(b), respectively. Note that the figure contains only the atoms and bonds within one supercell. A stereoscopic view shows more distinctly than the two-dimensional picture the tendency to fivefold, sixfold and sevenfold non-planar ring formation, which are connected to a porous disordered structure. Some of the statistical results are represented in table 3 and figures 3 and 4.

The mean values and standard deviations of both the bond length and the bond angles as well as the pair correlation functions agree well with experimental findings (see, e.g., Holzhueter (1986)) and theoretical results (Beeman *et al* 1984, Galli *et al* 1989).

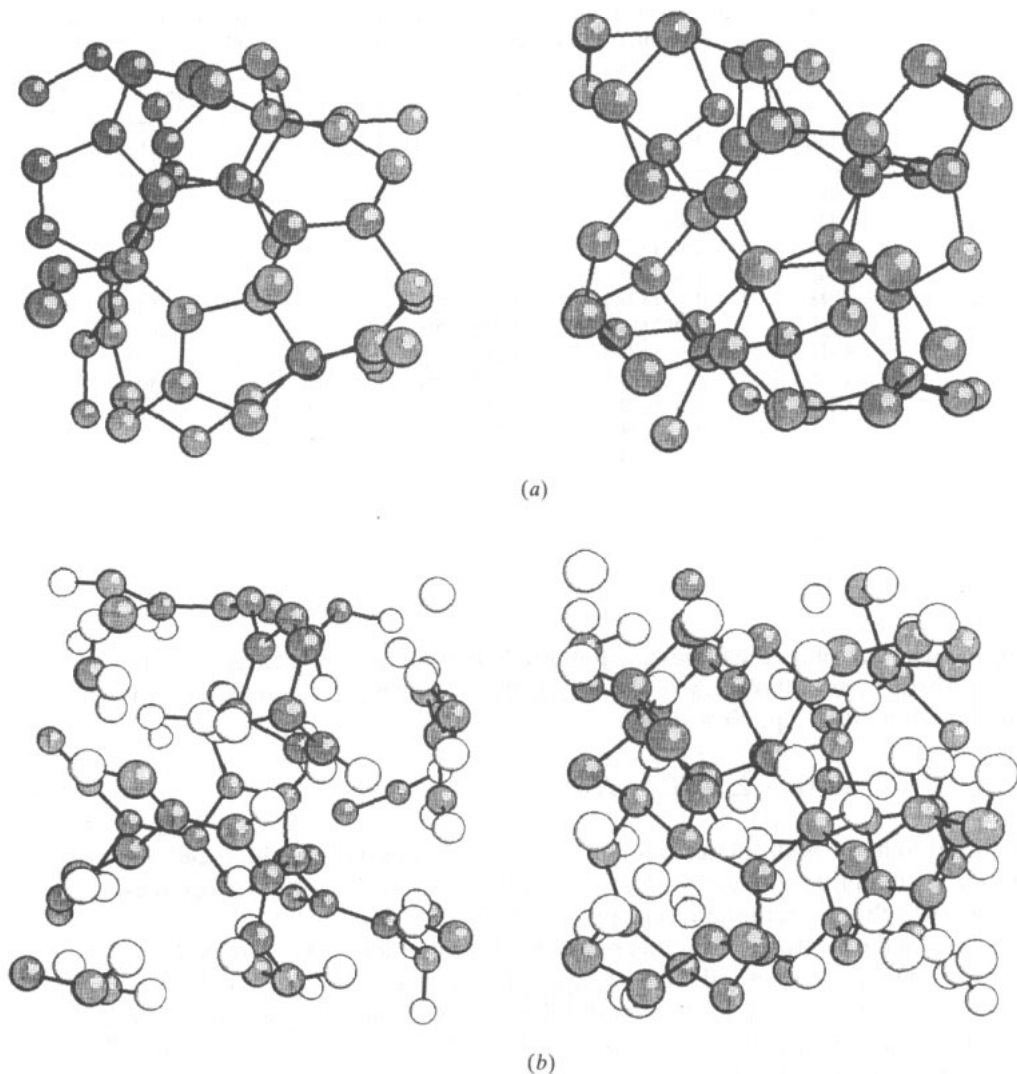


Figure 2. (a): *left*, C_{54} (2 g cm^{-3}) and *right*, C_{54} (3 g cm^{-3}). (b): *left*, $C_{55}H_{45}$ (1.6 g cm^{-3}) and *right*, $C_{55}H_{45}$ (2.4 g cm^{-3}) supercells: dark spheres, C; light spheres, H.

Table 3. Statistics of bond length and bond angles.

Model	Density (g cm^{-3})	sp^3 content (%)	Bond length (atu)				Bond angle (deg)	
			sp^2 - sp^2	sp^2 - sp^3	sp^3 - sp^3	C-H	C- sp^2 -C	C- sp^3 -C
C_{54}	2.0	13	1.42 ± 0.08	1.51 ± 0.03	1.54 ± 0.02	—	122 ± 16	109 ± 9
C_{54}	3.0	59	1.42 ± 0.07	1.55 ± 0.08	1.57 ± 0.06	—	118 ± 11	109 ± 11
$C_{55}H_{45}$	1.6	20	1.38 ± 0.07	1.50 ± 0.02	1.55 ± 0.02	1.07 ± 0.04	123 ± 14	107 ± 5
$C_{55}H_{45}$	2.4	49	1.40 ± 0.05	1.49 ± 0.03	1.53 ± 0.04	1.05 ± 0.03	120 ± 11	108 ± 11

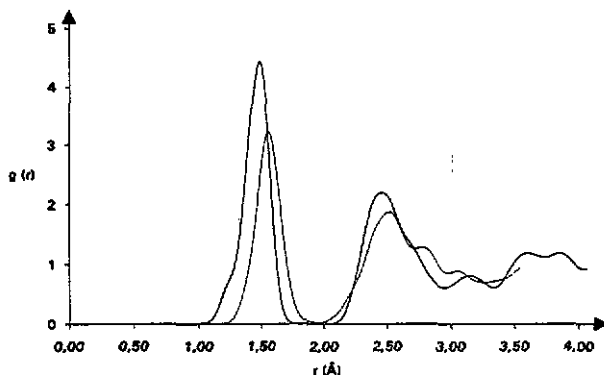


Figure 3. Pair correlation function for the structures in figure 2(a): 54 C atoms per supercell at 2 g cm^{-3} (—) and 3 g cm^{-3} (---).

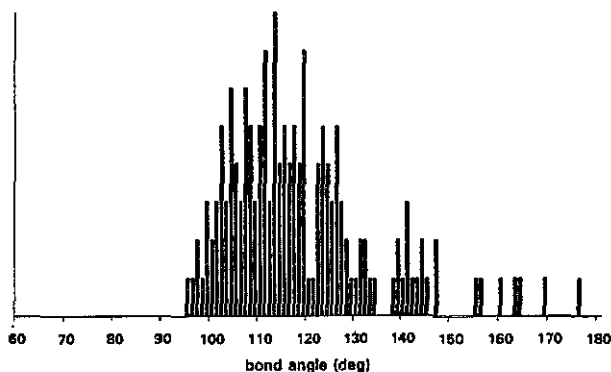


Figure 4. Distribution of bond angles for 54 C atoms per supercell at 2 g cm^{-3} .

Contrary to the work of Galli *et al* (1989) our carbon system contains a few twofold-bonded atoms at 2 g cm^{-3} , as you can also easily see from the bond angle distribution in figure 4, but in fact the definition of the coordination number is in some degree arbitrary. From our experience we think that the existence of two-fold-bonded atoms at such a small mass density is necessary to form a reasonably homogeneous structure. Kleber *et al* (1991) have found experimentally a much higher sp^3 content in *a*-C:H structures, e.g. 73% at 1.6 g cm^{-3} , but our sp^3 content in pure carbon agrees very well with the result of Galli *et al* (1989). One reason for this contradiction may be that the measuring of mass densities includes all mesoscopic holes in the structure which cannot be handled in microscopic calculations including only about 100 atoms per supercell. Therefore, very high sp^3 contents will probably belong to higher mass densities if mesoscopic holes are excluded.

The electronic DOS of all the presented structures are shown in figures 5 and 6. In pure amorphous carbon (figure 5) a sensitive dependence of the π DOS near the Fermi energy on the mass density and the sp^3 content is found. In the valence band at 2 g cm^{-3} there is probably a distinct peak from π electrons at -0.35 H but at 3 g cm^{-3} we have only one huge σ peak with a small π shoulder. The same is true for the comparison of

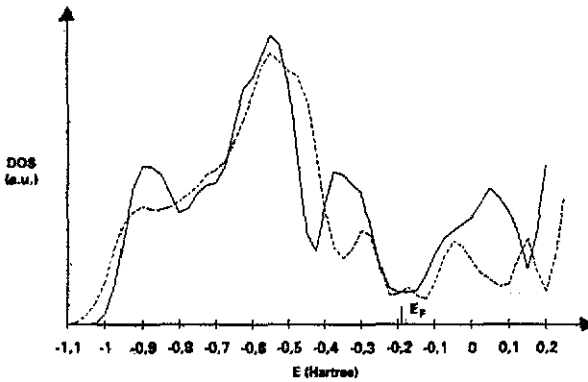


Figure 5. Electronic DOS for the structures in figure 2(a): 54 C atoms per supercell at 2 g cm^{-3} (—) and 3 g cm^{-3} (---).

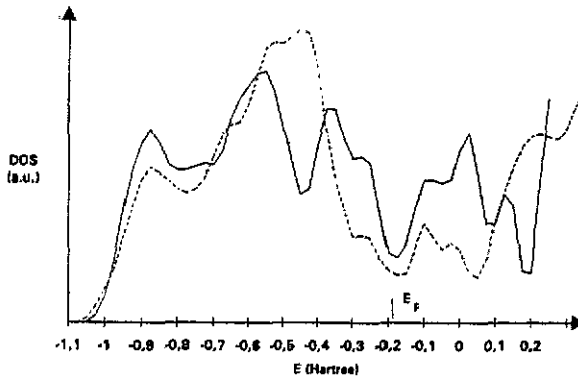


Figure 6. Electronic DOS for the structures in figure 2(b): 55 C and 45 H atoms per supercell at 1.6 g cm^{-3} (—) and 2.4 g cm^{-3} (---).

Table 4. Electronic band gaps of the generated models.

Model	Density (g cm^{-3})	Band gap (eV)
C_{54}	2.0	0.7
C_{54}	3.0	1.0
$\text{C}_{55}\text{H}_{45}$	1.6	2.2
$\text{C}_{55}\text{H}_{45}$	2.4	3.2

the a-C:H systems at different mass-densities in figure 6. The band gaps in table 4 result from an estimation by extrapolating the DOS near the Fermi energy to form square-root-like band edges. This estimation is necessary because the DOS curves in figures 5 and 6 are generated by Gaussian broadening of the discrete energy eigenvalues at the Γ point of the periodic supercell system.

4. Conclusion

A MD-DF approach using localized basis functions has been introduced for theoretical investigations of the density, C-H composition, clustering and medium-range order on the electronic gap behaviour in amorphous hydrocarbon films.

The MD method, shown to yield the correct ground-state geometry for C_n micro-clusters, C_nH_m molecules and crystalline modifications, can be established as a method for real MD simulations to study the influence of hydrogen on dynamical structure relaxation and chemical formulation in hydrogenated amorphous semiconductors.

A first application to dynamical structure simulation of a-C and a-C:H, starting from a random set of C and H atoms in a supercell with periodic boundary conditions, results in realistic metastable configurations with a well defined gap in the electronic DOS. This pronounced gap behaviour in electronically stable amorphous hydrocarbon films is crucial for further theoretical study of doping (efficiency and stability) in these materials.

As an important requirement the method allows one to include any kind of atom in the structure, provided that the short-range repulsive potential parameters can be fitted to describe the associated diatomic data. This well tested MD algorithm will be used in future on RISC workstations or other fast computers to allow realistic dynamical structure formation in heteronuclear amorphous systems of up to a few hundred atoms per supercell to be studied. Using the present method it will be consistent to study how the starting configuration (density, composition, predetermined clustering of atoms or molecular fragments) and the simulation regime (simulated annealing on quenching) in close relation to realistic thin-film deposition influences the physical behaviour and the stability of amorphous structures.

Acknowledgments

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