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Brief Reports

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Adiabaticity in first-principles molecular dynamics

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Car-Parrinello-like simulations critically depend on the ability to control the drift of the electronic wave functions away from the instantaneous ground state. This problem, particularly severe for metals, is gaining more importance as the time scale of such simulations increases. Here a method is proposed that solves the problem by introducing two separate thermostats for ions and electrons, without adding to the computational cost. A detailed analysis of the nonadiabatic behavior leads to a strategy that minimizes the resulting errors. An application of the method to molten aluminum is presented.

A few years ago Car and Parrinello[1] invented a scheme that unified molecular-dynamics techniques with the density-functional framework[2,3] for electronic structure calculations. This approach allows us to calculate the atomic motion directly from the underlying electronic structure. In contrast to standard molecular-dynamics techniques, in which the interactions between atoms are parametrized, with parameters adjusted to experimental data, the interactions in their method are obtained from first principles. The underlying idea of this technique is that a fictitious dynamics is introduced for the electronic wave functions that is treated in the same manner as the dynamics of the atoms by integrating Newton-type equations of motion.

Since the electronic wave functions of the density-functional framework[2,3] are meaningful only if the wave functions are in their ground state for each instantaneous atomic configuration, they must reside on the Born-Oppenheimer surface. This implies that the two subsystems, electronic wave functions and atomic positions, must not be in thermal equilibrium with each other; the temperature related to the electronic wave functions must be very low compared with the physically relevant temperature of the atomic subsystem. However, as thermal equilibrium is approached, the electronic wave functions tend to heat up and leave the Born-Oppenheimer surface, accompanied by a cooling of the atomic system.

An essential condition for the practicability of the Car-Parrinello method is that this heat transfer is sufficiently slow to allow simulations over long periods of time before the dynamics produces unphysical results. For insulators this is indeed the case, and simulations of up to a picosecond time scale typically can be performed without adjustment. However, there is a marked difference between the behavior of insulators and that of metals: for metals the heat transfer is very difficult to control; in insulators, there is a separation of the frequency spectra of the electronic and the ionic motions that is roughly proportional to the width of the electronic band gap divided by a fictitious mass parameter for the electronic degrees of freedom.[4] Since there is no band gap, this separation is absent in metals and hence the heat transfer can no longer be controlled by adjusting the mass parameter.

The common practice for metals, and for long simulations in general, has been to repeatedly quench the electronic system back to the Born-Oppenheimer surface, a method that adds appreciably to the computational cost and that, in addition, introduces noise to the simulation. Therefore, an approach that controls the individual temperature of the two subsystems and minimizes the perturbation of the atomic motion is highly desirable.

Such a method can be obtained from an extension of the constant-temperature molecular-dynamics scheme that has been introduced by Nosé[5,6] and subsequently reformulated by Hoover.[7] In the original scheme, one additional thermostating variable is introduced that is able to generate a canonical ensemble at a prefixed temperature. Subsequently, Nosé[8] generalized this idea by introducing several variables that can maintain different portions of the system at different temperatures. This option has been exploited very recently by Sprik[9] to perform classical simulations of polarizable systems.

In this paper we will extend these ideas to the first-principles molecular-dynamics technique of Car and Parrinello, and describe how in this way the temperatures of the electronic wave functions and the atomic positions can be kept at two different temperatures. The implementation is simple and does not add to the computational effort in any noticeable way. We will give guidelines that lead to a minimum perturbation of the physically relevant results. The implications of this method are illustrated with a practical example: aluminum at the melting point.

If we combine the two thermostats of Nosé[5–8] and the method of Car and Parrinello,[1] we obtain the following equations of motion for electronic wave functions Ψ_i and atomic positions R_i:

$$|\ddot{\Psi}_i\rangle\mu=-H|\Psi_i\rangle+\sum_j|\Psi_i\rangle\Lambda_{ji}-|\dot{\Psi}_i\rangle\dot{x}_e\mu\ , \tag{1}$$

$$M_i\ddot{R}_i=F_i-M_i\dot{R}_i\dot{x}_R\ . \tag{2}$$

The forces acting on the ions, F_i, and the fictitious forces acting on the electronic wave functions, $-H|\Psi\rangle$, are obtained from the corresponding partial derivatives of the total-energy functional $E(|\Psi_i\rangle,R_i)$ of the local-density approximation.[3] The matrix of Lagrange multipliers Λ_{ij} assures orthonormality of the wave functions. μ is a fictitious mass for the wave functions and M_i are the atomic masses. The last term of each equation is a friction term which couples wave functions and atom dynamics to the Nosé thermostats. These friction terms are governed by the dynamical variables x_e and x_R, which obey the following equations of motion:

$$Q_e\ddot{x}_e=2\left[\sum_i\mu\langle\dot{\Psi}_i|\dot{\Psi}_i\rangle-E_{\mathrm{kin},0}\right]\ , \tag{3}$$

$$Q_R\ddot{x}_R=2\left[\sum_i\tfrac{1}{2}M_i\dot{R}_1^2-\tfrac{1}{2}gk_BT\right]\ . \tag{4}$$

The fictitious kinetic energy of the electronic wave functions fluctuates about the mean value $E_{\mathrm{kin},0}$ and the average kinetic energy of the ions is $\frac{1}{2}gk_BT$, where g is the number of degrees of freedom for the atomic motion, k_B is the Boltzmann constant, and T is the physical temperature of the simulation. The masses Q_e and Q_R determine the time scales for the thermal fluctuations. These equations of motion conserve the total energy of the system,

$$\begin{aligned}E_{\mathrm{tot}}=&\sum_i\mu\langle\dot{\Psi}_i|\dot{\Psi}_i\rangle+\sum_i\tfrac{1}{2}M_i\dot{R}_i^2+E(|\Psi_i\rangle,R_i)\\&+\tfrac{1}{2}Q_e\dot{x}_e^2+2E_{\mathrm{kin},0}x_e+\tfrac{1}{2}Q_R\dot{x}_R^2+gk_BTx_R\ .\end{aligned} \tag{5}$$

It can be shown, under the assumption of ergodicity and small heat transfer between electronic and atomic dynamics, that both the fictitious dynamics of the wave functions and the atomic motion each form a canonical ensemble with different temperatures.

A proper choice of the value of $E_{\mathrm{kin},0}$ is not important for a physically relevant simulation: If, on the one hand, this value is too large, the electronic wave functions will depart from the Born-Oppenheimer surface and ultimately become meaningless. If, on the other hand, it is too small, the electrons cannot easily follow the atomic motion, which results in a retardation of the atomic motion.

In order to analyze the situation, we distinguish an adiabatic from a free contribution to the dynamics of the electronic wave functions. The adiabatic motion is given by the exact electronic ground state for each instantaneous atomic configuration. A free motion of the wave functions would be possible even for a static atomic arrangement. Ideally, the free motion should vanish. An estimate for the kinetic energy related to the adiabatic motion can be inferred from a model system of well-separated atoms. The adiabatic (atomic) wave functions of this model system follow the corresponding atom rigidly. Thus we can relate the fictitious kinetic energy of the system to the velocities of the atom. If we average over a canonical ensemble, we obtain the following expression under the simplified assumption that the atomic masses are identical:

$$E_{\mathrm{kin,ad}}=2k_BT\frac{\mu}{M}\sum_i\langle\Psi_i|-\tfrac{1}{2}\nabla^2|\Psi_i\rangle\ . \tag{6}$$

Here M stands for the mass of one atom. This value gives us a guideline for setting the average kinetic energy of the electronic wave functions.

In Fig. 1 the heat transfer is shown as a function of the preset average kinetic energy of the electrons for solid aluminum at the melting point. We can clearly distinguish two regimes which are separated at approximately the value of the kinetic energy calculated in Eq. (6). For very small values of $E_{\mathrm{kin},0}$, the heat transfer rises sharply to very high values. This is the region where the average kinetic energy is smaller than necessary for adiabatic motion of the electrons; the thermostat hinders the electrons from following the atomic motion, which in turn retards the atomic motion. Hence the dynamics of the atoms is strongly perturbed in this regime. If the average kinetic energy is larger than needed for the adiabatic motion, the heat transfer becomes virtually independent of $E_{\mathrm{kin},0}$. This is the regime in which the electrons are free to follow the atoms, and the additional kinetic energy results in deviations from the Born-Oppenheimer surface, which ultimately will lead to a deterioration of the results for the atomic motion. The optimum choice clearly lies just to the right of the transition region. As our estimate neglects fluctuations of the atomic kinetic energy, we should choose $E_{\mathrm{kin},0}$ somewhat larger than $E_{\mathrm{kin,ad}}$. We recommend a value that is about twice that given in Eq. (6).

From Fig. 1, it also becomes clear why the route of re-

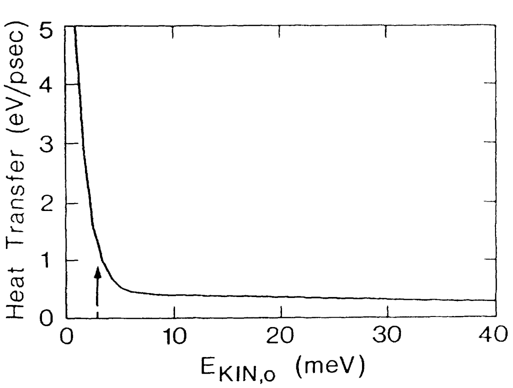

FIG. 1. Heat transfer as a function of the pre-fixed average fictitious kinetic energy $E_{\mathrm{kin},0}$ of the electronic wave functions for solid aluminum at the melting point. The arrow indicates the kinetic energy required for adiabatic motion of the electrons according to Eq. (6).

peatedly quenching the electronic wave functions to the Born-Oppenheimer surface is an unfortunate choice: as one frequently operates in the very left of the diagram, the heat transfer is very large. Contrary to common belief, the problem cannot be solved by quenching the system more frequently; with each quench the ions experience a kick, which corresponds to a transfer of a fixed amount of energy to the electrons, namely $E_{\text{kin,ad}}$. Hence, more frequent quenching of the electronic wave functions increases the perturbation of the atomic trajectories. The electronic and the atomic motion can only be decoupled adiabatically in this way if the wave functions are quenched after each single time step. Such a procedure, however, would be computationally exhaustive as it would increase the number of iterations for the electronic wave functions—and thus the total computational effort—typically by more than an order of magnitude.

In addition to $E_{\text{kin,0}}$, we have to determine the time scales for the thermal fluctuations of the electronic and atomic subsystems. The typical frequencies of the thermal fluctuations ω_R and ω_e are determined through the masses for the thermostats via $\omega_R=\sqrt{2gk_BT/Q_R}$ and $\omega_e=\sqrt{4E_{\text{kin,0}}/Q_e}$. It should be kept in mind that the Nosé thermostat alters the atomic dynamics and cannot reflect a realistic coupling to the environment that acts as a heat bath. Therefore, the period of the oscillation of the atomic thermostat shall be chosen larger than the typical time scale for the dynamical events of interest but, of course, shorter than the simulation time. The choice of the mass of the thermostat for the electrons is expected to influence the physically relevant results even less, as it acts directly only on the fictitious dynamics of the wave function. However, the frequency should lie above the phonon spectrum to avoid any interference effects.

The efficient implementation of the Nosé thermostat for the electronic wave functions, consistent with the Verlet algorithm used for integrating the equations of motion, is nontrivial. The problem is related to the fact that, in the Verlet algorithm, a velocity-dependent force usually requires a self-consistent cycle for the wave functions of the next time step. For the atomic positions this poses no problem. For the wave functions, however, this route would add appreciably to the computational effort, owing to the vast number of degrees of freedom for the wave functions and the need to simultaneously satisfy the constraint of orthonormal wave functions, which itself is implemented by an iterative solution. This problem, however, can be avoided by a simple trick: since the Verlet algorithm itself is only accurate up to second order in the time step, a consistent implementation of the Verlet algorithm requires the forces to be accurate only up to second order of the time step Δ. To this accuracy the velocity of x_e can be calculated from the present and the two preceding time steps,[10]

$$\dot{x}_e=\frac{3x_e(t)-4x_e(t-\Delta)+x_e(t-2\Delta)}{2\Delta}\;. \tag{7}$$

Next we decompose the equations of motion for the electronic wave functions, Eq. (1), into its discretized form. We apply the standard rules

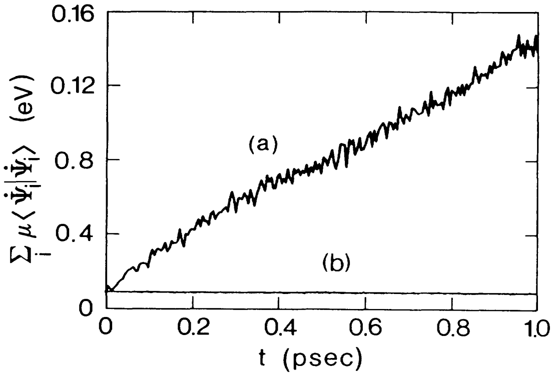

FIG. 2. Fictitious kinetic energy of the electronic wave functions versus time for liquid aluminum at the melting point (a) without and (b) with thermostating of the electrons. Both simulation runs start from identical initial conditions.

$$|\ddot{\Psi}\rangle=\frac{|\Psi(t+\Delta)\rangle-2|\Psi(t)\rangle+|\Psi(t-\Delta)\rangle}{\Delta^2}\;, \tag{8}$$

$$|\dot{\Psi}\rangle=\frac{|\Psi(t+\Delta)\rangle-|\Psi(t-\Delta)\rangle}{2\Delta}\;, \tag{9}$$

and resolve for $\Psi(t+\Delta)$,

$$|\Psi_i(t+\Delta)\rangle=|\Psi_i(t-\Delta)\rangle+\left[|\Psi_i(t)\rangle-|\Psi_i(t-\Delta)\rangle-H|\Psi_i(t)\rangle\frac{\Delta^2}{2\mu}\right]\frac{2}{1+\dot{x}_e\frac{\Delta}{2}}+\sum_j|\Psi_j(t)\rangle\Lambda_{ji}\frac{\Delta^2/\mu}{1+\dot{x}_e\frac{\Delta}{2}}\;. \tag{10}$$

This equation can be solved as usual, using the algorithm to satisfy the constraint to orthogonality described by Car and Parrinello.[11]

We have applied the technique to a simulation of solid and molten aluminum at the melting point. Here, we

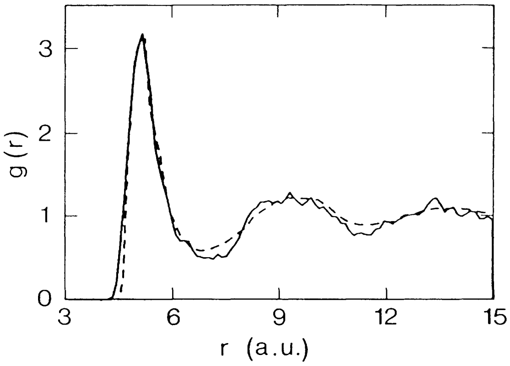

FIG. 3. Pair-correlation function for molten aluminum at the melting point obtained with the Car-Parrinello method (solid line) compared to the result of Jacucci *et al.* (Ref. 17) (dashed line).

have chosen the mass parameter for the electronic variables to be $\mu = 1000$ a.u. and the time step to be 10 a.u. We have used supercell geometry with 64 atoms per cell. The pseudopotentials are the separable version[12,13] of a Bachelet-Hamann-Schlüter type pseudopotential[14–16] with s nonlocality only and core radii of 1.5 and 1.3 a.u. for s- and p-type angular momenta, respectively. The **k**-point sampling has been reduced to a sampling of the Γ point. This approximation does not introduce a quasigap since the set of degenerate levels at the Fermi level is partially occupied.

Without applying a thermostat to the electronic wave functions, the fictitious kinetic energy of the electronic wave functions rapidly rises to unacceptable levels, as shown in Fig. 2. If, however, the temperature of the electrons is controlled according to the description given above, the dynamics is stable, with the electronic wave functions remaining close to the Born-Oppenheimer surface throughout the simulation. A qualitatively similar behavior is expected also for insulators, even though the rise of the fictitious kinetic energy without temperature control for the electronic wave functions would be orders of magnitude smaller. For *long* simulations, however, temperature control for the wave functions is mandatory even for insulators.

In Fig. 3 our calculated pair-correlation function for molten aluminum is compared with that calculated by Jacucci *et al.*,[17] which provides an excellent description of the experimental data. We also checked that the dynamics is not significantly altered through our scheme by calculating the diffusion constant D from the mean-square displacement of the ions. Our result is $D = 6 \times 10^{-5}$ cm^2/sec. Even though there is no measurement of D, theoretical estimates reported by Waseda[18] are $\sim 8 \times 10^{-5}$ cm^2/sec. We find the agreement satisfactory, given the semiquantitative nature of the theories on which the estimates are based.

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