Ethane: A Viscosity Surface Correlation Convenient for Engineers

S. Herrmann[1], E. Vogel[2], R. Span[3]

[1]Zittau/Goerlitz University of Applied Sciences, Zittau, Germany

[2]University of Rostock, Rostock, Germany

[3]Ruhr-University Bochum, Bochum, Germany

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Motivation - Problems and Tasks

Convenience for engineers

- Use of a Standard Database Program for Thermophysical Properties – consistent with respect of thermodynamic and transport properties: REFPROP[1]
- Consistency of the formulations for water:
  - Equation of state (EOS): Wagner and Pruss (2002)[2]
  - Viscosity η: Huber *et al.* (2009)[3]
  - Thermal conductivity λ: Huber *et al.* (2012)[4]

1 Lemmon, E. W.; Huber, M. L.; McLinden, M. O.: Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg (2013).

2 Wagner, W. and Pruss, A., *J. Phys. Chem. Ref. Data* **31**, 387-535 (2002).

3 Huber, M. L., Perkins, R. A., Laesecke, A., Friend, D. G., Sengers, J. V., Assael, M. J., Metaxa, I. M., Vogel, E., Mares, R. and Miyagawa, K., *J. Phys. Chem. Ref. Data* **38**, 101-125 (2009).

4 Huber, M. L., Perkins, R. A., Friend, D. G., Sengers, J. V., Assael, M. J., Metaxa, I. M., Miyagawa, K., Hellmann, R. and Vogel, E., *J. Phys. Chem. Ref. Data* **41**, 1-23 (2012).

Problems with consistency

Ethane – within REFPROP: EOS, η, λ – inconsistent

- - EOS: Bücker and Wagner (2006)[5]
  - η and λ: Friend *et al.* (1991)[6]
- - EOS – classical including the critical region, an additional parametric crossover EOS not needed
  - η – not including a critical enhancement, but using the classical Schmidt-Wagner EOS of Friend *et al.* (1991)
  - λ – including a critical enhancement according to a simplified crossover model by Olchowy and Sengers, but again based on the classical Schmidt-Wagner EOS of Friend *et al.* (1991)

5 Bücker, D. und Wagner, W., *J. Phys. Chem. Ref. Data* **35**, 205-266 (2006).

6 Friend, D. G., Ingham, H., und Ely, J. F., *J. Phys. Chem. Ref. Data* **20**, 275-347 (1991).

Motivation - Problems and Tasks | Problems with consistency

Problems with consistency

Ethane – improvement (?) of η and λ not used in REFPROP

- - EOS: Friend *et al.* (1991).
  - η: Hendl *et al.* (1994)[7]
  - λ: Vesovic *et al.* (1994)[8]
- - EOS – classical Schmidt-Wagner EOS and an additional parametric crossover EOS by Luettmer-Strathmann *et al.* (1992)[9] in the critical region
  - η and λ – including a critical enhancement according to the full crossover model by Olchowy and Sengers (1988)[10], complicated by implicitly defined functions and root-finding algorithms

$\rightarrow$ not practical for use in the daily work of an engineer

7 Hendl, S., Millat, J., Vogel, E., Vesovic, V., Wakeham, W. A., Luettmer-Strathmann, J., Sengers, J. V., and Assael, M. J., *Int. J. Thermophys.* **15**, 1-31 (1994).

8 Vesovic, V., Wakeham, W. A., Luettmer-Strathmann, J., Sengers, J. V., Millat, J., Vogel, E., and Assael, M. J., *Int. J. Thermophys.* **15**, 33-66 (1994).

9 Luettmer-Strathmann, J., Tang, S., Sengers, J. V., *J. Chem. Phys.* **97**, 2705-2717 (1992).

10 Olchowy, G. A.; Sengers, J. V., *Phys. Rev. Lett.* **61**, 15-18 (1988).

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Motivation - Problems and Tasks

Deviation from the equation of Hendl *et al.* (1994)

- Deviations up to -6% at ≈ 3.5 mol l^{-1} (≈ 120 kg m^{-3})
- ρ_c at 6.86 mol l^{-1}, T_c at 305.322 K

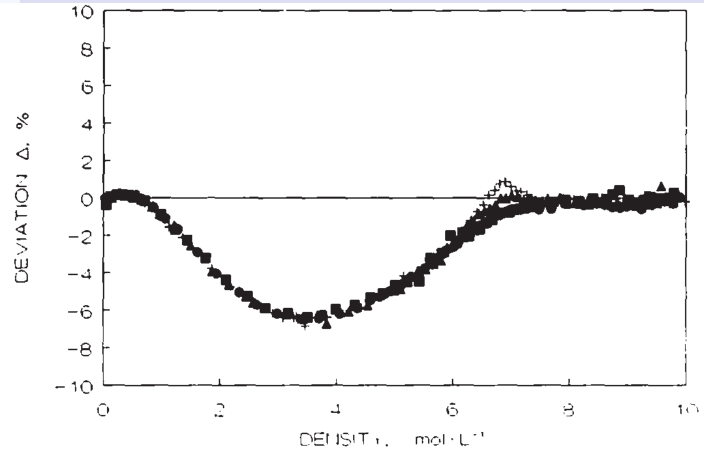


Fig. 3. Deviations, Δ, from the final excess correlation, Eq. (9), of the excess viscosity deduced from Iwasaki and Takahashi's data [43]: +, $T = 305.65$ K; ▲, $T = 305.85$ K; ●, $T = 306.15$ K; ■, $T = 306.45$ K. $\Delta = 100.0\,(\Delta\eta_{exp} - \Delta\eta_{cor})/\eta_{cor}$.

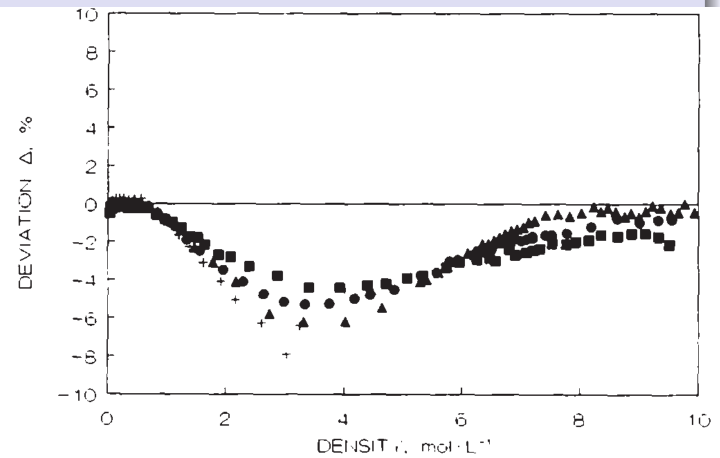


Fig. 4. Deviations, Δ, from the final excess correlation, Eq. (9), of the excess viscosity deduced from Iwasaki and Takahashi's data [43]: +, $T = 298$ K; ▲, $T = 308$ K; ●, $T = 323$ K; ■, $T = 348$ K. $\Delta = 100.0\,(\Delta\eta_{exp} - \Delta\eta_{cor})/\eta_{cor}$.

Motivation - Problems and Tasks

Deviation from the equation of Hendl *et al.* (1994)

- Deviations up to -6% and -4% at ≈ 120 kg m^{-3}

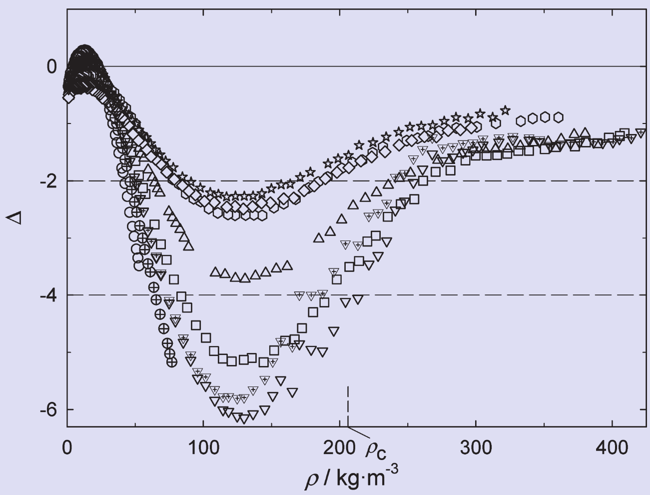


Figure 11. Comparison of re-evaluated experimental viscosity data of Wilhelm et al.[11] for ethane with calculated values, using the correlation by Hendl et al.[3] and measured values for temperature and calculated values for density. Deviations: $\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{cor}$. ○, 290 K; ⊕, 300 K; ▽, 310 K; ▽ with cross, 310 K, correlation without critical enhancement; □, 320 K; △, 340 K; ⬡, 370 K; ☆, 400 K; ◇, 430 K.

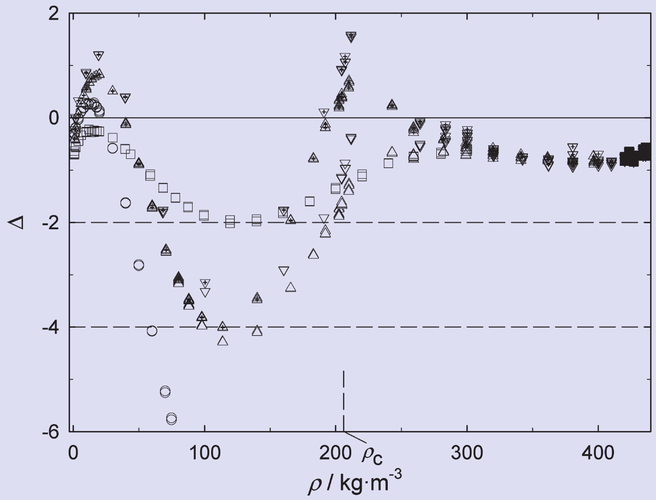


Figure 10. Comparison of experimental viscosity data for ethane with calculated values using the correlation by Hendl et al.[3] and measured values for temperature and density. Deviations: $\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{cor}$. ○, 293.15 K for ethane 3.5; △, 307.15 K for ethane 3.5; △ with cross, 307.15 K for ethane 3.5, correlation without critical enhancement; ▽, 307.15 K for ethane 5.0; ▽ with cross, 307.15 K for ethane 5.0, correlation without critical enhancement; □, 423.15 K for ethane 5.0.

Correlation Method Using Structure Optimization

Selection Criteria

- Feasibility of combination of different terms
- Requirement of reliable experimental data
- Use of simple functional dependencies, e.g., $\eta = \eta(T, \rho)$
- Successful correlation of viscosity surfaces for propane[11] and R134a[12] → Scalabrin *et al.*

Procedure

- Evaluation and classification of all available viscosity data
- Selection of terms for the complete fluid range of thermodynamic states including the near-critical region
- Assessment of the resulting correlation using statistical parameters and adequate description of experimental data

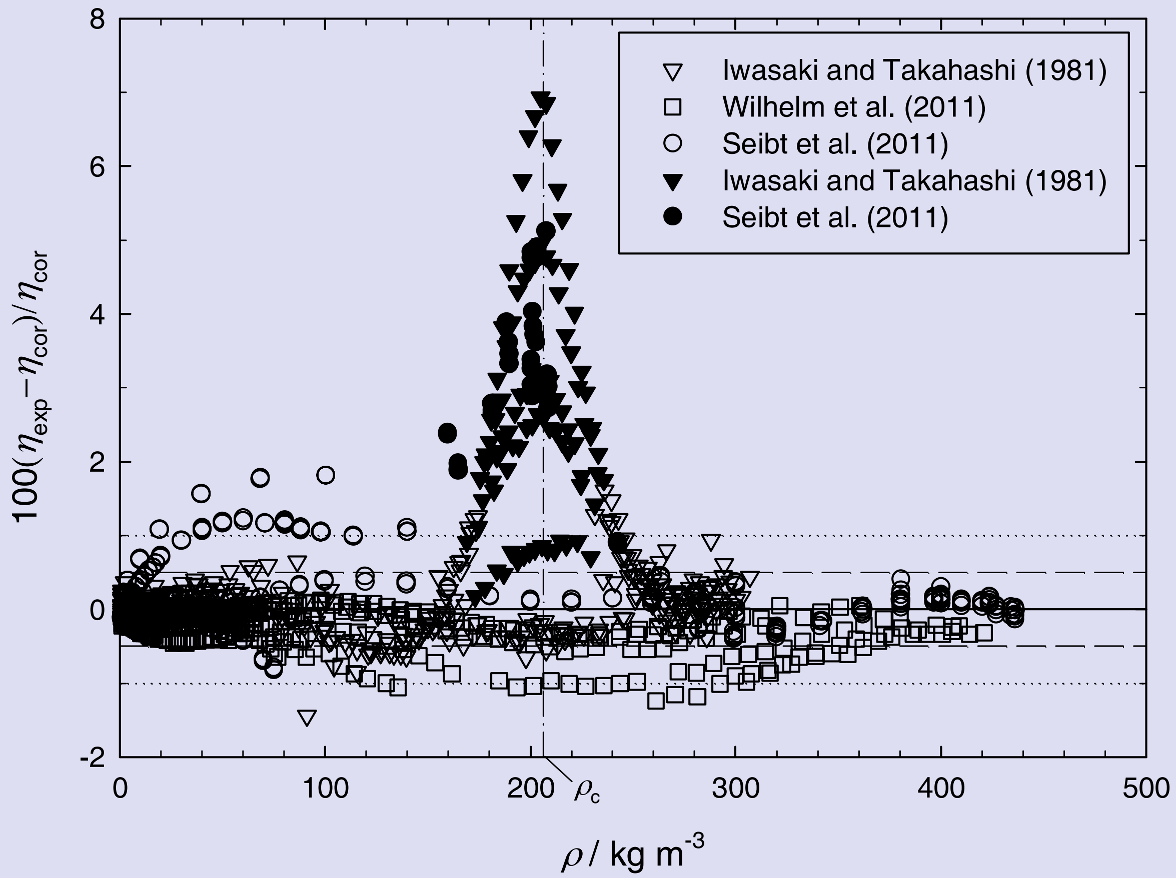
[11] Scalabrin, G.; Marchi, P.; Span, R.: *J. Phys. Chem. Ref. Data* **35**, 1415-1442 (2006).
[12] Scalabrin, G.; Marchi, P.; Span, R.: *J. Phys. Chem. Ref. Data* **35**, 839-868 (2006).

Primary experimental data — ethane

Authors	Year	Method[13]	Number of points	T K	ρ kg m^{-3}	$\Delta\eta/\eta$ %
Iwasaki, Takahashi	1981	OD	8	298–348	0	0.3
Hunter, Smith	1989	C	7	212–393	0	0.5
Hendl, Vogel	1992	OD	15	291–624	0	0.3
Wilhelm *et al.*	2011	VW	8	290–430	0	0.3
Seibt *et al.*	2011	VW	4	293–423	0	0.3
Kestin *et al.*	1971	OD	2	296–304	1	0.4
Kestin *et al.*	1977	OD	5	301–477	1	0.4–1.0
Abe *et al.*	1978	OD	5	298–468	1	0.4–1.0
Abe *et al.*	1979	OD	6	298–468	1	0.4–1.0
Swift *et al.*	1960	FC	13	193–303	293–537	2.5
Eakin *et al.*	1962	C	81	298–444	4–483	2.5
Carmichael, Sage	1963	RC	90	300–478	1–455	2.5
Iwasaki, Takahashi	1981	OD	417	298–348	1–307	0.7
Diller, Saber	1981	OQC	164	100–320	8–652	2.5
Diller, Ely	1989	OQC	70	295–500	22–483	2.5
Wilhelm *et al.*	2011	VW	630	290–430	1–421	0.7
Seibt *et al.*	2011	VW	315	293–423	1–436	0.5

[13] C, capillary; FC, falling cylinder; OD, oscillating disk; OQC, oscillating quartz crystal; RC, rotating cylinder; VW, vibrating wire

Ethane — Correlation without critical enhancement



Critical enhancement according to Bhattacharjee *et al.* (1981)[14]

- Viscosity η corresponds to an asymptotic power-law divergence:

$$\eta \approx \eta_{\mathrm{g}}(Q_0\xi)^{z_\eta} \ .$$

- Critical enhancement represents a multiplicative anomaly:

$$\eta_{\mathrm{c}} = \eta_{\mathrm{g}}[(Q_0\xi)^{z_\eta} - 1] \ .$$

- A crossover is needed $\longrightarrow$ complete global solution by Olchowy and Sengers (1988) for the mode-coupling theory:

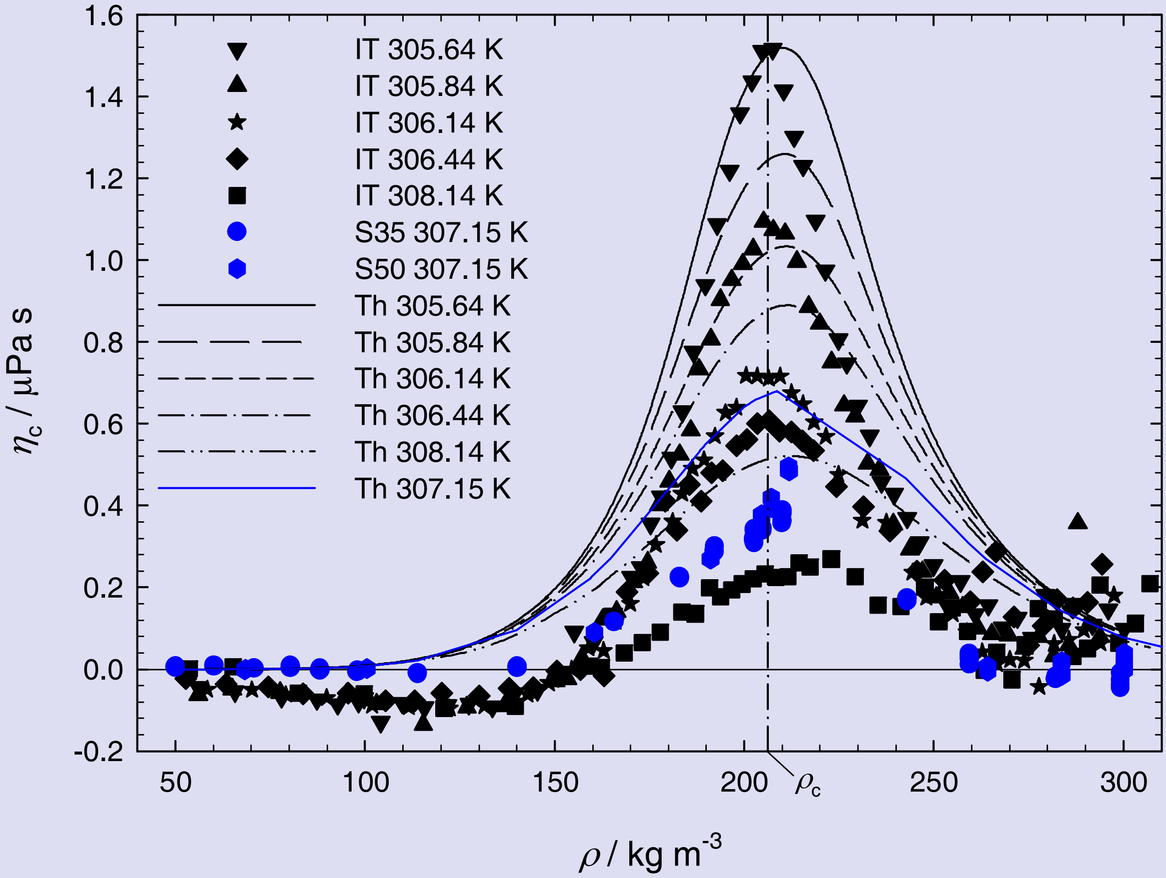
$$\eta_{\mathrm{c}} = \eta_{\mathrm{g}}[\exp(z_\eta H) - 1] \ .$$

- A simplified closed-form solution earlier developed (Bhattacharjee *et al.*) $\longrightarrow$ recently used for IAPWS water (Huber *et al.*, 2009):

$$\eta = \eta_{\mathrm{g}} \exp(z_\eta Y) \ , \qquad \eta_{\mathrm{c}} = \eta_{\mathrm{g}}[\exp(z_\eta Y) - 1] \ .$$

[14] Bhattacharjee, J. K.; Ferrell, R. A.; Basu, R. S.; Sengers, J. V., *Phys. Rev. A* **24**, 1469-1475 (1981).

Critical enhancement — comparison theory - experiment



Viscosity surface correlation for ethane

- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Bank of terms for the correlation:

$$\frac{\eta_{\text{bank}}(T,\rho)}{\mu\text{Pa s}} = \frac{\eta_0(T)}{\mu\text{Pa s}} A_0 + \sum_{i=0}^{8}\sum_{j=1}^{20} A_{ij}\tau^i\delta^j + \sum_{k=0}^{5}\sum_{l=1}^{5} A_{kl}\tau^k\delta^l\,\mathrm{e}^{-\delta} + \sum_{m=0}^{1} A_m\tau\delta\mu_m\,\mathrm{e}^{-\beta_m(\delta-\gamma_m)^2-\varepsilon_m|\tau-\zeta_m|}.$$

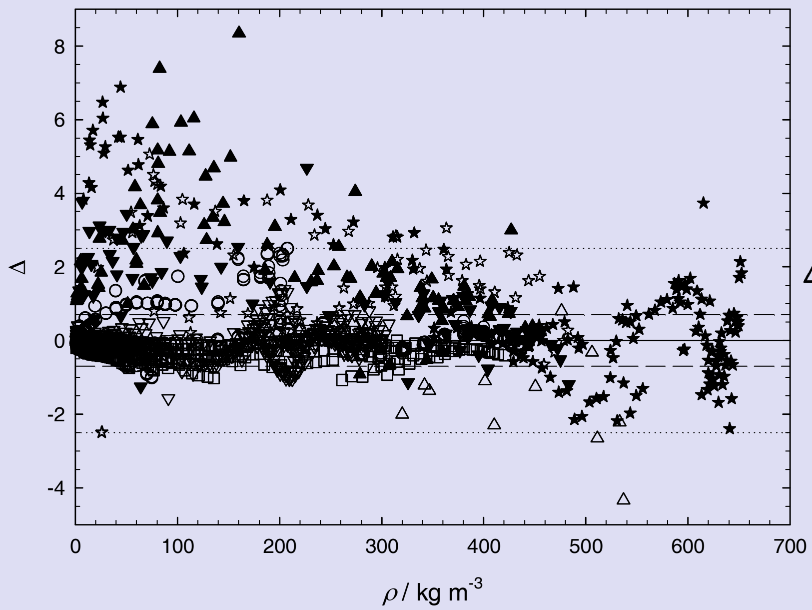
- Result for ethane:

$$\frac{\eta_{\text{cor},C_2H_6}(T,\rho)}{\mu\text{Pa s}} = \sum_{i=1}^{9} A_i\tau^{t_i}\delta^{d_i} + \sum_{i=10}^{12} A_i\tau^{t_i}\delta^{d_i}\,\mathrm{e}^{-\delta} + \sum_{i=13}^{14} A_i\tau\delta\,\mathrm{e}^{-\beta_i(\delta-1)^2-\varepsilon_i|\tau-1|}.$$

Comparison equation - experiment

Viscosity in the fluid region

- New and newly evaluated data are dominant
- Large deviations at small densities for former primary data
- Deviation of data in the near critical region $< \pm 2\%$



$$\Delta = 100\,\frac{\eta_{\text{exp}} - \eta_{\text{cor}}}{\eta_{\text{cor}}}$$

△, ▼, ▲, ★, ☆ earlier experimental data

▽, □ newly evaluated experimental data

○ new experimental data

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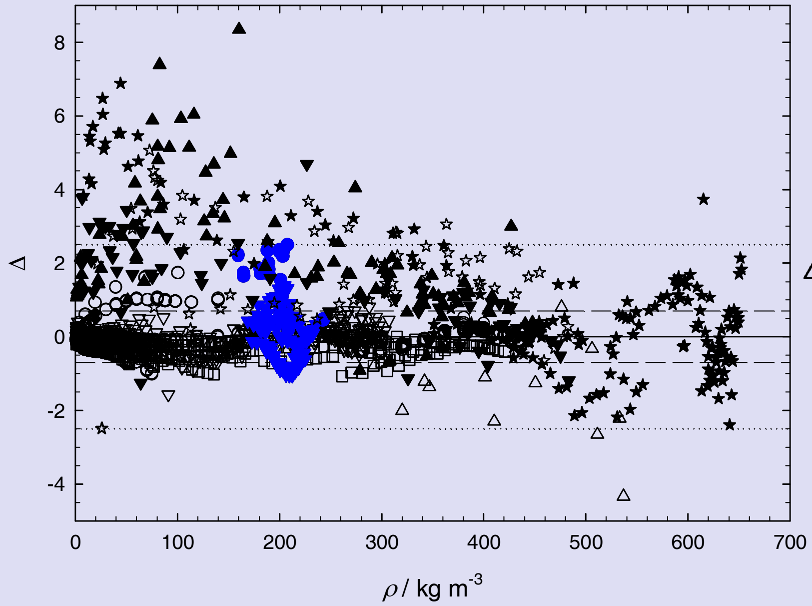

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- △, ▼, ▲, ★, ☆ earlier experimental data
- ▽, □ newly evaluated experimental data
- ○ new experimental data

Conclusion and Outlook

- New viscosity-surface correlation was generated for ethane based on new precise experimental viscosity data and an improved evaluation of older data
- The structure-optimisation method of Setzmann and Wagner (Ruhr-University Bochum) was used
- Critical enhancement was included according to the crossover approach by Bhattacharjee *et al.* (1981)

- Further work on propane, n-butane, and isobutane

→ precise data using the vibrating-wire viscometer are available for these fluids

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