

determined by the Monte Carlo results, it appears that the lower portion of the Hugoniot curve may lie in the solid region. As pointed out in reference 3, the apparent coexistence point on the lowest-temperature Monte Carlo isotherm is at a lower pressure than that predicted by the extrapolation of the experimental results. Thus the coexistence curve predicted by the Monte Carlo results probably lies somewhat to the right of the dashed curve of Fig. 2(b) and intersects the lower portion of the Hugoniot curve.

TABLE II. Shock Hugoniot calculated with the LJD equation of state.

$P(kb)$	Lennard-Jones potential [Eq. (2.4)]		Exp-six potential [Eq. (3.1)]		Exp-six potential [Eq. (3.2)]	
	V/V_0	$T(^{\circ}K)$	V/V_0	$T(^{\circ}K)$	V/V_0	$T(^{\circ}K)$
600	0.5137	21 230	0.4698	20 900	0.4121	22 863
500	0.5205	17 210	0.4791	16 920	0.4228	18 420
400	0.5292	13 310	0.4907	13 053	0.4359	14 195
300	0.5409	9 555	0.5062	9 335	0.4528	10 177
250	0.5487	7 743	0.5164	7 547	0.4638	8 244
200	0.5587	5 988	0.5292	5 819	0.4775	6 370
150	0.5722	4 306	0.5464	4 167	0.4957	4 570
100	0.5927	2 720	0.5720	2 616	0.5228	2 872
75	0.6083	1 976	0.5912	1 893	0.5430	2 077
50	0.6322	1 280	0.6199	1 221	0.5732	1 334
25	0.6778	652.5	0.6730	620.2	0.6291	668.6
20	0.6938	538.7	0.6911	512.6	0.6482	548.9
15	0.7151	430.0	0.7150	410.3	0.6734	435.4
10	0.7462	327.0	0.7494	314.2	0.7096	328.8
5	0.8003	229.4	0.8082	223.8	0.7716	229.4

The same set of isotherms and the shock Hugoniot were also calculated from the LJD cell theory.⁶ These calculations were done on the IBM 704. The Hugoniot curve was obtained by the iterative solution of Eq. (2.1), with the equation-of-state points calculated as needed. The results are given in Table II and are compared with the Monte Carlo results in Figs. 1 and 2.

Although the isotherms do not agree too well, particularly on the fluid side of the phase transition (which is of course not predicted by the cell theory), the two Hugoniot curves are quite close. Of course the isotherms shown give only the difference between the E or PV and the contributions of the regular lattice configuration, which is the same in both calculations. Examination of the results, shows, however, that the lattice values are less than half of the total above about 50 kb on the Hugoniot, so that the fact that the lattice contributions are the same cannot alone account for the agreement. It appears that the agreement is due mainly to the cancellation of the differences in PV and E when they are subtracted in the Hugoniot equation, plus

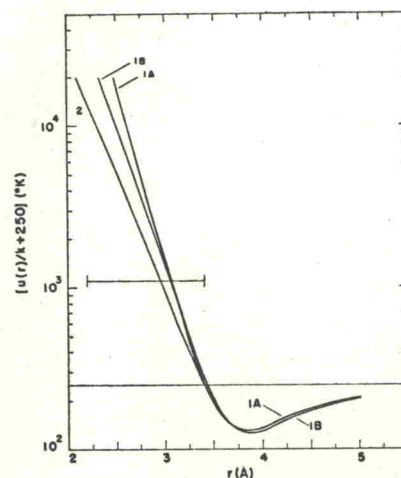


FIG. 3. Intermolecular potentials used in the calculations. (1A) Lennard-Jones 6-12, constants from second virial coefficient data [Eq. (2.4)] $\epsilon^*/k = 119.3^{\circ}K$, $r^* = 3.833$. (1B) Exp-six, constants from second virial coefficient and crystal data [Eq. (3.1)] $\alpha = 14$, $\epsilon^*/k = 123.2^{\circ}K$, $r^* = 3.866$ A. 2. Exp-six, constants from molecular scattering data for $2.2 \text{ A} < r < 3.4 \text{ A}$ [Eq. (3.2)] $\alpha = 12$, $\epsilon^*/k = 116$, $r^* = 3.87$ A. The range of distances covered by the scattering data is indicated by the vertical bars. To the right of the minimum, the attractive portion, not shown, lies between curves 1A and 1B.

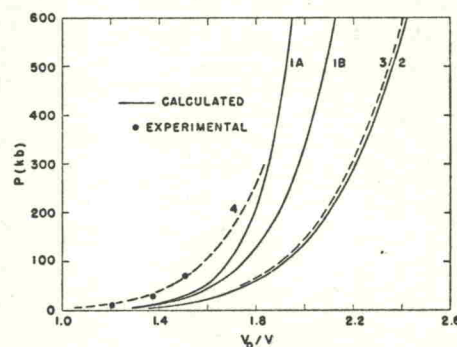


FIG. 4. Shock Hugoniot for liquid argon calculated with different pair potentials: Curves 1A, 1B, and 2 correspond to the potentials of Fig. 3. Curves 3 and 4 illustrate the effect of varying the potential parameters: 3. $\alpha = 12$, $\epsilon^*/k = 123.2$, $r^* = 3.866$. 4. $\alpha = 14$, $\epsilon^*/k = 123.2$, $r^* = 4.18$ A. Curve 4 also illustrates the change in r^* required to reproduce the available experimental data.

the fact that a part of the Hugoniot curve corresponds to a region in which the LJD and Monte Carlo isotherms are crossing.

3. EFFECT OF THE PAIR POTENTIAL

In addition to the Lennard-Jones form of the pair potential used above, the exp-six form has also been fit to second virial coefficient and crystal data, with the result¹²

$$u(r) = \frac{\epsilon^*}{1 - 6/\alpha} \left[\frac{6}{\alpha} e^{\alpha(1-r/r^*)} - \left(\frac{r}{r^*} \right)^{-6} \right] \quad (3.1a)$$

¹² E. W. Mason and W. E. Rice, J. Chem. Phys. 22, 843 (1954).