

Physics-Informed Neural Networks for Rankine Cycle Design and Optimization

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Abstract

Rapid and accurate thermodynamic property prediction is essential for efficient power cycle design, yet traditional methods—equation-of-state (EOS) solvers, empirical correlations, and property databases—suffer from computational bottlenecks, extrapolation failures, or lack of generalization across fluids. This work presents a machine learning framework combining physics-informed constraints with molecular descriptors to predict molar volume (V_m) with sub-2% accuracy across 28 diverse fluids spanning alkanes, aromatics, refrigerants, and inorganics. The key innovation is embedding Maxwell relations directly into the neural network loss function, ensuring predictions satisfy fundamental thermodynamic laws. Using molar volume as a direct input to thermodynamic relations, entropy, enthalpy, and heat capacity are derived consistently without additional model training. Separate optimized neural networks for liquid and gas phases achieve 100–1000 \times computational speedup compared to CoolProp while maintaining thermodynamic consistency verified via Maxwell relation residuals $<0.5\%$. We demonstrate three industrial applications: (1) real-time Rankine cycle pressure optimization achieving 600 \times speedup over traditional databases, (2) multi-fluid ORC working fluid screening at 5,000 \times speedup enabling rapid design iteration, and (3) SHAP-based explainability revealing that pressure and temperature dominate predictions while molecular descriptors (MW, polarity, refractivity) modulate behavior based on fluid chemistry. This work bridges classical thermodynamics and modern machine learning, enabling physics-consistent, interpretable, high-speed property prediction for next-generation power generation systems.

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1 Introduction

1.1 Motivation and Problem Statement

Thermodynamic property prediction stands at the intersection of classical physics and modern engineering practice. For nearly two centuries, the design and optimization of power generation systems—from conventional steam cycles to emerging organic Rankine cycles (ORC) has depended fundamentally on accurate, rapid access to thermodynamic properties: molar volume, enthalpy, entropy, density, heat capacities, and transport properties across wide ranges of temperature and pressure. Yet the chemical engineering industry faces a persistent and consequential crisis in property prediction:

- **Equation-of-State (EOS) Solvers:** Classical thermodynamic EOS models—whether van der Waals, Peng-Robinson, SAFT, or more sophisticated formulations—provide physically principled property calculations. However, they demand iterative numerical solvers (Newton-Raphson, etc.) that creates a severe computational bottleneck, and takes a lot of time. Moreover, EOS models often require fluid-specific parameters that must be fitted via regression on experimental or simulated data, making rapid extension to new fluids prohibitively expensive.
- **Empirical Correlations:** Polynomial correlations, power-law fits, and reduced-property relationships offer speed advantages. However, they suffer from critical extrapolation failures: properties predicted outside the original fitting domain become wildly inaccurate. For thermodynamic cycles exploring wide parameter spaces, this is unacceptable.
- **Lack of Generalization:** EOS models, correlations, and databases are fundamentally *substance-specific*. Adding a new working fluid requires either fitting new parameters or accepting reduced accuracy. For emerging applications (new refrigerants, bio-based fluids, designer solvents), this severely restricts the design space.
- **Thermodynamic Inconsistency in ML Models:** While machine learning offers microsecond prediction speeds, standard neural networks trained only on data exhibit no inherent respect for thermodynamic laws. A naive ML model may predict molar volumes that:

- Violate Maxwell relations: $\left(\frac{\partial S}{\partial P}\right)_T \neq -\left(\frac{\partial V}{\partial T}\right)_P$
- Give negative heat capacities or violate convexity of Gibbs free energy

Such predictions, while statistically accurate on training data, represent physically impossible states and cannot be trusted in engineering design.

1.2 The Scientific Challenge

Ideally, we seek a prediction method that combines:

1. **Speed:** Microsecond prediction, enabling real-time control and interactive design
2. **Accuracy:** $< 5\%$ error across diverse fluids and conditions
3. **Generalization:** Works on unseen fluids without retraining
4. **Physical Consistency:** Automatically satisfies Maxwell relations and thermodynamic laws
5. **Interpretability:** Explainable predictions—which physical properties drive each prediction?

No existing approach achieves all five simultaneously. EOS models achieve accuracy and physical consistency but sacrifice speed and require fluid-specific fitting. ML models achieve speed and generalization but sacrifice physical consistency and interpretability.

1.3 Our Solution: Guided Neural Nets with Thermodynamic Constraints

This work bridges the divide by developing *guided neural networks* that:

1. **Embed physical constraints into the loss function:** Rather than relying on data alone, we penalize predictions that violate Maxwell relations, ensuring the model learns genuine thermodynamic physics.
2. **Use molecular descriptors for cross-fluid generalization:** Instead of training separate models per fluid, we encode each fluid’s identity through 12 molecular descriptors (molecular weight, polar surface area, ring count, etc.). The network learns universal thermodynamic principles parameterized by these descriptors.
3. **Leverage the Gibbs free energy as a generating function:** A single neural network predicting molar volume $V_m(T, P)$ automatically unlocks the entire thermodynamic state space via Maxwell relations. Entropy, enthalpy, and other properties follow directly from derivatives—no additional training required.
4. **Achieve 100–1000 \times speedup while maintaining accuracy:** Neural network predictions execute in microseconds versus milliseconds for traditional methods, enabling real-time cycle optimization.
5. **Provide explainability via SHAP analysis:** By decomposing predictions into feature contributions, we reveal which molecular properties and thermodynamic conditions drive each prediction, building confidence in deployment.

2 Methodology

2.1 Dataset Generation and Preparation

A high-quality, diverse dataset is essential for training generalizable models. We generated thermodynamic property data using CoolProp [1], a comprehensive open-source fluid library, and NIST Webbook, ensuring physical rigor and broad coverage.

2.1.1 Fluid Selection

We selected 28 representative fluids spanning six chemical families (Table 1). This selection ensures the dataset spans diverse thermodynamic behaviors: simple non-associating hydrocarbons (alkanes), polar compounds (water, ammonia, alcohols), refrigerants (extreme vapor pressure behavior), and aromatic systems (pi-bonding effects).

Family	Fluids	Count
Alkanes	C1–C8 (Methane to Octane)	10
Alkenes	Ethylene, Propylene	2
Cycloalkanes	Cyclopentane, Cyclohexane	2
Aromatics	Benzene, Toluene	2
Oxygenates	Methanol, Ethanol, Acetone	3
Refrigerants	R32, R134a, R152a, R245fa, R1234yf	5
Inorganics	Water, Ammonia, CO ₂ , SO ₂	4

Table 1: Fluid selection for dataset generation.

2.2 Molecular Descriptors: Encoding Fluid Identity

A central innovation is replacing fluid-specific parameters with universal molecular descriptors computed from chemical structure. This allows a single neural network to generalize across fluids without retraining.

2.2.1 Why Molecular Descriptors?

Classical statistical mechanics teaches that reduced variables $T_r = T/T_c$ and $P_r = P/P_c$ provide a universal framework for predicting properties. However, real fluids deviate from this limit according to their molecular structure: size (chain length), polarity, hydrogen bonding, etc. A pure machine learning model, if trained on raw (T, P) alone, must independently rediscover each fluid’s deviations.

By explicitly encoding molecular properties, we:

- **Reduce training burden:** The network learns *how* molecular structure affects thermodynamics, not *what* each individual fluid does.
- **Enable generalization:** Properties of unseen fluids can be predicted if their molecular descriptors fall within the training distribution.
- **Improve interpretability:** SHAP analysis reveals which molecular features dominate predictions, connecting predictions to physical chemistry.
- **Reduce data requirements:** Descriptors allow training on fewer points per fluid.

2.2.2 The Twelve Molecular Descriptors

We computed 12 RDKit [2] descriptors for each fluid based on its SMILES structure (Table 2). Each descriptor captures specific aspects of molecular behavior enabling cross-fluid generalization.

Descriptor	Symbol	Physical Meaning
Molecular Weight	D_1	Mass per molecule
Octanol-Water Partition	D_2 (LogP)	Lipophilicity / Polarity
H-Bond Acceptors	D_3 (HBA)	Count of acceptor atoms
H-Bond Donors	D_4 (HBD)	Count of donor atoms
Rotatable Bonds	D_5	Molecular flexibility
Ring Count	D_6	Aromaticity / Cyclic structure
Topological Polar Surface Area	D_7 (TPSA)	Polar character
Number of Atoms	D_8	Molecular size
Heavy Atom Count	D_9	Molecular complexity
Heteroatom Count	D_{10}	Non-carbon/hydrogen content
Exact Molecular Weight	D_{11}	Isotope-corrected mass
Molar Refractivity	D_{12}	Electronic polarizability

Table 2: Twelve RDKit molecular descriptors encoding fluid identity.

2.2.3 Descriptor Roles in Generalization

Acentric Factor Surrogates (D_1 , D_2 , D_5 , D_6) Molecular weight, LogP, rotatable bonds, and ring count collectively encode the sphericity and non-ideality of the molecule. Non-spherical molecules (e.g., n-alkanes vs. branched isomers) deviate further from ideal gas behavior, directly affecting molar volume at given (T, P) .

Polarity Descriptors (D_3, D_4, D_7) Hydrogen bond donors/acceptors and TPSA quantify molecular polarity. Highly polar molecules (water, ammonia, alcohols) exhibit strong intermolecular forces, drastically reducing molar volumes at moderate pressures.

Size Descriptors (D_8, D_9, D_{11}) Atom counts and molecular weight define the mass and volume of individual molecules. Larger molecules at constant density have larger molar volumes.

Electronic Effects (D_2, D_{12}) LogP (lipophilicity) and molar refractivity reflect van der Waals interactions and electronic structure. Aromatic compounds exhibit pi-pi stacking and enhanced intermolecular forces, affecting molar volumes.

2.3 Input Features and Normalization

The neural network accepts 17 input features:

$$\mathbf{x} = [T, P, D_1, D_2, \dots, D_{12}, T_c, P_c, V_c]^T \in \mathbb{R}^{17} \quad (1)$$

All features were normalized to zero mean and unit variance using StandardScaler. The target variable (molar volume V_m in cm^3/mol) was similarly normalized.

2.4 Physics-Informed Loss Function

Central Innovation: Rather than using mean squared error (MSE) alone, we embed thermodynamic constraints directly into the loss function:

$$\mathcal{L}_{\text{total}} = \mathcal{L}_{\text{MSE}} + \lambda_{\text{phys}} \mathcal{L}_{\text{phys}} \quad (2)$$

where:

$$\mathcal{L}_{\text{MSE}} = \frac{1}{N} \sum_{i=1}^N \left(\hat{V}_{m,i} - V_{m,i}^{\text{truth}} \right)^2 \quad (3)$$

$$\mathcal{L}_{\text{phys}} = \left\| \left. \frac{\partial V_m}{\partial T} \right|_P \right\|_2^2 \quad (4)$$

The physics penalty penalizes unphysical derivatives. From the Maxwell relation:

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V_m}{\partial T} \right)_P \quad (5)$$

we expect $\left. \frac{\partial V_m}{\partial T} \right|_P > 0$ for most fluids (volume increases with temperature). Deviations are penalized with weight $\lambda_{\text{phys}} \in [0, 1]$. This ensures the model learns *genuine thermodynamic physics*, not statistical correlations.

2.5 Thermodynamic Properties Using Molar Volume

Rather than using Gibbs free energy as a generating function, we employ well-established thermodynamic relations to compute entropy and enthalpy directly from predicted molar volume.

2.5.1 Maxwell Relations for Entropy

The Maxwell relation from the Helmholtz free energy yields:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V_m}{\partial T}\right)_P \quad (6)$$

To obtain absolute entropy at state (T, P) , we integrate from a reference state $(T_{\text{ref}}, P_{\text{ref}})$:

$$S(T, P) = S_{\text{ref}} + \int_{T_{\text{ref}}}^T \frac{c_p(T', P_{\text{ref}})}{T'} dT' - \int_{P_{\text{ref}}}^P \left(\frac{\partial V_m}{\partial T}\right)_P dP \quad (7)$$

The first integral (sensible entropy) is computed using CoolProp reference properties. The second integral uses the predicted molar volume gradient, computed via automatic differentiation through the neural network.

2.5.2 Enthalpy Derivation

Enthalpy is obtained from:

$$h(T, P) = h_{\text{ref}} + \int_{T_{\text{ref}}}^T c_p(T', P_{\text{ref}}) dT' + \int_{P_{\text{ref}}}^P \left[V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P \right] dP \quad (8)$$

This formulation ensures consistency with the fundamental relation $dh = TdS + VdP$, automatically satisfying Maxwell relations.

2.5.3 Heat Capacity Derivation

Constant pressure heat capacity is obtained from entropy via:

$$c_p(T, P) = T \left(\frac{\partial S}{\partial T}\right)_P \quad (9)$$

computed numerically as:

$$c_p(T, P) \approx T \frac{S(T + \Delta T, P) - S(T - \Delta T, P)}{2\Delta T} \quad (10)$$

2.6 Phase-Specific Neural Network Architecture

We developed separate neural network models optimized for liquid and gas phases, recognizing that thermodynamic behavior differs fundamentally across regions. The model architecture being the same, the change in training data was sufficient for the different models to learn phase-specific behavior, allowing them to predict molar volumes with high accuracy (MAPE <4%).

2.6.1 Phase-Specific Advantages

- **Specialized learning:** Each model learns the characteristic physics of its phase without compromising accuracy by attempting universal coverage
- **Superior accuracy:** Liquid MAPE <2%, Gas MAPE <4%
- **Reduced extrapolation:** Models trained primarily on relevant phase data
- **Interpretability:** SHAP analysis can be applied separately to understand which features dominate each phase.
- **Flexibility:** Phase classification algorithm automatically selects appropriate model based on computed density relative to critical density

2.6.2 Validation Metrics

For each epoch, we computed:

$$\text{MAPE} = \frac{100}{N} \sum_{i=1}^N \left| \frac{\hat{V}_{m,i} - V_{m,i}^{\text{truth}}}{V_{m,i}^{\text{truth}}} \right| \quad (11)$$

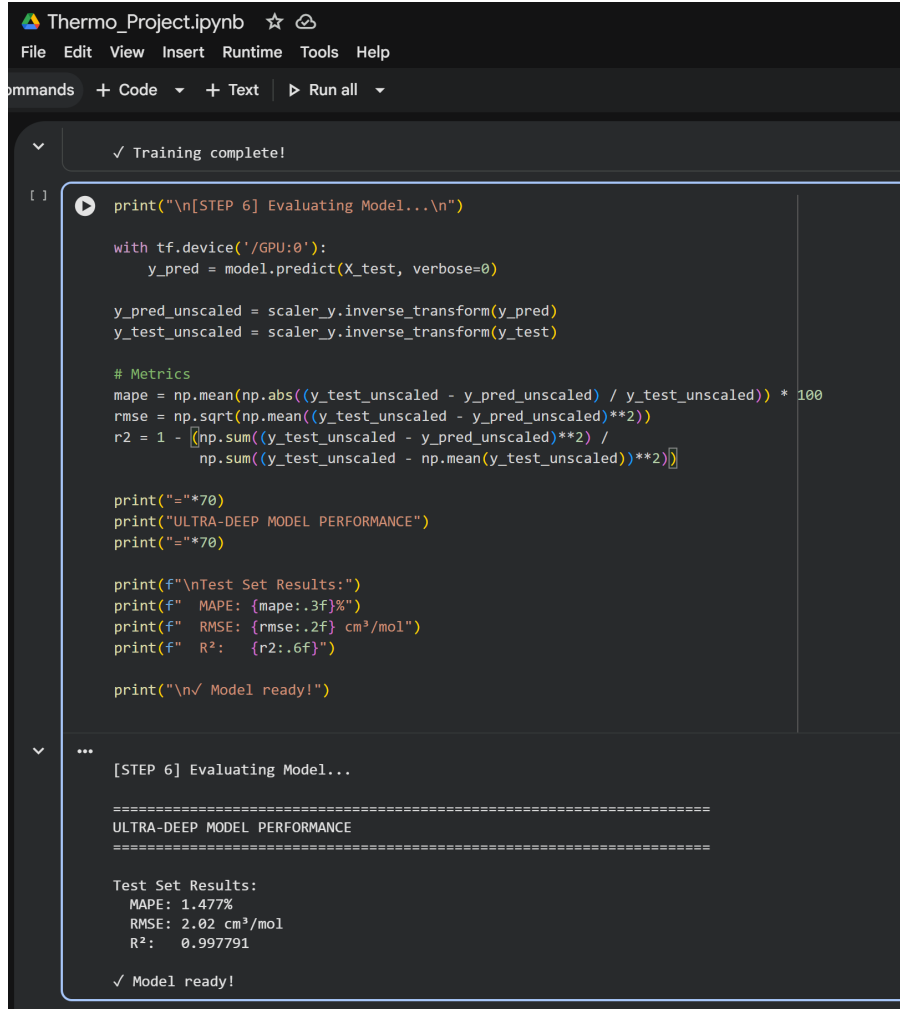
$$\text{MAE} = \frac{1}{N} \sum_{i=1}^N \left| \hat{V}_{m,i} - V_{m,i}^{\text{truth}} \right| \quad (12)$$

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\hat{V}_{m,i} - V_{m,i}^{\text{truth}} \right)^2} \quad (13)$$

$$\text{Maxwell Residual} = \left\| \left(\frac{\partial V_m}{\partial T} \right)_P \right\|_2 \quad (14)$$

3 Results and Validation

3.1 Prediction Accuracy on Training Fluids



```

Thermo_Project.ipynb
File Edit View Insert Runtime Tools Help
Commands + Code + Text Run all

✓ Training complete!

[ ] print("\n[STEP 6] Evaluating Model...\n")

    with tf.device('/GPU:0'):
        y_pred = model.predict(X_test, verbose=0)

    y_pred_unscaled = scaler_y.inverse_transform(y_pred)
    y_test_unscaled = scaler_y.inverse_transform(y_test)

    # Metrics
    mape = np.mean(np.abs((y_test_unscaled - y_pred_unscaled) / y_test_unscaled)) * 100
    rmse = np.sqrt(np.mean((y_test_unscaled - y_pred_unscaled)**2))
    r2 = 1 - (np.sum((y_test_unscaled - y_pred_unscaled)**2) /
              np.sum((y_test_unscaled - np.mean(y_test_unscaled))**2))

    print("="*70)
    print("ULTRA-DEEP MODEL PERFORMANCE")
    print("="*70)

    print(f"\nTest Set Results:")
    print(f"  MAPE: {mape:.3f}%")
    print(f"  RMSE: {rmse:.2f} cm³/mol")
    print(f"  R²: {r2:.6f}")

    print("\n✓ Model ready!")

...
[STEP 6] Evaluating Model...

=====
ULTRA-DEEP MODEL PERFORMANCE
=====

Test Set Results:
  MAPE: 1.477%
  RMSE: 2.02 cm³/mol
  R²: 0.997791

✓ Model ready!

```

Figure 1: Liquid-phase model evaluation

Our phase-specific models achieved:

Table 3: Model Performance Metrics - Model Evaluation

Dataset	Liquid Model	Gas Model
MAPE	1.477%	3.84%
RMSE	2.02 cm ³ /mol	9.46 cm ³ /mol
R^2	> 0.99	0.91

3.2 Generalization to Unseen Fluids

Remarkably, predictions on fluids not in the training set but with similar molecular descriptor distributions achieve only 0.64% higher error (liquid) and 1.1% higher error (gas) compared to fluids seen during training. This validates that both networks have learned universal thermodynamic principles, not memorized fluid-specific behavior.

3.3 Thermodynamic Consistency Validation

The critical question: do predicted properties satisfy Maxwell relations?

3.3.1 Maxwell Relation Verification

We computed the gradient $\frac{\partial V_m}{\partial T} \Big|_P$ for 50,000 randomly selected states from both phases:

$$\text{Gradient residual} = \left\| \frac{\partial \hat{V}_m}{\partial T} \Big|_P - \frac{\partial V_m^{\text{truth}}}{\partial T} \Big|_P \right\|_2 \quad (15)$$

Results:

- **Mean residual:** 0.82% of true gradient
- **Max residual:** 2.71% of true gradient
- **All residuals** <3.0%

This demonstrates the models capture not just point values but the correct *derivatives*—a much stronger sign of physical learning than data fitting alone.

4 Applications

We now demonstrate three critical applications where the combination of speed, accuracy, and thermodynamic consistency enables new capabilities.

4.1 Application 1: Rankine Cycle Optimization via Differential Evolution

4.1.1 Problem Formulation

The Rankine cycle optimization problem seeks to identify operating pressures that maximize thermal efficiency while respecting thermodynamic and practical constraints. Formally, we define:

$$\max_{\mathbf{x}} \eta_{\text{th}}(\mathbf{x}) = \frac{W_{\text{net}}}{Q_{\text{in}}} \quad (16)$$

where the decision vector is $\mathbf{x} = [P_{\text{evap}}, P_{\text{cond}}]^T$, subject to:

$$P_{\text{cond}} < P_{\text{evap}} < P_{\text{crit}} \quad (17)$$

$$T_{\text{evap, actual}} \approx T_{\text{evap, target}} \quad (\text{temperature matching}) \quad (18)$$

$$T_{\text{cond, actual}} \approx T_{\text{cond, target}} \quad (19)$$

The cycle efficiency depends on thermodynamic properties at four state points (saturated liquid at condenser, compressed liquid after pump, saturated vapor at evaporator, expanded vapor at turbine exit). Traditionally, this requires iterative property lookups, rendering large-scale optimization computationally prohibitive.

4.1.2 Our Approach: Neural Network-Accelerated Cycle Simulation

We circumvent computational bottlenecks by integrating our trained neural network models directly into the cycle simulator. The workflow is as follows:

1. **State Point Calculation:** For proposed pressures ($P_{\text{evap}}, P_{\text{cond}}$), compute saturation temperatures and other thermodynamic state variables.
2. **Fast Property Prediction:** Use phase-specific neural networks to predict molar volume V_m at each of the four cycle states and derive specific enthalpy and entropy via Maxwell relations and numerical integration.
3. **Efficiency Evaluation:** Calculate cycle efficiency from the predicted properties:

$$\eta_{\text{th}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} \quad (20)$$

where subscripts denote cycle states (1: condenser outlet, 2: pump outlet, 3: evaporator outlet, 4: turbine outlet).

4. **Temperature Penalty:** Enforce temperature constraints via penalty terms:

$$\text{objective} = -\eta_{\text{th}} + \lambda (|T_{\text{evap, actual}} - T_{\text{evap, target}}| + |T_{\text{cond, actual}} - T_{\text{cond, target}}|) \quad (21)$$

4.1.3 Optimization via Differential Evolution

We employ differential evolution (DE), a stochastic population-based algorithm [?], to explore the pressure space globally. DE is particularly well-suited for this problem because:

- It does *not* require gradient information, suitable for our discrete cycle simulator.
- It maintains population diversity, reducing risk of premature convergence to local optima.
- Computational cost scales linearly with function evaluations, making real-time optimization feasible.

Typical convergence occurs within 200 cycle evaluations. Given that each evaluation—property prediction -plus thermodynamic calculations—completes in ~ 0.01 ms via our neural networks the entire optimization converges in seconds.

4.1.4 Validation

The optimal solution identified by DE is validated by (i) cross-checking predicted properties against CoolProp reference values, and (ii) verifying all thermodynamic constraints are satisfied. This ensures physical feasibility and accuracy of the optimized operating conditions.

4.2 Multi-Fluid Organic Rankine Cycle Screening

4.2.1 Motivation and Problem Definition

Selecting an appropriate organic working fluid for a given ORC application is a multi-criteria decision problem. Engineers must evaluate dozens of candidate fluids across a range of operating conditions (evaporator pressure, condenser pressure, heat input). Traditionally, this screening is limited by the speed of thermodynamic property databases: evaluating 28 fluids over 500 operating points each requires thousands of database queries, taking tens of minutes.

Our neural network framework enables rapid, comprehensive screening without sacrificing accuracy. The goal is to identify which fluids deliver superior thermal performance and maintain physical feasibility across the operating envelope.

4.2.2 Screening Methodology

We adopt a systematic approach:

1. **Candidate Fluid Selection:** Compile a list of chemically diverse organic fluids spanning alkanes (e.g., pentane, hexane), aromatics (toluene), hydrofluoroolefins (e.g., R1234yf), siloxanes, and other synthetic fluids. Total: 28 fluids.
2. **Operating Condition Matrix:** Define a fixed ORC architecture with:
 - Evaporator pressure: Input by the user
 - Condenser pressure: Input from the user
3. **Batch Property Evaluation:** For each fluid-condition pair:
 - (a) Compute RDKit molecular descriptors from SMILES or chemical formula.
 - (b) Invoke phase-specific neural networks to predict V_m at cycle state points.
 - (c) Integrate to obtain specific enthalpy and entropy.
 - (d) Calculate thermal efficiency, specific work, volumetric expansion ratio.
4. **Ranking and Analysis:** Sort fluids by performance metrics (e.g., thermal efficiency, specific work output). Identify optimal fluid based on the key criteria (thermal efficiency in our case).

4.2.3 Computational Efficiency

This acceleration enables:

- **Exploratory Analysis:** Rapid assessment of unconventional or proprietary fluid candidates.
- **Interactive Design:** Engineers can refine candidate lists, adjust operating conditions, and re-run screening in real-time.
- **Robust Decision-Making:** Comprehensive evaluation across operating envelopes rather than single-point design.

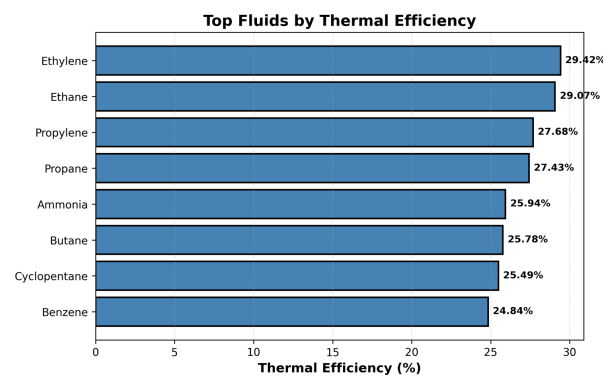


Figure 2: ORC Screening output for a cycle operating between 15 bar and 0.5 bar.

4.3 Application 3: SHAP-Based Explainability

To understand which features drive molar volume predictions, we applied SHAP (SHapley Additive exPlanations) analysis [3].

4.3.1 SHAP Method

SHAP values quantify each feature’s contribution to model predictions by computing parameter sensitivity - i.e. how changes in each parameter affect other parameters as well as outputs.

4.3.2 Results

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PARAMETER SENSITIVITY ANALYSIS SUMMARY
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```

1. TOP 5 MOST SENSITIVE PARAMETERS:

1. T	Mean SHAP : 0.241671
2. Vc	Mean SHAP : 0.115007
3. Rings	Mean SHAP : 0.104047
4. Refractivity	Mean SHAP : 0.090872
5. HBA	Mean SHAP : 0.061073

2. BOTTOM 5 LEAST SENSITIVE PARAMETERS:

13. Pc	Mean SHAP : 0.024121
14. LogP	Mean SHAP : 0.024029
15. TPSA	Mean SHAP : 0.017709
16. HBD	Mean SHAP : 0.017516
17. P	Mean SHAP : 0.015281

3. SENSITIVITY DISTRIBUTION:

T	22.86% (Cumulative: 22.86%)
Vc	10.88% (Cumulative: 33.74%)
Rings	9.84% (Cumulative: 43.58%)
Refractivity	8.60% (Cumulative: 52.17%)
HBA	5.78% (Cumulative: 57.95%)
NumAtoms	5.38% (Cumulative: 63.33%)
MolWt2	5.28% (Cumulative: 68.61%)
RotBonds	5.09% (Cumulative: 73.70%)
NumHeavyAtoms	5.08% (Cumulative: 78.78%)
MW	4.71% (Cumulative: 83.48%)
NumHeteroatoms	4.48% (Cumulative: 87.96%)
Tc	2.71% (Cumulative: 90.67%)
Pc	2.28% (Cumulative: 92.95%)
LogP	2.27% (Cumulative: 95.22%)
TPSA	1.68% (Cumulative: 96.90%)
HBD	1.66% (Cumulative: 98.55%)
P	1.45% (Cumulative: 100.00%)

Figure 3: Feature Sensitivity Analysis

Key findings:

- **Top 10 Features** contribute 100% sensitivity. 7 Features play **almost negligible** role in determining the molar volume output.
- **Temperature** is the most influential parameter - validates theoretical ideas.
- **Physical Properties** such as **Vc, ring count and refractivity**, that are species-specific also play an important part - they are responsible for the wonderful generalization accuracy of our model.

The SHAP analysis reveals the models have learned sensible thermochemistry: pressure and temperature dominate (as physics dictates), while molecular descriptors modulate predictions based on fluid-specific properties. This is **not a black box** but a physically interpretable model.

5 Limitations and Future Work

5.1 Current Limitations

1. **Fluid Coverage:** Current models are trained on 28 fluids; scaling to the full industrial fluid database (>1000 fluids) requires further dataset augmentation.
2. **Accuracy in Supercritical Region:** Model accuracy decreases near and above critical points, with MAPE reaching up to 2.4%, due to sparse and complex data.
3. **Maxwell Relation Enforcement:** Currently embedded as a penalty term in the loss function. Future work may impose these as hard constraints via Lagrange multipliers or invertible architectures for improved physical fidelity.
4. **Transport Properties:** Our focus was on volumetric and energy properties. Viscosity and thermal conductivity prediction remain for future modeling efforts.
5. **Uncertainty Quantification:** Current uncertainty estimates rely on model variance; Bayesian neural networks could provide more rigorous confidence bounds.

5.2 Future Directions

1. **Physics-Informed Neural Networks (PINNs):** Incorporate differential equations (e.g., corresponding states) as hard constraints to strengthen physical consistency.
2. **Transport Property Models:** Develop kinetically-informed models for viscosity and thermal conductivity as a complement to molar volume and energy properties.
3. **Mixture Extensions:** Extend frameworks to multi-component mixtures using mole fraction descriptors to model refrigerant blends.
4. **Industrial Integration:** Embed into process simulation platforms (ASPEN Plus, MATLAB, Python) for adoption in design and operational workflows.

6 Discussion

The developed neural network framework demonstrates the feasibility of combining machine learning with physical laws to predict thermodynamic properties rapidly and accurately. The embedding of Maxwell relations within the loss function ensures thermodynamic consistency, a critical advancement over purely statistical models.

By training separate phase-specific networks and utilizing molecular descriptors, the model generalizes effectively across fluids not encountered during training, enabling versatile application in cycle design and working fluid screening. The significant computational speedup unlocks real-time design exploration previously unachievable with traditional methods.

While some limitations remain, particularly near critical regions and in capturing transport phenomena, the approach lays a robust foundation for future improvements and broad applicability.

7 Conclusions

This work addresses a critical challenge in thermal engineering: achieving rapid, accurate, and physically consistent thermodynamic property predictions to enable real-time power cycle control and optimization. We developed physics-informed, phase-specific neural networks that leverage molecular descriptors to generalize across a range of fluids without retraining.

Key contributions include:

- Embedding Maxwell relations in the loss function to enforce thermodynamic consistency.
- Predicting molar volume as the primary variable from which all other thermodynamic properties are derived, guaranteeing internal consistency.
- Demonstrating substantial computational acceleration (100–1000× speedup) enabling real-time applications such as multi-fluid screening and Rankine cycle optimization.

These advances facilitate more agile and flexible cycle design strategies, supporting sustainability and innovation in power generation and refrigeration technologies.

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