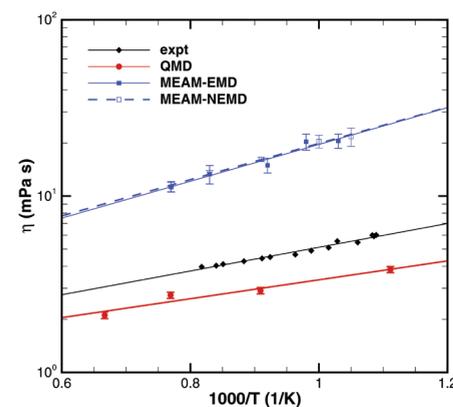


# Quantum Molecular Dynamics Simulations of Transport Properties in Liquid and Dense-Plasma Plutonium

Joel D. Kress, James S. Cohen, David P. Kilcrease,  
Daniel A. Horner, Lee A. Collins, T-1

We have calculated the self-diffusion coefficients and shear viscosity of plutonium in the liquid phase using QMD, and in the dense-plasma phase using OFMD, as well as in the intermediate warm dense matter regime with both methods. Our liquid metal results for viscosity are about 40% lower than measured experimentally. The QMD and OFMD results agree well at the intermediate temperatures. The calculations in the dense-plasma regime for temperatures from 50 to 5000 eV and densities about 1–5 times ambient are well fit by a simple power law in density and temperature. A Stokes-Einstein relationship of the viscosities and diffusion coefficients is found to hold well in both the liquid and dense-plasma regimes.

Fig. 1. (Color online) Shear viscosity of liquid plutonium as a function of inverse temperature: experimental results (diamonds, no error bars were given); present QMD calculations (circles, with statistical error bars); MEAM calculations by equilibrium molecular dynamics (EMD, solid squares) and by nonequilibrium molecular dynamics (NEMD, open squares). The straight lines are exponential (Arrhenius) fits to the data points.



Plutonium (Pu) ranks as the heaviest naturally occurring element given its presence in trace amounts within uranium ores. This distinction gives rise to several atypical properties when compared with standard metals. Plutonium has a very low melt temperature (913K) and contracts while melting (a property shared by water and some semimetals) and has poor electrical and thermal conduction characteristics, but has good elastic compressibility. While most noted in its role in nuclear explosions, plutonium has many applications such as supplying the heating element in radioisotope thermoelectric generators used in remote sensing stations and deep-space craft such as Cassini, and forming a principal component in closed fuel cycles for fast nuclear reactors as part of advanced energy initiatives. In contrast to the extensive experimental, theoretical, and computational efforts to elucidate the material properties of the solid allotropes, the liquid phase has remained relatively unexplored except around the melt temperature due to its highly reactive, corrosive, and radioactive nature. Measurements exist of the shear viscosity up to 1500K, as well as of various optical properties.

Given the paucity of information above melt, we have employed molecular dynamics simulation techniques to determine the transport properties, both diffusion and viscosity, of Pu from the liquid, through the Warm, Dense Matter (WDM), to the plasma regime over a broad range of temperatures [0.1–5 keV] and compressions [1–5x solid]. The WDM regime, although somewhat ill-defined, spans a range of densities between 1/100 and 100 solid and temperatures from about 1 eV to several hundred eV and marks a region that resembles a soup of various particle types including atoms, ions, free electrons, and even molecules in a highly transient state for which a quantum mechanical treatment obtains. As the temperature rises and

ionization increases, the particle interactions become more classical, signaling the beginning of a plasma environment. To examine this broad range of conditions, we applied quantum molecular dynamics (QMD) and orbital-free molecular dynamics (OFMD) simulations, both of which treat the electrons quantum mechanically and the nuclei classically. Our previous investigations on such systems as hydrogen and lithium hydride have demonstrated that for static (equation-of-state) and transport properties the semi-classical OFMD generally agrees well with QMD in intermediate temperature and density regimes and can effectively reach very high temperatures (~ 5 keV). The present work is described in a recently submitted paper [1].

The QMD simulations employed the Vienna ab initio Simulation Package (VASP), in which the electrons are treated fully quantum mechanically using a plane-wave finite-temperature density-functional-theory (FTDFT) description. In OFMD simulations, the kinetic energy of the electrons is treated in a semi-classical approximation, up to first order in the partition function of the electrons. The orbital-free procedure treats all electrons on an equal footing, albeit approximately, with no distinction between bound and ionized electrons.

To aid in the analysis of the simulation results, we consider three simple models/phenomenological forms for describing transport: kinetic theory, the Arrhenius equation, and the Stokes-Einstein relation. The latter gives a connection between the diffusion and shear viscosity through an expression

$$F_{se}[D, \eta] \equiv \frac{D\eta}{k_B T n_a^{1/3}} = C_{se}$$

with  $C_{se}$ , a constant and  $F_{se}$ , a shorthand notation for the relationship between the transport coefficients. Many prescriptions exist for determining the constant  $C_{se}$ . From the original derivations based on the

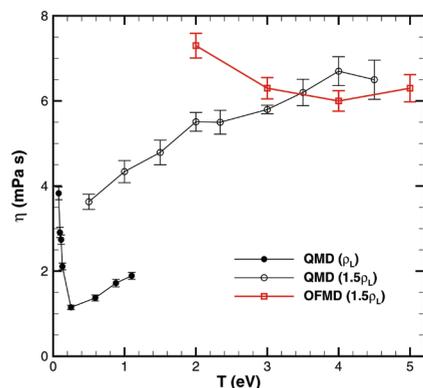


Fig. 2. (Color online) Viscosity of plutonium as a function of temperature in the WDM regime, calculated by the QMD method for densities of 17.44 g/cm<sup>3</sup> ( $\rho_L$ ; solid circles) and 26.11 g/cm<sup>3</sup> ( $1.5 \rho_L$ ; open circles) and by the OFMD method (open squares) at  $\rho = 26.11$  g/cm<sup>3</sup>. The straight line segments between data points are provided to only guide the eye and the error bars are statistical only.

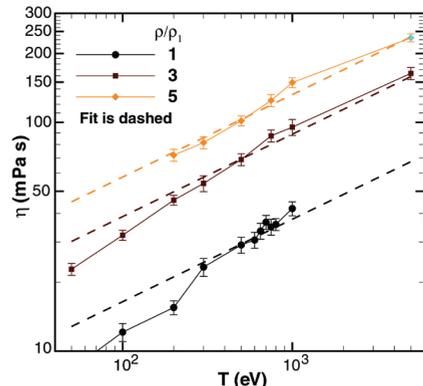


Fig. 3. (Color online) OFMD calculations of shear viscosity of dense-plasma plutonium with fit (dashed) with  $\rho_1 = 20$  g/cm<sup>3</sup>.

motion of a test particle through a solvent,  $C_{se}$  ranges from  $1/6\pi$  (0.053) or  $1/4\pi$  (0.080) depending on the limits of the slip coefficient from infinity (stick) to zero (slip) respectively. On the other hand, Chisolm and Wallace [2] determined an empirical value of  $0.18 \pm 0.02$ , based on a global fit to 21 liquid metals. We shall examine to what extent these phenomenological forms represent the behavior of Pu over the various regimes we explore.

In Fig. 1, we compare the experimentally-measured viscosity of liquid plutonium with results from our QMD simulations ( $N_a=54$ ) and the previous MEAM calculations [3], which employed a classical interatomic potential. A liquid (L) density of  $\rho_L = 17.44$  g/cm<sup>3</sup> was used in the QMD simulations at all four temperatures. The QMD results are about 40% lower than the experiment while the MEAM results are 3–4 times higher, making the MEAM viscosities 4–7 times larger than the QMD. In both cases, the differences with the experimental values are considerably larger than the theoretical error bars (no error bars were given in the report of the experiment). As can be seen from the points falling approximately on a straight line in the semilogarithmic plot, the results of both calculations, as well as the experiment, are fit fairly well by an Arrhenius form  $\eta = \eta_0 e^{-E_a/k_B T}$ .

We now raise the temperature while remaining near liquid density ( $\sim 20$  g/cm<sup>3</sup>) in order to enter the WDM regime. The QMD and OFMD results are shown in Fig. 2 as a function of temperature for two densities: 1)  $\rho_L = 17.44$  g/cm<sup>3</sup> for QMD, and 2)  $1.5 \rho_L = 26.21$  g/cm<sup>3</sup> for both QMD and OFMD.

We first examine the QMD results at liquid density,  $\rho_L$ . The viscosity displays a clear change in character as a function of temperature. Just above the melting temperature, the viscosity decreases with increasing T with an Arrhenius behavior typical of a liquid metal, whereas at higher temperatures, the viscosity steadily rises with temperature, resembling the behavior for a hard-sphere fluid or a partially ionized one-component plasma. This behavior represents a shift from processes dominated by the potential interactions to those controlled by the kinetics. This competition leads to a distinct minimum in the viscosity at around  $T \sim 0.4$  eV.

In addition, this transition regime provides an excellent test bed for comparing the QMD and OFMD approaches. Due to the number of active

electrons and the increasing number of states required for the diagonalization of the KS equations, the QMD becomes computationally prohibitive above about 5 eV for our choice of parameters. On the other hand, the need to represent detailed quantum mechanical interactions begins to wane as the temperature rises so that the OFMD gains greater validity. To this end, we have compared the QMD and OFMD at the higher density ( $1.5 \rho_L$ ), as displayed in Fig. 2. The results for the two formulations between 2 and 4 eV agree closely to within the statistical error bars for both  $D$  and  $\eta$ .

The Stokes-Einstein expression  $F_{se}[D, \eta]$  was calculated as a function of temperature, using the diffusion coefficients and viscosities from the OFMD at  $1.5 \rho_L$  and the QMD at  $\rho_L$  and  $1.5 \rho_L$ . The QMD and the OFMD results (not shown) are in relatively good agreement and bounded by the classical values of  $C_{se}$  from below and the Chisolm-Wallace liquid metal value from above. The QMD results between  $T=1100$  and 40,000 K for both densities are tightly distributed about a constant value of  $C_{se} = 0.11 \pm 0.01$ .

In Fig. 3, the shear viscosity  $\eta$  calculated with OFMD is shown for plutonium at temperatures between 50 eV and 5 keV and densities between 20 and 100 g/cm<sup>3</sup> or approximately solid density to five times compressed. The shear viscosity increases with temperature in this range. Some simplified models or limiting cases predict power-law dependences on temperature and density such as the hard-sphere approximation. Though such formulas are oversimplified, we have attempted to fit our numerical data on viscosity  $\eta$  over the whole temperature and density range. The resulting least-squares fit is  $\eta_{fit} = a_\eta T^{b_\eta} (\rho/\rho_0)^{c_\eta}$  (mPa sec) with  $a_\eta = 3.13 \pm 0.26$ ,  $b_\eta = 0.360 \pm 0.010$ , and  $c_\eta = 0.780 \pm 0.034$ , where  $T$  is in eV and  $\rho$  is in g/cm<sup>3</sup>. The fit of the viscosity, shown in Fig. 3, follows all the calculated points to within  $\sim 30\%$ , except for those at  $T=50$  eV and  $\rho/\rho_0 = 1$ . The fits improve as  $T$  increases.

[1] Kress, J.D., et. al., “Quantum Molecular Dynamics Simulations of Transport Properties in Liquid and Dense-Plasma Plutonium,” *Phys Rev E*, submitted; LAUR-10-07728 (2010).

[2] Chisolm and Wallace **NEEDED**

[3] Cherne, F.J., et al., *Phys Rev B* **67**, 092104 (2003).

**Funding Acknowledgments**

Advanced Simulation and Computing Program