The influence of boundaries on high pressure melting experiments

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At low pressure, free surfaces play a crucial role in the melting transition. Under pressure, the surface of the sample is acted upon by some pressure transmitting medium. To examine the effect of this medium on melting, we performed Monte Carlo simulations of a system of argon atoms in the form of a slab with two boundaries. We examined two cases, one with a soft and the other with a rigid medium at the boundaries. We found that in the presence of a rigid medium, melting resembles the mechanical lattice instability found in a surface-free solid. With a soft medium at the boundary, melting begins at the surface and at a lower temperature. The relevance of these results to experiment is discussed.

Phase diagrams of materials at high pressures and temperatures are of great interest due to their importance for geology and astrophysics, in particular understanding the Earth’s core [1]. For example, the melting line of iron under high pressure and temperature determines the locus of the solid-liquid interface inside the Earth’s core. The melting line of rare-gas solids is important for understanding the abundance of these gases in the Earth’s atmosphere [2].

Experimental studies of melting at high pressures are performed using the diamond anvil cell (DAC) [3] or the shock wave [4] technique. An ongoing controversy exists regarding the melting line of iron [5, 6] obtained by these two methods. It seems that the melting temperature, \( T_m \), determined using shock waves is systematically higher than that measured in the DAC experiments. This difference introduces a considerable uncertainty into the models of the Earth’s core [5]. In addition, Errandoiu [6] pointed out a systematic disagreement between melting temperatures of bcc transition metals measured in shock-waves and DAC experiments. Also in this case, \( T_m \) measured using shock-waves is noticeably higher than that obtained by extrapolation of DAC measurements. Several possible explanations were proposed to resolve this discrepancy, including the existence of an extra high P-T phase and an overshoot of the melting temperature due to the small time scale in shock-wave experiments [6].

We would like to suggest that the discrepancy between the melting temperatures determined by these methods results from different conditions present at the boundary of the sample. Inside a DAC, the sample is surrounded by a pressure transmitting medium. In shock-wave experiments the molten region inside the sample is bordered by relatively unstressed cold regions. In both cases, the sample has no free surface. It is well known that at zero pressure, the mechanism of melting differs depending on whether the sample does or does not have a free surface. The purpose of this study is to examine how the different types of boundary conditions systematically affect the melting transition at high pressures.

At zero pressure, theories describing the mechanism of melting [7] can be separated into two classes. The first one describes the mechanical melting of a homogeneous solid resulting from lattice instability [8–11] and/or the spontaneous generation of thermal defects (vacancies, interstitials, and dislocations) [12–17]. The second class treats the thermodynamic melting of solids, which begins at extrinsic defects such as a free surface or an internal interface (grain boundaries, voids, etc) [18–24]. From these studies it is clear that the value of the melting temperature is sensitive to whether or not the solid has a free surface. The thermodynamic melting temperature is systematically lower than the melting temperature of surface-free solids, and the liquid phase always nucleates on the least closely packed surface.

We now examine the question of whether this distinction affects the interpretation of high pressure experiments. Here, in order to maintain a high pressure, there can be no free surface. To shed light on this problem, we decided to simulate melting of samples with either “soft” or “rigid” boundaries. Specifically, we simulated a system of argon particles interacting via a pairwise Lennard-Jones (LJ) potential. In one case the argon was in contact with a rigid wall, represented by an infinite step function in the potential. In the second case we simulated solid argon in contact with a fluid neon layer. Our model crystal is a slab made of 44 atomic layers, and with two surfaces. (See Fig. 1). The argon atoms were subjected to periodic boundary conditions only along the x and y directions (parallel to the free surface). We studied two different low-index surfaces: Ar(011) with 25 atoms per layer, and Ar(001) with 32 atoms per layer. As a reference, we also simulated a surface-free solid sample with 864 atoms, by applying periodic boundary conditions in all directions.

In the laboratory, experimental conditions include a fixed pressure P, temperature T, and number of atoms N (NPT ensemble). We performed Monte Carlo (MC) simulations using this ensemble [25]. The LJ potential was truncated and shifted, with the cutoff distance, \( r_c \), chosen to be \( r_c = 2.1 \sigma \). The values of the parameters of the LJ potential are given in the Table.

The initial conditions in our simulations differed according to the type of boundary. For the case of hard
walls, the distance between the top surface layer of argon and the hard wall was set equal to the bulk interlayer distance. In the second case, the atoms of neon were initially arranged in a simple cubic lattice. Since the melting temperature, $T_m$, of neon is lower than that of argon at all pressures, this boundary layer melted immediately and remained fluid at all temperatures at which simulations were made. The interaction between the Ne-Ne and Ar-Ne atoms was modeled using the LJ potential with parameters (see the Table) taken from [26]. Each simulation was started at a low-temperature with a perfect fcc solid sample at a fixed pressure ($P > 1\text{GPa}$). The temperature of the sample was then gradually raised by 20K - 100K steps, (at low and high pressures respectively) and the sample was equilibrated. An equilibrium state was considered to be achieved when there was no significant variation (beyond the statistical fluctuations) of the total energy, pressure, volume and structure order parameter (the spatial Fourier transform along the [001] direction). The melting transition was indicated by a jump in the total energy and volume, simultaneous with the vanishing of the structure order parameter. To improve the accuracy in the vicinity of $T_m$, we used smaller temperature steps of 10 K, and increased the number of MC steps by a factor of six. Throughout this study, interactive visualization (the AViz program [27]) was implemented to observe sample disorder and melting.

The melting curves calculated for the case of the hard wall are shown in Fig. 2 for both the Ar(001) and Ar(011) samples. For comparison, the points showing $T_m$ of the surface-free solid are also shown. These points are in very good agreement with a simulation (solid curve in Fig. 2) of a surface-free solid made by Gomez et. al. [15]. It is seen that the argon sample bordered by hard walls melted at a temperature very close to that of a surface-free solid. The sample with the (011) surface melted at a slightly lower temperature than the sample with the (001) surface.

The melting curves calculated for the Ar bordered by fluid neon are shown in Fig 3 for the Ar(001) and Ar(011) samples. The curves are compared with that calculated for the surface-free solid. Within our resolution we did not observe a difference in $T_m$ between samples with the (001) and the (011) surface.

A comparison of the melting curves for the samples with soft and rigid boundaries shows that the sample bordered by the neon layer melted at a systematically lower temperature than the sample with the hard walls. Another important difference, shown in Fig. 4, is that premelting effects were absent in the sample with the hard walls, whereas in the case of the neon covered surface a gradual premelting was observed.

We interpret the above results as follows: the interactions with the hard wall seem to effectively inhibit the
FIG. 3: (Color online) Melting temperature as a function of pressure for the samples with a neon layer at each surface: the Ar(001) sample (triangles, blue online) and the Ar(011) sample (circles, red online). The black squares correspond to the (infinite) surface-free sample. The dotted line is drawn to guide the eye, and the solid line is taken from [15]. Error bars are smaller than the size of the symbols.

FIG. 4: (Color online) Snapshot of the Ar(001) slabs at pressure $P = 4.17$ GPa: (a) a sample with hard walls at $T = 740$ K ($T_m = 780$ K). (b) a sample with neon layers at $T = 625$ K ($T_m = 665$ K). Note the presence of premelting near the surface of the Ar-Ne sample.

FIG. 5: (Color online) The depression of the out-of-plane atomic vibration amplitude (circles, red online) relative to the in-plane vibration amplitude (squares), shown for the (001) sample with surface atoms bordered by a hard wall. The pressure is 20 GPa. The dotted lines guide the eye. Error bars are smaller than the size of the symbols.

out-of-plane motion of the surface atoms. This result is shown in Fig. 5. In contrast, the in-plane and out-of-plane RMS vibration amplitude in the sample bordered by fluid neon is approximately the same. Restriction of the out-of-plane motion suppresses thermal disordering of the surface. Absence of thermal disordering inhibits surface premelting and allows superheating up to the temperature at which crystal lattice becomes unstable. Consequently, superheating of argon bordered by hard walls is possible. The situation is analogous to the well-known experiment by Daeges et. al. [28] in which superheating of silver coated with gold was demonstrated (gold has a higher $T_m$ than silver).

In our opinion, the conditions in the simulations with the hard walls are similar to those found in the shock wave experiments. The simulations can be related to the experiments in the following way: Typically, the part of the solid which is compressed during the propagation of the shock wave is much smaller than the size of the sample. Therefore, the instability occurs inside a region surrounded by a relatively cold material, which can act as a hard wall. Further support for this conjecture comes from the work of Kanel et. al. [29] who clearly observed superheating of aluminum single crystals with the shock wave technique. Another example where superheating is distinctly observed is in the case of compressed argon bubbles inside an aluminum matrix [30]. In this experiment the free surface of the solid was eliminated and as a result the solid was superheated. Therefore, the melt-
ing transition is closer to mechanical melting triggered by lattice instability.

On the other hand, in DAC experiments the material under study is usually surrounded by a hydraulic medium [6] so that it surface is in contact with a rare-gas or some other inert material. In addition the heating is usually done by a laser which heats mainly the surface. This situation is close to our simulations with the fluid neon layer. According to the results of the simulations, melting in this case is more like thermodynamic melting.

Before concluding we remark that the LJ (6,12) potential is not accurate enough at high pressures to allow quantitative comparison with experiment [31–33]. However, we believe that the generic nature of our results is valid.

In conclusion, we simulated the melting of a solid in the presence of two types of pressure transmitting medium at the sample boundaries. We found that with the soft medium (liquid neon layers) melting is closer to thermodynamic, nucleating at the surface, while with the rigid medium (hard walls) the solid exhibits superheating and melts via a lattice instability. These results are related to high pressure melting experiments and appear to be consistent with systematic differences that exist between shock wave and DAC measurements. We believe that the disparities between the results of measurements obtained with these two techniques at least to some degree originate in the different conditions at the solid-liquid interface. We suggest that results obtained with a DAC technique should be compared with thermodynamic theories, while shock wave results should be compared with theories based on a mechanical instability.

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