Quantum Molecular Dynamics Simulations for Generating Equation of State Data

Michael P. Desjarlais

Pulsed Power Sciences
Sandia National Laboratories
Albuquerque, NM 87185

Abstract. Quantum molecular dynamics simulations based on density functional theory have emerged in recent years as a powerful tool for generating much needed data for equation of state development. We report here on some general issues, key equation of state landscape features, and specific results related to Hugoniot, isentrope and liquid-vapor critical point calculations.

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INTRODUCTION

Wide-range equation of state development has historically relied heavily on experimental data where available. Free energy functions with adjustable parameters are often tuned to the available data and well-trusted theoretical models. Most commonly available at higher pressures is shock Hugoniot data and cold curve data obtained with diamond anvil cell techniques. However, this leaves a large region of phase space unmapped by experiments and a great deal of uncertainty in modeling. For example, liquid-vapor critical points for metals have only been measured for the alkali metals and mercury, all of which have relatively low temperature critical points. As a consequence, even relatively well-understood materials like aluminum exhibit large variations in critical point pressure, density, and temperature within the different aluminum models available in equation of state models and databases. Principal and release isentropes are also key landscape features and contain important information on sound speeds and the Gruneisen $\Gamma$, which, if measured or accurately calculated, place constraints on the equation of state. However, high pressure isentrope data has only recently become available with the development of ramp-loading experimental techniques. Molecular dynamics based on density functional theory --- quantum molecular dynamics or QMD --- is a powerful method for generating synthetic data and mapping key landscape features. This short paper will discuss a few techniques for generating much needed data for equation of state development.
COMPUTATIONAL METHODS

The calculations discussed here were performed with the VASP code, a plane-wave density functional code [1]. Exchange and correlation functionals were of the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form. We use projector augmented wave (PAW) all-electron, frozen-core, potentials for the atoms [2]. We generally perform our calculations in the canonical ensemble with either velocity scaling or a Nosé-Hoover thermostat to regulate the temperature. Fermi statistics are used to thermally occupy the electronic degrees of freedom at the same temperature as the ions. The molecular dynamics simulations generally cover anywhere from 2 to 20 picoseconds of real time. Typical time-steps are on the order of 1 femtosecond. The number of atoms can range from several dozen to several hundred, depending on the material, region of phase space being modeled, and the number of valence electrons per atom.

HUGONIOT CALCULATIONS

The Hugoniot is the locus of single shock end states satisfying the Rankine-Hugoniot conditions for various particle velocities $u_p$. Hugoniot calculations are based on finding solutions to the Rankine-Hugoniot relations.

\[
\frac{\rho_1}{\rho_0} = \frac{U_s}{(U_s - u_p)}
\]

\[
U_s u_p = \frac{(P_1 - P_0)}{\rho_0}
\]

\[
E_1 - E_0 = \frac{P_1 + P_0}{2}(V_0 - V_1)
\]

In practice, the most straightforward approach to constructing the Hugoniot is to iteratively search over density or temperature for solutions of the energy conservation relation. There are numerous examples of these calculations in the literature and we won’t go in to much discussion here. Reference [3] demonstrates the calculations of 1st, 2nd, and 3rd shock Hugoniots for deuterium and also emphasizes the importance of obtaining convergence of both energy and stresses for accurate Hugoniot calculations. Hugoniot calculations for tungsten are shown in Fig. 1, with solid (BCC) tungsten at low pressures and liquid at high pressures. The Hugoniot is plotted in terms of the particle velocity $u_p$ and the shock velocity $U_s$. Also shown are linear fits (see inset) for the two regimes. Note that the crossing of the two asymptotic fits is not in general a reliable indication of the location of melt. The multipliers next to each QMD Hugoniot point indicate the compression relative to ambient density. The linearity of the

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Hugoniot \((u_p, U_s)\) relation in the two regimes is a common but by no means universal feature of Hugoniots.

**FIGURE 1.** The Hugoniot for tungsten, calculated for solid and liquid phases. Also shown are linear fits to the solid and liquid Hugoniot branches.

**ISENTOPE CALCULATIONS**

The calculation of isentropes is essentially a solution of the curve \(dS=0\), were \(S\) is the total entropy. Beginning with the total differential for the entropy in the Canonical Ensemble

\[
dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV
\]

and two Maxwell identities relating \(S\) to the pressure \(P\) and total energy \(E\)

\[
\frac{\partial S}{\partial T} = \frac{1}{T} \frac{\partial E}{\partial T} \quad \frac{\partial S}{\partial V} = \frac{\partial P}{\partial T}
\]

we construct an equation relating the temperature change along the isentrope to the volume change and the change and pressure relative to energy at constant volume:
\[
\frac{1}{T} \, dT = - \frac{\partial P}{\partial E/\partial T} \, dV = - \frac{\partial P}{\partial E} \bigg|_V \, dV.
\] (3)

Piecewise integration gives

\[
\frac{T_{i+1}}{T_i} = \exp \left[ - \int_{V_i}^{V_{i+1}} \frac{\partial P}{\partial E} \, dV \right].
\] (4)

Equation 4 is the foundation for the isentrope calculations. Note the integrand is $\Gamma/V$, where $\Gamma$ is the Gruneisen $\Gamma$. For regions of phase space where $\Gamma/V \sim$ constant, typically condensed matter systems, it is advantageous to approximate $\partial P/\partial E$ as piecewise linear for the purpose of carrying out the integration in Eq. 4. This leads to

\[
T_{i+1} = T_i \exp \left[ \frac{1}{2} \left( \frac{\partial P}{\partial E_i} + \frac{\partial P}{\partial E_{i+1}} \right) (V_i - V_{i+1}) \right].
\] (5)

Alternatively, for higher energy density conditions (e.g., release from a high pressure shock state) it is more advantageous to assume $V \, \partial P/\partial E$ is piecewise linear, which leads to

\[
T_{i+1} = T_i \exp \left\{ \left( V_i \frac{\partial P}{\partial E_i} - V_{i+1} \frac{\partial P}{\partial E_{i+1}} \right) - \frac{V_i V_{i+1}}{V_{i+1} - V_i} \left( \frac{\partial P}{\partial E_i} - \frac{\partial P}{\partial E_{i+1}} \right) \ln \frac{V_{i+1}}{V_i} \right\}.
\] (6)

For situations where $V \, \partial P/\partial E \sim$ constant, this simplifies to

\[
T_{i+1} \approx T_i \exp \left\{ - V_i \frac{\partial P}{\partial E_i} \ln \frac{V_{i+1}}{V_i} \right\}.
\] (7)

The step variables $\partial P/\partial E_i$ are determined by differencing two steady state calculations separated by slightly different temperatures, above and below the target temperature. In practice, long calculations may be necessary to get adequate convergence of the thermodynamic differences.

Figure 2 shows the results of this approach applied to aluminum starting from ambient conditions (circles), along with a quasi-isentrope obtained as a series of small shocks (diamonds), isentropic compression data [4] from Sandia’s Z machine, and isentropes from two SESAME tables. Note that the experimental data is adjusted for strength to compare with the hydrostatic equations of state and calculations. The Z isentrope data lies almost directly on top of the SESAME 3700 data and is difficult to separate in the plot. The density steps used in this isentrope calculation are on the order of 15% increase over the previous density iterant. These relatively large steps are possible because we are integrating Eq. 4 over a variable that is weakly varying.
We’ve also confirmed that the Gruneisen $\Gamma$ obtained through these calculations is in very good agreement with data. This approach is equally viable for release isentropes from shocked states and we have calculated release isentropes for aluminum from multi-Mbar states on the principal Hugoniot.

Figure 2. The aluminum isentrope from isentrope compression experiments on Z [4], two SESAME equations of state, a quasi-isentrope generated from a series of small shocks, and the calculated isentrope. The Z isentrope lies nearly on top of the SESAME 3700 isentrope and is difficult to distinguish in the plot. The Z data, SESAME 3700, and the QMD results are all in good agreement.

Figure 3 shows the temperature versus density for the same calculations and equations of state. (Temperature data wasn’t obtained on the Z experiments.) Here the difference between the isentrope calculation and the multiple shock quasi-isentrope is much more apparent.

LIQUID-VAPOR CRITICAL POINTS

Liquid vapor critical points have proven to be very difficult to obtain experimentally for the common metals of high energy density physics experiments. The main problem is maintaining and diagnosing under static conditions the high temperature and pressures required. However, this region of phase space is very important for modeling many current high energy density physics experiments. Aluminum shocked to several Mbar, will release in to the two-phase region. Exploding wires will expand and release into the two-phase region and this has
important ramifications on conductivities and current paths. An error in the location of the liquid-vapor critical point can have serious consequences for the fidelity of large-scale simulations. QMD simulations offer a possible alternative to high-pressure experiments for locating liquid-vapor critical points. In these simulations we are not trying to model the phase separation, but instead look for the critical point directly by searching for the diverging isothermal compressibility characteristic of the liquid-vapor critical point.

**FIGURE 3.** The temperature along the isentrope for two SESAME equations of state and the QMD calculations. Note the much more rapid temperature rise for the quasi-isentrope case. The QMD temperatures are very close to those in SESAME 3700.

For temperatures above the critical temperature, the pressure isotherms will be monotonically increasing with density. For temperatures below the critical temperature, mechanical instability and phase separation will be evident. Precisely on the critical isotherm, the derivative of pressure with respect to density will vanish, but not go negative. These calculations are very tedious. Long simulations are required to converge the thermodynamic variables, particularly the pressure, to the level of accuracy needed to identify the critical isotherm, and that will only be within a certain margin of error.

The plot in Fig. 4 illustrates the results of a long series of calculations searching for the critical isotherm for aluminum. The critical temperature is close to 6000K, with a critical density of 0.63 g/cc and a critical pressure of 1.8 kbar. The accuracy is on the order of 10% in temperature. The results of these calculations and results for neighboring isotherms were recently used by Lomonosov in building a new equation.
of state for aluminum [5]. Equations of state with much higher critical points for aluminum are readily found in the existing databases.

**FIGURE 4.** An approximate critical isotherm for aluminum at ~ 6000K. The critical density is around 0.63 g/cc and the critical pressure is approximately 1.8 kbar. The accuracy of this determination is on the order of 10% in temperature.

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