First International Conference on ORC Power Systems
Delft, September 23, 2011

SPEED OF SOUND OF
HEXAMETHYLDISILOXANE
AS WORKING FLUIDS FOR ORGANIC RANKINE CYCLES

Frithjof Dubberke and Jadran Vrabec
Working fluids for ORC power systems

- Working fluids play an important role for power cycle efficiency
- Design and optimization of power cycles depend on fluid properties
- Siloxanes are appropriate working fluids for ORC plants due to their fluid properties and environmental safety
- Hexamethyldisiloxane belongs to the wider class of organosilicone compounds
- Several ORC suppliers employ Hexamethyldisiloxane (MM)

Lack of accurate fluid property data for siloxanes may lead to sub-optimally designed ORC power cycles, reducing their efficiency.
Speed of sound — measurement principle

\[ c = \sqrt{\left( \frac{\partial p}{\partial \rho} \right)_s} \]

- Puls-echo technique
- Speed of sound is determined from propagation distance \( \Delta l \) and propagation time \( \Delta t \)

\[ c = \frac{2\Delta l}{\Delta t} \]

- Interference approach (Muringer et al. 1985)
Speed of sound – measuring cell

- Cell is made of stainless steel (1.4571)
  - good surface characteristics
  - well known thermal expansion coefficient
- Cell reflectors are polished
- Cell is enclosed in stainless steel cylinder and operates up to 180 MPa
Speed of sound — measuring apparatus

- Cell is embedded in a double copper thermostat which was isolated under vacuum conditions
- 4 layers of aluminum foil minimize thermal radiation losses
- PID controls cell temperature within 2 mK
- Electrical heating system operates up to 650 K

Construction by Gedanitz
Calibration and uncertainties

- Calibration of propagation distance as a function of thermal expansion coefficient was calibrated with purified water, based on the EOS by Wagner and Pruss, 2002 (IAPWS)

- Successfully tested on water, acetone and hexadecane

- Pressure sensor calibrated by deadweight tester up to 15 MPa

- Thermometers (PT 100) were calibrated up to 425 K (extrapolated to 650 K)

- Uncertainty is around 0.3%

- Intended operation range $T = 270… 650$ K, $p = 0…180$ MPa

- Hexamethyldisiloxane (MM), CAS-No: 107-46-0 (Merck purity $\geq 99\%$); degased in ultrasonic bath under vacuum
Fundamental EOS by Colonna et al., 2006

Massieu-Planck energy $\phi$  \quad $T = 300 \ldots 500$ K, $p = 0 \ldots 15$ MPa

\[ \frac{F}{RT} = \phi(\tau, \delta) = \phi^0(\tau, \delta) + \phi^{\text{res}}(\tau, \delta) \]

Ideal part

\[ \phi^0 = \ln \delta + c_\tau \ln \tau + \sum_{i=1}^{5} c_i \tau^{2-i} \]

Residual part

\[ \phi^{\text{res}} = \sum_{i=1}^{6} a_i \tau^{t_i} \delta^{d_i} + \sum_{i=7}^{12} a_i \tau^{t_i} \delta^{d_i} \exp(-\delta^{e_i}) \]

Total:

- 18 Parameters
- 14 Stat. mech. data (Ideal)
- 99 Exp. data (Residual)

Due to the fundamental formulation, all (static) thermodynamic properties are accessible by derivation.
EOS by Colonna et al.

Specific volume $[\text{m}^3/\text{kg}]$

Pressure $[\text{MPa}]$

- 573 K
- 473 K
- 420 K
- 360 K
- 300 K
Adjustment of EOS by Colonna et al.

![Graph showing pressure vs. specific volume for different temperatures: 573 K, 473 K, 420 K, 360 K, and 300 K. Each temperature has a series of data points represented by green triangles.](image)

TP $\rightarrow$ $\rho$ 56 points

**Specific Volume [m$^3$/kg]**

**Pressure [MPa]**

- 573 K
- 473 K
- 420 K
- 360 K
- 300 K

Adjustment of EOS by Colonna et al.
Adjustment of EOS by Colonna et al.

![Graph showing specific volume vs. pressure for different temperatures (573 K, 473 K, 420 K, 360 K, 300 K). The graph includes data points for $P - \rho - T$ (56 points) and $\rho_{sat}$ (26 points).]
Adjustment of EOS by Colonna et al.

Specific volume [m³/kg]

Pressure [MPa]

573 K
473 K
420 K
360 K
300 K

$P - \rho - T$
$
\rho_{\text{sat}}$
$C_p$

56 points
26 points
14 points
Adjustment of EOS by Colonna et al.

- \( P - \rho - T \) (56 points)
- \( \rho_{sat} \) (26 points)
- \( C_p^0 \) (14 points)
- Critical Data (3 points)

Critical Data:
- 26 points
- 56 points
- 3 points
- 14 points

Temperature and Pressure Points:
- 360 K, 420 K, 473 K, 573 K
- Specific volume [m³/kg]
- Pressure [MPa]
Adjustment of EOS by Colonna et al.

![Graph showing specific volume vs. pressure for different temperatures (573 K, 473 K, 420 K, 360 K, 300 K).]
Range of present experiments

![Diagram showing specific volume vs pressure for different temperatures (573 K, 473 K, 420 K, 360 K, 300 K). The x-axis represents specific volume [m³/kg] and the y-axis represents pressure [MPa]. Experimental data is indicated with red crosses.](image)
Experimental results at 413 K

- Speed of sound [m/s]
- Pressure [MPa]

Colonna et al.
- Experiment
Experimental results at 573 K

- **Speed of sound [m/s]**

  - 150
  - 200
  - 250
  - 300
  - 350
  - 400

- **Pressure [MPa]**

  - 6
  - 8
  - 10
  - 12
  - 14

- **Line**
  - Colonna

- **Points**
  - Experiment

Graph showing the relationship between speed of sound and pressure at 573 K.
Deviations to EOS by Colonna et al., 2006
Conclusion

- The measurement of the speed of sound is an efficient route to gather thermodynamic data on the fluid behavior.
- Such data are useful for the development of EOS.
- Even for well-known fluids such as MM, EOS can misrepresent their thermodynamic properties.
- Significant effort has to be invested in measurements and reliable predictive methods of thermodynamic properties.