Equations of state for mixtures: results from density-functional (DFT) simulations compared to high accuracy validation experiments on Z

R J Magyar, S Root and T R Mattsson
P.O. Box 5800, MS 1322, Albuquerque, NM 87185
E-mail: rjmagya@sandia.gov

Abstract. We report a computational and validation study of equation of state (EOS) properties of liquid / dense plasma mixtures of Xe and ethane to explore and to illustrate the physics of the molecular scale mixing of light elements with heavy elements. Accurate EOS models are crucial to achieve high-fidelity hydrodynamics simulations of many high-energy density phenomena such as inertial confinement fusion, planet interiors, and planetary impact. While the EOS is often tabulated for separate species, the EOS for arbitrary mixtures is generally not available, requiring properties of the mixture to be approximated by combining physical properties of the pure systems. The main goal of this study is to assess how accurate this approximation is under shock conditions. Density functional theory molecular dynamics (DFT-MD) at elevated-temperature and pressure is used to assess the thermodynamics of the xenon-ethane and xenon-deuterium mixtures. The simulations are unbiased as to elemental species and therefore provide comparable accuracy when describing total energies, pressures, and other physical properties of mixtures as they do for pure systems. In addition, we have performed shock compression experiments using the Sandia Z-accelerator on pure xenon, ethane, and various mixture ratios thereof. The DFT-based simulation results for the principle Hugoniot compare well with the experimental points. The predictions of different EOS mixing models for Xe-D are considered, and we find that a mixing rule based on pressure equilibration performs reliably well.

1. Equation of State Models for Mixtures

Computational models of planetary interiors [1], giant impacts [2], inertial confinement fusion[3], and many technological applications require detailed descriptions of material properties that are in part included as equations of state (EOS) tables. These are typically included for a finite set of materials that are described by EOSs. However, in many dynamic situations, materials will mix. Depending on the degree of mixture various models may be appropriate. Simulations often assume that a system is decomposed into a set of volumes consisting of known quantities of the materials described by EOSs. However, the description of any volume element is in general expected to be unlike the available EOSs if it contains more than one material. The materials within the volume may be unmixed or immiscible, out of thermodynamic equilibrium, or in an extreme case, homogenized to the molecular level. We consider the case where mixing has occurred at the molecular level, this is the extreme where interspecies quantum mechanics becomes most important and classical mixing models are expected to be most frustrated. Additionally, we consider mixtures in which the nuclei atoms of different species...
are in thermodynamic equilibrium. The conditions under which we study mixing rules are near the warm dense matter regime, several eV in temperature and several Mbar in pressure.

In this work, we use DFT-MD to probe the accuracy of various mixing rules. DFT-MD has had great success in predicting various properties of warm dense matter in comparison to experiment [4, 5]. There have been other previous uses of DFT-MD to examine the properties of mixtures [6–8]. For this study, we restrict our analysis to the description of binary mixtures of pure materials.

In this report, we present results for mixtures of Xe-ethane and Xe-D. The former is used as a validation study to check that DFT-MD provides reasonable results for mixtures, and the latter is used as a computational experiment to probe the validity of several mixture models. We also present an approximate mixture rule to obtain estimates of the Hugoniot for mixtures of materials where the pure material Hugoniots for the same pressure and temperature point are known.

EOSs relate the mass-density and temperature of a material to its pressure, energy per atom, and sometimes to entropy. For mixtures, empirical models have been developed to combine EOSs for an arbitrary composition. We consider three of the most commonly used schemes, each based on thermodynamic variables, mass composition, volume, and pressure respectively.

The ideal mixing rule is motivated by the universal gas law EOS and only depends on the fractional mass percentages, $x_A = \rho_A/\rho_{tot}$, of the components. By convention, $\rho_A < \rho_B$. The ideal pressure rule states

$$P = x_A P_A[\rho, T] + (1 - x_A) P_B[\rho, T], \quad (1)$$

where $P_A$ and $P_B$ are the EOSs for the pure systems at the total mass density $\rho = \rho_A + \rho_B$. This rule is provided as a base-line simplest physical model; however, it is not used in any significant modeling efforts.

The volume rule (the law of partial pressures, Dalton’s rule) accounts for the volume occupied by the mixture components and can be related to the fractional cell rules used in many hydrocodes. The is sometimes referred to as the law of additive pressures and can be thought of as chemically distinct species occupying discrete volumes. The volume rule gives the total pressure as

$$P = P_A[x_A \rho, T] + P_B[(1 - x_A) \rho, T]. \quad (2)$$

This mixing rule is sometimes used in planetary modeling.

The pressure rule (law of additive volumes, Amagat-Leduc model) requires that the pressures of the components be equal at a chosen mixture ratio, total volume, and temperature. The set of equations to be solved are

$$P_A[\tilde{\rho}_A, T] = P_B[\tilde{\rho}_B, T] \quad (3)$$

and

$$\frac{x_A}{\tilde{\rho}_A} + \frac{1 - x_A}{\tilde{\rho}_B} = \frac{1}{\rho}, \quad (4)$$

where $\tilde{\rho}$ is the effective density solved for each pure material. The pressure rule is the most rigorous of the set but still fails to account for enthalpies of mixing that result from inter species interactions. Note too that because of the numerically cumbersome non-linear solve, practical codes will often solve equations (3) and (4) approximately. Many hydrocodes use some variant of this rule. While these three rules are thermodynamically motivated, they are not fundamental laws of nature and can be a significant source of uncertainty in multi-material hydrocode simulations. There is therefore a need to validate the use of these approximate mixing rules.

Models exists to predict mixture viscosities, sound velocities, and opacities for example. Most hydrocodes require an energy term so we compare the analogous energy mixture methods as
well. The mixture energies can be obtained in a way that is similar to the rules suggested above. The ideal rule for energy of mixing is

$$E = x_A E_A[\rho, T] + (1 - x_A) E_B[\rho, T],$$

and the volume rule is

$$E = E_A[x_A \rho, T] + E_B[(1 - x_A)\rho, T].$$

The analog of the pressure mixing rule is a bit more complicated. The energy per atom is the number fraction weighted sum of the effective energy per atom at the equilibrated Amagat pressure,

$$E = y_A E_A[\tilde{\rho}_A, T] + (1 - y_A) E_B[\tilde{\rho}_B, T],$$

where Amagat’s rule equations (3) and (4) are satisfied to find $\tilde{\rho}_A$ and $\tilde{\rho}_B$ and

$$y_A = x_A / \left( x_A + (1 - x_A) \frac{m_A}{m_B} \right)$$

is the molar mixing ratio. $m_{A,B}$ are the atomic masses and $m_A < m_B$. The form of the energy equation differs from a simple substitution of energy for pressure in equation (3). This is because the pressure is still fixed according to Amagat’s rule, and from this pressure energies per kilogram are determined. The introduction of $y_A$ reflects that the total energy per atom is sum of energy per atom of each atom type.

The mixing models require well validated EOS models. For Xe, we use Xe5191 [9], a new high fidelity EOS. For D, we use D5263/D5365, often referred to as the Kerley 2003 EOS [10]. While we consider ethane in the validation study, we do not consider it when evaluating mixture models and thus do not require its EOS.

2. Density Functional Theory Molecular Dynamics

We use DFT-MD simulations to validate the mixing rules. DFT-MD is a first principles method that solves the quantum mechanical many electron problem for thermally equilibrated electrons and nuclei [11–13]. Nuclei are propagated along trajectories on the thermally-excited-electron Born-Oppenheimer surface to obtain thermodynamic properties. We use VASP 5.2 [14–18] to simulate an ensemble at fixed number, volume, and temperature with the AM05 generalized gradient density functional [19, 20] with strict convergence criteria [22]. In all the simulations, we chose a plane-wave cut off so that block-averaged pressures were converged to < 1%. The Badereski mean value point is used for the k-point sampling, an approximation that is found to provide a good combination of accuracy and efficiency for simulations of disordered systems above melt [21]. Further details of the method are reported elsewhere [9, 23–27].

We find it useful to re-normalize the EOS tables to isolate errors in the mixing models from errors in the pure materials EOSs. The motivation for this scaling is discussed in reference [26]. The scaling of the EOS tables proceeds as follows for each pure material:

$$\alpha = \frac{P_{EOS}[\rho, T]}{P_{DFT}[\rho, T]}$$

and

$$\alpha' = \alpha^{-1} C E^{EOS}[\rho, T] - E^{DFT}[\rho, T]$$

$C$ converts Joules per Kilogram to eV per atom as the EOS tables are usually given in the former. So, for an approximate mixture rule,

$$P^{Mix}[ho, x_A, T] = f[\alpha_d^{-1} P^{EOS}\rho, T], \alpha_{xe}^{-1} P^{XE, EOS}[ho, T], x_A]$$

(11)
and the energy is

$$E^{Mix,P}[\rho, x_A, T] = x_A \left( \alpha_D^{-1} C_D E^{D,EOS}[\bar{\rho}, T] - \alpha_D' \right) + (1 - x_A) \left( \alpha_X^{-1} C_X E^{X,EOS}[\bar{\rho}, T] - \alpha_X' \right).$$

(12)

The pressure mixing rule, of course, has $y_A$ instead of $x_A$.

3. Experimental Validation

We validate our DFT-MD simulations as being capable of describing mixtures of elements of vastly different atomic numbers by comparing simulations for Xe and ethane to shots that have been performed on the Z-machine. Details about the experiments and equipment can be found in references [24, 28]. Previous work by other researchers has explored mixing rules and DFT simulations for mixtures of light elements [6–8]. The validation study focuses on Xe-ethane as pure D is immiscible in Xe at conditions readily achievable in the Z-machine. Ethane can be considered as a proxy for a large density of liquid D to be shocked and mixed with Xe. The pure materials DFT-MD results have been validated against Z-machine experiments in previous work [24, 29].

For Xe-ethane, the number and type of atoms used in the simulations varied according to mixture ratio. The super cell used for the equimolar fraction contains 13 Xe atoms and 13 ethane molecules for a total of 117 atoms and a ratio $x_A = 0.19$. The equal mass density mixture super cell contains 5 Xe atoms and 18 ethane molecules for a total atom count of 149 and has the ratio $x_A = 0.5$. The reference states are inferred from experimental cryomixture data [30]. For the molar mixing $x_A = 0.19$, the reference state has a density of $\rho_{ref} = 1.676$ g/cc at a temperature 163K and a pressure < 10 kBar. For the mass mixing $x_A = 0.5$, the reference state has a density $\rho_{ref} = 1.054$ g/cc under similar conditions.

From the knowledge that along the Hugoniot each pressure, density, and temperature point is unique, we can identify a density for a given pressure. We assume that a mixture Hugoniot is shocked from the same initial conditions as known pure material Hugoniots. The approximate mixture density is found by selecting target pressures and looking up the effective densities along the pure Hugoniots. At a chosen pressure, the approximate density of the mixture Hugoniot is then a weighted sum of these densities:

$$\rho = \left( \frac{x_A \rho_A + (1 - x_A) \rho_B}{\rho_A} \right)^{-1}$$

(13)

A very crude approximation to the temperature is

$$T = x_A T_A + (1 - x_A) T_B$$

(14)

where $T_{A,B}$ are the temperatures along the pure material Hugoniots. This is an approximate use of Amagat’s rule since the EOS tables are referenced at different temperatures. Additionally, the result is approximate because it only approximately satisfies the Hugoniot conditions for the mixture.

Figure 1 shows the principle Hugoniot for shocked Xe-ethane 1:1 molar mixture and Z-machine data. The dark blue curve connects the blue points that are the results of DFT-MD simulations, and the magenta points with the error bars are preliminary Z machine results. The DFT-MD is slightly stiffer than the Z-data. A possible reason for this is that a small fraction of ethane failed to load in the Z target. The result is a slightly higher percentage of Xe than expected and a softening of the Z data. The reference Z density is $1.7 \pm 0.15$ g/cc. The pure Xe and ethane Hugoniots are shown for reference. In the limited set of 2 Z-points shown, we see good agreement. The discrepancy between the DFT results and the experimental data is likely
caused by the initial state of the mixture. For the pure substances, we know the initial density in the reference state accurately. For the mixture, we perform mass spectroscopy on the mixed gas bottle to determine the molar concentrations and determine the liquid density based on the data in reference [30]. After condensing to liquid in the target cell, we do not have a method for ensuring a uniformly distributed mixture of ethane and Xe. The time between condensing to liquid and executing the shock experiment is minimized, but the potential for demixing still exists. The final state pressure and density are determined the measured shock velocity in the mixture and using monte carlo impedance matching to a known standard [24, 28].

4. Evaluation of mixing rules using DFT-MD simulations

We study the accuracy of mixing rules on a mixture of Xe and D. There is limited interspecies
chemistry, but significant dissociation of D in the temperature range studied. We expect the largest potential for interspecies chemistry and the potential for breakdown in approximate mixing models would occur at the one to one molar ratio of Xe to D.

Figure 2 shows the various mixing rules applied to a mixture of Xe-D at several Mbar and 10000 K. The DFT-MD results are the straight black lines. Amagat’s rule is the dashed blue line that essentially lies atop the DFT results. The long-dashed red lines and the short dashed black lines are the ideal and volume rule results respectively. Neither provides a very accurate description of the mixture under these conditions. The result can be rationalized by realizing that the ideal rule samples an effectively higher pressure region of a concave up pressure verse density relationship for both materials, so a weighted average is still likely to be too high in pressure. The volume rule predicts the converse since it samples a too low region of the EOS.

Figure 3. 3 Mbar isobars at various temperature 5000 K, 10000 K, 20000 K. Labeling is the same as figure 2.

The results do not vary strongly with temperatures at these compressed densities and elevated pressures. Figure 3 shows that the pressure rule remains highly accurate over a wide range of temperatures. The other models grow more inaccurate with temperature.

Figure 4. Energy per atom of Xe-D mixes of various composition. Labeling is the same as figure 2.

The energy of the mixture can also be tested. Figure 4 shows the energy per atom using various mixing rules. Surprisingly, the pressure rule provides an extremely accurate model for the energy of mixtures.

The density scaling of the EOS is arbitrary and might have introduced systematic errors into this analysis. To test this, we performed EOS free tests of Amagat’s rule by comparing the ratio of the predicted density to the density resulting from DFT-MD simulations. In figure 5,
Figure 5. Ratio (green line) of the DFT-MD density and a density predicted by assuming the exactness of Amagat’s rule for various mixture compositions of Xe-D.

we show that the predicted ratio deviates by at most a few percent in the difficult $x_A$ region where we have one to one ratios of Xe to D. Nevertheless, the rule remains remarkably robust.

By comparing DFT-MD simulations and the rules for total pressure and energy from various mixing rules, we find that Amagat’s rule works reliably in the multi Mbar and several thousand degree temperature range. This result is likely because of limited interspecies chemistry under these conditions, but it’s degree of accuracy ($<1\%$ in pressure) is surprising nonetheless. The energies predicted are likewise highly accurate. The results presented here are found by scaling appropriate equations of state when assessing the approximate mixture models, but it is highly unlikely that an analysis using more accurate equations of state that are unscaled would find different qualitative results since the degree of scaling is relatively small typical only a few percent. The main finding is that, in this pressure and temperature regime, the dominant inaccuracies are incurred from the underlying EOS models of the pure materials rather than the use of Amagat’s rule.

5. Conclusions

We have highlighted a scheme for combining DFT-MD and experimental validation studies to assess EOS mixing models. We provided some of examples of how this works in practice. We have validated several DFT-MD calculations of mixtures under multi Mbar and 1000s of Kelvin conditions showing that DFT-MD can provide accurate predictions for total pressure and energy under these conditions. Using this validation, we turned the analysis towards approximate mixing models and used DFT-MD to show that a mixing rule based off Amagat’s pressure equilibration scheme provides both accurate pressures and energy given accurate pure materials equations of state. The result is surprising since at these temperatures the electrons are highly thermally excited and the system is expected to behave non-classically. Nevertheless, interspecies chemistry is expected to be limited and that is helping the accuracy of the Amagat rule.

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