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Mass Transport Properties of Pu/DT Mixtures from Orbital Free Molecular Dynamics Simulations

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Abstract. Mass transport properties (shear viscosity and diffusion coefficients) for Pu/DT mixtures were calculated with Orbital Free Molecular Dynamics (OFMD). The results were fitted to simple functions of mass density (for ρ=10.4 to 62.4 g/cm^3) and temperature (for T=100 up to 3,000 eV) for Pu/DT mixtures consisting of 100/0, 25/75, 50/50, and 75/25 by number.

Obtaining transport coefficients for Pu/DT mixtures of different $Pu_xDT_{(1-x)}$ compositions as functions of temperature and mixture density is a tedious task. Quantum molecular dynamics (MD) simulations can be employed, as in the case of pure Pu or pure DT. However, due to the presence of the heavy constituent Pu, simulations of Pu/DT mixtures proceed so slowly that only a limited number of numerical data points in the (x, ρ, T) phase space can be obtained. To finesse this difficulty, transport coefficients for mixture compositions x=0.25, 0.50, and 0.75 have been calculated. The ultimate goal (future work) will be: 1) to combine the results with those for pure Pu (x=1) and pure DT (x=0) and derive interpolation formulae for all x = [0,1], and; 2) explore reproducing the mixture simulation results from the pure DT and Pu results using mixing rules. For Pu, the corresponding transport coefficients were obtained earlier from quantum molecular dynamics simulations. In these simulations, the quantum behavior of the electrons was represented using an orbital free (OF) version of density functional theory, and ions were advanced in time using classical molecular dynamics. The total pressure of the system, $P = nk_BT/V + P_e$, is the sum of the ideal gas pressure of the ions plus the electron pressure. The mass self-diffusion coefficient for species i, D_i , and the shear viscosity, η, are computed from the appropriate autocorrelation function [1].

The details of similar OFMD calculations on LiD/U are described in Ref. [2], on pure Pu as described in Ref. [3], and for DT for $2 < T < 10$ eV and $2 < \rho < 20$ g/cm^3 as described in Ref. [4] and $10 < T$ 100 eV and $0.5 < \rho < 5$ g/cm^3 as described in Ref. [5]. Results for DT for T > 100 eV will be described in future work [6] with regards to H/Ag mixtures. The results (shear viscosity, η, and self-diffusion coefficients D_i for i=Pu, D, T, and "DT") from the OFMD simulations using typically N=108 atoms were fit over a range of mass densities (for ρ=10.4 to 62.4 g/cm^3) and temperatures (for T=100 up to 3,000 eV). For the 50/50 (by number) Pu/DT mixtures both three-component (Pu with explicit D and T atoms, Pu/D/T=50/25/25) and two-component simulations (Pu with composite "DT" atoms) were performed. For the latter, "DT" was a hydrogenic ion (Z=1) of atomic mass A=5/2. After verifying that the two-component mixtures yield results consistent with the three-component mixtures, simulations for the 25/75 and 75/25 mixtures were conducted with only two-components for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV. Since the two-component simulations use twice as many light atoms of a

given type compared to the three-component simulations, the statistics of the motion of the light atoms is improved by a factor of $\sqrt{2}$.

Our numerical data on viscosity and mass diffusion over the entire temperature and density range are fitted to formulas inspired by Dufreche and Clerouin based on their study [7] of dense fluid hydrogen [T in eV, ρ in g/cm^3, and $X=(\rho/T^3)$]:

$$\eta = T^{5/2} \exp(a + b \ln(X) + c [\ln(X)]^2 + d [\ln(X)]^3) \text{ mPa·s}, \quad (1)$$

$$D = T^{5/2}/\rho \exp(a' + b' \ln(X) + c' [\ln(X)]^2 + d' [\ln(X)]^3) \text{ cm}^2/\text{s}. \quad (2)$$

Before discussing the results we summarize the findings:

Shear viscosity (Pu/DT ratio by number)
50/50: $\log_{10}(\eta) = -0.8468 + 2.5 \log_{10}(T) + 0.6207 \log_{10}(X)$, R=0.995
25/75: $\log_{10}(\eta) = -0.5071 + 2.5 \log_{10}(T) + 0.6400 \log_{10}(X)$, R=0.987
75/25: $\log_{10}(\eta) = -0.6183 + 2.5 \log_{10}(T) + 0.6635 \log_{10}(X)$, R=0.997
100/0: $\log_{10}(\eta) = -0.3930 + 2.5 \log_{10}(T) + 0.7169 \log_{10}(X)$, R=1.000
0/100: $\log_{10}(\eta) = -1.5455 + 2.5 \log_{10}(T) + 0.20161 \log_{10}(X)$, R=1.000

Light Ion Self-diffusion (Pu/DT ratio by number)
50/50: $\log_{10}(D_D) = -1.5144 + \log_{10}(T) - 0.6925 \log_{10}(\rho)$, σ =8.4%, R=0.980
50/50: $\log_{10}(D_T) = -1.6343 + \log_{10}(T) - 0.6684 \log_{10}(\rho)$, σ =11.2%, R=0.955
50/50: $\log_{10}(D_{DT}) = -1.5575 + \log_{10}(T) - 0.6829 \log_{10}(\rho)$, R=0.978
25/75: $\log_{10}(D_{DT}) = -1.6361 + \log_{10}(T) - 0.6401 \log_{10}(\rho)$, R=0.986
75/25: $\log_{10}(D_{DT}) = -1.5939 + \log_{10}(T) - 0.6751 \log_{10}(\rho)$, R=0.987

Heavy Ion Self-diffusion (Pu/DT ratio by number)
50/50: $\log_{10}(D_{Pu}) = -2.6259 + 0.4435 \log_{10}(T) - 0.4435 \log_{10}(\rho)$, σ =10.2%, R=0.979
25/75: $\log_{10}(D_{Pu}) = -2.6068 + 0.4215 \log_{10}(T) - 0.4215 \log_{10}(\rho)$, R=0.976
75/25: $\log_{10}(D_{Pu}) = -2.6059 + 0.4517 \log_{10}(T) - 0.4517 \log_{10}(\rho)$, R=0.982
100/0: $\log_{10}(D_{Pu}) = -2.8103 + 0.4952 \log_{10}(T) - 0.4952 \log_{10}(\rho)$, R=0.989

with η in mPa-sec, D_i in cm^2/sec, ρ in g/cc, and T in eV. σ=standard deviation of the relative difference between the OFMD results and the fit and R=goodness of fit.

In Figs. 1-4 the scaled OFMD results (shear viscosity, Pu, D, and T self-diffusion) are shown, along with linear least squares fit to the Dufreche/Clerouin inspired fitting functions for the three-component OFMD simulations of Pu/DT mixtures. The shear viscosity was fit to first and second order in $\log_{10}(X)$. The second order fit showed negligible improvement, so first order fits were carried out for the shear viscosities for the other mixtures considered later. When the self-diffusion coefficents were fit to the exact Dufreche/Clerouin form, agreement was less than satisfactory. Other expansion variables were tried with the following choices providing the best overall fit as given above in the summary. For the light ion self-diffusion, a fixed scaling of unity (vs. 5/2) of $\log_{10}(T)$ and a fitted linear scaling for $\log_{10}(\rho)$ worked best. For the heavy ion

self-diffusion, a fitted linear scaling for $\log_{10}(T)$ and $\log_{10}(\rho)$ worked best. For all four mass transport coefficients, the relative difference between the OFMD results and the chosen fitting formula is quite good over the entire range of temperatures and densities (σ=16% or better and goodness of fit of R=0.979 or better). In Fig. 5, the effective "DT" self-diffusion coefficients, constructed from the average of the mass-scaled self-diffusion coefficients for D and T, D_{DT}= ½ $(2/2.5)^{½}$ D_D + ½ $(3/2.5)^{½}$ D_T, are also fitted to the light-ion fitting function for comparison with the 25/75 and 75/25 mixtures results, since the latter were only carried out as two-component simulations. Some two-component simulations were carried out for 50/50 mixtures and the resulting "DT" self-diffusion coeffients agreed with the mass-scaled approximations to within the uncertainty of the three-component simulations. In Fig. 6, the Schmidt number $Sc_i = n/D_i$, where n = kinematic viscosity = η/ρ, is plotted vs. the various cases (points in ρ, T phase space) considered in this work for the three-component simulations over the full range of T and ρ. (There are more cases for Pu relative to D and T because the 50/50 simulations for ρ=62.4 g/cm^3 were two-component performed with "DT".) Note that the lightest species (D) diffuse quickest and vice versa (Pu), as Sc_D and Sc_T fluctuate about a value of ~0.02 and Sc_{Pu} flucuates about a value of ~3.

In Figs. 7-10 the scaled OFMD results (shear viscosity, Pu, and "DT" self-diffusion and Pu/"DT" mutual diffusion) are shown for the two-component OFMD simulations of Pu/DT mixtures 25/75 by number. Also shown are the linear least squares fit of each fitting function that gave the best fit for the 50/50 mixture. As in the case for the 50/50 mixtures, the relative difference between the OFMD results and the fit is quite good over the entire range of temperatures and densities (goodness of fit of R=0.976 or better). In Fig. 11 for the 25/75 mixtures the Darken approximation is tested: $D_{12}=x_1D_2+x_2D_1$, where D_{12} is the predicted mutual diffusion coefficient, x_1 and x_2 are the mole fractions of components 1 and 2, respectively and D_1 and D_2 are the self-diffusion coefficients in the two-component binary mixture. Motivated by the fitting funciton, the log of the ratio of the actual mutual diffusion coefficient relative to the Darken result is plotted on the y-axis vs. $\log[1/\rho]$ on the x-axis. Perfect agreement is represented by the constant line for y=0. Note that for many of the simulations, the Darken approximation agrees with the actual result to 50% or better, although there are some outliers.

In Figs. 12-15, the scaled OFMD results (shear viscosity, Pu, and "DT" self-diffusion and Pu/"DT" mutual diffusion) are shown for the two-component OFMD simulations of Pu/DT mixtures 75/25 by number. Also shown are the linear least squares fit of each fitting function that gave the best fit for the 50/50 mixture. As in the case for the 50/50 and 25/75 mixtures, the relative difference between the OFMD results and the fit is quite good over the entire range of temperatures and densities (goodness of fit of 0.982 or better).

In Figs. 16 and 17, the scaled OFMD results (shear viscosity and Pu self-diffusion) are shown for the OFMD simulations for pure Pu [2]. Also shown are the linear least squares fit of each fitting function that gave the best fit for the 50/50 mixture. As in the case for all of the Pu/DT mixtures 50/50 and 25/75 mixtures, the relative difference between the OFMD results and the fit is quite good over the entire range of temperatures and densities.

For the 100/0 mixture (pure DT), the simple Extended Wallenborn-Baus (EWB) formula [8] for shear viscosity for Coulomb coupling Γ<1 was recast into the fitting function formula. OFMD simulations of shear viscosity for pure DT at elevated temperatures are very computationally demanding since small MD timesteps are needed to resolve the motion of light ions moving at extremely high velocities. We have verified that the EWB formula agrees well with a limited set of OFMD simulations for T=200 and 500 eV between 0.2 and 2 g/cm^3.

In summary, in order to interpolate over the Pu number fraction x, we express the fitting formulae as

$$\log_{10}(\eta) = a + 2.5 \log_{10}(T) + b \log_{10}(\rho/T^3)$$
$$\log_{10}(D_{DT}) = a + \log_{10}(T) - b \log_{10}(\rho)$$
$$\log_{10}(D_{Pu}) = a + b \log_{10}(T) - b \log_{10}(\rho),$$

where a and b are functions of x (see Table I). The following trend is observed for all three fits to the OFMD simulations: as x increases from 0.25 to 0.50 to 0.75, a is not monotonic and b is nearly constant. Finally, note that the a and b coefficents for the shear visocity of pure DT (0/100) are significantly different than the values for the 25/75 Pu/DT mixture, consistent with the results of classical MD simulations of heavy/light ion mixtures [8,9] and with the preliminary OFMD simulations for Ag/H mixtures [6].

Table I. Coefficients for the fitting functions for the mass transport coefficients. n/a=not applicable.

Pu/DT	η	η	D_{DT}	D_{DT}	D_{Pu}	D_{Pu}
x/(1-x)	a	b	a	b	a	b
0.00/1.00	$2.848\text{x}10^{-2}$	$2.161\text{x}10^{-1}$	-	-	n/a	n/a
0.25/0.75	$3.111\text{x}10^{-1}$	$6.400\text{x}10^{-1}$	$2.312\text{x}10^{-2}$	$6.401\text{x}10^{-1}$	$2.473\text{x}10^{-3}$	$4.215\text{x}10^{-1}$
0.50/0.50	$1.423\text{x}10^{-1}$	$6.207\text{x}10^{-1}$	$2.770\text{x}10^{-2}$	$6.829\text{x}10^{-1}$	$2.366\text{x}10^{-3}$	$4.435\text{x}10^{-1}$
0.75/0.25	$2.408\text{x}10^{-1}$	$6.635\text{x}10^{-1}$	$2.547\text{x}10^{-2}$	$6.751\text{x}10^{-1}$	$2.478\text{x}10^{-3}$	$4.517\text{x}10^{-1}$
1.00/0.00	$4.046\text{x}10^{-1}$	$7.169\ \text{x}10^{-1}$	n/a	n/a	$1.548\text{x}10^{-3}$	$4.952\text{x}10^{-1}$

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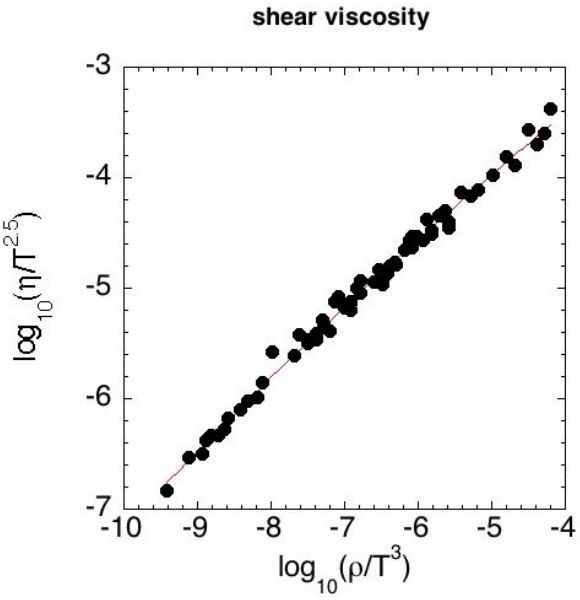

Fig. 1. OFMD simulation results for a 50/50 Pu/DT mixture (x=0.5) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 3,000 eV: Scaled shear viscosity $\log_{10}(\eta/T^{5/2})$ vs. $\log_{10}(\rho/T^3)$ (solid points). Linear fit to results (red line).

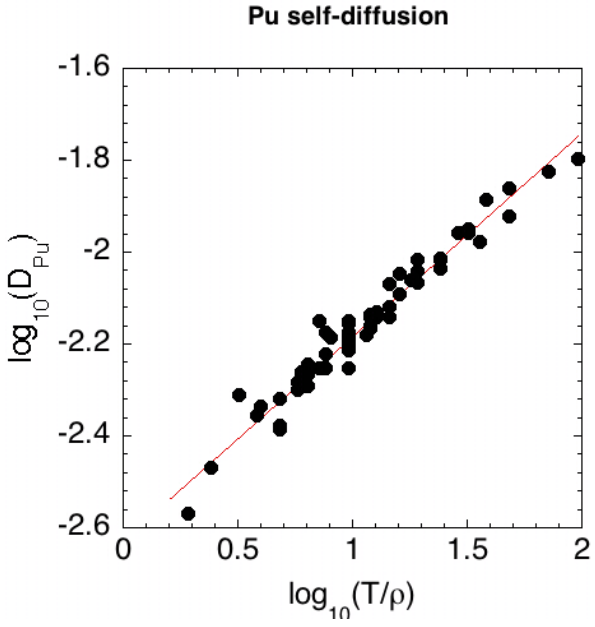

Fig. 2. OFMD simulation results for a 50/50 Pu/DT mixture (x=0.5) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 3,000 eV: Pu self-diffusion $\log_{10}(D_{Pu})$ vs. $\log_{10}(T/\rho)$ (solid points). Linear fit to results (red line).

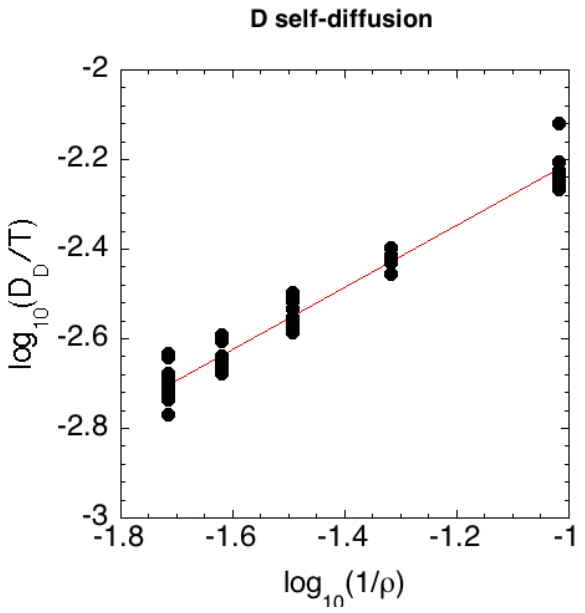

Fig. 3. OFMD simulation results for a 50/50 Pu/DT mixture (x=0.5) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 3,000 eV: Scaled deuterium self-diffusion $\log_{10}(D_D/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

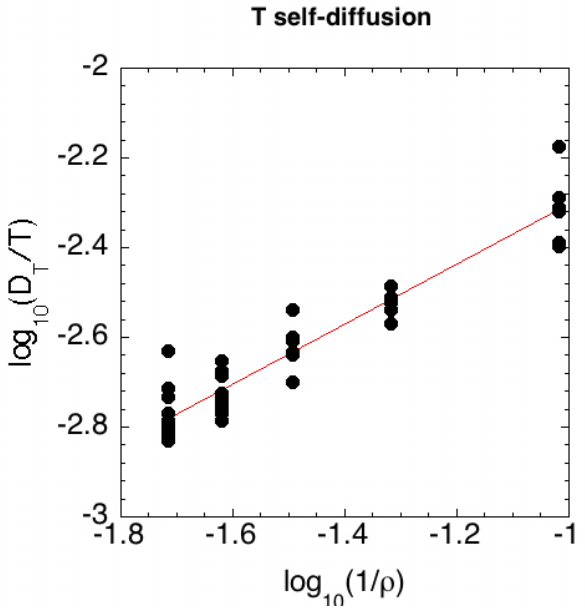

Fig. 4. OFMD simulation results for a 50/50 Pu/DT mixture (x=0.5) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 3,000 eV: Scaled tritium self-diffusion $\log_{10}(D_T/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

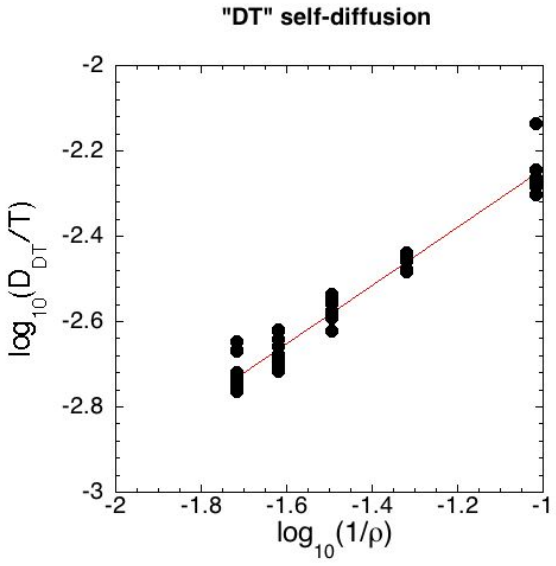

Fig. 5. OFMD simulation results for a 50/50 Pu/DT mixture (x=0.5) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 3,000 eV: Scaled "DT" self-diffusion $\log_{10}(D_{DT}/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

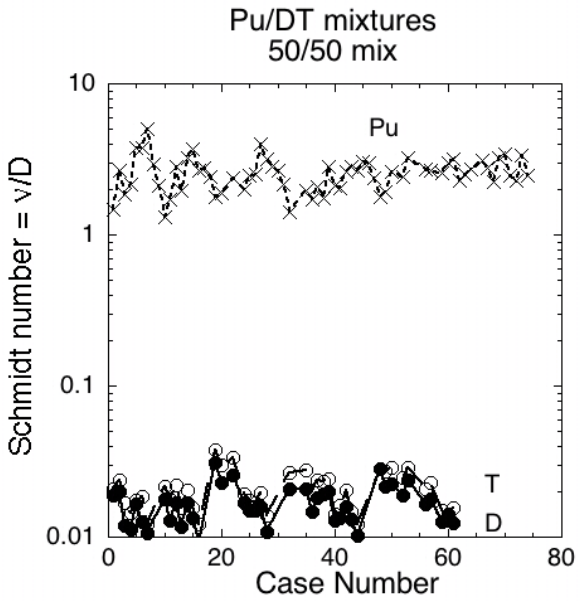

Fig. 6. OFMD simulation results for a 50/50 Pu/DT mixture (x=0.5): Schmidt numbers for representative cases T=100 to 3000 eV, ρ=1.8 to 62.4 g/cm^3.

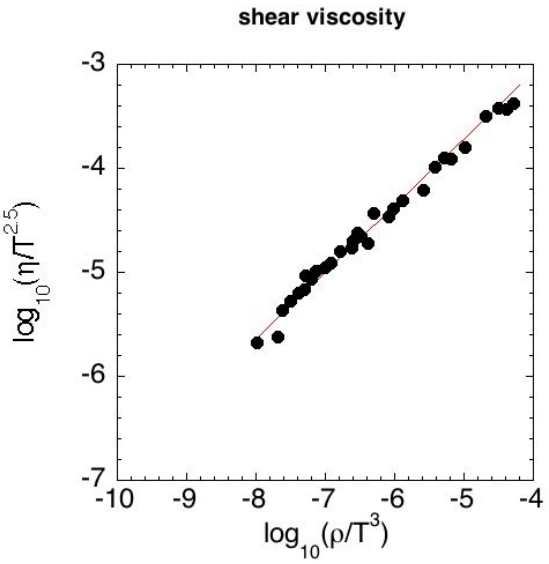

Fig. 7. OFMD simulation results for a 25/75 Pu/DT mixture (x=0.25) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Scaled shear viscosity $\log_{10}(\eta/T^{5/2})$ vs. $\log_{10}(\rho/T^3)$ (solid points). Linear fit to results (red line).

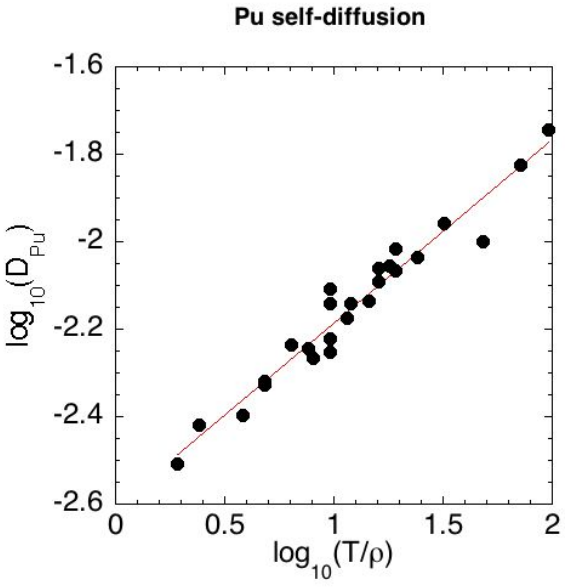

Fig. 8. OFMD simulation results for a 25/75 Pu/DT mixture (x=0.25) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Pu self-diffusion $\log_{10}(D_{Pu})$ vs. $\log_{10}(T/\rho)$ (solid points). Linear fit to results (red line).

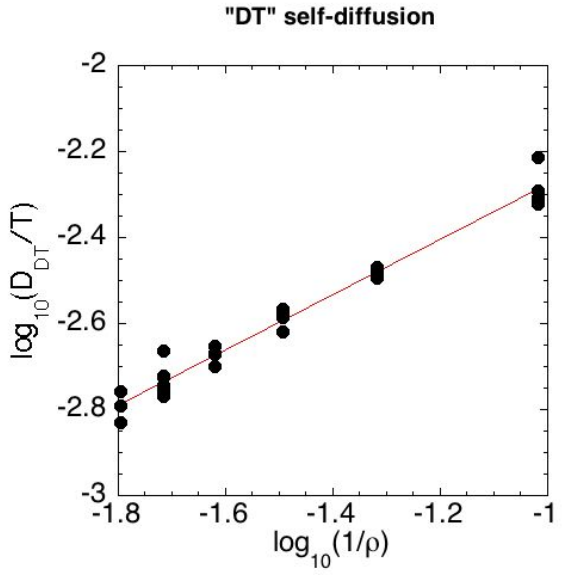

Fig. 9. OFMD simulation results for a 25/75 Pu/DT mixture (x=0.25) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Scaled "DT" self-diffusion $\log_{10}(D_D/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

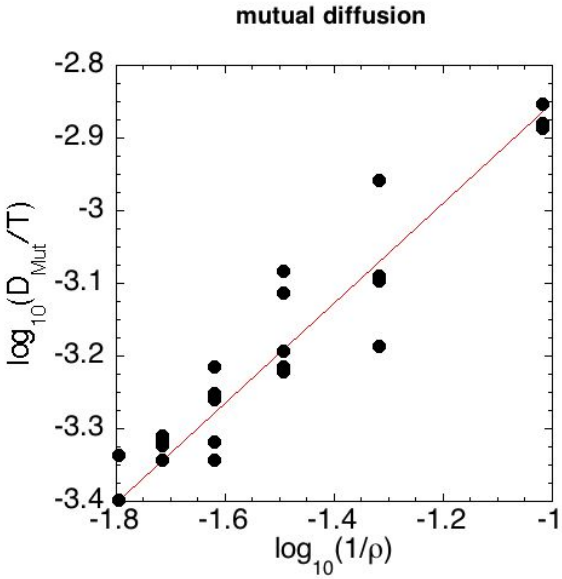

Fig. 10. OFMD simulation results for a 25/75 Pu/DT mixture (x=0.25) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Scaled mutual diffusion $\log_{10}(D_{Mut}/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

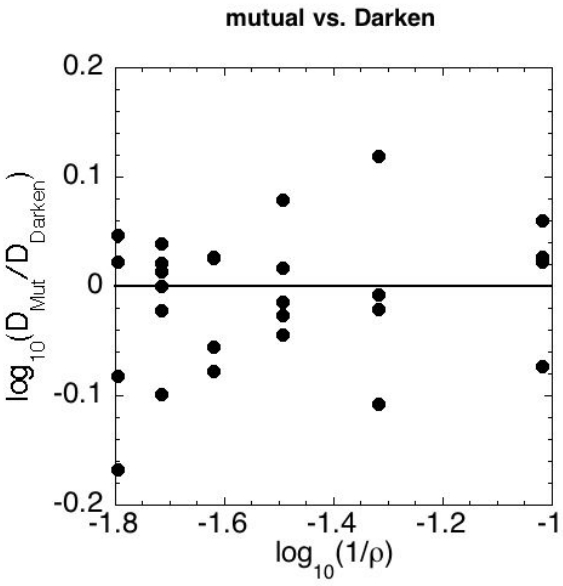

Fig. 11. OFMD simulation results for a 25/75 Pu/DT mixture (x=0.25) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Log_{10} of the ratio of (full mutual diffusion/Darken formula) vs. $\log_{10}(1/\rho)$ (solid points).

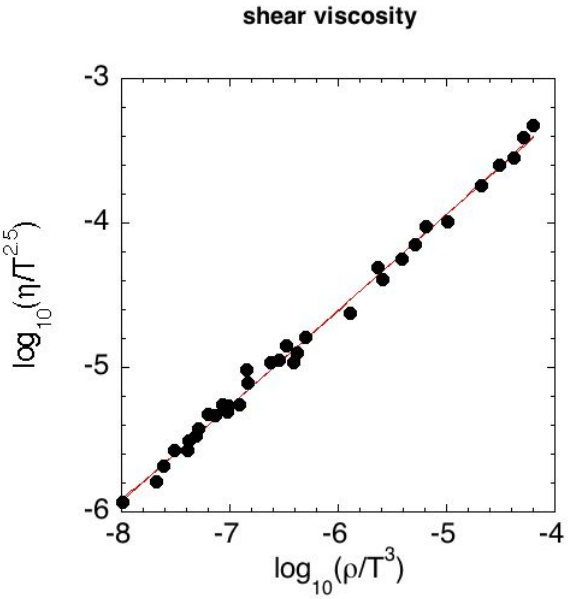

Fig. 12. OFMD simulation results for a 75/25 Pu/DT mixture (x=0.75) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Scaled shear viscosity $\log_{10}(\eta/T^{5/2})$ vs. $\log_{10}(\rho/T^3)$ (solid points). Linear fit to results (red line).

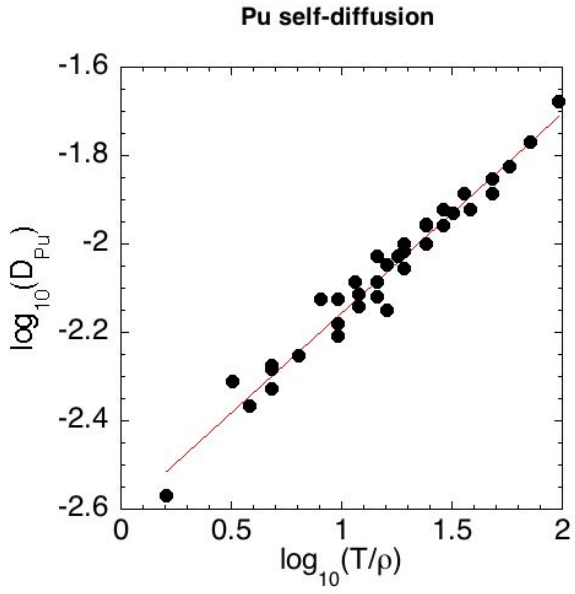

Fig. 13. OFMD simulation results for a 75/25 Pu/DT mixture (x=0.75) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Pu self-diffusion $\log_{10}(D_{Pu})$ vs. $\log_{10}(T/\rho)$ (solid points). Linear fit to results (red line).

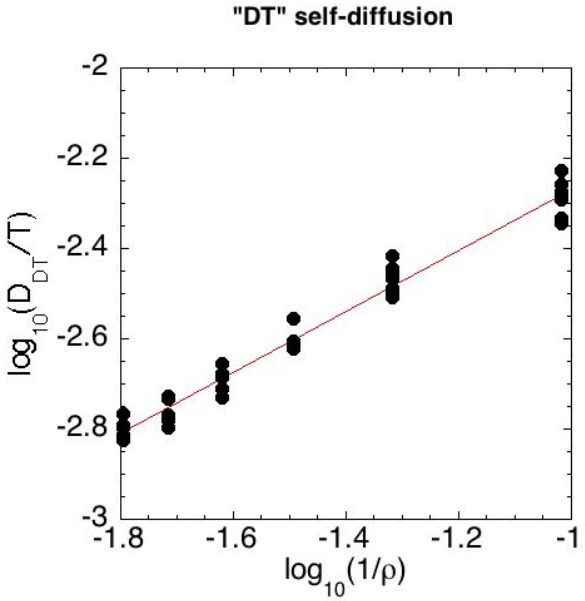

Fig. 14. OFMD simulation results for a 75/25 Pu/DT mixture (x=0.75) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Scaled "DT" self-diffusion $\log_{10}(D_D/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

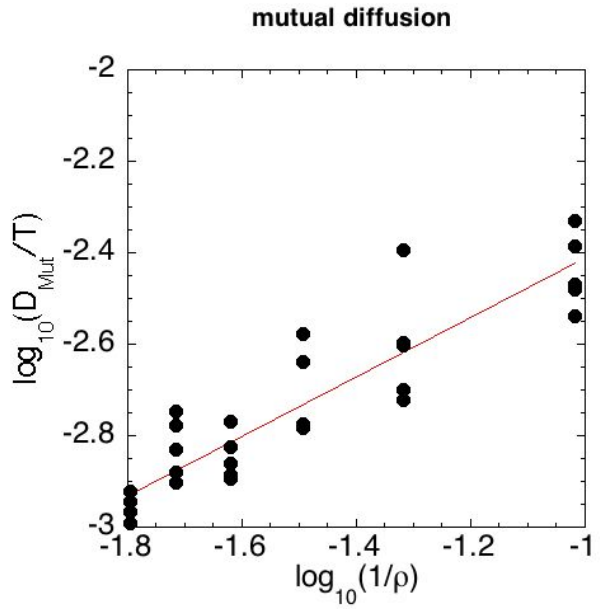

Fig. 15. OFMD simulation results for a 75/25 Pu/DT mixture (x=0.75) for ρ=10.4 to 62.4 g/cm^3 and T=100 to 1,000 eV: Scaled mutual diffusion $\log_{10}(D_{Mut}/T)$ vs. $\log_{10}(1/\rho)$ (solid points). Linear fit to results (red line).

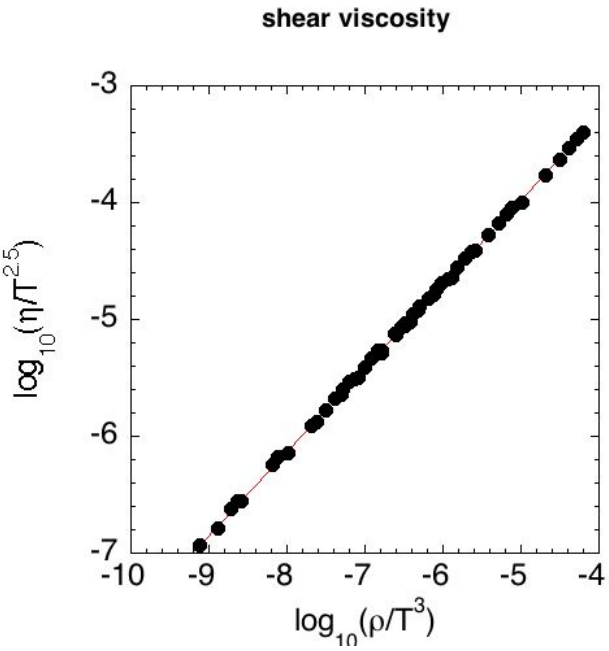

Fig. 16. OFMD simulation results for pure Pu [2] for ρ=20 to 100 g/cm^3 and T=50 to 5,000 eV: Scaled shear viscosity $\log_{10}(\eta/T^{5/2})$ vs. $\log_{10}(\rho/T^3)$ (solid points). Linear fit to results (red line).

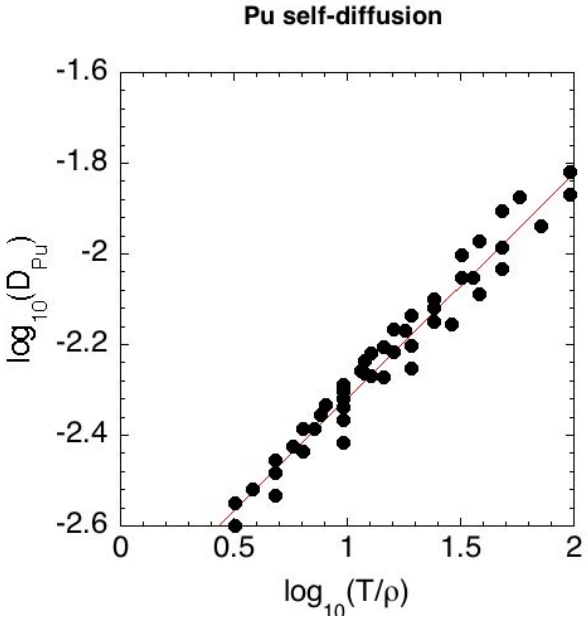

Fig. 17. OFMD simulation results for pure Pu [2]] for ρ=20 to 100 g/cm^3 and T=50 to 5,000 eV: Pu self-diffusion $\log_{10}(D_{Pu})$ vs. $\log_{10}(T/\rho)$ (solid points). Linear fit to results (red line).