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A SUMMARY AND REVIEW OF HYDROGEN THEORETICAL
EQUATION-OF-STATE MODELS AT
LAWRENCE LIVERMORE LABORATORY

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ABSTRACT

We present a review and analysis of the hydrogen equations of state (EOS) at use at Lawrence Livermore Laboratory (LLL). Careful comparisons to experimental data and among EOS's are performed and evaluated. We find that the new LLL hydrogen EOS (EOS95) and its representations produce the best agreement with experimental data and hydrodynamic simulation studies.

INTRODUCTION

Due to its functional importance and fundamental primacy, the physics of hydrogen* has been studied for more than 20 years at LLL. During this period there has been continuous evolution of our ability to model the high pressure thermodynamics of hydrogen. The history of this evolution is complicated and may be obscure in details. In this report we attempt to present a complete review of the studies of hydrogen from 1972 through 1979, including critical evaluations and plots showing a large set of comparisons.

DESCRIPTION AND HISTORICAL REVIEW OF PRIMARY DATA BASES

Table 1 presents the history and evolution of the hydrogen EOS. Tabulated are (1) the primary data base (PDB) name representing the full primary set of numerical EOS data; (2) the LLL's H-Division EOS Reference File (HERF) number where references to the physics codes and construction methods used in generating the PDB can be found; (3) the analytic fit EOS (AFEOS) name given to the analytic representation of the PDB; (4) the biquadratic Lagrange tabular EOS (BQLEOS) number referring to the BQL representation generated from the PDB; (5) the EOS name associated with the giant planet studies (GPEOS);

*For simplicity throughout this report, the terms hydrogen or H_2 will be used to describe work carried out on hydrogen or deuterium.

(6) a brief descriptor of the EOS; and (7) an index to a brief discussion of the origin of the PDB. The key to the origin index in Table 1 follows.

1. The original LLL hydrogen EOS (1960 to 1962), was primarily the work of Gilda Harris (circa 1962). Constructed from the low density CONARI* code of Harris and Trulio with an interpolation region to join onto Cowan TFD at high pressures.
- 2a. A composite modern LLL EOS was constructed in 1972. This work was reported in UCID-16095¹ and was compared in detail to K042. This PDB forms a partial basis for two later LLL EOS's (EOS66 and EOS95). The AFEOS K049 was a very difficult, restricted range fit in ρ, E space.
- 2b. A substantially modified EOS from EOS6/72, is fully documented in Astrophys. J. 199, 255 (1975).² Taking partial advantage of LASL and LLL hydrogen shock wave experiments, the EOS was generated in 1973, with slight modifications made in 1974. This EOS was used in work published on giant planet evolution and was not used in LLL hydrocode libraries.
3. Original H_2 EOS from Los Alamos Scientific Laboratory (LASL) was generated by G. Kerley in 1972 and documented in Phys. Earth Plan. Int.³ The AFEOS 37 is a restricted range fit.
4. A revision to the Kerley PDB (KNEW) just cited was made in 1973 and was received in 1975 at LLL. It is currently the LASL standard hydrogen EOS. A restricted range fit, AFEOS 55A, was also generated.
5. The modern analytic fit to KNEW. This fit is valid over a wide range. The fit was constrained to reproduce the PDB, but was not required to reproduce the experimental data.
6. A rectangularized modified grid extension of EOS6/72 was required for generating a BQL tabular EOS. Thermodynamic consistency (TDC) modifications were also made. This was the LLL standard H_2 PDB before 1978. It was used in unpublished 1977-78 giant planet studies, but was found less than satisfactory (led to cool interiors). The AFEOS K0109 was constrained to reproduce the shock data and produce a wide range (full ρ, E coverage) fit.

*The CONARI Code was the predecessor to BEAST, which then became FMIN.

7. A revised and extended modification of EOSREV1 which has been described in detail in two informal memos (refer to H. Graboske for details) and a paper.⁴ This is now the standard LLL H₂ EOS. The AFEOS K095A was forcibly normalized to fit all experimental data and covers the full ρ, E range.

The following intercomparisons of PDB's, AF's, and tabular EOS's are primarily aimed at a threefold comparison between EOS66, KNEW, and EOS95, the major LLL and LASL standards. A very detailed earlier comparison of the first and second PDB's has already been documented, and since they have both been superseded by the three more recent standards, we will not consider them here.

TABLE 1. History and description of hydrogen EOS's.

PDB	HERF	GPEOS	AFEOS	BQLEOS	ORIGIN ^a	DESCRIPTOR
Lost	--	--	K042	--	1	1960 Primal H ₂ EOS
EOS6/72	36		K049	275	2a	First modern LLL EOS 1972-73
EOSREV1	--	T9JHYD			2b	Revision of EOS6/72
KFILEFIX	37	--	37	--	3	Kerley LASL H ₂ EOS 1972
KNEW	55	--	55A ^b	--	4	Revised Kerley LASL H ₂ EOS 1973
KNEW	55	--	55B ^c	--	5	New AF to KNEW 1978
EOS66	66	EHYDGP3	K0109		6	Extended, modified EOS6/72-1975
EOS95	95	T9HYDJ5	K095A	277	7	Extension and revision of EOSREV1- 1978

^a See text for explanation and key to numbers.

^b Generated by the H-Division PARFAIT code.

^c Generated by the H-Division VITUS code. All subsequent AFEOS were generated with this code.

INTERCOMPARISONS OF PRIMARY DATA BASES

There are no general standards to assess the overall quality of an EOS. However, a specific set of practical standards for hydrogen has been developed in H Division over the years. The following criteria have been applied here:

1. Thermodynamic stability (TDS) and consistency (TDC). (See UCIR 811⁵ for a quantitative analysis of these criteria.)
2. Agreement with experimental data. This is the crucial test for any theoretical model. The full set of experiments included here is as follows:
 - a) 300-K isotherm (Amagat tables)--ideal gas thermodynamics
 - b) Stewart 20-K isotherm to 20 kbar⁶--cryogenic high pressure data.
 - c) Single-shock Hugoniot data--the van Thiel⁷ 40-kbar point, and the 210-kbar point⁸--P, ρ , E data on the shock compressed liquid. There exists a set of independent single-shock experimental data for hydrogen from R. Dick,⁹ ranging from 25 to 150 kbar. Ross¹⁰ has analyzed these data in connection with his study of the LLL-General Motors deuterium shock experiments and concludes that although Dick's data do not agree with van Thiel *et al.*, the size of the uncertainties in the two sets of data are sufficiently large that a single intermolecular potential can produce a theoretical Hugoniot lying within the error bars of both works. Therefore we are referencing only the LLL-GM experimental data, and acknowledging that the LASL-Dick data would also be valid for comparisons.
 - d) Double-shock Hugoniot data--the van Thiel *et al.*⁸ reflected shock point at 870 kbar.

The data used in this study are listed in Table 2.

Although the data are sparse, and the shock data are not of high accuracy, they are all we have, and they do prove difficult to match with precision. Our comparison procedure uses interrogation codes to calculate isotherms (20 K and 300 K), principal Hugoniots (single-shock loci), and reflected Hugoniots (double-shock loci), as well as the various T-relations (TDC indicators), and alternate forms of isentropes (TDC and TDS indicators of a different type).

TABLE 2. Hydrogen-deuterium experimental data.

	T, eV	ρ , mg/m ³	P, Mbar	E, Mbar $\cdot$ cm ³ /g
Stewart pt.	0.0043079	0.4	0.02	0.012 (scaled for D ₂)
H ₂ single shock	0.094791	0.387	0.0395	0.0651 (scaled for D ₂)
D ₂ single shock	0.38776	0.584	0.210	0.8995
D ₂ double shock	0.603188	1.202	0.870	1.375
Amagat tables:	0.02585	1.2575×10^{-3}	7.7707×10^{-6}	
	0.02585	3.4132×10^{-3}	2.1259×10^{-5}	
	0.02585	6.1078×10^{-3}	3.8422×10^{-5}	
	0.02585	8.8024×10^{-3}	5.5936×10^{-5}	
	0.02585	1.1497×10^{-2}	7.3814×10^{-5}	
	0.02585	2.0479×10^{-2}	1.3623×10^{-4}	
	0.02585	3.0180×10^{-2}	2.0906×10^{-4}	
	0.02585	4.2754×10^{-2}	3.1355×10^{-4}	
	0.02585	5.3533×10^{-2}	4.1349×10^{-4}	
	0.02585	6.0718×10^{-2}	4.8651×10^{-4}	
	0.02585	7.3293×10^{-2}	6.2848×10^{-4}	
	0.02585	8.2225×10^{-2}	7.4259×10^{-4}	

The key point of these comparisons is to examine how well the different PDB's exhibit TDC and TDS, how well they match the set of experimental data, and how they agree or disagree with each other. To show the rather complex nature of the two EOS surfaces $[P(T, \rho), E(T, \rho)]$, we present them in Figs. 1 and 2 for EOS95, the current LLL standard EOS. The other PDB's resemble this surface reasonably closely on the scale used here to show the full temperature and density range, from 1×10^{-4} eV to 100 keV, and from 10^{-9} to 3.5×10^4 g/cm³.

In Fig. 3, the shock loci computed for EOS66 are compared with the three shock data points. The principal Hugoniot is 20% too high at the 40-kbar point, and almost 200% too high relative to the 210-kbar point. These serious discrepancies demonstrate that the modifications performed to generate EOS66 from EOSREV1 (which agreed much better with the experimental data) have rendered it dangerously inaccurate. However, the reflected shock, started from its correct P_1 (210 kbar), ρ_1 (0.584 Mg/m³), E (0.8995 Mbar $\cdot$ cm³/g) values comes very close to the experimental point. It should be noted that if the reflected-shock calculation were initiated from the 210-kbar level on the theoretical Hugoniot (rather than the correct experimental value), this agreement would be lost. Also, we see from Fig. 4, that the 20-K isotherm (only

the 20-kbar point is plotted) and the 300-K isotherm are very accurately matched by this PDB. Overall this PDB is reasonable, but its principal Hugoniot is so far off the experimental values that it is not a good choice to use in hydrodynamic calculations.

The KNEW PDB is used to calculate similar principal and reflected-shock loci, and is compared to the same experiments, shown in Fig. 5. The single-shock locus is in very good agreement with the shock data, being exact at 40 kbar, and 10% high at 210 kbar. However, the 870-kbar point lies 25% below the KNEW prediction, a serious discrepancy. The 20-K, 300-K isotherms are plotted in Fig. 6, showing excellent agreement with the experimental data. Also present in this PDB is the two-phase (molecular-metallic) region at 2 Mbar. This data base is quite good, and except for the disagreement with the reflected shock data, is acceptable for hydrodynamic modeling.

The third PDB, EOS95, is used for a similar comparison, as shown in Figs. 7 and 8. The agreement with all three shock points is quite good, the theoretical shock loci lying about 10% high relative to the 210- and 870-kbar points. This agreement has, of course, been forced, in that this 1978 EOS was renormalized to match the experiment as closely as possible. The reason it does not match exactly is that the energy surface was renormalized to render it TDC (as best possible with our existing numerical interpolation codes); this second renormalization moves the theoretical shock loci slightly away from the experimental data. However, this EOS represents the best match to the data of the three standard EOS's under discussion.

The shock loci computed from KNEW and EOS66, compared in Fig. 9, show large discrepancies on the principal Hugoniot for $100 \leq P(\text{kbar}) \leq 10,000$. The double-shock loci show a maximum second-shock compression of about 2.4 g/cm^3 , and the differences between these two tracks are good indicators of the differences one would see in isentropic paths over this same density range. In Fig. 10, the two shock loci are shown compared to the experimental data. In Fig. 11, the 20-K and 300-K pressure isotherms are compared, both agreeing with the static, isothermal data. There is a cohesive loop in the KNEW surface 20-K isotherm not present in EOS66, and a two-phase region in both KNEW isotherms at approximately 2 Mbar, also not present in EOS66.

A more significant comparison is shown in Fig. 12, showing the shock loci calculated from KNEW and EOS95. These EOS's show excellent agreement on the principal Hugoniot to 250 kbar, but diverge dramatically from there. At 3 Mbar they predict densities on the Hugoniot that differ by a factor of 2.

Along the reflected shock locus, disagreement increases to 25% at 1 Mbar and again significant differences are seen near maximum compression. The double-wave structure in the EOS95 shock loci are due to pressure dissociation of the H_2 molecule (the first, large peak) and then pressure ionization of the H atom (the second, small peak). These features are much less pronounced in the KNEW shock loci. A higher resolution view of these two Hugoniot is shown in Fig. 13, together with the shock data. Here the differences between the models are magnified, showing that although they are very close to the shock data at 210 kbar, and not too bad at 870 kbar, yet they differ dramatically just slightly higher in pressure. In Fig. 14, the theoretical isotherms are compared to the static isothermal data, both agreeing well. The cohesive loop and two-phase region in the KNEW model are absent from the EOS95 surface.

A final comparison is given between KO42 and KNEW in Fig. 15 and between KO42 and EOS95 in Fig. 16. The scale of these figures is much larger than the foregoing plots, so that the actual large discrepancies between KO42 and both standard PDB's are reduced. However, KO42 is off at 40 kbar by a factor of two in pressure, and at 210 kbar by 25%. In the 500-kbar to 5-Mbar range it is qualitatively different than either modern Hugoniot. From about 15 Mbar upwards it agrees roughly with both standard Hugoniot, which is to be expected as they are all based on TF theory in this regime. In sum, the KO42 surface is a very bad approximation to either the experimental data, or the modern EOS surfaces accepted as standards.

INTERCOMPARISON OF ANALYTIC-FIT EOS'S

For use in hydrodynamic simulation codes, the PDB's must be converted to either analytical fits or fast tabular interpolation forms. In this section we will review the analytic fit EOS representations. These range from a simple Grüneisen model, to polynomial forms, to the most complex LLL method--the 28-term ratio of polynomial form (28 ROP for brevity). This sequence describes an evolutionary trend in AFEOS's that occurred over the period 1963-1978. The early simpler AF's (Grüneisen and polynomial) are fast but are limited in range usually to the 1-to-10-Mbar pressure range, and to a segment of $P(E,\rho)$ surface lying near or between the principal Hugoniot and the principal adiabat. Points that lay well away from this surface segment could be in error (relative to the PDB) by many orders of magnitude. Also, severe

pathologies (poles, negative pressures, negative compressibilities) would also occur over extensive regions. In the last few years, the more complex 28 ROP was designed to represent the entire $P(E,\rho)$ surface, and eliminate or greatly reduce singularities and negative P 's and B_T 's. It could extrapolate in all directions very accurately, and was given the capability of being "laced" or strongly tied to either selected parts of the PDB surface or to a selected set of the experimental data. Various demonstrations of these capabilities will be evident as we analyze and exhibit the various hydrogen AFEOS surfaces. Our analysis of fit adequacy (by use of extensive plot comparisons) is based on earlier assessments that used the rms error of $(|P_{\text{fit}} - P_{\text{PDB}}|/P_{\text{PDB}})$ as a key adequacy criterion, together with a non-pathological surface in the limited $P(E,\rho)$ range between the principal Hugoniot and the principal adiabat. Due to poor analysis tools, previously accepted fits would pass the above tests, yet be a poor match to the experimental data. They could include pathologies, substantially distort certain hydrodynamic paths, or significantly amplify existing distortions in the PDB. To ensure that these defects are detected, we chose the set of plots that will be discussed later in this report. It should be noted that these AFEOS are intended for pure hydrodynamic modeling, so they represent P as a function of E and ρ , the temperature variable being eliminated. Also, they are least squares fits, so the AF surfaces are only approximations to the exact PDB surface, typical rms deviations of the pressures ($\Delta P/P$) being in the range of 3 to 10%. There are times when a fit to the PDB is also forced to fit experimental data points where the PDB does not pass exactly through the experimental data. In this case there are two noncongruent surfaces presented to the fitting code, thereby resulting in deviations from one or the other. Such discrepancies will be noted in comparisons to follow.

The AF's examined in this study include: KO49, a restricted range fit to the EOSREV1 PDB (or an earlier predecessor of this PDB), which was not forced to either PDB or experimental data; KO109, a recent wide range AF to EOS66 and constrained to the three shock data points; AF 55A, an early AF to the KNEW PDB with a restricted range and not force fit; AF 55B, a refit of KNEW which was forced to fit the PDB in the 100-kbar to 10-Mbar range and was applicable over a wide range; and AF 95A, a wide range fit to EOS95, forced to fit the three shock data points. These fits are evaluated in terms of their rms fit to the underlying PDB, as given in the various HERF reports.¹¹ The plots discussed here show how the overall $P(E,\rho)$ surface is covered by an AF

generated surface. Figure 16 shows how the restricted-range AF's depart radically from the correct EOS surface outside their range of fit, where is an accurate $P(E,\rho)$ AF surface is depicted for hydrogen.

First we examine the K049 AF surface, used from 1974-76 for certain studies. This surface (Fig. 17) is reasonable from 0.1 to 100 g/cm³ and either pathological or grossly in error outside that range. In Fig. 18, all those points where $\Delta P/P$ (fit minus PDB over the PDB value, i.e., fractional pressure error) exceeds 20% is plotted, showing concentrations of error in three areas. The area where no errors greater than 20% are found is the range over which the fit was made. A more significant comparison is given in Fig. 19, where the principal Hugoniot and reflected shock paths are given for K049 and for EOS66. The agreement is quite good up to 20 Mbar, which covers the main area of interest. A higher resolution plot, Fig. 20, shows the agreement of these models with the experimental shock data. Typical of AF's (also visible in Fig. 19) is their inability to follow structure or rapid change in the PDB surface. One unfortunate feature of K049 is that it gives a much stiffer double-shock locus than the PDB, thus missing the 870-kbar point by 200 kbar. This AFEOS is clearly a poor choice for hydrogen, at least in the pressure density range given in Fig. 20.

Next let us examine the two AF's made to the LASL KNEW database. An earlier AFEOS, described in HERF37 was a restricted range AF to an earlier Kerley D₂ EOS, but this is superseded by the fits described here. In Fig. 21, the AF 55A surface is calculated over the full T,ρ range of the KNEW PDB, showing its character as a restricted range fit with severe pathologies at lower densities and higher temperatures. For reasons that are not clear to us, both the LLL and LASL hydrogen data bases were rather difficult to model by good AF's. The $\Delta P/P \geq 20\%$ error points are superimposed on this same surface in Fig. 22. The region of good fit is very restricted. The final comparison for this fit, Fig. 23, shows a reflected-shock path for AF 55A that lies 500 kbar below the same path calculated from the KNEW PDB at the density of the 870-kbar shock experiment. This set of curves identified AF 55A as a very poor EOS representation, which distorted the surface too badly to be usable. We proceeded to carry out a higher quality fit using the VITUS code, the result designated as AF 55B.

The resulting AFEOS surface is illustrated in Fig. 24, showing an excellent wide range AF, which will extrapolate nicely to high and low ρ , and to high T . There are no evident pathologies (although sharp singularities

can exist and not be visible in such a plot due to the point spacing). The $\Delta P/P \geq 20\%$ error points are concentrated along the low temperature isotherms in the range $1 \leq \rho/\rho_{liq} \leq 100$, as is reasonable due to the strong curvature of these isotherms and the discontinuities produced by the two-phase region (1.5 to 2 g/cm³). A further comparison of the principal Hugoniot and 210-kbar (initial pressure) double-shock locus, in Fig. 25, shows very good replication of the PDB paths by the AF. A higher resolution plot, Fig. 26, shows how good this fit is, only losing perfect registration where the Hugoniots exhibit rapid curvature. By lacing or forcing the AF tightly to the PDB surface, this AFEOS gives a hydrodynamic representation that is very close to the PDB itself. Note that by choosing to force the fit to the PDB and not to the experimental data, the double-shock locus predicted by AF 55B will lie some 400 kbar above the 870-kbar experimental point, as does the PDB locus. A final comparison, Fig. 27, is between AF and PDB along the 20-K and 300-K isotherms. The deviation of the 20-K isotherm is probably due to not being included in the data set that was used to produce AF 55B. Also, we see that the fits do a good job of "smoothing" through the phase transition.

The next AFEOS to be considered is K0109, the AF to the EOS66 PDB. The full ρ, T range surface generated by the K0109 AF is displayed in Fig. 28, showing the same wide range, excellent extrapolatory character and apparent freedom from pathology as seen in the previous fit. The same clustering of $\Delta P/P \geq 20\%$ errors in the $1 \leq \rho/\rho_{liq} \leq 100$, low T range is seen, again due to rapidly changing character of the pressure surface here (Fig. 29). An additional set of error points is evident, at low density and in the $1\text{-to-}10\text{-e}^4$ range. These points are here because EOS66 contains a detailed treatment of the H₂ molecular dissociation (the lower irregular band, 10^{-7} to 10^{-2} g/cm³) and the H-ionization regions (the upper band), which are only treated apparently in an average form in the KNEW data base. In Fig. 30, the principal Hugoniot and double-shock locus are given for both K0109 and EOS66. The AF was fit to EOS66 with a strong weighting toward the experimental shock points, and the result of such a procedure is evident. Where the PDB Hugoniot passes far above the 210-kbar point, the AF Hugoniot lies quite close to it. However, the price paid for trying to force the AF to pass through two noncongruent surfaces (the PDB and the surface defined by the three shock points) shows by the cutoff of the AF principal Hugoniot at 500 kbar, indicating there were convergence problems in continuing the calculation beyond this point. This pathology is probably related to the force-fitting

procedure, but this does not necessarily imply that this AFEOS will cause hydrodynamic problems as the codes use a von Neumann Q to generate shock states. As seen in Fig. 31, the reflected-shock locus from the AF lies 200 kbar above the experimental point, which is poor but acceptable. A final comparison of the 20-K and 300-K isotherms is given in Fig. 32, for the K0109 and EOS66 surfaces, again compared to the experimental data. Registration is excellent at 300 K, and adequate for 20 K at $\rho < \rho_{\text{liq}}$. The K0109 AFEOS represents an actual improvement over the PDB (EOS66) from which it was generated, in that it is a close fit overall, and produces a much better principal Hugoniot. However, the severe deficiencies of EOS66 make K0109 a less desirable choice than the newer EOS to be described.

The final hydrogen EOS, EOS95, was a further modification of the LLL sequence, attempting to improve the overall quality by forcing a match to the experimental data. The AF 95A fit to this surface is illustrated in Fig. 33, showing the same high quality wide range features as seen for K0109. The quality of this fit was so good that there were very few errors greater than 10%. The $\Delta P/P \geq 10\%$ error points are superimposed on the AF 95A surface in Fig. 34, far fewer in number than previous fits, but still located in the low-T, medium-density region and along the dissociation and ionization zones. In Fig. 35, the two standard-shock loci are plotted. The inability of these analytic fits to follow rapidly changing surfaces is more evident in this surface which has more structure and detail than any of the others. A closer comparison of the shock loci is given in Fig. 36, as well as the experimental data. The fit passes almost exactly through the experimental shock data, as expected, but the pressure dissociation loops are displaced relative to the PDB Hugoniot. A final comparison is given for the 20-K and 300-K isotherms with the static data in Fig. 37. Again the agreement is good. Our final assessment is that EOS95 and its AF, 95A, are the best available hydrogen thermodynamic models available at present.

INTERCOMPARISON OF THE TABULAR BQL EOS REPRESENTATIONS

A second and completely different type of numerical representation of the EOS primary data base is the use of some numerical interpolation algorithm chosen to fit the data, which is then reduced to a tabular array (two-dimensional, usually in T and ρ) stored for pressure and internal energy in a material properties library. Two different forms used by us are

the biquadratic Lagrange interpolation (BQL) and the EVOL form,⁴ a bilinear interpolation in logarithmic variables, with EOS derivatives computed by a higher order method and also tabulated along with the two EOS's.

In Fig. 38, a high resolution plot of the two shock loci from BQL275 and the EOS66 primary data base are compared to the experimental shock points. The BQL EOS is unfortunately even farther away from the data than the PDB loci, that is, the fit procedure producing the tabular form has distorted the surface slightly, but in a way that worsens its Hugoniot predictions. BQL275 should be avoided for modeling hydrogen at pressures below 50 Mbar.

The comparison of the principal Hugoniot and the double-shock locus are shown in Fig. 39, for BQL277 and the EOS95 PDB. As is evident, the agreement is excellent, the double loop structure in both PDB loci being closely represented by the tabular EOS curves. The only deviations are in the range of 4 to 50 kbar and are unimportant. A closer comparison of these same curves is presented in Fig. 40, this time with the experimental shock data added. The BQL shock paths are as good as those derived directly from the PDB; the 210-kbar point lying exactly on the BQL principal Hugoniot. The maximum discrepancies (above 50 kbar) between the two sets of shock loci are no more than 10% in pressure, and are usually less. A final test of the BQL 277 surface is given in Fig. 41, where the 20-K and 300-K isotherms from BQL 277 and EOS95 are compared, and the static isothermal experimental data are added. The 300-K isotherm is accurately represented, but the 20-kbar, 20-K static point is not, probably due to the truncation of the PDB data used in the actual BQL fit generation (data below room temperature are often deleted from PDB's, if present, because they are not generally relevant to hydrocode simulations). Overall, the BQL representation of EOS95 is quite good, and is adequate to represent the LLL standard hydrogen EOS until either an improved theoretical model is completed, or better, until improved experimental shock data are acquired.

It is worth emphasizing here how important experimental shock data have been, as they represent the extreme limit, in temperature and density, of our true knowledge of the hydrogen EOS. Clearly more shock data, of higher accuracy and in the higher pressure regime are very badly needed if we are to improve our thermodynamic models.

HYDRODYNAMIC SENSITIVITY STUDIES

Studies of how a material's thermodynamic properties affect its hydrodynamic response in different conditions have been carried out for a variety of materials in different geometries and different pressure-temperature regimes. Two such studies have been documented for hydrogen, and some data for a third will be briefly discussed here.

The first documented hydrogen EOS hydrodynamic analysis is basically a comparison of high pressure hydrodynamic response between the AF EOS's, K042 and K049. The basic conclusion was that there were substantial reasons for preferring K049 over K042. The second documented study, by Marino,¹² which was recently completed, consisted of a hydrodynamic analysis assessing the adequacy of the analytic fits of the two standard PDB's, KNEW and EOS95.

In addition to these studies, G. Carlson has provided some density-temperature loci that are of interest in applying the hydrogen EOS. A sequence of high pressure, high compression points are plotted in Fig. 42, where the given values are energy, E , and density, ρ . From these E, ρ values pressures were calculated from a selection of the various EOS forms and then were plotted. Also included are the three shock data points, both the experimental P, ρ values, and the various EOS predictions for these points.

We see that AF 95A does the best job of matching the experimental Hugoniot points. In addition, there are large differences (on the order of 40%) between EOS's along the Carlson track. AF 55B approaches and agrees with AF 95A at high compressions, where K042 remains in poor agreement along the entire path. For high compression, high energy applications, AF 55B and AF 95A are equivalent. However, at low compressions, the differences can be substantial and AF 95A is probably the best representation in that regime.

SUMMARY AND CONCLUSIONS

Throughout this study, we have found EOS 95 and its representations to be the best data set for a wide range of applications. Its agreement with experiment is good and its use in hydrodynamic studies has given very satisfactory results.

There is a need, however, for more high quality experimental data in order to better define the compression regime of hydrogen. This will not only help in constraining the representations, but can also give definition to the EOS surface where we have had little help from theoretical models.

In addition, EOS'95 does not include the molecular-metallic phase transition (as KNEW has) and this should be considered in the next generation of the hydrogen EOS.

ACKNOWLEDGMENTS

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FIG. 1. Pressure EOS as a function of ρ , with T as a parameter for EOS95 for the full T, ρ range.

FIG. 2. Energy EOS for EOS95 for the full T, ρ range.

FIG. 3. Principal Hugoniot, and reflected-shock locus from the 210-kbar point, calculated from EOS66 PDB, compared to the (a) 40- and (b) 210-kbar single-shock experimental data points, and the (c) 870-kbar double-shock point.

FIG. 4. The 20-K and 300-K pressure isotherms from EOS66, compared to the experimental data.

FIG. 5. Principal Hugoniot (PH) and reflected-shock locus (RSL) from the 210-kbar point, calculated from KNEW PDB compared to the experimental data (x).

FIG. 6. The KNEW PDB 20-K and 300-K isotherms, compared to the experimental data.

FIG. 7. The EOS95 PDB principal and reflected Hugoniot, compared to the shock experiments.

FIG. 8. The EOS95 PDB 20-K and 300-K isotherms, compared to the experimental data.

FIG. 9. Shock loci (PH and RSL) from KNEW and EOS66.

FIG. 10. Shock loci from KNEW and EOS66 compared to the experimental data.

FIG. 11. The 20-K and 300-K isotherms from KNEW and EOS66 compared with static data.

FIG. 12. Shock loci from KNEW and EOS95. Note the qualitative differences in these two theoretical models that appear above 200 kbar on the PH and above 1 Mbar on the RSL.

FIG. 13. Shock loci from KNEW and EOS95 compared to the experimental shock data.

FIG. 14. The 20-K and 300-K isotherms from KNEW and EOS95, compared to the static isothermal data.

FIG. 15. Principal Hugoniot from KO42 (computed by performing shock compressions using the KOVEC code) and KNEW.

FIG. 16. Principal Hugoniot from KO42 and EOS95.

FIG. 17. KO49 AFEOS (pressure as a function of ρ for constant energy as a parameter) evaluated over the T, ρ range of EOS66.

FIG. 18. KO49 AFEOS $\Delta P/P \geq 20\%$ pressure errors relative to EOS66 PDB values.

FIG. 19. KO49 principal and reflected-shock loci compared to equivalent EOS66 paths.

FIG. 20. KO49 and EOS66 shock loci compared to the shock data.

FIG. 21. 55A AFEOS
evaluated over the T, ρ
range of KNEM.

FIG. 22. 55A AFEOS with
 $\Delta P/P \geq 20\%$ points.

FIG. 23. Shock loci from 55A AFEOS and the KNEW PDB, compared to shock data. Note that the poor quality analytic fit comes much closer to the 870-kbar experimental point due to weighting.

FIG. 24. 55B AFEOS evaluated over the T, ρ range of KNEW. $\Delta P/P \geq 20\%$ error points superimposed, showing a high quality fit to the underlying data.

FIG. 25. Principal Hugoniot and reflected shock locus from AF55B compared to the same tracks computed from KNEW PDB.

FIG. 26. Shock loci from AF55B and KNEW, compared to shock data.

FIG. 27. The 20-K and 300-K isotherms from AF55a and KNEW, compared to the static isothermal data.

FIG. 28. KO10; AFEOS evaluated over the full P, ρ range of EOS66 PDB.

FIG. 29. K0109 AFEOS with $\Delta P/P \geq 20\%$ error points are superimposed.

FIG. 30. Principal Hugoniot and double-shock locus from K0109 and EOS66 compared.

FIG. 31. Shock loci from K0109 and EOS66 compared with experimental shockwave data.

FIG. 32. The 20-K and 300-K isotherms from K0109 and EOS66 compared to the experimental data.

FIG. 33. AF95A pressure surface evaluated over the full T, ρ range of EOS95.

FIG. 34. Segment of same surface with $\Delta P/P \geq 10\%$ error points superimposed.

FIG. 35. Principal Hugoniot and reflected-shock locus calculated from AF95A and the EOS95 PDB. Even the very high quality AF does not give $P(\rho, E)$ surfaces which track the PDB Hugoniot closely at all points. Weighting the AF to the experimental data may be responsible.

FIG. 36. The two shock loci from AF95A and EOS95, compared to the experimental shock data.

FIG. 37. The 20-K and 300-K isotherms from AF95A and EOS95, compared to the static isothermal data.

FIG. 38. Principal Hugoniot and double-shock locus from BQL275 (trace) and EOS66 (dash), compared to the experimental data.

FIG. 39. Principal Hugoniot and double-shock locus from BQL277 and EOS95.

FIG. 40. Two shock loci from BQL277 and EOS95, compared to the experimental data.

FIG. 41. The 20-K and 300-K isotherms from BQL277 and EOS95, compared to the experimental data.

FIG. 42. Carlson's P, η sequence, as evaluated by different EOS's, shown as curves. The Hugoniot points for the single- and double-shock points for the different EOS's are also shown with the experimental data.

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