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Equation of state of mixtures: density functional theory (DFT) simulations and experiments on Sandia's Z machine

R. J. Magyar*, **S. Root***, **T. A. Haill***, **D. G. Schroen**†, **T. R. Mattsson*** **and D. G. Flicker***

**Sandia National Laboratories, Albuquerque, NM 87185*
†*General Atomics, Albuquerque, NM 87185*

Abstract. Mixtures of materials are expected to behave quite differently from their isolated constituents, particularly when the constituents atomic numbers differ significantly. To investigate the mixture behavior, we performed density functional theory (DFT) calculations on xenon/hydrogen (deuterium) mixtures. Since the DFT simulations treat electrons and nuclei generically, simulations of pure and mix systems are expected to be of comparable accuracy and we present a method to simulate mixtures at constant pressure, an approach that makes comparisons between different mix models straightforward.

Keywords: mixtures, xenon, deuterium, EOS, DFT-MD

INTRODUCTION

Many applications of hydrocodes require knowledge of mixtures at high pressures and temperatures. For example, mixing rules are critical to models of internal confinement fusion [1, 2], and the earths core [3, 4], and the interiors of giant gas planets [5, 6] as well as solar convection models [7]. An important question is whether models of mixed systems are valid under intense pressures and high temperatures. Typically in these codes, mix properties are modeled through a blending of the equations of state (EOS) of pure constituents.

Mixtures of materials are often studied at constant pressure while the proportions of the mix components are varied. This happens for example during a chemical reaction at standard conditions. Since pressure is an intensive variable, it affects all consituents of a equilibrated system in a similar fashion. To compare existing data and to develop models for use in hydrocodes, it is important to be able to numerically study mixtures at fixed average pressure. We have developed an algorithm and script to control the pressure in density functional based molecular dynamics simulations. In particular, we present results of the mix of Xe and D at high pressure as a model system.

One of the most successful ways to experimentally probe GPa pressures and kK temperatures is through shock experiments. These experiments are often quite expensive and challenging to preform over a wide range of mixture compositions. On the other hand, theoretical methods have been shown to be tremendously predictive in modeling materials in this pressure and temperature regime. In particular, density functional molecular dynamics (DFT-MD) has been used with great success to study warm dense matter [8, 9, 10]. Using supercomputers, simulations across a broad range of mix compositions can be performed in a reasonable time-span and at modest cost. The DFT-MD calculations treat the electrons and nuclei generally so mixture calculations are not distinct and are expected to provide comparable results to pure system calculations. In DFT-MD, no particular theoretical bias is built into the mix calculations whereas empirical models are constructed with particular physical models in mind.

In order to extract useful results from DFT mixture simulations, a method to model fixed pressure mixing is needed. A constant pressure simulation can be achieve in a DFT-MD calculations using an numeri-

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cal barostat. However, this introduces additional degrees of freedom to the calculation making comparison of various mixture compositions difficult. An alternative approach is to find a fixed average pressure can be achieved through an iterative process. In this proceeding, we propose a simple scheme to perform these target pressure simulations with a quantum mechanical molecular dynamics formalism.

COMPUTATIONAL TOOLS

Density functional theory molecular dynamics (DFT-MD) is the computer simulations of the motion of many nuclei with thermally excited electrons. 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.

Central to the goal of predictive simulations in density functional theory (DFT) [11, 12] is the need for convergence [13]. The DFT-MD simulations were performed with VASP 5.1.40 [14, 15, 16], a plane-wave projector augmented-wave (PAW) core function code. [17, 18] using stringent convergence settings [13]. Steady-state simulations in the NVT ensemble used a Nosé-Hoover thermostat with velocities scaled to control temperature in the ramped-temperature simulations. 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 [20]. We could choose several exchange-correlation functionals but report the results for only one generalized gradient method, AM05 [21, 22]. Results within the local density approximation were comparable. Note that D is used in place of H in these MD calculations because it allows for longer time-steps. It is expected that the mixture calculations are of comparable accuracy.

A shell script performs the search for the supercell dimensions that contain a system with a time averaged pressure at a fixed nuclear and electronic temperature. This is done by adjusting the lattice scale and performing a DFT-MD 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 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 statistics are collected to provide a meaningful average pressure. This typically requires 400-800 fs steps. Once the target pressure is achieved, a longer simulation (2-4 ps) 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 barostat is that at each time step, the system is not constrained to a chosen pressure.

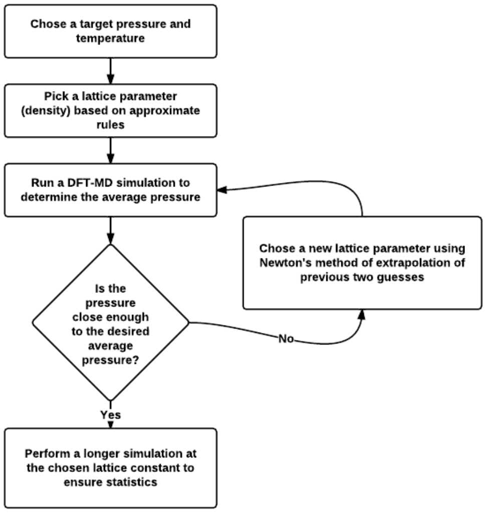

FIGURE 1. Flowchart depicting the algorithm used to find the fixed average pressure. This scheme is run until the longer time simulation is also within the desired pressure window.

MODELS OF MIXTURES OF PURE MATERIALS

The fixed average pressure method is particularly useful to examine the fidelity of mixing models. We restrict our analysis here to the description of the total pressures of binary mixtures of pure materials. Three of the most commonly used pressure mixing models are the ideal, volume, and pressure rules. The ideal mixing rule is based off 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

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

where P_A and P_B are the equations of state for the pure systems at the total density ρ. This mixing rule is sometimes used in planetary modeling.

The volume mixing rule accounts for the relative sizes of the mixture components and can be related to the fractional cell rules used in many hydrocodes. The volume rule gives the total pressure as

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

Notice the position of x_A. This means that the EOS for the pure materials will be sampled far from the total density point, ρ.

The pressure mixing rule requires that the partial pressures of the components be equal at a chosen mix ratio. The set of equations to be solved are

$$P_A[\rho_A,T] = P_B[\rho_B,T] \tag{3}$$

and

$$\frac{x_A}{\rho_A} + \frac{1-x_A}{\rho_B} = \frac{1}{\rho}. \tag{4}$$

The pressure rule 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.

LIQUID MIXTURE OF XENON AND DEUTERIUM

As a test case, we present results for a Xe-D mixture. This system represents a very idealized situation where two mostly non-interacting elements coexists at high pressure. Earlier computational work has demonstrated that DFT-MD calculations of pure Xe and pure D are highly reliable [8, 9].

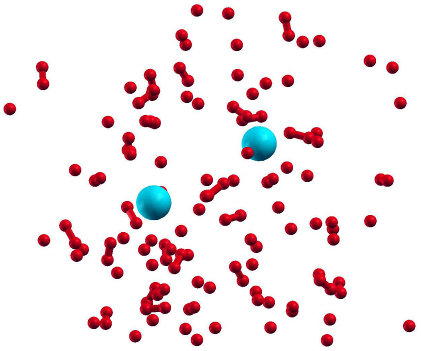

FIGURE 2. Xe-D mixture at $\rho = 5.4$ g/cc and T=10kK.

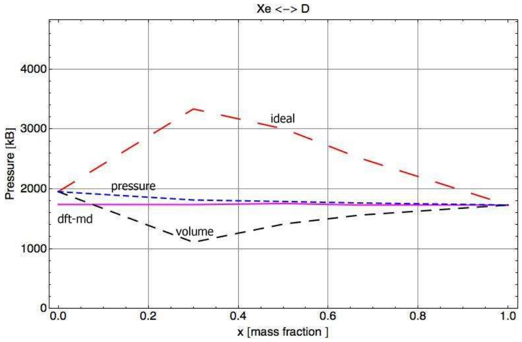

FIGURE 3. Xe-D mixture at 1.8Mbar and T=10kK.

Figure 2 illustrates a supercell used in the simulations. Xe and D are mixed at a 0.5 mass ratio,10kK, and compressed density of 5.4 g/cc resulting in a multi MBar pressure. At this elevated temperature and pressure, most of the D molecules are dissociated.

Figure 3 presents the results for the same Xe-D mix at a slightly different pressure of 1.8 MBar and 10kK. The DFT results are obtained using the fixed target pressure scheme. The DFT-MD results in total density and pure component densities that are in turn inputted into various mixing models. The mixing models combine equations of state for pure Xe and D to predict the pressure of the mixtures. It is apparent that the ideal mixing law grossly over estimates the pressure of the mixtures at these higher densities and temperatures. The volume mixture model underestimates the predicted pressure by a comparable percentage. The pressure mixing model performs reliably well compared to the DFT-MD results. The performance of the mixing models can be understood as follows. First, it must be recalled that at fixed temperature the pressure of a material increases at a higher power than linear with density, and the non-linear behavior affects how the ideal and volume mixing rules perform. The idea rule samples higher pressures and combines the results using a linear mix of pressures. Because of the superlinear 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 smaller densities resulting in a smaller than accurate mix prediction. The pressure rule on the other hand samples the equation of state at pressures that are commensurate with the given densities. The pressure rule still slightly underestimates the mix pressure (this can be seen if the pure Xe point is scaled to the DFT result). The reason of this is that the pressure rule does not account for the inter species forces which in this system would enhance the pressure slightly. In energy term, this is the enthalpy of mixing and may be positive or negative depending on the chemistry between the pure species.

CONCLUSIONS

In this proceedings we have introduced a simple algorithm to obtain fixed pressure simulations of materials that is straightforward to implement external to a DFT-MD code and provides computational results that are comparable across a range of mixture compositions. We show how this analysis provides information about approximate mixing rules using the example of of a Xe-D mix.

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REFERENCES

1. H.U. Rahman, N. R., F.J. Wessel, and Ney, P., *J. Plasma Physics*, **75**, 749 (2009).
2. H.U. Rahman, N. R., P.H. Ney, and Wessel, F., *Atrophys. Space Sci.*, **323**, 51 (2009).
3. D. Alfe, M. J. G., and Price, G. D., *J. Chem. Phys.*, **116**, 7127 (2002).
4. S. Ostanin, D. D. L. V. J. B., A. Afle, and Price, G., *Geophysical Research Letters*, **33**, L06303 (206).
5. W.Lorenzen, B., and R.Redmer, *Phys. Rev. Lett.*, **102**, 115701–1 (2009).
6. H.F.Wilson, and Militzer, B., *Phys. Rev. Lett.*, **104**, 121101–1 (2010).
7. Jiayu Dai, Y. H., and Yuan, J., *The Astrophysical Journal*, **721**, 1158 (2010).
8. Desjarlais, M. P., *Phys. Rev. B*, **68**, 064204 (2003).
9. S.Root, J. C. D. H., R.J.Magyar, and Mattsson, T., *Phys. Rev. Lett.*, **105**, 085501–1 (2010).
10. J.H. Carpenter, S. R. R. M. D. H., D.G. flicker, and Mattsson, T., *New models and hydrocodes for shock wave processes in condensed matter* (2011).
11. Hohenberg, P., and Kohn, W., *Phys. Rev.*, **136**, B864 (1964).
12. Kohn, W., and Sham, L. J., *Phys. Rev.*, **140**, A1133 (1965).
13. Mattsson, A. E., Schultz, P. A., Desjarlais, M. P., Mattsson, T. R., and Leung, K., *Modelling Simul. Mater. Sci. Eng.*, **13**, R1 (2005).
14. Kresse, G., and Hafner, J., *Phys. Rev. B*, **47**, R558 (1993).
15. Kresse, G., and Hafner, J., *Phys. Rev. B*, **49**, 14251 (1994).
16. Kresse, G., and Furthmüller, J., *Phys. Rev. B*, **54**, 11169 (1996).
17. Bloechl, P., *Phys. Rev. B*, **50**, 17953 (1994).
18. Kresse, G., and Joubert, D., *Phys. Rev. B*, **59**, 1758 (1999).
19. Mermin, N., *Phys. Rev.*, **137**, A1441 (1965).
20. Mattsson, T. R., and Desjarlais, M. P., *Phys. Rev. Lett.*, **97**, 017801 (2006).
21. Armiento, R., and Mattsson, A. E., *Phys. Rev. B*, **72**, 085108 (2005).
22. Mattsson, A. E., Armiento, R., Paier, J., Kresse, G., Wills, J. M., and Mattsson, T. R., *J. Chem. Phys.*, **128**, 084714 (2008).