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**THEORETICAL EQUATION OF STATE FOR SIMPLE
LIQUIDS AT HIGH PRESSURES**

BY HERMENZO D. JONES

RESEARCH AND TECHNOLOGY DEPARTMENT

26 MARCH 1981

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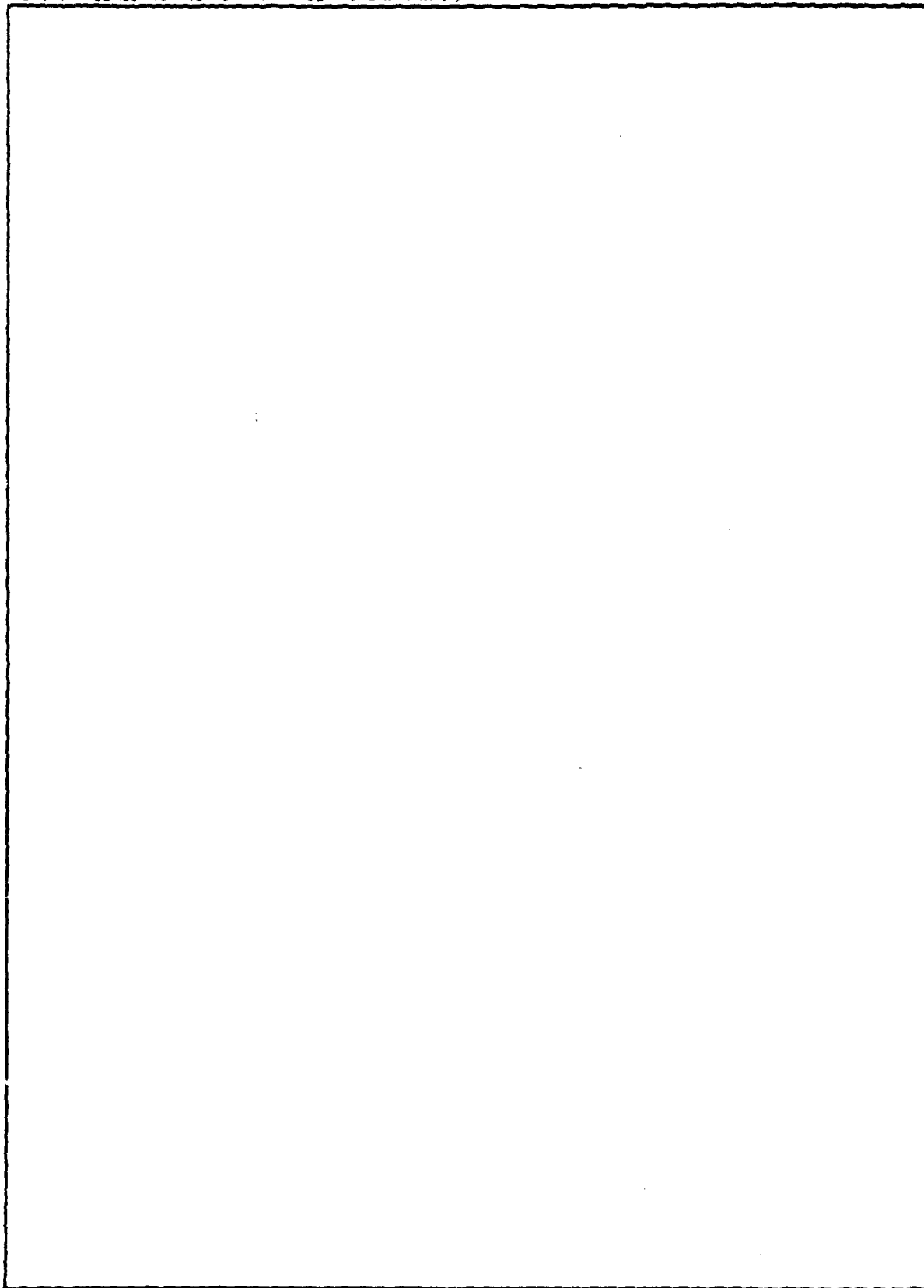
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FOREWORD

A description of simple, dense fluids based on intermolecular forces has been investigated utilizing liquid-state perturbation theory. This work is applicable to the modeling of reaction products of explosives. Funding for this work was provided by both the Independent Research and Explosives 6.2 Block Programs at the Naval Surface Weapons Center.


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INTRODUCTION

A description of even simple liquids in the high pressure domain is a problem of extreme complexity. Aside from the work of Ross¹, who employs a variational technique, most efforts have been directed towards lattice theory approximations; but it is well known that the latter are inadequate. However, perturbation theory appears to provide a simple, but accurate characterization of dense liquids.

The formalism of Weeks, Chandler and Anderson² is employed to describe fluids whose molecules interact via a spherically symmetric modified Buckingham (exp-6) potential. It is assumed that the repulsive forces provide the dominate contribution to the properties of dense fluids. The intermolecular potential is divided into a reference part which is repulsive in character and a perturbation which is attractive. Division of the potential is carried out so that the resulting free energy is a minimum or essentially constant with respect to the break point as suggested by Ree³. With the prescription of Verlet and Weis (VW),⁴ the radial distribution function for the reference system is akin to one for hard spheres with a diameter which is a function of the temperature and density. First-order properties can be written analytically aside from several, simple numerical integrals.

Within the above framework several calculations are performed. The isothermal compressibility and internal energy are computed for a system governed by an exp-6 intermolecular potential for high temperatures and pressures and are compared to Monte Carlo (MC) predictions⁵. Then properties for a real system, liquid nitrogen, are considered. It is assumed that the internal modes are unchanged from the gaseous state. Retention of the free rotation is based on the observations of Smith, et al⁶ which indicates that there is a transition from free rotation in the solid- β phase to hindered rotation in the solid- α phase.

¹Ross, M., Phys. Rev. A8, 1466 (1973).

²Weeks, J. D., Chandler, D. and Anderson, H. C., J. Chem. Phys. 54, 5237 (1971).

³Ree, F. H., J. Chem. Phys. 64, 4601 (1976).

⁴Verlet, L., and Weis, J., Phys. Rev. A5, 939 (1972).

⁵Ross, M. and Alder, B. J., J. Chem. Phys. 46, 4203 (1967).

⁶Smith, A. L., Keller, W. E. and Johnston, H. L., Phys. Rev. 79, 728 (1950).

Moderate temperature isotherms and a shock Hugoniot are calculated and are compared to experimental data^{7,8}.

THEORY

The perturbation theory to be discussed here is based on the assumption that the repulsive intermolecular forces provide the dominant characteristics of the material. This technique, originated by Weeks, et al², should be quite applicable to the high pressure domain.

It is assumed that the intermolecular interaction is spherically symmetric and is taken as

$$\phi(r) = v_0(r) + w(r) , \quad (1)$$

where $v_0(r)$ is the reference potential with repulsive character and $w(r)$ is the attractive perturbation. The reference potential is given by

$$v_0(r) = \begin{cases} \phi(r) - \phi(\lambda) & r \leq \lambda \\ 0 & r > \lambda \end{cases} , \quad (2)$$

and the perturbation is taken as

$$w(r) = \begin{cases} \phi(\lambda) & r < \lambda \\ \phi(r) & r > \lambda \end{cases} , \quad (3)$$

where

$$\phi(r) = \epsilon \left\{ (6/\alpha) \exp[\alpha(1-r/r_m)] - (r_m/r)^6 \right\} / (1-6/\alpha) . \quad (4)$$

The potential parameters denote the usual quantities. Specifically, ϵ is the well depth, α is the steepness parameter, and r_m is the position of the minimum of the potential. Historically, the potential is divided at the minimum^{2,4}; however, Ree³ demonstrated that the region of applicability could be extended to the high density domain with the additional flexibility of a variable λ . Hence λ is here taken as a variational parameter.

⁷Robertson, S. L. and Bann, Jr., S. E., J. Chem. Phys. 50, 4560 (1969).

⁸Dick, R. D., J. Chem. Phys. 52, 6021 (1970).

Using standard techniques⁹ the free energy can be written as a perturbative series in inverse temperature, which is well suited for the shock wave domain. The result for the excess free energy per particle is

$$f = f_0 + \rho/2 \int d\vec{r} w(r) g_0(r) + \dots, \quad (5)$$

where f_0 and $g_0(r)$ are the free energy per particle and radial distribution function for the reference system, respectively, and the number density is denoted by ρ . In this work only the two leading terms in the expansion of Equation 5 are retained.

The steep, discontinuous behavior of $v_0(r)$ is reminiscent of a hard sphere potential. Application of a functional Taylor expansion¹⁰ yields the result that the free energy of the reference system is identical to second-order with that for hard spheres with a temperature and density-dependent hard sphere diameter, so that

$$f_0 \approx f_{Hs}, \quad (6)$$

where

$$g_0(r) = e^{-\beta v_0(r)} y_{Hs}(r), \quad (7)$$

and

$$g_{Hs}(r) = e^{-\beta \phi_{Hs}(r)} y_{Hs}(r). \quad (8)$$

The hard-sphere diameter is determined from the condition

$$\int d\vec{r} \left\{ e^{-\beta v_0(r)} - e^{-\beta \phi_{Hs}(r)} \right\} y_{Hs}(r) = 0. \quad (9)$$

This is the requirement that the long wavelength structure factors for the reference system and the hard-sphere system be equal.

Combination of the results of VW with the Percus-Yevic description of the hard-sphere system¹¹ yields analytic results for the thermodynamic state variables aside from several simple, numerical integrals. The compressibility and excess internal energy per particle are obtained from analytic derivatives of the free energy as

$$Z = \beta p/\rho = 1 + \rho \left(\frac{\partial f}{\partial \rho} \right)_{\beta} \quad (10)$$

and

$$E = \left(\frac{\partial (\beta f)}{\partial \beta} \right)_{\rho}.$$

⁹Zqanzig, R. W., J. Chem. Phys. 22, 1420 (1954).

¹⁰Anderson, H. C., Chandler, D. and Weeks, J. D., J. Chem. Phys. 56, 3812 (1972).

¹¹Wertheim, M. S., Phys. Rev. Lett. 10, E501 (1963).

It was found that the compressibility defined in this manner rather than the original analysis of VW compared more favorably with MC results in higher pressure and temperature region.

RESULTS AND DISCUSSION

The isothermal properties for a typical exp-6 potential with the parameters

$$\begin{aligned}\alpha &= 13.5 \quad , \\ r_m &= 3.85 \times 10^{-10} \text{ m} \quad , \\ \epsilon/k &= 122^{\circ}\text{K} \quad ,\end{aligned}$$

are given in Table 1. Here, the reduced temperature is defined as $T^* = kT/\epsilon$, and the reduced density is taken as $\rho^* = (r_m^3/\sqrt{2})\rho$. For a material such as argon, the lower temperature isotherm ranges from 2.5 GPa to 16.6 GPa, while the higher temperature isotherm varies from 16 GPa to 100 GPa. It is seen that perturbation theory is in excellent agreement with Monte Carlo calculations, except for the very high density regions for the respective isotherms. In both instances these larger deviations result from the entrance into the meta stable region for the hard-sphere reference system.

To consider a real system, moderate temperature isotherms for liquid nitrogen are computed. The values of the potential parameters are taken as

$$\begin{aligned}\alpha &= 13.6 \quad , \\ r_m &= 4.12 \times 10^{-10} \text{ m} \quad , \\ \epsilon/k &= 100.0^{\circ}\text{K}\end{aligned}$$

The compressibility as a function of the pressure is shown in Figure 1. The solid curves are the perturbative predictions, and the circles represent the experimental data. It is seen that the calculation exhibits very good agreement with the data, with a maximum error of 5%. Thus, the theory describes the liquid quite well in the moderate pressure and temperature range.

As a final application of this technique, the shock compression of liquid nitrogen is considered. The initial conditions for the material are given as $T_0=77^{\circ}\text{K}$ and $\rho_0=8.1 \times 10^2 \text{ kg/m}^3$. The same potential parameters used in the previous calculation of moderate temperature isotherms are used for this computation. In this calculation a value of volume for the compressed state was chosen, and then a value of the temperature was found by iteration to satisfy the energy conservation condition,

$$E - E_0 = \frac{1}{2} (P+P_0)(V_0-V) \quad , \quad (12)$$

TABLE 1
THERMODYNAMIC PROPERTIES FOR EXP.-6 POTENTIAL

$T^* = 20$

Monte Carlo ⁵			Perturbation Theory	
ρ^*	Z	βE	Z	βE
.9	3.27	.28	3.30	.28
1.0	3.81	.38	3.83	.38
1.25	5.52	.73	5.56	.75
1.50	8.07	1.34	7.85	1.32
1.75	11.34	2.17	10.3	2.13

$T^* = 100$

1.264	3.06	.55	3.09	.57
1.473	3.71	.74	3.71	.74
1.768	4.81	1.08	4.75	1.06
2.431	8.17	2.20	7.57	2.03
2.701	9.86	2.78	9.11	2.78

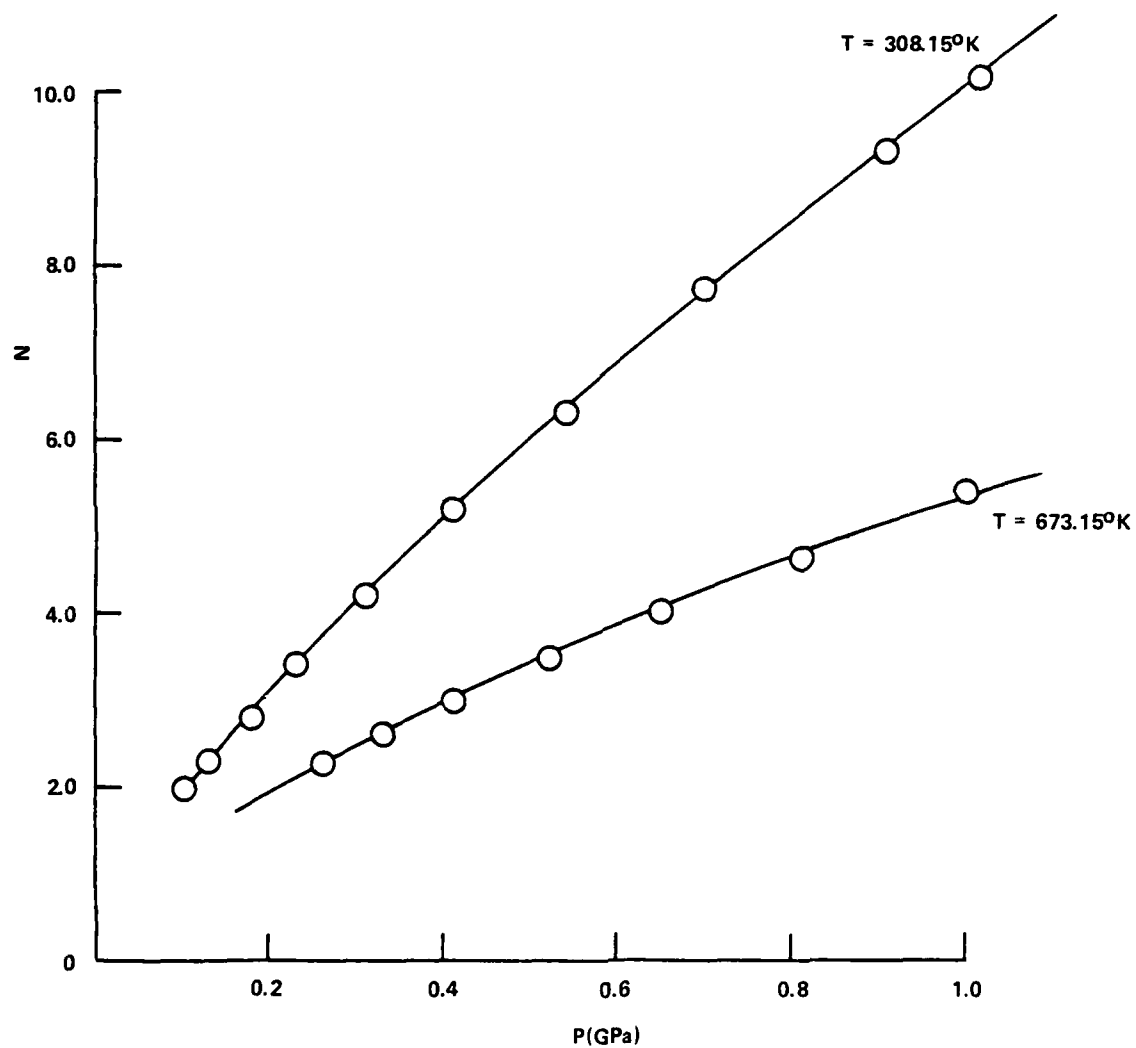


FIGURE 1 COMPRESSIBILITY VS. PRESSURE FOR LIQUID NITROGEN

where the zero subscript refers to material in the undisturbed state ahead of the shock front. In Equation (12), E and v are the total specific energy and specific volume, respectively.

The theoretical shock Hugoniot in the pressure-volume plane for liquid nitrogen is compared with the experimental data⁸ in Figure 2. The data could be interpreted as having a cusp in the 14 GPa region, signalling the onset of a phase transformation; however, there is good agreement between the present calculation and experiment. Similar results are exhibited in Figure 3 in the shock velocity particle velocity plane. The decline in the slope is well characterized by the single-phase computation. For completeness, the theoretical Hugoniot is presented in Table 2.

SUMMARY

Thermodynamic properties for high temperatures and pressures have been calculated using an exp-6 potential and liquid-state perturbation theory. The results were in good agreement with MC computations, except for extremely dense states which are close to the phase line of the hard sphere reference system. Theoretical predictions for the compressibility of liquid nitrogen for moderate temperatures were in accord with the experimental data. The calculated shock Hugoniot for liquid nitrogen was also in close agreement with experimental results. It is apparent that the theoretical technique utilized in the calculations provides a convenient and accurate description of simple fluids in the moderate as well as high-pressure domains.

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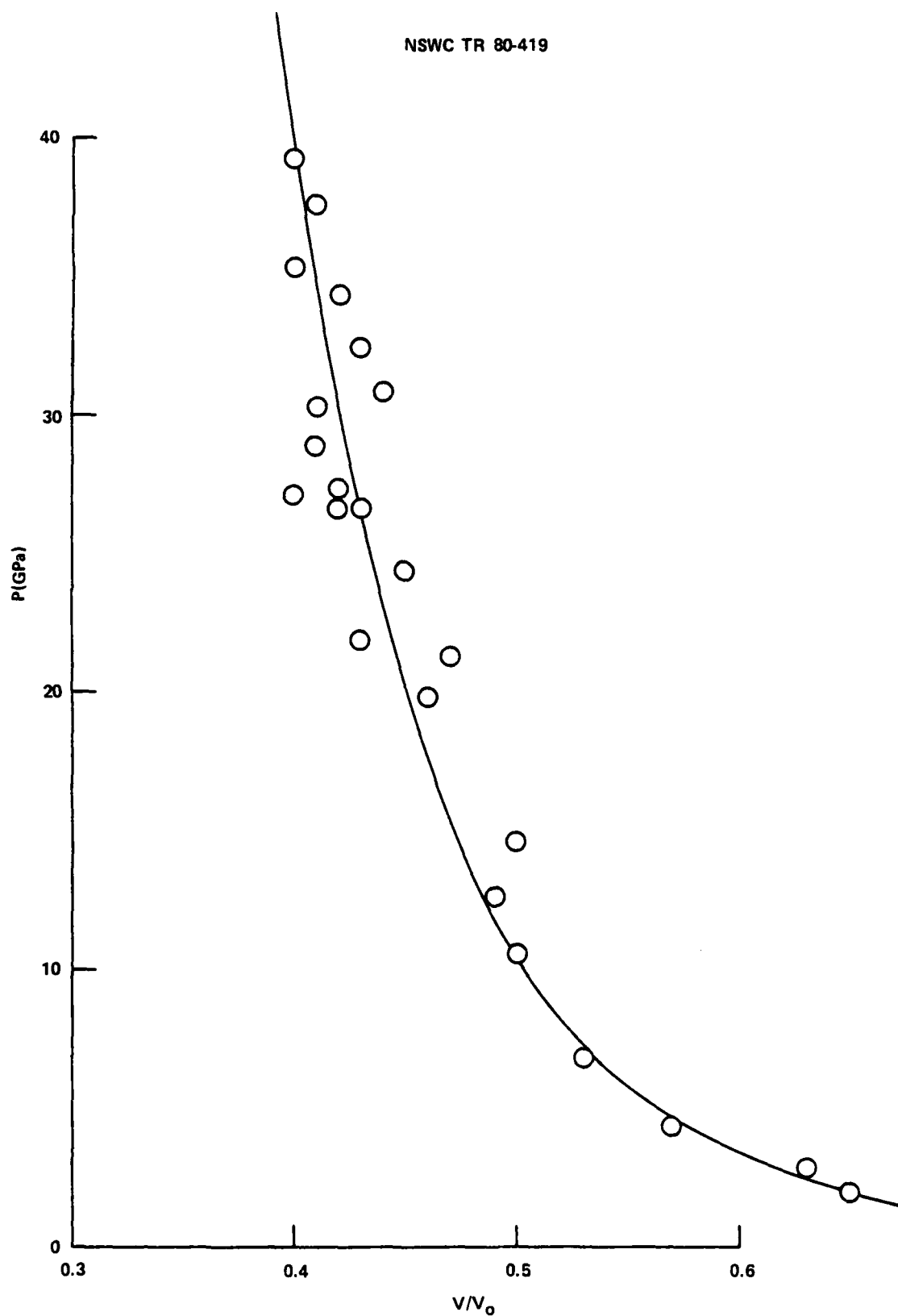


FIGURE 2 SHOCK PRESSURE VS. RELATIVE VOLUME FOR LIQUID NITROGEN

TABLE 2
SHOCK HUGONIOT FOR LIQUID NITROGEN

v/v_0	P(GPa)	T(°K)	U(km/sec)	U_p (km/sec)
.653	1.86	316.2	2.56	0.89
.628	2.47	418.3	2.84	1.06
.570	4.83	874.7	3.70	1.59
.531	7.56	1446	4.44	2.08
.501	10.7	2137	5.12	2.55
.494	11.6	2348	5.30	2.68
.468	16.0	3364	6.05	3.22
.448	20.5	4486	6.73	3.72
.432	25.3	5714	7.37	4.19
.419	30.0	6977	7.94	4.61
.409	34.2	8134	8.41	4.97
.400	39.0	9467	8.90	5.34

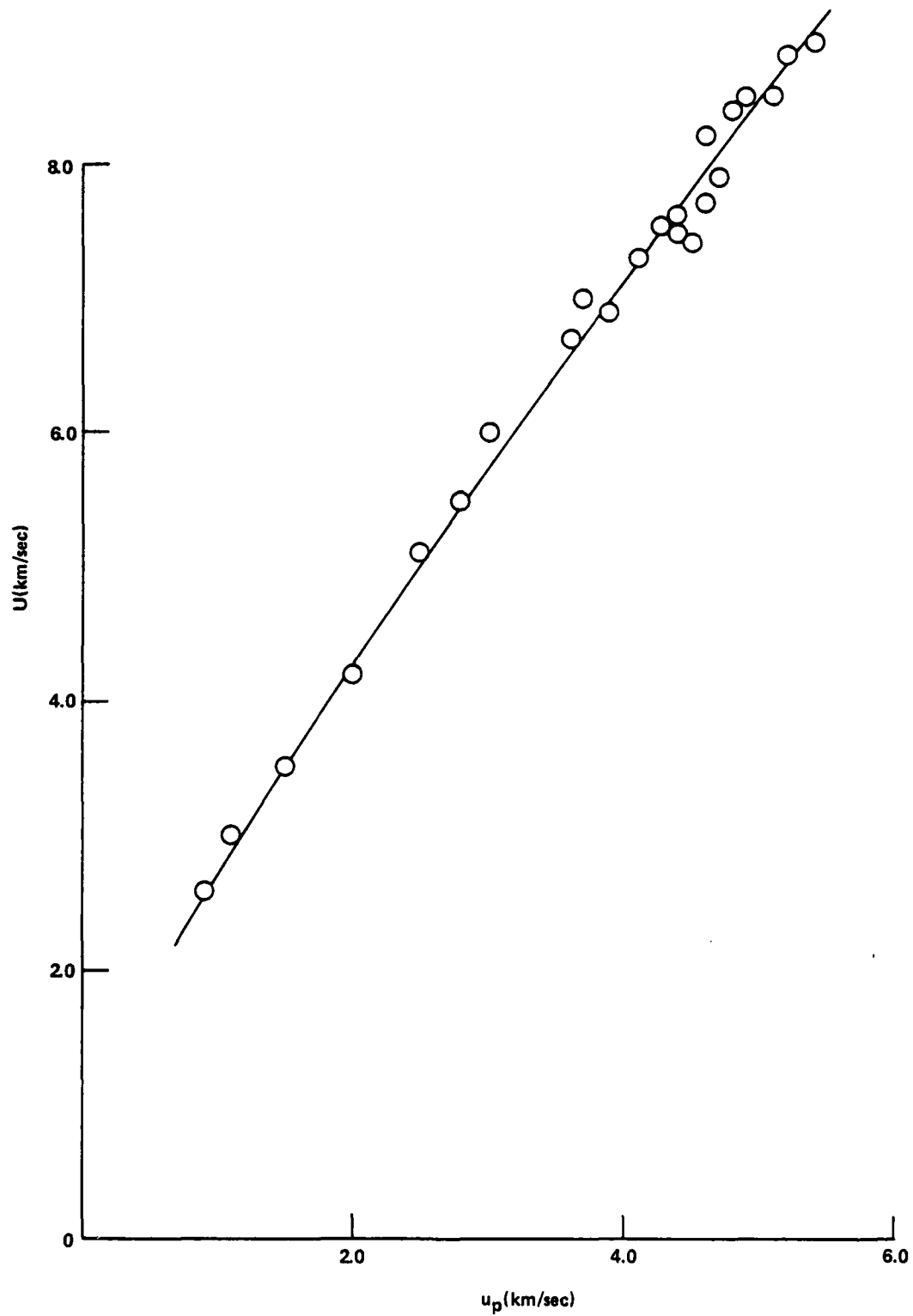


FIGURE 3 SHOCK VELOCITY VS. PARTICLE VELOCITY FOR LIQUID NITROGEN

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