Supporting Information: Development of thermodynamically-consistent machine-learning Equations of State: Application to the Mie fluid

Gustavo Chaparro and Erich A. Müller*

Department of Chemical Engineering, Sargent Centre for Process Systems Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

E-mail: e.muller@imperial.ac.uk

The loss function, Eq. (S.1), used to train the FE-ANN EoS includes information from first-order derivative properties (Z and U^*) and second-order derivative properties (C_V^*, γ_V^*, $\rho^* \kappa_T^*$, α_P^*, γ and μ_{JT}^*). In the main article, the effect of different relative weights, Eq. (S.2), for the second-order derivative properties was discussed for $w_i =$, 0, 1/20, 1/10 and 1. Other values of relative weights (1/50 and 1/5) were also studied. The results of these models are found in Table S1.

$$
\begin{aligned}
\mathcal{L}^{prop} = \frac{1}{N_p} \sum_{i=1}^{N_p} & \omega_Z (Z_{i,MD} - Z_{i,model})^2 + \omega_{U^*} (U^*_{i,MD} - U^*_{i,model})^2 \\
& + \omega_{C_V^*} (C^*_{V,i,MD} - C^*_{V,i,model})^2 + \omega_{\gamma_V^*} (\gamma^*_{V,i,MD} - \gamma^*_{V,i,model})^2 \\
& + \omega_{\rho^* \kappa_T^*} (\rho^* \kappa^*_{T,i,MD} - \rho^* \kappa^*_{T,i,model})^2 + \omega_{\alpha_P^*} (\alpha^*_{P,i,MD} - \alpha^*_{P,i,model})^2 \\
& + \omega_{\gamma} (\gamma_{i,MD} - \gamma_{i,model})^2 + \omega_{\mu_{JT}^*} (\mu^*_{JT,i,MD} - \mu^*_{JT,i,model})^2
\end{aligned}
\tag{S.1}
$$

with

$$
\omega_i = \frac{w_i}{\sigma_i^2} \tag{S.2}
$$

Table S1: Trained FE-ANN EoS results[a, b].

Input Features	w_i[c]		100×MSE							
			Z	U^*	C_V^*	γ_V^*	$\rho^*\kappa_T^*$	α_P^*	γ	μ_{JT}^*
α_{vdw}, ρ^*, T^*	0	Train	0.42	10.92	17.82	4.37	0.66	3.83	24.95	11.30
		Test	**0.32**	11.20	17.38	**3.12**	1.18	3.86	27.78	8.11
	1/50	Train	1.99	3.43	2.07	14.58	0.37	1.08	1.36	6.64
		Test	1.98	**3.27**	2.01	13.43	0.35	0.93	1.55	7.26
	1/20	Train	2.55	5.56	1.52	15.58	0.39	0.90	1.63	7.39
		Test	2.49	5.19	1.45	14.56	0.36	0.82	2.09	7.82
	1/10	Train	2.01	4.78	0.90	11.32	0.29	0.82	1.30	5.78
		Test	2.05	4.76	0.82	12.73	0.28	0.70	**1.48**	6.09
	1/5	Train	5.34	6.46	0.46	16.49	0.23	0.54	1.47	4.77
		Test	6.01	6.47	**0.46**	18.99	**0.26**	**0.64**	1.93	**4.56**
	1	Train	31.44	29.53	0.65	60.45	0.51	0.68	3.01	5.05
		Test	34.63	31.74	0.72	71.85	0.53	0.95	3.63	4.67
α_{vdw}, ρ^*, $1/T^*$	0	Train	0.21	2.16	11.94	2.33	0.92	2.47	26.58	11.73
		Test	0.16	1.97	11.54	1.40	3.10	2.90	28.11	10.99
	1/50	Train	1.99	7.44	2.85	5.57	0.49	1.37	1.62	7.24
		Test	2.52	8.02	2.77	6.73	0.48	1.29	1.78	7.52
	1/20	Train	0.18	0.55	0.35	0.79	0.15	0.62	0.89	5.50
		Test	**0.14**	**0.32**	0.33	**1.05**	0.15	0.57	**1.03**	5.72
	1/10	Train	0.26	0.83	0.32	0.83	0.11	0.49	0.88	4.61
		Test	0.26	0.64	**0.28**	1.37	**0.12**	**0.56**	1.21	**4.51**
	1/5	Train	0.43	1.30	0.27	1.20	0.10	0.43	1.09	4.44
		Test	0.42	1.03	0.25	2.13	0.13	0.65	1.73	4.07
	1	Train	7.87	9.02	0.37	7.22	0.27	0.55	2.15	4.82
		Test	8.03	8.57	0.34	10.26	0.29	0.76	2.72	4.20

[a] All the models consider a 4-layered neural network, activated using the tanh activation function and 45 neurons each. All models were trained for 20000 epoch using a learning rate of $\alpha = 10^{-6}$ and the ADAM optimiser. [b] Smallest test MSE deviations are highlighted in **bold**. [c] w_i is the relative weight used for the second-order derivative properties in the loss function. This relative weight is set to 1 for the compressibility factor (Z) and internal energy (U^*). See Eq. (S.2) for further details.

1 FE-ANN EoS results for selected Mie Fluids

The main article presents the results of the FE-ANN EoS using α_{vdw}, ρ^* and $1/T^*$ as input features and trained using a relative weight of $w_i = 1/20$ for second-order properties for the Lennard-Jones fluid ($\lambda_r = 12$ and $\lambda_a = 6$). This section complements those results for other Mie fluids: $\lambda_r = 16$, 20, 24 and 30 and $\lambda_a = 6$.

In Figures S1, S3, S5 and S7, the pressure isotherms for the mentioned Mie Fluids are shown. Similarly, in Figures S2, S4, S6 and S8, a list of second-order derivative properties are shown: (a) Isochoric Heat Capacity, (b) Isothermal Compressibility, (c) Thermal Expansion Coefficient, (d) Isobaric Heat Capacity, (e) Joule-Thomson Coefficient, (f) Thermal Pressure Coefficient.

For simplicity, all the figures shown below share the same nomenclature for symbols and lines. This is:

- Solid lines are FE-ANN EoS calculations
- Dashed lines are SAFT-VR-Mie EoS calculations
- Molecular dynamics data: (□) $T^* = 0.9$, (□) $T^* = 1.0$, (□) $T^* = 1.3$, (□) $T^* = 2.8$, (□) $T^* = 6.0$.

1.1 $\lambda_r = 16$ and $\lambda_a = 6$

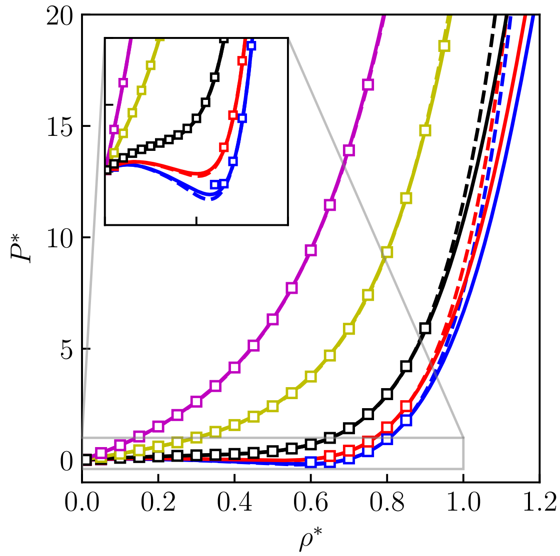

Figure S1: Pressure isotherms for the Mie fluid ($\lambda_r = 16$ and $\lambda_a = 6$).

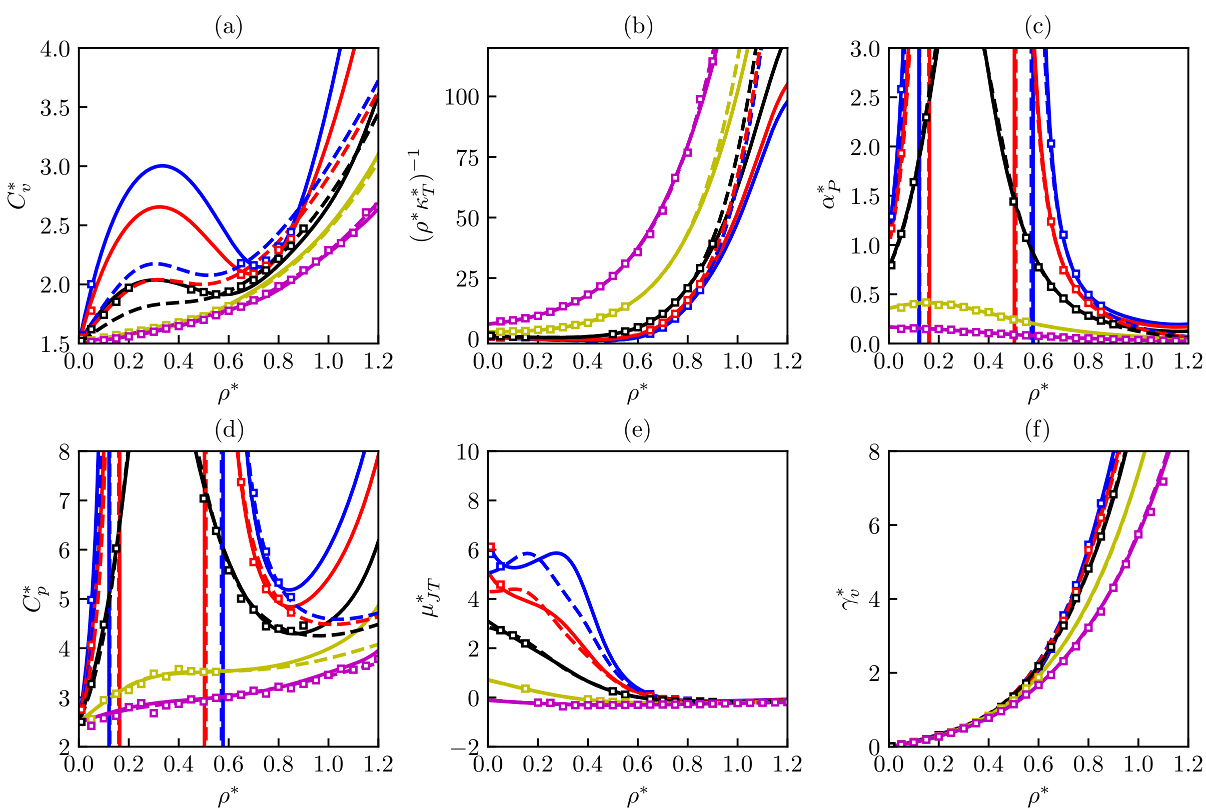

Figure S2: Second-order derivative properties isotherms for the Mie fluid ($\lambda_r = 16$ and $\lambda_a = 6$).

1.2 $\lambda_r = 20$ and $\lambda_a = 6$

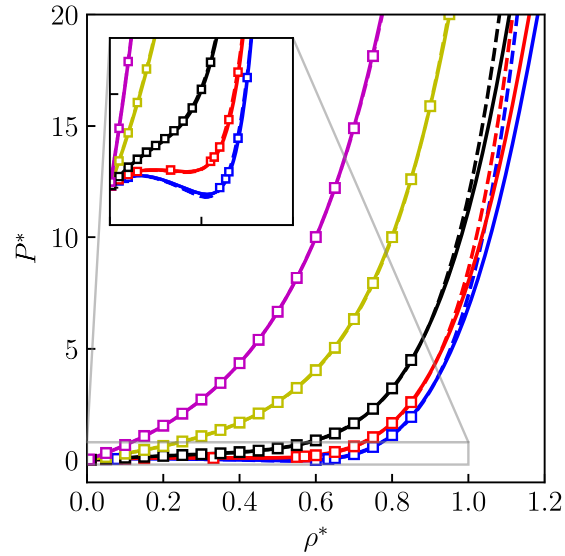

Figure S3: Pressure isotherms for the Mie fluid ($\lambda_r = 20$ and $\lambda_a = 6$).

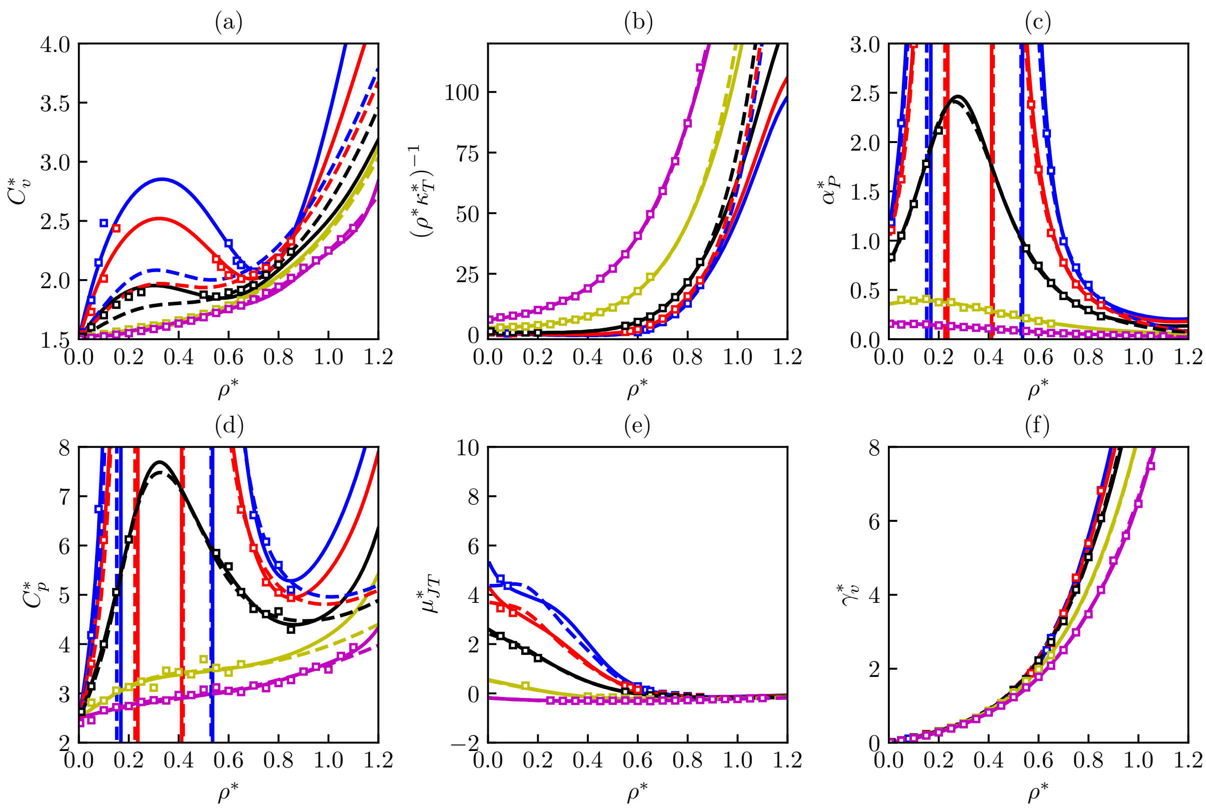

Figure S4: Second-order derivative properties isotherms for the Mie fluid ($\lambda_r = 20$ and $\lambda_a = 6$).

1.3 $\lambda_r = 24$ and $\lambda_a = 6$

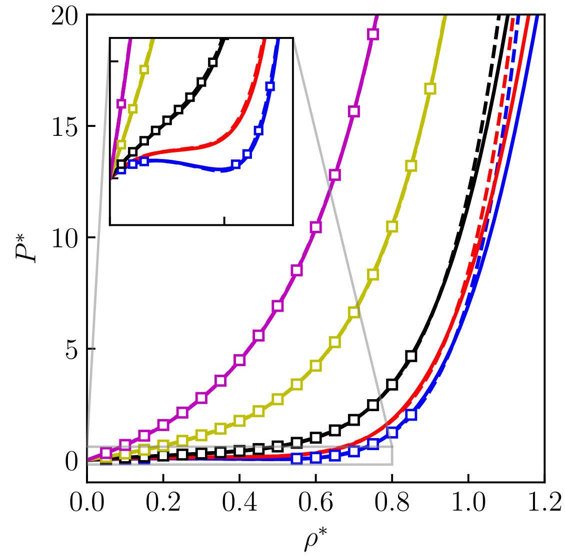

Figure S5: Pressure isotherms for the Mie fluid ($\lambda_r = 24$ and $\lambda_a = 6$).

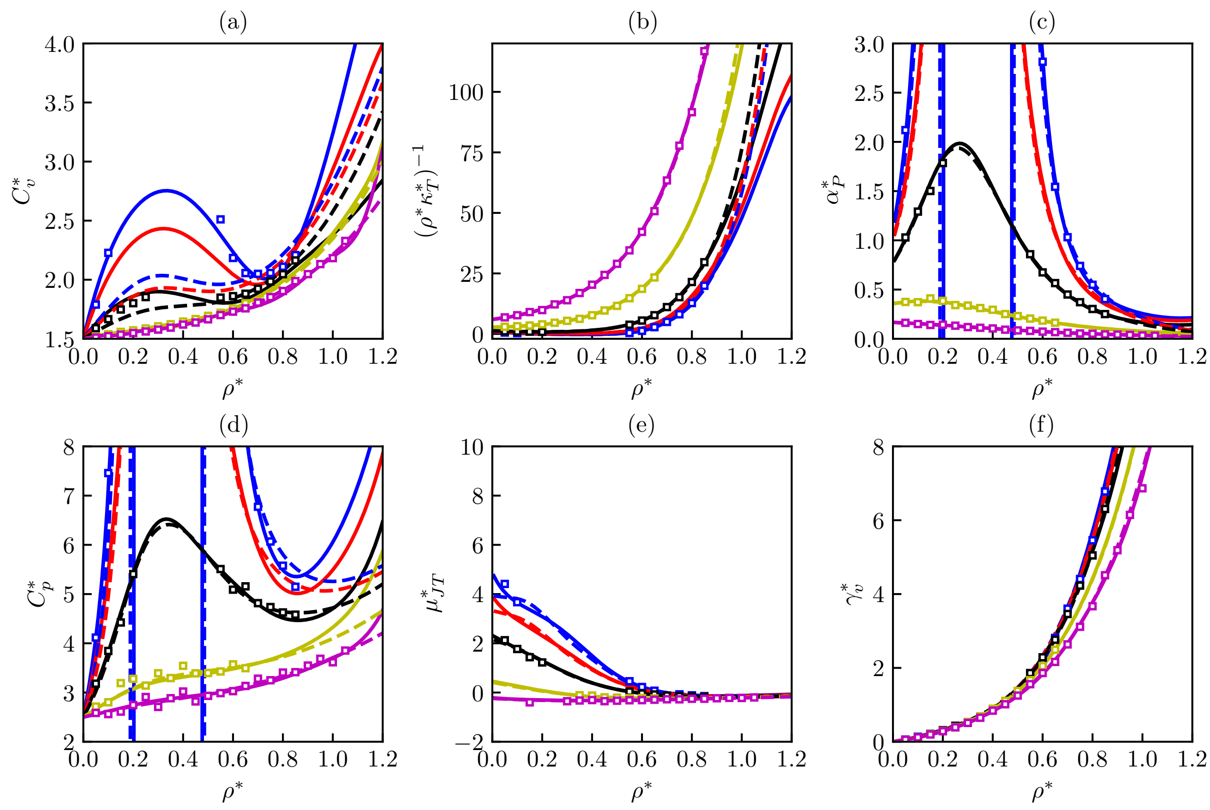

Figure S6: Second-order derivative properties isotherms for the Mie fluid ($\lambda_r = 24$ and $\lambda_a = 6$).

1.4 $\lambda_r = 30$ and $\lambda_a = 6$

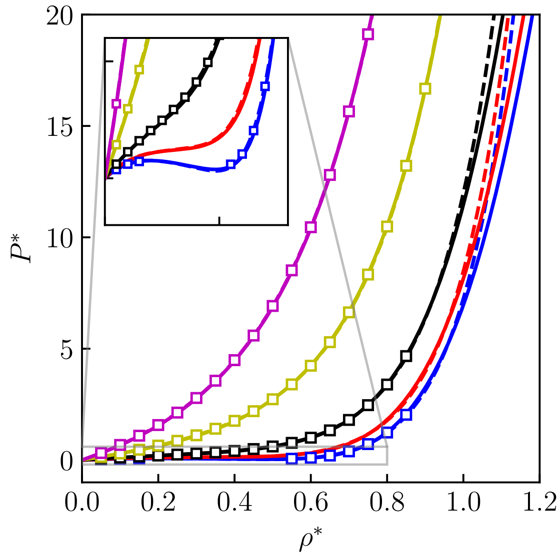

Figure S7: Pressure isotherms for the Mie fluid ($\lambda_r = 30$ and $\lambda_a = 6$).

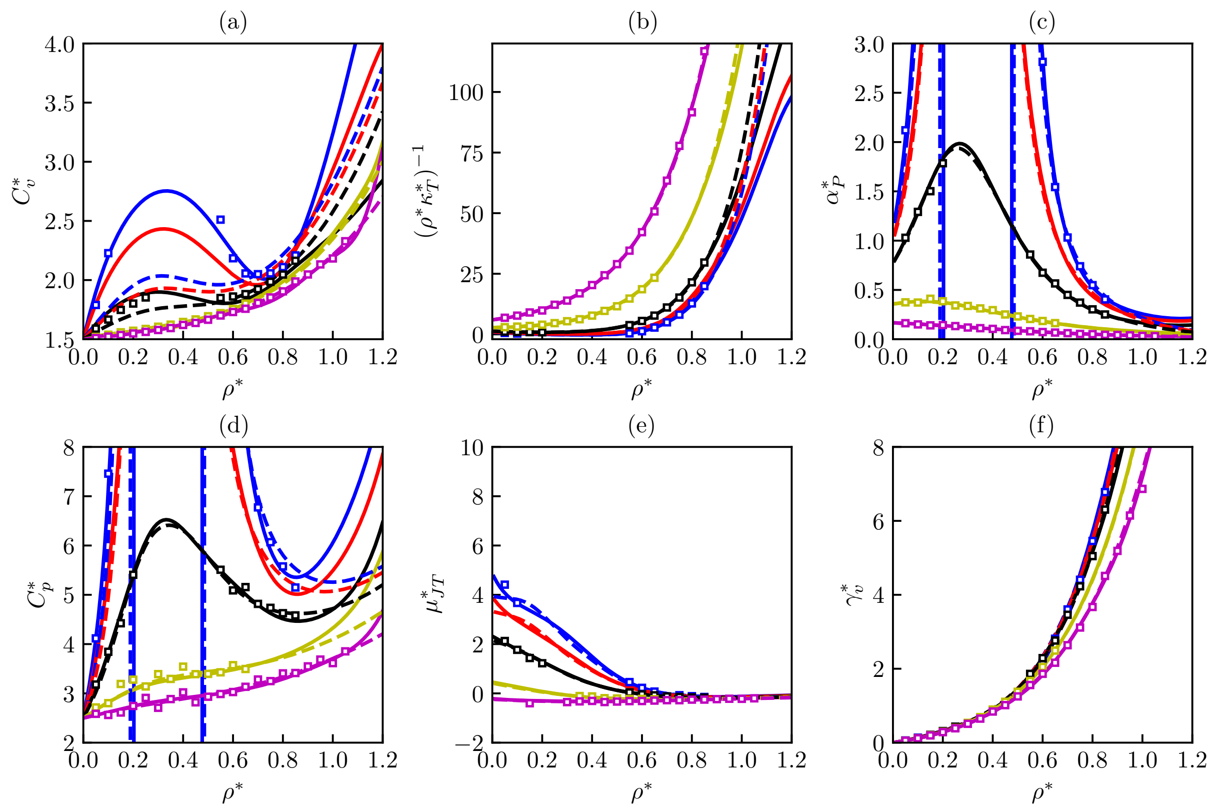

Figure S8: Second-order derivative properties isotherms for the Mie fluid ($\lambda_r = 30$ and $\lambda_a = 6$).