First-Principles Molecular Dynamics Simulations of Disordered Materials

Roberto Car and Michele Parrinello, Trieste

(Scuola Internazionale Superiore di Studi Avanzati)

Modern computer simulations based on molecular dynamics (MD) consist of calculating numerically the trajectory of motion of a number of atoms, usually ranging from a few tens up to a few thousands, during a time span of picoseconds. This allows us to study the statistical mechanical properties of complex systems, provided that the relevant spatial and temporal correlations are contained within the finite size and time of the simulation. Numerical experiments make accessible microscopic details of the atomic motion that would not otherwise be available in real experiments. Microscopic models of real materials may be studied with MD techniques in a wide area of current interest that includes crystal growth and epitaxy, melting, ion implantation, defect motion, laser annealing, amorphous structures, surface and interface reconstruction [1].

MD assumes that the adiabatic Born-Oppenheimer (BO) approximation holds and that atomic motion obeys classical mechanics. This works well in most cases of interest. In addition, the interatomic potential energy surface is usually modelled in terms of simple empirical pair potentials. For real materials this is often a poor approximation and large effort has recently been devoted to the atomistic modelling of materials beyond pair potentials. In spite of the progress made in this direction, the construction of reliable and transferable many-body potentials remains a very difficult task. A more satisfactory and more accurate approach would be to derive the interatomic potential directly from first principles, *i.e.* from the electronic groundstate. Accurate techniques for handling the electronic problem are available, based on density functional (DF) methods which exactly recast the quantum many-body problem into a set of self-consistent single-particle Schrödinger equations. These may be solved numerically by adopting a simple local density approximation (LDA) for exchange and correlation. The resulting energy surfaces are surprisingly accurate as shown by the wide success of such methods in predicting the properties of simple structures [2]. However, DF calculations were usually considered to be far too demanding for direct application to MD simulations.

The situation has changed in the last few years with the introduction of a new approach that efficiently combines MD and DF methods (MD-DF). In this scheme one considers a fictitious dynamical system whose potential energy surface is a functional of both electronic and nuclear degrees of freedom. The scheme does not require separate self-consistent electronic calculations for all nuclear configurations. All degrees of freedom are relaxed simultaneously. Under appropriate conditions, the nuclear dynamics generated in the fictitious parameter space closely reproduces the BO dynamics of the nuclei, making the MD-DF approach an efficient scheme for first-principles MD simulations [3].

In what follows we briefly outline the MD-DF method and review a few of its recent applications to disordered bulk condensed phases. These applications show that the scheme describes quite accurately some relatively complex phases and processes of materials. We do not cover the applications to cluster physics, since these will be the object of a forthcoming article in *Europhys. News* [4]. Similarly, we do not consider applications where the MD-DF scheme, or some suitable modification of it, has been used to perform efficiently more traditional electronic structure calculations for large systems [5].

Molecular Dynamics in the Coupled Electron-nucleus Parameter Space

Let us denote by $\Phi(\{\mathbf{R}_I\})$ the classical BO potential energy surface of a multiatomic system, whose spatial configurations are $\{\mathbf{R}_I\}$. The (standard) MD trajectories are solutions of the Newton's equations of motion:

$$M_I\ddot{\mathbf{R}}_I = -\partial\Phi/\partial\mathbf{R}_I \qquad (1)$$

According to DF theory, $\Phi(\{\mathbf{R}_I\})$ results from minimizing the total energy functional $E[n(\mathbf{r}),\{\mathbf{R}_I\}]$ with respect to the occupied orthonormal single-particle orbitals $\{\psi_i\}$ that represent the electronic charge density $n(\mathbf{r}) = \Sigma_i \mid \psi_i(\mathbf{r}) \mid ^2$. The functional E is a sum of several contributions, namely the electrostatic interaction energy between the nuclei, the single-particle (quantum) kinetic energy of the electrons, the interaction energy of the electrons with the external nuclear potential, the average electrostatic interaction energy between the electrons, and, finally, the exchange and correlation energy of the electrons, where all the information on the many-body Fermi character of the problem is contained. All terms can be explicitly calculated without approximation, with the exception of the exchange and correlation term E_{xc}, for which the so-called LDA is adopted. This consists of assuming that $E_{xc} = \int d\mathbf{r} n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r}))$, where $\varepsilon_{xc}(n)$ is the exchange and correlation energy per particle of a homogeneous electron gas with density n, which is known with sufficient accuracy.

In standard electronic structure calculations the minimum problem relating Φ to E results in self-consistent Schrödinger equations. We do not follow this approach. Instead we treat $E[n(\mathbf{r}),\{\mathbf{R}_I\}]$ as the potential energy surface of a *fictitious classical dynamical system* consisting of the nuclear plus the electronic degrees of freedom, *i.e.* $\{\mathbf{R}_I\}$ and $\{\psi_i\}$, respectively. The corresponding equations of motion are:

$$\mu\psi_i(\mathbf{r},t) = - \tfrac{1}{2}\, \delta E/2\delta\psi_i^*(\mathbf{r},t) + \sum_j \Lambda_{ij}\psi_j(\mathbf{r},t) \qquad (2a)$$

$$M_I\ddot{\mathbf{R}}_I = -\partial E/\partial\mathbf{R}_I(t), \qquad (2b)$$

where μ is an adjustable parameter, M_I are nuclear masses, and Λ_{ij} are lagrangian multipliers used to impose the orthonormality between the wavefunctions.

With modern supercomputers Eqs. 2 can be integrated numerically even for relatively complex systems. In general, the nuclear trajectories so obtained and those generated with Eq. 1 do not coincide, but one can choose the parameter μ so as to make the electronic dynamics sufficiently faster than the nuclear. As a consequence, there is little mixing between slow nuclear and fast electronic degrees of freedom. Thermal equilibration requires a very long time and nuclear trajectories, initially lying on the BO surface, deviate only very slowly

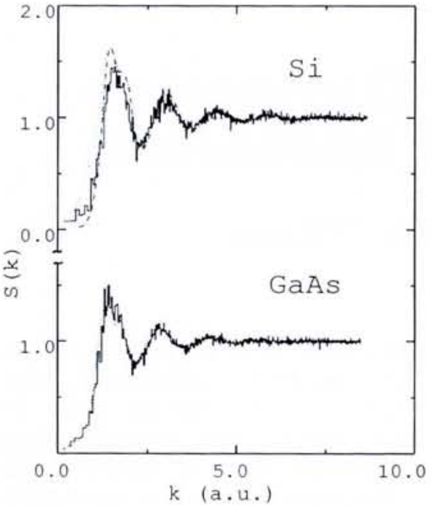

Fig. 1 — Theoretical (full line) and experimental (dotted and dash-dotted line) structure factor of liquid Si and GaAs. The noise in the theoretical results reflects the finite statistics in the computed averages. Data from two different experiments are reported for Si.

from it. This dynamics may be called *classical adiabatic dynamics*. It allows simulation of the motion of the nuclei without the need for a separate self-consistent electronic minimization at every time step.

As usual in classical MD simulations, one can relate the average value of the kinetic energy *(K)* to the temperature of the system. Under the conditions of classical adiabatic dynamics in the MD-DF scheme one can define two temperatures: an electronic temperature T_c, related to the average (classical) kinetic energy of the electrons

$$<K_c> = <\Sigma_i \int d\mathbf{r}\mu \,|\psi_i(\mathbf{r})|^2>,$$

and a nuclear temperature T_I, related to the average nuclear kinetic energy

$$<K_I> = <\tfrac{1}{2}\Sigma_I M_I \mathbf{R}_I^2>.$$

When $T_c \ll T_I$, the electronic degrees of freedom simply oscillate around the minimum of $E[n(\mathbf{r}),\{\mathbf{R}_I\}]$, while continually readjusting to the new minimum as the nuclei evolve. Then the temperature T_I corresponds to the physical temperatures of the system. Thermal treatments, such as annealing and quenching, can be simulated by varying the particle velocities.

A distinctive feature of the MD-DF scheme is that one generates at the same time the nuclear trajectories and the corresponding ground-state electronic charge densities and potentials. One can therefore follow directly the evolution of the chemical bonds resulting from atomic motion. In addition, one can compute consistently electronic properties, like single-particle densities of states, conductivities etc., that were usually considered outside the scope of MD simulations.

Liquids with Directional Bonds

Elemental covalent semiconductors, like Si, undergo remarkable structural changes upon melting. The coordination number, which is 4 in the crystalline phase, increases to an average value exceeding 6, indicating a collapse of the tetrahedral network. At the same time they lose their semiconducting character, becoming metals. They are, however, quite different from more traditional close packed liquid metals, suggesting that directional covalent bonds may be present also in the liquid. Compound semiconductors, like GaAs, show a similar behaviour, *i.e.* increase in the coordination and strong increase in the electrical conductivity upon melting.

Generally speaking, our knowledge of the microscopic properties of molten semiconductors is very poor. Basically, one does not know much more than the structure factor *S(k)* obtained in diffraction experiments. Simple theories of the liquid structure do not apply, and molten semiconductors have long been a great challenge for MD simulations, in view of the complete failure of a simple description in terms of pair potentials. While very accurate DF calculations existed for different crystalline phases of elemental and compound semiconductors, no such calculations were available for the liquid phases, where one could only speculate on the basis of assumed similarities with crystalline metallic phases that may exist under pressure, like the β-Sn, the simple cubic or the simple hexagonal structure, which have coordination numbers between 6 and 8.

Molten semiconductors constitute therefore an ideal test case for the MD-DF scheme and very recently simulations have been performed for liquid Si [6] and GaAs [7]. Both calculations used periodically repeated MD cells containing 64 atoms in a volume fixed by the experimental density at the melting point. The resulting structure factors *S(k)* are compared with experimental diffraction data in Fig. 1. The agreement is very good, particularly in view of the fact that the only empirical parameter of the calculations was the atomic density, while all other information was derived from the atomic numbers of the constituent atoms.

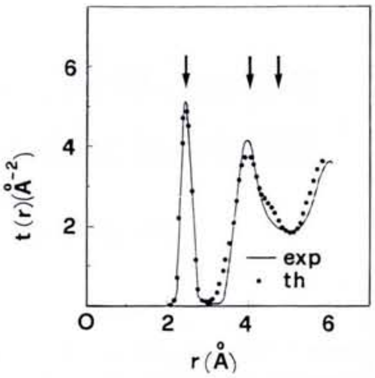

Fig. 3 — RDF t(r) *of amorphous Si.* t(r) = 4πrρg(r), *where* ρ *is the average density and* g(r) *is the pair correlation function. The theoretical curve has been convoluted with the experimental resolution function. The arrows indicate peak positions in the perfect crystalline structure.*

It is interesting to see what changes in the chemical bonds and in the electronic structure accompany the disruption of the tetrahedral network. The microscopic electronic charge density of liquid systems is at present inaccessible from experiments but can be readily obtained from MD-DF simulations. Plots of the valence charge density of an instantaneous liquid configuration in Si are compared with the corresponding quantity in the crystal in Fig. 2. This provides

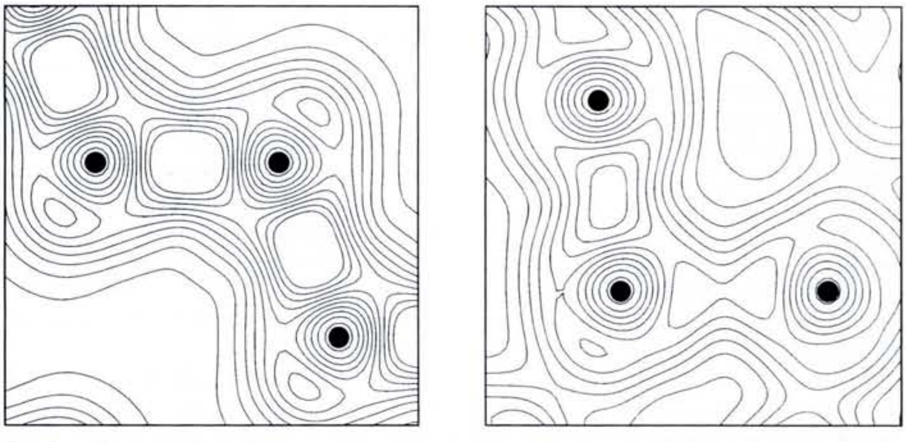

Fig. 2 — Contour plots of the valence charge density of crystalline (left hand side) and liquid Si (right hand side). Atoms are indicated by the black circles. In the crystalline case one can clearly see a chain of covalent bonds, corresponding to the maxima of the valence charge density between pairs of adjacent atoms. Somewhat weaker covalent bonds are also apparent in the liquid configuration represented on the right hand side.

direct evidence for the persistence of directional covalent bonds in molten semiconductors.

Covalent Amorphous Systems

For both fundamental and technological reasons, there is great interest in understanding the local order in amorphous semiconductors and how it affects their mechanical and electrical properties. In MD-DF simulations amorphous structures can be generated by quenching from the melt. This is not the common experimental technique for preparing amorphous semiconductors, essentially because achievable cooling rates are too slow and result in (re-)crystallization. Laser annealing experiments have shown, however, that amorphous Si can be generated by very fast cooling of the liquid. Even in this case the cooling rates are orders of magnitude smaller than in computer experiments. As a consequence the computer generated structures usually contain a large amount of defects. They are nonetheless remarkably similar to real materials in many respects.

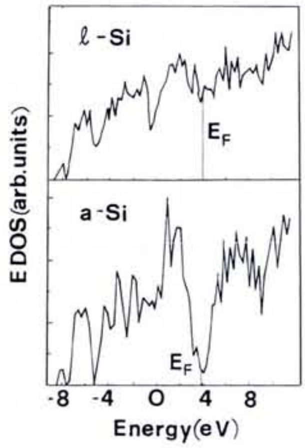

Fig. 4 — Electronic density of states for liquid (upper panel) and amorphous (lower panel) Si. The finite energy resolution reflects the finite size of the simulation box. The averages have been calculated over 12 and 32 different configurations for liquid and amorphous Si respectively.

An amorphous Si structure has been generated using the MD-DF method with a periodically repeated 54-atom cell, whose volume has been adjusted to the appropriate density [8]. The calculated radial distribution function (RDF) is compared with the experimental data in Fig. 3. The RDF, which is simply related to $S(k)$, measures the average atomic density as a function of the radial distance from a tagged atom. Remarkably, the integrated area under the first peak of the RDF, which gives the local coordination, is very close to 4, indicating that the tetrahedral network has been recovered. This process is certainly favoured by the presence of directional bonds in the liquid. The recovering of fourfold coordination is accompanied by the formation of a gap in the electronic density of states, signalling a transition from metal to semiconductor. This is shown in Fig. 4.

Amorphous carbon is another example of a covalent amorphous system that has been recently simulated with the MD-DF method [9]. From a technologi-

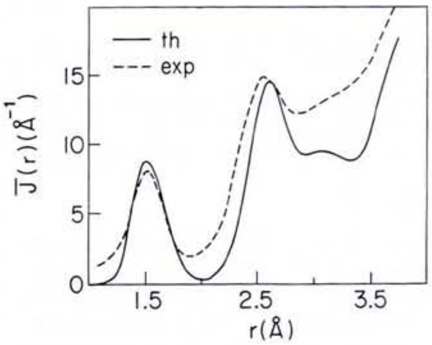

Fig. 5 — Theoretical (full line) and experimental (dotted line) RDF **J**(r) *of amorphous C.* **J**(r) = $4\pi r^2 \rho g(r)$, *where* ρ *is the average density and* g(r) *is the pair correlation function. The theoretical* **J**(r) *has been convoluted with the experimental resolution function.*

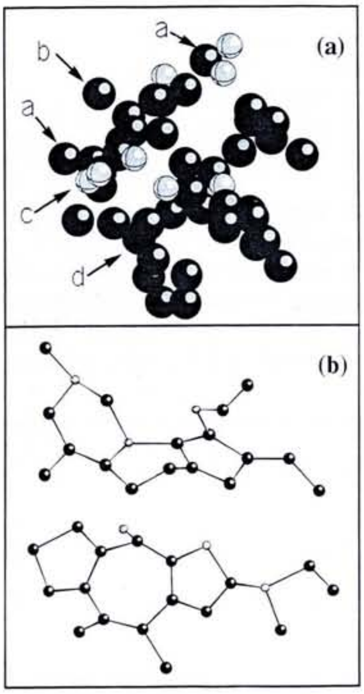

Fig. 6 — Microscopic structure of the computer-generated amorphous C network: the entire set of atoms belonging to the MD cell (a) and several 5-, 6-, and 7-fold ring structures of which the system is composed (b). Black and grey spheres indicate 3- and 4-fold coordinated atoms, respectively.

cal point of view α-C is very attractive, since it combines semiconducting properties, in some way similar to graphite, with a much higher hardness. Disordered forms of carbon are thought to consist of a mixture of threefold and fourfold coordinated atoms, as in graphite and diamond, respectively. The simultaneous presence of two coordinations depends on a delicate balance of different electronic binding forces and makes the simulation of α-C particularly challenging.

The RDF obtained with a 54-atom MD cell is reported in Fig. 5. The corresponding microscopic structure is shown in Fig. 6a, which displays the entire set of atoms belonging to one MD cell. Several 5-, 6- and 7-fold ring structures are shown in Fig. 6b. One sees that disorder introduces 5- and 7-fold rings, in addition to the 6-fold graphitic ones. Five and 7-fold rings are usually coupled as in carbon azulene molecules. Although the structure is truly three dimensional, the atoms are arranged into several *thick planes*, two of which, labelled (a) and (b) in Fig. 6a, are roughly parallel to each other. Four-fold coordinated atoms, indicated by the grey spheres, show a tendency to clustering and bind together the locally planar structures. Thus they contribute significantly to the hardness of the system.

Meetings

Corrections and Up-dates

Dates Interchanged, Schools

25-29 Sept. Bad Honnef, FRG
DPG-Schule für Physik, Kurs IV:
Physik in der Mikroelektronik
J. Debrus, Physikzentrum Bad Honnef,
Hauptstr. 5, D-5340 Bad Honnef
A: 2.6.89 / 60 / German /
DPG and WE-Heraeus-Foundation /
DM 375.– all incl.

2-6 Oct. Bad Honnef, FRG
DPG-Schule für Physik, Kurs V:
Nichtlineare Dynamik in Festkörpern
J. Debrus, Physikzentrum Bad Honnef,
Hauptstr. 5, D-5340 Bad Honnef
A: 2.6.89 / 60 / German /
DPG and WE-Heraeus-Foundation /
DM 375.– all incl.

New, Workshop

20 Nov. 1989 Rijnhuizen, NL
3rd European Workshop on Free Electron Lasers; collaboration between research institutes and industry
A. Nijsen-Vis, FOM, Postbus 1207,
NL-3430 BE Nieuwegein
Tel. ++31 (3402) 31 224

In conclusion, we have presented only a few applications of the MD-DF approach to liquid and amorphous semiconductors, but they are sufficient to demonstrate the power of the method.

REFERENCES

[1] For a recent overview see *Molecular-Dynamics Simulation of Statistical-Mechanical Systems*, eds. G. Ciccotti and W.G. Hoover (North-Holland, Amsterdam) 1986.

[2] See, for instance, the review articles in *Theory of the Inhomogeneous Electron Gas*, eds. S. Lundqvist and N.H. March (Plenum, New York) 1983.

[3] For a recent review, see Car R. and Parrinello M., in Proceedings of the NATO Advanced Research Workshop *Simple Molecular Systems at Very High Density*, Les Houches, France, 1988 (NATO ASI Series - Plenum Publishing Co.), in press.

[4] Andreoni W. and Echt O., *Europhys. News*, to be published.

[5] Payne M.C., Bristowe P.D. and Joannopoulos J.D., *Phys. Rev. Lett.* **58** (1987) 1348; Allan D.C. and Teter M.P., *Phys. Rev. Lett.* **59** (1987) 1136.

[6] Štich I., Car R. and Parrinello M., to be published.

[7] Zhang Q.M., Chiarotti G., Selloni A., Car R. and Parrinello M., to be published.

[8] Car R. and Parrinello M., *Phys. Rev. Lett.* **60** (1988) 204.

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

EPS Divisions, Sections and Group
Astronomy and Astrophysics Division
  Solar Physics Section
Atomic and Molecular Physics Division
  Atomic Spectroscopy Section
  Chemical Physics
  Electronic and Atomic Collisions
  Molecular Physics
Condensed Matter Division
  Liquids Section
  Low Temperature Physics Section
  Macromolecular Physics
  Magnetism
  Metal Physics
  Semiconductors and Insulators
  Surfaces and Interfaces
High Energy & Particle Physics Division
Interdivisional Groups on Accelerators,
  Computational Physics, Exptl. Physics Control
  Systems, History, Physics for Development
Nuclear Physics Division
Optics Division
Plasma Physics Division
Quantum Electronics Division

Europhysics News is the official journal of the European Physical Society which comprises 29 National Societies, Academies and Group, about 4000 Individual Members and 75 Associate Members. Governing bodies of EPS are the General Meeting, Council and an elected Executive Committee responsible for detailed policy. EPS promotes the collaboration of physicists throughout Europe, organising and harmonising conferences and publications, improving physics education, encouraging physics applications, awarding scholarships to sponsored schools in Erice. EPS publishes in addition to *Europhys. News, Europhysics Letters* (in partnership with national societies), *European Journal of Physics* (in partnership with The UK Inst. of Phys.), and *European Conference Abstracts*. Individual Members receive *Europhys. News* free of charge (price to insts: Sw.Fr. 90.-/a), *Europhys. Lett.* at Sw.Fr. 125.-/a (insts. 1050.-), rebates on many other publications and on conference fees. From Jan. 1989, membership fee for Individual Members belonging to an EPS member society is: Sw.Fr. 48.-/a; independent mbrs: Sw.Fr. 144.-/a; mbrs of a Collaborating Society: Sw.Fr. 60.-/a.

Editor: E.N. Shaw

Editorial Board:
F. James, M. Lehmann, M. Mayor, J. Muller, J.M. Richard, M. Siegrist

Editorial and Advertising Office at the EPS Secretariat

Address: EUROPEAN PHYSICAL SOCIETY
P.O. Box 69,
CH-1213 Petit-Lancy 2
Switzerland

Telephone: Geneva (22) 793 11 30
Telex: 428 024 eps ch
Telefax: (22) 793 13 17 **NEW**

Printed by: Pfirter frères sa
CH-1213 Petit-Lancy/Switzerland