Figure S1: Computed structure factors, $S(q)$, of compressed liquid Na at the melting temperatures indicated in Figure 1 of the manuscript. The $S(q)$'s are computed by Fourier transforms of the g(r)'s averaged over a minimum of 5 ps after equilibration of the liquid has been achieved (that sometimes took more than 30 ps). g(r) are windowed by a fermi function at half the cell size, with a width of 0.5 angstroms. The $S(q)$'s are shifted on the y-axis by a value of 0.1 x P(GPa), where $P$ is the corresponding pressure.

Figure S2: Computed pair correlation functions, g(r), of compressed liquid Na (solid curves) at the melting temperatures indicated in Fig. 1 of the manuscript. The g(r)'s of the heated solids near melting are also drawn (dashed lines) for selected pressures. The g(r)'s are computed directly from the atomic coordinates and averaged over at least 5 ps simulations of the equilibrated systems. Pressure and temperature values are the same as on Figure 1. The g(r)'s are shifted along the y-axis by a value of 0.1 times the pressure value in GPa.

Figure S3: Distance distributions in molten Na under pressure. The distributions to the 1st, 2nd... up to the 24th nearest neighbour (n.n.) are drawn for 9 different pressures in the liquid state (upper 9 sets of curves). The area under each individual curve is normalized to unity. The distributions of the 6th, 8th, 12th, 14th, 16th, 18th and 24th n.n. are emphasized with bold curves and their evolution between 3 and 59 GPa is indicated with dotted arrows. It is evident that no major changes occur in the relative positions in the first 12 neighbours, but the others are shifting towards smaller distances. Here $r_6$ is taken as the distance unit in order to identify changes in the local ordering independent of the volume decrease under pressure (as an homothetic modification of the structure would show no variations in the curves). These curves are used to compute the data plotted in Figure 2A of the manuscript. The two bottom sets of curves are the distributions obtained from the disordered solid models (fcc, bcc) with a Gaussian disorder of 10% of $r_1$ which corresponds to the observed Debye-Waller factor in our simulations at 600K and 40 GPa. These two curves are also plotted in Figure 2B of the manuscript. The change in distance distributions seen in these curves is similar to the evolution observed in the liquid phases (though the 14th neighbour distribution shows little change).