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(High-Density) Polyethylene (Marlex)

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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F. Dowell

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

A SIMPLE EOS FOR "LINEAR" (HIGH-DENSITY) POLYETHYLENE (MARLEX)

by

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ABSTRACT

A simple equation of state (EOS) for "linear" (high-density) polyethylene (Marlex) was generated and added to the T-4 Sesame EOS Library as material number 7180. This new EOS for Marlex reproduces the experimental shock Hugoniot data for the initial state density ρ_o = 0.954 g/cm^3 or Mg/m^3.

INTRODUCTION

In this report, the generation of a simple equation of state (EOS) for Marlex, i.e., "linear" (high-density) polyethylene is presented. This EOS reproduces the experimental shock Hugoniot data for Marlex, thus fulfilling the primary purpose of this EOS to describe the compression region. The PVT (pressure-volume-temperature) data from this EOS are also compared with some data from static measurements and found to be reasonably good, given the simplicity of the models used to generate the EOS and given the dependence of PVT properties on the degree of crystallinity of the particular polyethylene sample being studied.

METHOD

A simple EOS for Marlex was generated using two computer codes, CANDIDE[1] and PANDA.[2,3] CANDIDE uses Thomas-Fermi-Dirac (TFD) theory to calculate the thermal electronic contributions to the EOS; PANDA uses various models to calculate the other contributions to the EOS and to combine these results with the TFD results from CANDIDE to form an EOS.

For reasons of tractability, the models used to generate the simple EOS described here for Marlex do not explicitly treat Marlex as a polymer; however, experimental data for Marlex are used in these models, and thus the polymeric nature of Marlex is implicitly included at least in parts of the EOS. The repeat unit in a Marlex chain is CH_2. Therefore, Marlex was modeled as an average atom with an average atomic number of 8/3 and an average atomic weight of 4.6757. A reference density of $0.95399 \simeq 0.954$ Mg/m^3 at pressure $P = 0$ and temperature $T = 298.15$ K was used.

The thermal electronic contributions were calculated by CANDIDE run in its standard mode with an exchange constant of 2/3. The other contributions to the EOS were generated from PANDA in the manner described in the following paragraphs:

The solid lattice vibrations were calculated by a solid-gas interpolation scheme,[2] which reduces to a Debye model at low temperatures and high densities and which reduces to an ideal gas at high temperatures or low densities. This solid-gas interpolation scheme was matched with a virial expression at the density $\rho = 0.954$ Mg/m^3; this virial expression was used for $\rho < 0.954$ Mg/m^3.

The cold curve ($T = 0$ K isotherm) was calculated from experimental shock Hugoniot data assuming[2] a Mie-Gruneisen EOS. The following fit (accomplished with the computer code LEASTS[4]) to the Marlex shock Hugoniot data[5] for the initial state density $\rho_o = 0.954$ Mg/m^3 was used:

$$U_s = 2.8233 + 1.6810\ U_p - 0.0339\ U_p^2 \quad , \quad 0.7 < U_p < 5.4 \quad ,$$

where U_s is the shock velocity and U_p is the particle velocity; U_s and U_p are given in units of mm/μs or km/s. This fit ignores a very small transition[6] around $U_p = 3.3$ km/s.

The Gruneisen function γ and the Debye temperature θ were calculated with the Thompson formulas.[2] A reference γ of 0.739 at ambient temperature and pressure was chosen for use in the calculations; this reference γ was calculated from experimental values of the constant pressure heat capacity[7] $C_p = 1.874$ J/[g•K], the isentropic bulk modulus[5] $B_S = 4.48$ GPa, the thermal expansion coefficient[8] $\alpha = 2.95 \cdot 10^{-4}$ K^{-1}, and the density ρ for Marlex. The reference θ at ambient conditions was calculated by PANDA[2] using the experimental U_s-U_p intercept, the average atomic weight, the density ρ, and a Poisson's ratio of 1/3.

At $\rho = 0.949$ Mg/m^3, the cold curve was matched to an analytic Lennard-Jones (LJ) formula with FACLJ = 2 (corresponding to an r^{-6} attractive term, where r is the separation distance between the two members of the pair involved in the LJ pair potential). This LJ formula was used for $\rho \leqslant 0.949$ Mg/m^3. The solid binding energy E_b was set equal to −1.6836 MJ/kg, in order to set the zero of energy at $P = 0$ and $T = 298.15$ K.

The PANDA code was also used to match the cold curve at high densities to the TFD model. The match density was calculated by the PANDA code.[2]

The cohesive energy E_{coh} is the heat of vaporization of the solid at 0 K. E_{coh} for an average atom in a CH_2 segment in a polyethylene chain can be estimated from experimental data.[9] However, in the EOS described here for Marlex, an E_{coh} of 4.00 MJ/kg was used in order that the pressures on the cold curve at low densities are not positive (and do not pass through a maximum)--problems encountered with smaller values of E_{coh}, including the value estimated from Ref. 9. As with branched (low-density) polyethylene[10] and with Teflon,[11] an E_{coh} considerably larger than that estimated from Ref. 9 is needed for Marlex to meet this requirement on the cold curve.

The TFD results from CANDIDE were combined with the other EOS contributions calculated with PANDA. This merger was accomplished with the PANDA code using the default parameters in PANDA.[2]

Pressure, energy, and Helmholtz free energy tables for Marlex as a function of temperature and density have been calculated in the manner described above and added to the T-4 Sesame EOS Library under material number 7180. The following kinds of pressure, energy, and Helmholtz free energy tables were added: 301 (total EOS), 303 (ion plus cold curve, i.e., 305 plus 306), 304 (thermal electron), 305 (ion, including zero point), and 306 (cold curve; no zero point).

DISCUSSION

The simple EOS described in this report for Marlex reproduces the experimental shock Hugoniot data[5] of Marlex for the initial state density ρ_0 = 0.954 Mg/m^3. (See Figs. 1 and 2.) This EOS does not address the matter of the glass transitions or the melting transition.[12]

Values of pressure, energy, and negative Helmholtz free energy for every other isotherm from the total EOS tables calculated for Marlex are plotted versus density in Figs. 3-5.

In Table I, some densities calculated at different pressures and temperatures from the EOS of this report for Marlex are compared with densities from static experimental PVT data.[13-15] The densities marked "from Ref. 13" were calculated using a fitting equation in Ref. 13 for the experimental data from Ref. 14. In Table I, the relative deviations between the densities calculated with the EOS of this report and the densities from the static experiments fall between 0% and 4.48%, with one exception. This exception is a relative deviation of 10.9% for the density[15] at $P = 1.0133 \cdot 10^5$ Pa and $T = 476.2$ K. The sample of Marlex in Ref. 15 was in the melt (liquid) state at $P = 1.0133 \cdot 10^5$ Pa and $1014.3 \cdot 10^5$ Pa at $T = 476.2$ K and would appear to have been close to the melting transition at $P = 2027.5 \cdot 10^5$ Pa at the

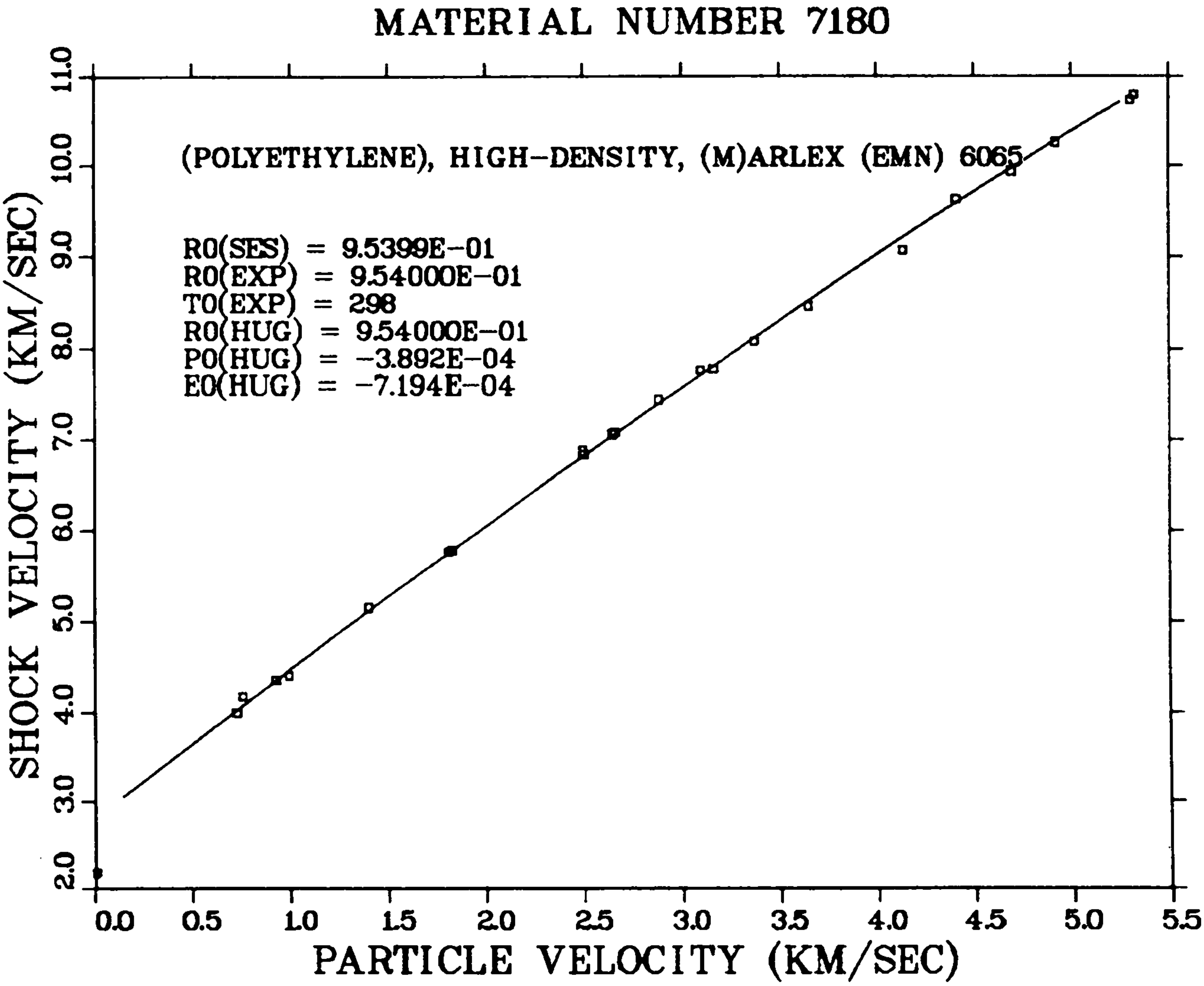

Fig. 1. Comparison of model and experimental shock velocity U_s vs particle velocity U_p for initial state density $\rho_o = 0.954$ Mg/m^3. The line is generated from the total EOS tables. The boxes are the experimental shock Hugoniot data points plotted from the LASL Shock Hugoniot Data File.[17] Initial densities (RO) are in Mg/m^3, initial temperature (TO) is in degrees Kelvin, initial pressure (PO) is in GPa, and initial energy (EO) is in MJ/kg. "SES" refers to the Sesame total EOS tables, and "EXP" refers to the experimental Hugoniot information. Here, PO(HUG) and EO(HUG) are calculated from the total EOS tables using RO(HUG) = RO(EXP).

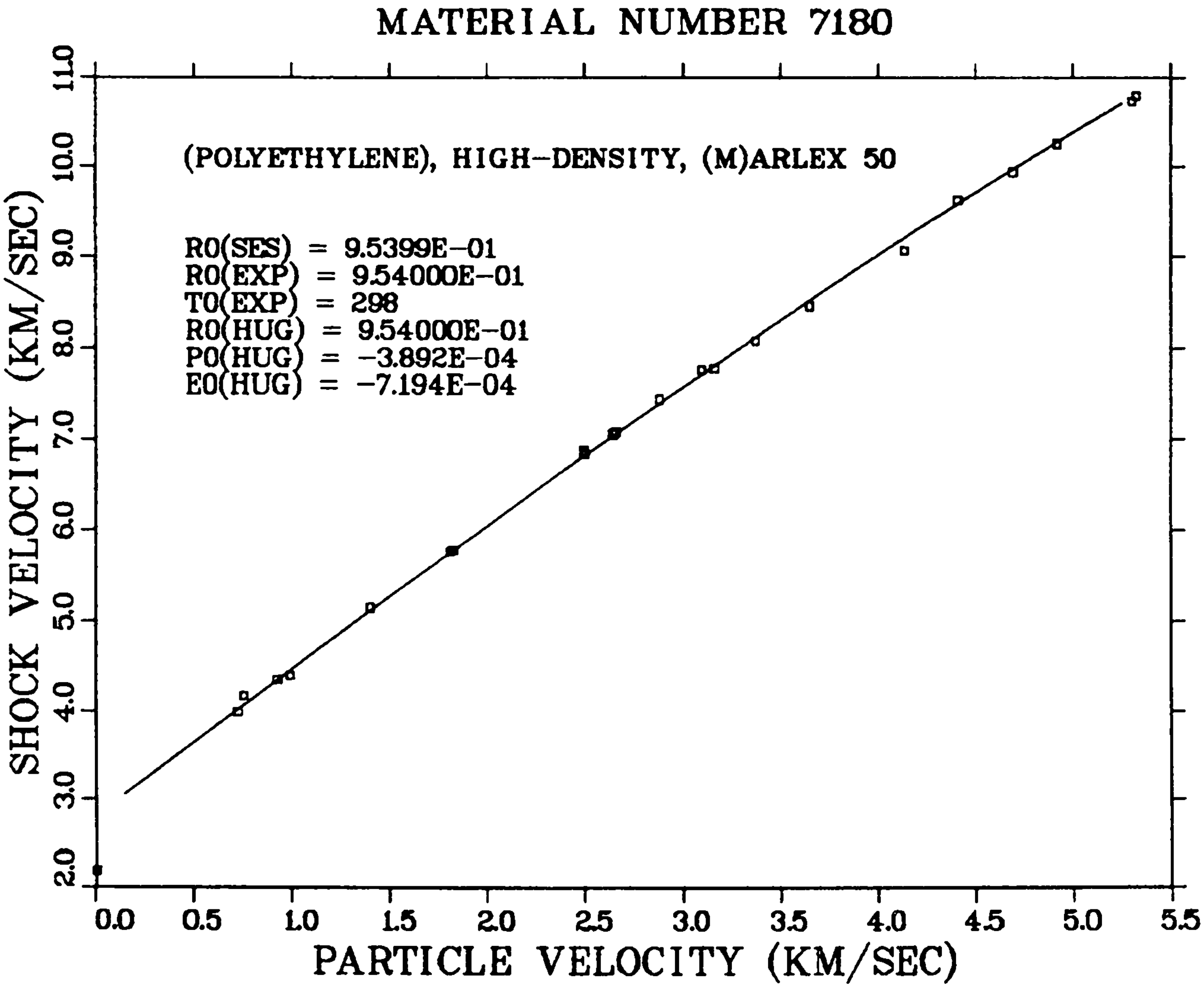

Fig. 2. Comparison of model and experimental shock velocity U_s vs particle velocity U_p for initial state density ρ_0 = 0.954 Mg/m^3. The line is generated from the total EOS tables. The boxes are the experimental shock Hugoniot data points plotted from the LASL Shock Hugoniot Data File.[17] Initial densities (RO) are in Mg/m^3, initial temperature (TO) is in degrees Kelvin, initial pressure (PO) is in GPa, and initial energy (EO) is in MJ/kg. "SES" refers to the Sesame total EOS tables, and "EXP" refers to the experimental Hugoniot information. Here, PO(HUG) and EO(HUG) are calculated from the total EOS tables using RO(HUG) = RO(EXP).

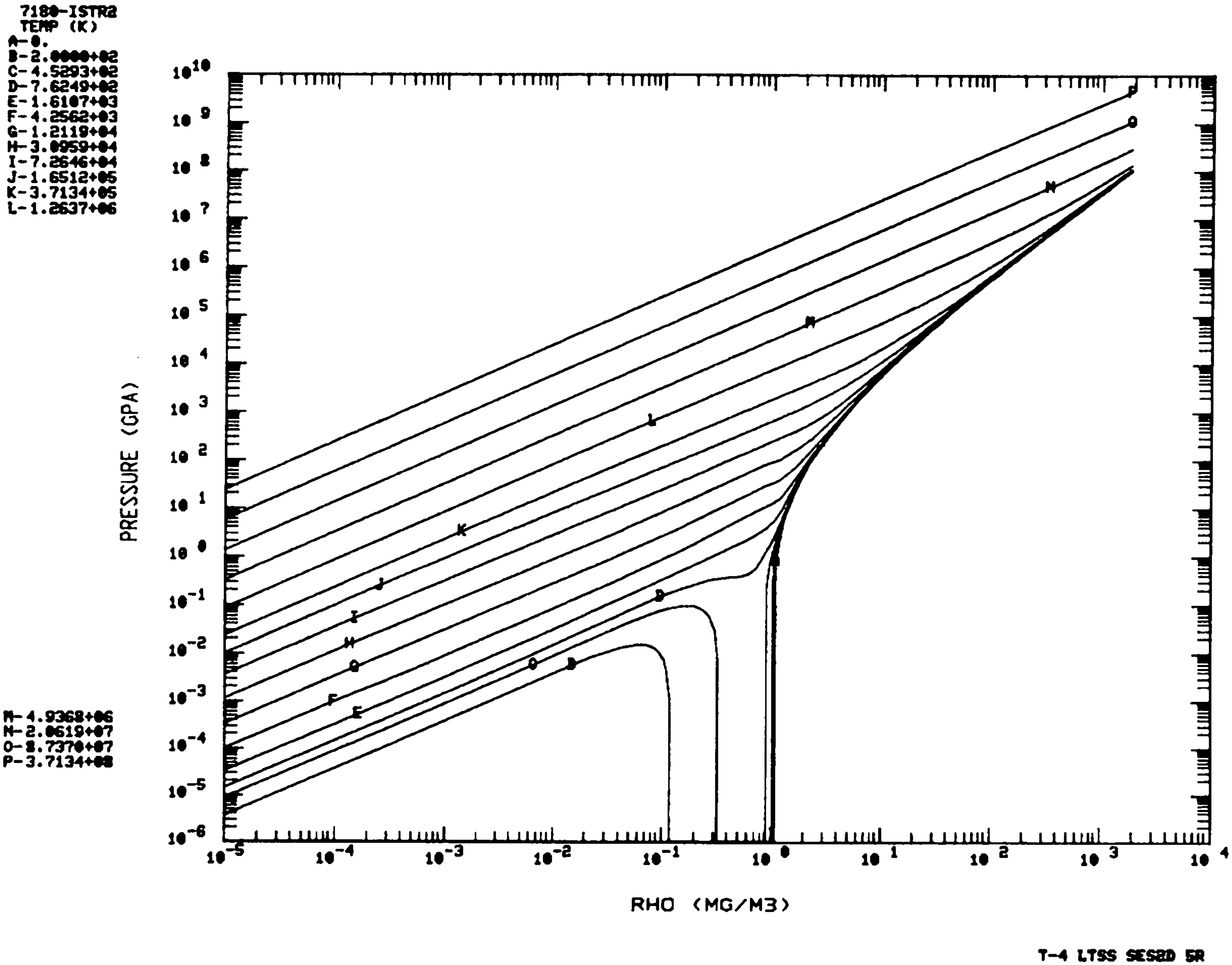

Fig. 3. Some pressure vs density isotherms from the total EOS tables for Marlex.

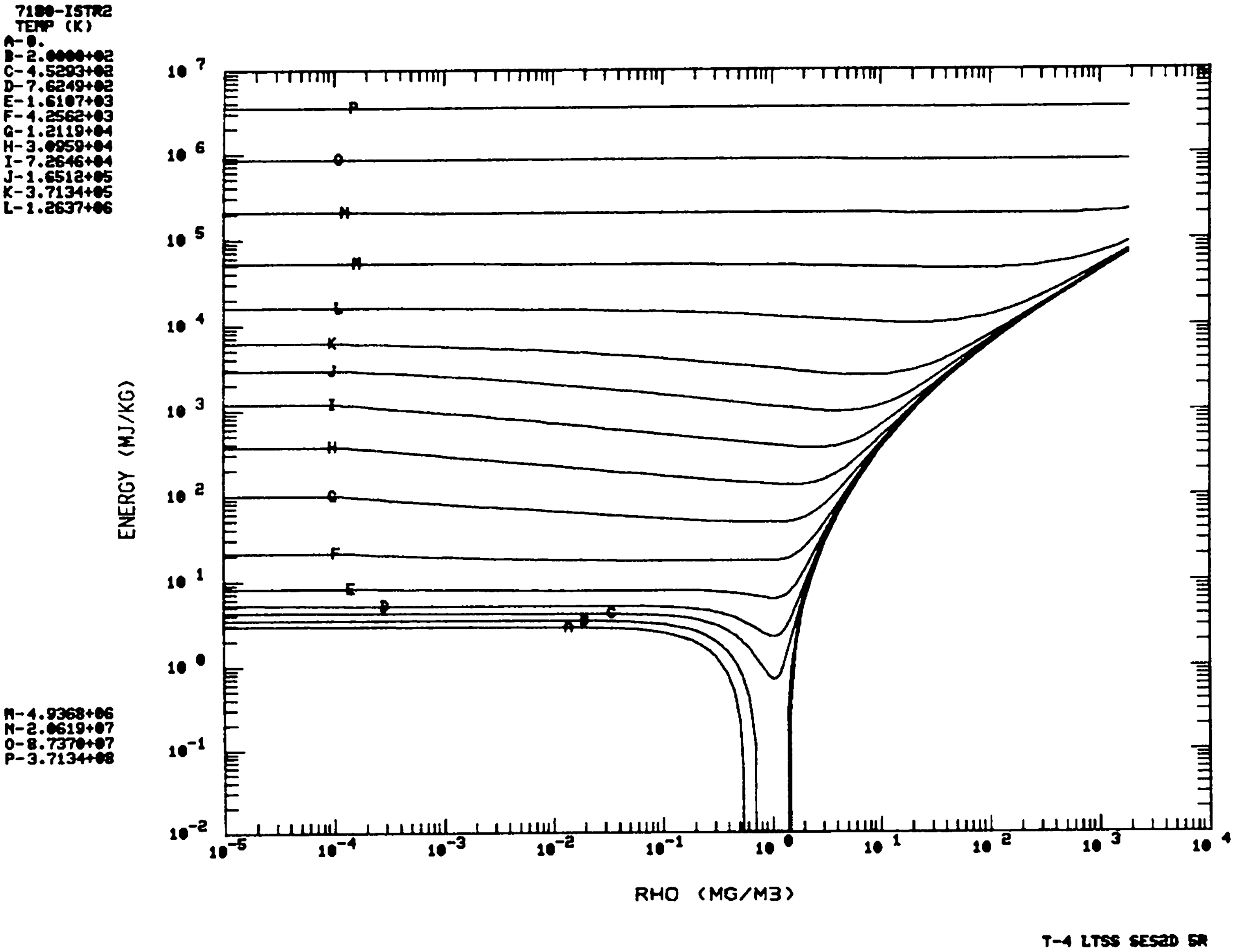

Fig. 4. Some energy vs density isotherms from the total EOS tables for Marlex.

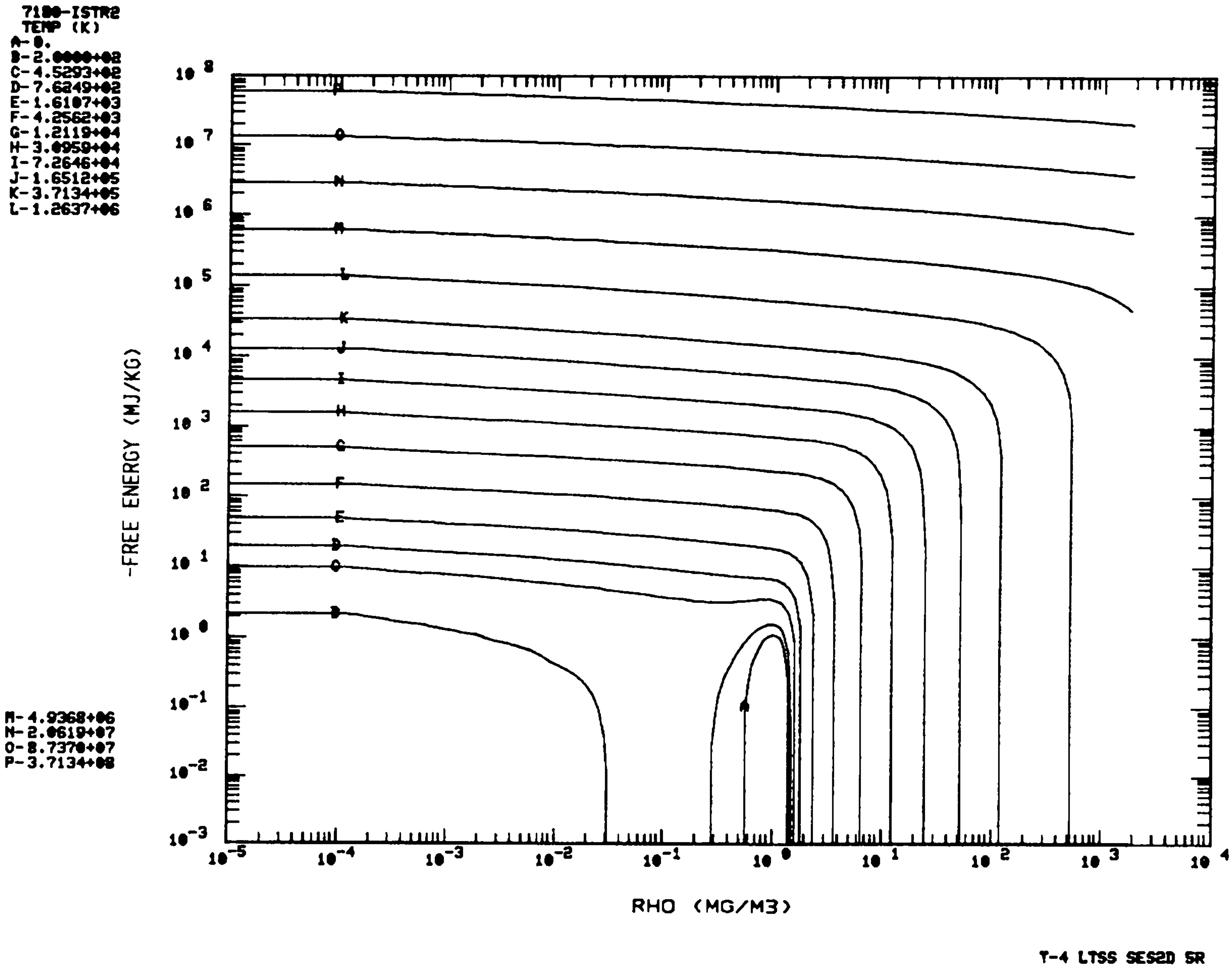

Fig. 5. Some negative Helmholtz free energy vs density isotherms from the total EOS tables for Marlex.

TABLE I. Comparison of densities calculated at different pressures and temperatures from the EOS of this report for Marlex with densities from static experimental PVT data.

P	T = 298 K			T = 372.9 K			T = 476.2 K		
	ρ EOS	ρ Ref. 13	rel. devia.	ρ EOS	ρ Ref. 15	rel. devia.	ρ EOS	ρ Ref. 15	rel. devia.
(10^5 Pa)	(Mg/m^3)	(Mg/m^3)	(%)	(Mg/m^3)	(Mg/m^3)	(%)	(Mg/m^3)	(Mg/m^3)	(%)
1.0133	0.954	0.954	0	0.9147	0.9398	2.67	0.8387	0.7564	10.9
1013.3	0.968	0.977	0.95						
1014.3				0.9318	0.9702	3.96	0.8653	0.8424	2.72
2026.5	0.980	0.995	1.48						
2027.5				0.9473	0.9917	4.48	0.8877	0.8949	0.80
5066.3	1.014	1.034	1.96						
8106.0	1.043	1.062	1.83						

same $\underline{T}$. (See also Ref. 16 for the melting temperatures of polyethylene under pressure.) It should be noted that the simple EOS of this report does not treat the liquid state per se.

It should be noted that the static experimental PVT data in Table I fall between the $\underline{P}$ and $\underline{V}$ of the initial (unshocked) Marlex samples and the $\underline{P}$ and $\underline{V}$ of the first data point for the shocked samples.[5] Not surprisingly, the best agreement between the densities from the EOS of this report and the densities from the static data seems to be for those PV points that appear to lie closest to the shock Hugoniot[5] used in the generation of the simple EOS of this report.

It should be noted that the density of a Marlex sample at a given $\underline{T}$ and $\underline{P}$ depends on the degree of crystallinity of the sample.[12] At 298 K at ambient pressure, the densities of the EOS of this report and of the sample of Refs. 13 and 14 were both 0.954 Mg/m^3. At 292.6 K at ambient pressure, the densities of the EOS of this report and of the sample of Ref. 15 were 0.957 Mg/m^3 and 0.973 Mg/m^3, respectively. At least some of the discrepancies between the densities in Table I may very well be due to differences in the crystallinities of the Marlex samples whose behavior is being compared.

It is not possible at present to comment on the accuracy of the EOS of this report at densities smaller than those of the compression region.

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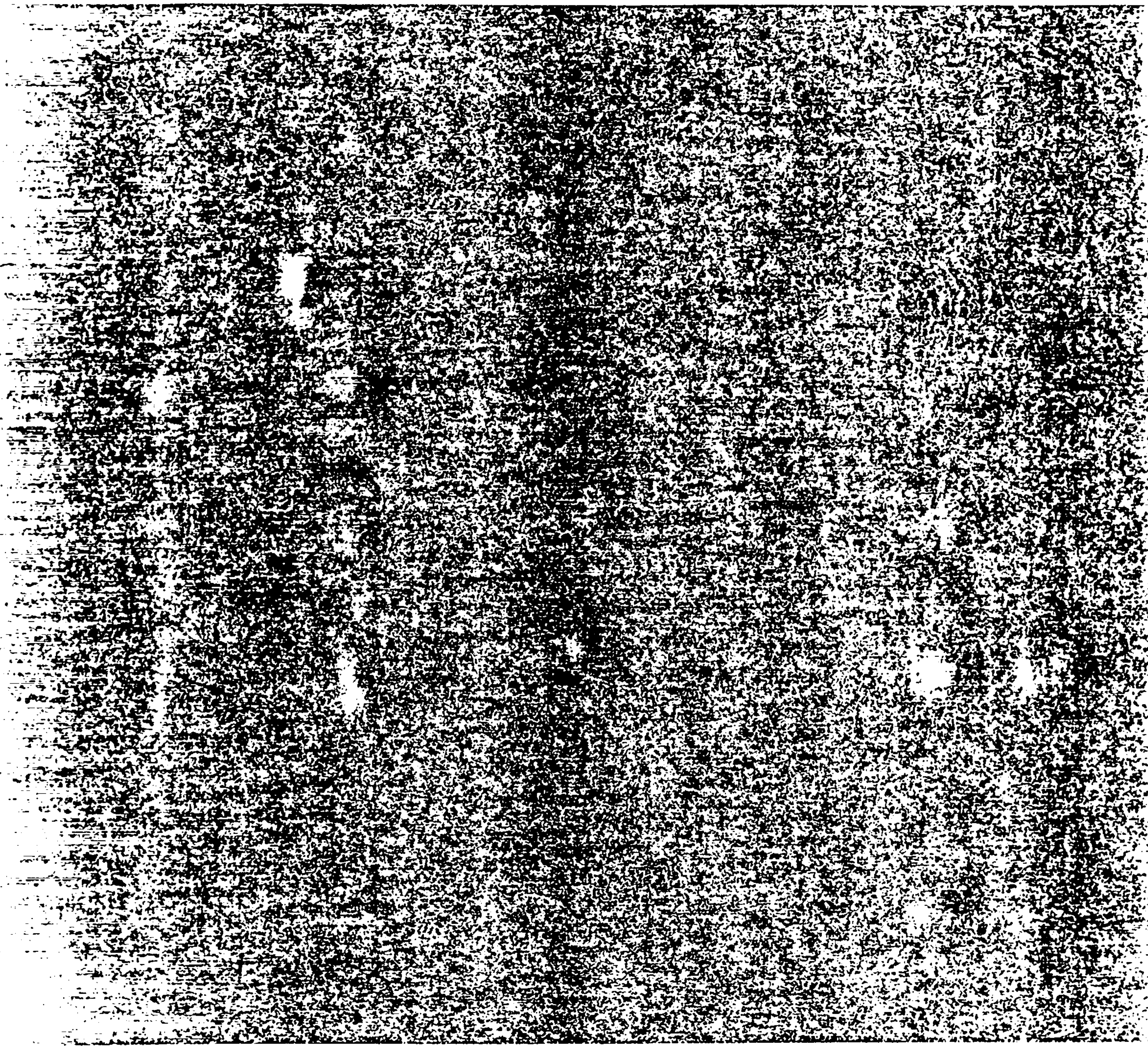

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