SHORT COMMUNICATIONS

SHOCK COMPRESSION AND MELTING OF SOLID ARGON

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Some years ago, David and the author[1] calculated the conditions that exist behind strong shock fronts in materials obeying the theoretical Lennard-Jones and Devonshire (LJD) equation of state,[2] which was originally proposed as a description of the behaviour of simple monatomic liquids. We compared the calculated shock conditions with experimental data for the shock compression of liquid argon, and concluded that the theory consistently underestimates the volume by about 12%. However, we remarked in a footnote that, at that time, it had become apparent that the LJD theory is really more appropriate to the solid state than to the liquid. It is based on a model in which a particular molecule is contained in a cell bounded by its nearest neighbours; the molecule can move within its cell subject to the forces between it and its neighbours, whose positions are assumed to be fixed. Barker[3] has pointed out that this model is essentially that of an anharmonic Einstein crystal, and David and the author[4] have shown that it gives an excellent description of the volumetric behaviour of *solid* argon at hydrostatic pressures up to 20 kbar (1 kbar $\equiv 10^8$ N m^{-2} $\equiv$ 986·92 atm).

Recently, Skalyo, Dick, and Warnes[5] have measured the shock-wave compression of solid argon, starting at atmospheric pressure and 75°K, and reaching a maximum shock pressure of 640 kbar and a density 2·16 times the normal value. It is therefore now possible to compare the LJD shock-wave theory with more appropriate experimental data than have existed before. To that end, the earlier calculations have been extended to lower temperatures and smaller volumes. In the notation used previously,[1] the intial values of the reduced pressure and temperature in Skalyo's experiments are $P^* = 0{\cdot}0024$ and $T^* = 0{\cdot}626$, and the corresponding values of the reduced volume and internal energy have been calculated to be $V^* = 1{\cdot}019$ and $E^* = -6{\cdot}533$, based on an effective 6–12 intermolecular pair potential with parameters $\sigma = 3{\cdot}405$ Å, $\epsilon/k = 119{\cdot}8$°K.[6] From these starting conditions, the locus (Hugoniot) of points which can be reached in single shock-wave

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[4] David, H. G., and Hamann, S. D., *J. chem. Phys.*, 1963, **38**, 3037.

[5] Skalyo, J., Dick, R. D., and Warnes, R. H., *Bull. Am. phys. Soc.*, 1968, **13**, 578.

[6] Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids." p. 1110. (John Wiley: New York 1954.)

compression has been traced by simultaneously satisfying the Rankine–Hugoniot relations and the LJD equation.[1] The results are plotted in the P–V plane in Figure 1 and the P–T plane in Figure 2. The plots have been limited to a maximum pressure 200 kbar because the experiments showed an apparent transition at 220 kbar, which may be associated with partial ionization of the argon.

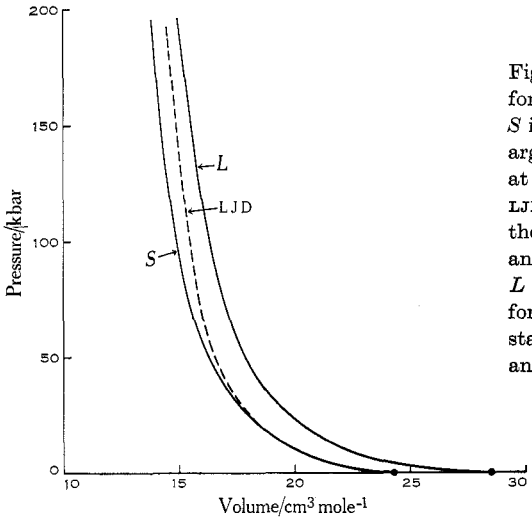

Fig. 1.—Pressure–volume relationships for the shock compression of argon. *S* is the experimental Hugoniot for argon initially in the *solid* state at 75°K and atmospheric pressure.[5] LJD is the corresponding theoretical Lennard-Jones and Devonshire curve. *L* is the experimental Hugoniot for argon initially in the *liquid* state at 86°K and atmospheric pressure.[8]

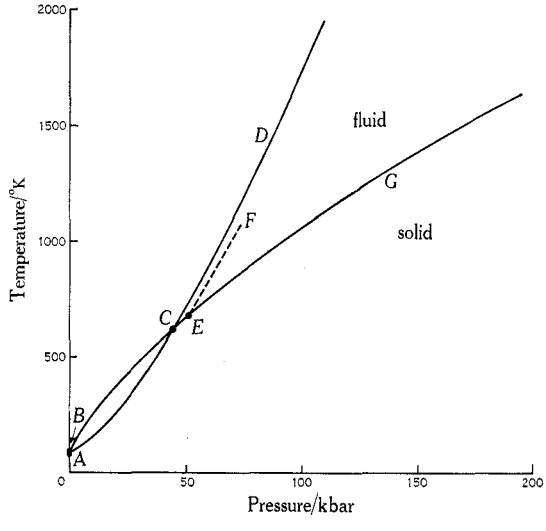

Fig. 2.—Pressure–temperature relationships for argon. *ACD* is the calculated Hugoniot for argon initially in the solid state at 75°K and atmospheric pressure. *BCG* is the melting curve of argon.

It will be seen in Figure 1 that the agreement between the calculated and experimental Hugoniot P–V curves is almost exact below 30 kbar and is still quite good at 150 kbar, where the theoretical and experimental volumes differ by only

5%. The deviation is in the direction to be expected from other evidence[7] that the repulsion between argon atoms in close contact is less than the 6–12 potential predicts. For comparison, Figure 1 also shows the experimental Hugoniot for liquid argon, compressed from an initial state at 86°K and atmospheric pressure.[8]

The good agreement between theory and experiment justifies use of the LJD theory to estimate the temperatures reached in shock compression, which are not directly measurable. Figure 2 shows the theoretical relationship between temperature and pressure along the Hugoniot *ACD*, and also the experimental melting curve for argon, *BCG*, extrapolated from 18 kbar by the Simon formula:[9]

$$P = 2{\cdot}263[(T/83{\cdot}2)^{1{\cdot}5}-1] \qquad (P \text{ in kbar, } T \text{ in } ^\circ\text{K})$$

It is apparent that the shock Hugoniot enters the fluid region at *C* and that at higher pressures partial or complete melting must occur. The region of partial melting can be determined from the criterion, derived by Kormer *et al.*,[10] that the temperature rise ΔT needed to produce complete melting is approximately equal to $\Delta H_m/C_V$, where ΔH_m denotes the molar enthalpy change for melting at the point *C*, and C_V denotes the molar heat capacity of solid argon at constant volume at the same point. Combining a calculated LJD value of $C_V(T,P) = 2{\cdot}62\boldsymbol{R}$ with the value $\Delta H_m \simeq 1470$ J mole^{-1}, obtained by extrapolating Lahr and Eversole's measurements,[9] gives $\Delta T = 67$°K. It follows that the course of the Hugoniot in the *P–T* plane must be *ACEF* rather than *ACD*, *CE* being the mixed-phase region. In the region *AC*, from 0 to 45 kbar, the shocked argon remains solid; between *C* and *E*, from 45 to 50 kbar, part of the thermal energy of compression is absorbed in melting and the temperature rise is not as great as it would have been along *CD*; when melting is complete at *E*, the Hugoniot resumes a path *EF* which is closely parallel to *CD* since ΔH_m is small compared with the total energy of compression.

Although the discontinuities associated with melting are quite apparent in the *P–T* plot of Figure 2, they are likely to be much less so in the *P–V* relationship, which is one that is determined experimentally. The only effect on the curves in Figure 1 would be the appearance of small and opposite changes of slope of a few per cent[11] at 45 and 50 kbar. These changes are too small to be detected and it can be assumed that the experimental Hugoniot passes smoothly from the solid to the fluid phase at about 50 kbar. The upper part of the curve *S* in Figure 1 therefore depicts the behaviour of the fluid phase, and the fact that it is well represented by the LJD theory indicates that the cell model is a good one for fluids as well as solids, provided the density is about twice the normal liquid density.

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