Residual Entropy Scaling Model for the Viscosity of CO_2- and H_2- Containing Fluids

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Introduction

The viscosity of working fluids directly influences their flow characteristics, making it a critical fundamental property for system design and the development of key components. In CCUS systems and hydrogen-based industrial applications, accurate viscosity predictions for CO_2- and H_2-containing fluids form the foundation of a wide range of research efforts. This study focuses on CO_2 and H_2 as primary components, selects fluids relevant to CCUS and hydrogen industries, and develops a residual entropy scaling model for viscosity prediction.

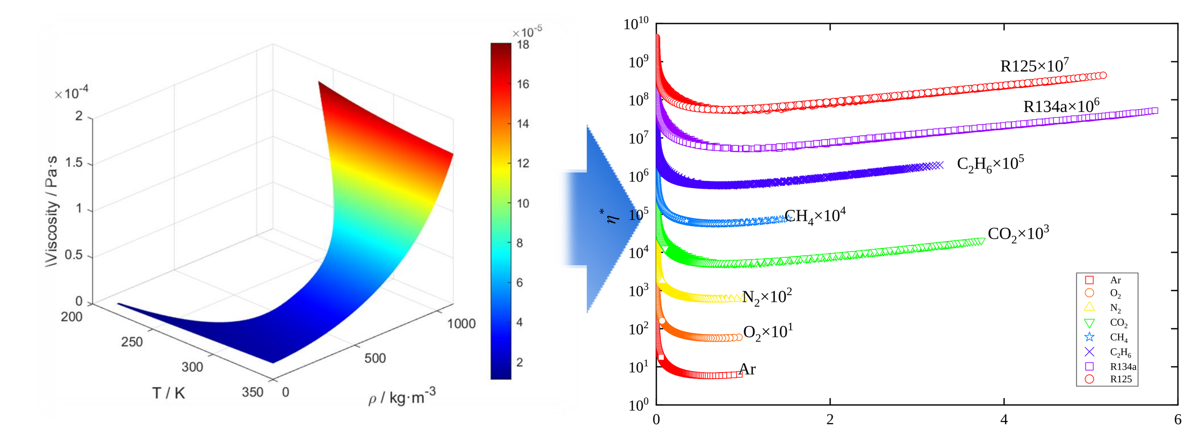
What and Why is RES?

In 1977, Rosenfeld observed the dimensionless viscosity $\ln(\eta^*)$ exhibits an approximately linear correlation with the residual entropy $s^r(T,\rho) = s^{real}(T,\rho) - s^{ideal}(T,\rho)$:

$$\ln(\eta^*) \propto -s^r / Nk_B \qquad \eta^* = \frac{\eta}{\rho_N^{2/3}(mk_BT)^{1/2}}$$

The approach of investigating the relationship between transport properties and residual entropy is referred to as residual entropy scaling (RES).

Traditional models of transport properties primarily focus on establishing direct relationships with temperature-pressure (T-p) or temperature-density (T-ρ) conditions. In contrast, RES simplifies this process by correlating transport properties with residual entropy via a univariate relationship. Since residual entropy is determined by the equation of state, extensive research achievements in thermodynamic properties can be leveraged.



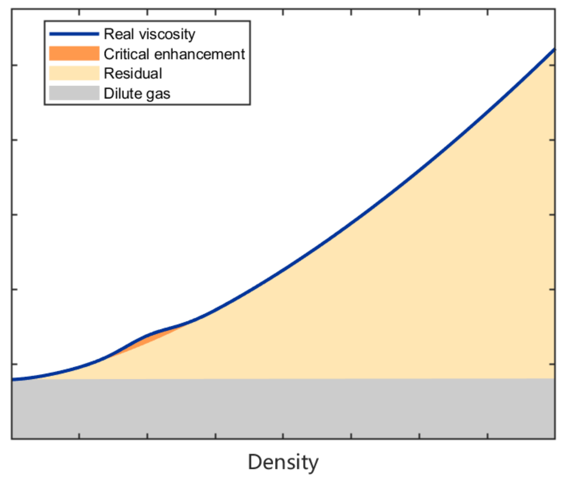
The dimensionality reduction capability of residual entropy scaling

Target Fluid

Fluid name	Molar mass (g/mol)	Fluid name	Molar mass (g/mol)
Ar	39.948	CH_4	16.0428
CO	28.0101	N_2O	44.0128
CO_2	44.0098	N_2	28.0135
H_2S	34.0809	O_2	31.9988
H_2	2.0159	SO_2	64.0638

Method

Transport property models typically consist of three components: dilute-gas, residual, and critical terms. In the dilute gas limit, only two-body interactions are considered. As density increases, complex many-body effects arise, captured by the residual term. Near the critical point, singular behavior occurs, necessitating the inclusion of a critical term.



*A schematic of the **viscosity** variation with density along a near-critical isotherm for carbon dioxide. Note that for viscosity, the influence of the critical term is **minimal**, and therefore the critical term can be set to **zero**. However, for **thermal conductivity**, the effect of the critical term is **significant**, and thus a critical enhancement term is typically required.*

In this work:

- Dilute gas: Chapman-Enskog (CE) solution.

$$\eta_{CE} = \frac{5}{16}\sqrt{\frac{mk_BT}{\pi}}\frac{1}{\sigma^2\Omega^{(2,2)*}}$$

- Residual: RES + Rainwater-Friend's virial term.

$$\ln\left(\frac{\eta}{\eta_{\text{dilute}}}\right) = B_{\eta,\text{RES}}s^+ + \sum_{i=0}^{3} n_i (s^+)^i$$

$$B_{\eta,\text{RES}} = \sum_{i=0}^{4} a_i \left(T^*\right)^{-i}$$

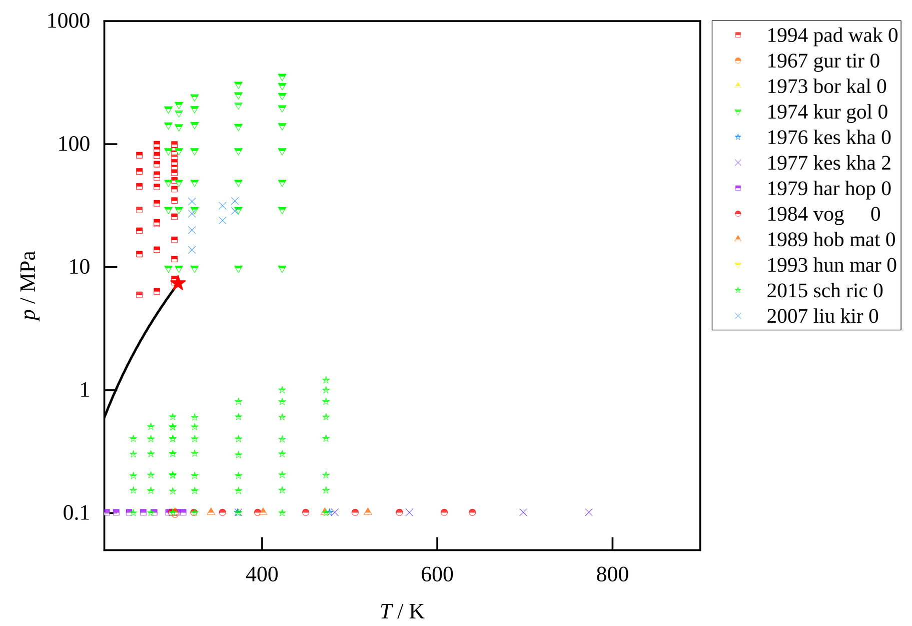
- Critical enhancement: Ignored.

For mixtures, a simple mixing rule is applied:

$$B_{\eta,\text{mix}} = \sum x_i B_{\eta,i} \qquad n_{j,\text{mix}} = \sum x_i n_{j,i}$$

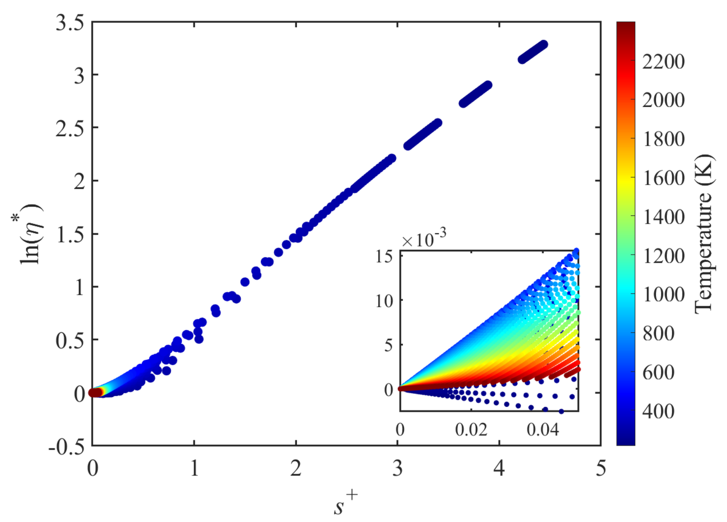
Fitting Process

Experimental data for both pure substances and mixtures have been collected for fitting. For $B_{\eta,\text{RES}}$ and certain fluids, due to insufficient experimental data, REFPROP calculated values are used for fitting.



Experimental data distribution for CO_2. The black line represents the vapor-liquid equilibrium line for carbon dioxide, and the red pentagram represents the critical point. Legend format: Year, first author's abbr., second author's abbr., S.N.

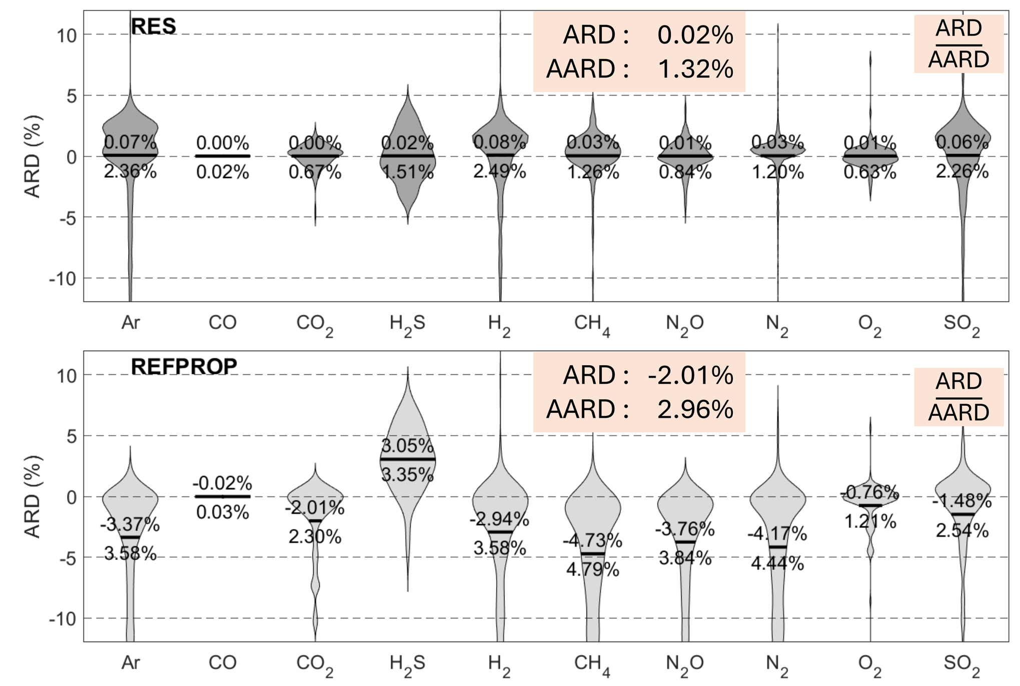
Firstly, REFPROP calculated values are used for the validation of the RES method. Taking CO_2 as an example, it can be observed that there is a univariate relationship between viscosity and the dimensionless residual entropy s^+. Moreover, in the enlarged plot for $s^+ < 0.05$ the viscosity follows the Rainwater-Friend theory, where the logarithmic dimensionless viscosity shows a linear relationship with residual entropy, with the slope depending on temperature.



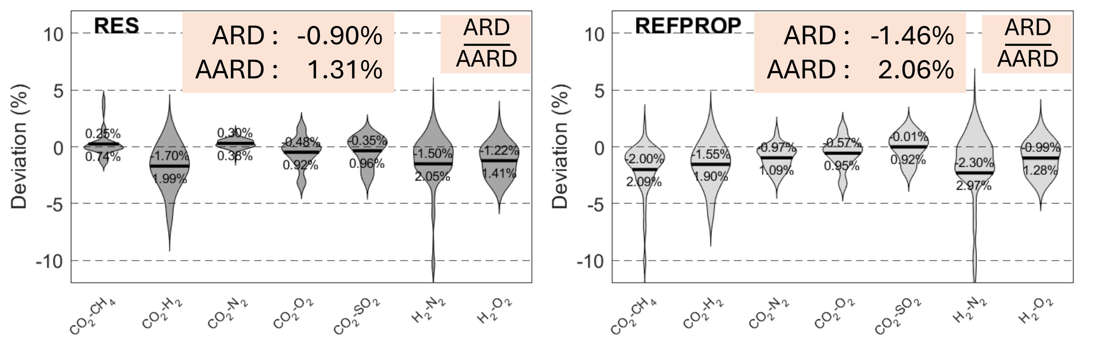
The relationship between dimensionless viscosity and residual entropy for CO_2, with data generated by REFPROP 10.0. The inset in the lower right corner magnifies the region where the dimensionless residual entropy is less than 0.05. Each data point is color-coded according to temperature, with deeper red hues indicating higher temperatures.

Residual entropy is calculated using REFPROP 10.0, and the parameters in the residual term are fitted based on the collected experimental database.

Results



*Statistical distribution of calculation deviations for pure substances. **ARD** refers to the average relative deviation, while **AARD** represents the average absolute relative deviation*



Statistical distribution of calculation deviations for mixtures.

In all, the RES model proposed in this work achieves an AARD of 1.32% for pure substances and 1.31% for mixtures, both lower than those of REFPROP. Among seven mixtures with available experimental data, the RES model achieves lower AARD in four cases and maintains comparable performance in the remaining three. Notably, these improvements in mixture predictions are achieved without introducing any additional fitting parameters.

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