$\alpha = 14, \epsilon^*/k = 123.2 \,°\text{K}, r^* = 3.866 \text{ A}.$ (3.1b)

The repulsive portions of these two potentials (Lennard-Jones and exp-six) differ somewhat, but are both much "harder" than the molecular scattering results of Mason and Amdur,[2] who have found that the exp-six form with

$\alpha = 12, \quad \epsilon^*/k = 116 \,°\text{K}, \quad r^* = 3.87 \text{ A},$ (3.2)

reproduces the molecular scattering data quite well and has an attractive portion quite close to that of Eq. (3.1). This potential is undoubtedly the most nearly correct one for the present calculations, in which the repulsive portion dominates.

Therefore, we have used the LJD equation of state to calculate the shock Hugoniot of liquid argon using this potential as well as those determined from second virial coefficient data, Eqs. (3.1) and (2.2), (2.4). These pair potentials are shown in Fig. 3, and the corresponding shock Hugoniots are given in Table II and Fig. 4.

In order to illustrate the effects of changing the adjustable parameters in the potential function, the dashed curves of Fig. 4 were calculated. The effect of changing α only, in Eq. (3.1a) can be seen by comparing curves 1B and 3; of changing ϵ^* only, by comparing 2 and 3; and of changing r^* only, by comparing 1B and 4. Curve 4 is also used for another purpose below.

In all of the calculated Hugoniots except that shown in Fig. 2, only a single shell of neighbors was included in the calculation of the cell partition function. In calculating the lattice energy, all shells of neighbors were included for the Lennard-Jones
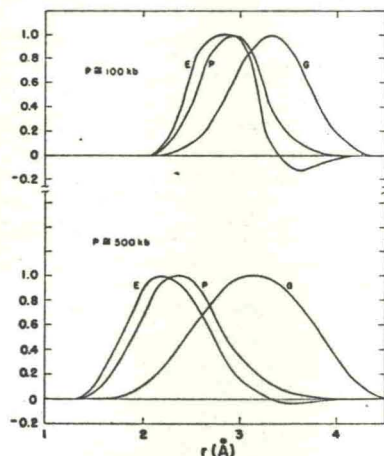

FIG. 5. Normalized weighting functions and integrands for the LJD cell integrals transformed to the form of integrals over the intermolecular separation r. Upper curves: for $P \cong 100$kb on the shock Hugoniot 2 of Fig. 4; lower curves: for $P \cong 500$kb on the same shock Hugoniot. Here G is the weighting function, P is the integrand for $(PV/RT - 1)$ and E is the integrand for E'/RT.

potential, but for the exp-six potential only one shell was included in the repulsive term. This was done partly for simplicity, since for an exponential repulsion the ratio of the entire lattice energy to the single-shell energy is a fairly strongly increasing function of density. Also, it seems likely that the inclusion of all shells in the calculation of the repulsive energy would probably give too large a result at high densities, since the exponential term remains relatively large at intermediate distances.*

4. DISCUSSION

In order to show the relative importance of different intermolecular distances in these calculations, we have obtained in the appendix a weighting function which gives the relative weight with which each intermolecular distance occurs in the cell integrals of the LJD equation of state. This weighting function is given in Eq. (A12), and can be regarded as a pseudo radial distribution function in the sense that it gives the LJD equation of state when it is used in place of the radial distribution function $g(r)$ in the general statistical mechanical expressions for pressure and excess internal energy

$$\frac{E'}{RT} = \frac{2\pi N}{VkT} \int_0^\infty u(r)g(r)r^2 \, dr \qquad (4.1)$$

$$\frac{PV}{RT} - 1 = -\frac{2\pi N}{VkT}\frac{1}{3}\int_0^\infty \frac{du(r)}{dr} \, g(r)r^3 \, dr.$$

The weighting function consists of the sum of a continuous function and a Dirac delta-function. The continuous portion of the normalized weighting function and the corresponding integrands of Eqs. (4.1) are plotted in Fig. 5 for values of T and V corresponding to pressures of about 100 and 500 kb on curve 2 of Fig. 4. The delta-function (not shown) lies at the maximum of the weighting function, and has the opposite sign and an area equal to half that under the weighting function curve. As expected, the repulsive portion of the potential is the determining factor, and the range of distances of greatest importance coincides roughly with the range of the molecular scattering results shown in Fig. 3.

The available experimental measurements of the shock Hugoniot[5] consist of x-ray densitometry measurements of the density behind the shock wave.

* In order to obtain some idea of the effect of omitting the second and third shells of neighbors in calculating the cell integrals, the Hugoniot curve of Fig. 2 was also calculated in this way. The resulting curve was displaced slightly to the right—by about 0.01 in V_0/V.

The effect of omitting the additional shells of neighbors in calculating the lattice contribution for the repulsive term of the exp-six potential is somewhat smaller than this.