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# THERMODYNAMIC SCALING OF VISCOSITY APPLIED TO MIXTURES: MIE FLUIDS AND REAL FLUIDS

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In this work, we have tested the ability of the so-called “thermodynamic scaling” to deal with the shear viscosity of mixtures. For this purpose we have performed extensive Non-Equilibrium Molecular Dynamics simulations on the Mie  $n$ -6 fluids to define a general scheme to tackle the problem. Interestingly, the viscosity scaling has been found to be well respected in such model fluids (pure and mixtures) as well as in real mixtures using a simple mixing rule.

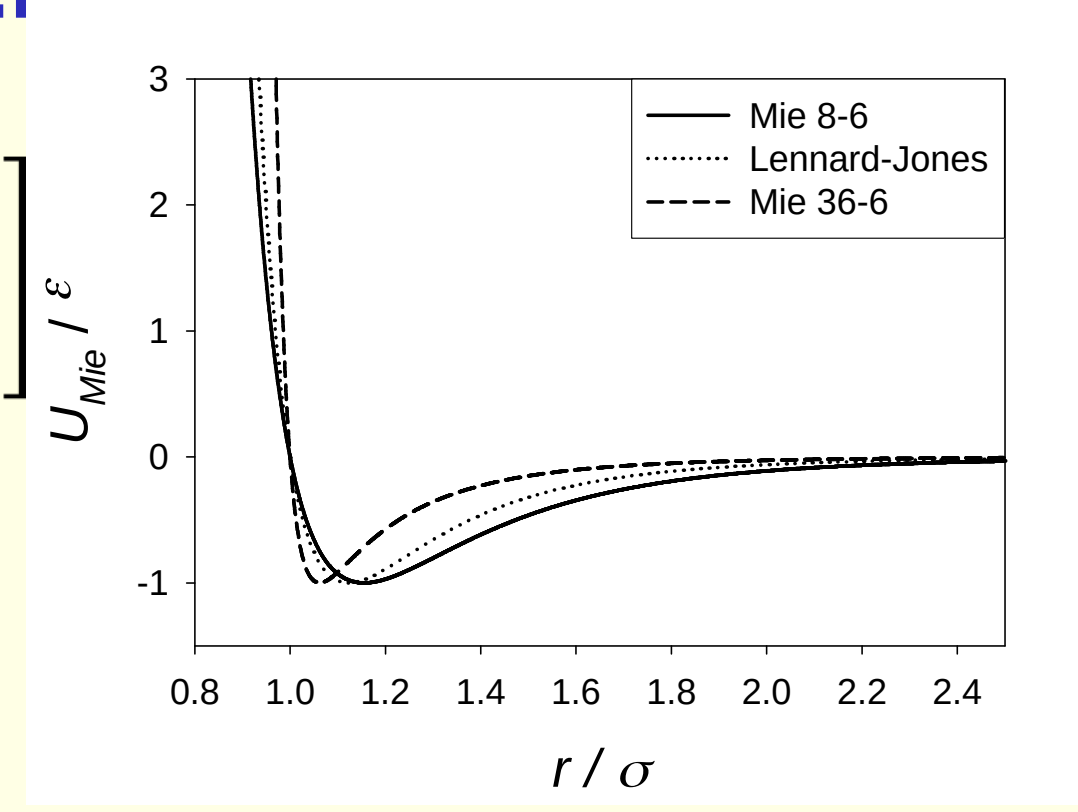
## THEORY

### THE MIE FLUID MODEL

Spheres interacting through :

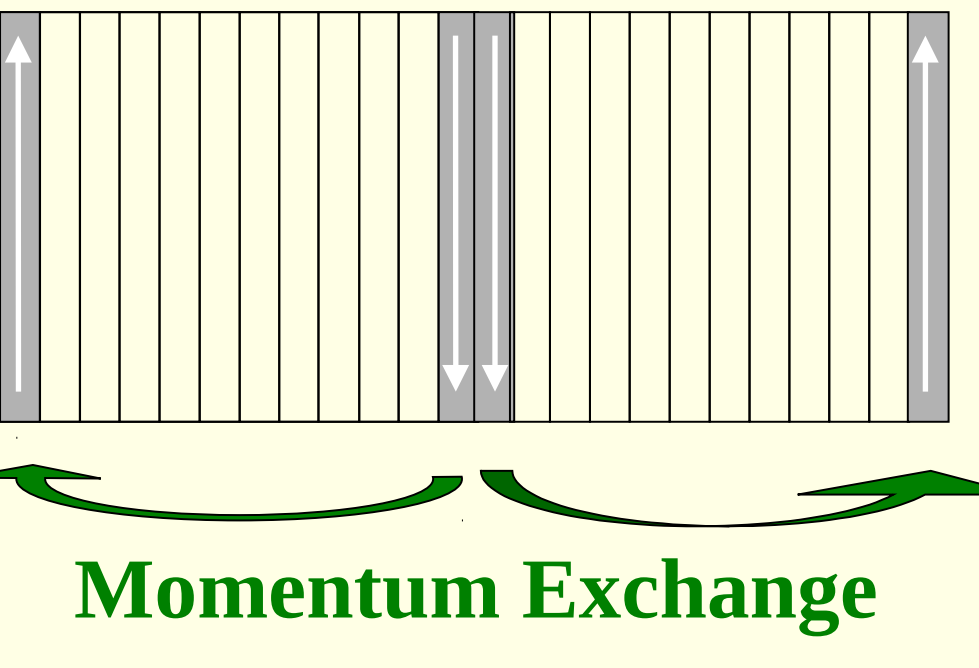
$$U_{Mie}(r) = \frac{n}{n-6} \left(\frac{n}{6}\right)^{\frac{6}{n-6}} \epsilon \left[ \left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6 \right]$$

Three parameters :  $n, \epsilon, \sigma$   
 $8 \leq n \leq 36$ , Lennard-Jones:  $n=12$



### MOLECULAR DYNAMICS

Non-Equilibrium Molecular Dynamics scheme :



Müller-Plathe Scheme  
 1500 particles,  $1.5 \cdot 10^7$  time-steps  
 Exchange frequency : 500

Shear viscosity is directly accessible

### THERMODYNAMIC SCALING

Reduced residual viscosity scales as:

Ashurst and Hoover approach

$$\eta_{res}^r = f\left(\frac{\rho^\gamma}{T}\right) \quad \text{where} \quad \eta^r = \eta \frac{\rho_n^{-2/3}}{(Mk_B T)^{1/2}} \quad \text{and} \quad \eta_{res} = \eta - \eta_0$$

The zero-density viscosity,  $\eta_0$ , is computed by Chapman-Enskog relation

$f$  is an unknown function and  $\gamma$  is a parameter

### VISCOSITY MODELING

Semi-empirical relation :

$$\eta_{res}^r = b_1 \left[ e^{b_2 X^{b_3}} + b_4 X^{b_5} - 1 \right] \quad \text{where} \quad X = \frac{\rho^{*\gamma}}{T^*} \quad \text{and} \quad b_i : \text{fitting parameters}$$

Dimensionless units :  $T^* = \frac{k_B T}{\epsilon}$ ,  $\rho^* = \frac{N_T \sigma^3}{V}$  and  $\eta^* = \eta \frac{\sigma^2}{\sqrt{M\epsilon}}$

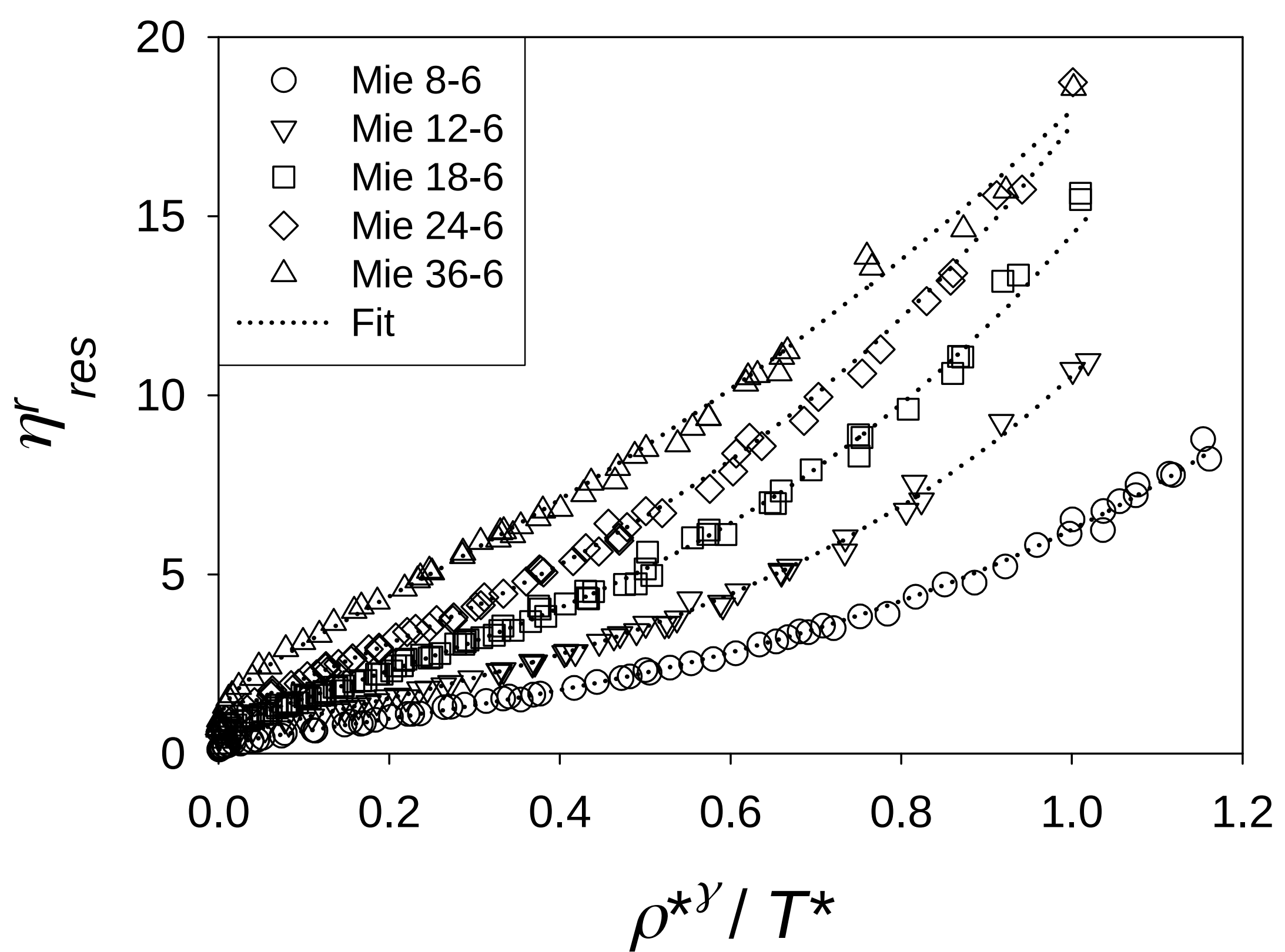
It allows to determine unambiguously  $\gamma$

## RESULTS

### MIE PURE FLUIDS

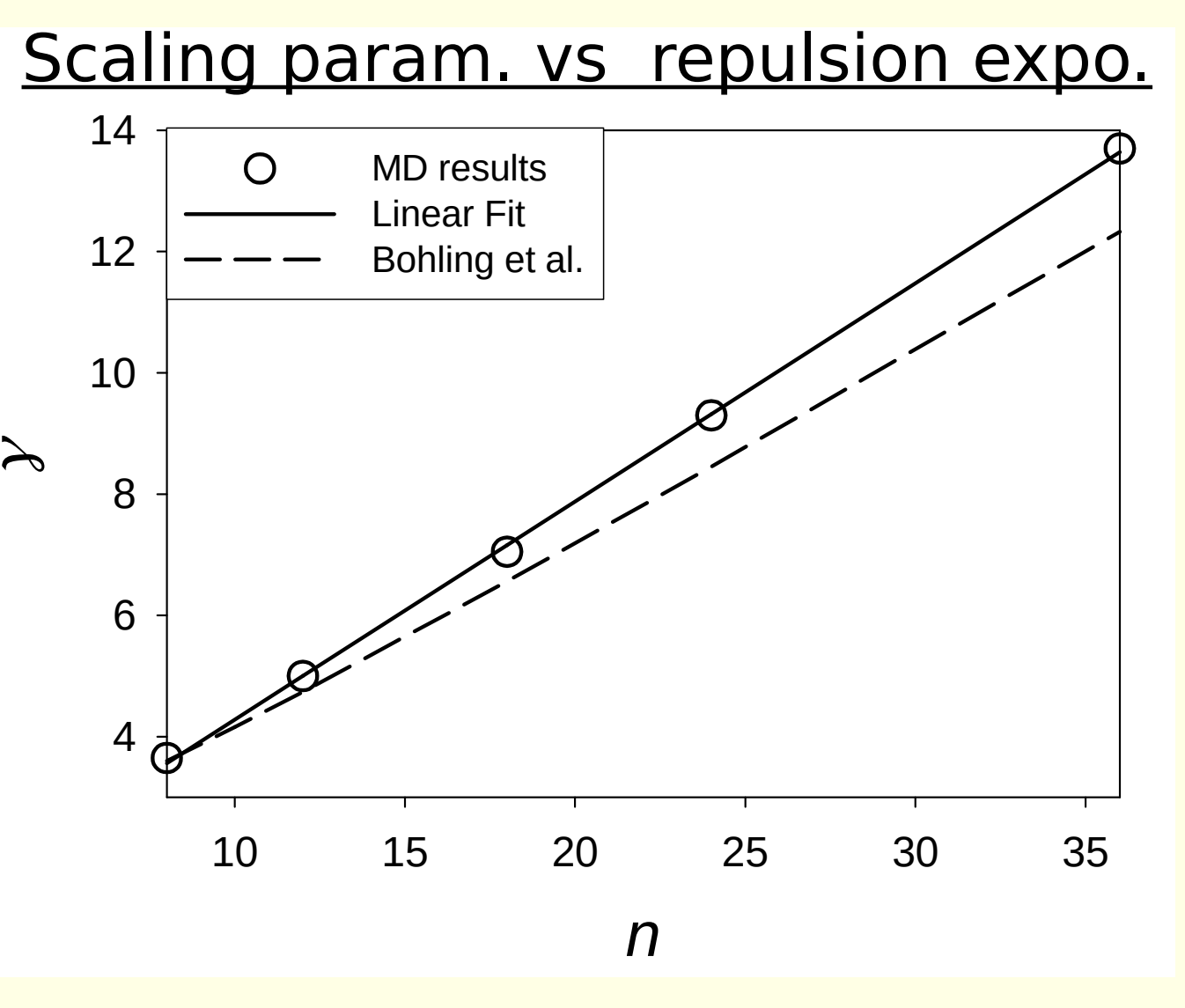
Gas, liquid and supercritical states are covered

Mie  $n$ -6 fluids viscosity scaling



The semi-empirical relation allows to correlate well the NEMD results. For a given dimensionless state,  $\eta$  increases with  $n$

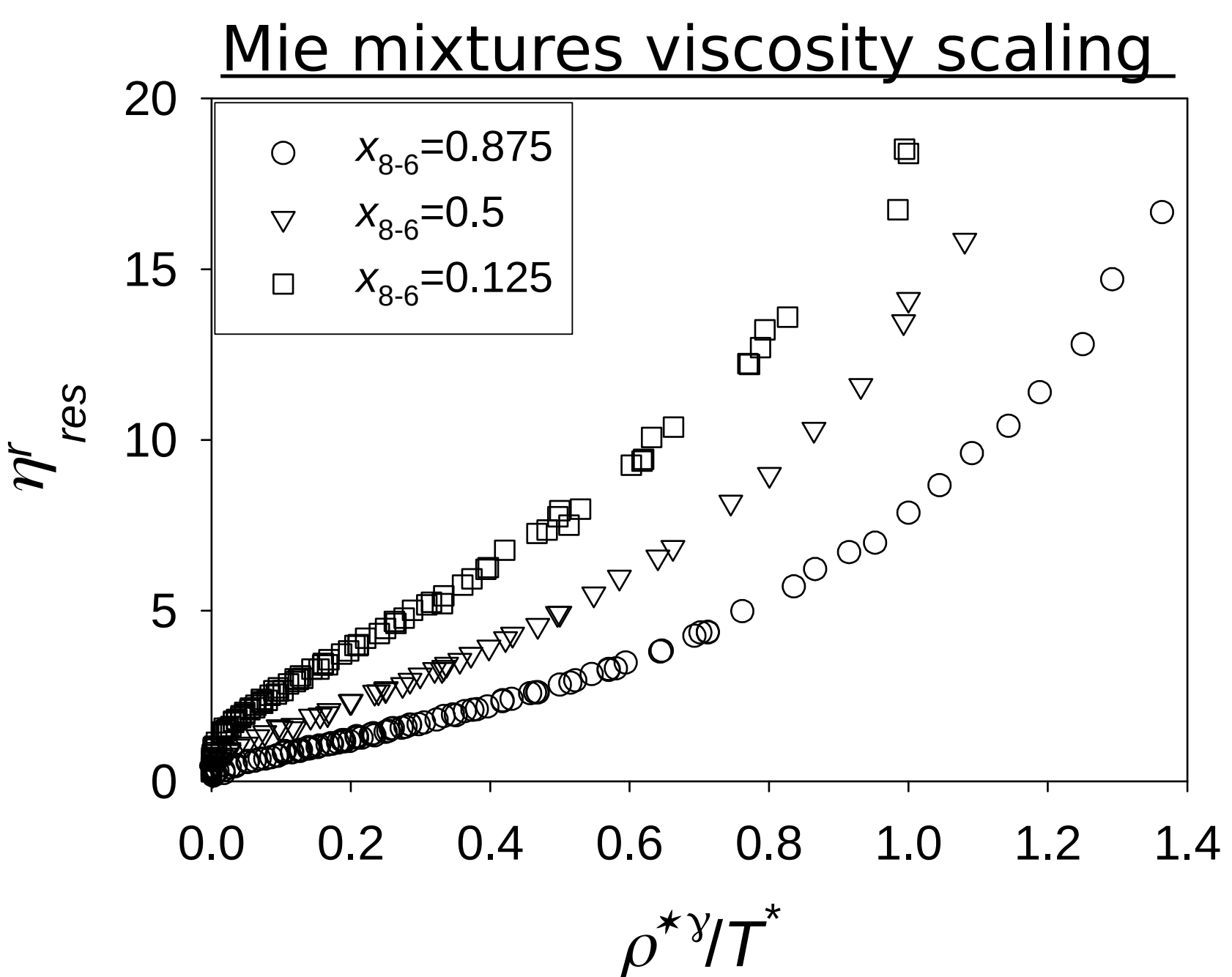
The scheme yields deviations below 10 %



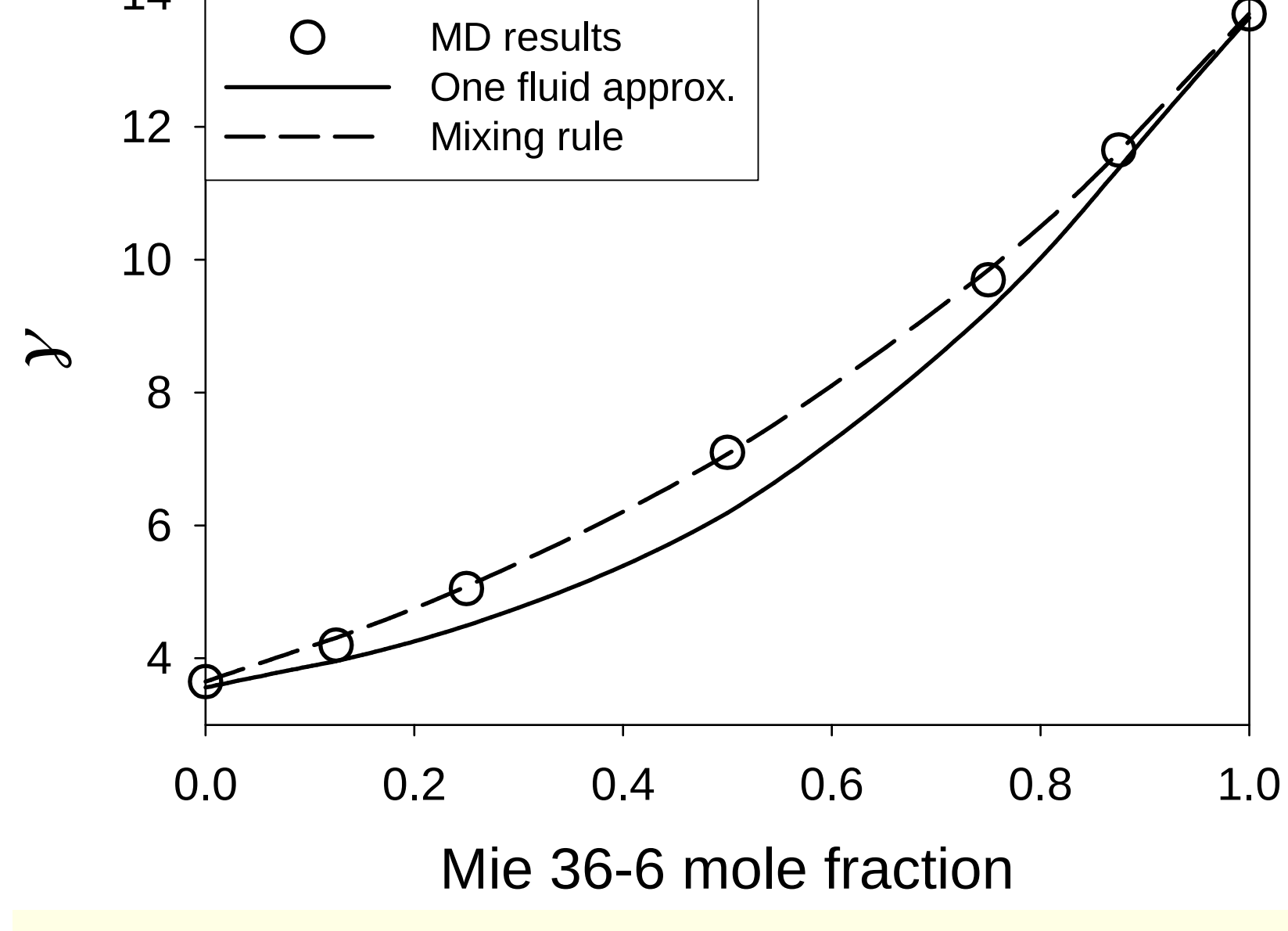
As expected,  $\gamma$  increases with  $n$  (linearly)  
 In soft sphere fluids  $\gamma = n/3$  but in Mie fluids :  
 $\gamma \approx n/2.78$   
 Bohling et al. relation yields a reasonable estimate  
 The Mie fluid allows to test very  $\gamma$  asymmetric mixtures !

### MODEL AND REAL MIXTURES

Binary mixtures of Mie 8-6 and Mie 36-6 fluids

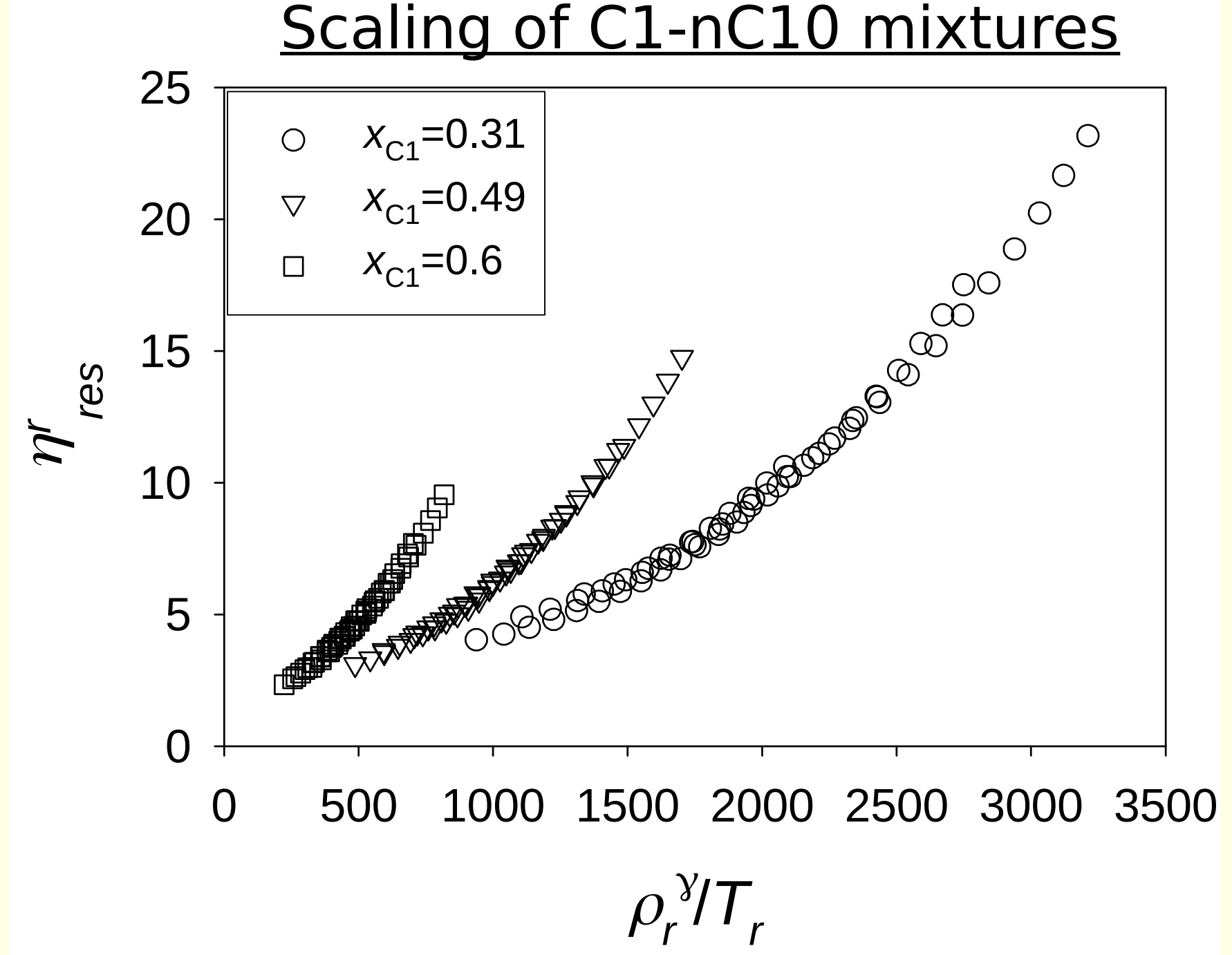


Scaling param. vs concentration



The application of the thermodynamic scaling is adequate to deal with Mie fluids mixtures (deviations < 10 %)

The most efficient mixing rule is :  $\ln(\gamma_{mix}) = \sum x_i \ln(\gamma_i)$



293-373 K, 20-140 MPa  
 Canet et al. Data

The proposed scheme seems efficient for real mixtures !  
 Tested on a alcohol-alkane as well

Thermodynamic scaling of viscosity in mixtures is applicable with a simple mixing rule

Work in progress :

1. Application of the mixing rules to other real mixtures, with a special focus on  $\gamma$  asymmetric ones
2. Extend the scheme to be used in a predictive manner, i.e. define a strategy to estimate the  $b_i$  parameters

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