First-principles molecular dynamics simulations at high pressure

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1. – Introduction

In this lectures I will review recent developments in the atomistic simulation of matter at extreme conditions of pressure and temperature. The idea of simulating the behavior of matter by directly solving on the computer the Newton's equations for a collection of atoms has been first proposed by E. Fermi [1] in the '40s, although the first systematic studies started only later, in the '60s, thanks to the pioneering work of A. Rahman [2]. Since then, the exponential increase in the computer power and the continuous refinement of the simulation techniques have turned computer simulations from a toy model of statistical physics into an extremely valuable and predictive tool [3]. The application of atomistic simulations is now widespread in many fields of condensed matter physics, materials science, and chemistry.

High pressure phenomena is one of the fields that have benefited more from computer simulations. In fact, contrary to experiments, where every minor increase in the maximum achievable pressure is considered as a major technical challenge, atomistic simulations at high pressure just require to confine the same number of particles in a smaller simulation box, with periodic boundary conditions, to achieve arbitrarily high pressures. This statement is of course too simplistic. Reducing the average interatomic distances

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poses in fact a number of methodologically problems that have challenged theorists for decades. In the first place, thermodynamics imposes that pressure – and not volume – be the expernal "knob" that one should fix. Suppose that we are interested in the phase transformation of a material from phase A to phase B, with a large volume collapse (e.g. carbon from graphite to diamond). If we were to confine our collection of carbon atoms in a simulation box of fixed shape and volume, initially fitting the shape of the graphite crystal, then the direct transformation of the atomic positions from the graphite to the diamond lattice would be strongly hindered by the energy cost (elastic energy in the case of a uniform strain or surface energy in the case of creation of voids) required to fit the diamond lattice in the same box. In other words, if the number of atoms and the volume are both conserved, then density changes – a crucial driving force in most pressure-induced transitions – are not allowed.

An even more challenging problem for atomistic simulation is the choice of the inter-atomic potential. Evolving the Newton's equations

$$(1) \qquad \ddot{\mathbf{R}}_I = -\frac{1}{M_I}\frac{\partial V}{\partial \mathbf{R}_I}(\mathbf{R}_1, ... \mathbf{R}_N) \quad I = 1, N$$

for a collection of N atoms with positions $\{\mathbf{R}_1, \mathbf{R}_2, ... \mathbf{R}_N\}$, implies that the force field, or more precisely, the potential $V(\mathbf{R}_1, \mathbf{R}_2, ... \mathbf{R}_N)$ of interaction among them is given. A very convenient way to construct interatomic potentials consists in approximating them through appropriately chosen functional forms tailored to capture the physics of the system under consideration. The parameters of the functional form are then adjusted to fit known experimental properties (e.g. equilibrium volumes, distances, bulk moduli, etc.). The simplest example is the case of condensed rare gases, where atoms can be reasonably well approximated by rigid spheres, so that the potential is typically approximated by a sum of pair (two-body) interatomic contributions

$$(2) \qquad V(\mathbf{R}_1, \mathbf{R}_2, ... \mathbf{R}_N) = \frac{1}{2} \sum_{i,j=1,N} \Phi(\mathbf{R}_i - \mathbf{R}_j) \quad i \neq j$$

with Φ having a repulsive (attractive) character at short (long) distances, and a minimum at a distance roughly corresponding to the equilibrium (zero-pressure) interatomic spacing. However, for the vast majority of materials the approximation of eq. (2) is too crude, and more complex functional forms have been introduced, that include three-body and higher-order terms, or even with an explicit dependence on the local atomic environment. In the study of high pressure phenomena the problem of constructing a reliable interatomic potential is particularly severe. When pressure is increased, in fact, interatomic distances vary over of wide range, often wider than the range of validity of a given functional form. It turns out that in most cases it is impossible to reproduce with the same functional form the behavior of a material at completely different conditions of pressure and temperature. This is particularly true when pressure induces chemical and/or electronic changes, but may also be the case for simple metals, as will be shown in in Section 2.6 .

The problem of determining the best functional form for V ceases to exist if we look instead for a brute force derivation of V from "first principles", based on the laws of quantum mechanics. Although by doing so the complexity of the problem increases dramatically, implying for example that a much smaller number of atoms can be simulated and for much shorter times than conventional simulations, the accuracy of the results obtained from such a first-principles approach is unparalleled. Thanks to the availability of increasingly powerful computer and to the methodological advances described in the following sections, first-principles simulations have now become a reliable and predictive tool to investigate the behavior of matter at high-pressure, complementing experiments when these are available, and extending our knowledge to conditions of pressure and temperature presently unreachable in the laboratory.

2. – Molecular Dynamics

2`1. *Basic concepts*. – Molecular dynamics, or MD for short (for historical reasons we keep calling the method "molecular" dynamics even if the dynamical entities are actually the atoms) consists of solving the Newton's equations (1) for a collection of atoms whose positions are constrained within a simulation box defined by the three edges $\mathbf{a}, \mathbf{b}, \mathbf{c}$, or equivalently by the 3×3 matrix $\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$. Periodic boundary conditions are applied in order to mimic the extended system and minimize the energy cost of a free surface (in the absence of periodic boundary conditions even for a simulation box containing as much as 10^3 atoms half of the atoms would be at the surface). The dynamics are evolved by discretizing Newton's equations with a sufficiently small but finite time step (typically of the order of $10^{-16} \div 10^{-15} s$). The overall simulation time depends on the complexity of the potential and on the number of atoms. It can range from $10^{-9} s$ in the case of "empirical" potentials (where the number of atoms can reach a few millions), down to a $10^{-11} s$ for first-principles simulation (where the number of atoms is limited to about 10^2). Analysis of the atomic trajectories provides information on the structural (lattice parameters, interatomic distances, angles, etc.), thermodynamical (thermal expansion, heat capacity, phase diagrams, etc.) and dynamical (vibrations, elastic constants, transport, diffusion, viscosity, etc.) properties of the system under study. I refer the reader to textbooks [4, 5] and to a collection of relevant papers [6] for further details.

2`2. *Molecular dynamics at constant pressure*. – In order to overcome the limitations, illustrated in Section I, deriving from the choice of a fixed simulation box, Parrinello and Rahman [7, 8] have extended the earlier idea, due to Andersen [9], of allowing the volume of the box to adjust according to the required pressure, and transformed the simulation box into a fully dynamical variable, driven by an appropriate equation of motion.

Let us consider a generic simulation box described by the matrix h_{ij}. The position $\mathbf{R}_I$ of an atom in the box can be written as:

$$(3) \qquad \mathbf{R}_I = \mathbf{h}\mathbf{S}_I$$

where $\mathbf{S}_I$ is the "scaled" position of atom I, whose components vary between 0 and 1.

In standard MD the cell (the matrix $\mathbf{h}$) is fixed, and the dynamics for the independent degrees of freedom $\{\mathbf{R}_I\}$ are obtained from the lagrangian

$$(4) \qquad \mathcal{L}_V = \frac{1}{2}\sum_{I=1}^{N} M_I |\dot{\mathbf{R}}_I|^2 - V(\mathbf{R}_1, ..., \mathbf{R}_N) \quad .$$

In the Parrinello-Rahman method, $\mathbf{h}$ and $\mathbf{S}_I$ are both independent degrees of freedom, and their dynamics are obtained from the modified lagrangian

$$(5) \qquad \mathcal{L}_P = \frac{1}{2}\sum_{I=1}^{N} M_I |\mathbf{h}\dot{\mathbf{S}}_I|^2 - V(\mathbf{h}\mathbf{S}_1, ..., \mathbf{h}\mathbf{S}_N) + \frac{1}{2}W\mathrm{Tr}(\dot{\mathbf{h}}^t\dot{\mathbf{h}}) - P\Omega, \quad .$$

where P is the pressure we want to impose (it is a parameter that has to be fixed at the outset), Ω is the cell volume, itself a function of $\mathbf{h}$ ($\Omega = \mathrm{Det}(\mathbf{h})$), and W is the inertial "mass" of the cell, a fictitiuous parameter that controls the time scale of the cell dynamics. Three major differences can be noticed in eq. (5), with respect to (4). First, since we want to impose pressure (P) as the external thermodynamical variable, the correct thermodynamical potential is now the enthalpy $H = E + P\Omega$, and therefore the lagrangian (5) contains an additional $-P\Omega$ term. Second, the cell dynamics requires a (fictitiuous) kinetic energy associated with the cell parameters; this is the third term in the right-hand side of (5). Third, the kinetic energy of the atoms is written, in (5), in terms of the "internal" velocity $\mathbf{h}\dot{\mathbf{S}}_I$, which differs from $\dot{\mathbf{R}}_I$ by the term $\dot{\mathbf{h}}\mathbf{S}_I$. All these differences are required for a proper thermodynamic treatment of pressure, and it can actually be proven that lagrangian (5) samples exactly the isobaric ensemble of statistical mechanics [10].

The equations of motion that can be derived from the lagrangian (5) are:

$$(6a) \qquad \ddot{S}_I^\alpha = -\frac{1}{M_I}\frac{\partial V}{\partial R_I^\beta}{h^t}_{\beta\alpha}^{-1} - G_{\alpha\beta}^{-1}\dot{G}_{\beta\gamma}\dot{S}_I^\gamma,$$

$$(6b) \qquad \ddot{h}_{\alpha\beta} = \frac{1}{W}\left(\Pi_{\alpha\gamma} - P\delta_{\alpha\gamma}\right)\Omega {h^t}_{\gamma\beta}^{-1} \quad ,$$

where greek letters are cartesian indices, summation over repeated indices is assumed, and where

$$(7) \qquad G_{\alpha\beta} = h_{\gamma\alpha}h_{\gamma\beta} \quad .$$

The stress tensor Π is defined as

$$(8) \qquad \Pi_{\alpha\gamma} = \frac{1}{\Omega}\left(\sum_I M_I V_I^\alpha V_I^\gamma - \frac{\partial V}{\partial h_{\alpha\delta}}h_{\delta\gamma}^t\right) \quad ,$$

with

$$(9) \qquad V_I^\alpha = h_{\alpha\gamma}\dot{S}_I^\gamma \quad .$$

The equations of motion ($6a$) for the atomic positions are modified with respect to the standard Newton's equations (1) by the addition of a term that accounts for the variation of the metric tensor G, while a new equation of motion (eq. $6b$) is introduced for the cell parameters. The dynamics of the cell parameters in ($6b$) is controlled by the unbalance between the imposed pressure P and the instantaneously calculated value of the stress tensor (8). At equilibrium ($\ddot{h} = 0$) the shape and volume of the cell will be such that the internal stress coincides with the external pressure P. During the dynamics, however, the cell edges fluctuate dynamically around the equilibrium position.

It is not difficult to show [11] that the lagrangian (5) has the constant of motion

$$(10) \qquad H_P = \frac{1}{2}\sum_I M_I V_I^2 + V(\mathbf{R}_1, ..., \mathbf{R}_N) + P\Omega + \frac{1}{2}W\mathrm{Tr}(\dot{\mathbf{h}}^t\dot{\mathbf{h}}) \quad ,$$

which corresponds to the enthalpy H of the system, apart for the last term, which becomes negligible for large N (its contribution to H at equilibrium is $\frac{9}{2}k_BT$).

Although the lagrangian (5) allows the exploration of the constant-pressure statistical ensemble for every value of W, this is only true in priciple, i.e. if averages are taken over an infinitely long simulation time. In practice, the choice of W is dictated by the need to ensure the most efficient coupling with the "real" degrees of freedom, namely the atomic coordinates $\mathbf{S}_I$. In fact, if the goal of the simulation is to reproduce a phase transition, the cell parameters have to respond as quickly as possible to the tendency of the atoms to move from the positions characterising the initial phase to those corresponding to the new phase.

After the original work of Parrinello and Rahman [7] several variants of the constant-pressure MD methodology have been proposed. Instead of considering the cell matrix $\mathbf{h}$ as the dynamical variable, a fictitiuous dynamics on the strain tensor [12] or on the metric tensor [13] has been shown to prevent occasional spurious rotations of the cell matrix. MD under non-isotropic compression conditions has also been shown to be feasible with a suitable modification of the cell dynamics and has been used to simulate transformations under uniaxial stress [8]. More recently, a technique to force the MD to satisfy the Hugoniot compression curve has been developed and tested [14], and a new method to study phase transitions in clusters proposed [15, 16]. Finally, it should be mentioned that although here we have only focused on MD at constant pressure, a very similar methodology exists to force the dynamics to sample the canonical ensemble (constant temperature) [17], and that the two techniques can be merged, with a few caveats [18] .

2˙3. *First-principles MD*. – Here we will concentrate on the problem of determining a reliable interatomic potential, to be used in the MD equations (6). The approach we will follow starts from the "first principles", namely from the fundamental quantum mechanical laws that govern the behavior of a collection of electrons and nuclei. Although we know very well what these laws are – the Schrödinger equation for the coupled electrons-nuclei system – solving them on the computer without any further approximation would

require an exceptional effort, many orders of magnitude more than what is available at present in terms of computer memory and speed. The first approximation we are going to introduce is the so called "adiabatic", or Born-Oppenheimer approximation [19]. This approximation stems from the consideration that electrons react much faster than nuclei to external perturbations, due to their smaller mass. As a consequence, electrons can be considered to be always in their ground state, for every instantaneous nuclear configuration $\{\mathbf{R}_1, ..., \mathbf{R}_N\}$. Therefore, the interaction potential V can be expressed as

$$(11) \qquad V(\mathbf{R}_1, ..., \mathbf{R}_N) = \langle \psi_\circ | H_e(\mathbf{R}_1, ..., \mathbf{R}_N) | \psi_\circ \rangle$$

where $\psi_\circ$ is the *electronic* ground state wavefunction calculated for the nuclear configuration $\{\mathbf{R}_1, ..., \mathbf{R}_N\}$, according to the Hamiltonian

$$(12) \qquad H_e = -\sum_{i=1,N_e} \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i=1,N_e}^{j=1,i-1} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} -$$

$$-\sum_{i=1,N_e}^{I=1,N} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I=1,N}^{J=1,I-1} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \quad ,$$

where N_e is the number of electrons and Z_I the atomic number of atom I. It is worth to stress that the Hamiltonian (12) acts on the electrons, and depends on $\{\mathbf{R}_1, ..., \mathbf{R}_N\}$ only parametrically. This implies that the ground state wavefunction $\psi_\circ$ will also depend parametrically on $\{\mathbf{R}_1, ..., \mathbf{R}_N\}$, i.e. a different wavefunction is obtained for every nuclear configuration. Although the problem has been simplified considerably, finding $\psi_\circ$ for the Hamiltonian (12) is still an impossible task, at least for systems with more than a few electrons, because of the many-body nature of the electron-electron Coulomb interaction (second term in the right-hand side of (12)). Among the approximations that allow to overcome the problem, those based on density functional theory are probably among the most widespread and accurate, particularly when dealing with relatively large systems (hundreds of electrons or more). Density functional theory (DFT) is an *exact* theory that allows one to recast the problem of finding the many-electron ground state of (12) into the problem of finding the ground state of a system of independent electrons in a potential that explicitly depends on the electron density [20, 21]. Although the theory is formally exact, approximations have to be made in order to derive the functional form of the potential. The most common of these approximations is the so-called local-density approximation (LDA), whereby the potential is approximated locally with the functional form of the uniform electron gas, which is known almost exactly from numerical calculations [22]. The LDA can be systematically improved by adding contributions from the local gradient of the density (gradient corrections, or GGA). A discussion of how different GGA functionals perform in different systems would go beyond the scope of these lectures, so I refer the interested reader to the vast literature existing on the subject [23].

A final approximation that is commonly made in first-principles calculations is to assume that core states are actually frozen to their atomic shape and energy. Orthogonalization of the valence states to the core states is ensured by the replacement of the electron-nuclei Coulomb potential, the third term in the right-hand side of (12), with a so-called "pseudopotential", whose scattering properties are constrained to be identical to those of the full atomic potential. A database of pseudopotentials for almost every element of the periodic table has been published [24]. When the basis set over which the wave functions are expended consists of plane waves, a very popular choice in first-principles codes, smoother pseudopotentials [25] may be less demanding in terms of basis set size.

The above approximations have finally brought the problem into the category of those that can be nowadays solved numerically on a powerful computer. To summarize, a rough flow chart of how the MD time step is accomplished in a first-principles MD code consists of (a) choosing an initial set of nuclear positions $\{\mathbf{R}_1, ..., \mathbf{R}_N\}$, (b) solving the electron hamiltonian (12), i.e. determining the ground state wave function for that particular nuclear configuration, (c) calculating the forces on the nuclei as the derivative of the potential (11) [N.B. this can be accomplished either numerically, by finite differences, or by exploiting the so called Hellman-Feynman theorem, whereby the derivative of the potential can be expressed as the expectation value of the derivative of the Hamiltonian in (11), on the ground state wave function], (d) evolving the Newton's equations for all nuclei with a finite time step Δt, i.e. determining the new set of nuclear positions corresponding to time $t + \Delta t$, and finally going back to (b) with the new set of positions. This procedure is iterated for a large number of time steps, depending on the system and on the property under study. In order to integrate Newton's equations properly, the time step Δt of integration must be much smaller than the fastest period of oscillation of the nuclei. Because typical periods (vibrations, phonons, etc.) are in the $10^{-14} - 10^{-12}$ s range, typical Δt are in the range of a fraction of a fs, which means that a ps of simulation requires about 10^4 time steps. One of the computationally heavier steps of a first-principles MD simulation is the determination of the ground state wave function. Considering that this step has to be repeated 10^4 times, most of the methodological effort has been focused to the search of efficient ways to update the wave function from one time step to the next one. Most of the differences bewtween existing codes for first-principles MD [CASTEP (Cambridge), VASP (Vienna), CPMD (Stuttgart/Zürich), PARATEC (Berkeley) and FPMD (Trieste), just to name a few] can be ascribed to different techniques in the way wave functions are evolved.

2'4. *The Car-Parrinello method.* – A rather original and very efficient way to evolve the wave functions has been proposed in 1985 by Car and Parrinello [26]. Instead of solving very accurately the Hamiltonian (12) at each time step, they relaxed the constraint that the wave function be exactly in the ground state. The exact solution was replaced by a fictitious dynamics of the wave function about the exact ground state. Although applied in a completely different context, it is easy to see the analogy with the ideas that underlie the constant-pressure MD technique discussed in Section 2.2 . Also in that case,

in fact, the need to adjust the shape and volume of the simulation cell in order to equilibrate pressure was fulfilled by introducing a fictitious dynamics on the cell parameters, which were allowed to vary dynamically with the second order (Newton's like) equations of motion ($6b$). In the Car-Parrinello method the solution of the Hamiltonian (12), which is equivalent to minimize the right-hand side of (11) with respect to the wavefunction, is replaced by the dynamical evolution of the following "extended" Lagrangian

$$(13) \quad \tilde{\mathcal{L}}_V = \frac{1}{2}\sum_i \mu\langle\dot{\psi}_i|\dot{\psi}_i\rangle + \frac{1}{2}\sum_I M_I\dot{\mathbf{R}}_I^2 - E\left[\{\psi_i\},\{\mathbf{R}_I\}\right] + \sum_{ij}\Lambda_{ij}\left(\langle\psi_i|\psi_j\rangle - \delta_{ij}\right).$$

where E is the DFT functional, expressed here in terms of the wave functions and, parametrically, of the positions of the nuclei, μ is a fictitious mass that can be used to control the time scale of the electronic dynamics, and Λ_{ij} are Lagrange multipliers that ensure the orthogonality of the wave functions. The equations of motion that can be obtained from the above Lagrangian are:

$$(14a) \qquad\qquad \mu\ddot{\psi}_i = -\frac{\delta E}{\delta\psi_i} + \sum_j \Lambda_{ij}\psi_j$$

$$(14b) \qquad\qquad \ddot{\mathbf{R}}_I = -\frac{1}{M_I}\frac{\partial E}{\partial\mathbf{R}_I}.$$

Eq. ($14a$) defines the dynamics of the wave functions, which will oscillate (by virtue of the second order time derivative) around the equilibrium condition

$$(15) \qquad\qquad \frac{\delta E}{\delta\psi_i} = \sum_j \Lambda_{ij}\psi_j \quad .$$

Notice that eq. (15) is the mathematical rephrasing of the DFT prescription of minimising the DFT functional E with respect to variations of the (orthogonal) set of orbitals. Eq. ($14b$) instead coincides with Newton's equation (1) and the first-principles potential (11), with the only difference that the wave functions in ($14b$) are not at the exact ground state. As shown in [27], the period of oscillation of the wave functions around the ground state scales with $\mu^{\frac{1}{2}}$, which means that for a sufficiently small value of μ the oscillations can be made much faster than the typical time scales of the dynamics of the nuclei. In this limit, the effect of the fast oscillations averages out on the time scale of the dynamics of the nuclei, and the resulting net force on the nuclei is very similar to the force that would be calculated with the electrons in their ground state [28]. Further details on the Car-Parrinello method can be found in review papers [29, 30].

2˙5. *First-principles MD at constant pressure*. – Merging the constant-pressure method described in Section 2.2 with the first-principles Car-Parrinello method described in Section 2.4 is not completely straightforward, and requires some care in the definition of how the wave functions change upon cell rescaling [31, 32, 33]. The problem can be tackled by

starting from the Car-Parrinello Lagrangian (13) and expressing all spatial coordinates, both electronic ($\mathbf{r}$) and nuclear ($\mathbf{R}$), in terms of scaled coordinates, $\mathbf{r} = \mathbf{hs}$ and $\mathbf{R} = \mathbf{hS}$, as already done in (3). The constant-pressure dynamics can now be introduced by adding to the original Car-Parrinello Lagrangian (13) the last two terms of the constant-pressure Lagrangian (5). This yields the first-principles constant-pressure Lagrangian:

$$(16) \quad \tilde{\mathcal{L}}_P = \frac{1}{2}\mu\sum_i \int d\mathbf{s}\,|\dot{\psi}_i(\mathbf{s})|^2 + \frac{1}{2}\sum_{I=1}^N M_I|\mathbf{h}\dot{\mathbf{S}}_I|^2 - E\left[\{\psi_i\},\{\mathbf{hS}_I\}\right] +$$

$$+ \sum_{ij}\Lambda_{ij}\left(\int d\mathbf{s}\,\psi_i^*(\mathbf{s})\psi_j(\mathbf{s}) - \delta_{ij}\right) + \frac{1}{2}W\mathrm{Tr}(\dot{\mathbf{h}}^t\dot{\mathbf{h}}) - P\Omega \quad,$$

with the following definition of the wave function in scaled coordinates:

$$(17) \qquad\qquad \psi(\mathbf{s}) = \sqrt{\Omega}\ \psi_h(\mathbf{r}) = \sqrt{\Omega}\ \psi_h(\mathbf{hs})$$

where ψ_h is the wave function expressed in terms of the real coordinate $\mathbf{r}$, and ψ is the wave function in scaled coordinates. Notice that ψ in (17) is correctly normalized when the integral is performed on $d\mathbf{s}$. Notice also that by using definition (17) we neglect, in the fictitious kinetic term (first term of Eq. 16), the contribution due to the deformation of the cell, as already done for the nuclear coordinates (see eq. 9).

The equations of motion for wave functions, nuclear positions and cell that follow from Lagrangian (16) are:

$$(18a) \qquad\qquad \mu\ddot{\psi}_i = -\frac{\delta E}{\delta\psi_i^*} + \sum_j \Lambda_{ij}\psi_j$$

$$(18b) \qquad\qquad \ddot{S}_I^\alpha = -\frac{1}{M_I}\frac{\partial E}{\partial R_I^\beta}h^{t\,-1}_{\beta\alpha} - G_{\alpha\beta}^{-1}\dot{G}_{\beta\gamma}\dot{S}_I^\gamma,$$

$$(18c) \qquad\qquad \ddot{h}_{\alpha\beta} = \frac{1}{W}\left(\Pi_{\alpha\gamma} - P\delta_{\alpha\gamma}\right)\Omega h^{t\,-1}_{\gamma\beta},$$

Eq. (18a) coincides with the equation of motion (14a) derived in Section 2.4, with the only difference that ψ is here defined in a slightly different way [see eq. (17)]. Eq. (18b) coincides with the constant-pressure equation of motion (6a) for the nuclear positions. Finally, eq. (18c) coincides with constant-pressure equation of motion (6b), with the difference that here the stress tensor Π is calculated from first-principles [34] .

2`6. *Empirical potentials from first-principles simulations.* – Although a first-principles approach to the determination of the interatomic potential is in most cases mandatory, the very short time scales and small sizes that can be afforded nowadays imply that a number of properties, in particular those that require long thermalization times or large spatial scales cannot be obtained entirely from first principles. Among these properties we can list high-temperature elastic constants, thermal conductivity, phase relations, mechanical properties (rheology), etc. In most of these cases, simulation times of *ns* and

box sizes as large as 10^4 atoms are required to extract statistically meaningful information. An effective trade-off consists of generating empirical potentials that reproduce with the best possible accuracy the first-principles interatomic potential. This approach has been vastly explored in the past, mostly by fitting the parameters of appropriate functional forms to selected low-pressure properties of the materials under study, such as elastic constants, lattice parameters, defect energies, etc [35]. Alternatively, the parameters can be fitted to the ab-initio calculated force constants and geometries of simple molecular analogues [36]. Finally, in the force-matching method the potential is required to fit the forces calculated from first principles on a number of different configurations ranging from clusters, surfaces and bulk solids [37]. It has been shown, however, that all the above procedures have intrinsic limitations, mostly due to our ignorance of the exact functional form of the interatomic potential. In the case of aluminium metal, for example, it has been shown that even including about 170 atomic configurations leads to a potential with an energetical accuracy of only ~ 0.10 eV/atom [38]. A common requirement in all the approaches explored so far has been that the potential must be able to reproduce the first-principles results in a large variety of physical, chemical, or thermodynamical situations. However, when this requirement is relaxed, and the potential is required to reproduce the behavior of a material only at a specific condition (e.g. of pressure and temperature), then its accuracy can be dramatically increased [39]. Application of this method to the study of compressed iron will be illustrated in Section 3.10 .

3. – Applications

3˙1. *Silicon*. – Silicon has been often a benchmark system for new first-principles methodologies. Technically speaking silicon is appealing because of the simple (diamond) structure, the affordable size of the plane-wave basis set needed to describe its electronic states, and for the rather good performance of the LDA. The first prediction of pressure-induced transitions with first-principles methods was indeed carried out for silicon [40]. Silicon was also chosen for the first application of the Car-Parrinello method [26] and of the constant-pressure extension of the Car-Parrinello method [31]. In Ref. [31] a spontaneous transformation from diamond to simple hexagonal was observed in the simulation at about 30 GPa, roughly 15 GPa above the transition reported in experiments. Similar results have been obtained in subsequent works [41, 42]. These results, together with the observation that the simulation did not give the β-Sn and *Imma* phases, experimentally observed in a narrow pressure range between 11 and 16 GPa [43], illustrate very clearly the limitations of a simulation approach to phase transitions. In the real system, phase transitions take place in the vast majority of cases through nucleation of the new phase around a seed that may consists of a thermal fluctuation, or a defect, or anything else that perturbs locally the initial phase and allows to overcome locally the energy barrier between the initial and the final phase. The limited size and time scale of the simulations do not allow the simulated system to sample sufficiently large regions of the phase space. Therefore, fluctuations are hindered and the transition takes place only when a global

mechanical instability is approaching. In the case of silicon, for example, it is known that a mechanical (phonon) instability occurs in the diamond structure at about 30 GPa [44], in nice agreement with the transition pressure in the simulation. This suggests that great care has to be used when extracting transition pressures from simulations. On the other hand, the simulations correctly predict the stability of the simple hexagonal phase at high pressure, a non trivial result considered the dramatic change in the electronic structure brought about by the transition, a feature that could be hardly captured without a first-principles description.

3.2. Carbon. – Carbon is probably the first system where first-principles MD simulations have been used to explore the high-pressure behavior. Constant-volume simulations of the compressed liquid have shown that the average coordination at megabar pressures is slightly less than four, indicating that the density of the compressed liquid might be lower than that of the compressed solid (diamond) at the same pressure [45]. Although this behavior is "normal", it indicates that liquid carbon is substantially different from liquid silicon, which is instead known, both from experiment and from simulations, to be denser than its solid. The normal behavior of carbon implies that its melting slope dT/dP is positive according to the Clausius-Clapeyron relation. This is consistent with recent shock-wave experiments [46]. Simulations at extremely high pressure indicate however that the melting slope might eventually become negative [47], due to an increase in coordination in the liquid from four to about six and to the concomitant stability of four-fold coordinated solid phases up to at least 1000 GPa. In fact, simulations in the solid phase suggest that not only a six-fold coordinated phase (simple cubic) becomes enthalpically favored only above 2300 GPa, but they also indicate that a transition to the simple cubic phase might be hindered by very large energy barriers. Instead, kinetics might favor the transition of carbon from diamond into a different six-fold coordinated cubic structure, named SC4, at about 3000 GPa [48]. At lower pressures, constant-pressure first-principles MD has been used to study the transformation path of graphite to diamond. The transformation has been shown to proceed through an intermediate state consisting in the sliding of the graphite planes from the ABAB stacking characteristic of hexagonal graphite, the most stable form of carbon at ambient conditions, into an orthorhombic AB'AB' stacking, from where perfectly 4-fold coordinated cubic or hexagonal diamond was obtained [49]. Finally, simulations under non-isotropic stress [8] have been performed on diamond with the aim of clarifying its stability and properties at the tip of a loaded diamond anvil [50]. It was found that diamond becomes mechanically unstable when the differential stress (the difference between the radial and the vertical stress) exceeds 200 GPa [51], a condition that may be reached in a diamond anvil for sample pressures exceeding 300 GPa [52].

3.3. Hydrogen. – The high-pressure phase diagram of hydrogen is reviewed elsewhere [53]. It consists of a low pressure phase I where molecules are centered on the sites of a *hcp* lattice, but are free to rotate around their center of mass, of an intermediate broken-symmetry phase II, where molecular rotations are hindered by the crystal field,

of a high-pressure phase III, characterized by a strong infrared activity, and by one (or more) liquid phase(s) above melting. Here we summarize the hints provided by first-principles simulations. A large number of authors have focused on the low-temperature portion of the phase diagram. Simulations on H_2 at low temperature are particularly challenging because of the need to include the possibility that the unit cell be large [54], combined with the very large number of points needed to sample the Brillouin zone [55]. This required the development of a new method for Brillouin zone integration, based on perturbation theory [56]. Simulations in phase II have helped understand its crystal structure, which on the basis of MD within the gradient-corrected LDA is either $Pca2_1$ or $P2_1/c$ [57]. Simulations in phase III have suggested that the infrared activity might be due to a grouping of molecules in triplets [58]. More recently, it has been shown that most of the structures proposed so far are actually unstable mechanically, whereas structures with a layered triangular-like arrangement of molecules might be favored [59]. None of the above simulations has attempted to study the insulator-metal transition, expected to occur at sufficiently elevated pressures, because of intrinsic problems in the LDA (or GGA) approximation close to the metallic transition [60]. However, attempts to search for compounds where hydrogen metallization takes place at lower pressures have been made [61]. All the simulations described so far have assumed that the nuclei (protons) behave as classical particles, i.e. they obey Newton's equation. This approximation is not fully correct for hydrogen, where quantum effects are certainly important, e.g. in preserving rotational disorder in phase I down to very low temperatures. Path-integral MD simulations [62, 63] in phases I, II, and III have shown that the degree of order increases with pressure, and that quantum effects increase the localization of the protons, contrary to elementary considerations [63].

At high temperature, first-principles simulations have been carried out to investigate the structure of the liquid at various conditions of pressure and temperature. At relatively low temperatures ($\sim$ 3000 K) and high pressures ($>$ 150 GPa) the liquid was found to be mostly monoatomic [64], although peculiar filamentary structures have been observed [65]. The conductivity calculated with a Kubo-Greenwood formulation [64] appears to overestimate by almost one order of magnitude the conductivity measured along the multiple-shock compression curve achieved in gas-gun experiments [66]. Although this may indicate a problem in the determination of temperature in experiments, the discrepancy might also be attributed to the insufficient size of the simulation box. Determinations of the pressure-vs-density equation of state along the principal Hugoniot of deuterium [67, 68] are in strong disagreement with laser-shock experiments [69], simulations showing a much smaller compressibility than experiments. Inclusion of spin in the description of electronic states improves, but only marginally, the agreement [70]. At variance with multiple-shock experiments, however, theoretical conductivities calculated [71] along the principal Hugoniot agree with optical reflectivity data [72] . Applications of first-principles simulations to the understanding of the interiors of the giant planets Jupiter and Saturn [73] have shown that the sound velocity of dense hydrogen is not compatible with available planetary models, and have suggested that helium is fully miscible in hydrogen [74], again contrary to evidences from planetary modeling [75]. It is

clear that more work needs to be done in order to resolve this discrepancies, for example by repeating the simulations with larger simulation cells.

3'4. *Oxygen*. – Among the diatomic molecules, O_2 stands out for its magnetic moment ($S = 1$), caused by the exchange interaction between electrons in the two-fold degenerate $\pi^\star$ molecular orbitals. Magnetism controls most of the low-pressure and low-temperature properties of solid molecular oxygen, including its crystal structure and its insulating antiferromagnetic electronic structure [76]. Upon compression, intermolecular electronic hopping eventually overcomes the on-site exchange interaction, leading to a paramagnetic metal. The ζ-O_2 phase, observed above 96 GPa [77] has in fact been reported to be metallic [78]. First-principles simulations have been used to investigate how the transition takes place and to give some insight on the crystal structure of ζ-O_2, so far little contrained by experiments. In order to account for the magnetic moments in the low pressure phases, the local spin density approximation (LSDA) has been used. In the LSDA both the total electronic density and the magnetization density are optimised independently at each time step. The magnetization density correctly disappeared at high pressure, during the simulation [79], and concomitantly a new peak appeared in the structure factor of the simulation cell, indicating a trasformation to a new phase. Further refinement of the crystal structure found in the simulation [79] lead to a satisfactory agreement with the experimental positions of the X-ray diffracted peaks of the ζ-O_2 phase [77].

3'5. *Carbon oxides*. – Carbon monoxide (CO) and carbon dioxide (CO_2) are among the most stable molecules known in nature. In both molecules, however, the carbon atom is in a different hybridization state than the sp^2 or sp^3 states that characterize carbon in its elemental dense forms, graphite or diamond, respectively. The dramatic decrease in the intermolecular distances caused by the application of moderate pressures (a few tens of GPa) leads in both molecules to polymerization and formation of extended covalent solids, with carbon in sp^2 or sp^3 hybridisation. In CO, evidence that the molecular solid transforms into a denser yellowish substance above 5 GPa has been reported [80]. Infra-red spectroscopy measurements on the compressed sample have later revealed the polymeric nature of the compressed phase [81]. First-principles MD simulations on CO have also observed polymerization, and have identified recurrent structural units (C_4O five-membered rings) as peculiar of the CO polymer [82]. The simulation have also been used to attribute peaks in the infra-red spectra to speficic vibrational modes of the polymer. In the case of CO_2, pressure-induced polymerization has also been observed experimentally [83] and calculated theoretically [84, 85]. Polymerization pressures in CO_2 are around 50 GPa, slightly larger than in CO. In first-principles MD simulations the transformation took place at about 100 GPa [84], but since the transition involves substantial electronic changes and formation of new bonds, it is likely that a large energy barrier prevents the transition to take place at the correct thermodynamic pressure in simulations. Remarkably, simulations at different temperatures yielded rather different results. At high temperature ($\sim$ 2000 K) the molecular solid transformed into an

amorphous solid, while at lower temperatures ($\sim$ 1000 K) it transformed into a perfectly ordered crystal, with a peculiar layer-like structure [84].

3`6. *Hydrocarbons.* – The fate of methane (CH_4) at very high pressures and temperatures has important implications for our understanding of the interiors of Neptune and Uranus [75]. Shock-wave experiments show evidence of a transition that has been initially interpreted as due to full dissociation of CH_4 into its consituent elements, carbon and hydrogen [86]. First-principles simulations have suggested that a more subtle chemistry may pre-empt full dissociation. Formation of hydrocarbons of molecular weight higher than methane has in fact been reported on the basis of constant-pressure simulations at 100 GPa and 4000 K [87]. Evidence for hydrocarbon formation has been later confirmed by static laser-heated diamond-anvil cell experiments [88], although at a considerably lower pressure than in the simulations.

Acetylene (C_2H_2) is known to polymerize in the pressure range 3.5-14 GPa [89]. First-principles simulations at constant pressure do reproduce the polymerization [90], but once again at a considerably higher pressure (25 GPa). However, simulations indicate also that a self-trapped exciton on a single, *cis*-bent molecule in crystalline acetylene is a very effective polymerization seed at lower pressure ($<$ 9 GPa), much closer to the experimental pressure range. This suggested that the reaction might be sensitive to light irradiation, as later confirmed [91]. Further compression from the polymeric phase yielded, in the simulations, an amorphous hydrogenated carbon phase with a very large proportion of sp^3-like carbon atoms [92].

3`7. *Water and Ammonia.* – Water (H_2O) and ammonia (NH_3) are, with methane, the main consituents of the giant planets Neptune and Uranus, where they are subjected to pressures up to a few hundred GPa and temperatures up to a few thousand Kelvin. Whereas in the low-pressure condensed phases molecules are held together by hydrogen bonds, extreme conditions have the effect of reducing the relative strength of the hydrogen bond, either by thermal induced partial breaking of the directional O-H$\cdots$O linkage, or by its pressure-induced symmetrization. First-principles simulations have reproduced the pressure-induced symmetrization at low temperature [93, 94], although the precise value of the transition pressure could only be obtained by properly treating quantum effects on the protons [95, 96]. The calculated infrared activity of ice across the symmetrization [97] compares favorably with experiments. At high temperature, partial collapse of the hydrogen bonding has been observed close to the critical point [98, 99], and its almost complete collapse has been reported at 10 GPa and 600 K [100]. At higher pressures and temperatures water becomes completely ionised, as a two-component fluid above melting and as a superionic phase below melting and for temperature above 2000 K [101]. Ionic conductivities in the fluid compare rather well with shock-wave measurements [102] at similar conditions. Finally, H_2O is predicted to become metallic at temperatures exceeding 7000 K and pressures above 300 GPa [101].

3`8. *Other hydrogen-bonded systems: H_2S and HBr.* – Hydrogen disulfide (H_2S) and hydrogen bromide (HBr) are typically classified as hydrogen-bonded systems. The

strength of the hydrogen bond in both systems is however weaker than in water. The weakness of the hydrogen bonding in H_2S has been shown, by first-principles simulations, to be responsabile for the large fluctuations of the S atoms around their average positions in high-pressure phase IV [103]. This leads to the dynamical formation of short-lived S-S bonds whose presence would be consistent with experimental scattering data [104]. Simulations at higher pressures indicate that the H_2S molecular entity disappears completely in phase V. The structure of phase V is in fact characterized by the presence of charged SH_3^+ and SH^- species, while in phase VI hydrogen atoms intercalate between sulfur sheets. Full dissociation into into elemental crystalline hydrogen and sulfur could not be ruled out however [105].

Simulations of HBr have shown that, contrary to water, the hydrogen bond is here weaker than the isotropic dispersive interactions. This results in a disordered rotator phase (phase I), with fluctuating hydrogen bonds up to pressures exceeding 10 GPa. Disorder is predicted to lead, at higher pressures, to cooperative proton-transfer dynamics [106, 107]. Further compression leads to the transition to the hydrogen-bond ordered phase III, where the hydrogen bond approaches and finally reaches its symmetrized state [107]. A dielectric catastrophe follows, causing formation of H_2 and possibly Br_2 species [107, 108].

3˙9. Silicates and other Earth's materials. – The high-pressure behavior of silica (SiO_2) has attracted a remarkable attention in the last decades, due to its relevance in materials science and geophysics [109]. First-principles simulations have only recently started to address this system. Simulations of quartz above its thermodynamical stability limit have shed light on the structure of the intermediate ordered phase observed prior to amorphization [110]. The direct transformation of cristobalite into stishovite has also been reported, and the microscopic path elucidated [111]. Finally, the simulations suggest that octahedral (six-fold) coordination persits in SiO_2 up to pressures of 1400 GPa, where a new nine-fold coordinated structure is predicted to become favored [111].

Magnesium silicate perovskite ($MgSiO_3$), the major component of the Earth's lower mantle, has been studied with first-principles MD with the aim of determining its low temperature crystal structure [112] and elastic constants [113] and its thermoelasticity at the temperatures of the Earth's mantle [114, 115, 116].

Simulations were used to determine the preferential absorption site of a proton (H^+) in the various polymorphs of Mg_2SiO_4 [117], as well as to study the microscopic mechanisms responsible for the pressure-induced hydrogen sublattice amorphization in $Mg(OH)_2$ and $Ca(OH)_2$ [118] .

3˙10. Iron. – Among the materials of geophysical interest, iron has recently received a lot of attention. Iron is the main constituent of the Earth's core, and is found in the liquid state, possibly mixed with light impurity, in the outer core, whereas deeper in the inner core it solidifies because of pressure. Among the long standing question that first-principles simulations have started to address we can list the melting temperature at the pressure of the inner/outer core boundary, the elastic properties of the solid at inner core

conditions, and the miscibility of light elements in the liquid at outer core conditions. The determination of the melting temperature has been address independently in two works [39, 119]. Two rather different approaches have been followed in the two works. In the first one [119], the melting temperature has been determined by means of thermodynamic integration [120] from a reference potential. In the second approach [39], a very accurate empirical potential has been fitted to the first-principles MD trajectories and melting has been determined with a straightforward two-phase coexistence method with the empirical potential. Unfortunately the two methods yield melting temperatures that differ by about 1300 K (6700 K versus 5400 K). The two approaches however agreed on a number of other thermodynamical quantities including latent heat and volume jump at melting. Elastic constants at Earth's inner core conditions were shown to be consistent with seismic data [39]. For what concerns the outer core, various thermodynamical and structural properties of compressed liquid iron have been calculated [121], including the viscosity coefficient [122]. The effect and solubility of light elements in liquid iron has been studied in the case of oxygen [123] and sulfur [124, 125], and important implications for the temperature and composition of the Earth's core have been drawn [126]

3˙11. *Other simple metals*. – The *hcp*-to-*bcc* pressure-induced transformation in Magnesium (Mg) has been simulated with constant-pressure first-principles MD, and the transformation path (Burgers mechanism) has been confirmed [127]. Simulations on Rubidium (Rb) along the melting curve yielded structural information in good agreement with experiments. A change in the compression mechanism observed at about 6 GPa has been explained in terms of a pressure-induced electronic s-to-d transition[128]. The localization (Mott transition) in expanded Rb, close to the critical point, has been attributed to the large ionic fluctuations[129].

4. – Perspectives

First-principles simulations have experienced a tremendous impetus in the last decade. Nonetheless, a number of major challenges still remain to be solved. Conceptually, improvements over the conventional approximations to DFT would be extremely welcome, although this is admittedly a field where important developments do not seem to be close to our horizons. Extending the number of properties that can be extracted from first-principles simulations is instead a field where important progresses have been made recently, or are in the progress of being made. Increasing the size and time scales of the simulations is also a challenge that requires continuous effort, both from the technical (software) point of view and from the point of view of methodologies that allow to alleviate the effort required to solve the electronic problem.

* * *

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