

Ab Initio Molecular Dynamics for *d*-Electron Systems: Liquid Copper at 1500 K

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We show that an *ab initio* molecular-dynamics scheme based on Vanderbilt ultrasoft pseudopotentials and a plane-wave expansion for the electronic orbitals allows one to perform accurate calculations for large systems containing tightly bound *d*-electron states. We use a novel real-space double-grid technique to deal efficiently with the localized augmentation functions in the core region. We apply our scheme in a full molecular-dynamics simulation of liquid copper at a temperature of 1500 K and find structural and dynamical properties that are in excellent agreement with experimental data.

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The *ab initio* molecular-dynamics (MD) scheme of Car and Parrinello (CP) [1] has been very useful to study structural, dynamical, and electronic properties of large atomic aggregates that model low-symmetry systems such as clusters, surfaces, liquid, and amorphous materials [2]. This method allows one to perform parameter-free MD simulations in which the forces acting on the atoms are derived from the electronic ground state within density-functional theory. This approach has been mostly used in connection with a plane-wave pseudopotential (PP) treatment of the valence electrons. This has so far prevented the application of this method to the tightly bound *d*-electron states of noble and transition metals, which in standard norm-conserving PP formulations [3] require a prohibitively large number of plane waves.

To date the most widely used approaches for accurate first-principles calculations of the electronic structure of *d*-band metals are based on techniques such as the linearized-augmented-plane-wave (LAPW) or the linearized-muffin-tin-orbital (LMTO) methods [4]. Although in principle it is possible to compute accurate interatomic forces within these schemes [5, 6], the computational demand of such calculations has so far prevented direct application to MD simulations. As a consequence, realistic structural models of disordered noble and transition metal systems could only be constructed by means of empirical or semiempirical interatomic potentials [7, 8]. However, only in the context of *ab initio* MD is the subtle interplay between interatomic forces and electronic properties treated in a fully self-consistent way. This level of sophistication is still missing in the case of noble and transition metals.

Recently our group has developed an efficient *ab initio* MD scheme based on plane-wave techniques in connec-

tion with the ultrasoft PP's proposed by Vanderbilt [9] to deal with strongly localized electron states [10]. This approach has been successfully applied to study ice under high pressure [11].

In this Letter, we further extend this scheme to deal with the tightly bound *d*-electron states of noble and transition metals. In order to achieve this result we improve the formulation in several ways, the most important being the introduction of a novel real-space double-grid technique to treat the rapidly varying localized augmentation functions in the core region. We first test the accuracy of our technique with a calculation of the Cu dimer. Then, we show that large systems can be afforded by performing the first *ab initio* MD simulation for a system like liquid copper (*l*-Cu), whose electronic states are among the most difficult to treat in a plane-wave PP formulation. Our simulated liquid sample has structural and dynamical properties that are in excellent agreement with experimental data.

In the Vanderbilt PP scheme one works with optimally smooth pseudo wave functions $\psi_n(\mathbf{r})$, which coincide with the true valence orbitals outside a given core radius r_c . Within the core region, the difference between true and pseudo wave functions is described in terms of localized augmentation functions $Q_{ij}(\mathbf{r})$, so that the total valence electron density can be written as

$$n_v(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 + \sum_{ij} \rho_{ij} Q_{ji}(\mathbf{r}). \quad (1)$$

Here the indices i and j denote an atomic reference state and $\rho_{ij} = \sum_n \langle \beta_i | \psi_n \rangle \langle \psi_n | \beta_j \rangle$, where the $\beta_i(\mathbf{r})$ are localized functions that span the core space. In this scheme the augmentation functions $Q_{ij}(\mathbf{r})$ are the only functions which still require a relatively high plane-wave cutoff. In the case of first row elements such as oxygen, a suffi-

ciently accurate representation of the charge density (1) could be achieved by smoothening the $Q_{ij}(\mathbf{r})$ within an inner core region ($r_{\text{in}} < r_c$) in such a way as to preserve the lowest moment of the electronic charge and by using a Fourier cutoff equal to 4 times the energy cutoff of the pseudo wave functions. The above procedure is not sufficient for a d -electron element like Cu, since in this case the augmentation functions $Q_{ij}(\mathbf{r})$ are a dominant contribution to the electron density and require a considerably higher Fourier cutoff. Thus, we propose the following: (i) The functions $Q_{ij}(\mathbf{r})$ are decomposed in terms of functions of total angular momentum L , which are then smoothened using L -dependent inner radii, in such a way as to preserve *all* the moments of the charge distribution. (ii) Two *different* FFT grids are used: a coarse grid which is defined by 4 times the cutoff of the pseudo wave functions as in conventional plane-wave calculations, and a significantly denser grid whose spatial mesh is defined by the large Fourier cutoff required by the $Q_{ij}(\mathbf{r})$. (iii) We adopt a real-space formulation to exploit the fact that the $Q_{ij}(\mathbf{r})$ are *localized* within the core region defined by r_c .

Point (i) allows an accurate smoothening of the $Q_{ij}(\mathbf{r})$ and reduces the need for high Fourier components, since these are mainly related to the high- L components of the Q_{ij} for which one can use larger r_{in} . Points (ii) and (iii) allow us to use a significantly larger cutoff for the $Q_{ij}(\mathbf{r})$ without significantly increasing the computational cost. The coarse grid is used to calculate the smooth part of the electron density [the first term on the right-hand side of Eq. (1)] and to apply the full local potential to the pseudo wave functions. The dense grid is used to evaluate the $Q_{ij}(\mathbf{r})$ in real space. In practice this is done by performing Fourier interpolations of the $Q_{ij}(\mathbf{r})$ inside small boxes, which contain the core region and move with the ions. The number of operations needed for these interpolations does not depend on the size of the system but only on the size of the core region. Fourier transforms on the dense grid covering the entire simulation cell are only used to compute the total Hartree potential and to transfer functions such as the exchange and correlation potential, the smooth part of the charge density, and the full local potential from real to reciprocal space or vice versa. The above procedure not only significantly reduces the total number of operations associated with the Q_{ij} but also has a total cost that scales only linearly with size [neglecting the $\log(\text{size})$ factor in the FFT's], instead of quadratically as it would result if the real-space formulation were not used.

In order to illustrate our method we apply it to Cu, which we take as a prototype element with very localized d -electron states. We constructed a nonrelativistic ultrasoft PP for Cu, using two reference energies for each angular momentum ($l = 0, 1, 2$) in a slightly excited electronic valence configuration $3d^{9.5}4s^14p^{0.5}$. The core radii were taken to be $r_{cs} = 2.1$, $r_{cp} = 2.4$, $r_{cd} = 2.0$ a.u., while inner radii r_{in} ranging from 0.6 a.u. (for $L = 0$) up to

1.2 a.u. (for $L = 4$) were used. Exchange and correlation effects were treated within LDA using Perdew and Zunger's interpolation formulas [12]. The above choice of parameters allows one to achieve very good convergence using an energy cutoff of only 18 Ry for the pseudo wave functions and of 200 Ry for the augmentation functions $Q_{ij}(\mathbf{r})$. We checked the accuracy of our technique by performing calculations for a Cu dimer using a periodically repeated simple cubic cell of side 16 a.u. The results are reported in Table I, where they are compared with experiment [13], with an accurate calculation using a real-space method [14], and with a well converged calculation using norm-conserving PP's [15]. The agreement between the three calculations in Table I is extremely good showing (i) the accuracy of the PP's, and (ii) the good convergence of the calculations. We remark that while a cutoff of 300 Ry was used for the pseudo wave functions in Ref. [15], only an 18-Ry cutoff was used in the present calculation. A plane-wave cutoff similar to ours would be needed in a LAPW calculation for the same system.

Next, in order to simulate l -Cu, we considered a relatively large system consisting of a periodically repeated simple cubic cell of side $a = 16.467$ a.u. containing 50 atoms [16] at a density corresponding to the experimental density of l -Cu at the melting point ($\rho = 7.97$ g/cm³ at $T_M = 1356$ K [17]). During the MD simulation, we let the atomic coordinates and the electronic pseudo wave functions at the Γ point of the supercell evolve according to the CP equations of motion in the presence of two Nosé-Hoover thermostats [18], having masses Q_p and Q_e , associated with the ions and with the electrons, respectively [19]. The ionic thermostat was used to keep the average ionic temperature of the simulation equal to a preset value T , whereas the electronic thermostat was used to keep the total classical kinetic energy of the electronic degrees of freedom always very close to a preset value $E_{\text{kin},0}$. $E_{\text{kin},0}$ must be much smaller than the total ionic kinetic energy, but at the same time it must be large enough to allow the classical electronic degrees of freedom of mass μ to follow adiabatically the motion of the ions. In this way long MD simulations do not require subsequent electronic reoptimizations, since the two thermostats continuously extract from the electrons

TABLE I. Bonding length r_e , cohesive energy D_e , and vibrational frequency ω_e for Cu₂: experimental value [13], as calculated with a real-space method (RS) [14], with a norm-conserving PP (NCP) [15], and in the present work [27]. The binding energies are given with respect to non-spin-polarized atoms.

	r_e (a.u.)	D_e (eV)	ω_e (cm ⁻¹)
Experiment	4.195	1.97	264.5
RS	4.124	3.35	292.0
NCP	4.07	3.18	295.1
Present	4.12	3.14	277.5

and give back to the ions the energy that is transferred from the latter to the former, due to a nonperfectly adiabatic CP evolution. As a consequence the departure of the electrons from the Born-Oppenheimer (BO) surface does not increase with time. This is particularly important to simulate metallic systems that are characterized by a persistent and non-negligible transfer of energy from the ionic to the electronic degrees of freedom.

In our simulation we used a time step of 10 a.u. (0.24 fs) and masses $\mu = 1500$ a.u., $Q_p = 5 \times 10^6$ a.u., and $Q_e = 7.5 \times 10^4$ a.u., respectively. $E_{\text{kin},0}$ was set equal to 0.95 eV, i.e., about a tenth of the average ionic kinetic energy and only slightly larger than the value that, according to a simple estimate given in Ref. [19], would be necessary to follow adiabatically the ionic motion. With this choice of parameters, the global constant of motion [18, 19] is found to drift at a rate of 0.012 meV/ps, which is negligible on the time scale of our simulation.

Initially the atoms were given a simple cubic arrangement in which 14 vacancies were randomly created. After minimizing the electronic energy, the system was first allowed to evolve microcanonically. Then the electronic energy was re-minimized and the system was coupled to the thermostats. The externally set temperature was gradually decreased from the naturally acquired value of about 2000 K to the chosen value of 1500 K. At the same time we observed a rapid evolution of the system towards more closely packed configurations. This is not surprising since the starting atomic configuration had an average coordination of less than 6 which is rather unphysical for bulk Cu. After allowing for equilibration we let the system evolve at $T = 1500$ K for a total time of 2 ps during which we measured various physical quantities. We checked that the deviation from the BO surface did not increase with time. As a matter of fact, at two atomic configurations along the MD trajectory, one after approximately 1 ps and the other at the very end of the simulation, the total (potential) energy of the system of 50 atoms was found to lie above the BO surface by 0.62 and 0.53 eV, respectively. Notice that a total energy shift of about 0.5 eV, or, equivalently, of less than 0.002 eV per electron state, is substantially smaller (by about a factor of 20) than the total ionic kinetic energy and is also smaller (by a factor of 2–3) than the average fluctuation of the ionic kinetic energy in our sample. This is a typical situation in *ab initio* MD simulations [20]. As an additional check that the electrons remain very close to the instantaneous ground state all along the simulation, we compared the occupied single-particle eigenvalues obtained from the CP dynamics with those obtained from energy minimization and found only negligible differences.

In Fig. 1 we report the radial correlation function $g(r)$ of *l*-Cu as obtained from our simulation and we compare it with experimental data taken at two different temperatures [17], one below and one above $T = 1500$ K used in our calculation. Notice that in spite of the small size

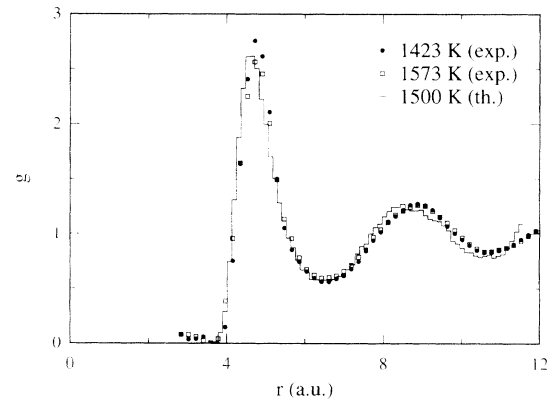


FIG. 1. Radial pair correlation function for liquid Cu. The histogram is a result of the present theory. Experimental data are from Ref. [17]. Theory: peaks at 4.62 a.u. and at 8.45 a.u., coordination number equal to 12.5. Experiment (1413 K): peaks at 4.86 a.u. and at 9.07 a.u., coordination number equal to 11.3.

of our simulation box ($a/2 = 8.23$ a.u.) we have been able to measure the correlation function up to $r = 10$ a.u., using the technique of Ref. [21] to include data obtained from the corners of the cube. This allows us to fully include the second peak of $g(r)$ in our measurement. Overall the agreement between theory and experiment is excellent, with only a few percent underestimate of the binding distances in the simulation data, an effect that was already present in the dimer calculation. We notice that, although a good radial correlation function for *l*-Cu can also be obtained with empirical methods, such as, e.g., the embedded atom approach [7], the good result found in our parameter-free calculation indicates that our PP LDA scheme gives an accurate description of the potential energy surface of *l*-Cu.

Not only static but also dynamic properties can be obtained from our simulation. In particular we have calculated the self-diffusion coefficient D by analyzing the mean squared displacement of the ions in our sample. We find $D = (2.8 \pm 0.2) \times 10^{-9}$ m²/s, to be compared with experimental values of $D = 4.6 \times 10^{-9}$ m²/s and of $D = 6.0 \times 10^{-9}$ m²/s at $T = 1413$ and 1533 K, respectively [22], which we consider a satisfactory agreement, in view of the strong temperature dependence of D . We should remark that although our simulated sample shows good liquidlike behavior, we do not know the precise value of its melting point.

Finally, we report in Fig. 2 the electronic density of states of *l*-Cu as obtained from the calculated single-particle eigenvalues. The average was taken over 150 configurations generated at regular intervals during the MD run for what concerns the occupied states, while for the unoccupied states we have only used the two configurations at which we performed the electronic minimizations referred to above. In the same figure we also report a calculation of the density of states of crystalline Cu

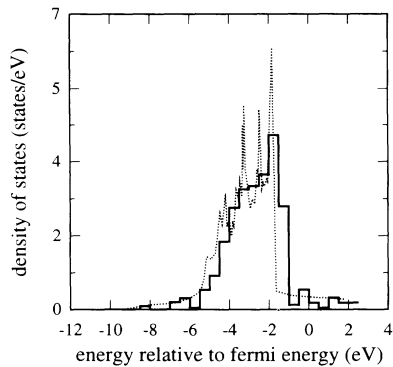


FIG. 2. Density of states vs energy for liquid Cu as obtained in the present theory. The dotted line is the density of states of crystalline Cu (from Ref. [23]). The Fermi level is at zero energy.

from Ref. [23]. Since the density of states for the liquid is obtained with a one-point (Γ) sampling of the Brillouin zone, it is not expected to be accurate. However, the metallic character of the system is evident from the absence of a gap at the Fermi level [24]. Overall, the electronic density of states appears to change only slightly when going from the crystal to the liquid, in agreement with early photoemission data for *l*-Cu [25] and with recent theoretical calculations for liquid transition metals [26].

In conclusion, we have shown that *ab initio* MD simulations for large systems containing *d*-electron elements are feasible. This will allow the study of systems such as transition metal clusters, liquid and amorphous noble and transition metals, metallic surfaces, or transition metal oxides, using the same advanced techniques to treat structural relaxation effects that have been so far available only in the case of simple *s-p* bonded systems.

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