A hydrogen equation of state for ion beam-driven compression experiments

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Abstract
Full scale equations of state (EOS) covering solid, fluid and plasma as needed for applications in warm dense matter physics are difficult to establish. We demonstrate how such an EOS can be constructed from available data.

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1. Introduction and requirements

One of the most important physical quantities for high-energy density physics studies is the equation of state. No matter what kind of warm dense matter experiment is conducted, the equation of state (EOS) is either investigated or used to investigate other material properties. Furthermore, it is well known that the quality of predictions for a variety of experiments strongly depends on the reliability of the EOS for the materials under consideration. Today vast parameter spaces have been studied, both theoretically and experimentally. The problem one faces is that there exists a variety of different methods, each only applicable in a small area, with errors and uncertainties not well known. Some of these approaches even disagree with each other.

Even for the simplest element, hydrogen, there is no standard equation of state representing the state of the art knowledge. This is counterproductive as substantial advances in fusion research or astrophysics depend on such a standard table. However, an arbitrarily patched EOS table is not appropriate. We require that the following characteristics are met: experimental data are preferred, the experiments should however obtain EOS data directly, without model-dependent data analysis. If this cannot be achieved, then first principle simulations in the physical picture without assumptions about phase transitions, interactions, ionization state, dissociation state etc shall be used. Classical calculations or the chemical picture shall only be used in parameter regions where the form of the effective interaction has been established by either experiment or first principle theory and where composition and phase do not change. With this in mind, the EOS should cover all known phases, that is gas, fluid, molecular solid and the plasma state consisting of partially dissociated, partially ionized, fully ionized, and the high pressure metallic fluid state.
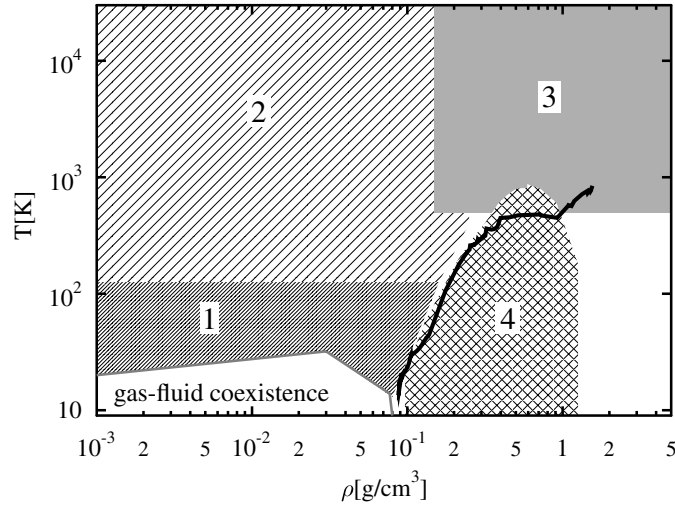
Figure 1. Density–temperature grid for the hydrogen EOS: NIST and MC data were used in area 1. The Saumon & Chabrier EOS covers region 2. DFT–MD simulations were used in region 3. Solid hydrogen is found in region 4. The gas–fluid coexistence region at low temperatures is indicated. In the white area at the bottom right, the EOS is not known. The black line is part of the compression path of the experiment described in [1].

Special attention is given here to the solid state. It is not of direct use for experiment and theory of warm dense matter. However, it represents the initial state of the material before being compressed and heated, and a substantial amount of the compression path of many experiments lies within this phase [1].

2. EOS models for the different parameter regions

According to the requirements, we constructed a hydrogen EOS for predictions for a dynamic compression experiment as possible at the Gesellschaft für Schwerionenforschung Darmstadt [1–3].

The density–temperature region covered by our EOS is shown in figure 1. It spans eight orders of magnitude in the pressure. Phases covered reach from the cryogenic gas/fluid/solid at around 10 K at very low pressure to the high-temperature/high-density metallic fluid phase to be found in the centre of giant gas planets. In addition, figure 1 contains a path of compression as encountered for the hydrogen next to the driver in the cylindrical compression experiment described in [1].

In the different regions indicated in figure 1, the EOS was determined as follows. For low temperatures and low densities (region 1), we used experimentally well-established data from NIST [4]. These are complemented by classical Monte Carlo simulations using the Ross–Ree–Young intermolecular potential [5]. Both methods agree very well in the region above the critical temperature. The NIST data include the gas–solid and gas–liquid phase transition of hydrogen as well as some data above the critical point. The EOS of Saumon and Chabrier (S&C) [6, 7] provides data for low-density and high-temperature systems (region 2). Strictly speaking, the method used by S&C does not satisfy the requirements from above. However, there exists a well-defined mathematical procedure that maps the physical to the chemical picture in this parameter region. Thus, the approach is well justified.

Furthermore, comparison with analytical theory as well as with first principle simulations gave excellent agreement. The high-density fluid (region 3) spans molecular and atomic/metallic hydrogen. Here, the EOS was described by means of density functional molecular dynamics simulations (DFT-MD) [8, 9] which allows for a fully quantum-mechanical treatment of the electrons and strong correlations in the ion component. DFT-MD calculations and the S&C EOS overlap. There are disagreements between the data of those two approaches [8]. DFT-MD data were usually preferred in such cases.

For the molecular solid phase (we include only the disordered phase I) in region 2, we combined experimental data [10] and density functional calculations (DFT) up to the highest pressure for which the melting line is known, that is 200 GPa [11]. We used abinit and norm conserving pseudopotentials from the fhi code[1] [12, 13].

The system was initially prepared in the hcp (A3) crystal structure with hydrogen molecules of random orientation at the lattice points. The ratio between the lattice constants is $c/a \sim 1.63$ at low pressure, and it decreases with pressure as found in experiment [14–16]. DFT calculations were run on three unit cells of this lattice. First, the system's structure was optimized using the Broyden–Fletcher–Goldfarb–Shanno procedure. Then, pressure and energy were calculated from the electronic ground state using the stress theorem. We used 108 hydrogen atoms in the supercell. The cutoff for the planewave expansion of the electronic wavefunction was 40–100 Hartree. The Brillouin zone was sampled at the gamma point only. The exchange correlation contribution of the electrons was modelled using the Perdev–Burke–Ernzerhof generalized gradient approximation [17].

Finally, the discrete EOS data points of experiments and simulations can be very well represented by fitting a Vinet EOS formula [18]

$$P(V, T) = \frac{3K_0(T)(1 - x)}{x^2} \exp\{\xi(1 - x)\}, \tag{1}$$

$$E(V, T) = E_0(T) + \frac{9K_0(T)V_0(T)}{\xi^2}\{1 + [\xi(1 - x) - 1]\exp\{\xi(1 - x)\}\}.$$

Here, E_0 and V_0 are the values for the zero pressure equilibrium energy and volume respectively, $x = (V/V_0)^{1/3}$ and $\xi = \frac{3}{2}(K_0'(T) - 1)$. $K_0(T) = -V[\partial P/\partial V]_T$ is the isothermal bulk modulus and $K_0'(T) = [\partial K(T)/\partial P]_0$ its pressure derivative at zero pressure. Best fit values for the zero Kelvin isotherm are $V_0[\text{cm}^3\text{ mol}^{-1}] = 23.234$, $K_0[\text{GPa}] = 0.166$, $K_0' = 7.102$. Information for temperatures above absolute zero can be obtained within the Debye model. Pressure and energy contribution due to lattice vibrations are given by

$$P_{\text{th}} = \frac{3RT}{V}\gamma D\left(\frac{\Theta_D}{T}\right), \qquad E_{\text{th}} = 3k_B T D\left(\frac{\Theta_D}{T}\right). \tag{2}$$

γ is the thermal Grueneisen parameter, D is the Debye integral of order 3 and Θ_D is the Debye temperature [16]

$$\gamma = \frac{1}{C_V}\left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial P}{\partial V}\right|_T, \qquad D(x) = \frac{3}{x^3}\int_0^x \frac{t^3}{e^t - 1}\,dt. \tag{3}$$

Results obtained with this formalism are presented in figure 2. There is very good agreement between DFT calculations and measurements. DFT-MD and DFT ground-state calculations are consistent with each other. Starting from the zero Kelvin isotherm (the fit is indistinguishable from the calculated curve), it is now easy to obtain a full EOS for phase I of the solid as needed by utilizing equations (2) and (3) and the experimentally determined pressure-dependent Debye temperature [14–16].

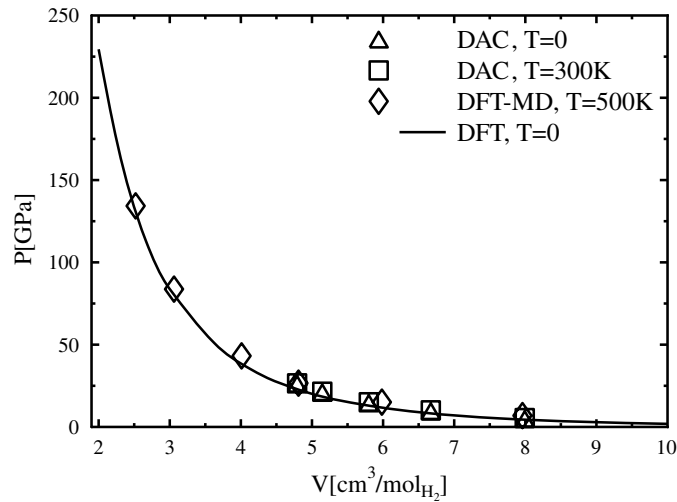[1] Copyright ABINIT group (M Mikami *et al*) 2003–2005.

Figure 2. Isotherm of the pressure for the molecular solid in the randomly oriented hcp phase (phase I). Diamond anvil cell (DAC) measurements were taken from [16]. DFT-MD simulations as reported in [8]. The fitted isotherm not shown, it agrees with the $T = 0$ DFT curve.

3. Summary

The presented EOS was successfully used to predict the capabilities of a new compression experiment [1]. The EOS tables in the present form still lack thermodynamic consistency at the boundaries between the different methods. In future thermodynamic consistency will be achieved via a free energy surface [19] which will make it also possible to recover the phase transitions. At this point, the EOS will be made public.

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