the Monte Carlo ntial, Eq. (2.4)].

$T(^{\circ}K)$	
11 900	
9 360	
4 330	
3 120	
2 390	
1 401	
760	
569	

re at the given vas then used Eq. (2.1a) was -of-state quanation. it temperature isotherms. The . discussed in $T/\epsilon^* = 2.74,$ isotherms also. oints on these in Figs. 1(a) only a disconable transition. rm was then t temperature. e Carlo points interpolation.) niot point was om the LJD cood agreement

luced thermof pair potential from second-

33 A, (2.4)

ven in Table I in in Fig. 2(b) imental solidthe empirical appears that id region. To ci of Hugoniot 1(b). Although tion is poorly

Chem. Phys. 23, ndon) A225, 393 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 lowesttemperature 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.

 $_{\rm TABLE}$ II. Shock Hugoniots calculated with the LJD equation of state.

Lennard-Jones potential [Eq. (2.4)]			Exp-six potential [Eq. (3.1)]			Exp-six potential [Eq. (3.2)]			
P(kb) V/V_0	I	'(°K)	V/V_0	T	(°K)	V/V_0	T	(°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	ĩ	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)] $\epsilon^*/k = 119.3$ °K, $r^* = 3.833$. (1B) Exp-six, constants from second virial coefficient and crystal data [Eq. (3.1)] $\alpha = 14$, $\epsilon^*/k = 123.2$ °K, $r^* = 3.866$ A. 2. Exp-six, constants from molecular scattering data for 2.2 A < r < 3.4 A [Eq. (3.2)] $\alpha = 12$, $\epsilon^*/k = 116$, $r^* = 3.87A$. 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 Hugoniots 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).