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What's in an Equation of State?

A Traditional View

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John H. Carpenter

Center for Computing Research

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Overview

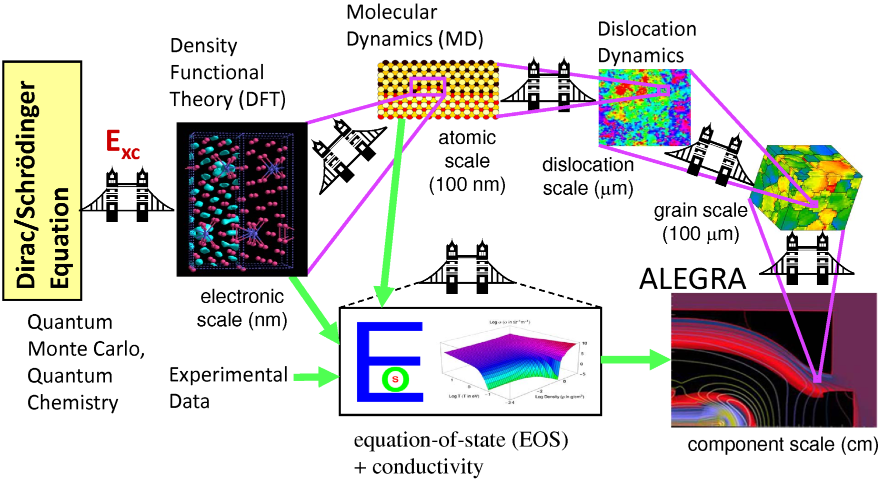
Why "Traditional"?

A high-level view of Equations of State (EOS):

- Preliminaries
- Modeling
- Data
- Tabulation
- Critiques
- Breaking With Tradition

Preliminaries

The Big Picture



- EOS/conductivity/strength models are closure relations for the hydrocode governing equations.
- EOS typically split off of the full stress tensor via the trace.
- Closure relations have strong multi-scale character, reflected in how we build EOS models.

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A Bit of Thermodynamics

Nomenclature:

density (ρ), temperature (T), pressure (P), internal energy (E), entropy (S), enthalpy (H), Helmholtz free energy (F), Gibb's free energy (G)

Thermodynamic Potentials:

- Depend upon two variables, e.g. $F(\rho, T)$ and $E(\rho, S)$.
- Can be inverted to other forms, e.g. $E(\rho, S) \rightarrow S(\rho, E)$
- Related through Legendre transforms, e.g. $F = E + TS$.
- Have combined first and second law expressions, e.g.:
  - $dF = -SdT - PdV$
  - $dE = TdS - PdV \rightarrow dS = \frac{1}{T}dE + \frac{P}{T}dV$

Thermodynamic Relations:

- Calculus is the language of thermodynamics
- Variables are all related through the governing potential space
- Relations allow calculation of complex derivatives in the native potential space, e.g. sound speed:

$$c_s^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \left(\frac{\partial P}{\partial \rho}\right)_T + \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \left(\frac{\partial T}{\partial E}\right)_\rho$$

A "complete" EOS model must specify a full thermodynamic potential.

Modeling

Modeling Paradigms

Code solvers typically operate in (ρ,E) space:

- Need $P(\rho, E)$, $T(\rho, E)$ and other variables.
- Appropriate potential is $S(\rho, E)$.

Paradigm 1: analytic models in $S(\rho, E)$ form

- Mie-Grüneisen forms common ($P(\rho, E) = X(\rho) + Y(\rho)E$)
  - often incomplete
- More complicated models not tabulated.

Paradigm 2: invert from models built in $F(\rho, T)$ form

- Natural form for using statistical mechanics ($F = -k_B T \log Z$)
- Models usually tabulated, and in (ρ, T) space (SESAME)
- Allows for very costly/complex models

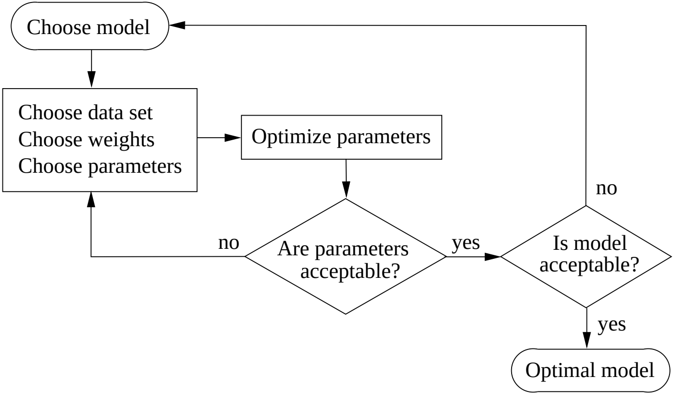
Herein focus will be on Paradigm 2, with the end goal of producing a SESAME table.

Model Building Flowchart

Three key aspects to model building:

- Choose the model and data
- Optimize the model parameters
- Tabulate the model

Iteration of these steps occurs until satisfied with result.



Model Assumptions

Helmholtz free energy split:

$$F(\rho, T) = F_c(\rho) + F_i(\rho, T) + F_e(\rho, T)$$

- Individual phases built from set of submodels
- Submodels may contain one or more F_i components
- Models evaluable at arbitrary locations

Several phase models may be joined to form a multi-phase model.

- Stable phase has lowest Gibb's free energy $G(P, T)$.
- Phase transitions where $G_1(P, T) = G_2(P, T)$.

Common Models

Cold curve models:

- Parametrized forms (Birch-Murnaghan, Vinet)
- Series expansions – fit to desired behaviors
- Spline forms – directly represent DFT data

Thermal ionic models:

- Simple physics based (Debye, Einstein)
- Semi-empirical forms (Cowan, JDNUC, Generalized Metal)
- Variational models (soft-spheres, CRIS)

Thermal electronic models:

- Semi-empirical forms (Generalized Metal)
- Average-atom models (Thomas-Fermi (TF), TF-Dirac, TF-Kirzhnits, QSM)
- Effective medium (INFERNO, Pergatorio)
- Direct DFT/OFDFT calculations

Data

Calibration Data Overview

Data Type	Constrained Variables	Target Models
0 K DFT	$P\ E\ (\rho)$	F_c
Static compression	$P\ (\rho, T)$	$F_c\ F_i$
Shock compression DFT-MD Shock	$P\ E\ \rho\ T\ u\ D\ (T_0, \rho_0)$	$F_c\ F_i\ F_e$
Isobaric expansion	$C_P\ S\ H\ \rho\ K\ (T, P)$	$F_i\ F_e$
Heated DAC DFT-MD Phases	P phase (T)	$F_i\ F_e$
DFT-MD Vaporization	$P\ E\ (\rho, T)$	$F_i\ F_e$

Parameter optimization performed both by hand and automatically using local minimization in a stepwise process:

- Solid cold/ionic parameters to solid data
- Liquid cold/ionic parameters to low T liquid data
- Liquid parameters to all liquid data
- Solid parameters to all data (phase included)

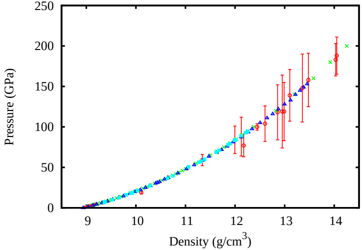
Copper Data and Model Notation

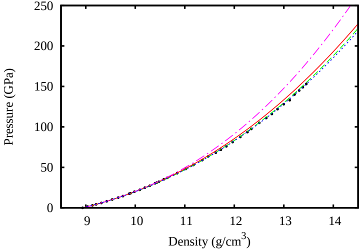
Examples of the data types and how models match them will appear as follows:

- Data will be plotted on the left with lines and points.
- Table results will be plotted on the right.
  - Data (and/or surrogate data model) shown as points.
  - Copper table 3325 – red line (mine)
  - Copper table 3320 – green line (Kerley)
  - Copper table 3336 – blue line (LANL)
  - Copper table 3331 – magenta (ANEOS)
- All copper models have solid and fluid phases with melt and vaporization.
- All tables have Maxwell constructions in the vapor dome except 3336.

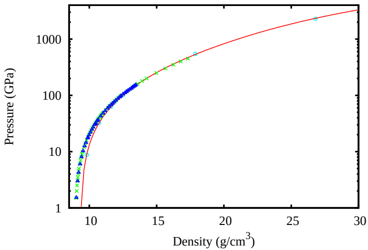
Cold Curve/Static Compression

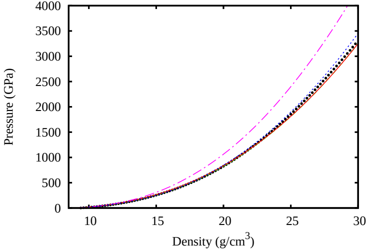
Static data – Diamond anvil cell (DAC) and piston experiments





DFT calculations augment DAC at high compression

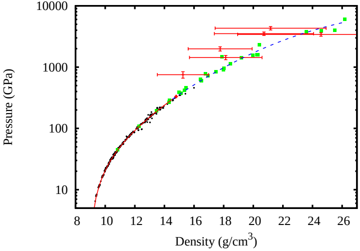




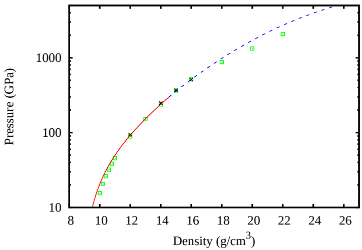
Constrains F_c and F_i.

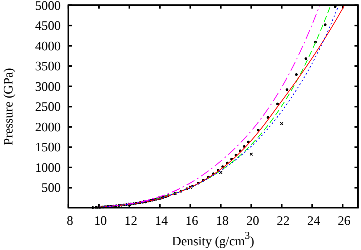
Shock Compression

Experimental Hugoniot with linear and quadratic fits



Theoretical Hugoniot and final results





Constrains F_c, F_i, F_e.

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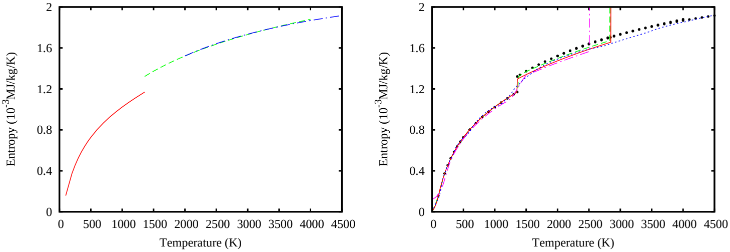
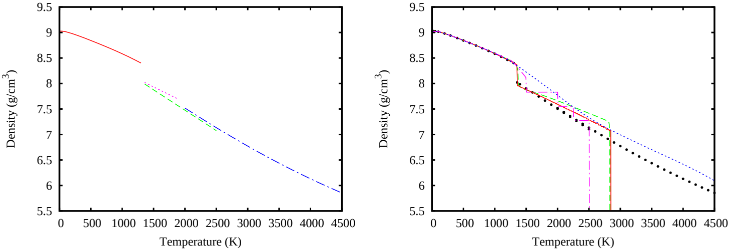
Isobaric Expansion

Entropy from heat capacity measurements – IEX at high temperature



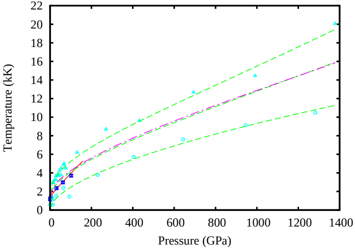
Density from dilatation measurements, sinkers, and IEX.

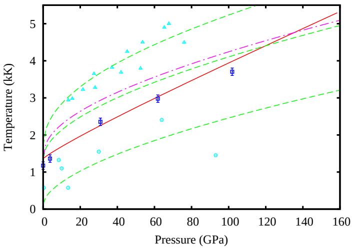


Constrains F_i and F_e.

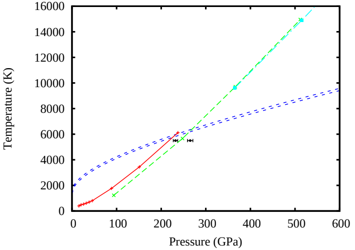
Melting

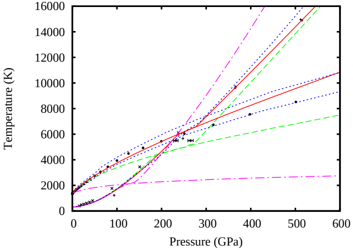
DFT calculations – red line is experimental curve.





Shock melt points arbitrarily placed at 5000*K*.





Constrains F_i and F_e.

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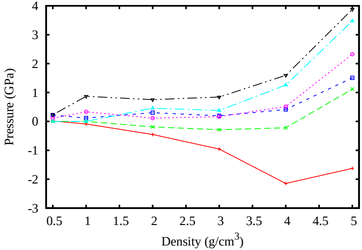
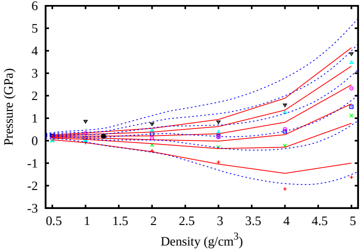
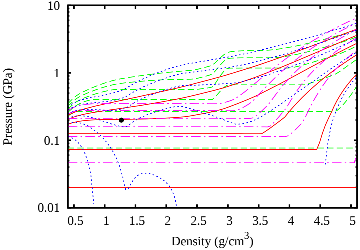
Vaporization

Van der Waals loops for 3325 directly from model (6 temperatures)



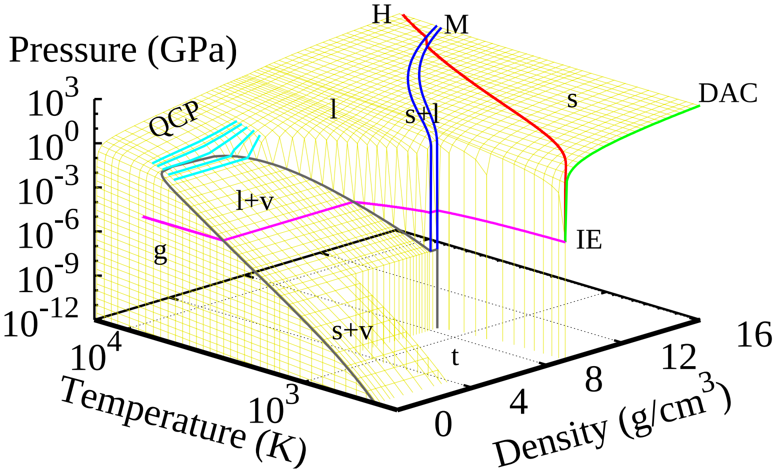


Maxwell constructions of tables. 3325 critical point is black dot.



Internal energy data (not shown) also available from DFT-MD.
Constrains F_i and F_e.

Visual Data Summary



- Data provides skeleton across most of the range of interest
- Models must interpolate/extrapolate the remaining surface

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Tabulation

Best Tabulation Practices

Tabulation goals:

- Speed up state computation in the codes.
- Represent the analytic EOS appropriately.

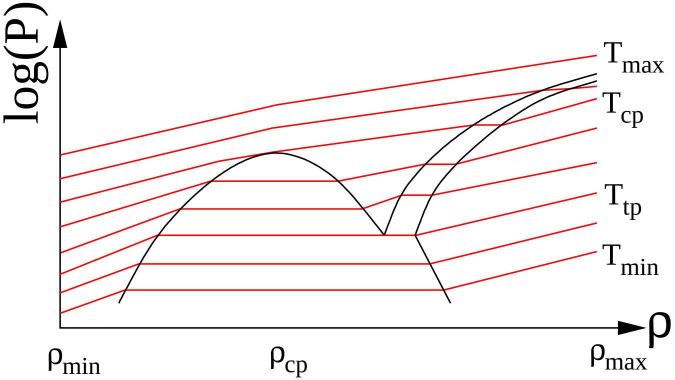
Problems:

- In general practice the first goal has taken precedence either intentionally or through carelessness.
- Rectangular grid SESAME tables cannot naturally follow curves or represent discontinuities on curves.
  - SESAME style tables contain at least P and E on an arbitrary rectangular (ρ, T) grid.
- Reverse interpolation on the energy table does not always give a consistent temperature state. $(E_0 \neq E(\rho, T(\rho, E_0)))$
- Inconsistent thermodynamics between $P(\rho, E)$ and $T(\rho, E)$.
- Meta-stable and equilibrium states do not play well together.

Best practices:

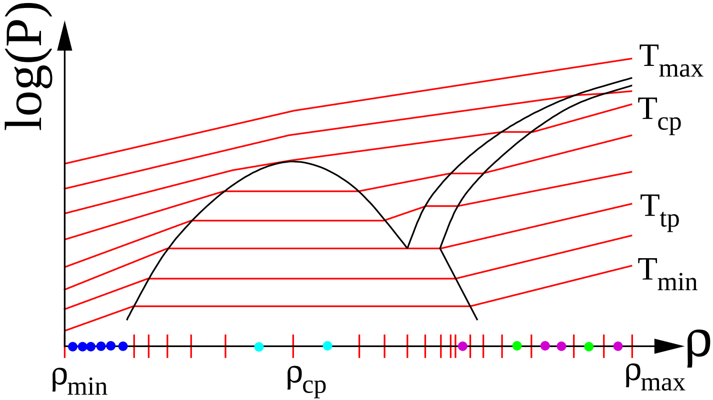
- Conform SESAME grid as well as possible to phase boundaries.
- Create fine-enough grid to make derivatives reasonable.
- Check the table for anomalous behavior before releasing.

Tabulation: Temperature Grid



1. Determine phase boundary topology
2. Choose pressure spacing at critical density
3. Compute equi-spaced temperatures
4. Choose min temperature for Maxwell constructions
5. Eliminate temperatures for interpolation efficiency and accuracy

Tabulation: Density Grid



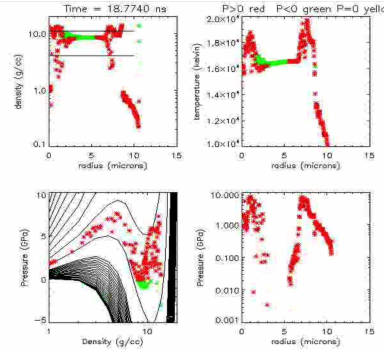
- Temperature grid fixed
- Add density points
  1. Phase boundary intersections
  2. Ensure point in Maxwell construction
  3. Meet linear, log, and relative spacing constraints

Critiques

Tabulation: Meta-stable Phase States

Van der Waals loops or Maxwell constructions?

- Vapor dome tabulation practice is not consistent
- Other groups typically use loops, Sandia constructions
- Maxwell constructions guarantee a valid state everywhere
- Van der Waals loops give some meta-stable behavior
- Codes cannot currently handle region between spinodals
- Do you trust the state of material that traverses this region?



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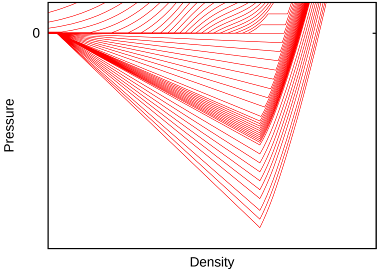
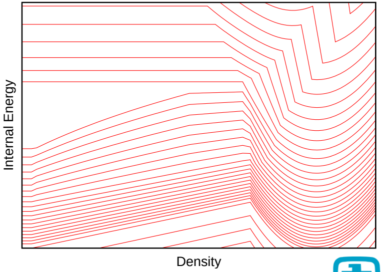
Tabulation: (Meta-stable) Tensile States

Combining equilibrium and meta-stable states in single table

- Often only for tensile states
- Temperature boundary at boiling or triple point
- Multiple issues:
  - Unphysical region at densities smaller than minimum pressure
  - Encounter interpolation difficulties across the boundary
  - Resolve by using fake values that mitigate the issues
  - Does your code use these values?





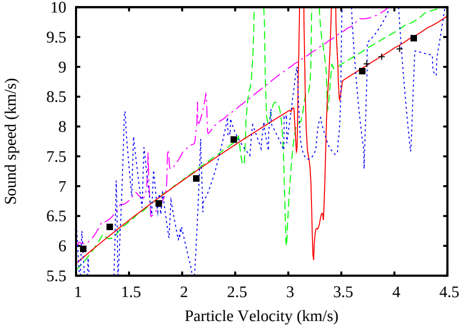
Derivative Issues: Sound Speed

Recall the formula for sound speed:

$$c_S^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \left(\frac{\partial P}{\partial \rho}\right)_T + \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \left(\frac{\partial T}{\partial E}\right)_\rho$$

- Requires 3 derivatives on the tables
- Requires the sum to be positive
- Extremely sensitive to these values
- Extremely important for stable time steps ($\Delta t \sim c_S^{-1}$) and dissipation (artificial viscosity $\sim c_S$)

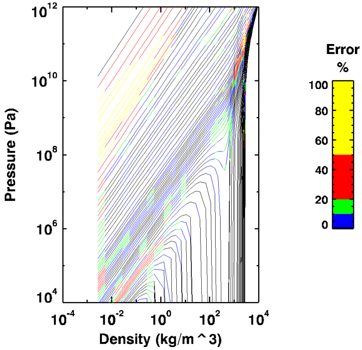
Sound speed along Hugoniot:



Derivative Issues: Thermodynamic Consistency

Is $S(\rho, E)$ really a state function?

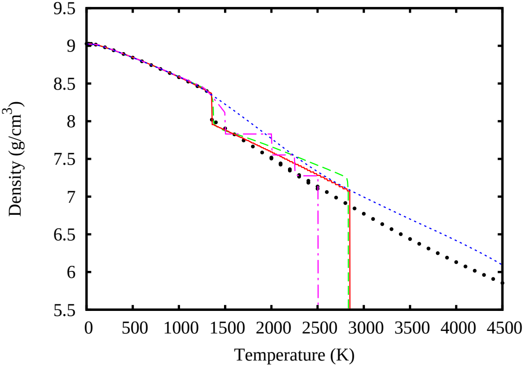
- Integration between two points should be identical regardless of path.
- Consistency of $P(\rho, E)$ and $T(\rho, E)$ surfaces:
  $\rho^2 \left(\frac{\partial T}{\partial \rho}\right)_E = T \left(\frac{\partial P}{\partial E}\right)_\rho - P \left(\frac{\partial T}{\partial E}\right)_\rho$
- Often tested in (ρ, T) space:
  $\rho^2 \left(\frac{\partial E}{\partial \rho}\right)_T = P - T \left(\frac{\partial P}{\partial T}\right)_\rho$
- Results for LANL 3718 (aluminum) shown in plot.



What Does "EOS Model" Mean?

EOS table and interpolation scheme is the real "EOS model"

- Codes actually query it for thermodynamic closure states
- Let's pick on 3325 and Sandia's codes:
  - ALEGRA simulation with 3325 and backup linear interpolation
  - ALEGRA simulation with 3325 and sound speed modifications
  - CTH simulation with 3325 and bad state clipping
  - Saying "Copper 3325" describes none of these accurately
  - They are not even the same as the model used to build 3325
- Ambient thermal expansion is one example (stair steps).



Breaking With Tradition

The state of traditional EOS model development is not without issues:

- Lack of data to constrain models
- Subjectivity toward goodness of models
- Tabulation accuracy issues
- Meta-stable state representation problems

We can do better and are actively working on such:

- More accurate EOS models and calculation methods
- UTri format to improve table fidelity
- Automation of core model and table building activities
- Strongly coupled EOS and conductivity
- Integrated UQ information for EOS/conductivity sensitivity
- Kinetics models for meta-stable state breakdown
- Recoupling strength models and EOS with UQ information