Shear viscosity of refrigerants
Experiments - Modelling

Guillaume Galliero
Jean-Patrick Bazile, Jean-Luc Daridon
Laboratoires des Fluides Complexes et leurs Réservoirs
UMR 5150 TOTAL-CNRS-UPPA

Journées Fluides de travail pour la production de froid

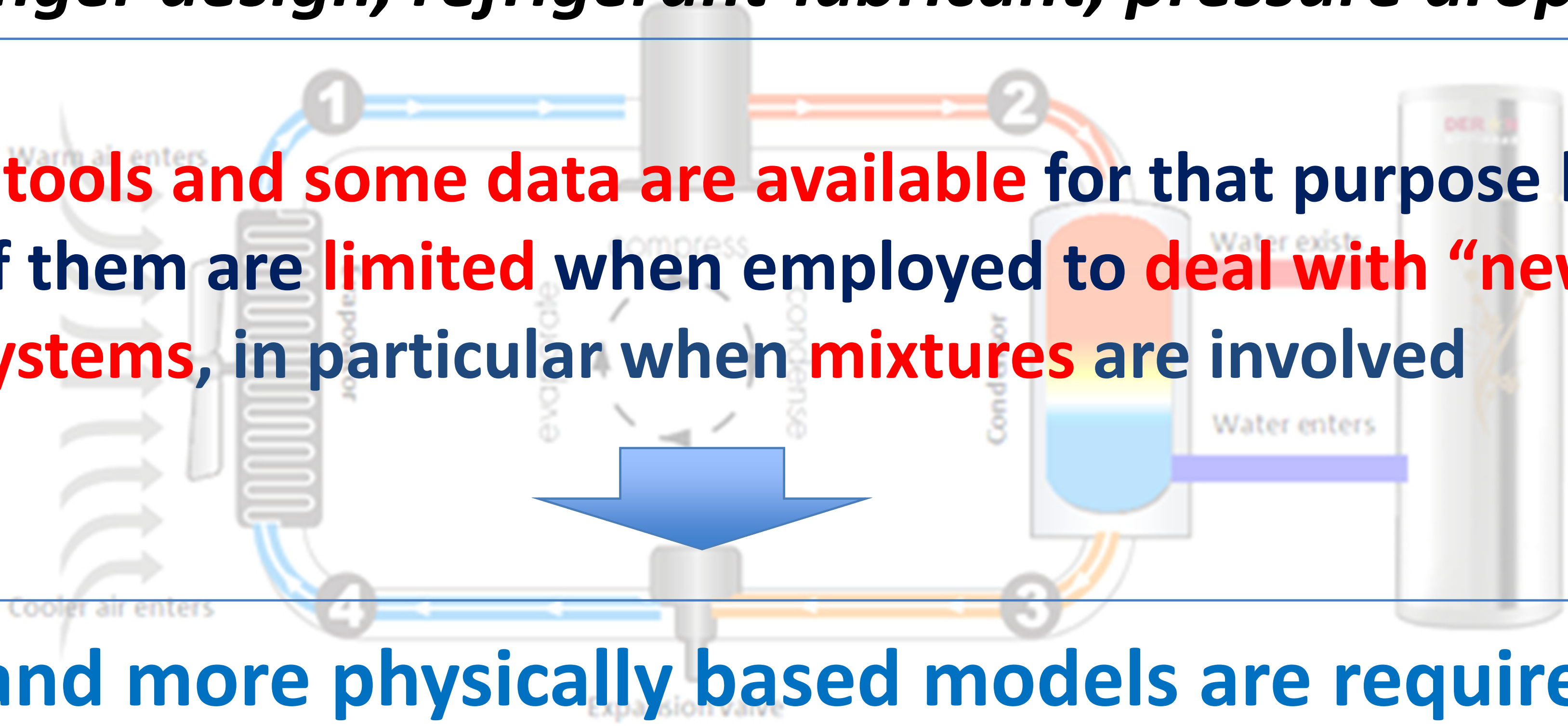
Mercredi 15 mars 2017

CONTEXT AND ISSUES

GLOBAL CONTEXT AND ISSUES

Accurate thermophysical properties of refrigerants are crucial for the design of cold production systems

Shear viscosity is one of these required quantities :
Exchanger design, refrigerant-lubricant, pressure drop …



Various tools and some data are available for that purpose but most of them are limited when employed to deal with "new" systems, in particular when mixtures are involved

Data and more physically based models are required

« Measuring » Shear viscosity

Two (shear) "viscosities" *(+ one bulk):*

✓Dynamic viscosity ($\mu = \tau/\dot{\gamma}$) in Pa.s

✓Kinematic viscosity ($\nu = \mu/\rho$) in m^2/s

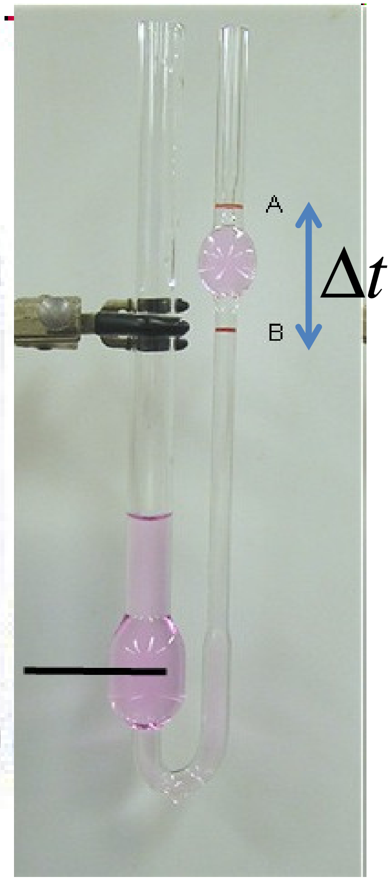
EXPERIMENTAL METHODOLOGY

Rotational Type	Tube Type	Wave Type
Cone and plate	*Capillary*	*Vibrating wire*
Rot. Cylinder	*Falling body*	*QCM*
…	…	…
Rheological behavior	**Most used methods**	**Absolute viscosity**

Ubbelodhe capillary viscometer (P_{atm})

0.2 to 30 000 mm²/s

μ **dev. +/- 1%**



Poiseuille law

+ Pressure gradient

+ Calibration (k)

$$\nu(0.1, T) = k * \Delta t$$

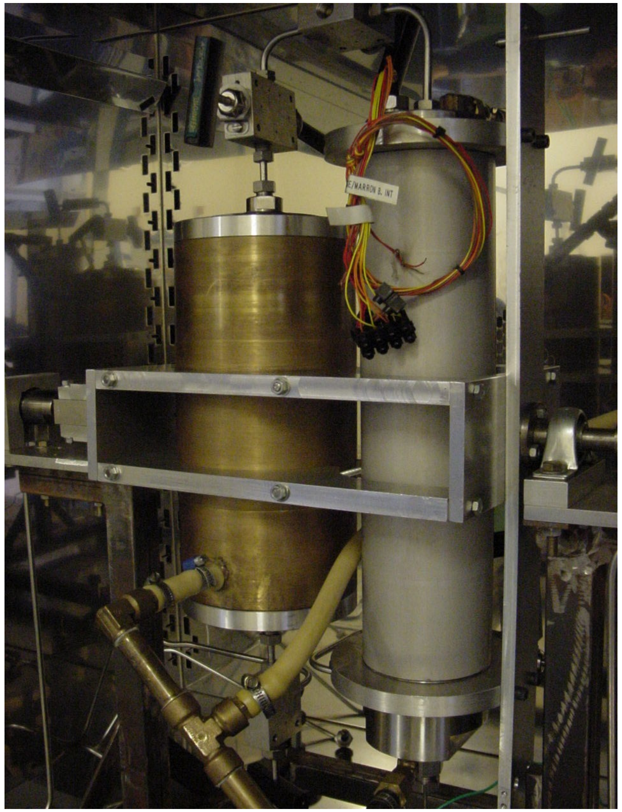
Anton Paar densimeter

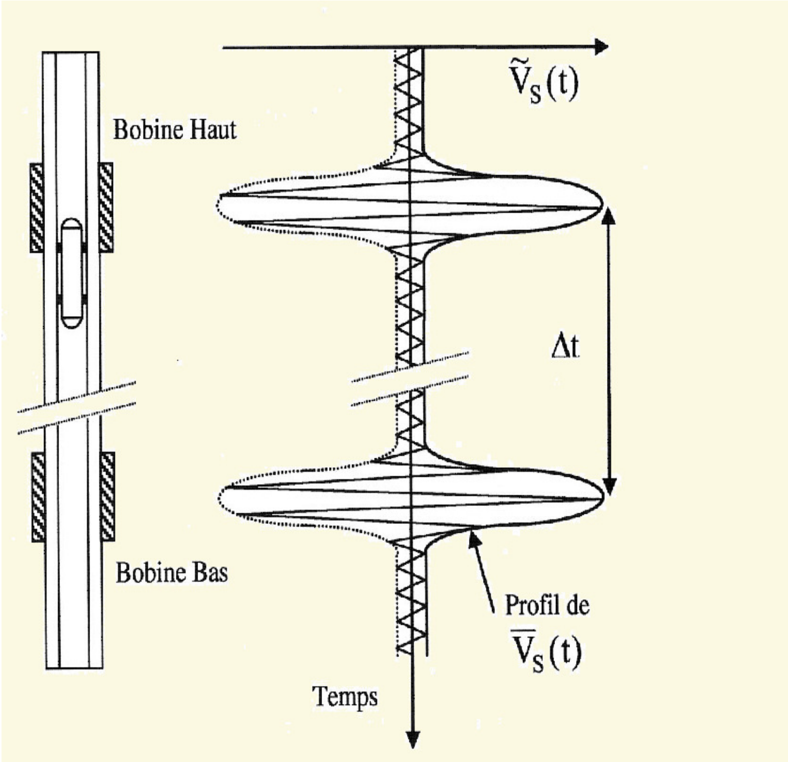
$$\mu = \nu / \rho$$

Similar methods under pressure are available

OPTION 1: FALLING BODY

Falling body viscometer (1 - 2000 bars)





Applicable to liquids, gas, live oils …

Stokes law

+ Calibration (K)

0.3 to 500 mPa.s

μ dev. +/- 3%

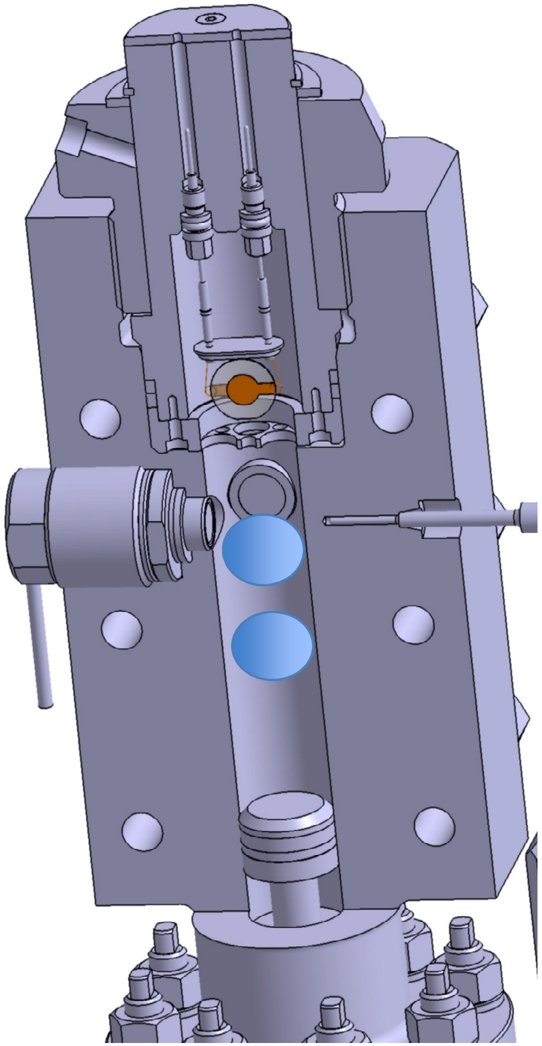
$$\mu(T,P) = K(P,T)\ (\rho_{solid} - \rho_{fluid})\Delta t$$

+ Anton Paar densimeter

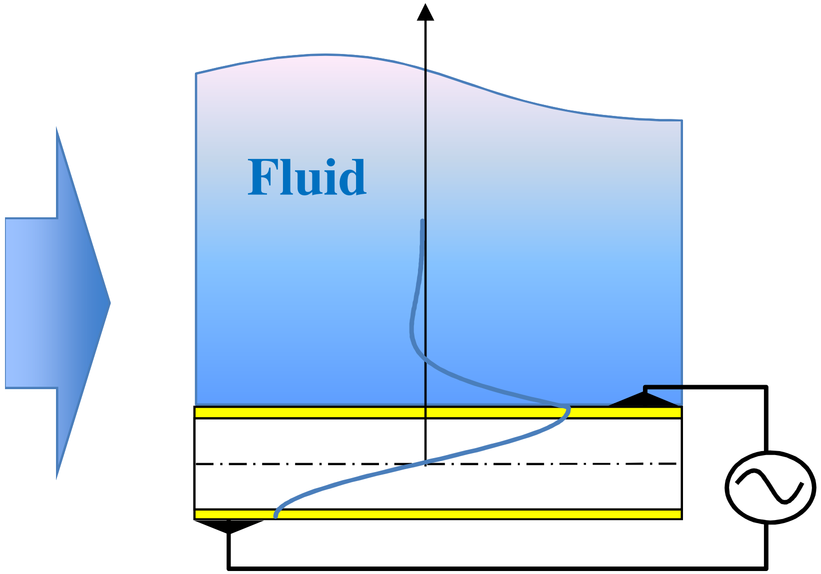
Boned and co-workers

OPTION 2: QCR (1/2)

Quartz Crystal Resonator (1 - 2000 bars)



Piezo-sensor

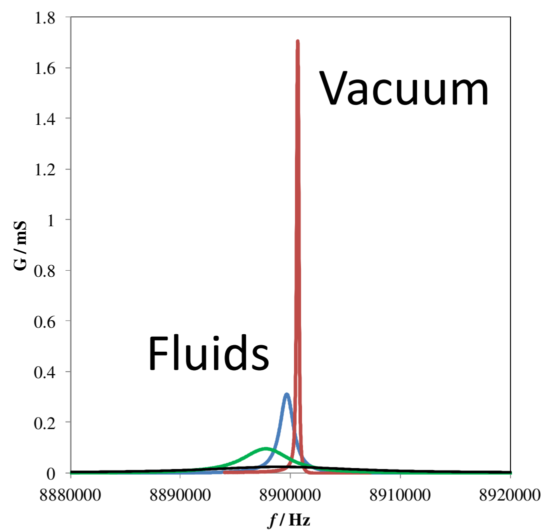


Viscosity affects:

Resonant frequency

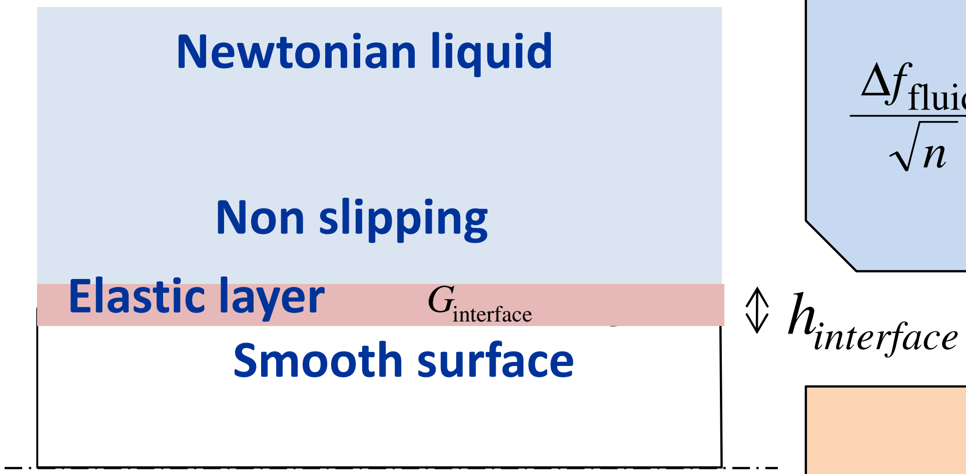
Amplitude of the resonance

$$\Delta\tilde{f}_n = \Delta f_n + i\Delta\Gamma_n$$



OPTION 2: QCR (2/2)

Quartz Crystal Resonator (1 - 2000 bars)



$$\frac{\Delta f_{\text{fluid}}}{\sqrt{n}} = -4\sqrt{n}\,\frac{f_0^{2}}{\sqrt{\rho_q\mu_q}}\,\rho h_{\text{interface}} - 2\,\frac{f_0^{3/2}}{\sqrt{\pi\rho_q\mu_q}}\sqrt{\rho\eta_{\text{fluid}}}$$

$$\frac{\Delta\Gamma_{\text{fluid}}}{\sqrt{n}} = 2\,\frac{f_0^{3/2}}{\sqrt{\pi\rho_q\mu_q}}\sqrt{\rho\eta_{\text{fluid}}}\left(1+R_{\text{interface}}\right) = c$$

Dev <2% up to 100 MPa
Dev <4% 100 -200 MPa

QCR allows measuring viscosity by two methods

✓ Resonance frequency : absolute but sensitive to pressure

✓ Dissipation : relative

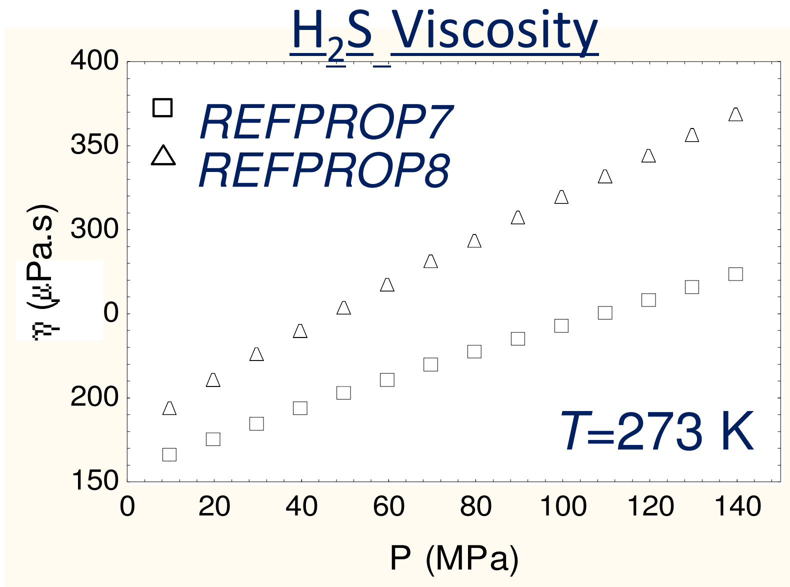
Daridon and co-workers

EXPERIMENTAL MEASUREMENTS: DATA GENERATION

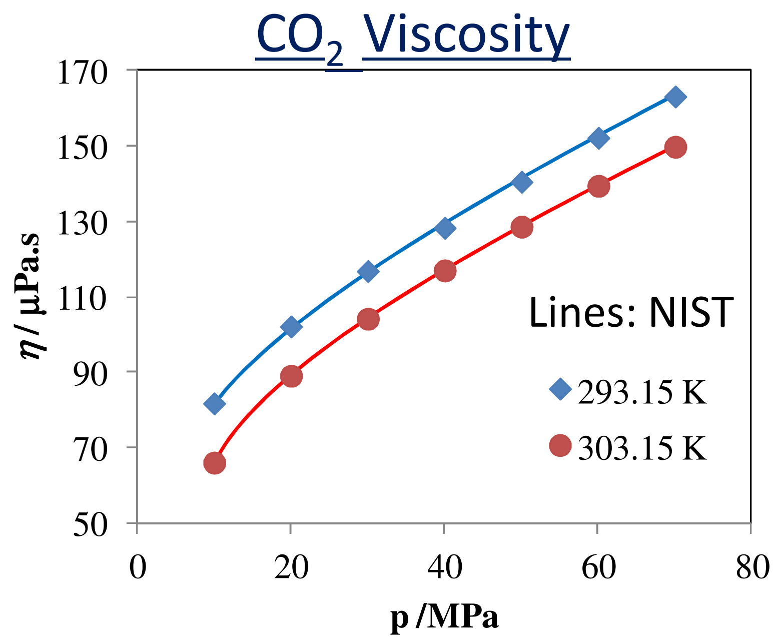
Be careful with "ref." data (even NIST)

Not that much accurate viscosity data in particular on mixtures and "new" products

E.g. HFO: R1234yf (<10), R1234ze(E)(<5)



Our apparatus + our experience could allow to obtain accurate data on various "new" refrigerants



NUMERICAL METHODOLOGY

Molecular Model
Force Fields

Molecular Simulations

Molecular Dynamics

“Exact” emerging properties
$\mu, \rho \ldots$

Test/Development of Theories

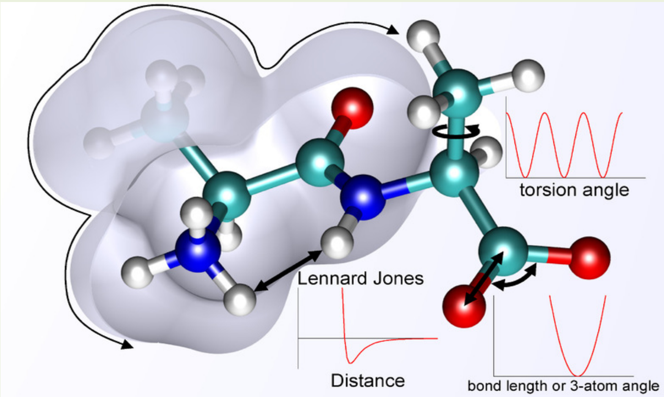
Pseudo-experimental Data

IVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

INSTITUT CARNOT ISIFoR

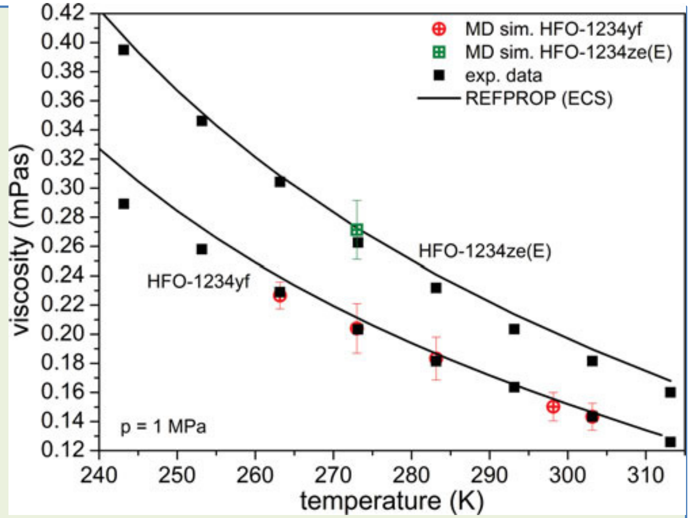
Computing Shear Viscosity from MD simulations

Option 1: Detailed molecular model



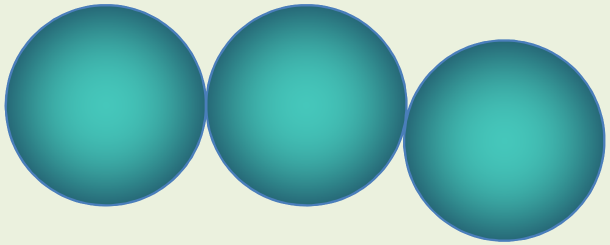
Molecular Simu

Dozens of parameters
Hours to Days



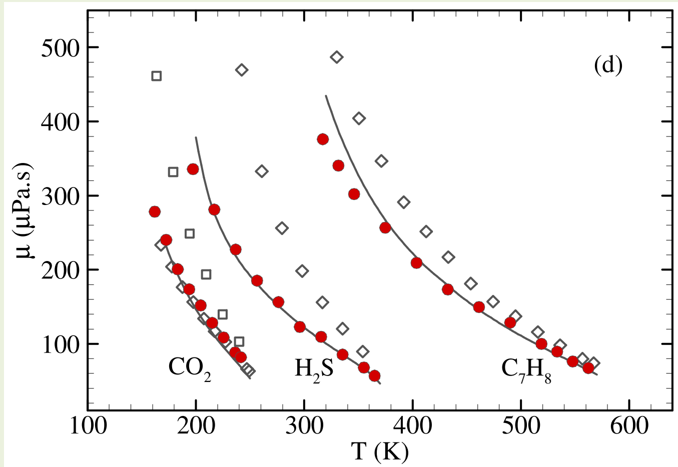
✓ Can produce quasi-experimental thermophysical data *Raabe, 2016*

Option 2: Coarse Grained model



Mol Sim/Theory

3 to 6 parameters
Milliseconds to hours



✓ Is compatible with engineering requirements *Galliero et al., 2017*

More details to come in Bernard Rousseau talk …

MODELING SHEAR VISCOSITY

Correlations	Coresp. states	Liquid theory
Vogel	*Supertrapp*	*Free volume*
Arhenius	*Lennard-Jones*	*Thermo. scaling*
…	…	…

Most problems arise when dealing with mixtures !

Modeling viscosity: Two modern approaches

In dense fluids it has been shown that *(Dyre and coworkers)* **:**

Transport property

$$\boldsymbol{\mu^r = F\left(\rho^\gamma/T\right)}$$

"Excess" entropy

$$S^r = G\left(\rho^\gamma/T\right)$$

where

$$\mu^r = \mu\frac{\rho^{-2/3}}{\sqrt{Mk_BT}}$$

$$S^r = \frac{S - S_0}{Nk_B}$$

γ is a material property constant (can be deduced from fluctuations)

On a isomorph, ρ^γ/T, viscosity and entropy are constant !

$$\boldsymbol{\mu^r = \alpha e^{-\beta S^r}}$$

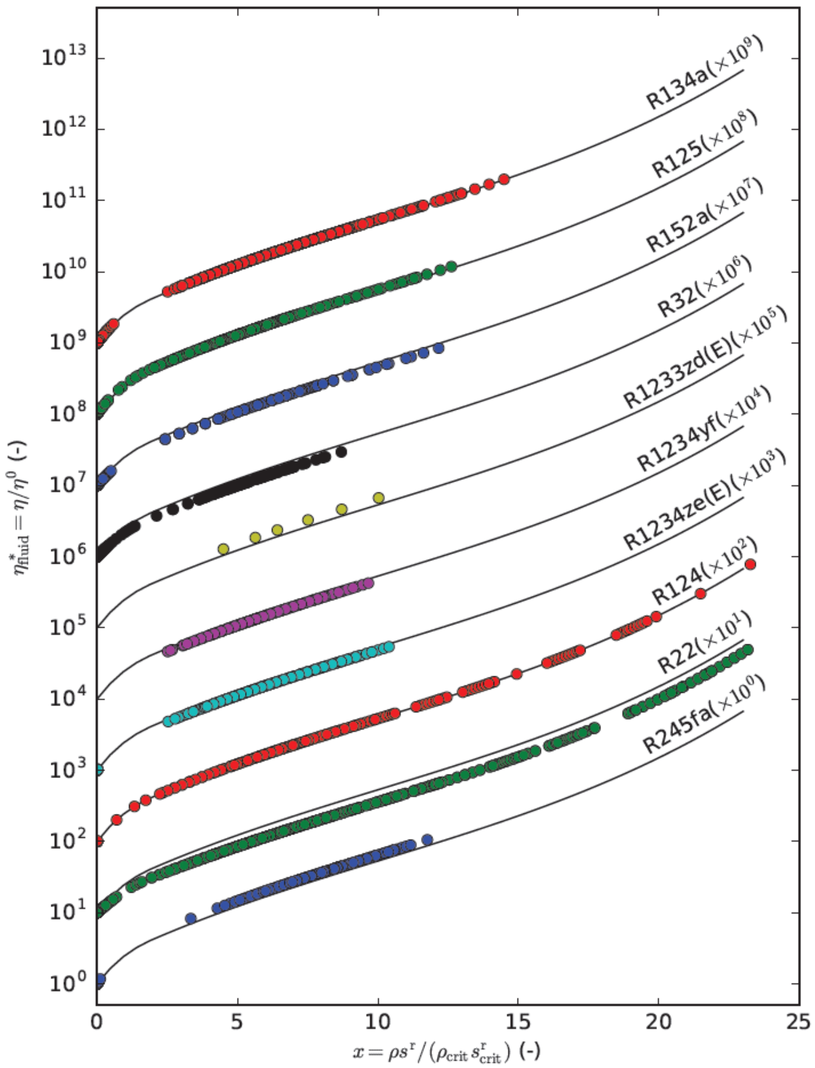
(Rosenfeld, PRA, 1977)

This approach is applicable to many fluids including refrigerants

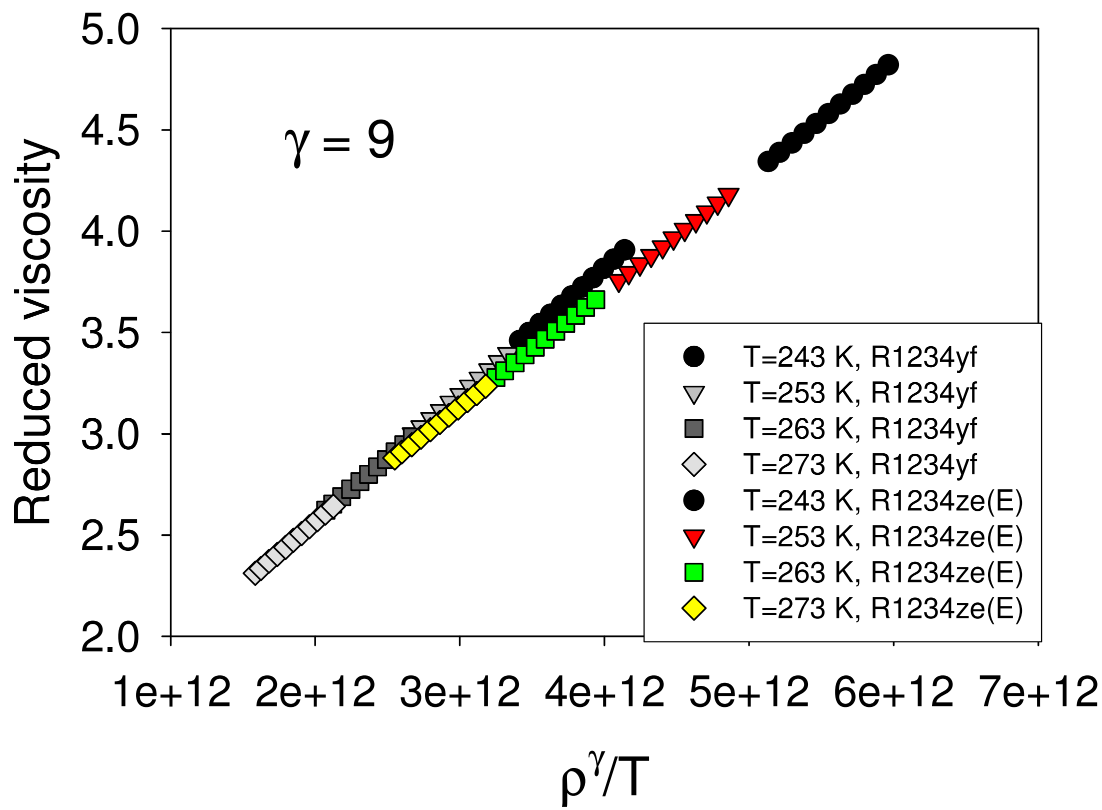
(Galliero et al., Gross et al. …)

MODELING VISCOSITY: SCALING

Excess entropy scaling (Bell, 2016)



Thermodynamic scaling (REFPROP 9.1)



Is interesting to check data consistency and to develop correlations

Extension to mixtures in progress

CONCLUSIONS

CONCLUSIONS

Among required thermophysical properties to design cold production systems, viscosity should not be forgotten

Accurate data are scarce for « new » fluids, in particular on mixtures

Additionnal measurements are required (and feasible) !

Molecular simulations could be a viable alternative

Even if still largely correlative, new models are available to estimate shear viscosity of a large class of fluids

Thank you for your attention