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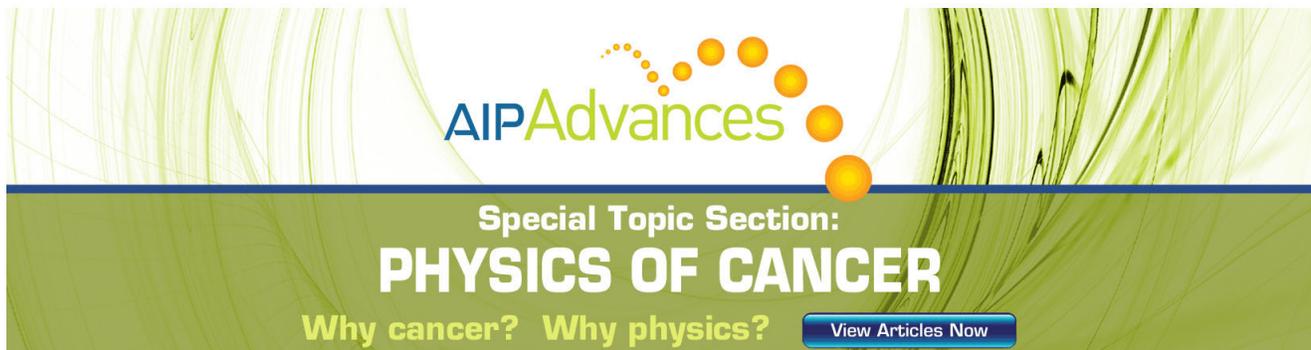
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Mixing of equations of state for xenon-deuterium using density functional theory

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We report on a theoretical study of equation of state (EOS) properties of fluid and dense plasma mixtures of xenon and deuterium to explore and illustrate the basic physics of the mixing of a light element with a heavy element. Accurate EOS models are crucial to achieve high-fidelity hydrodynamics simulations of many high-energy-density phenomena, for example inertial confinement fusion and strong shock waves. While the EOS is often tabulated for separate species, the equation of state for arbitrary mixtures is generally not available, requiring properties of the mixture to be approximated by combining physical properties of the pure systems. Density functional theory (DFT) at elevated-temperature is used to assess the thermodynamics of the xenon-deuterium mixture at different mass ratios. The DFT 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. The study focuses on addressing the accuracy of different mixing rules in the temperature range 1000–40 000 K for pressures between 100 and 600 GPa (1–6 Mbar), thus, including the challenging warm dense matter regime of the phase diagram. We find that a mix rule taking into account pressure equilibration between the two species performs very well over the investigated range. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4793441>]

I. INTRODUCTION

The physical properties of a fluid/dense plasma mixture of two pure materials (elemental or molecular) have several contributing factors: the properties of the pure components, inter-species volume exclusion, pressure equilibration, entropy increase, inter-species chemical bonding, modification of pure species properties in mixture environment, chemical transmutation of pure materials, and heat release from chemical reactions. While at elevated temperatures and pressures, the details of chemical reactions should become less relevant, homogeneous mixtures are still expected to behave quite differently from what one might expect from studying the pure constituents.

The properties of mixtures of materials under multi megabar pressures and kilokelvin temperatures are important in many aspects of the physical sciences such as geoscience,¹ planetary physics,^{2–4} astrophysics and plasma physics.^{5–7} Mixture models are critical in the multi-physics simulations required to design experiments, for example, in tight coupling inertial confinement fusion (ICF) experiments. In particular, the properties of a mixture of xenon and deuterium are important in modeling gas-puff z-pinch fusion experiments.^{5–8} The pressure and temperature ranges investigated in this work are 1–40 kK and 1–6 Mbar, a range very difficult to access experimentally but at the same time one where density functional theory (DFT) based quantum molecular dynamics (QMD) simulations have been demonstrated to be reliable. This range is relevant to the design of inertial confinement experiments where mixing models play a critical role in understanding the imploding cavity. A second important reason for choosing a xenon and deuterium mixture is that DFT/QMD methods have been validated separately for the two pure systems.^{9,10}

In most hydrodynamics codes, atomic mixtures are described by creating a new equation of state (EOS) model for the mixture as a fundamental material or by combining equation of state information about pure materials. The former is time consuming and expensive, so the use of mixing models is prevalent in practical codes.

Mixing rules have previously been studied in the context of DFT/QMD within Kohn-Sham (KS) orbital based formalisms and orbital free (OF) approximations. For mixtures of gold and aluminum, it was found that the volume and pressure rules successfully predict the total pressure of mixtures while the latter rule outperforms the former for properties such as the optical conductivity.¹¹ Zerah *et al.* found that a partial pressure excess mixing rule outperformed total pressure mixing within the orbital free approximation in simulations of He-Fe and D-Cu mixtures.¹² Work on Li-H combining OF-MD and Kohn-Sham density functional theory molecular dynamics (KS DFT/QMD) found about 10% accuracy on the pressure mixing rule with derived properties less accurately reproduced.^{13,14} Early work on high pressure mixing was done in the context of planetary and geological science.^{1,3,4} The fixed average-pressure scheme, used in this work and described in Sec. II, was applied to Xe-D in Ref. 15. This current work used the methods developed in Ref. 15 to examine a broader range of conditions and to develop a mix rule test that does not rely on access to (tabular) EOS models.

II. METHOD

In this work, we restrict our analysis to the description of the total pressures of binary mixtures of pure materials. Equations of state typically map the density and temperature of a material to pressure, energy, and sometimes to entropy.

For mixtures, empirical models have been developed to combine equations of states for pure materials into an EOS for an arbitrary composition. Three of the most commonly used pressure mixing models are based on thermodynamic variables: mass composition, volume, and pressure. We consider three such rules here and the resulting pressures.

The ideal mixing rule is based on the universal gas law and only depends on the fractional mass percentages, $x_A = \rho_A / \rho_{Tot}$, of the components. The ideal pressure rule states,

$$P = x_A P_A[\rho_{Tot}, T] + (1 - x_A) P_B[\rho_{Tot}, T], \quad (1)$$

where P_A and P_B are the equations of state for the pure systems at the total mass density ρ_{Tot} . If ideal gas models are applied for the EOSs of the pure materials, this becomes Dalton's rule. 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 relative sizes of the mixture components and can be related to the fractional cell rules used in many hydrocodes. This 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

$$P = P_A[x_A \rho_{Tot}, T] + P_B[(1 - x_A) \rho_{Tot}, T]. \quad (2)$$

Notice the position of x_A within the argument of the EOS tables. This means that the EOS for the pure materials will be sampled far from the total density point, ρ_{Tot} . 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 mix ratio, total volume, and temperature. The set of equations to be solved are

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

and

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

where $\widetilde{\rho}$ is the effective density solved for each pure material. The pressure rule not only requires the numerical solution of a non-linear set of equations but also results in a thermodynamically consistent result. 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. Also, note that because of the numerically cumbersome non-linear solve, practical codes will often solve these equations 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.

Other common mixing rules use non-thermodynamic indicators such as scaled isotope number, effective ionization

potentials, or atomic densities to combine EOSs. These rules are not expected to have wide ranges of applicability as the choice of mixing indicators set domains of validity. For example, ionization potential methods should work well when the interspecies mixing is dominated by a limited number of charge transfer interactions. When the pure materials become significantly altered by the transferred charge, we would expect drastic deviations from accuracy.

To test the mixing models, we require equations of state for the pure materials. For Xe, we used Xe5191,¹⁵ a new high fidelity EOS that was recently developed to improve existing models in the temperature and pressure range. For D, we used D5263/D5365, often referred to as the Kerley 2003 EOS.¹⁶

To assess the fundamental accuracy of the mixing rules, we restrict the analysis to the important thermodynamic state descriptor, pressure, and have developed a target pressure scheme within the NVT ensemble.¹⁵ We perform a set of DFT/QMD calculations at various mixture ratios of Xe and D at a thermostatically controlled temperature. For each DFT/QMD run, we adjust the overall cell size so that the average pressure over several DFT/QMD steps is near a target value. This scheme provides a set of mix ratios and material densities that have the same pressure in the simulations. The resulting set of densities and mix ratios can be plugged into various mixing models typically used to combine equations of state (EOSs) of the pure materials. The resulting predictions will typically differ from the *exact* DFT result. Comparison of the models to the *exact* DFT results provides useful details about the approximate rules and the relative intrinsic errors of mixing models. The DFT/QMD results provide the total densities at which the mixing rules are tested. However, the pressures of the pure materials used in the mixing rules are read from EOS tables. Thus, mixing rule results give different pressures than the DFT-MD simulations.

In DFT/QMD the motion of many nuclei with thermally excited electrons is followed step by step. The internal forces are calculated based on the finite temperature charge density and ionic positions. The electrons are treated fully quantum mechanically and mutually interacting. The fundamentals of the theory are outlined in Refs. 17–19. Central to the goal of predictive simulations in DFT (Refs. 17 and 18) is the need for convergence. The DFT/QMD simulations were performed with VASP 5.1.40,^{22–24} a plane-wave projector augmented-wave (PAW) core function code^{26,27} using stringent convergence settings.²⁵ Steady-state simulations in the canonical or number-volume-temperature (NVT) ensemble used a Nosé-Hoover thermostat. Complex k-point sampling with mean-value point $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ was used due to its high precision for disordered structures at high temperature. We use Mermin's finite temperature formulation,¹⁹ which is critical for high energy-density applications.²⁸ We could choose several exchange-correlation functionals but report the results for only one generalized gradient method, AM05.^{20,21} Results within the LDA were comparable.

A shell script searches for the supercell volume that contains a system with a target averaged pressure given a fixed nuclear and electronic temperature. This is done by adjusting the lattice scale and performing a DFT/QMD simulation.

After choosing two initial lattice sizes, the lattice scale is adjusted according to a Newton's method to find a new cell-size that more closely yields the desired pressure until within a given tolerance (about 1%). Figure 1 shows the search algorithm schematically. Care must be taken that each simulation is run long enough to eliminate transitional noise and that enough steps are calculated to provide a meaningful average pressure. This typically requires 400–800 femtoseconds steps. Once the target pressure is achieved, a longer simulation (4 picosecond) is run to ensure that the sampling is adequate. If the longer simulation does not yield the desired pressure, then the entire scheme was reinitialized using the semi-optimized lattice scale. The key difference between this algorithm and a barostat is that at each time step, the system is not constrained to a chosen pressure as we still have an NVT ensemble (Figs. 2 and 3).

III. RESULTS

Fig. 4 shows the pressures resulting from inputting the partial densities from the reference DFT calculations into various mixing rules. The extent to which a material is mixed is described by the mass mixing ratio, $x = \rho_D / \rho_{Tot}$.

The EOS tabulated values and the DFT/QMD pressure values disagree by 16.3% for pure D and 5.6% for pure Xe. This disagreement is for several reasons. First of all, the EOS is tabulated to cover a wide range of thermodynamic states with the kK and Mbar range forming only a small subset. In order to reproduce the entire EOS with desired accuracy, it is possible that regions of EOS phase space may differ in accuracy by several percent. This would be

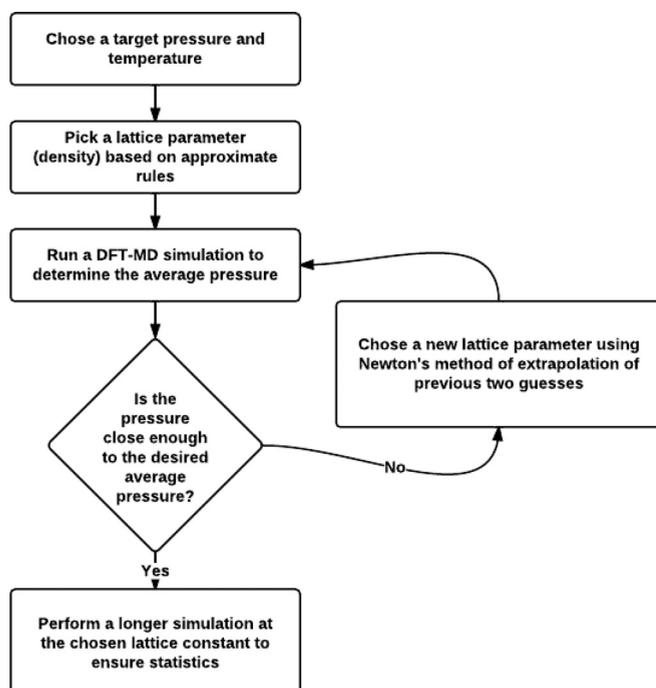


FIG. 1. Flowchart depicting the algorithm used to find the fixed average pressure within the NVT ensemble. This scheme is repeated until a 4 ps simulation is within the desired pressure window. Reprinted with permission from T. R. Mattsson and R. J. Magyar, "Shock compression of condensed matter-2009," AIP Conf. Proc. **1426**, 1196 (2009). Copyright 2009 American Institute of Physics.

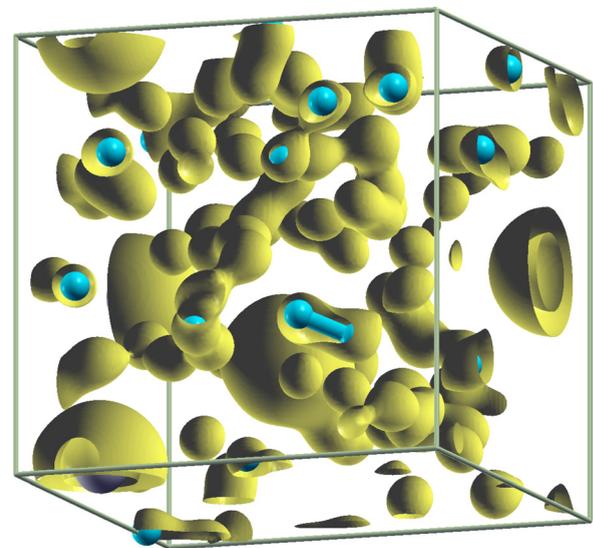


FIG. 2. Snapshot of the electron charge density contour of a Xe-D mixture with mass ratio $x = 0.3$ and density $\rho = 3.514$ g/cc from a DFT/QMD AM05 calculation. The yellow surface is the isodensity surface value 0.8 at 1 Mbar and 5kK. Deuterium atoms are blue and xenon atoms are light purple.

especially true for points away from the Hugoniot and other measured states. Second, in its practical implementation, DFT is an approximate theory and would not be expected to match the experiment perfectly. Although experience with calculations in this range suggests the accuracy should be high. For example, in recent work on the Hugoniot of Xe (Ref. 9) in this P-T regime, the accuracy is about 1%. Similarly, DFT/QMD simulations of hydrogen agree well with experiment.¹⁰ Thus, the DFT/QMD descriptions of the pure systems Xe and D have been separately validated and shown to agree well with experiment (Fig. 5).

The principle focus of this work is the accuracy of using approximate mixing rules combined with high fidelity

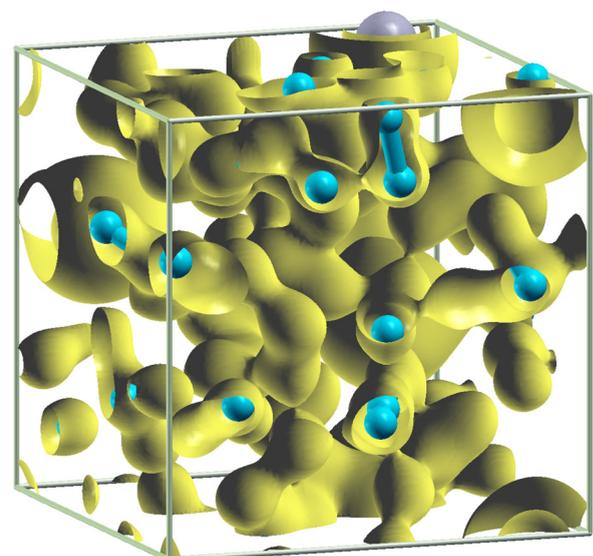


FIG. 3. Snapshot of the electron charge density contour of a Xe-D mixture with mass ratio $x = 0.3$ and density $\rho = 5.069$ g/cc from a DFT/QMD AM05 calculation. The yellow surface is the isodensity surface value 0.8 at 3 Mbar and 10 kK. Deuterium atoms are blue and xenon atoms are light purple. Note that much of the valence charge of Xe has been removed and is shared in a delocalized fashion amongst deuterium atoms.

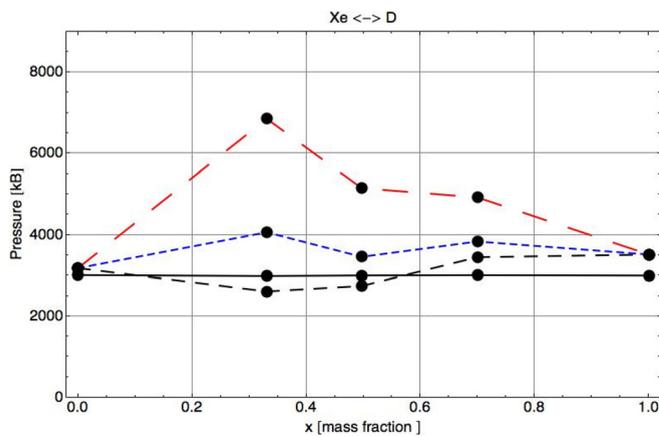


FIG. 4. The curves show the exact (DFT/QMD with AM05—flat black) results for the explicit mixture at 10 kK and 3 Mbar and the results of mixing rules constructed using pure material EOS: ideal—long-dashed red, volume—dashed black, and pressure—short-dashed blue. The maximum errors occurs around the mixing ratio of $x = 0.3$ and is expected to peak at a 1:1 molar mixture corresponding to $x = 0.015$. The total density ρ varies from 15.71 g/cc on the left to 1.932 g/cc on the right. The EOS models used are D5365 and Xe5191. The DFT/QMD and EOS values for the pure materials differ by 5.6% for Xe and 16.3% for D.

equations of state for the pure materials. However, we have seen that the high fidelity EOS results and the DFT/QMD results can disagree for pure materials. This is mostly like the result of a wide ranging EOS table failing to capture this region of phase space in order to maximize global accuracy. However, the DFT/QMD results might also differ from experimental accuracy but unlikely by as large an amount as is seen here.

In order to reduce errors associated with the EOS and DFT/QMD mismatch, we multiply the pressure given by the EOS tables by factor chosen so that the pure materials coincide with the DFT/QMD results for this temperature. This scales the EOS table but this is not expected to alter the conclusions of this study. The plots hence isolate the errors generated by the mixing rules themselves. In further plots, the pure material EOS results are therefore scaled to match the DFT which is expected to be more accurate providing a better measure of the absolute error of the mixing-rules.

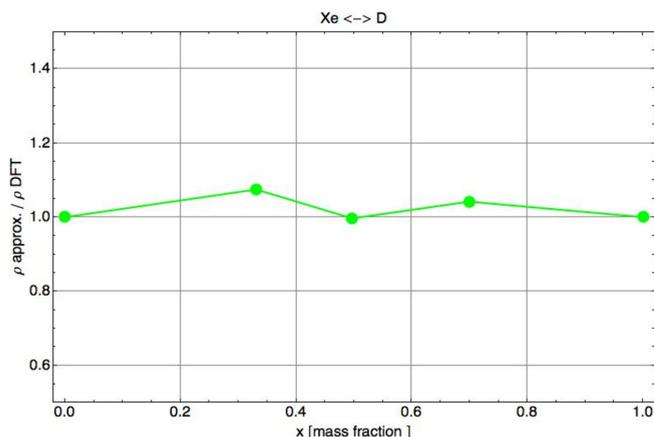


FIG. 5. Ratio of the density found using the calculated partial densities from Amagat's rule, Eq. (4), and the individual species densities at target pressure to the actual total density. This is an exclusively DFT way of testing Amagat's rule without evoking approximate EOS values.

By choosing the pressures and temperatures, the resulting densities are significantly higher than those typically encountered for these materials along the shock Hugoniot for the pure systems. This is because we have maintained much lower temperatures for given pressures than one would have on the Hugoniot curve. To achieve these pressures, therefore, requires higher densities at the lower temperatures.

The DFT rules are expected to provide accurate pressures within a few percent of the pure systems since the DFT/QMD method is very general, the error in the calculations of the mixtures should be bounded by the errors of the pure systems.

We see that the pressure rules outperform the ideal and volume rules at these temperatures and pressures. The volume rule underestimates, and the ideal rule drastically overestimates the pressures.

To verify the main conclusion of this work that the pressure mixing rule is highly valid, we only performed a related DFT/QMD analysis. We do this by appealing to Eqs. (3) and (4). If Amagat's rule was to provide an accurate representation of mixing then both equations would be simultaneously satisfied for the exact density, ρ_{Tot} , and mixture ratio, $x = \rho_D / \rho_{Tot}$, of the physical system. The pressure comes from DFT/QMD calculations of the explicit mixed system, and the effective densities, $\widetilde{\rho}_{A,B}$, at the target pressure can be obtained from DFT/QMD calculations instead of using tabular EOS values using Eq. (3). In general given these inputs, we expect the second equation (4) to hold only if Amagat's rule is exact. The resulting plot 5 shows the ratio of right over left sides of Eq. (4) for DFT/QMD only simulations. This ratio provides a useful measure of when the pressure mixing rule can be expected to effectively treat mixing in hydrocodes. It is important to notice that no EOS data has been used in this method to test the mixing rule, and, thus, no complications requiring linear scaling of EOS tables that was needed for the earlier analysis is required. We see that the pressure mixing rule indeed performs quite well with errors in the density less than 10%. As seen in the earlier plots, the errors tend to peak in the Xe rich side most likely as the inter-species chemistry is expected to peak at molar one-to-one ratio corresponding to $x = 0.015$. This one-to-one ratio is of interest here because xenon and deuterium are known to form xenon-dideuteride under certain low temperature conditions. The analysis in this paper is at much higher temperatures and pressures, and while elevated temperature and pressure play competing roles in bond formation, under the multi-megabar conditions, we expect an overall tendency for reduced bond order. Thus, we expect that at most each xenon can react with one deuterium atom under these conditions leading to the estimate of a one-to-one ratio for the maximum inter-species chemistry. Curiously, the density errors seem to show a bimodal nature with minima by construction at the extreme values and a surprise minima at $x = 0.5$. It is unclear why a system with equal mass proportions of Xe and D should be well described. This is perhaps the result of a cancellation of errors between the numerical challenges of modeling the D rich mixture versus the intrinsic errors of using a pressure mixing rule to describe the system towards the molar-mixing maximum.

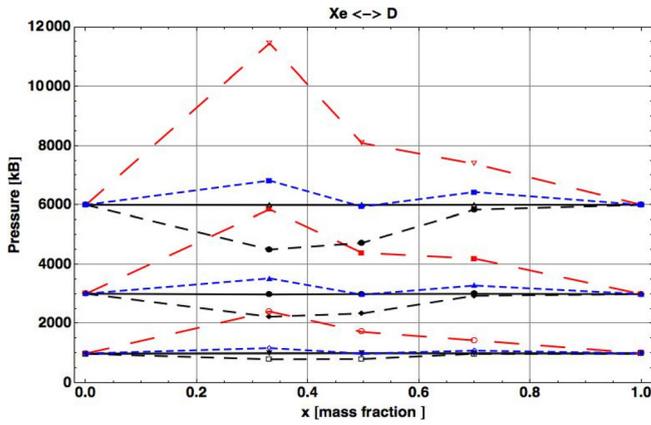


FIG. 6. The curves show the exact (DFT/QMD with AM05—flat black) results for the explicit mixture at 10 kK and 1, 3, and 6 Mbar and the results of mixing rules constructed using pure material EOS: ideal—long-dashed red, volume—dashed black, and pressure—short-dashed blue.

In Fig. 6, we show how the relative accuracy of various mixing rules changes with pressure. The 3 Mbar results from Fig. 4 are re-plotted here using the rescaling discussed above. Several important trends can be observed. First, the relative inaccuracy of the ideal mixing rule grows substantially with increasing pressure. This is true also of the volume mixing but the plot suggests that below 1 Mbar, the volume mixing rule is reasonably reliable. Also, note that at 3 Mbar, the rescaling process brings the pressure rule to comparable absolute accuracy as the volume rule. As the unscaled results do not isolate fundamental deficiencies of the scaling rules from systematic DFT inaccuracies, this later result suggests that at 3 Mbar and above, the pressure rule is expected to be more reliable. The pressure mixing rule remains reliable at high pressures with the dominant errors coming from the EOS of the pure systems scaled away. It is most striking that the volume mixing rule becomes relatively more inaccurate at higher pressures. This is because at higher pressures mixture atoms are much closer to each other and inter-atomic attractive forces play an important role.

The reliable performance of the mixing models can be understood as follows. First, it must be recalled that at fixed

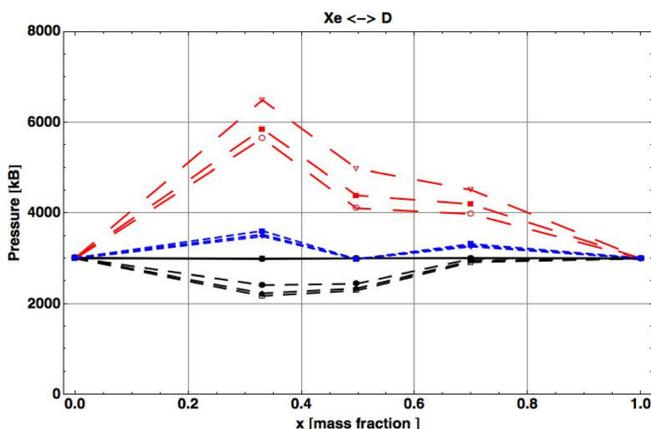


FIG. 7. Mixing scans at 3 Mbar and $T = 5$ kK, 10 kK, and 20 kK. The curves show the pressures predicted by various mixing rules using pure materials EOS or DFT data: Exact(DFT/QMD with AM05)—flat black, Ideal—long-dashed red, volume—dashed black, and pressure—short-dashed blue.

TABLE I. Root mean square errors over sampled mass mixture compositions (x) for various mixing rules versus results of DFT/QMD using AM05 for Xe-D mixtures.

Pressure	Temperature	RMS Errors/Ave from mixing rules		
		Ideal	Volume	Pressure
1 Mbar ^a	10 kK	0.44	0.06	0.11
1 Mbar	10 kK	0.33	0.05	0.05
3 Mbar ^a	10 kK	0.32	0.06	0.10
3 Mbar	10 kK	0.23	0.05	0.04
6 Mbar ^a	10 kK	0.27	0.05	0.08
6 Mbar	10 kK	0.20	0.07	0.03

^aDenotes that raw equation of state models are used for both pure systems; otherwise, the EOS values of the pure systems are scaled to match the DFT/QMD results for the pure materials.

temperature, the pressure of a material increases with a higher power law than linear with density, and the non-linear behavior affects how the ideal and volume mixing rules perform. The ideal rule samples higher pressures and combines the results using a linear mix of pressures. Because of the super-linear behavior of the isothermal pressure versus density curves for the pure EOSs, a higher than accurate pressure from the ideal rule is expected. In a similar fashion, the volume rule samples lower densities resulting in a smaller than accurate mix prediction. The pressure rule, on the other hand, samples the EOS at pressures that are commensurate with the actual mixture. The pressure rule still slightly underestimates the mix pressure. The reason for this is that the pressure rule does not account for the inter-species forces beyond lowest order which in this system would enhance the pressure slightly.

Fig. 7 shows how the mixing rules perform over a range of temperatures. While there is some variation with temperature, the general trends and performance are relatively unaffected by the temperature of the system. Based on this result, the dominant criteria for determining ranges of validity of mixing rules is total pressure.

Table I shows the relative root mean squared difference between the various mixing rules and DFT for total pressure at the calculated mixing ratios. The errors given by the volume mixing rule do not depend strongly on the scaling of the pure systems EOS tables, while the higher pressure rule results are significantly dependent on the quality of the EOS tables. An interesting conclusion of this work is that the error associated with the EOS, especially the D EOS, is larger than the error introduced for this mixture by using the pressure mixing rule.

IV. SUMMARY AND DISCUSSION

Hydrodynamics simulations of high energy density physics (HEDP) phenomena require a detailed knowledge of the equation of state of the constituents of the problem as well as their mixtures. In this paper, we analyzed how the pressure is described by different mix rules as compared to high-fidelity DFT/QMD simulations. It is found that in the multi megabar and kilokelvin range, mixture models using EOS information of the pure components that are based on equilibrated pressures perform with higher accuracy than the

uncertainty of the underlying EOS models. The mixture considered here, xenon-deuterium, has limited inter-species chemistry, and it is not clear to what extent these conclusions would hold in cases with significant chemistry between the species.

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