



# A proposed experimental platform for measuring the properties of warm dense mixtures: Testing the applicability of the linear mixing model



James Hawreliak

Institute for Shock Physics, Washington State University, Pullman, WA 99164, USA

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## ABSTRACT

This paper presents a proposed experimental technique for investigating the impact of chemical interactions in warm dense liquid mixtures. It uses experimental equation of state (EOS) measurements of warm dense liquid mixtures with different compositions to determine the deviation from the linear mixing model. Statistical mechanics is used to derive the EOS of a mixture with a constant pressure linear mixing term (Amagat's rule) and an interspecies interaction term. A ratio between the particle density of two different compositions of mixtures,  $K(P, T)$ :  $ii$ , is defined. By comparing this ratio for a range of mixtures, the impact of interspecies interactions can be studied. Hydrodynamic simulations of mixtures with different carbon/hydrogen ratios are used to demonstrate the application of this proposed technique to multiple shock and ramp compression experiments. The limit of the pressure correction that can be measured due to interspecies interactions using this methodology is determined by the uncertainty in the density measurement.

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## 1. Introduction

One of the most exciting discoveries in science has been the observation of planets outside of our solar system [1]. The number of confirmed exoplanets has grown into the 1000s offering insight into the diverse outcomes of exosystem formation in our galaxy [2]. Some of these observations challenge the models used to describe planetary formation and evolution [3]. For example, some transiting gas giant planets appear anomalously large based on their mass and the composition of the star they orbit [4]. One possible explanation for the discrepancy is uncertainties in the equation of state (EOS) used to predict the interior of these planets [5]. Varying the compressibility of the interior EOS of these planets by 30% was used to match the observations [6]. The EOS plays an important role in the understanding of planetary interior as it constrains the temperature, pressure and density towards the planetary core and ultimately leads to conclusions about the structure and processes that occur in the interior of planets [8,9]. Changes in pressure, density, temperature and their gradients in the interior of a planet will have direct impact on the calculated energy transport, conduction, and convection of matter [10,11]. Large gas and ice giant planets are mixtures of hydrogen, helium, oxygen, carbon, nitrogen and other elements, so their interior EOS models must include chemical interactions in mixtures over a broad range of pressures and temperatures. Warm dense mixtures in the interior of these planets present challenges for EOS modeling due to the

chemical interactions that vary with composition. Dynamic compression is the only means of achieving the relevant temperatures and pressures in the laboratory to study the properties of these mixtures in extreme conditions.

A common approach to build an EOS for a non-ideal gas mixture is to calculate the specific volume of the mixture based on a linear combination of the component species specific volumes at the same pressure and temperature (Amagat's rule) [12]. This method assumes the species are inert, ignoring chemical interactions. This must be true at high-temperatures and low-densities where all systems act like an ideal gas. However, for the densities and temperatures relevant to planetary interiors and inertial confined fusion (ICF) science the interaction between species could be significant. Mixtures of hydrogen and helium have been extensively studied through simulation [7], due to their astrophysical relevance, but little experimental data exists studying mixtures in extreme conditions [13–15]. Models of particle interactions without atomic physics like hard sphere or Coulomb charge interactions were initially used to test linear mixing approaches [16]. Recent simulations using quantum molecular dynamics and density functional theory, which include atomic interactions for many hundreds of particles, have shown deviations from Amagat's rule [17–19]. These sophisticated calculations can provide a better understanding of mixtures. What is lacking is experimental data at the relevant conditions to test the importance of chemical interactions in extreme thermodynamic conditions. This requires a technique that can investigate chemical interactions in dynamic compression experiments because these are the only laboratory experiments that can reach the relevant conditions.

E-mail address: [James.Hawreliak@wsu.edu](mailto:James.Hawreliak@wsu.edu)

This paper studies the feasibility of a proposed experimental approach for investigating the impact of interspecies interactions on the thermodynamic properties of warm dense liquid mixtures. Hydrodynamic simulations are used to demonstrate how the error bars associated with dynamic compression experiments can be overcome to isolate the deviation from a linear mixing model. It begins with a derivation of the EOS of a dense liquid mixture. The EOS is broken up into Amagat's rule and a pressure correction term related to the interspecies interactions. The radial distribution functions are maintained in the derivation as a link between the thermodynamic properties and the microscopic interactions that could be investigated with x-ray scattering experiments [20]. A ratio,  $K(P, T)i:ii$ , of the particle densities of mixtures of different compositions of the same species is derived by equating the pressure of two different mixtures. Comparing many  $K(P, T)$  ratios of different mixture combinations is used to determine the deviation from the linear mixing model.

## 2. Equation of state for warm dense mixtures

The EOS of a warm dense liquid mixture is assumed to be similar to a dense fluid, no long length-scale structure of the particles. In this derivation only pair-wise interactions between particles are considered. Using statistical mechanics the EOS of a dense liquid is given by [21]

$$P = \frac{Nk_B T}{V} - \frac{2\pi}{3V} \sum_{IJ} n_I n_J V_J \int_0^\infty \left( \frac{d}{dr} u_{IJ}(r) \right) g_{IJ}(r) r^3 dr \quad (1)$$

where  $\frac{Nk_B T}{V}$  is the ideal gas term with  $N/V$  being the total particle density of  $N$  particles in the system volume  $V$ .  $T$  is the temperature and  $k_B$  the Boltzmann constant. The subscript  $I$  and  $J$  identify species-specific terms.  $n_I = N_I/V_I$  is the particle density for  $N_I$  particles occupying a volume  $V_I$  for species  $I$ , where  $N = \sum N_I$  is the total number of particles. The particles are free to move through the system volume  $V$ , but an individual species,  $I$ , will fill a portion of the volume defined as  $V_I$ .  $g_{IJ}(r)$  is the radial distribution function and  $u_{IJ}(r)$  is the interaction potential between species  $I$  and  $J$ . Collecting the terms for each species,  $I$ , Eq. (1) can be written as Amagat's rule with a correction term,

$$P = \sum_I \frac{x_I n}{n_I} \left[ \frac{N_I k_B T}{V_I} - \frac{2\pi}{3} n_I^2 \int_0^\infty \left( \frac{d}{dr} u_{II}(r) \right) g_{II}(r) r^3 dr \right] - P_C \quad (2)$$

$$P_C = \sum_{I \neq J} \frac{2\pi}{3V} n^2 x_I x_J \frac{V_I}{V_I} \int_0^\infty \left( \frac{d}{dr} u_{IJ}(r) \right) g_{IJ}(r) r^3 dr.$$

where the particle fraction of an individual species in the mixture is expressed as  $x_I = N_I/N$  and  $1 = \sum x_I$  for the total particle density of  $n = N/V$ . The term  $P_C$  is the pressure correction to the linear mixing model due to the interaction between the particles of different species. The pressure for a species in the mixture is

$$P_I = \frac{N_I k_B T}{V_I} - \frac{2\pi}{3} n_I^2 \int_0^\infty \left( \frac{d}{dr} u_{II}(r) \right) g_{II}(r) r^3 dr. \quad (3)$$

For an inert mixture the correction term goes to zero,  $P_C = 0$ , and the total pressure from Eq. (2) is

$$P = \sum_I \frac{x_I n}{n_I} P_I \quad (4)$$

Applying the constant pressure condition of Amagat's rule to all the species,  $P = P_I$ , Eq. (4) reduces to  $1 = \sum_I \frac{x_I n}{n_I}$  or  $V = \sum_I V_I$ . Using Amagat's rule,  $V_I$  is the specific volume of the pure species independent of composition. The objective is to use this EOS formulation to find experimental observables that can be used to investigate the correction to the pressure due to mixing,  $P_C$ .

### 2.1. Comparing mixtures of different compositions: $K(P, T)i:ii$ ratio

Comparing a ratio of the particle density between different compositions of mixtures of the same species can be used to

investigate the pressure correction term (for example polystyrene, methane and pure carbon are mixtures of hydrogen and carbon). Setting the pressure from Eq. (2) equal for two mixtures of different composition, superscripts  $i$  and  $ii$  denote the mixture compositions, with two species, subscripts  $A$  and  $B$ , at the same temperature,

$$P = \frac{x_A^i n^i}{n_A^i} P_A^i + \frac{x_B^i n^i}{n_B^i} P_B^i + P_C^i = \frac{x_A^{ii} n^{ii}}{n_A^{ii}} P_A^{ii} + \frac{x_B^{ii} n^{ii}}{n_B^{ii}} P_B^{ii} + P_C^{ii} \quad (5)$$

where  $P_A^i$  and  $n_A^i$  are the component pressure and particle density respectively of species  $A$  in mixture composition  $i$ , and  $n^i$  is the total particle density of composition  $i$ . Assuming thermodynamic equilibrium and that  $P_C < P$  for both mixtures  $P \approx P_A^i \approx P_B^i \approx P_A^{ii} \approx P_B^{ii}$ ,  $n_A^i \approx n_A^{ii} \approx n_A(P, T)$ , and  $n_B^i \approx n_B^{ii} \approx n_B(P, T)$  a ratio between two compositions  $i$  and  $ii$ ,  $K(P, T)i:ii$ , is defined as

$$K(P, T)i:ii = \frac{x_A^i n^i - x_A^{ii} n^{ii}}{x_B^{ii} n^{ii} - x_B^i n^i} = \frac{n_A(P, T)}{n_B(P, T)} + K_C \quad (6)$$

$$K_C = \frac{n_A(P, T)}{x_B^{ii} n^{ii} - x_B^i n^i} \frac{P_C^i - P_C^{ii}}{P} \quad (7)$$

where  $x_A^i$  is the particle concentration of species  $A$  in mixture  $i$ . The ratio uses the particle density measurements,  $n^i$  and  $n^{ii}$ , of the two compositions and the known particle concentrations determined by the initial sample.

Three mixtures would be compared,  $i$ ,  $ii$ , and  $iii$  to give three ratios  $K(P, T)i:ii$ ,  $K(P, T)i:iii$ , and  $K(P, T)ii:iii$ . The ratios are still valid if two of the mixture compositions contain only a single species. In the limit where there are no interactions between the particles of different species (Amagat's rule),  $P_C^{iii} = P_C^i = P_C^{ii} = 0$  and the term  $K_C$  in all ratios goes to zero. In this limiting case the  $K(P, T)$  ratios will have a dependence on pressure and temperature but not on composition,  $i$ ,  $ii$  and  $iii$ , so  $K(P, T)i:ii = K(P, T)i:iii = K(P, T)ii:iii = n_A(P, T)/n_B(P, T)$ . The objective is to use these ratios when they are not equal to investigate the correction to the linear mixing model.

## 3. Hydrodynamic simulations of warm dense mixtures

The application of  $K(P, T)i:ii$  ratios require achieving the same pressure and temperature state in materials of different composition. Shock experiments are a means of achieving high pressures and temperatures, but the principle Hugoniot follows a single trajectory through pressure temperature space determined by the material. Due to the variation in temperatures and pressures between the compositions in single shock experiments it is not possible to investigate the deviation from the linear mixing model with  $K(P, T)i:ii$  ratios. That is why it is proposed that  $K(P, T)i:ii$  ratios are calculated from ramp and multiple shockwave compression experiments. Hydrodynamic simulations demonstrate how ramp compression experiments can be used to achieve the same pressure temperatures in mixtures of different compositions.

Hydrodynamic simulations [22] of an aluminum pusher and impactor driving multiple shock and ramp waves into samples of porous graphite (1.75 g/cm<sup>3</sup>), porous polystyrene (0.9 g/cm<sup>3</sup>), and liquid methane (0.44 g/cm<sup>3</sup>), are used to demonstrate the use of  $K(P, T)$  ratios to investigate warm dense mixtures. The initial densities of the samples are chosen such that the shock and ramp waves will generate similar high-pressure and high-temperature states. Fig. 1 shows the (a) pressure and (b) temperature as a function of time for the simulations. The temperature is predominantly set by the initial shock. Fig. 2 plots the trajectory in temperature-pressure space for each sample from the simulations between 1850 ns and 2000 ns. Ideally this would be the same curve for all three materials, however, because of the differences in impedance the compression isentropes follow different paths.

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