Ab Initio Molecular Dynamics Study of First-Order Phase Transitions: Melting of Silicon

Osamu Sugino[1,2] and Roberto Car[1,3]
[1]Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), PHB-Ecublens, CH-1015 Lausanne, Switzerland
[2]Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305, Japan
[3]Department of Condensed Matter Physics, University of Geneva, CH-1211 Geneva, Switzerland

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We present a scheme to compute the thermodynamic properties and the phase stability of materials based on parameter-free microscopic quantum theory. Taking silicon as an example we show that properties like the specific entropy, the specific volume, or the heat capacity of a solid and a liquid can be calculated accurately. In particular, we can locate the solid-liquid phase boundary and compute how thermodynamic properties change upon melting. This greatly extends the range of first-principles predictions of materials properties.

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Prediction of phase transformations of real materials from first-principles microscopic quantum theory is a long standing goal of condensed matter physics. Considerable progress in this field has been achieved, over the last decade, on the basis of accurate quantum-mechanical calculations of the electronic total energy of simple substances, using density-functional theory (DFT) within the local density approximation (LDA) for exchange and correlation. Although limited to the zero temperature phase diagram, these studies were extremely useful to understand and to predict pressure induced phase transitions in crystalline solids [1].

In principle it would be possible to extend these calculations to finite temperature with *ab initio* molecular dynamics (MD) techniques [2], which allow one to sample thermal fluctuations by means of atomic trajectories generated with DFT-LDA forces. However, as usual within MD simulations, an accurate location of the boundaries of first-order phase transformations would be hampered by hysteresis effects associated with short simulation time, periodic boundary conditions, etc. A possible way out consists of calculating separately the chemical potentials of each coexisting phase in order to find its range of stability as a function of p and T. Such calculations are possible within classical MD simulations [3] and have been used, for instance, to study the melting transition of silicon (Si) [4] as modeled by the Stillinger-Weber (SW) potential [5]. However, no attempts have been made so far to study in this way first-order phase transitions within *ab initio* MD, although recently, combined MD and DFT-LDA techniques have been used to compute free energies of point defects in crystalline solids [6–8].

In this paper, we report on a scheme to calculate finite temperature thermodynamic properties of materials within the *ab initio* Car-Parrinello (CP) method [2]. Our approach is based on isobaric-isothermal MD simulations combined with a recently proposed technique to compute free-energy differences [9]. In particular, taking the melting transition in Si at zero pressure as an example, we show that transition temperatures, heats of fusion, and volume discontinuities at melting can be calculated from microscopic quantum theory. Our results are in good agreement with experiment indicating that the overall accuracy of DFT-LDA is similar for zero and finite temperature properties. Even a delicate quantity like the melting temperature, which defines the boundary between two phases as different as a metallic liquid and a semiconducting crystal, can be predicted within 20% accuracy. This is similar to the DFT-LDA accuracy in predicting the transition pressure between the diamond and the β-tin phases of crystalline Si [10,11].

Under typical experimental conditions of constant pressure and temperature, the basic thermodynamic quantity is the chemical potential. This cannot be obtained directly from MD simulations, but its derivatives can be computed from temporal averages along isobaric-isothermal MD trajectories [3]. Hence, a free energy or chemical potential difference $\Delta\mu$, between an actual and a reference system, can be calculated by integrating a chemical potential derivative along a reversible thermodynamic path connecting the actual system of Hamiltonian $\mathcal{H}_1$ to the reference system of Hamiltonian $\mathcal{H}_0$, i.e.,

$$\Delta\mu = \int_0^1 d\lambda \frac{d\mu}{d\lambda} = \int_0^1 d\lambda \langle \mathcal{H}_1 - \mathcal{H}_0 \rangle_\lambda . \qquad (1)$$

Here $\langle \cdots \rangle_\lambda$ stands for a temporal average along an isobaric-isothermal MD trajectory generated from the Hamiltonian $\mathcal{H}(\lambda) = \lambda\mathcal{H}_1 + (1 - \lambda)\mathcal{H}_0$. Under ergodic conditions this is equivalent to an ensemble average. If the free energy of the reference system is known, Eq. (1) allows one to compute the chemical potential of the actual system.

For sufficiently close end systems, the thermal averages in Eq. (1) can be calculated with short MD runs. It is therefore convenient to split the calculation into two steps by introducing an intermediate classical reference system which, ideally, should be as close as possible to the actual quantum system. Then short MD runs can be used to calculate $\Delta\mu$ between the actual DFT-LDA and the intermediate reference system, while long MD runs can be used for the less demanding calculation of $\Delta\mu$ between the intermediate and final reference systems. In the present case we take SW Si as an intermediate reference system: This provides a reasonably good model of Si, for which the free energies of crystalline and liquid phases are already known [4].

In order to compute $\Delta\mu$, we find it convenient to adopt a dynamical method [9]. In this approach the parameter λ depends on time and switches slowly (adiabatically) from $\lambda(t_0) = 0$ to $\lambda(t_1) = 1$. Then Eq. (1) can be rewritten as

$$\Delta\mu = \int_{t_0}^{t_1} (\mathcal{H}_1 - \mathcal{H}_0) \frac{d\lambda(t)}{dt} dt . \qquad (2)$$

This has the important conceptual advantage that $\Delta\mu$ is obtained from a single isobaric-isothermal MD trajectory generated by the time-dependent Hamiltonian $\mathcal{H}(\lambda(t))$.

We used isobaric-isothermal CP simulations [12] to describe the DFT-LDA quantum system. By letting the cell volume fluctuate according to Andersen's [13] prescription, the average pressure of the simulation was kept equal to a preset value, taken here equal to zero. A choice of 0.04 a.u. for the volume mass ensured coupling between volume and thermal fluctuations. The ionic temperature was controlled by a Nosé thermostat with mass equal to 2.5×10^5 a.u. Following Ref. [14], an additional thermostat was used to keep the electrons close to their instantaneous ground state with the following choice of parameters (see Ref. [14]): $Q_e = 21.5$ a.u./atom and $E_{\text{kin},0} = 1.4 \times 10^{-4}$ a.u./atom. To speed up the numerical integration of the CP equations, we used a mass preconditioning scheme [15] which allowed us to use a time step $\Delta t = 0.34$ fs.

We adopted a plane-wave pseudopotential approach using a norm-conserving Bachelet-Hamann-Schlüter (BHS) pseudopotential [16] with s and p nonlocality. LDA exchange and correlation energies and potentials were parametrized as in Ref. [17]. The nonlocal part of the pseudopotential was computed in real space [18]. A large fraction of the tests were made with a pseudopotential softer than BHS but, since this pseudopotential introduced small errors, particularly in the enthalpy difference between liquid and solid, all our final results were based on the more accurate, albeit computationally more expensive, BHS potential.

We used the same number of plane waves N_{PW} at different volumes and added a correction $\Delta E_{\text{tot}}/N$ to the total energy per atom, to account for incomplete convergence with plane waves. Since, for large N_{PW}, $\Delta E_{\text{tot}}/N$ basically only depends on the density, we calculated it for a simple reference system and fitted its variation with N_{PW} and the cell volume Ω by the formula $\Delta E_{\text{tot}}/N = -A \exp\{-B(N_{\text{PW}}/\Omega)\}$, with appropriate values for the parameters A and B [19]. We checked, with fully converged calculations on selected crystalline and liquid structures, that convergence errors were reduced to less than 1% in the equilibrium volume and to less than 7 meV/atom in the total energy.

We also considered the effect of different cell sizes and different sets of k points for Brillouin zone integration. Some tests are reported in Fig. 1. They indicate that both the enthalpy difference between liquid and solid and the specific volume of the liquid are well converged with a 216-atom cell and Γ, or with a 64-atom cell and four special k points [20]. This implies that convergence is slower for electronic than for atomic structure. Indeed we found that average structural properties of the liquid, such as the pair correlation function and the bond angle distribution, depend little on the cell size and on the k points. Basically, these properties were the same in the present and in previous calculations by Štich, Car, and Parrinello [21], which were performed at a constant volume with a 64-atom cell and Γ. We therefore decided to use a 64-atom cell and four special k points in all our calculations. Size effects are also small for SW Si, in which case the chemical potential calculated with a 64-atom cell differs by less than 0.01 eV/atom from that obtained by Broughton and Li [4] with a 512-atom cell.

We computed $\Delta\mu$, i.e., the chemical potential difference between DFT-LDA and SW Si, by numerically evaluating the integral in Eq. (2). This required us to compute the difference between the DFT-LDA and the SW total energy function along an MD trajectory in which the electrons were evolved in CP fashion in the usual way, while the ions responded to forces that were adiabatically switched from those corresponding to the SW energy function to the CP forces. We found that a switching time of about 0.7 ps (i.e., about 10 times the shortest vibrational period of the solid) was sufficient to compute $\Delta\mu$ with an accuracy of about 0.02 eV/atom for both the liquid and the solid at

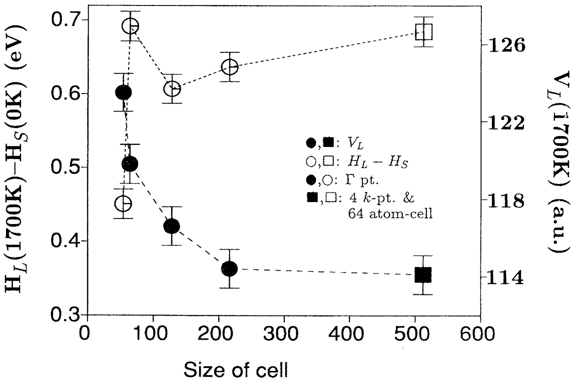

FIG. 1. Cell size and k-point dependence of the enthalpy and the specific volume of l-Si at $T = 1700$ K. The calculation was done using the soft pseudopotential. The enthalpies are referred to the solid at $T = 0$ K. Circles correspond to Γ-point calculations and squares to four k-point calculations with a 64-atom cell, which is equivalent to Γ-point sampling in a cubic 512-atom cell.

high temperature. The relatively short switching time is a measure of the similarity between SW and DFT-LDA Si. Finally, we computed the absolute DFT-LDA chemical potential by adding to $\Delta\mu$ the known chemical potential of SW Si [4].

The results are displayed in Fig. 2, where all the chemical potentials are referred to the solid at $T = 0$ K, which includes also a correction for zero-point motion of 0.06 eV/atom for crystalline Si in the diamond structure. The statistical errors of the simulation, as indicated by the error bars, are approximately equal to 0.02 eV/atom for all the data points. The available experimental data are also reported in the figure.

For the liquid we only know from experiment the chemical potential and the entropy at melting. The entropy gives the slope of the chemical potential curve. We note that theoretical and experimental slopes are approximately the same, and the theoretical curve is only shifted downward by approximately 0.12 eV/atom. This is a remarkable achievement considering the large difference in structure and bonding between the semiconducting solid and metallic liquid phases. Recent calculations for crystalline Si at $T = 0$ K have shown that the DFT-LDA total energy is approximately 0.26 eV/atom higher than the essentially exact result of diffusion quantum Monte Carlo calculations [22]. Our findings suggest that the DFT-LDA total energy of liquid Si should be even closer to the corresponding exact result. This can be understood on the basis of the more homogeneous character of the electronic density of the liquid. As we see in Fig. 2, a relative error of the order of 0.1 eV/atom in the chemical potentials is sufficient to make an error of about 300 K in the melting temperature T_m. In our opinion this is a satisfactory result for DFT-LDA. On general grounds an accuracy of the order of 0.01 eV/atom in the chemical potentials would be necessary to locate T_m with an accuracy of better than 100 K. This is well beyond the accuracy of electronic structure calculations.

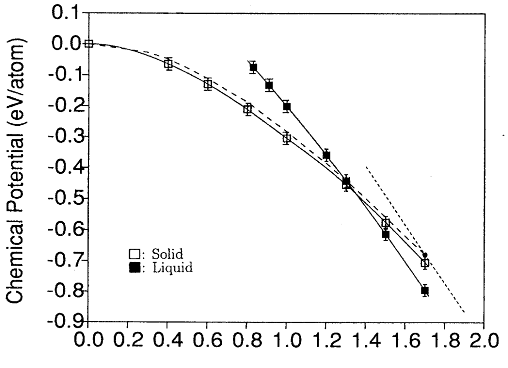

FIG. 2. Chemical potential for *s*-Si (open squares) and *l*-Si (filled squares). Full lines correspond to theory and broken lines to experiment.

A more detailed comparison between theory and experiment is given in Table I, where we report several calculated thermodynamic properties at melting together with their corresponding experimental values. All calculations are based on temporal averages over equilibrated MD runs lasting for about 1.5 ps.

We notice that the errors in the absolute entropies of the solid and liquid are only 7% or less, indicating that *ab initio* MD trajectories measure accurately the motional disorder at T_m. The typical errors in the enthalpies and in the latent heat of fusion ΔH_{sl} are of the order of 0.1 eV/atom, as expected from the overall accuracy of DFT-LDA. Good agreement between theory and experiment is also found for the specific heats at constant pressure which have been calculated both from the definition $C = -T(d^2\mu/dT^2)_p$ and from the fluctuation-dissipation formula $k_B T^2 C = \langle \delta H^2 \rangle_{pT}$, giving consistent results within the statistical errors of our simulation.

The next quantities in Table I are the specific volumes and the thermal expansion coefficients. It is well known that DFT-LDA gives lattice constants of most materials within a few percent error. This error is less than 1% for crystalline Si. Here we find that also the volume variation with temperature is given very accurately. In particular, the theoretical volume discontinuity at melting $\Delta V/V_s$ agrees with experiment within the error bar of the calculation and the experimental uncertainties. Notice that, as a result of the breaking of the tetrahedral bonding network, the thermal expansion coefficient of the liquid is about an order of magnitude larger than that of the solid both theoretically and experimentally.

Finally, we consider dT_m/dp, i.e., the derivative of the melting temperature with pressure, which can be ob-

TABLE I. Thermodynamic properties at the theoretical and at the experimental melting point.

	This work (LDA)	Experiment
T_m (K)	$1.35(10) \times 10^3$	$1.685(2) \times 10^3$[a]
S_s	$6.9(1)k_B$	$7.4k_B$[b]
S_l	$9.9(2)k_B$	$11.0k_B$[b], $10.7k_B$[c]
H_s (eV/atom)	$H_s(0\text{ K}) + 0.33(2)$	$H_s(0\text{ K}) + 0.41$[b]
ΔH_{sl} (eV/atom)	0.35(2)	0.52[b], 0.47[c]
C_s (eV/K atom)	$3.0(4) \times 10^{-4}$	3.03×10^{-4}[d]
C_l (eV/K atom)	$2.7(4) \times 10^{-4}$	3.03×10^{-4}[d]
V_s [(a.u.)^3/atom]	$1.350(5) \times 10^2$	1.380×10^2[a]
$\Delta V/V_s$	10(1)%	11.9%[e], 9.5%[c]
α_s (K^{-1})	$0.3(1) \times 10^{-5}$	0.44×10^{-5}[a]
α_l (K^{-1})	$4.8(5) \times 10^{-5}$	5.2×10^{-5}[d]
dT_m/dp (K/GPa)	$-50(5)$	-38[a]

[a] Ref. [23].
[b] Ref. [24].
[c] Ref. [25].
[d] From Ref. [4].
[e] Ref. [26].

tained from the Clausius-Clapeyron equation $dT_m/dp = T_m \Delta V/\Delta H_{sl}$. The negative sign of dT_m/dp indicates that the liquid is denser than the solid.

In the present calculation, as usual in implementations of *ab initio* MD, the ions were in thermal equilibrium at finite temperature while the electrons were close to their instantaneous ground state at $T = 0$ K. Finite temperature effects on the electrons should be small, since T_m is small on the scale of the occupied electronic bandwidth. We estimated the magnitude of these effects at melting, using the calculated electronic density of states for a few selected ionic configurations and by replacing the Kohn-Sham total energy functional with the Mermin free-energy functional at finite T. We found negligible (less than 0.01 eV/atom) effects for the semiconducting solid. The corrections are more important but still not larger than a few hundredths of an eV/atom for the metallic liquid. In this case they lead to an increase of the entropy and of the enthalpy by $0.2k_B$ and by 0.01 eV/atom, respectively. These effects are of the same order of the statistical errors of the calculation and were not included in Table I.

In conclusion, we have shown that finite temperature thermodynamic properties of real materials can be calculated from first principles. Our results indicate that DFT-LDA describes accurately highly anharmonic situations and that it is able to predict the relative stability of phases such as a liquid and a solid. We expect that calculations based on the general methods presented in this paper should be useful to elucidate aspects of the phase diagrams and to predict properties of materials, particularly under extreme pressure and/or temperature conditions, that are difficult to attain experimentally.

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