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First-principles calculation of the melting curve and Hugoniot of tin

S. Bernard* and J. B. Maillet
CEA-DIF, Département de Physique Théorique et Appliquée, BP12, 91680 Bruyères-le-Châtel, France

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By performing extensive first-principles and classical molecular-dynamics (MD) simulations, we have calculated the melting curve of tin, up to 50 GPa by direct phase coexistence, and its Hugoniot curve up to 200 GPa, using an equilibrium MD technique, the so-called Hugoniostat. In both cases, our results are in good agreement with recent shock-wave experiments, but indicate that the temperatures on the Hugoniot at very high pressures might be higher than previously thought. We also predict that the shoulder on the first peak of the liquid structure factor disappears under pressure, in connection with structural changes in the liquid.

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Dynamical simulation of complex processes such as melting or the propagation of shock waves at the atomic scale is a field of growing interest,[1] due to the increasing computer power and efficiency of the codes.

As for metals, effective potentials of more or less complex functional forms can be fitted (either on experimental data or on quantum calculations), that satisfactorily reproduce the physical properties of the material, on a given thermodynamic domain. Yet, there is no guarantee to the transferability of such potentials to very different thermodynamic conditions, and for example, to the high (P,T) states reached behind a shock front, or close to melting at high pressure. To overcome this, fully *ab initio* calculations would be the solution. However, they still suffer from severe size and time limitations, especially when it comes to dynamical phenomena involving large time and size scales, so a reliable alternative is still necessary.

We have recently proposed[2] such an alternative, the so-called optimal potentials (OP) technique, that couples quantum and classical molecular dynamics.

We start by generating, at a given (P,T) point of interest, the "largest" (i.e., in size and time) *ab initio* MD trajectory that we can afford. We then select a set of uncorrelated atomic configurations along the *ab initio* trajectory and fit empirical potentials of a given functional form by requiring that they accurately reproduce (within 1% in the case of tin) the first-principles atomic forces and stress tensor on these configurations.[3] These optimal potentials explicitly depend on the *ab initio* thermodynamic state, and mimick very precisely the *ab initio* dynamics. They can then be used for extensive classical MD simulations, and produce first-principles quality thermodynamic data (some of them possibly out of reach of *ab initio* calculations) *at* (or close to) that reference state. Such optimal potentials are hardly transferable to strongly different thermodynamic conditions.

One possible application of the OP method is the determination of melting at a given pressure by a solid-liquid coexistence method.[4]

As the melting temperature T_m at pressure P is not known *a priori*, it is determined by the following iterative procedure. Starting from a trial melting temperature T_m^0, an *ab initio* trajectory is generated at (P,T_m^0), from which we fit an OP. The melting temperature T_m^1 of this potential is computed. An *ab initio* trajectory is generated at (P,T_m^1), and a new OP is determined, whose melting temperature is T_m^2. The procedure is iterated until $|T_m^i - T_m^{i-1}| < 100$ K (at most three times in all our calculations). Of course, OP's can be generated either from liquid trajectories only, from solid trajectories, or from both. T_m is unaffected by the initial choice of T_m^0, provided that it is reasonable. At each *ab initio* step, it is possible to find a whole class of potentials that satisfy the required accuracy, and produce the same thermodynamic quantities (e.g., melting temperature, enthalpy or volume differences, elastic constants, etc.) within the error bars.[5]

If the system undergoes electronic structure changes upon melting, it is no more possible to represent both the solid and the liquid at melting by a single potential, which is implied in the solid-liquid coexistence technique. But our procedure can be adapted: the OP's fitted on the solid and those fitted on the liquid can be used to calculate free-energy differences by thermodynamic integration and thus deduce the melting temperature at P.

In a first paper,[2] we have calculated the melting line of iron, up to earth's core pressure conditions. We will here focus on the melting line of tin.

Tin has recently been the subject of shock-waves experiments[6] and an "experimental" melting line up to 25 GPa has been proposed. During plate impact experiments, in some shots, a singularity was observed upon release in the interface velocity recordings. It was interpreted as the sign of melting, and the authors have developed a simple three-phase mixture model,[7] so as to propose corresponding temperatures, which are extremely difficult to directly measure in such experiments.

All our *ab initio* calculations are based on a finite temperature extension of density-functional theory within local-density approximation, and on a pseudopotential description of the valence electrons ($5s$ and $5p$ states) with the ion core.[8] Our results for the solid phases are in good agreement with experimental data.[9]

In all the classical MD simulations, atoms interact through modified embedded atom model (MEAM) potentials.[10] Such potentials, which include many-body contributions through angular forces, have proven to be well suited for a variety of metals and for tin.[11]

At ambient pressure, we calculate a melting temperature for the β-tin phase of 450 K, which compares well with the true experimental one (510 K). The enthalpy change upon melting is $\Delta H_m = 0.05$ eV/atom (expt. 0.073) and the rela-

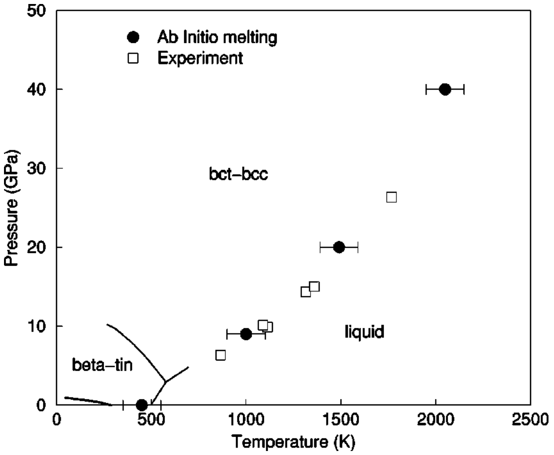

FIG. 1. Melting curve of tin.

tive volume change $\Delta V/V=2.58\%$ (expt. 2.3). We actually estimate the uncertainty on our calculations around 100 K at most. For the other pressures that we considered, the solid phase is tetragonal centered $(c/a=0.9)$, as predicted by the pseudopotential, the bct-to-bcc transition occurring beyond 50 GPa at $T=0$ K. The *ab initio* sample contains 144 atoms for the β-tin phase and 256 atoms for the bct one. We obtain the following set of points on the melting line: (10 GPa, 990 K), (20 GPa, 1490 K), (40 GPa, 2150 K), all of them with uncertainty ±100 K.

As can be seen on Fig. 1, our temperatures are consistent with the ones calculated with the simple mixture model.

We have also analyzed the structure of the liquid close to melting, at low and high pressure.

On Fig. 2, we have plotted the calculated structure factors of liquid tin at (0 GPa, 550 K), (20 GPa, 1550 K), and (40 GPa, 2150 K), i.e., above the melting line, but still close to it, so that our state-dependent potentials do not lose their accuracy. At ambient pressure, our structure factor is in striking agreement with the experimental one.[12] In particular, we reproduce the shoulder on the right of the first peak of the structure factor, which disappears for the two higher pressures. This shoulder can be correlated with the presence in the liquid of tetrahedral fragments, reminiscent of the β-tin structure.

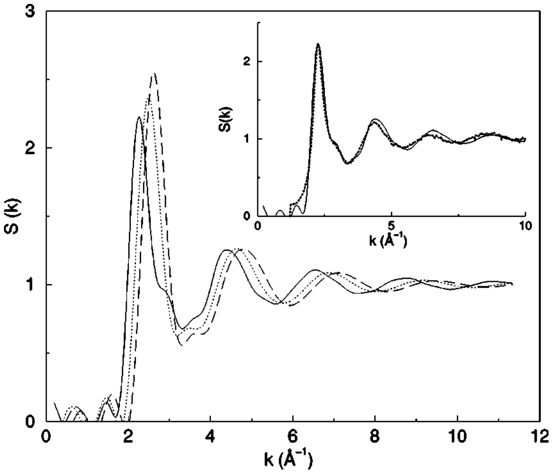

FIG. 2. The calculated structure factor of liquid tin; solid curve (0 GPa, 550 K), dotted line (20 GPa, 1550 K), and long dashed line (40 GPa, 2150 K). Inset: comparison with experiment at (0 GPa, 550 K).

At high pressure, these anisotropies are lost and liquid tin behaves like a regular liquid. They also disappear progressively at low pressure upon heating. Yet, it seems unlikely that there could exist a liquid-liquid phase transition in tin.

Another challenging problem is the *ab initio* calculation of Hugoniot curves, i.e., the (P,V,E) points in the thermodynamic diagram accessible to a material, after shock loading. They obey the Hugoniot equation of energy conservation before and after the shock:

$$E=E_0+\frac{1}{2}(P+P_0)(V_0-V), \tag{1}$$

where E is the internal energy per atom and subscript "0" refers to thermodynamic quantities in the initial unshocked state.

The recently proposed uniaxial Hugoniostat[13] is an equilibrium MD technique that simulates both thermodynamic and structural properties of shocked crystalline solids and fluids.

In this method, an initial uniaxial compression $\epsilon=V/V_0$ is applied to the system, and the dynamical evolution of the system is computed using modified equations of motion (EOM), which constrain the system to satisfy the Hugoniot relation at each time step.

The implementation of the uniaxial Hugoniostat method in *ab initio* calculations is straightforward: it follows the same formalism as for a Nosé thermostat[14] i.e., an additional term is included in the equation of motion for the ions and the EOM for the electrons is unchanged.[15]

In a first step, we have calculated the full Hugoniot curve of tin using a single classical potential (any of the MEAM potentials constructed for the melting study, plus a previously published MEAM potential fitted on thermodynamic macroscopic quantities[11]) for all compressions and for the unshocked state.

None of these potentials was able to describe the Hugoniot curve on the whole pressure range. Moreover, all the calculated curves strongly departed from the experimental data, confirming that the use of a single effective potential is not adequate for simulations of a real material on a wide pressure-temperature range.

In a second step, we have calculated the Hugoniot curve fully *ab initio*.

We performed first-principles simulations for different compression factors up to $V/V_0=0.55$, the starting solid phase being β tin. Our results are displayed in Figs. 3 and 4.

It is interesting to compare our predictions, not only with experiment, but also with effective equations of state (EOS) values, like the SESAME ones.[16] These comparisons are displayed on Figs. 3 and 4.

For the shock Hugoniot curve plotted in a $(P,V/V_0)$ diagram (Fig. 3), a good agreement is found between experimental data, *ab initio* results, and effective EOS.

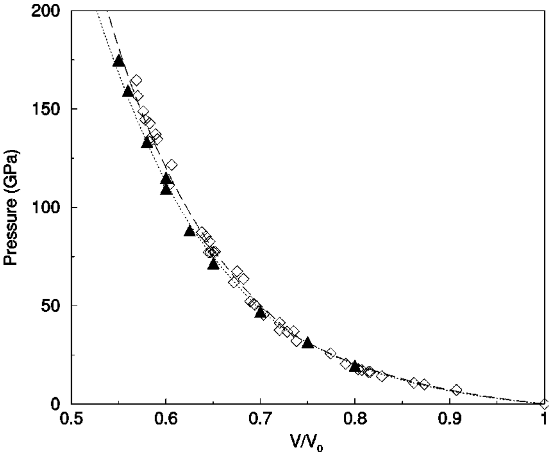

FIG. 3. Hugoniot curve plotted in a (P,V) diagram using the *ab initio* Hugoniostat technique. The dotted and dashed lines represent EOS (1) and (2), empty and filled triangles represent experimental data and *ab initio* results, respectively.

More interesting is the plot in the (P,T) diagram (Fig. 4).

Below 50 GPa, some discrepancies between *ab initio* and experimental results are observed. They come from the fact that the system is supposed to be solid and to exhibit a phase transition from the initial β-tin structure to a body-centered-tetragonal (bct) or body-centered-cubic (bcc) structure. Constant volume *ab initio* simulations do not reproduce this solid-solid phase transition, and instead our material melts at lower pressures than in experiments. This is due to the fact that our simulation cell is not allowed to change shape. In principle, the constant Hugoniot MD technique could be coupled with Parrinello-Rahman MD, but the resulting equations of motion are not straightforward to implement.

Up to 100 GPa, there is an overall reasonable agreement. However, above 100 GPa, *ab initio* temperatures on the Hugoniot start departing from the SESAME ones, and our calculations predict increasingly higher temperatures on the Hugoniot at very high pressures than assumed in the SESAME-like EOS.

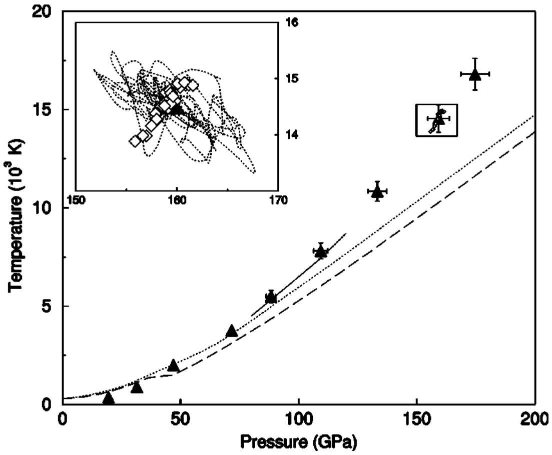

FIG. 4. Hugoniot curve of tin plotted in a (P,T) diagram. The dotted and dashed lines represent EOS (1) and (2), and filled triangles are our *ab initio* values. Solid line represents the EOS obtained with the three-phase mixture model. In inset, the *ab initio* trajectory for $V/V_0 = 0.56$; the solid triangle is the *ab initio* averaged value and diamonds represent the averaged Hugoniostat value with a large cell for several optimal potentials fitted on the *ab initio* trajectory (see text).

Till recently, it was very difficult to measure temperatures in shock experiments, and in order to build effective EOS, one had to make assumptions, usually on the variation of constant volume specific heat with pressure and temperature in the liquid. The calculated temperatures are very sensitive to this law. We have calculated C_v along the Hugoniot, and we find that it slightly decreases with pressure, whereas in the effective EOS models it turns out to be either constant or slightly increasing. This is consistent with our higher temperatures.

One could argue about the transferability of our pseudopotential to pressures of the order of 200 GPa and temperatures of 15 000 K. To shed light on this point, we have also tested a pseudopotential that includes the $4d$ electrons in the valence. The calculations are considerably heavier. Yet, the predicted temperatures on the Hugoniot are not changed.

Finally, we have also checked size effects in our classical simulations by fitting optimal potentials on Hugoniostat *ab initio* trajectories, and running Hugoniostat classical simulations with large cells.

The results are displayed in the inset in Fig. 4 for a compression of 0.56 (only the time averaged values of the pressure and the temperature are shown). The agreement between the *ab initio* and classical results is good, and no size effect is evidenced. Moreover, the dispersion of the classical MD results can give an estimate of the error bar on the *ab initio* Hugoniot point.

One should stress here that, if there is a size effect in the *ab initio* sample (which we have verified not to be the case here), this method is, by essence, unable to overcome it.[17] The same procedure has been used for other compression factors, and the same adequacy between classical MD and *ab initio* results has been found.

As a conclusion, by coupling first principles and classical molecular dynamics through the optimal potentials technique, we have calculated the melting line and the shock Hugoniot curve of tin. Close to melting, at low pressure, liquid tin is anisotropic, being reminiscent of β-tin structural features. On the contrary, we predict that above 10 GPa, and close to melting tin behaves like a regular liquid. Diffraction data in liquid tin at high pressure would be desizable. As for the Hugoniot equation of state, the agreement with experimental data is very good in (P,V) coordinates, but our *ab initio* simulations predict higher temperatures at very high pressures than calculated with effective EOS. This confirms the urgent need for reliable temperature measurements in shock-waves experiments. Meanwhile, extensive *ab initio* calculations could be helpful to revisit effective EOS tables. As for theory, work is in progress to apply our methodology to more complex systems, such as alloys and molecular systems.

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[*] Electronic address: stephane.bernard@cea.fr

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[7] This model is based upon a simple mixing law and minimization of Gibbs free energy; each phase is described by a Mie-Grüneisen equation of state, with constant specific heat C_v and constant Γ/V, where Γ is the Grüneisen coefficient. The individual EOS were fitted on an exhaustive set of experimental data (Ref. 6).

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$$\chi=-\frac{\dot{P}(V_0-V)}{4E_{kin}}. \tag{2}$$

The constraint is then satisfied at each time step. In the classical MD simulations, on the contrary, the Nose-Hoover approach was chosen, where the constraint is satisfied on average.

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