First principles simulations of direct coexistence of solid and liquid aluminium

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First principles calculations based on density functional theory, with generalised gradient corrections and ultrasoft pseudopotentials, have been used to simulate solid and liquid aluminium in direct coexistence at zero pressure. Simulations have been carried out on systems containing up to 1000 atoms for 15 ps. The points on the melting curve extracted from these simulations are in very good agreement with previous calculations, which employed the same electronic structure method but used an approach based on the explicit calculation of free energies [1].

The calculation of melting properties of materials using computer simulations has a long history. Two main approaches have traditionally been used. The first is based on the direct simulation of solid and liquid in coexistence [2–5,17]. The second on the calculation of the free energy of solid and liquid [7–10,18], with the melting point (p, T) determined by the condition of equality of the Gibbs free energies of liquid and solid, $G_{\text{liq}}(p, T) = G_{\text{sol}}(p, T)$. The two approaches must clearly give the same answer once all the sources of errors have been brought under control. These works were originally carried out using classical model potentials, with parameters usually adjusted to reproduce some known experimental properties of the material, or fitted to *ab-initio* calculations. The advantage of using these classical potentials is that they are relatively simple, so that computer simulations could easily be carried out on large systems and for long time. The main disadvantage, however, is that the transferability of these potentials is not always guaranteed, so that the accuracy of the predictions is sometimes questionable. In 1995 Sugino and Car [11] showed that it was actually possible to use density functional theory (DFT) [12] techniques to calculate the melting temperature of materials truly from first principles, i.e without relying on any adjustable parameters. They chose the melting of silicon as a test case, and using the local density approximation (LDA) they calculated the Gibbs free energy of solid and liquid using thermodynamic integration. This is a well known statistical mechanics technique to compute free energy differences between two systems [13]. The idea is to use a simple system for which the free energy is known as a reference system, and then compute the free energy difference between the *ab-initio* and the reference system, which is equal to the reversible work done in adiabatically switching the potential energy from one system to the other. An attractive feature of this method is that the final result is totally independent on the choice of the reference system. In practice, however, this method can only work if one is able to find a reference system which is as close as possible to the *ab initio* system, so that the computational effort needed to calculate the free energy difference between the two

systems is reduced to the minimum. Using this method, Sugino and Car found a zero pressure melting temperature about 20% lower than the experimental datum. This may seem not particularly good, but it has to be remembered that no adjustable parameters were inputed in the calculations, nor any experimental data other than the Plank's constant and the mass and charge of the electron. Recently, we have argued [14] that this non-perfect agreement between LDA results and experiments is probably due to non-cancelling LDA errors between the solid and liquid. The reason is that the two phases have very different properties: the liquid is six-fold coordinated and the solid four-fold coordinated, the liquid is a metal and the solid an insulator, so it is not surprising that the LDA errors in the two phases may be different. We have repeated the LDA calculations of Sugino and Car using similar techniques and found the same melting temperature. However, we have also shown that if the generalised gradient corrections (GGA) are used, then the melting temperature of silicon comes out in much closer agreement with the experiments [14].

Since the work of Sugino and Car [11] a number of first principles based calculations of melting points and melting curves have followed. In some cases the free energy approach has been used [15,16,19,20,1], while other methods relied on fitting a model potential to first principles simulations and calculating melting properties with the model potential [3–5]. The advantage of the free energy approach is that it is unbiased, provided all sources of technical errors are brought under control. A disadvantage of the method is that it is intrinsically complex. On the other hand, the coexistence approach is relatively simple to apply, but has the main disadvantage of relying on good quality fitting and, more importantly, transferability of the model for at least a simultaneous good description of solid and liquid. Recently, we have shown that provided that the model potential is reasonably close to the *ab-initio* system [21], it is possible to correct for the (small) differences between the model and the full *ab-initio* system using a perturbational approach to thermodynamic integration, and that once the corrections are applied the results coincide with those obtained using the

free energy approach [22].

The coexistence approach has been used extensively in the past to calculate the melting properties of various materials. In the constant volume constant internal energy (NVE ensemble) approach to the method it has been shown that liquid and solid can coexist for long time, provided V and E are appropriately chosen [2,22]. The average value of the pressure p and temperature T over the coexisting period then give a point on the melting curve. Size effects have also been studied quite extensively, and it was shown that correct results can be obtained in systems containing more than 500 atoms [5,6].

Here I have exploited recent advances in computer power and algorithms developments to use direct DFT calculations for simulating solid and liquid aluminium in coexistence near zero pressure. This work combines the simplicity of the coexistence approach with the accuracy provided by DFT, and in some respect represents a shift of paradigm, whereby the main effort is transferred from the human to the computer. The temperature at which solid and liquid coexist are found to be in good agreement with our previous results obtained with the free energy approach [1], so that these results also provide additional evidence that our techniques to calculate free energies are sound.

The calculations have been performed with the VASP code [23], with the implementation of an efficient extrapolation of the charge density [24], ultrasoft pseudopotentials [25] with a plane wave cutoff of 130 eV, and generalised gradient corrections. The simulations have been performed in the NVE ensemble on systems containing 1000 atoms ($5 \times 5 \times 10$ cubic supercell), with a time step of 3 fs and a convergency threshold on the total energy of 2×10^{-7} eV/atom. With these prescriptions the drift in the microcanonical total energy was less than 0.3 K/ps. The total length of the simulations were typically 15 ps. The volume per atom was chosen to be $V = 18.5$ Å^3, which is close to the average of the volumes of solid and liquid at the zero pressure melting point calculated in our previous work [1]. Electronic excitations have been included within the framework of finite temperature DFT. The simulations have been performed using the Γ point only, and spot checked with Monkhorst-Pack [26] ($2 \times 2 \times 1$) and ($4 \times 4 \times 2$) **k**-point grids. Calculations with the Γ point predict a small non-hydrostatic stress tensor with a difference of about $p_z - (p_x + p_y)/2 = -2$ kB between the components of the stress parallel to the solid-liquid interface, p_x and p_y, and that perpendicular to the interface, p_z. The pressure $p = (p_x + p_y + p_z)/3$ is essentially exact and the three off-diagonal components of the stress tensor fluctuate around zero average, so that there is no shear stress on the cell. With Γ the total energy is wrong by ≈ 5 meV/atom, and it is likely that the error is almost equally shared by the liquid and the solid parts, so that the resulting error on the melting temperature is most probably negligible [27]. A correction term of 2.7 kB due to the lack of convergency with respect to the plane wave cutoff has been added to the calculated pressures. The systems have been monitored by inspecting the average number density in slices of the cell taken parallel to the boundary between solid and liquid. In the solid region this number is a periodic function of the slice number, and in the liquid part it fluctuates randomly around its average value.

The zero pressure crystal structure of aluminium is face-centred-cube (fcc), so I have assumed that melting occurs from this structure. To prepare the system I have used the inverse power classical potential employed in Ref. [1]. This model has been tuned to the same *ab-initio* system used here, so it is a good starting point for the present calculations. The preparation procedure follows Ref. [22]. A perfect crystal is initially thermalized at 800 K, then the simulation is stopped, half of the atoms are clamped and the other half are freely evolved at very high temperature until melting occurs, then the liquid is thermalized back at 800 K [28]. At this point the system is being freely evolved in the NVE ensemble using DFT.

As explained in Ref. [22], for each chosen volume there is a whole range of internal energies for which different amount of solid and liquid are in coexistence. Provided that the energy is not too low (high) so that that the whole system freezes (melts), a whole piece of melting curve can be obtained for any fixed volume. In this work I have performed 3 simulations with 1000 atoms, all at the same volume but with different amounts of total energy, which therefore provide three distinct points on the melting curve. In all simulations coexistence was obtained for the whole length of the runs. In Fig. 1 I display the density profile, calculated by dividing the simulations cell into 100 slices parallel to the solid-liquid interface, corresponding to the last configuration of one of these simulations. Fig. 2 contains the calculated temperature (upper panel) and pressure (lower panel) for this particular simulation, and shows that they oscillate stably around their average values $T \approx 820$ K and $p \approx 5.5$ kB [29]. In order to test the reliability of the lengths of these simulations I have performed additional runs on system containing 512 atoms ($4 \times 4 \times 10$ cubic supercell), which could be simulated for up to 40 ps. Temperature and pressure from one of these runs are displayed in Fig. 3. It is clear that all the information needed to extract useful values for p and T is contained in any time window of $\approx 5 - 10$ ps, which provides confidence that the simulations for the large systems are long enough. A more detailed inspection of the figures reveals the presence of anti-correlated oscillations in pressure and temperature, which correspond to fluctuations in the total amount of solid and liquid in the system. These fluctuations seem absent in the simulations with 1000 atoms, but they would probably develop if the runs could be extended. In any case, they do not affect the average value of p and T.

It has been pointed out that non-hydrostaic conditions artificially raise the free energy of the solid, and therefore lower the melting temperature [6]. To investigate the effect on the melting temperature due to the present non-hydrostatic conditions I have used the model potential used in Ref. [1]. The model showed a difference $p_z - (p_x + p_y)/2 = 0.5$ kB when simulated with the same cell as the *ab-initio* system with 1000 atoms. To estimate the systematic error on the melting temperature I have performed an additional simulation using a slightly elongated cell at the same volume, so that non-hydrostaticity was reduced to less than 0.1 kB. The decrease of melting temperature in this second simulation was less than 10 K. A similar effect is expected for the *ab-initio* system, so that I estimate a systematic error due to non-hydrostatic conditions to be at worse of the order of 20 K.

In Fig. 4 I report the values of p and T calculated here in comparison with the low end of the melting curve calculated in Ref. [1] The agreement between the present finding with 1000 atoms and the free energy approach results is extremely good. The results obtained from the simulations with 512 atoms display melting temperatures higher by about 50 K, although they are still compatible with the results obtained with the free energy approach within the combined error bars. In order to test if the cause of this size effect was due to inadequate **k**-point sampling, I have performed a simulation using a $(2\times2\times1)$ **k**-point grid on a system with 512 atoms for ≈ 6 ps. The length of this simulation is too short to draw definite conclusions, but it indicates that the pressure may be underestimated by $\approx 1-2$ kB and the temperature over-predicted by ≈ 20 K. This would bring the results in somewhat better agreement with those obtained with the larger system, and also with the calculations based on the free energy approach (which were fully converged with respect to size and **k**-point sampling) [1]. Notice that these results do not agree perfectly with the experimental zero pressure melting temperature of aluminium (933 K) [30]. We have argued in our previous work [1] that this disagreement is due to inadequacy of the GGA to predict the vibrational properties of the solid. We have also suggested that this inaccuracy can be rationalised in terms of the errors in the equation of state, and devised a simple way to correct for it. In Table 1 I report the calculated GGA lattice constant, the bulk modulus and the cohesive energy compared with the experimental data. Following Gaudoin et al. [32], I also report the experimental values adjusted for the absence of zero point motion effects, which is missing in the present calculated values. It is evident that the GGA predicts a zero pressure lattice constant for Al which is too large, or, which means that at the correct lattice constant GGA predicts a positive pressure of about 16 kB. It follows that the GGA zero pressure melting point is actually the melting point at a negative pressure of about -16 kB, which is about 120-130 K lower.

In summary, I have shown here that it has become possible to directly simulate solid and liquid in coexistence using density functional theory techniques. This method combines the advantages of being relative easy to use and provide DFT accuracy. It is inevitably computationally very intensive, and these calculations have only been possible thanks to an access onto the 3.5 Teraflop/s machine (IBM p690 Regatta with 1280 processors). The cost of each molecular dynamics step for the 1000 atoms system was between 3 and 4 minutes on 128 processors of the machine. However, as large computer resources become routinely available this method should find widespread applicability in the future. The present results are in very good agreement with our previous findings based on the direct calculations of free energies, and therefore also support the reliability of those techniques.

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[27] Even in the unlikely worse case scenario in which this error was borne entirely by the solid (or entirely by the liquid), this would result in a wrong prediction of the melting temperature by only about 30 K.

[28] The temperature of 800 K has been chosen because it is close to the DFT-GGA melting temperature previously calculated [1].

[29] In fact, the simulation reported in Fig. 2 has been spawn from a previously well equilibrated simulation with a different value of total energy. The time needed to equilibrate the system the first time *ab-initio* was switched on from the classical regime was about 1 ps.

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	Experiment	GGA
E	3.39 (3.43)	3.43
B	76 (81)	73
a_0	4.049 (4.022)	4.05

TABLE I. Experimental values for the cohesive energy E^c (eV/atom) [31], the bulk modulus B (GPa) [30] and the lattice constant a_0 (Å) [30]. In parenthesis are the adjusted values for the effect of zero point motion [32]. The calculated GGA values have been obtained from a fit to a Birch-Murnaghan equation of state [33], and they do not include zero point motion effects.
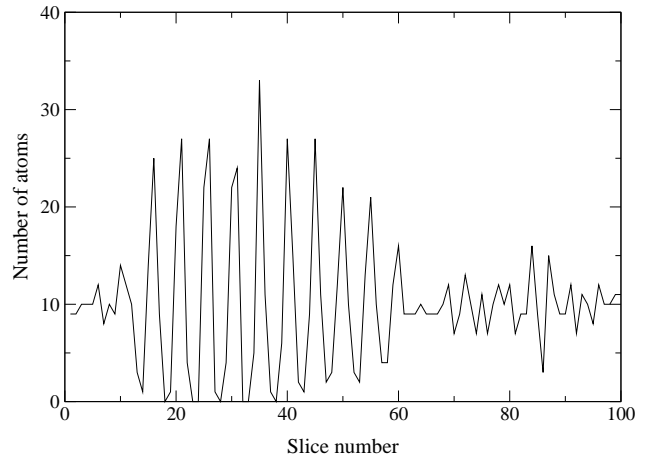

FIG. 1. Density profile in a simulation of solid and liquid Al coexisting at zero pressure. The system is divided in slices of equal thickness (0.42 Å) parallel to the solid-liquid interface, and the graph shows number of atoms in each slice. Simulations were performed on a system of 1000 atoms using density functional theory.
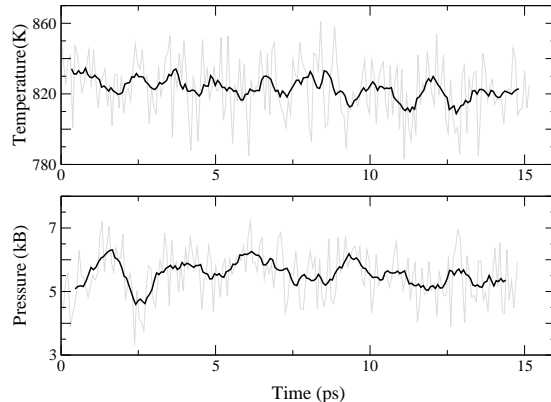

FIG. 2. Time variation of temperature (upper panel) and pressure (lower panel) during a simulation of solid and liquid Al in coexistence. Simulations were performed on a system of 1000 atoms with density functional theory. Gray lines: actual data; black lines: running averages over a 0.75 ps period.
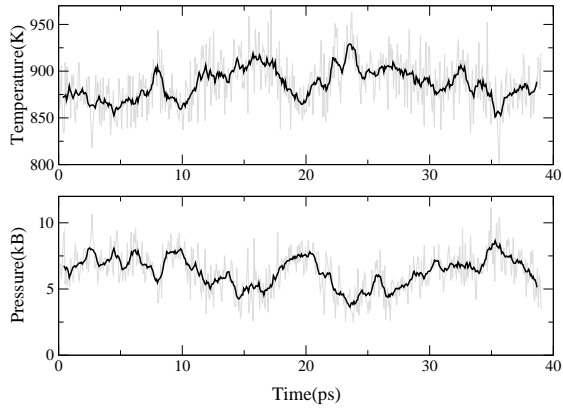
FIG. 3. Time variation of temperature (upper panel) and pressure (lower panel) during a simulation of solid and liquid Al in coexistence for a system containing 512 atoms. Gray lines: actual data; black lines: running averages over a 0.75 ps period.
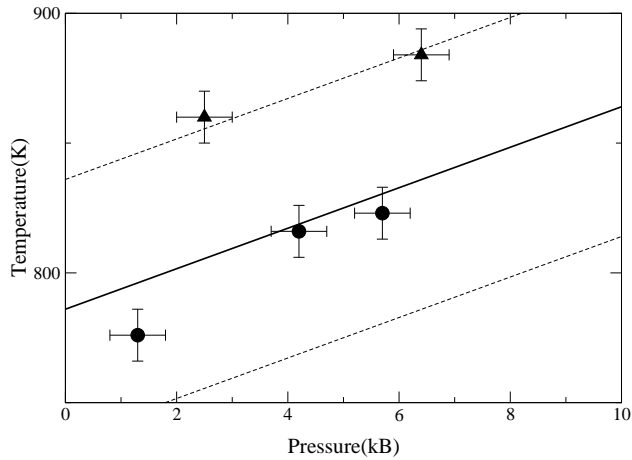

FIG. 4. Temperatures and pressures at which liquid and solid coexist in simulations containing 1000 atoms (circles) and 512 atoms (triangles). The solid line is the lower end of the melting curve calculated using the free energy approach in Ref. [1] (see text), light dashed lines represent error bars.