Determining Melt Curves from Liquid X-ray Diffraction

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Abstract

From an XRD pattern, the density of a substance can be obtained. On the melt curve, which can be reached from release of a shock, the solid and liquid coexist. At this point they will have equal pressures and temperatures. This extra condition should allow the pressure and temperature to be determined from the densities extracted from XRD pattern of the solid and liquid.

Modern experimental developments such as the X-ray Free Electron Laser and Single Photon Energy Dispersive X-ray diffraction, combined with improved computational power, have allowed the field of liquid XRD to develop further.

This project has relevance to geophysics as the Earth's central pressure is 0.37 TPa and supergiant planets have central pressures in the range 1 to 10 TPa. The solid to liquid transitions in planetary cores determine the outer and inner core boundaries, and therefore affect any magnetic fields.

Liquid x-ray diffraction

XRD is primarily used as a method to determine crystal spacing. However, from the average distance between atoms in a liquid, a series of rings can be seen in the diffraction pattern, as illustrated by Figure 1.

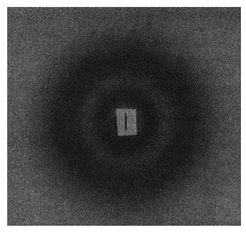


Figure 1. An example of an experimental x-ray diffraction pattern obtained from an amorphous substance. Figure from [1] for cellulose acetate with CuKα radiation.

The first peak occurs at 0.95 multiplied by the atomic diameter [1]. In addition to the average density, structural patterns can be seen, which roughly correspond to the coordination numbers from the solid state [1, 2], shown in Figure 2.

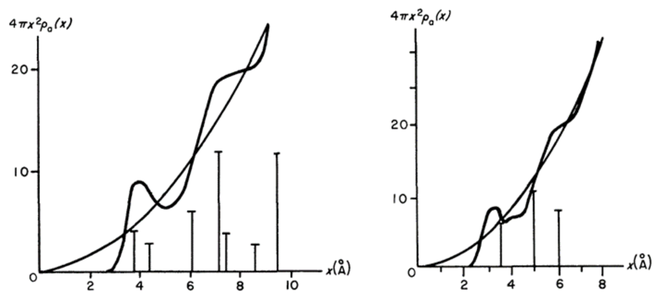


Figure 2. Density functions for two liquid metals: Na at 400^oC (left) and Li at 200^oC (right). Figures from [1].

This structure is due to the approximately spherical shells within the liquid. The positions of neighbours when in the crystal structure are also shown in Figure 2, and these roughly correspond to the positions of the shells [2].

As for a solid, the density alone is insufficient to calculate pressure and temperature. There may be other factors influenced by temperature, such as intensity and breadth of the peaks, which could be investigated further.

Previous work

This method is based on observations made during a laser shock compression experiment of Bi to 10 GPa at LCLS [3].

The experiment was carried out at a much lower pressure, and although the effect was observed, it was assumed to occur at the known phase boundary rather than being used to determine the boundary.

The path of decompression after the shock wave can be seen in Figure 3. The latent heat of melting acts as a sink of energy, causing the path to travel along the melt curve instead of the isentrope.

This process could be repeated, with different shock forces used, in order to reach different points on the Hugoniot, in order to trace out the melt curve.

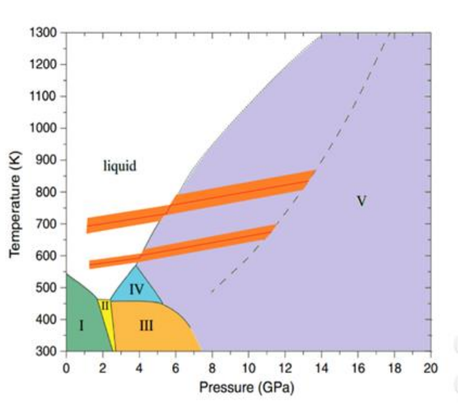


Figure 3. Schematic diagram showing the path of a release of a shock in Bi along isentropes and the melt curve. Figure adapted from [3]. The dashed line shows the Principle Hugoniot, and the dotted line shows the melt curve

Method

Simulations are being carried out using LAMMPS [4, 5]. LAMMPS (Large scale Atomic/Molecular Massively Parallel Simulator) is a classical MD simulator distributed by Sandia National Laboratories.

A shock can be modelled using a Hugoniotstat fix (an NPT simulation with a pressure dependent target temperature).

From this, the position of the atoms at each timestep, as well as atomic and bulk properties, are calculated. The output was visualised using Ovito [6,7].

Initial results

The diffraction patterns can be generated by taking the Fourier transform of the atom positions outputted from LAMMPS. For Si, prominent solid peaks at Q = 2.9 $Å^{-1}$ and 5.4 $Å^{-1}$ can be seen, and liquid peaks at 4.8 $Å^{-1}$ and 6.6 $Å^{-1}$ in the example XRD pattern shown in Figure 4.

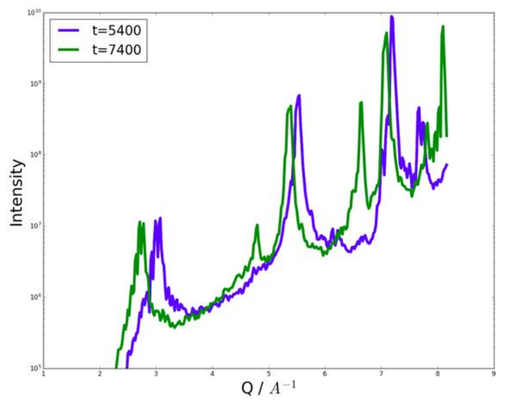


Figure 4. XRD pattern of the solid and liquid coexisting during decompression (green) and the solid it formed from (blue). Times after the shock in ps is in the legend.

The position of the liquid peak corresponds to the nearest neighbour distance, and so can be used to find density. In Figure 5 the link between the peak position and bulk density is given.

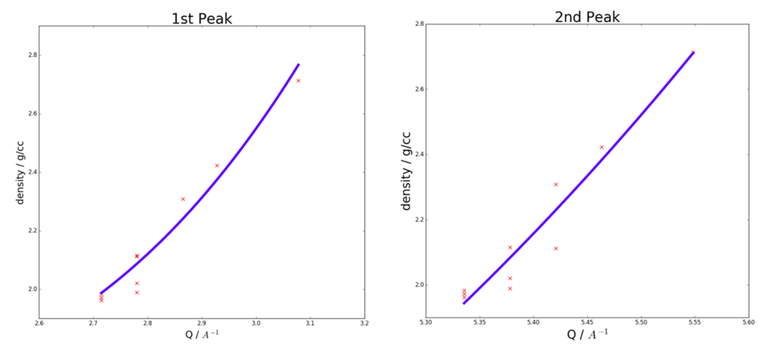


Figure 5. Graphs illustrating the relationship between Q and liquid density.

The csp (centro symmetry parameter) is used as a measure of lattice disorder. The distribution of csp values, in Figure 6, are distinct for solids and liquids. This has therefore been the primary method for determining whether atoms in the simulations are in a solid or liquid environment, for the purpose of calculating their temperature and pressure.

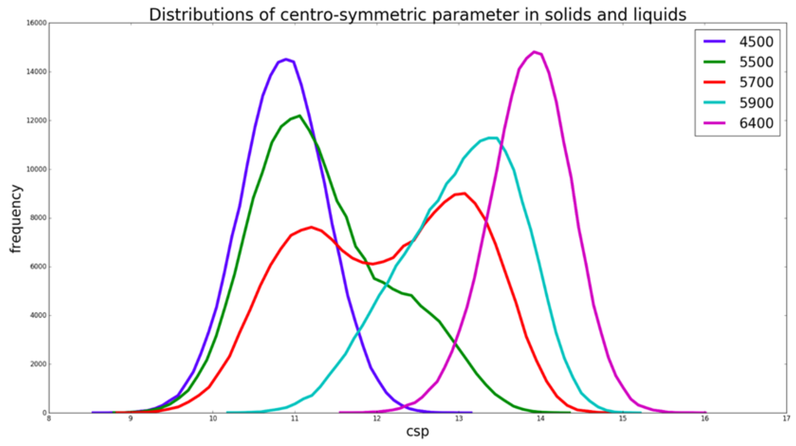
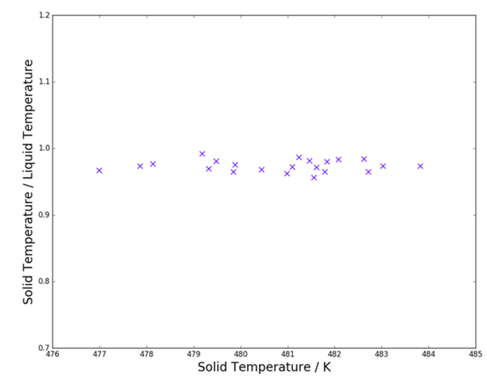


Figure 6. The distributions of csp, with times after the shock in ps given in the legend.

The temperatures and pressures of the solids and liquids were calculated and found to be equal, validating the reasoning for this method. The temperatures at coexistence are shown in Figure 7.

Figure 7. The temperature of solids and liquids were found to be equal at coexistence within 1% error.



Conclusion and further work

Using the method described in this poster, it should be possible to experimentally calculate melt curves at high pressures. This is expected to be carried out at an X-ray Free Electron Laser facility, once it has been fully tested by simulations.

Further work is needed in determining pressure and temperature, in order to get from MD results to determining the melt curve.

This would have applications to High Energy Density physics, particularly geophysics.

References

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