
SUPPLEMENTARY INFORMATION: DEVELOPMENT OF A HELMHOLTZ FREE ENERGY EQUATION OF STATE FOR FLUID AND SOLID PHASES VIA ARTIFICIAL NEURAL NETWORKS

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Supplementary Information needed for developing a continuous equation of state capable of modeling fluid and solid phases (FE-ANN (s) EoS). This framework has been applied to the Mie particle in the main article. The Supplementary Information covers the following items:

- Supplementary Note 1: Helmholtz free energy thermodynamics
- Supplementary Note 2: Mie particle reduced units
- Supplementary Note 3: Mie particle database
- Supplementary Note 4: Training and performance of the FE-ANN(s) EoS
- Supplementary Note 5: Phase equilibria predicted by the FE-ANN(s) EoS
- Supplementary Note 6: Critical exponents predicted by the FE-ANN(s) EoS
- Supplementary Note 7: Second-order derivative properties obtained from the FE-ANN(s) EoS

Supplementary Note 1: Helmholtz free energy thermodynamics

The intensive Helmholtz free energy ($\tilde{A}$) is a function of the molar density (ρ) and absolute temperature (T). This state function is useful as its derivatives are related to experimentally accessible thermophysical properties¹. The first order derivatives are related to the entropy ($\tilde{S}$) and pressure (P) as follows:

$$\tilde{S} = - \left(\frac{\partial \tilde{A}}{\partial T} \right)_{\rho} \quad (\text{S1a})$$

$$P = \rho^2 \left(\frac{\partial \tilde{A}}{\partial \rho} \right)_T \quad (\text{S1b})$$

Then, other fundamentals state functions such as the internal energy ($\tilde{U}$), enthalpy ($\tilde{H}$), and Gibbs free energy ($\tilde{G}$) can be obtained from the Helmholtz free energy. For a pure component, the Gibbs free energy, Eq. (S2c), is equivalent to

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the chemical potential (μ).

$$\tilde{U} = \tilde{A} + T\tilde{S} = \tilde{A} - T \left(\frac{\partial \tilde{A}}{\partial T} \right)_\rho \quad (\text{S2a})$$

$$\tilde{H} = \tilde{U} + \frac{P}{\rho} = \tilde{A} - T \left(\frac{\partial \tilde{A}}{\partial T} \right)_\rho + \rho \left(\frac{\partial \tilde{A}}{\partial \rho} \right)_T \quad (\text{S2b})$$

$$\tilde{G} = \tilde{A} + \frac{P}{\rho} = \tilde{A} + \rho \left(\frac{\partial \tilde{A}}{\partial \rho} \right)_T \quad (\text{S2c})$$

The second-virial coefficient (B) is obtained from the residual Helmholtz free energy.

$$B = \left(\frac{\partial \tilde{A}^{\text{res}}}{\partial \rho} \right)_T \bigg|_{\rho=0} \quad (\text{S3})$$

Finally, other thermophysical properties such as the isochoric and isobaric heat capacities ($\tilde{C}_V$ and $\tilde{C}_P$, respectively), thermal expansion coefficient (α_P), isothermal compressibility (κ_T), thermal pressure coefficient (γ_V) and Joule-Thomson coefficient (μ_{JT}) are related to the second-order derivatives of the Helmholtz free energy.

$$\tilde{C}_V = \left(\frac{\partial \tilde{U}}{\partial T} \right)_\rho = -T \left(\frac{\partial^2 \tilde{A}}{\partial T^2} \right)_\rho \quad (\text{S4a})$$

$$\alpha_P = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = \left(\frac{\partial P}{\partial T} \right)_\rho / \left[\rho \left(\frac{\partial P}{\partial \rho} \right)_T \right] \quad (\text{S4b})$$

$$\rho \kappa_T = \left[\left(\frac{\partial P}{\partial \rho} \right)_T \right]^{-1} \quad (\text{S4c})$$

$$\gamma_V = \left(\frac{\partial P}{\partial T} \right)_\rho = \frac{\alpha_P}{\kappa_T} \quad (\text{S4d})$$

$$\tilde{C}_P = \left(\frac{\partial \tilde{H}}{\partial T} \right)_P = \tilde{C}_V + \frac{T}{\rho} \frac{\alpha_P^2}{\kappa_T} \quad (\text{S4e})$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_{\tilde{H}} = \frac{1}{\rho \tilde{C}_P} [T \alpha_P - 1] \quad (\text{S4f})$$

The Helmholtz free energy derivatives are needed to characterize important regions of the phase diagram, such as the critical point, triple point, and phase boundaries. The definitions below are valid for pure substances.

Critical point

The critical point is an inflection point in the $P - \rho$ diagram. Mathematically speaking, it corresponds to the point where the first- and second-density derivatives of the pressure are zero, as shown below.

$$\left(\frac{\partial P}{\partial \rho} \right)_T = 2\rho \left(\frac{\partial \tilde{A}}{\partial \rho} \right)_T + \rho^2 \left(\frac{\partial^2 \tilde{A}}{\partial \rho^2} \right)_T = 0 \quad (\text{S5a})$$

$$\left(\frac{\partial^2 P}{\partial \rho^2} \right)_T = 2 \left(\frac{\partial \tilde{A}}{\partial \rho} \right)_T + 4\rho \left(\frac{\partial^2 \tilde{A}}{\partial \rho^2} \right)_T + \rho^2 \left(\frac{\partial^3 \tilde{A}}{\partial \rho^3} \right)_T = 0 \quad (\text{S5b})$$

This set of equations (S5) is solved numerically to find the critical density (ρ_c) and critical temperature (T_c). Then, the critical pressure (P_c) is obtained by evaluating Eq. (S1b) at the found solution.

Triple point

At the triple point, a vapor (v), liquid (l), and solid (s) phase coexist at the same temperature and pressure. The triple point (tr) is found by solving the following system of equations.

$$T_{\text{tr},v} = T_{\text{tr},l} = T_{\text{tr},s} \quad (\text{S6a})$$

$$P_{\text{tr},v} = P_{\text{tr},l} = P_{\text{tr},s} \quad (\text{S6b})$$

$$\mu_{\text{tr},v} = \mu_{\text{tr},l} = \mu_{\text{tr},s} \quad (\text{S6c})$$

The system of equations (S6) is numerically solved for the triple temperature (T_{tr}), vapor density ($\rho_{\text{tr},v}$), liquid density ($\rho_{\text{tr},l}$) and solid density ($\rho_{\text{tr},s}$). The pressure and chemical potential are obtained by evaluating Eqs. (S1b) and (S2c), respectively.

Two-phase equilibria

Vapor-Liquid (VLE), Solid-Liquid (SLE), and Solid-Vapor (SVE) Equilibria involve thermal, mechanical, and chemical equilibria between two different phases (I and II). The following system of equations governs phase equilibrium.

$$T_{\text{I}} = T_{\text{II}} \quad (\text{S7a})$$

$$P_{\text{I}} = P_{\text{II}} \quad (\text{S7b})$$

$$\mu_{\text{I}} = \mu_{\text{II}} \quad (\text{S7c})$$

The system of equations (S7) is solved numerically for the density of two distinguishable phases (ρ_{I} and ρ_{II}) at a given temperature. In the case of VLE, the temperature is narrowed by the triple and critical temperatures (i.e., $T_{\text{tr}} < T_{\text{I}} = T_{\text{II}} < T_{\text{c}}$). In the case of SVE, the temperature must be below the triple temperature (i.e., $T_{\text{tr}} > T_{\text{I}} = T_{\text{II}}$). Finally, in the case of SLE, the temperature must be above the triple temperature (i.e., $T_{\text{tr}} < T_{\text{I}} = T_{\text{II}}$). The pressure and chemical potential are obtained by evaluating Eqs. (S1b) and (S2c), respectively. Numerical methods for efficiently solving these equations have been discussed elsewhere^{1,2}.

The system of equations (S7) is equivalent to solving the Maxwell area rule.

$$\int_{1/\rho_{\text{II}}}^{1/\rho_{\text{I}}} P(\rho) d\left(\frac{1}{\rho}\right) = P_{\text{eq}} \cdot \left(\frac{1}{\rho_{\text{I}}} - \frac{1}{\rho_{\text{II}}}\right) \quad (\text{S8})$$

In Eq. (S8), the ρ_{I} and ρ_{II} are the equilibrium densities, $P(\rho)$ is the pressure as a function of density and $P_{\text{eq}} (= P_{\text{I}} = P_{\text{II}})$ is the equilibrium pressure.

Supplementary Note 2: Mie particle reduced units

This work focuses on systems interacting through a truncated Mie potential, Eq. (S9).

$$\mathcal{U}^{\text{Mie}} = \begin{cases} \mathcal{C}^{\text{Mie}} \epsilon \left[(\sigma/r)^{\lambda_{\text{r}}} - (\sigma/r)^{\lambda_{\text{a}}} \right] & \text{if } r \leq 5\sigma \\ 0 & \text{if } r > 5\sigma \end{cases} \quad (\text{S9})$$

$$\mathcal{C}^{\text{Mie}} = \frac{\lambda_{\text{r}}}{\lambda_{\text{r}} - \lambda_{\text{a}}} \left(\frac{\lambda_{\text{r}}}{\lambda_{\text{a}}} \right)^{\frac{\lambda_{\text{a}}}{\lambda_{\text{r}} - \lambda_{\text{a}}}}$$

In Eq. (S9), $\mathcal{U}^{\text{Mie}}$ refers to the interaction energy between two Mie particles, ϵ is the energy scale, σ is the shape parameter, which is loosely related to the diameter of a particle and r is the center-to-center distance between two particles. Finally, λ_{r} and λ_{a} are the repulsive and attractive exponents, respectively. Molecular dynamics simulations and the FE-ANN(s) EoS are formulated using reduced units, which is equivalent to setting σ , ϵ , monomer mass, M , and the Boltzmann constant, k_{B} , to 1. The definition of relevant thermophysical properties in reduced units are summarized in Supplementary Table 1.

Supplementary Note 3: Mie particle database

The database used in this work considers VLE, SLE, second virial coefficients, and thermophysical properties of the Mie Particle. The database can be accessed on the following GitHub repository: <https://github.com/gustavoohm/feanns-eos>⁴.

Supplementary Table 1: Definition of physical quantities in reduced units.

Quantity	Symbol	Units	Dimensionless Definition ^{a, b, c}
Time	τ	s	$\tau^* = \tau / \sigma \sqrt{M/\epsilon}$
Mass	m	g mol ⁻¹	$m^* = m/M$
Density	ρ	mol m ⁻³	$\rho^* = \rho N_{\text{av}} \sigma^3$
Temperature	T	K	$T^* = T k_{\text{B}}/\epsilon$
Pressure	P	Pa	$P^* = P \sigma^3/\epsilon$
Entropy	$\tilde{S}$	J K ⁻¹ mol ⁻¹	$S^* = \tilde{S}/N_{\text{av}} k_{\text{B}}$
Helmholtz free energy	$\tilde{A}$	J mol ⁻¹	$A^* = \tilde{A}/N_{\text{av}} \epsilon$
Internal energy	$\tilde{U}$	J mol ⁻¹	$U^* = \tilde{U}/N_{\text{av}} \epsilon$
Enthalpy	$\tilde{H}$	J mol ⁻¹	$H^* = \tilde{H}/N_{\text{av}} \epsilon$
Gibbs free energy	$\tilde{G}$	J mol ⁻¹	$G^* = \tilde{G}/N_{\text{av}} \epsilon$
Isochoric heat capacity	$\tilde{C}_V$	J K ⁻¹ mol ⁻¹	$C_V^* = \tilde{C}_V/N_{\text{av}} k_{\text{B}}$
Thermal expansion coefficient	α_P	K ⁻¹	$\alpha_P^* = \alpha_P \epsilon/k_{\text{B}}$
Isothermal compressibility	κ_T	Pa ⁻¹	$\kappa_T^* = \kappa_T \epsilon/\sigma^3$
Thermal pressure coefficient	γ_V	Pa K ⁻¹	$\gamma_V^* = \gamma_V \sigma^3/k_{\text{B}}$
Isobaric heat capacity	$\tilde{C}_P$	J K ⁻¹ mol ⁻¹	$C_P^* = \tilde{C}_P/N_{\text{av}} k_{\text{B}}$
Joule-Thomson coefficient	μ_{JT}	K Pa ⁻¹	$\mu_{\text{JT}}^* = \mu_{\text{JT}} k_{\text{B}}/\sigma^3$

^aSuperscript (*) refers to a reduced property. ^b $N_{\text{av}} = 6.02214076 \cdot 10^{23} \text{ mol}^{-1}$ is the Avogadro constant³, $k_{\text{B}} = 1.380649 \cdot 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant³ and M is the mass of a single monomer. ^c σ is the shape parameter in meters, and ϵ is the potential well depth of the Mie potential in Joules. See Eq. (S9).

The Mie particle database is an augmented version of the database used in previous work⁵. This database additionally includes the second-virial coefficient data and thermophysical properties of FCC Mie crystals.

The second virial coefficient is analytically obtained as follows⁶:

$$B^* = -2\pi \int_0^\infty \left[\exp\left(\frac{-\mathcal{U}^{*, \text{Mie}}}{T^*}\right) - 1 \right] r^{*2} dr^* \quad (\text{S10})$$

In Eq. (S10), B^* refers to the second virial coefficient at temperature T^* , $\mathcal{U}^{*, \text{Mie}} (= \mathcal{U}^{\text{Mie}}/\epsilon)$ is the dimensionless Mie interaction energy and r^* is the dimensionless center-to-center between two Mie particles.

The FCC solid simulations are performed on the outer boundaries of the Solid-Liquid Equilibria (SLE). The SLE of the Mie particles is computed using the freeze method, which is thoroughly described in Ref.⁷. The freeze method generates good-quality initial guesses (equilibrium densities and temperature) to obtain liquid-solid separation in molecular dynamics simulations. The final simulation box consists of an elongated simulation box with approximately 8000 Mie particles. The simulation is equilibrated for 10^6 timesteps in the NVT ensemble, and then statistics of the systems are accumulated every 1000 timesteps for further $8 \cdot 10^6$ timesteps. The equilibrium pressure is taken as the normal component (P_{zz}) of the pressure tensor, and the equilibrium densities are obtained by analysis of the density profile.

The ranges and number of data points for each thermophysical property are shown in Supplementary Table 2. The temperature-density distribution of the data points is shown in Supplementary Figure 1.

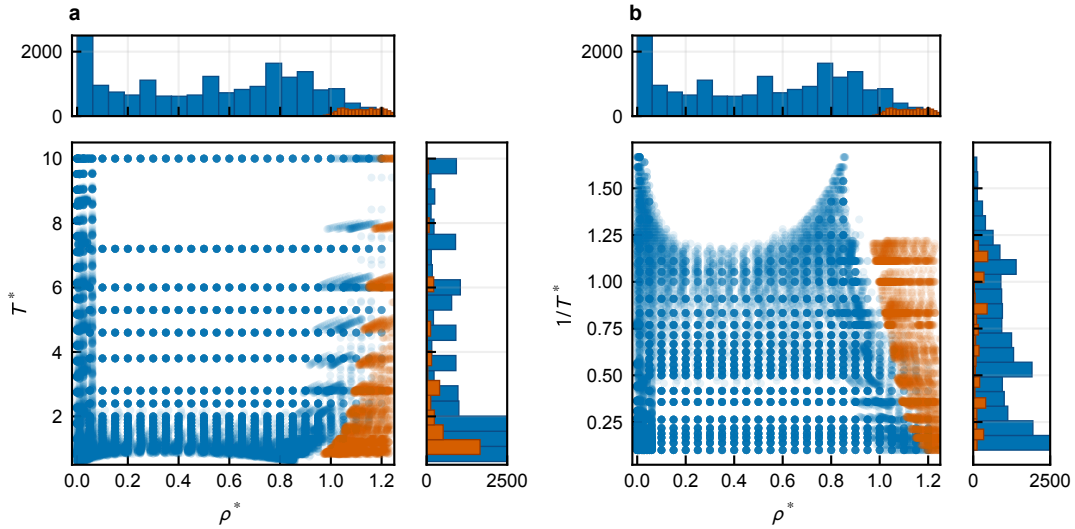
Supplementary Note 4: Training and performance of the FE-ANN(s) EoS

The loss function to train the FE-ANN(s) EoS consists of two parts. The first part corresponds to the mean squared error (MSE) with respect to the available data, Eq. (S11a). The second part consists of thermodynamic constraints to impose a thermodynamically consistent behavior, Eq. (S11b) and Eq. (S11c). The total loss, $\mathcal{L}$, is the sum of all these losses.

Supplementary Table 2: Mie particle database description.^a

Descriptor	Symbol	# of data points	Min value	Max value
Repulsive Exponent ^b	λ_r	—	7	34
Attractive Exponent ^b	λ_a	—	6	6
Density	ρ^*	—	1.000e−6	1.250
Temperature ^c	T^*	—	0.600	10.000
Property				
Compressibility factor ^d	Z	24873	2.500e−4	24.087
Internal energy	U^*	24873	−8.827	22.563
Second virial coefficient ^e	B^*	3080	−9.928	1.574 717
Isochoric heat capacity	C_V^*	20913	1.500	3.294
Isobaric heat capacity	C_P^*	18806	2.500	23.290
Adiabatic index ^f	γ	17578	1.113	8.825
Thermal pressure coefficient	γ_V^*	20991	10.000e−7	16.914
Thermal expansion coefficient	α_P^*	20111	0.015	8.056
Isothermal compressibility	κ_T^*	20081	1.385e−3	1.305e6
Joule-Thomson coefficient	μ_{JT}^*	14565	−0.503	10.930

^a Descriptors and thermophysical properties are reported in reduced units. See Supplementary Table 1. ^b Repulsive and attractive exponent of the Mie potential, Eq. (S9). ^c Temperature range used in molecular dynamics simulations. ^d Compressibility factor, $Z = P^*/\rho^*T^*$. ^e Second virial coefficient obtained in the temperature range from 0.951 to 39.620. ^f Adiabatic index (heat capacity ratio), $\gamma = C_P^*/C_V^*$.



Supplementary Figure 1: **Mie particle database distribution.** **a.** Temperature-density ($T^* - \rho^*$). **b.** Temperature inverse-density ($1/T^* - \rho^*$). Blue points are fluid data points, and orange points are solid data points.

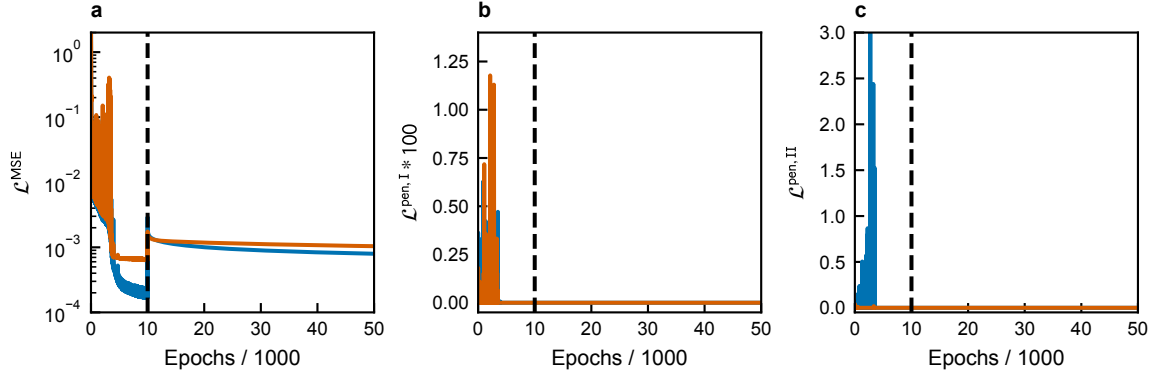
$$\mathcal{L}^{\text{MSE}} = \sum_i \frac{w_i}{\sigma_i^2 N_{P,i}} \sum_j \left(y_{i,j}^{\text{pred}} - y_{i,j}^{\text{true}} \right)^2 \quad (\text{S11a})$$

$$\mathcal{L}^{\text{pen, I}} = \frac{1}{N_P} \sum_j \min \left[0, C_{V,j}^{*,\text{pred}} \right]^2 \quad (\text{S11b})$$

$$\mathcal{L}^{\text{pen, II}} = \frac{1}{N_P} \sum_j \min \left[0, \left(\frac{\partial^2 A^*}{\partial \rho^{*2}} \right)_{T^*,j} \right]^2 \quad (\text{S11c})$$

In Eq. (S11a), $\mathcal{L}^{\text{MSE}}$ refer to the MSE loss. This loss is a weighted average of the squared error of a thermophysical property. Here, σ_i^2 , w_i , and $N_{P,i}$ are the variance, relative weight, and number of data points of the property i . This loss function considers first-order properties such as the compressibility factor (Z), internal energy (U^*), and second virial coefficient (B^*), as well as second-order properties such as the isochoric heat capacity (C_V^*), isothermal compressibility (as, $\rho^* \kappa_T^*$), thermal expansion coefficient (α_P^*), thermal pressure coefficient (γ_V^*), adiabatic index ($\gamma = C_P^*/C_V^*$) and the Joule-Thomson coefficient (μ_{JT}^*). The penalty loss functions, Eq. (S11b) and Eq. (S11c), are soft constraints to the model. $\mathcal{L}^{\text{pen}, I}$ enforces all the predicted isochoric heat capacities to be positive, and $\mathcal{L}^{\text{pen}, II}$ imposes the pressure to be an increasing function of the density. The latter constraint is only applied to data points in which temperature is supercritical ($T^* > T_c^*$) and outside the SLE boundaries ($|\rho^* - \rho^{*\text{SLE}}| > 0.05$).

The FE-ANN(s) EoS is trained using the ADAM optimizer⁸ with a batch size of 32 and a train/test split of 90/10. The training is a two-step process. The history of these losses is shown in Supplementary Figure 2. The FE-ANN(s) EoS is trained in two stages. The first 10000 epochs only consider first-order thermophysical properties (i.e., $w_i = 0$ for second-order properties) using a learning rate α equal to 10^{-4} . In the second step, the FE-ANN(s) EoS is trained for a further 40000 epochs, considering first-order properties with a relative weight equal to 1 and second-order properties with a relative weight equal to 1/100 using a learning rate α equal to 10^{-6} . In both training steps, the penalty loss functions, Eq. (S11b) and Eq. (S11c), are considered in the loss function. Finally, the trained FE-ANN(s) EoS performance for the train and test data are shown in Supplementary Table 3 and Supplementary Figure 3.

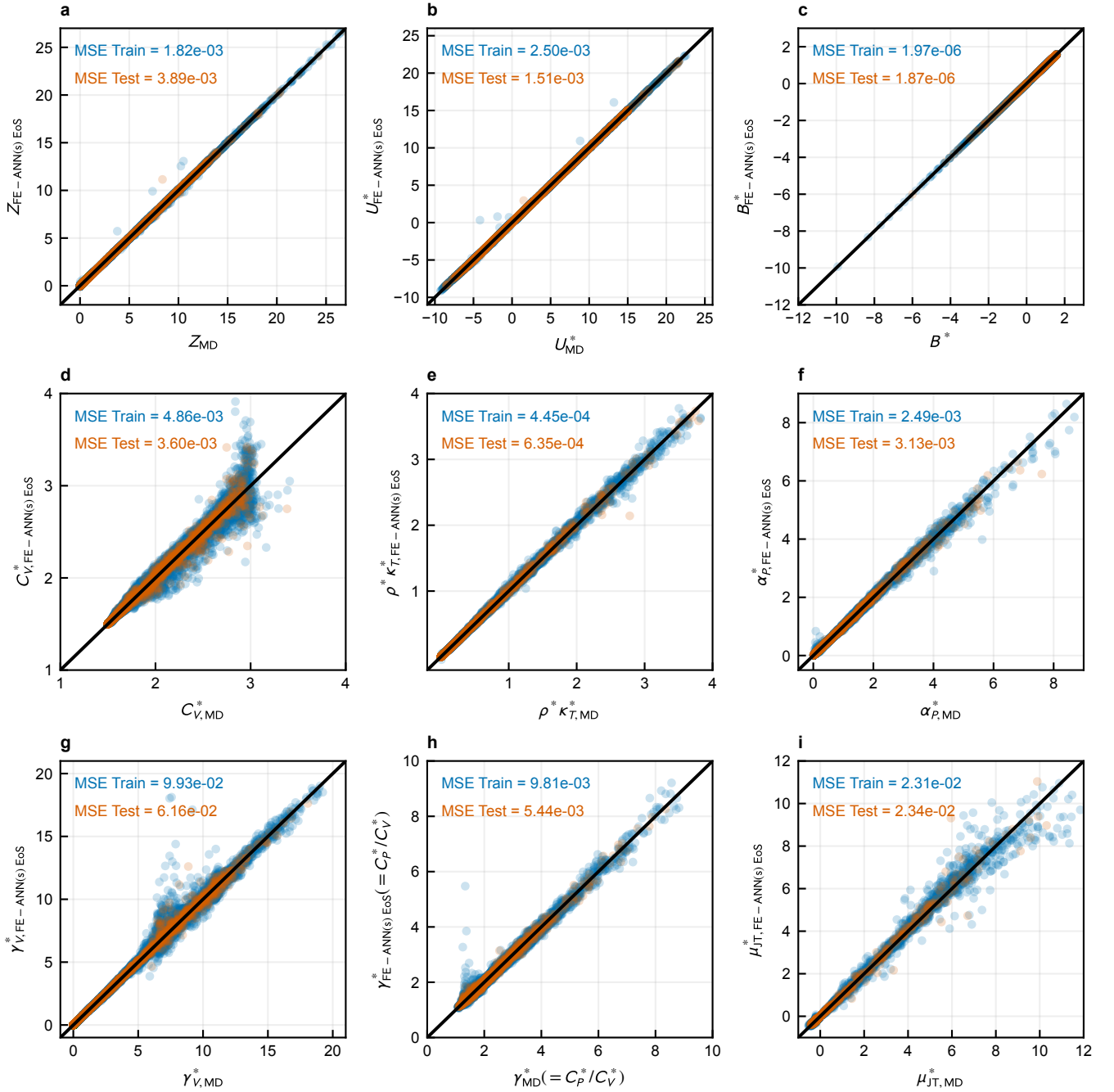


Supplementary Figure 2: **History of FE-ANN(s) EoS training.** **a.** $\mathcal{L}^{\text{MSE}}$ loss. **b.** $\mathcal{L}^{\text{pen}, I}$ penalty. **c.** $\mathcal{L}^{\text{pen}, II}$ penalty. $\mathcal{L}^{\text{MSE}}$, $\mathcal{L}^{\text{pen}, I}$, and $\mathcal{L}^{\text{pen}, II}$ computed as Eq. (S11). Blue lines are train data, orange lines are test data, and the dotted vertical line refers to the epoch at which training with second-order properties starts.

Supplementary Table 3: FE-ANN(s) EoS squared error distribution for selected thermophysical properties.^a

Property		Min	Max	Median	Mean
Z	Train	3.49e-15	7.52e+00	2.92e-05	1.46e-03
	Test	2.98e-13	7.37e+00	3.18e-05	5.86e-03
U^*	Train	2.73e-13	1.99e+01	7.03e-05	1.97e-03
	Test	1.35e-10	9.82e+00	7.41e-05	6.54e-03
B^*	Train	2.19e-15	1.06e-04	2.76e-07	1.44e-06
	Test	5.42e-11	9.93e-05	3.20e-07	1.83e-06
C_V^*	Train	2.90e-19	1.91e+01	1.31e-04	4.74e-03
	Test	8.57e-18	7.09e-01	1.55e-04	2.96e-03
$\rho^* \kappa_T^*$	Train	2.38e-14	2.26e-01	1.42e-06	4.04e-04
	Test	1.32e-15	3.77e-01	1.37e-06	5.85e-04
α_P^*	Train	3.70e-14	1.62e+00	3.21e-05	1.97e-03
	Test	2.98e-11	1.47e+00	2.95e-05	2.97e-03
γ_V^*	Train	4.95e-28	4.28e+02	2.14e-04	9.70e-02
	Test	3.52e-27	9.05e+00	2.46e-04	4.92e-02
γ	Train	4.15e-15	4.86e+01	1.21e-03	1.04e-02
	Test	1.45e-10	5.88e-01	1.20e-03	5.62e-03
μ_{JT}^*	Train	8.95e-12	1.02e+01	6.23e-05	2.08e-02
	Test	7.43e-10	3.99e+00	6.15e-05	1.34e-02

^a Squared error obtained as: $\left(y_i^{\text{pred}} - y_i^{\text{true}}\right)^2$.



Supplementary Figure 3: **Parity plots for thermophysical properties predicted by the trained FE-ANN(s) EoS.**

a. Compressibility factor. **b.** Internal energy. **c.** Second virial coefficient. **d.** Isochoric heat capacity. **e.** Isothermal compressibility, **f.** Thermal expansion coefficient. **g.** Thermal pressure coefficient. **h.** Adiabatic index. **i.** Joule-Thomson coefficient. Blue points: train data set, orange points: test data set. MSE obtained as: $MSE = \frac{1}{N_P} \sum_i (y_i^{\text{pred}} - y_i^{\text{true}})^2$.

Supplementary Note 5: Phase equilibria predicted by the FE-ANN(s) EoS

The phase diagram of selected Mie particles has been computed using the FE-ANN(s) EoS, SAFT-VR-Mie EoS⁹ and the multiparameter EoS proposed by Pohl *et al.*¹⁰. These last two EoSs were used from the `teqp` package¹¹. Two-phase equilibria were obtained by numerically solving the system of equations (S7). The comparison between the different EoSs and the molecular simulation data is shown in Supplementary Figure 4. It can be observed that the three EoSs predict a similar VLE phase envelope for the selected Mie particles. The parity plots, Supplementary Figure 4d, reveal that these predictions are in good agreement with molecular simulation data for the saturated densities, pressure, and internal energy change. It must be noted that the SAFT-VR-Mie EoS and the EoS proposed by Pohl *et al.* are designed to model the fluid phase. Hence, they predict VLE for temperatures below the triple point. Contrarily, the FE-ANN(s) EoS predicts a triple point and can additionally model solid-fluid equilibria, such as solid-liquid and solid-vapor equilibria, as observed in Supplementary Figure 4, the SLE predictions of the FE-ANN(s) EoS are in good agreement with the molecular simulation data.

Supplementary Note 6: Critical exponents predicted by the FE-ANN(s) EoS

The critical exponents are suitable for describing the critical behavior predicted by an equation of state. These exponents are relevant because of analogies between different systems (i.e., fluid and ferromagnetic systems) and because they can be compared to experimental observations. For further discussion about critical exponents and phase transitions, the reader is referred to the books of Stanley¹² and Yeomans¹³. The critical exponent " λ " of a property " f " is defined as follows:

$$\lambda \equiv \lim_{\varepsilon \rightarrow 0} \frac{\ln |f(\varepsilon)|}{\ln |\varepsilon|} \quad ; \text{ where } \varepsilon = \frac{T^* - T_c^*}{T_c^*} \quad (\text{S12})$$

In Eq. (S12), ε is a measure of how far the system is from the critical temperature (T_c^*). The following critical exponents are studied here:

α and α' exponents

The α and α' exponents are related to the critical behavior of the isochoric heat capacity, C_V^* , as follows.

$$C_V^* = \begin{cases} \mathcal{A}'(-\varepsilon)^{-\alpha'} (1 + \dots) & ; \text{ where } \varepsilon < 0 \text{ and } \rho^* = \rho_l^* \\ \mathcal{A}\varepsilon^{-\alpha} (1 + \dots) & ; \text{ where } \varepsilon > 0 \text{ and } \rho^* = \rho_c^* \end{cases} \quad (\text{S13})$$

In Eq. S13, $\mathcal{A}$ and $\mathcal{A}'$ are proportionality constants. The α' exponent is obtained for saturated subcritical conditions (i.e., $T^* < T_c^*$) and the α exponent is obtained for supercritical conditions (i.e., $T^* > T_c^*$). These two exponents can differ in value.

β exponent

The β exponent is related to the shape of the coexistence curve near critical conditions. This exponent is defined as follows.

$$\frac{\rho_l^* - \rho_v^*}{2\rho_c^*} = \mathcal{B}(-\varepsilon)^\beta (1 + \dots) \quad ; \text{ where } \varepsilon < 0 \quad (\text{S14})$$

In Eq. (S14), $\mathcal{B}$ is a proportionality constant, ρ_l^* and ρ_v^* are the saturated liquid and vapor densities, and ρ_c^* is the critical density. The difference between the liquid and vapor densities ($\Delta\rho^* = \rho_l^* - \rho_v^*$) is commonly known as the order parameter. The β exponent can only be defined for subcritical temperatures.

γ and γ' exponents

The γ and γ' exponents are related to the critical behavior of the isothermal compressibility, κ_T^* , as follows.

$$\frac{\kappa_T^*}{\kappa_{T^*,0}^*} = \begin{cases} \mathcal{C}'(-\varepsilon)^{-\gamma'} (1 + \dots) & ; \text{ where } \varepsilon < 0 \text{ and } \rho^* = \rho_l^* \\ \mathcal{C}\varepsilon^{-\gamma} (1 + \dots) & ; \text{ where } \varepsilon > 0 \text{ and } \rho^* = \rho_c^* \end{cases} \quad (\text{S15})$$

In Eq. S15, $\mathcal{C}$ and $\mathcal{C}'$ are proportionality constants, $\kappa_{T^*,0}^*$ refers to the isothermal compressibility of an ideal gas evaluated at the critical density and temperature, i.e., $\kappa_{T^*,0}^* = 1/(\rho_c^* T_c^*)$. The γ' exponent is obtained for saturated subcritical conditions (i.e., $T^* < T_c^*$) and the γ exponent is obtained for supercritical conditions (i.e., $T^* > T_c^*$).

δ exponent

The δ exponent describes the changes in pressure with density along the critical isotherm.

$$\frac{P^* - P_c^*}{P_c^{*,\circ}} = \mathcal{D} \left| \frac{\rho^* - \rho_c^*}{\rho_c^*} \right|^\delta \text{sign}(\rho^* - \rho_c^*) \quad ; \text{ where } \varepsilon = 0 \quad (\text{S16})$$

In Eq. S16, $\mathcal{D}$ is a proportionality constant, $P_c^{*,\circ} = \rho_c^* T_c^*$ is the ideal gas pressure evaluated at the critical point, and ρ^* and ρ_c^* are the density and critical density, respectively. The sign function is defined as $\text{sign}(x) = -1$ if $x < 0$, 0 if $x = 0$ and 1 if $x > 0$.

The definitions of these critical exponents (Eqs. (S13), (S14), (S15), and (S16)) can be linearized using a $\ln$ function. Hence, the critical exponent can be obtained by fitting the slope of " f " with respect to ε in the $\ln$ scale. We obtained the critical exponents of the FE-ANN(s) EoS for different $(\lambda_r, 6)$ Mie particles. The fitting was done for different ranges of a reduced property (temperature or density), and the obtained values were averaged. The fitting ranges for each critical exponent are found in Supplementary Table 4.

The critical exponents obtained by the FE-ANN(s) EoS are shown in Supplementary Figure 5. It is noticed that FE-ANN(s) EoS predicts an unphysical critical behavior for the heat capacity of low-repulsive systems (i.e., $\lambda_r = 7$ or 8). On these systems, the FE-ANN(s) EoS predicts a negative α' , which implies an incorrect temperature dependence of C_V^* . The predictions of the FE-ANN(s) EoS slightly change depending on the repulsive exponent. The β exponent is close to 0.5, the α' and α exponents are close to zero, the γ' and γ exponents are close to 1, and the δ exponent is close to 3. Remarkably, these values are in agreement with the values obtained by mean-field theory¹², even though this theory has not been embedded into the FE-ANN(s) EoS formulation.

Supplementary Table 4: Ranges used to fit the critical exponents from the FE-ANN(s) EoS.^a

Critical exponent	Property	Min value	Max value
α', β , and γ'	T_r^b	[0.98, 0.998]	0.99999
α , and γ	T_r^b	1.00001	[1.002, 1.02]
δ	ρ_r^c	[0.98, 0.998]	[1.002, 1.02]

^a Critical exponents as defined by Eqs. (S13), (S14), (S15), and (S16). ^b Reduced temperature: $T_r = T^*/T_c^*$ ^c Reduced density: $\rho_r = \rho^*/\rho_c^*$

Supplementary Note 7: Second-order derivative properties obtained from the FE-ANN(s) EoS

Isotherms of second properties predicted by the FE-ANN(s) EoS and its comparison against molecular simulation data are shown in Supplementary Figure 6 for selected Mie particles ($\lambda_r = 12, 16$ and 20 and $\lambda_a = 6$).

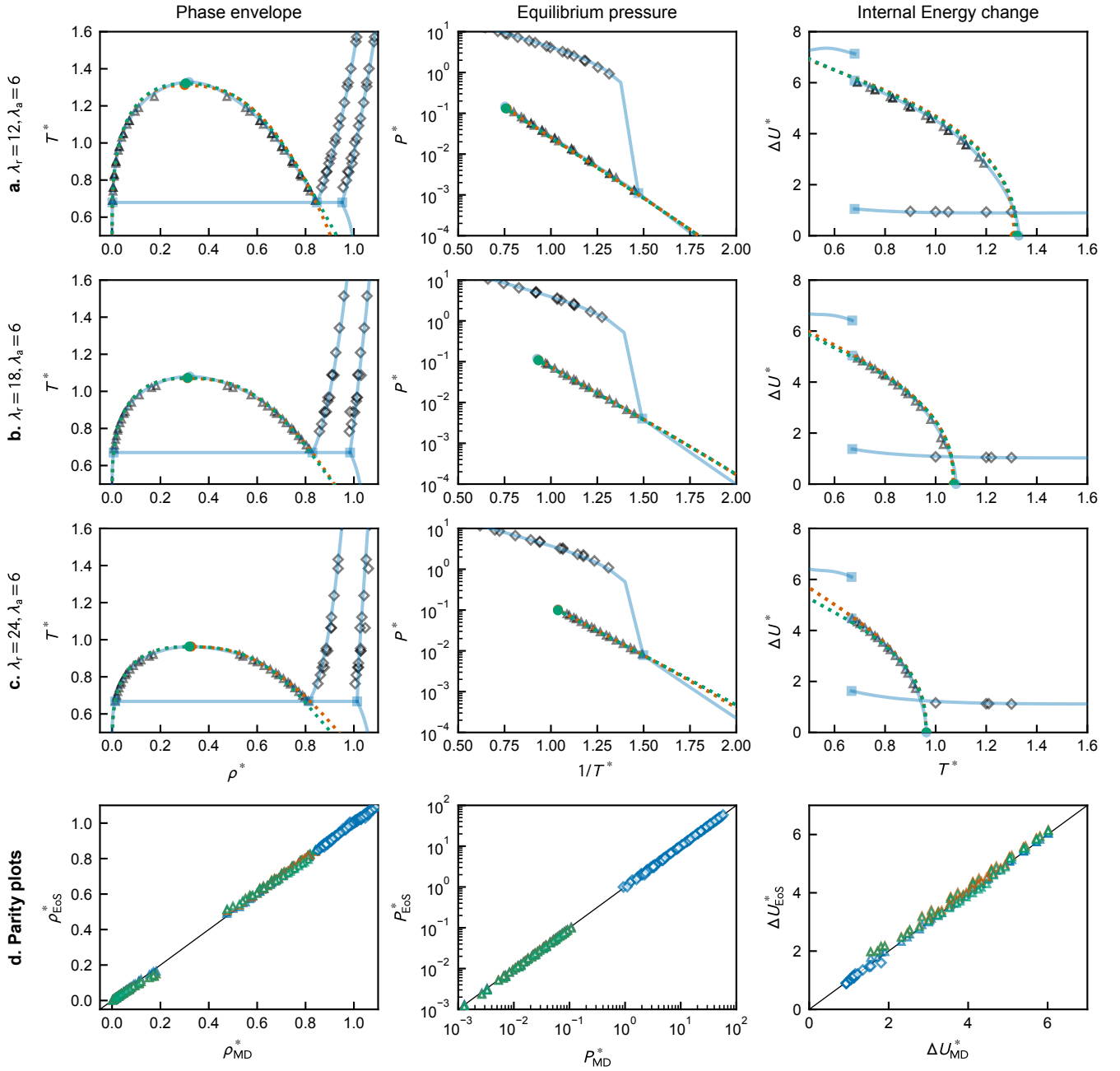
The definition of some derivative properties in Eqs. (S4), such as the thermal expansion coefficient, isothermal compressibility, and isobaric heat capacity can be rearranged to unveil the dependence of these properties with respect to the pressure first density derivative (i.e., $(\partial P^*/\partial \rho^*)_{T^*}$).

$$\alpha_P^* = \left(\frac{\partial P^*}{\partial T^*} \right)_{\rho^*} \bigg/ \left[\rho^* \left(\frac{\partial P^*}{\partial \rho^*} \right)_{T^*} \right] \quad (\text{S17a})$$

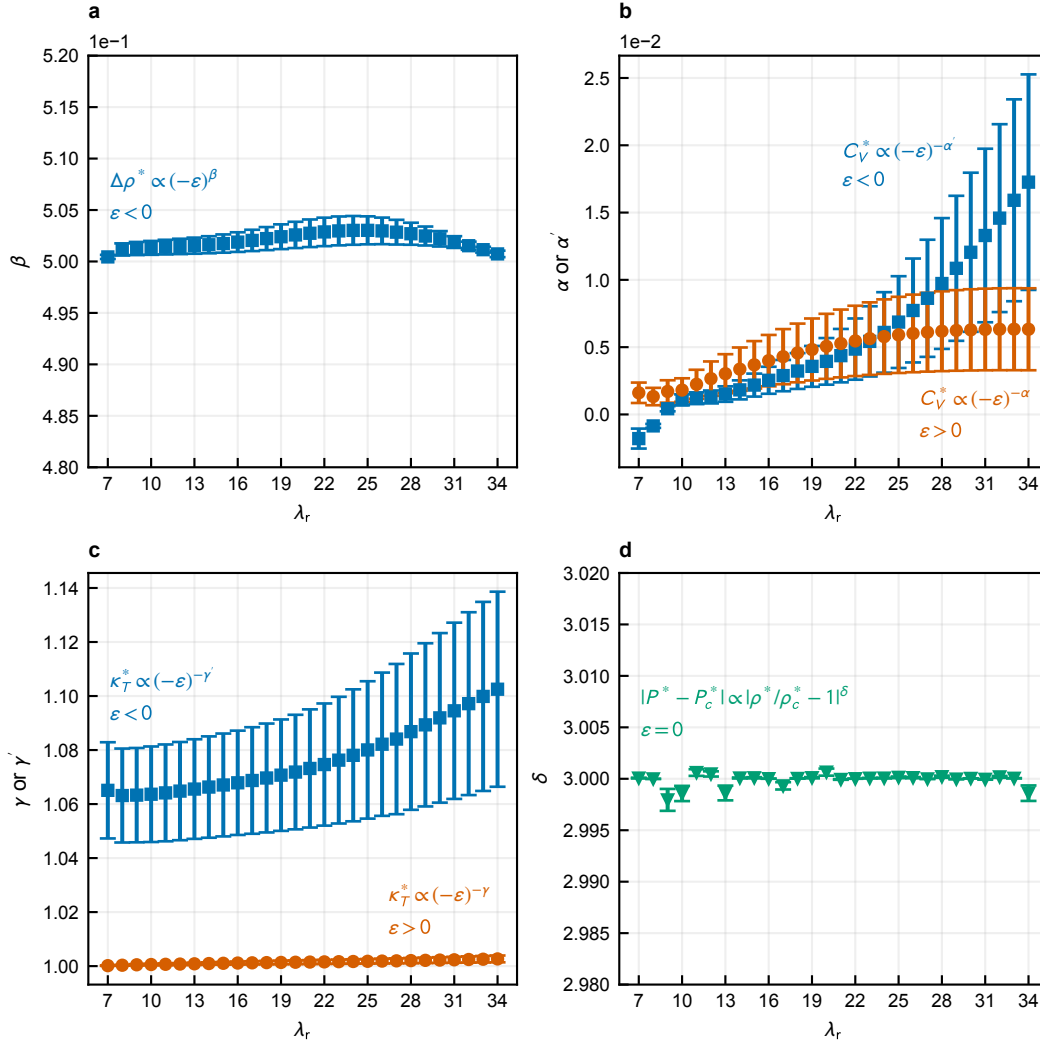
$$\kappa_T^* = 1 / \left[\rho^* \left(\frac{\partial P^*}{\partial \rho^*} \right)_{T^*} \right] \quad (\text{S17b})$$

$$C_P^* = C_V^* + \left[T^* \left(\frac{\partial P^*}{\partial T^*} \right)_{\rho^*} \right] \bigg/ \left[\rho^{*2} \left(\frac{\partial P^*}{\partial \rho^*} \right)_{T^*} \right] \quad (\text{S17c})$$

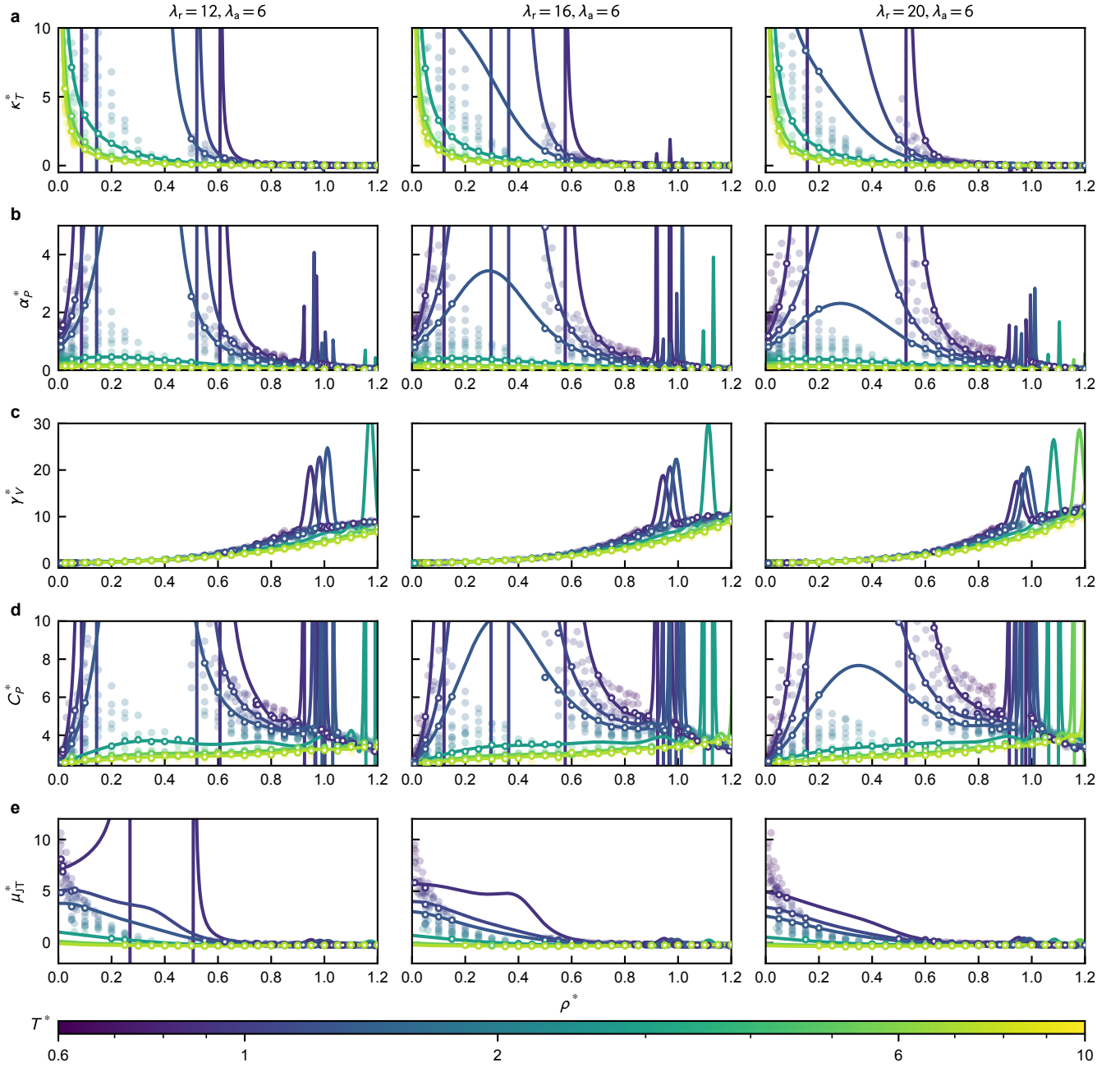
From Eqs. (S17), it can be observed these derivative properties are related to the inverse of $(\partial P^*/\partial \rho^*)_{T^*}$. This dependence implies a divergence behavior at the spinodal limits and critical point, where this derivative is zero (i.e., $(\partial P^*/\partial \rho^*)_{T^*} = 0$). This divergence is observed in Supplementary Figure 6a, b, and d by vertical lines of the isotherms.



Supplementary Figure 4: **Comparison of phase equilibria of selected (λ_r -6) Mie particles with different Equations of State.** **a.** $\lambda_r = 12, \lambda_a = 6$ (Lennard-Jones particle). **b.** $\lambda_r = 18, \lambda_a = 6$. **c.** $\lambda_r = 24, \lambda_a = 6$. **d.** Parity plots. Left column: phase envelope, center column: equilibrium pressure and right column: internal energy change ($\Delta U^{a \rightarrow b} = U^b - U^a$). Blue lines and symbols refer to FE-ANN(s) EoS results, orange lines, and symbols refer to SAFT-VR-Mie EoS⁹ results, and green lines and symbols refer to the EoS developed by Pohl *et al.*¹⁰. Empty grey symbols refer to molecular dynamics results obtained in this work. Triangle and diamond symbols refer to VLE and SLE results, respectively.



Supplementary Figure 5: **Critical exponents of $(\lambda_r, 6)$ Mie particles.** **a.** β critical exponent, Eq. (S14). **b.** α or α' critical exponents, Eq. (S13). **c.** γ or γ' critical exponents, Eq. (S15). **d.** δ critical exponent, Eq. (S16). Departure from critical temperature obtained as: $\varepsilon = (T^* - T_c^*)/T_c^*$. The blue square symbol refers to the critical exponent obtained for subcritical temperatures ($\varepsilon < 0$) at saturated conditions. Orange circles refer to critical exponents obtained for supercritical temperatures ($\varepsilon > 0$) and evaluated at the critical density. Green inverted triangles refer to the critical exponent computed at the critical isotherm ($\varepsilon = 0$). Error bars refer to the standard deviation from fitting the critical exponent to different ranges. See Supplementary Table 4 for further details.



Supplementary Figure 6: **Second order properties of selected Mie particles.** **a.** Isothermal compressibility. **b.** Thermal expansion coefficient. **c.** Thermal pressure coefficient. **d.** Isobaric heat capacity. **e.** Joule-Thomson coefficient. Left column: $\lambda_r = 12, \lambda_a = 6$ (Lennard-Jones particle), center column: $\lambda_r = 16, \lambda_a = 6$ and right column: $\lambda_r = 20, \lambda_a = 6$. Solid lines represent the following isotherms: $T^* = 0.9, 1.1, 1.3, 2.8, 5.3$, and 7.2 obtained with the FE-ANN(s) EoS. Solid empty circles represent the molecular dynamics (MD) result of the aforementioned isotherms. Transparent circles represent the data points available from the database. The divergent behavior (vertical lines) of some of these properties (isothermal compressibility, thermal expansion coefficient, and isobaric heat capacity) is a consequence of the dependence of the properties with respect to the inverse of $(\partial P^*/\partial \rho^*)_{T^*}$, see Eqs. (S17). At the spinodal and critical points, this derivative is zero (i.e., $(\partial P^*/\partial \rho^*)_{T^*} = 0$), producing a diverging behavior of these properties.

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