LA-UR-15-27354
Approved for public release; distribution is unlimited.

Title: SESAME 7363: A New Li(6)D Equation of State

Author(s): Sheppard, Daniel Glen
Kress, Joel David
Crockett, Scott
Collins, Lee A.
Greeff, Carl William

Intended for: Report

Issued: 2015-09-21

SESAME 7363: A New ^{6}LiD Equation of State

Daniel Sheppard, Joel D. Kress, Scott Crockett, Lee A. Collins, and Carl Greeff
(Dated: September 10, 2015)

A new Equation of State (EOS) for Lithium 6 Deuteride (^{6}LiD) was created, SESAME 7363. This EOS was released to the user community under "eos-developmental" as SESAME 97363. The construction of this new EOS is a modification of a previously released EOS, SESAME 7360[1]. SESAME 7360 is too stiff (5-10% excess pressure) at high compressions and high temperatures (ρ = 4-110 g/cm^3, T = 30-10,000 eV) compared to orbital-free density-functional theory. SESAME 7363 is softer and gives a better representation of the physics over this range without compromising the agreement with the experimental and simulation data that SESAME 7360 was based on.

The goal in creating SESAME 7363 was to preserve the compression behavior of SESAME 7360 for ambient and shock conditions, where agreement with experimental and simulation data was already good, while softening the high temperature behavior so the equation of state (EOS) would more rapidly converge to the ideal gas limit which is predicted by orbital-free density-functional theory (DFT).

The EOS code OPENSESAME is based on the assumption that the Helmholtz free-energy (F) can be separated into three pieces,

$$F(\rho,T) = F_{\rm cold}(\rho, T=0) + F_{\rm nuc}(\rho,T) + F_{\rm ele}(\rho,T). \quad (1)$$

where $F_{\rm cold}(\rho)$ is the cold-curve, $F_{\rm nuc}(\rho,T)$ is the nuclear model (contribution from thermal motion of the atoms), and $F_{\rm ele}(\rho,T)$ is the excitation of the electrons. $F_{\rm cold}(\rho)$ dominates the compression behavior of an EOS for low temperatures and is the primary input for insuring that the principle Hugoniot calculated from the EOS matches all of the data accessible from single-shock experiments. For ^{6}LiD we assume a Mie-Grüneisen form for EOS which allows for a cold-curve to be extracted from a fit the the shock (u_s) vs particle (u_p) speed along the principle Hugoniot[2]. At moderate compression ($\eta = \rho/\rho_0 = 1.5 - 3.0$) the cold-curve changes over to a cold-curve calculated from a Thomas-Fermi-Dirac (TFD) average atom model. This softens the cold-curve at high densities where the Mie-Grüneisen form becomes too stiff. There is almost no contribution of $F_{\rm ele}(\rho,T)$ to the total free-energy at low temperatures but once temperature is of order 1 eV this term makes a significant contribution to the EOS. There is no shell structure or relativistic effects in TFD but it does become exact at very high temperature and high pressure. $F_{\rm nuc}(\rho,T)$ was developed by J.D. Johnson[3] (jdjnuc) and contains a Debye vibrational model in the solid phase with a standard Debye temperature ($\Theta_{\rm D}$) and function $\gamma(\rho/\rho_0)$ which has a single maximum at $0 < \eta < 1$, and is typically set so $\gamma(\eta = 0) = 1$ and slowly decays so that $\gamma(\eta \to \infty)$ is a fixed value on the order of 2/3. $\gamma = 2/3$ is based on the theoretical value for γ of an ideal gas. The jdjnuc model also contains a Lindemann melt model at which point the heat capacity ($C_{\rm v}$) decays from $3k_{\rm B}$ to the ideal gas limit of $\frac{3}{2}k_{\rm B}$ as T$\to\infty$. $k_{\rm B}$ is the Boltzmann constant.

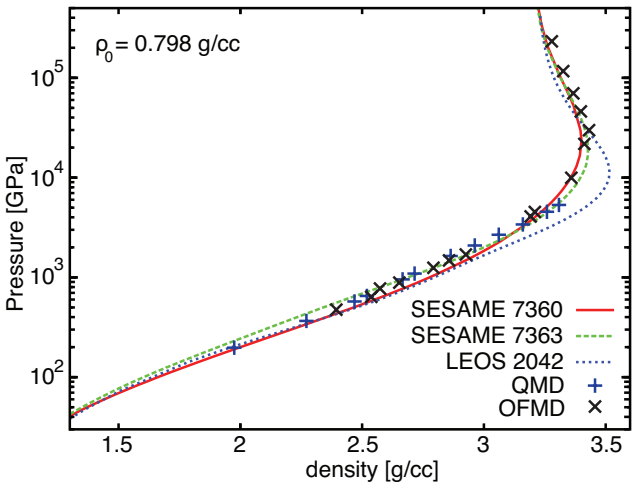

FIG. 1: Hugoniot for ^{6}LiD with initial density $\rho_0 = 0.798$g/cm^3. Blue plus signs are KSMD calculations and black crosses are OFMD results bootstrapped to KSMD results. Results from SESAME 7360 and 7363 are red solid and green dashed lines, respectively. Livermore's LEOS 2042 is shown as a blue dotted line.

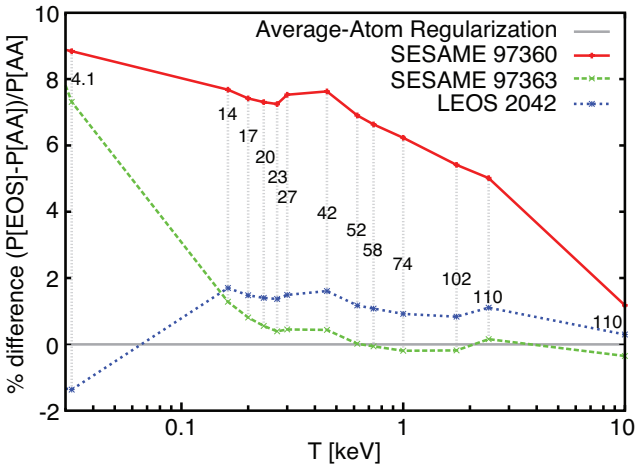

FIG. 2: Percent difference in pressure relative to an average-atom calculation. Results from SESAME 7360 and 7363 are red solid and green dashed lines, respectively. Livermore's LEOS 2042 is shown as a blue dotted line. The density of each calculated point is indicated from 4.1 to 110 g/cm^3.

The simplest way to reduce the pressure at high compression is to reduce γ_∞ and increase $d\gamma$ (a parameter which controls how fast $\gamma(\eta)$ goes to γ_∞). Reducing γ_∞ had the adverse effect of distorting the fits to the Hugoniot while not significantly reducing the over-pressure at high compression. $\gamma(\rho_0)$ cannot be modified without adverse effects on reproducing the thermal expansion data. The $\gamma(\eta)$, in jdjnuc, does not have enough flexibility to both compensate for the Hugoniot match while γ decays enough not to have residual over-pressures at high compression. In practice, models need to represent an accurate picture over 6-7 orders of magnitude in ρ and 10 orders of magnitude in T.

The solution to modifying the ^{6}LiD EOS for SESAME 7363 was to extend the u_s/u_p fit along the principle Hugoniot to include both experimental and theoretical calculations based on Kohn-Sham (KS) DFT molecular dynamics (MD) simulations[1] to $\rho \sim 3.3$ g/cm^3. In SESAME 7360 u_s/u_p was fit to only experimental data[4], which extended to $\rho \sim 1.3$ g/cm^3. This new cold-curve is stiffer at intermediate compressions and is able to match the Hugoniot with a smaller contribution from $F_{\rm nuc}(\rho, T)$. Figure 1 shows the principle Hugoniot calculated from SESAME 7363 and 7360 in addition to comparisons to Livermore's LEOS 2042. The extra compressibility in LEOS 2042 is due to an electronic model based on PURGATORIO[5] which contains shell structure. In principle, this discrepancy between PURGATORIO and TFD could be addressed using KS-MD, a level of theory which also contains shell structure. However, in practice, computational demands limit the KS-MD simulations to T<30 eV[1].

Extracting the cold-curve from a much wider compression range gave enough flexibility in $F_{\rm nuc}(\rho, T)$ to match new calculations based on a Thomas-Fermi-Perdew-Zunger (TFPZ) orbital-free-DFT regularization average-atom model[6] (denoted "AA"), using $Z_{\rm avg}$=2 and $A_{\rm avg}$=4g/mol while maintaining a good match to shock-data. We verified that AA pressures agree well with orbital-free-DFT MD simulations for T > 50 eV. Figure 2 shows the percent difference in pressure from the AA calculations, which we consider the best physics in this regime. Although LEOS 2042 better matched the AA pressures compared to SESAME 7360, our new release of SESAME 7363 eliminates the ∼2% over-pressure that still persists in LEOS 2042.

We suspect that the decay of C_v(T) as T increases, in jdjnuc, is partially to blame for high temperature dependence on $\gamma(\eta)$. More calculations are needed to study this issue in depth. We would emphasize that a concerted effort is needed to refine and develop new physics based models that are robust and accurate over a wider range of density and pressure space. The multiphase effort at LANL is taking a significant step in the right direction.

[1] D. Sheppard, J. D. Kress, S. Crockett, L. A. Collins, and M. P. Desjarlais, Phys. Rev. E **90**, 063314 (2014).
[2] G. I. Kerley, *User's manual for* PANDA*: a computercode for calculating equations of state* (Los Alamos National Laboratory Laboratory REPORT LA-8833-M, Los Alamos NM, 1981).
[3] J. D. Johnson, High Press. Res **6**, 277 (1991).
[4] S. P. Marsh, *LASL Shock Huginiot Data* (University of California Press, Berkeley CA, 1980).
[5] B. Wilson, V. Sonnad, P. Sterne, and W. Isaacs, J. Quant. Spectrosc. Radiat. Transfer **99**, 658 (2006).
[6] F. Lambert, J. Clérouin, and G. Zérah, Phys. Rev. E **73**, 016403 (2006).