Quantitative prediction of the phase diagram of alkanes in polar solvents

B. M. Mognetti[1*], L. Yelash[1], P. Virnau[1], W. Paul[1], K. Binder[1], M. Müller[2], L. G. MacDowell[3], and M. Oettel[1]

1- Institut für Physik, Johannes Gutenberg–Universität, Mainz, Germany
2- Institut für Theoretische Physik, Göttingen, Germany
3- Dpto. de Quimica Fisica, Universidad Complutense, Madrid, Spain

* SPEAKER

New Developments in Computational Physics
Leipzig 27/11/2008

OUR RESEARCH

- Development of a Coarse Grained model (CGm) for complex fluids (solvents+polymers)
  - Realistic $\Rightarrow$ predictive
  - Simplified $\Rightarrow$ accessible to numerical investigations (MC and EOS)

- We consider dipolar (NH_3, N_2O, H_2S, ...) and quadrupolar solvents (CO_2, C_6H_6, ...) and their mixtures with alkanes (C_nH_{2n+2})
  - We improve the previous Lennard-Jones CGm (P. Virnau et al. JCP **121**, 2169) by including a *polar spherically averaged* interaction (B.M. Mognetti et al. JCP **128**, 104501)

- GOAL: avoid the use of *ad-hoc* extra parameters in mixing rules $\Rightarrow$ PREDICTIVITY (no mixture experiments to fix the CGm)

$$\epsilon_{sp} = \xi\sqrt{\epsilon_s\epsilon_p}$$

PLAN OF THE TALK

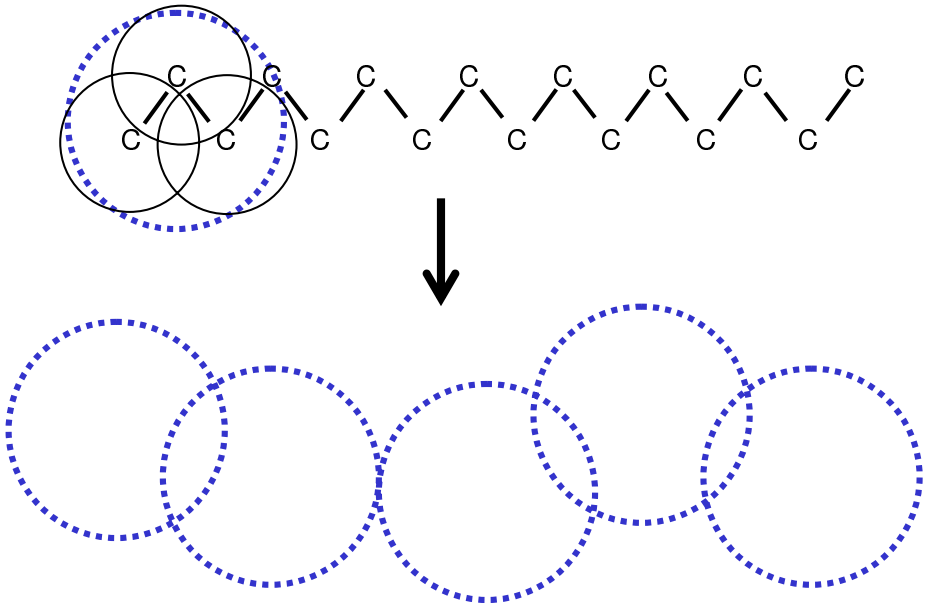
- The CGm for quadrupolar solvents: deriving the model and its validation using pure component experimental result

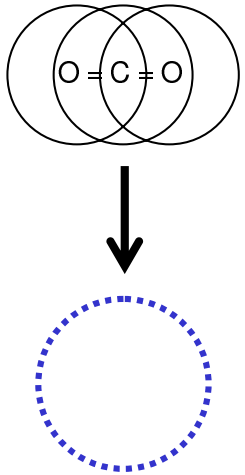
- The CGm for dipolar solvents: deriving the model and its validation using pure component experimental result

- Mixture phase diagram: validation of the new model using mixture with alkanes
  - Comparison with the previous modeling (LJ and and $\xi < 1$)
  - Comparison of the small residual discrepancies with apolar mixtures ones

- Conclusion

COARSE GRAINING



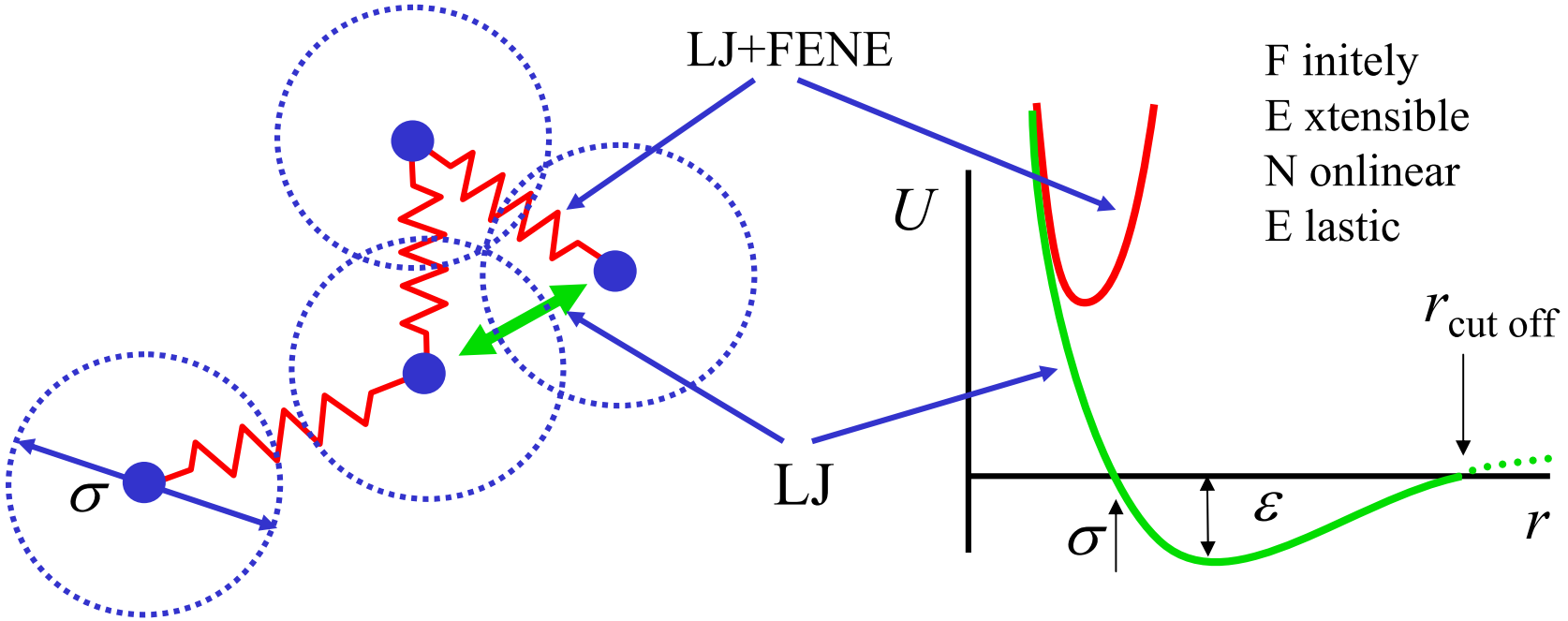


$C_{16}H_{34}$ - chain of 5 monomers

CO_2 - a single LJ-bead

Bead–spring model : LJ+FENE potential

A bead-spring model for chain molecules: Lennard-Jones plus FENE potential



$$U_{\text{FENE}}(r) = -33.75 \ln\left(1 - \left(\frac{r}{1.5\sigma}\right)^2\right)$$

EOS can be derived for LJ+FENE!

THE MODEL (dipolar) PCCP, submitted

- We start from the Stockmayer potential SM, LJ+DD beads

$$V^{(\mathrm{F,D})} = 4\epsilon_s[(\frac{\sigma_s}{r})^{12} - (\frac{\sigma_s}{r})^{6}] + \frac{\mu^2}{r^3}[\vec{n}_i \cdot \vec{n}_j - \frac{3}{r^2}(\vec{n}_i \cdot \vec{r}_{ij})(\vec{n}_j \cdot \vec{r}_{ij})]$$

- Averaging over $\vec{n}_i$, $\vec{n}_j$ $\Rightarrow$ isotropic short ranged potential (G. Stell et al. Mol. Phys. **27**, 1393)

$$\begin{aligned} V^{(\mathrm{A},D)} &= 4\epsilon_s[(\frac{\sigma_s}{r})^{12} - (1+\lambda)(\frac{\sigma_s}{r})^{6}] \\ \lambda &= \frac{1}{12}\frac{\mu^4}{\epsilon_s {\sigma_s}^6 k_B T} = \lambda_c \frac{T_c^{\mathrm{exp}}}{T} \end{aligned}$$

- ϵ_s, σ_s and λ_c determined using T_c^{exp}, ρ_c^{exp} and μ^{exp} (or an adjusted value of dipolar moment μ^{adj})

THE MODEL (quadrupolar)

JCP, **108** (2008); PRE **77** (2008)

- Solvent molecules $\Rightarrow$ (LJ+QQ)-beads

$$V^{(\mathrm{F},Q)} = 4\epsilon_s\Big[\left(\frac{\sigma_s}{r_{ij}}\right)^{12} - \left(\frac{\sigma_s}{r_{ij}}\right)^{6}\Big] + \frac{3Q^2}{4r_{ij}^5} f(\Omega_i,\Omega_j)$$

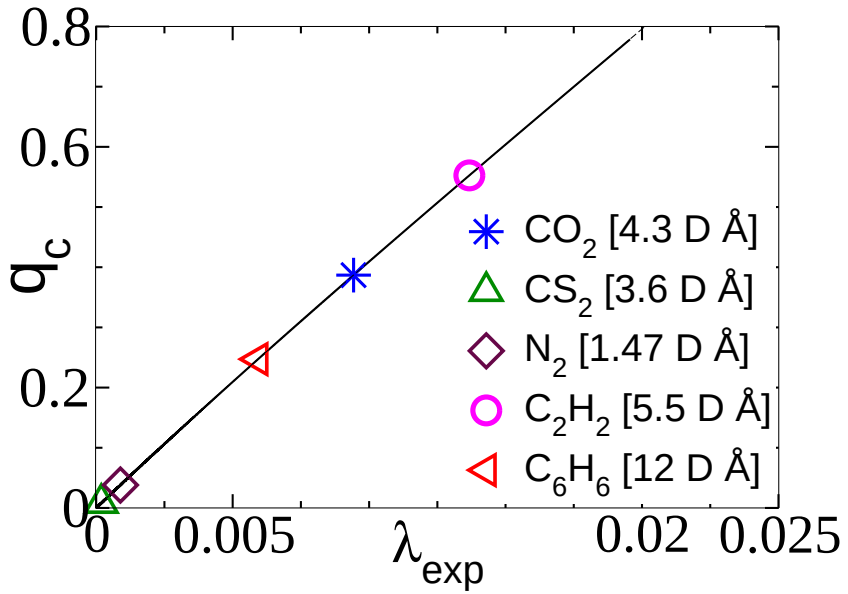
- Averaging over Ω_i $\Rightarrow$ isotropic potential (G. Stell et al. Mol. Phys. **27**, 1393; E. Müller et al. Ind. Eng. Chem. Res. **42**, 4123)

$$\begin{aligned} V^{(\mathrm{A},Q)} &= 4\epsilon_s\Big[\left(\frac{\sigma_s}{r_{ij}}\right)^{12} - \left(\frac{\sigma_s}{r_{ij}}\right)^{6} - \frac{7}{20} q_c \frac{T_c^{\mathrm{exp}}}{T}\left(\frac{\sigma_s}{r_{ij}}\right)^{10}\Big] \\ q_c &= \frac{Q^4 {\sigma_s}^{-10}}{\epsilon_s k_B T_c^{\mathrm{exp}}} \end{aligned}$$

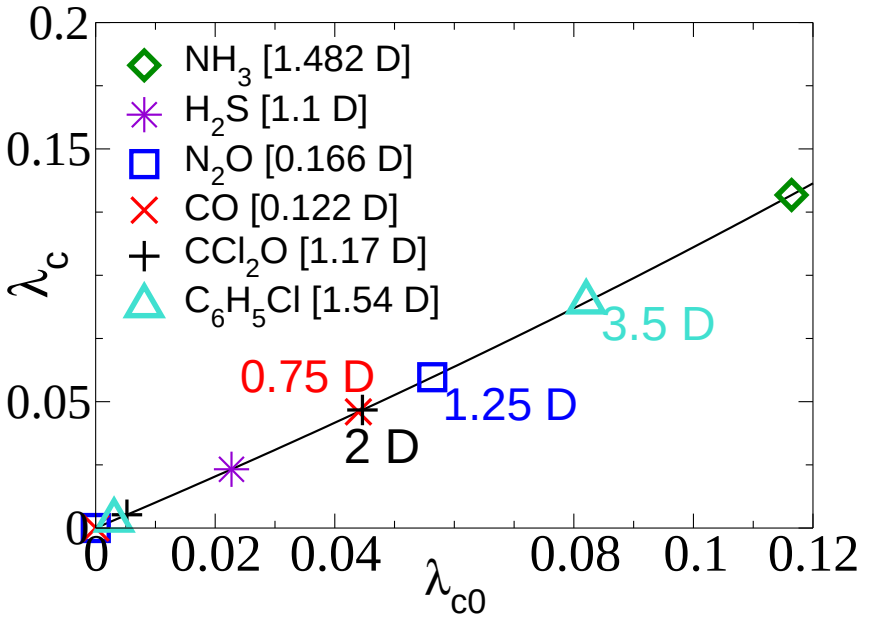
- ϵ_s, σ_s and q_c determined using T_c^{exp}, ρ_c^{exp} and Q^{exp} (or an adjusted value of quadrupolar moment Q^{adj})

DERIVING ϵ_s, σ_s, $\begin{cases}\lambda_c \\ q_c\end{cases}$ from T_c^{exp}, ρ_c^{exp}, $\begin{cases}\mu \\ Q\end{cases}$

$$T_c^{\text{exp}} = \frac{T_c^* \epsilon_s}{k_B} \qquad \rho_c^{\text{exp}} = \frac{\rho_c^* M_{\text{mol}}}{{\sigma_s}^3} \qquad q_c = \frac{Q^4 {\sigma_s}^{-10}}{\epsilon_s k_B T_c} \qquad \lambda_c = \frac{1}{12}\frac{\mu^4}{\epsilon_s {\sigma_s}^6 k_B T}$$



$$\lambda_{\text{exp.}} = \frac{Q^4}{(k_B T_c)^2}\left(\frac{\rho_c N_A}{M_{\text{mol}}}\right)^{10/3}$$

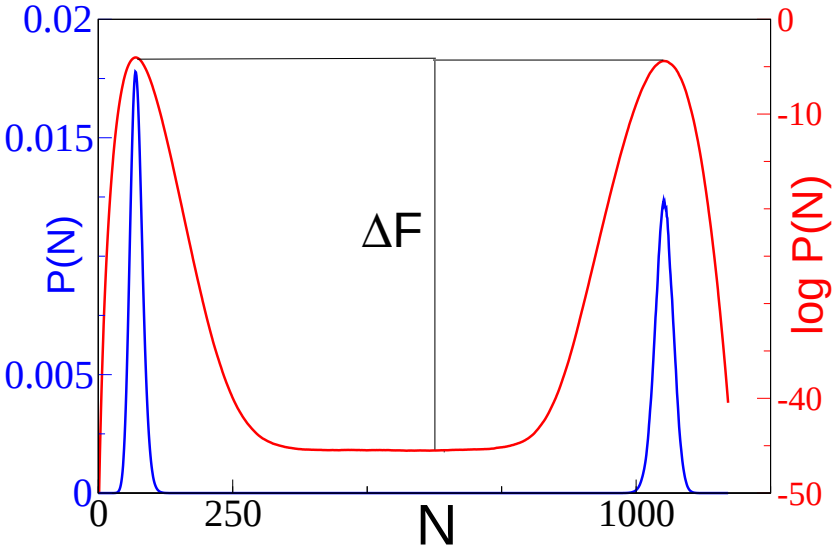


$$\lambda_{c0} = \frac{1}{12}\frac{\mu^4}{\epsilon_0 {\sigma_0}^6 k_B T_c}$$

ϵ_0 and σ_0 being the parameters for the uncut LJ potential (i.e. if μ=0)

THE MC METHODS Virnau et al., JCP **120**, 10925

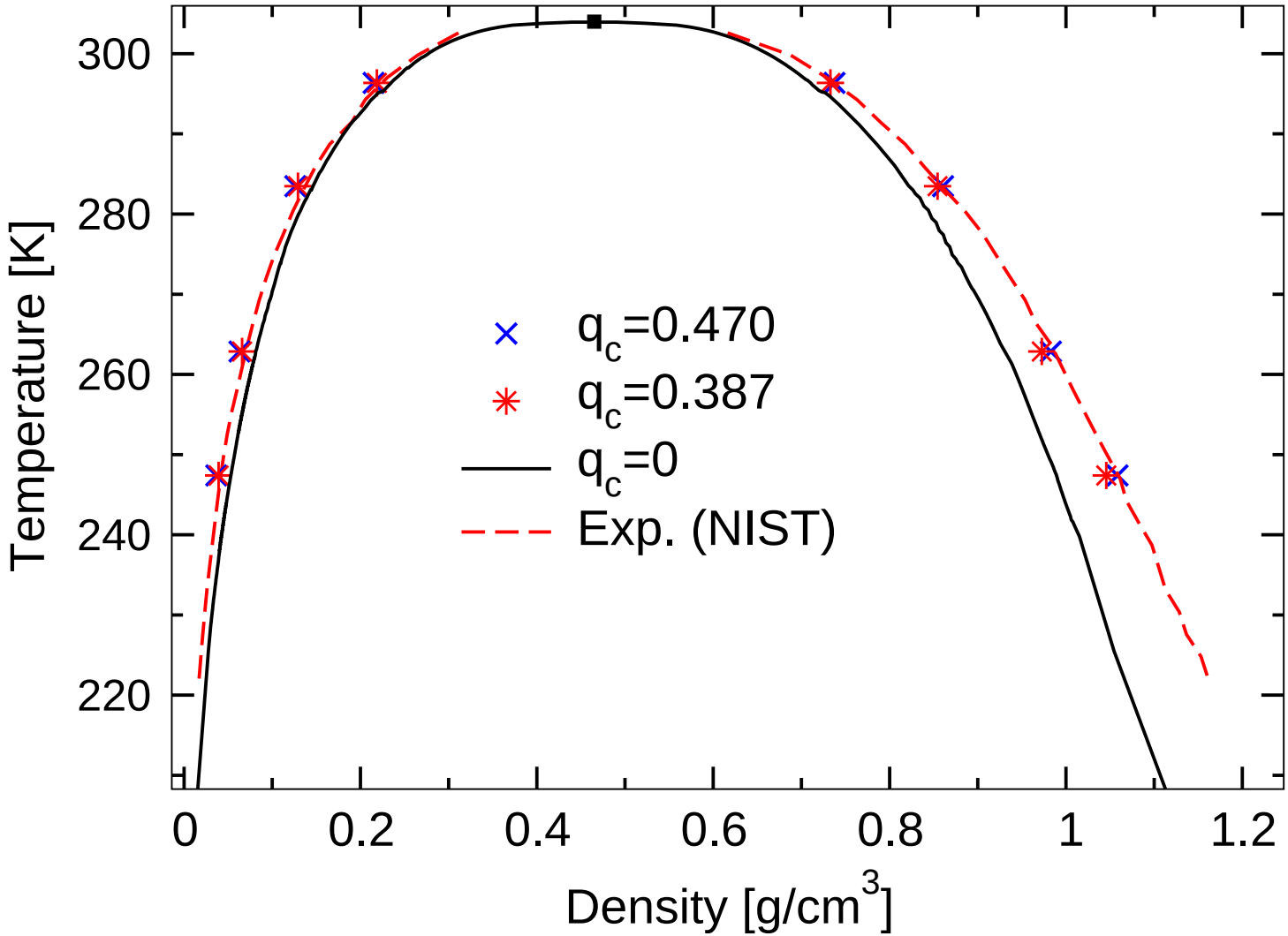
- Successive Umbrella Sampling
  - Algorithm constrained to sample configurations with n or n+1 particles (if n+2 or n-2 particles are generated the move is rejected)
  - In such a way P(n+1)/P(n) is determined
  - Spanning in n one is able to reconstruct P(n) and F(n)= log P(n) with the interface tension (Binder PRA**25**, 1982) $\gamma = \Delta F/2L^2$



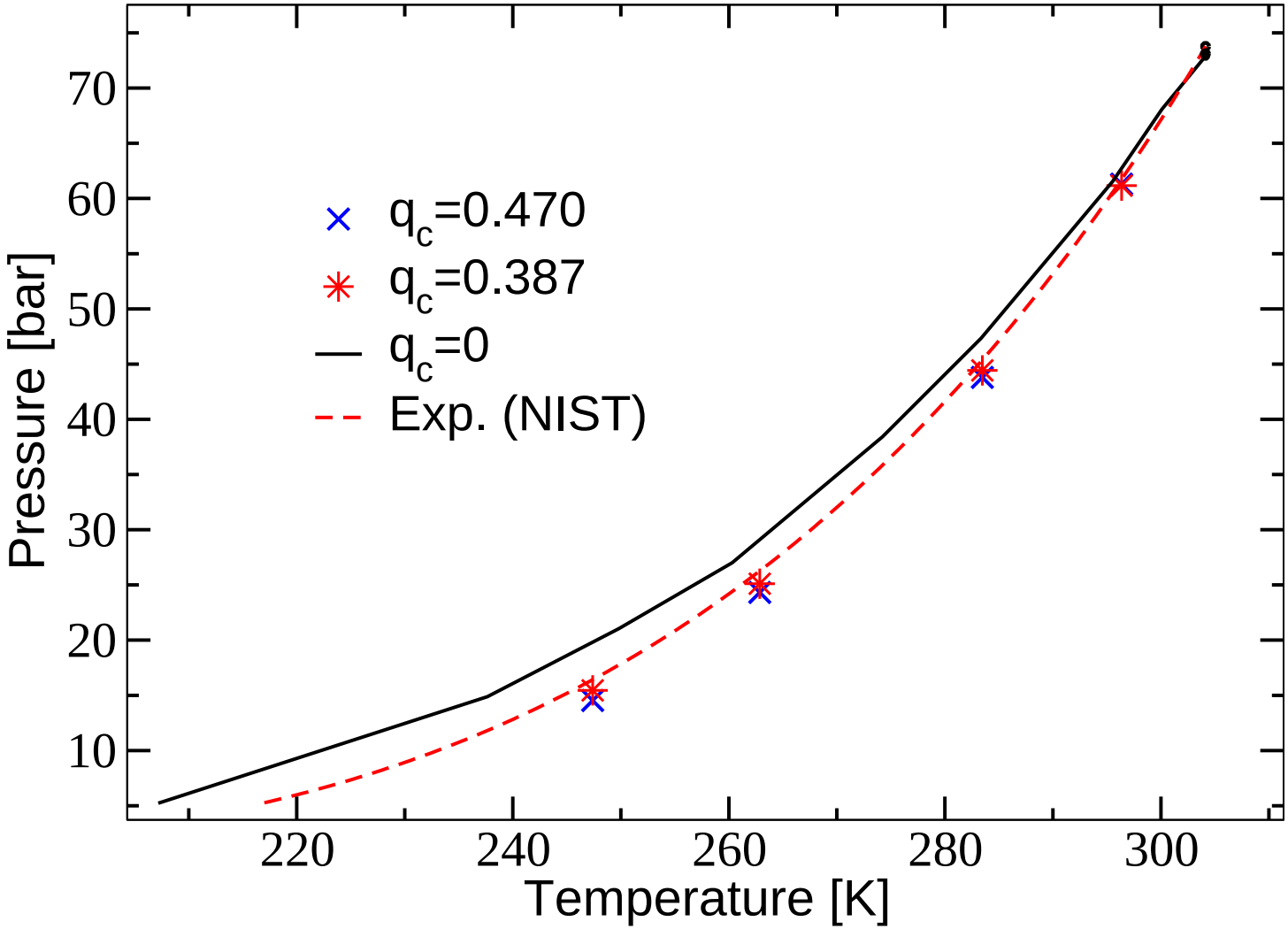
PURE QUADRUPOLAR SUBSTANCES

J. Chem. Phys. **128**, 104501, (2008)

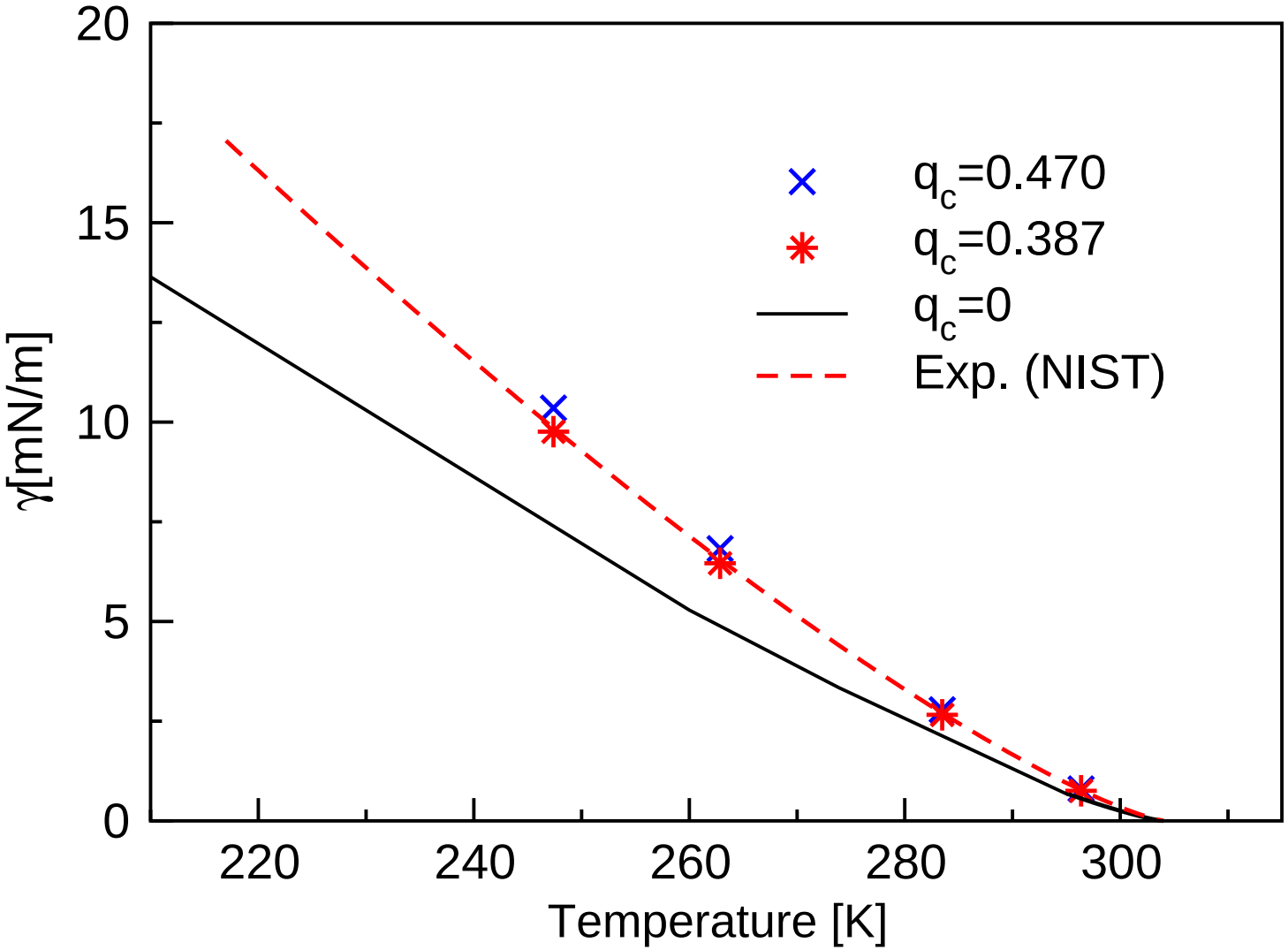
CO_2: Q_{exp} (q_c=0.387) and Q_{adj} (q_c=0.470)



CO_2: Q_{exp} (q_c=0.387) and Q_{adj} (q_c=0.470)

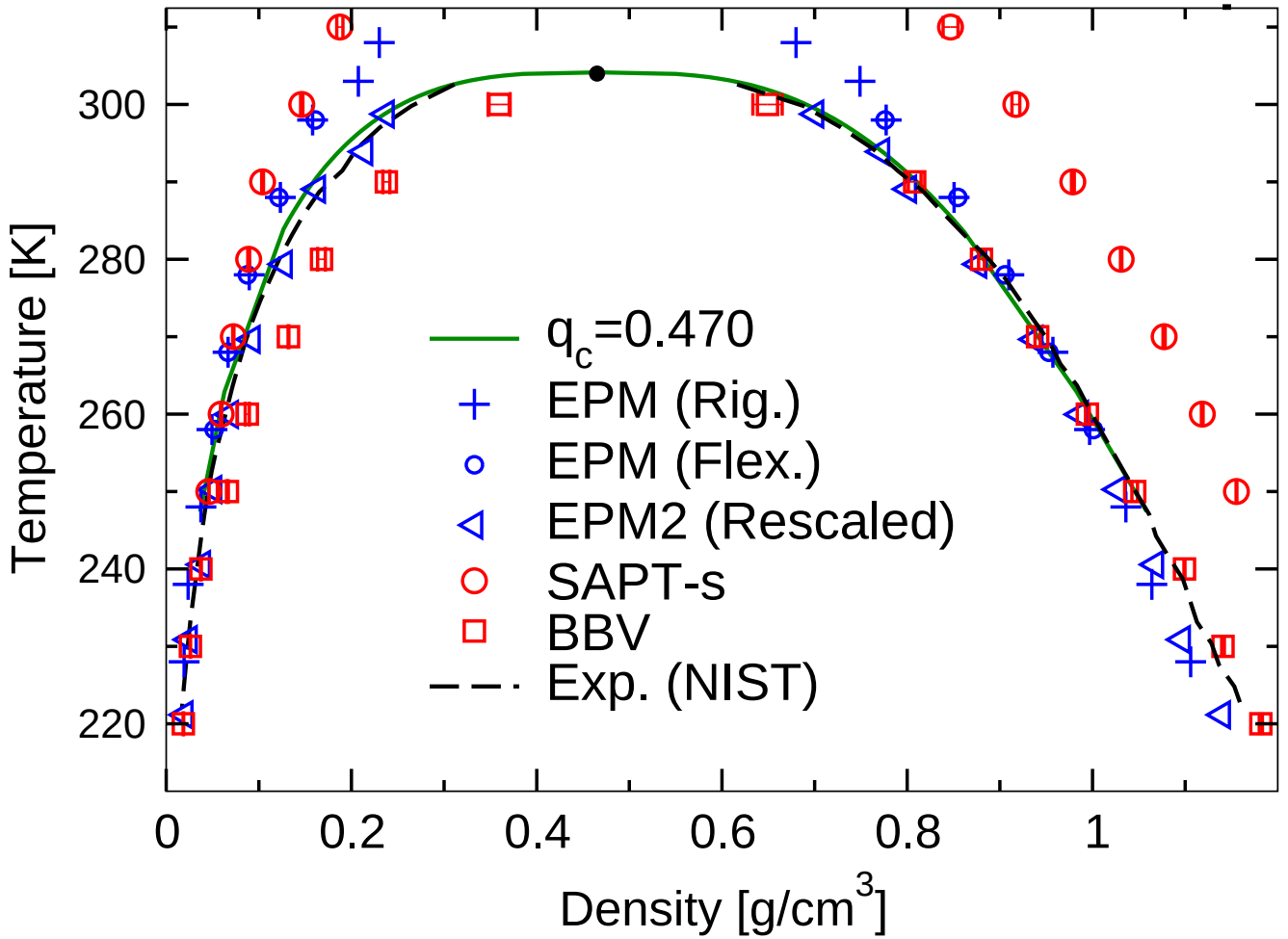


CO_2: Q_{exp} (q_c=0.387) and Q_{adj} (q_c=0.470)



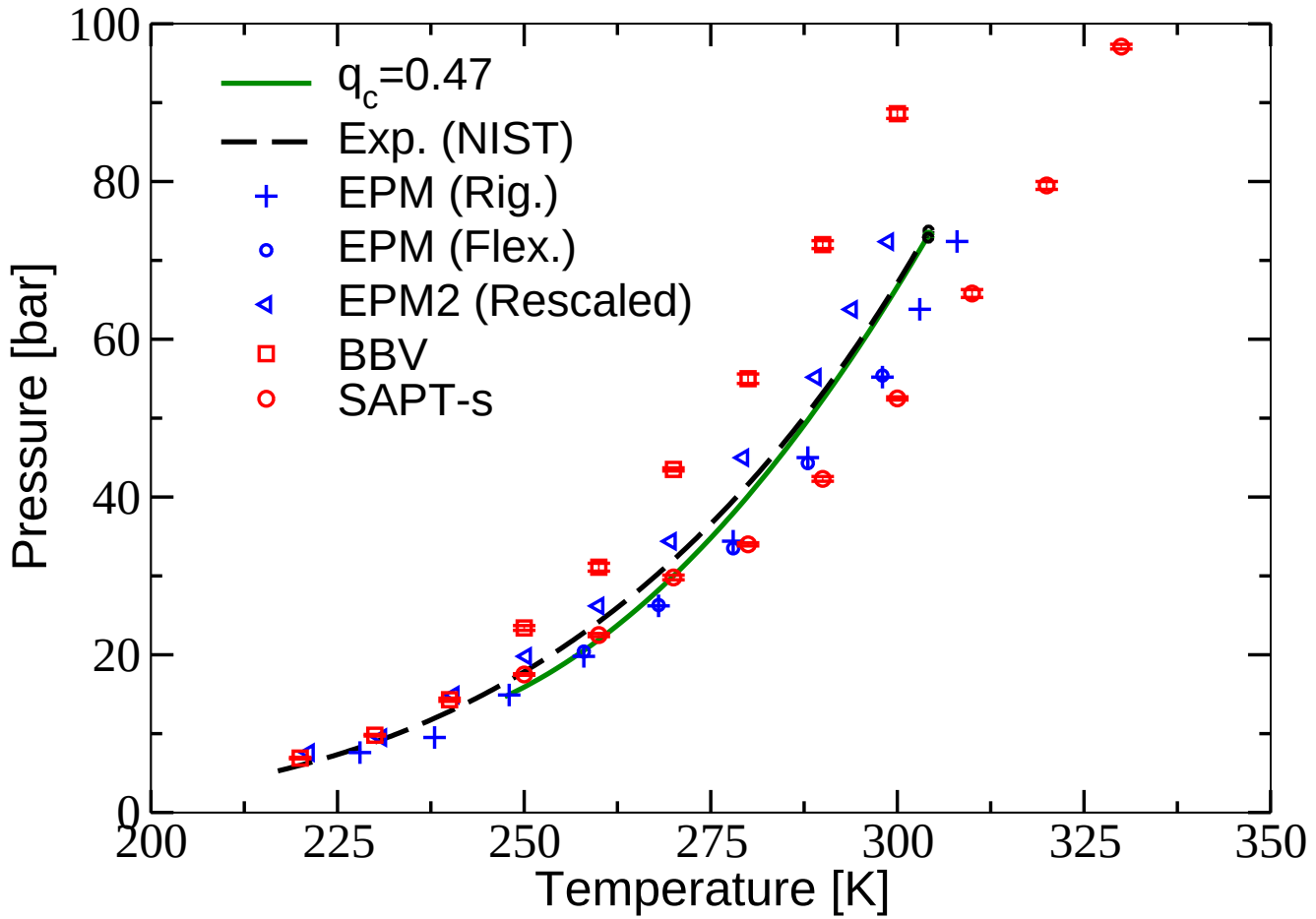
CO_2 ATOMISTIC MODELS

We also perform well when compared to fully atomistic models (which are too complicated for mixtures)

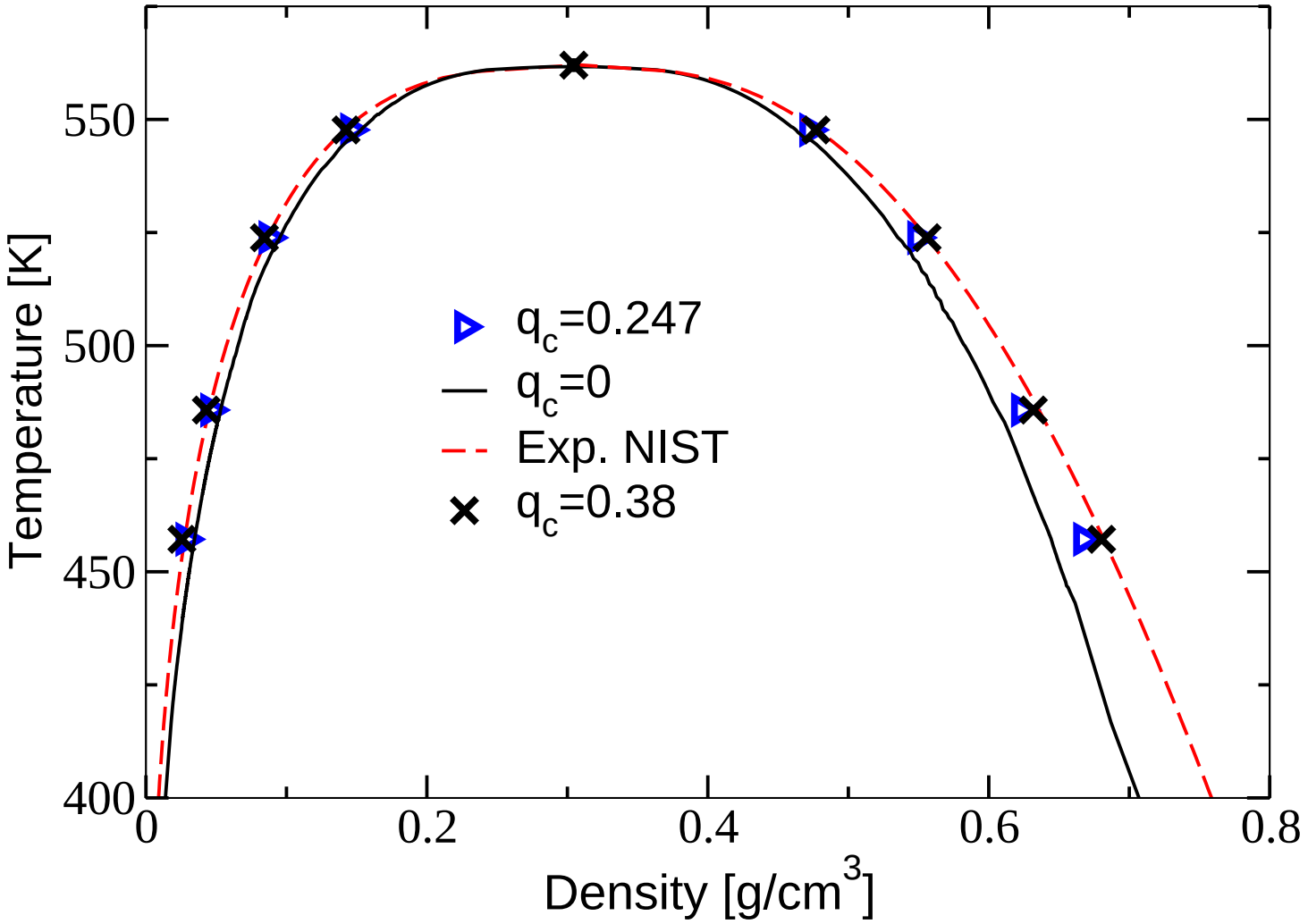


CO_2 ATOMISTIC MODELS

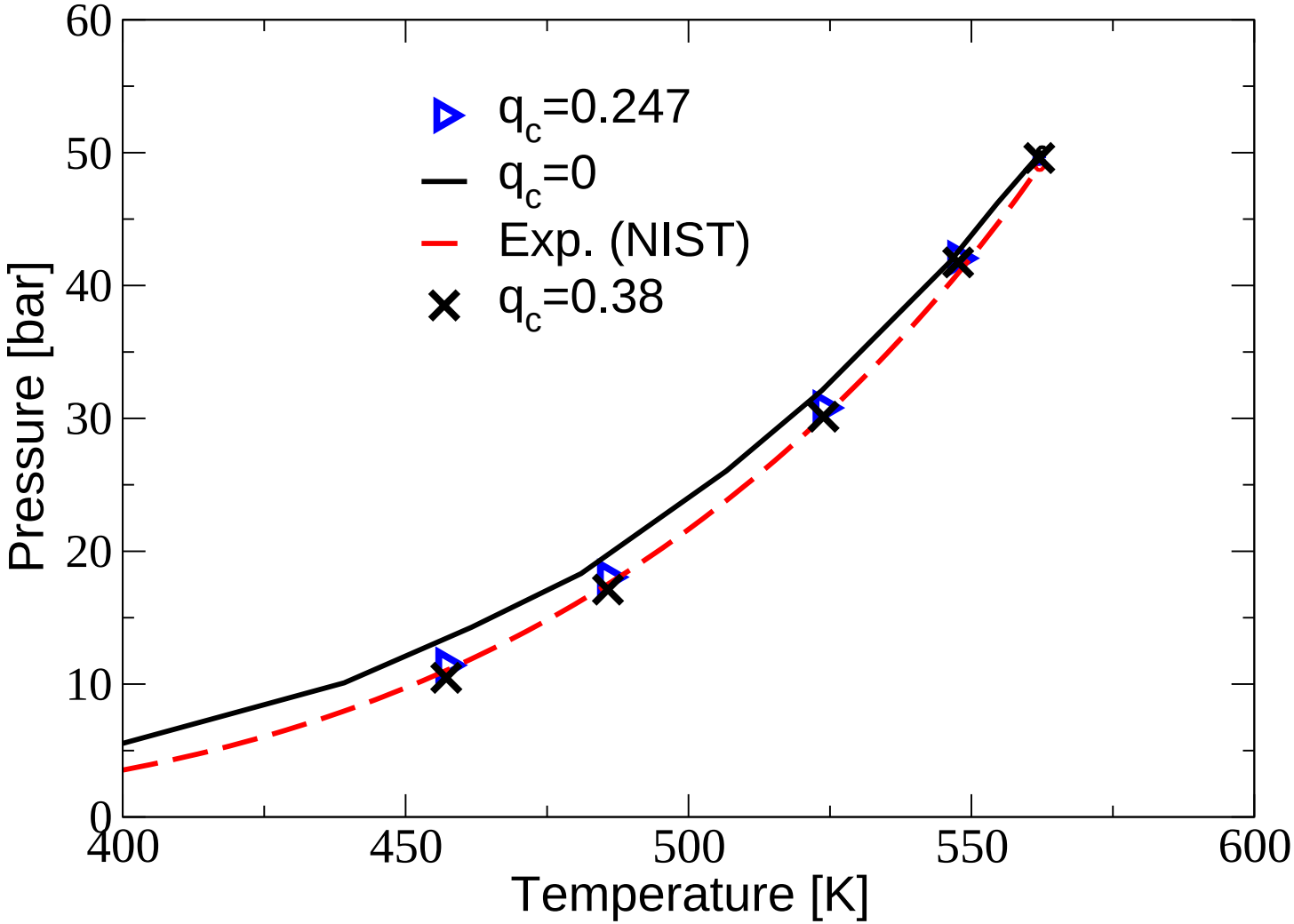
We also perform well when compared to fully atomistic models (which are too complicated for mixtures)



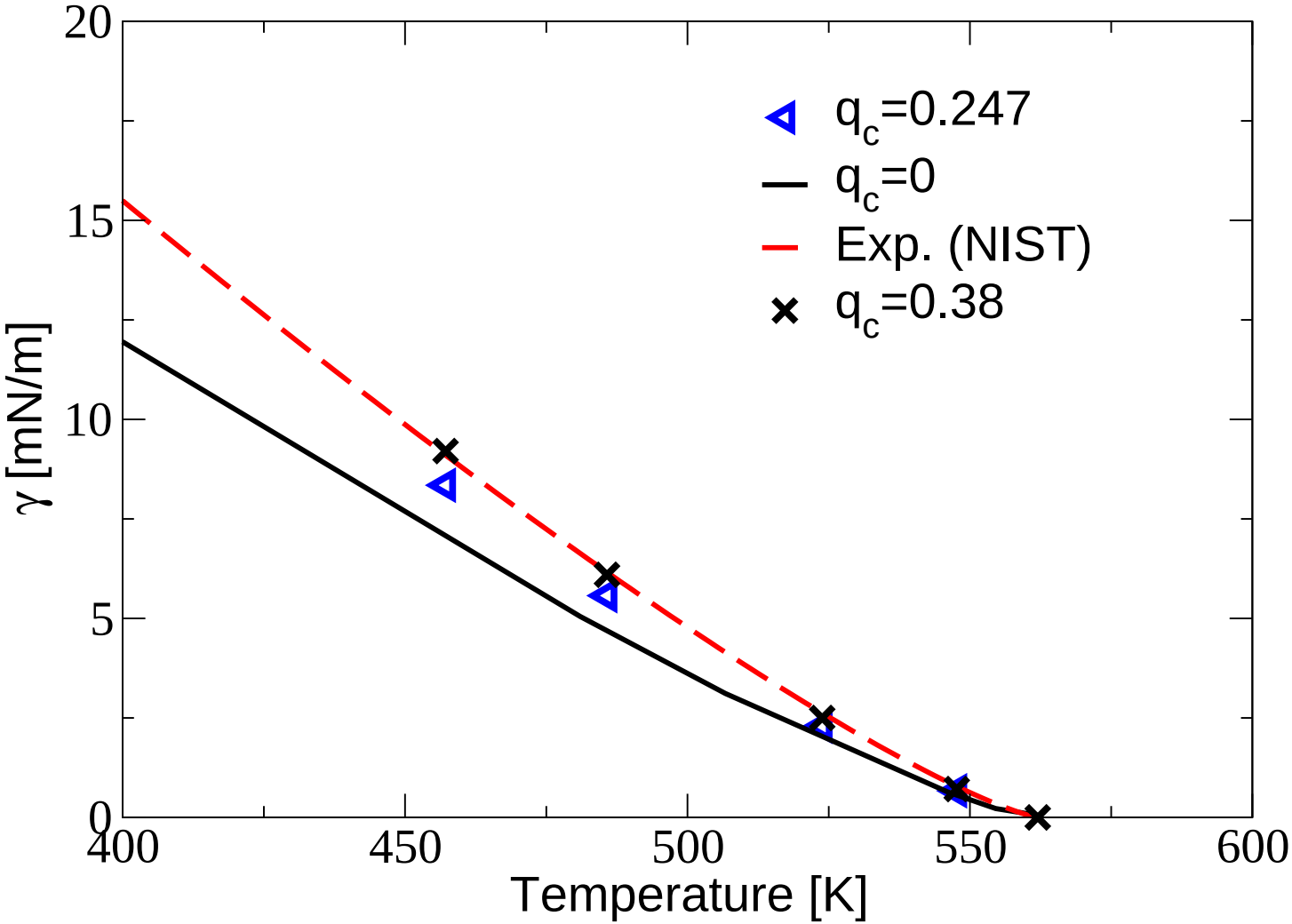
C_6H_6: $Q_{exp} = 12$DÅ(q_c=0.247) and $Q_{adj} = 13.4$DÅ(q_c=0.38)



C_6H_6: $Q_{exp} = 12$DÅ(q_c=0.247) and $Q_{adj} = 13.4$DÅ(q_c=0.38)



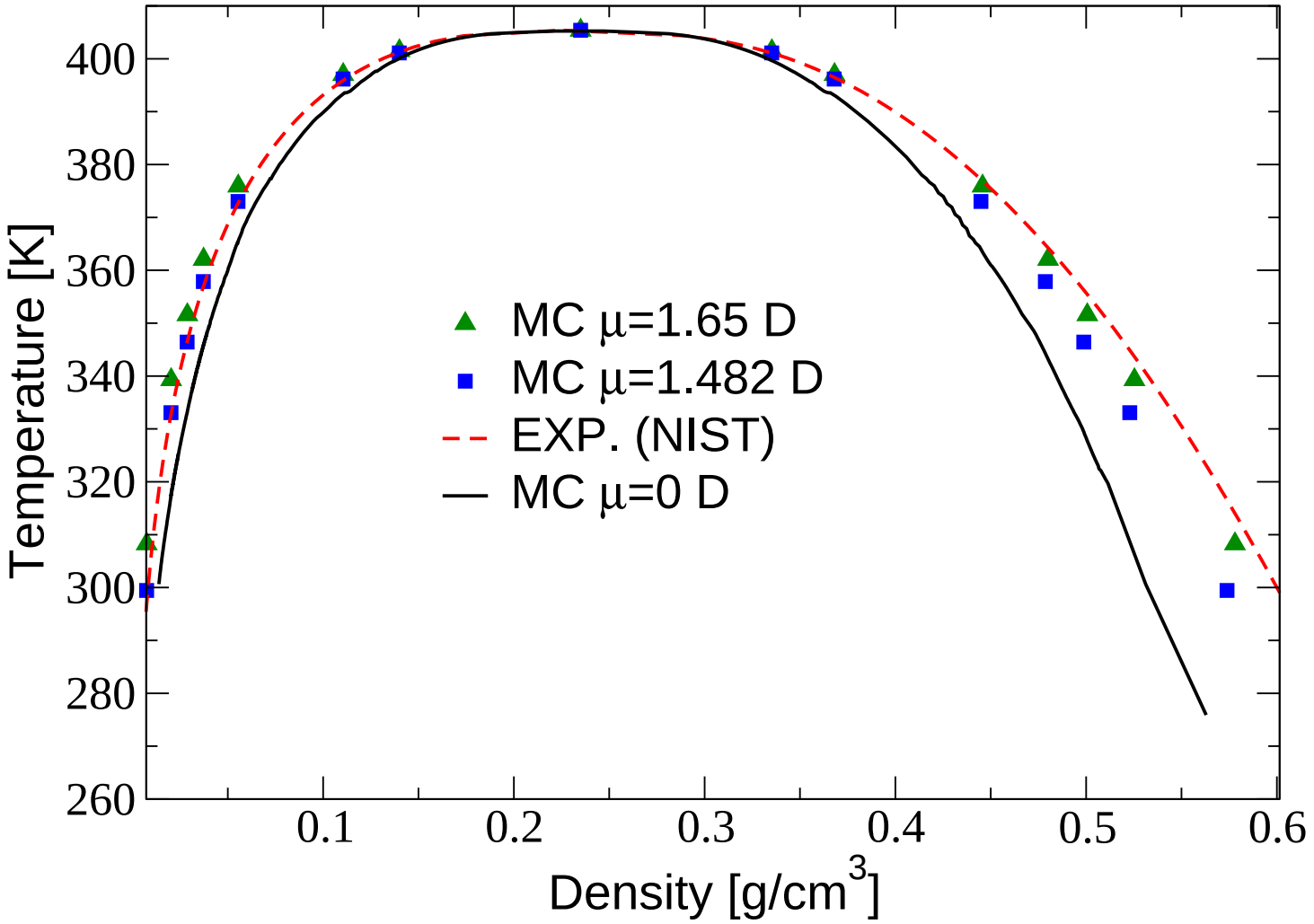
C_6H_6: $Q_{exp} = 12$DÅ(q_c=0.247) and $Q_{adj} = 13.4$DÅ(q_c=0.38)



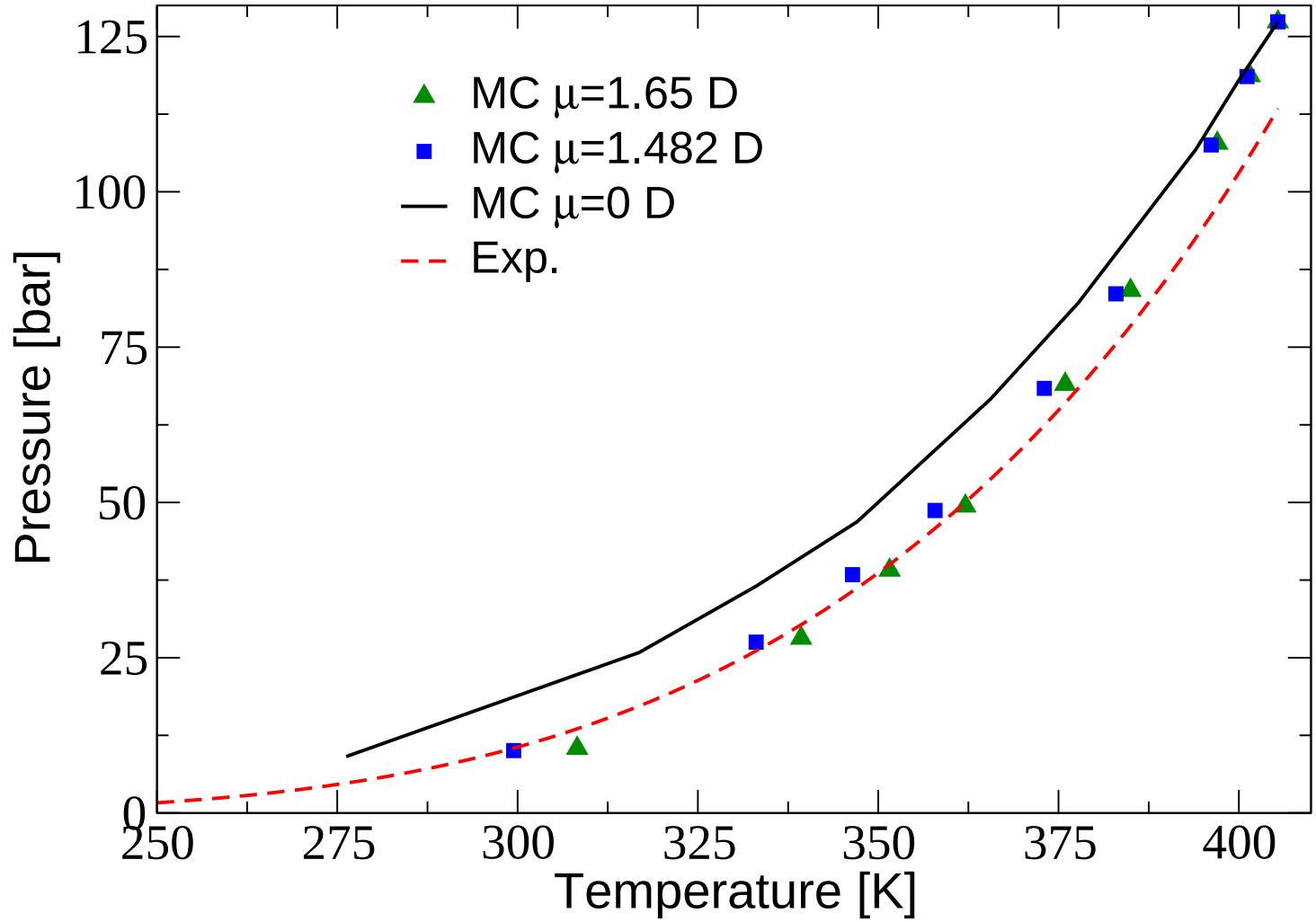
PURE DIPOLAR SUBSTANCES

Phys. Chem. Chem. Phys., submitted

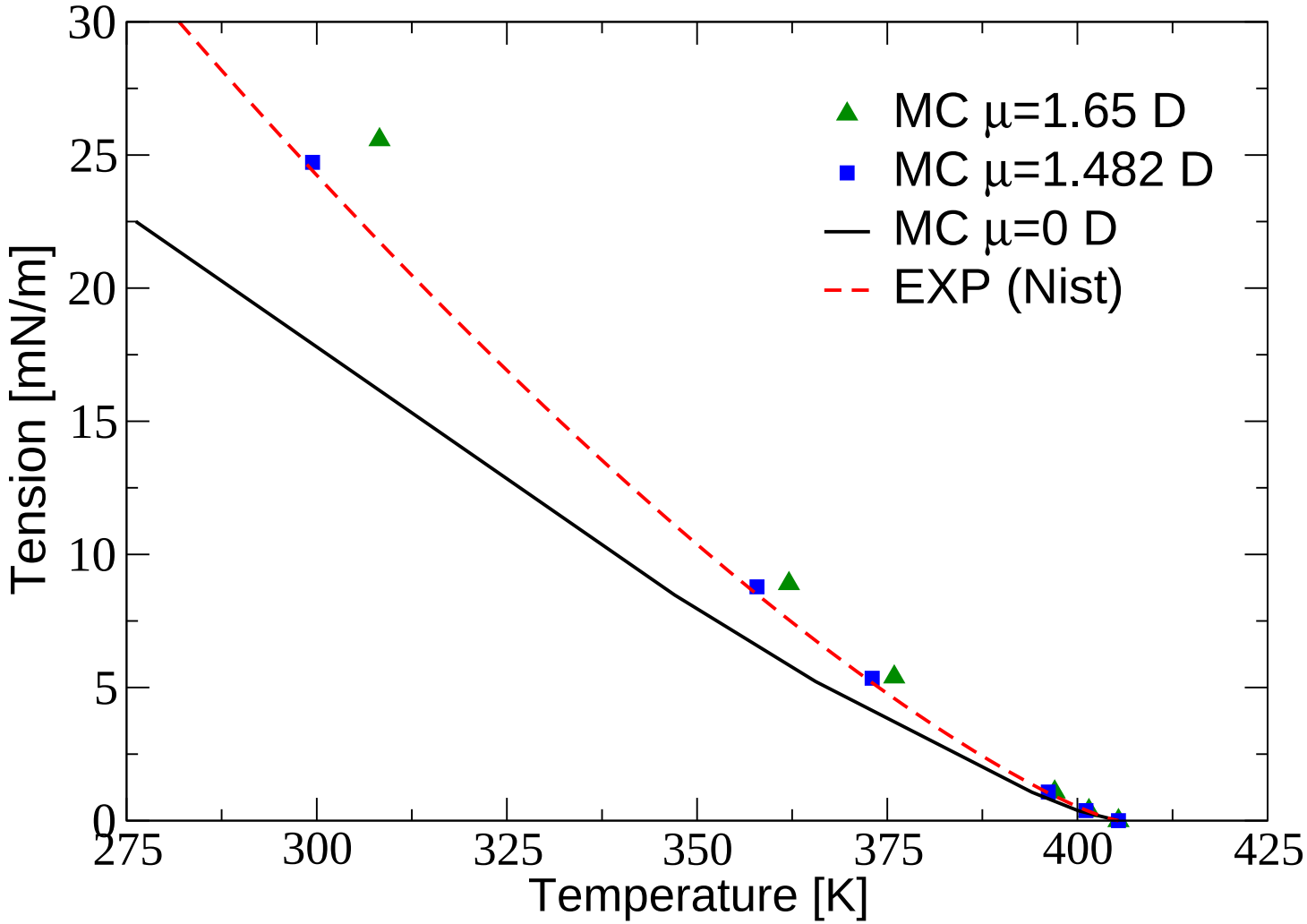
NH_3: μ_{exp}=1.482D (λ_c=0.131) and μ_{adj}=1.65D (λ_c=0.218)



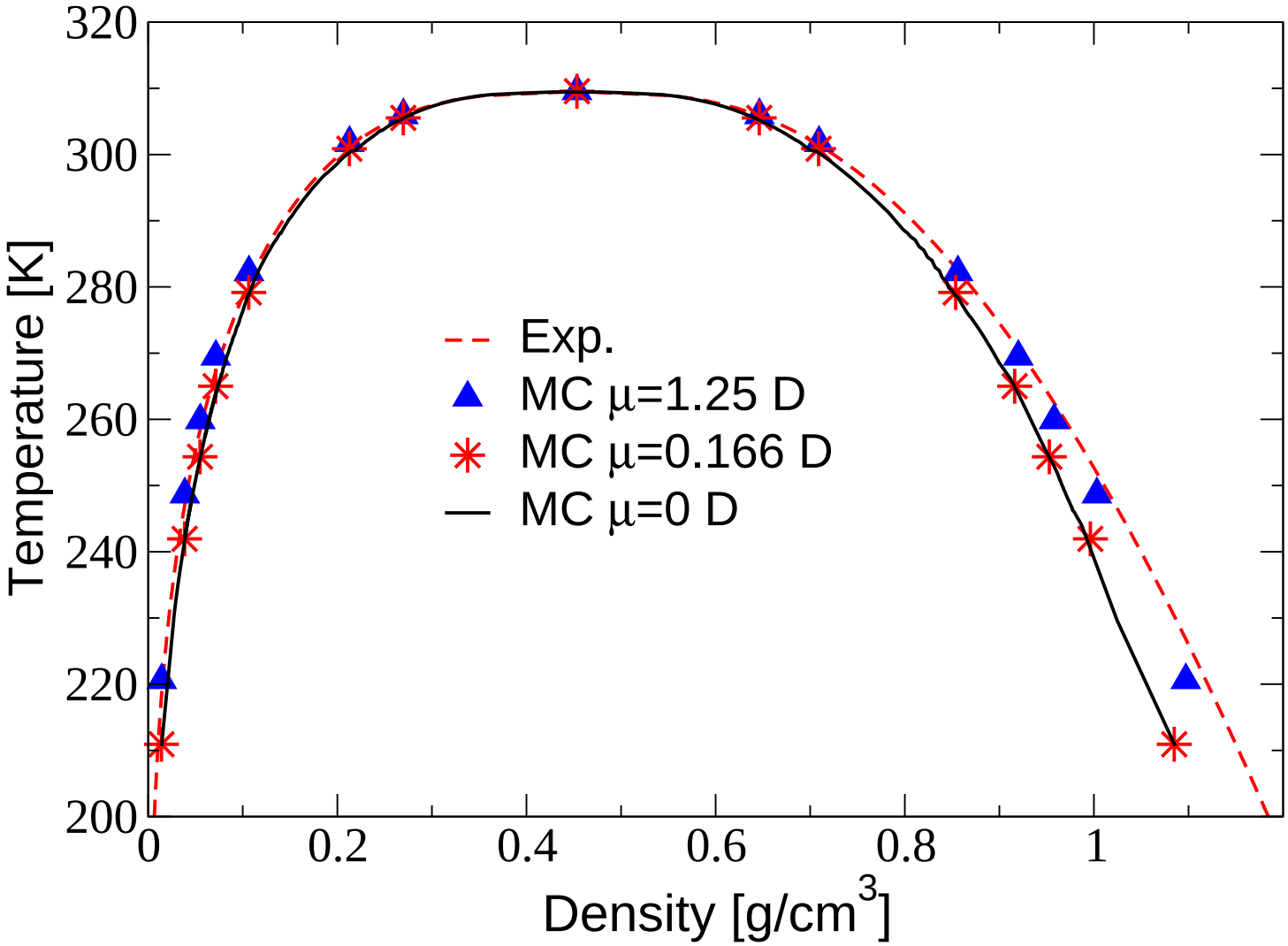
NH_3: μ_{exp}=1.482D (λ_c=0.131) and μ_{adj}=1.65D (λ_c=0.218)



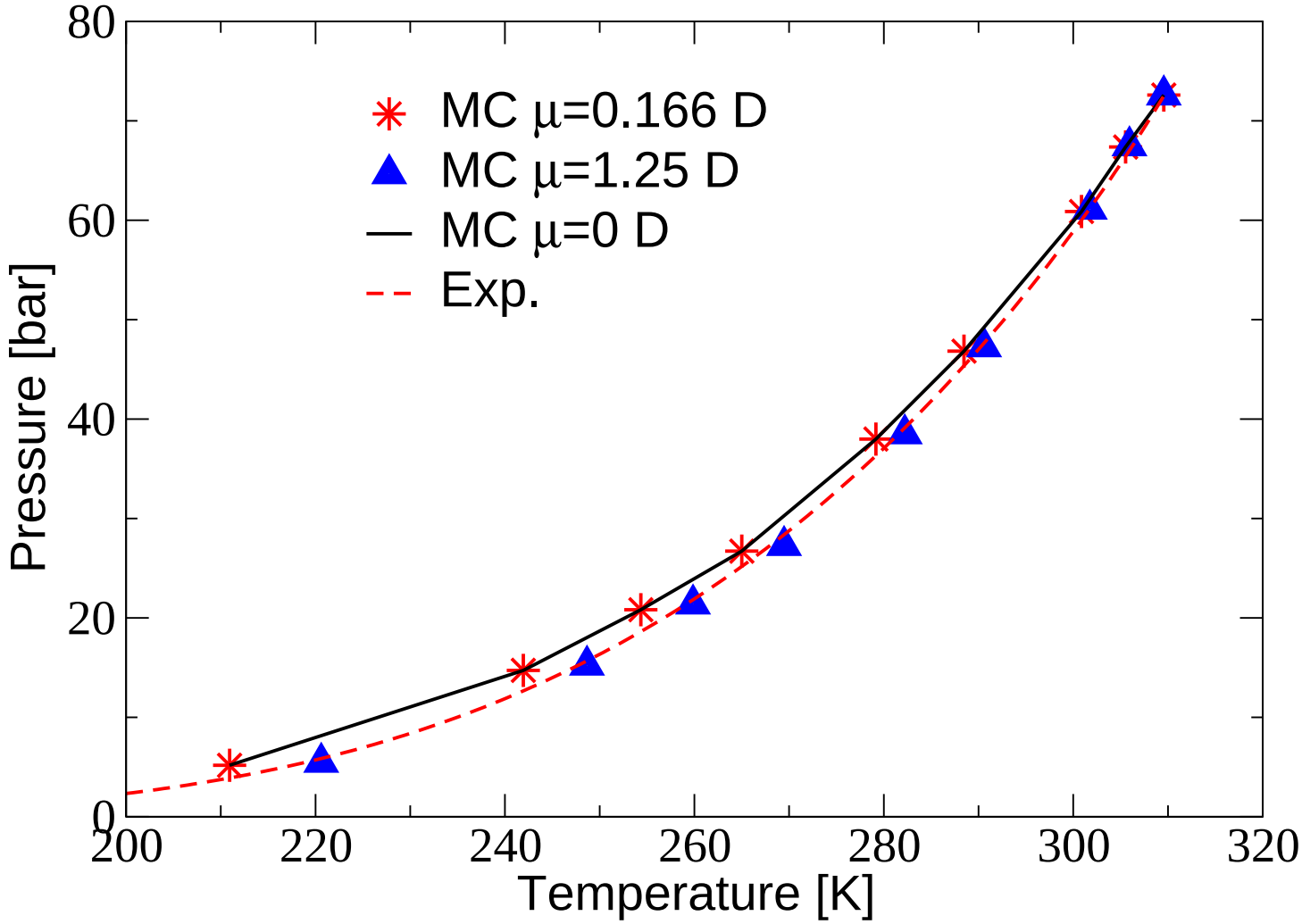
NH_3: μ_{exp}=1.482D (λ_c=0.131) and μ_{adj}=1.65D (λ_c=0.218)



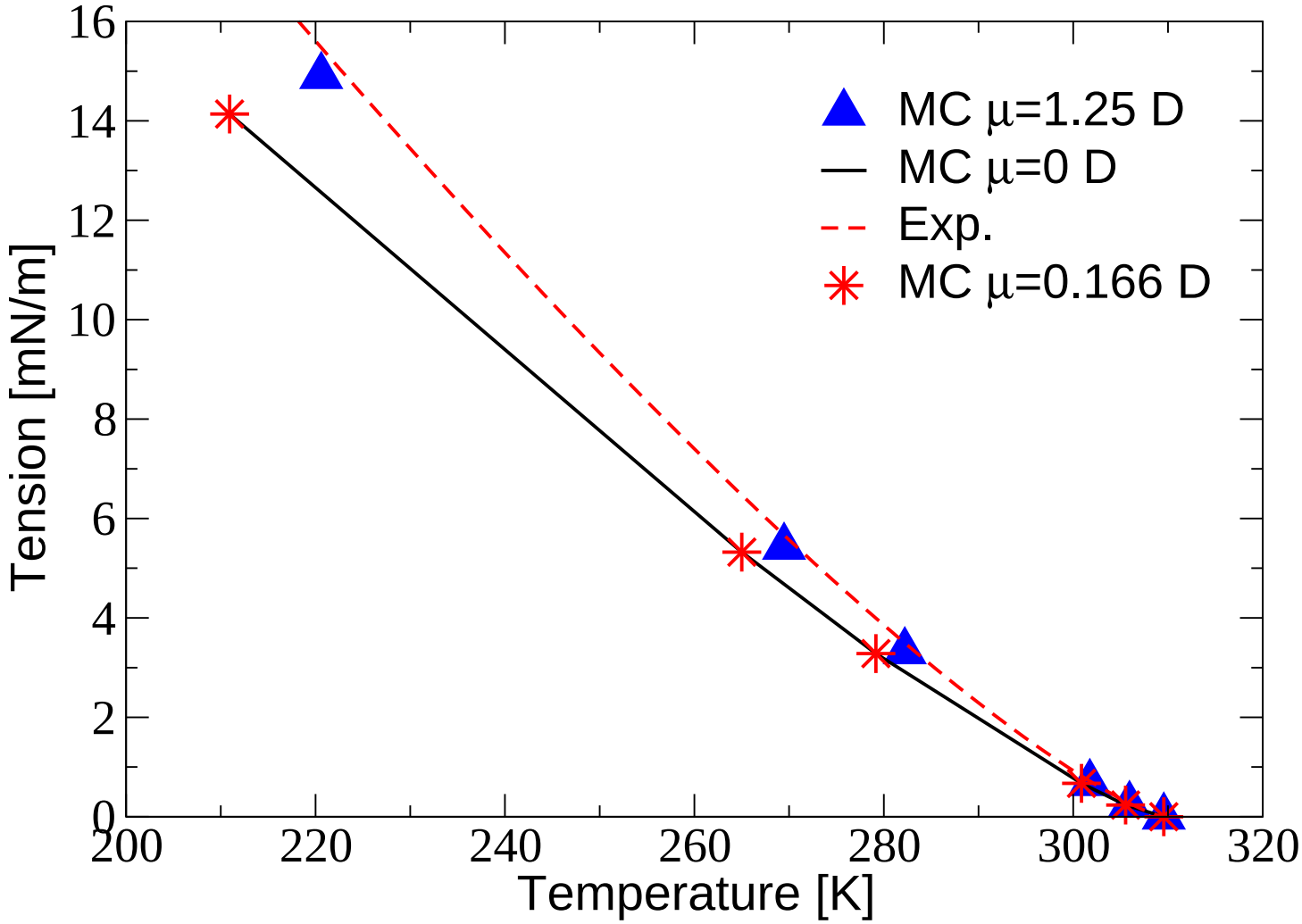
N_2O: μ_{exp}=0.166D (λ_c=1.75·10^{-5}) and μ_{adj} = 1.25D (λ_c=0.060)



N_2O: μ_{exp}=0.166D (λ_c=1.75·10^{-5}) and μ_{adj} = 1.25D (λ_c=0.060)

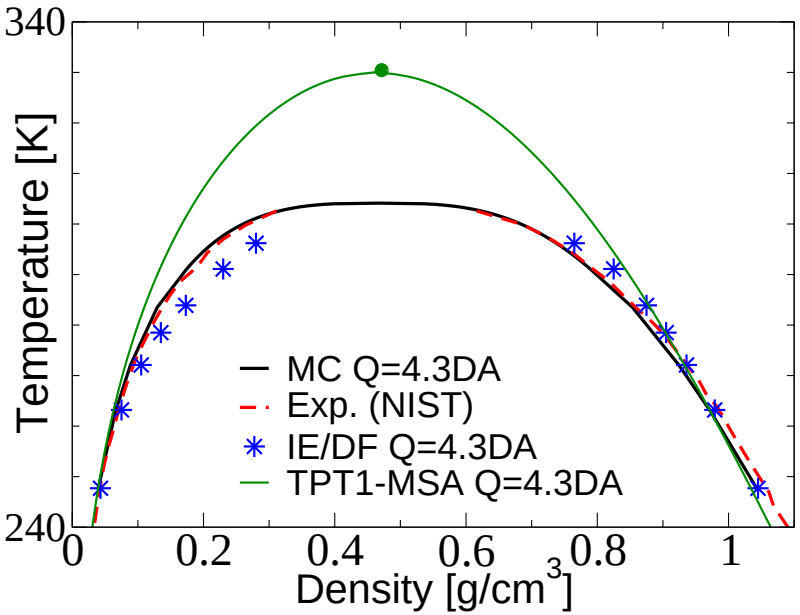


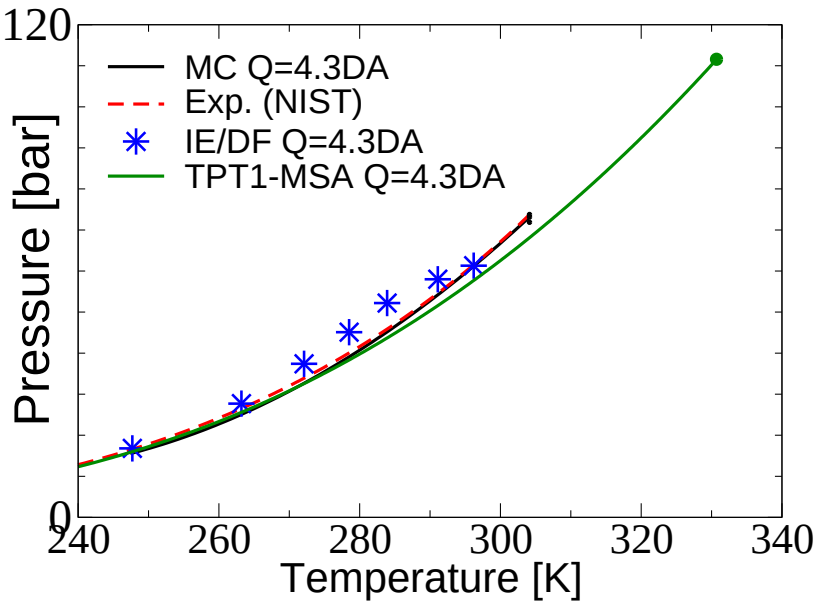
N_2O: μ_{exp}=0.166D (λ_c=1.75·10^{-5}) and μ_{adj} = 1.25D (λ_c=0.060)



POLAR FLUIDS WITH ALKANES

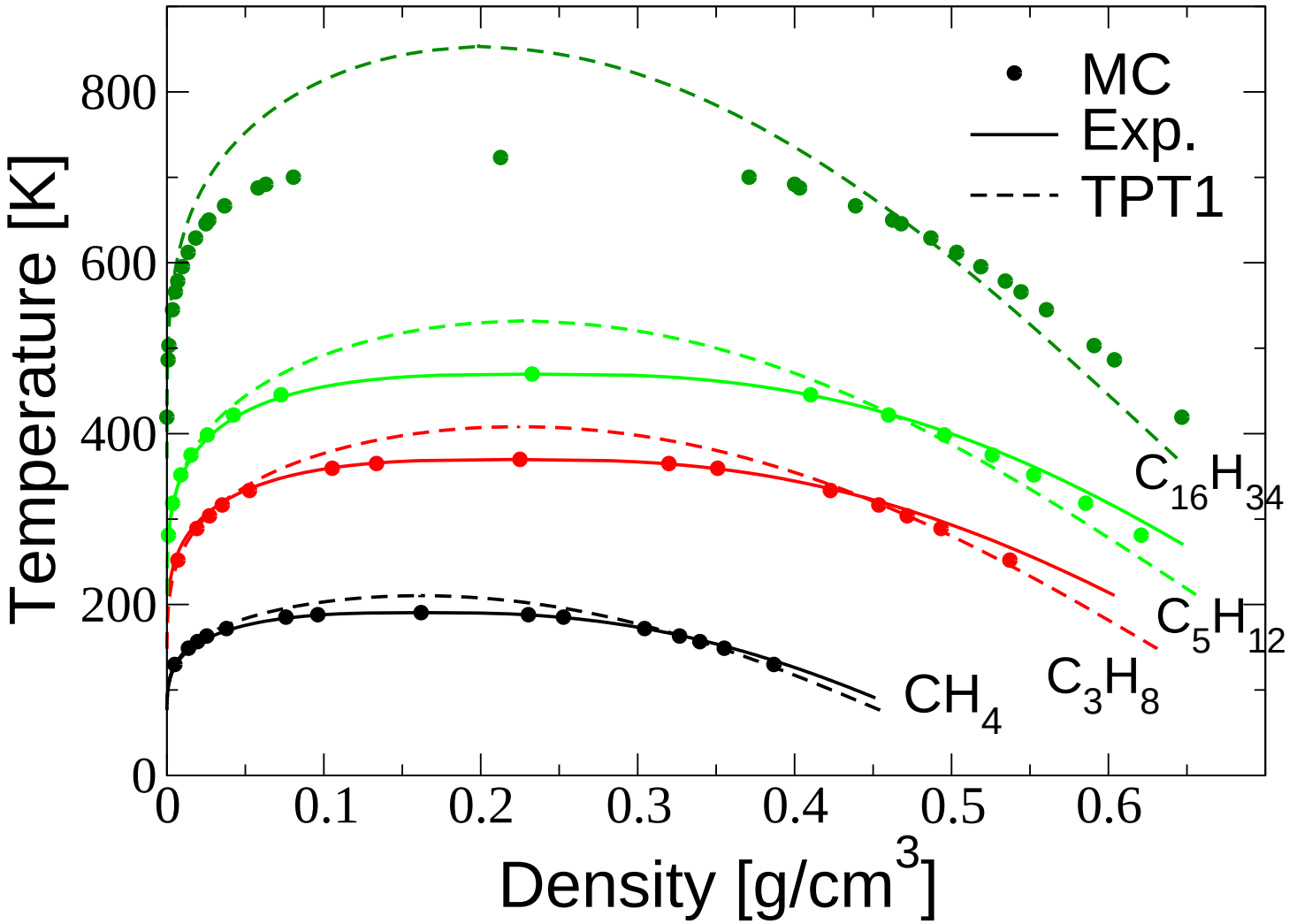
- Two methods
  - EXPENSIVE SIMULATIONS
  - TPT1 – MSA FAST BUT INACCURATE IN THE CRITICAL REGION (L. G. MacDowell)



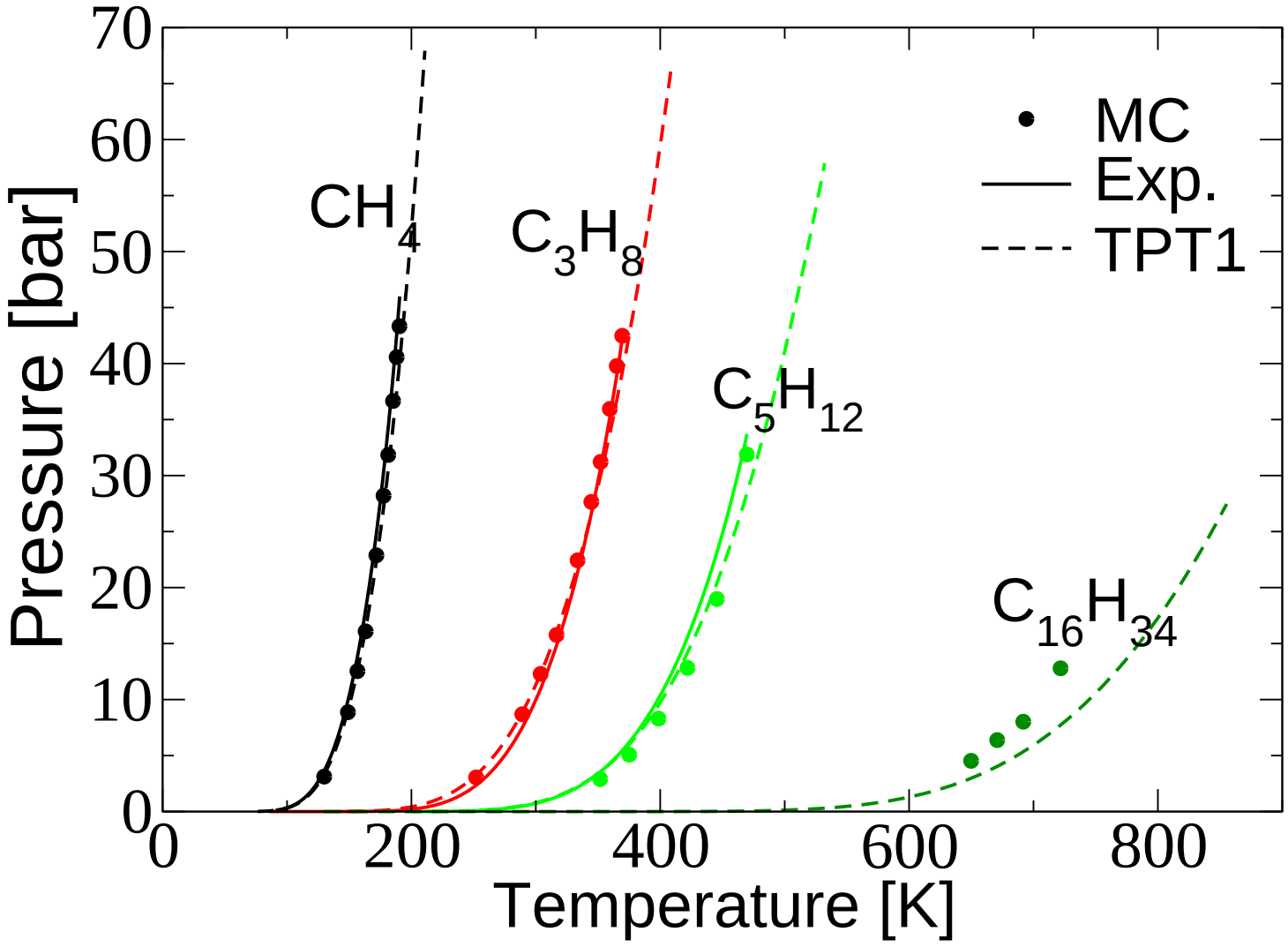


- QUADRUPOLAR EXAMPLES (CO_2). IE/DF an integral equation-density functional theory (M. Oettel)

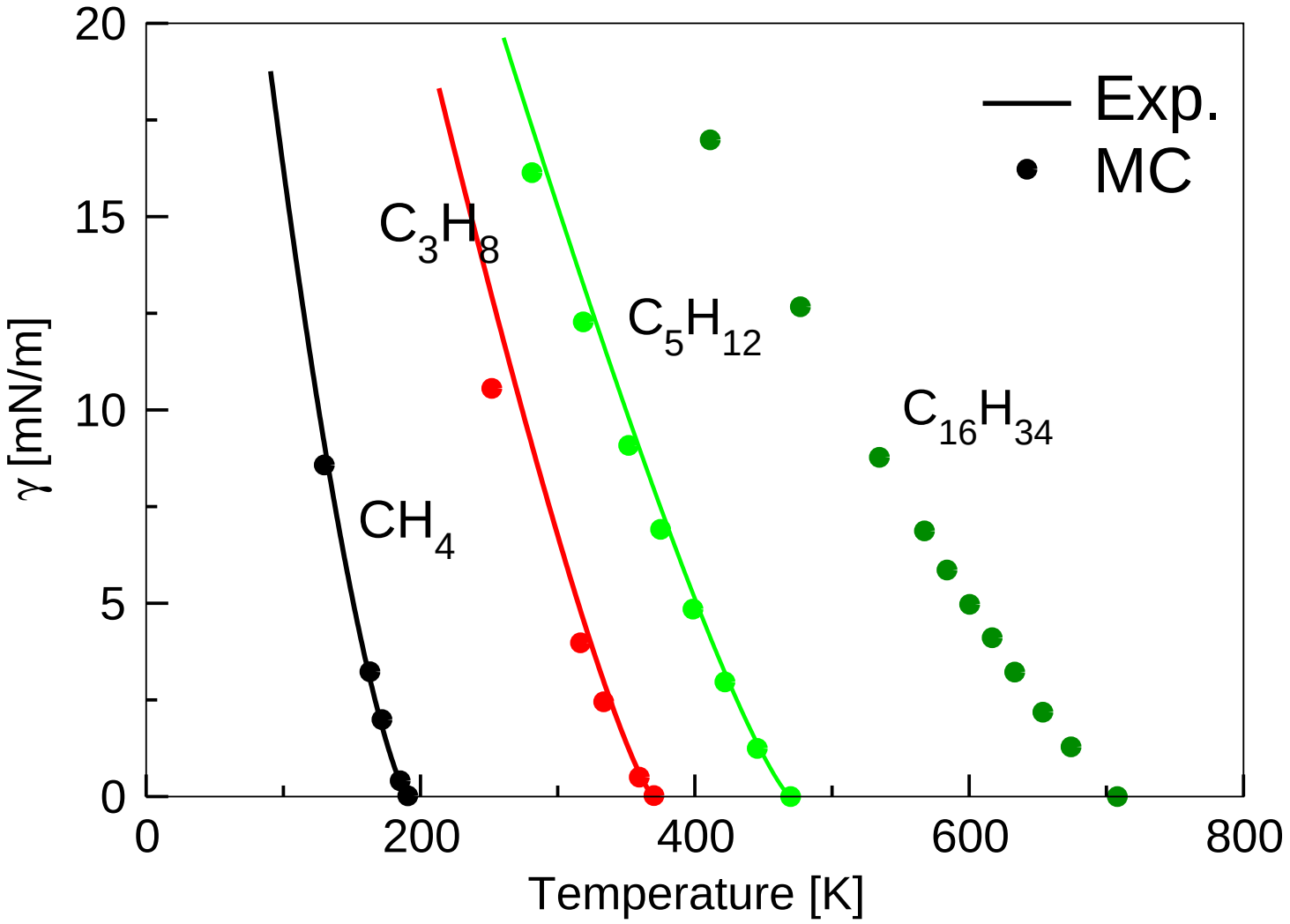
ALKANES PHASE DIAGRAM (P. Virnau)



ALKANES PHASE DIAGRAM (P. Virnau)



ALKANES PHASE DIAGRAM (P. Virnau)

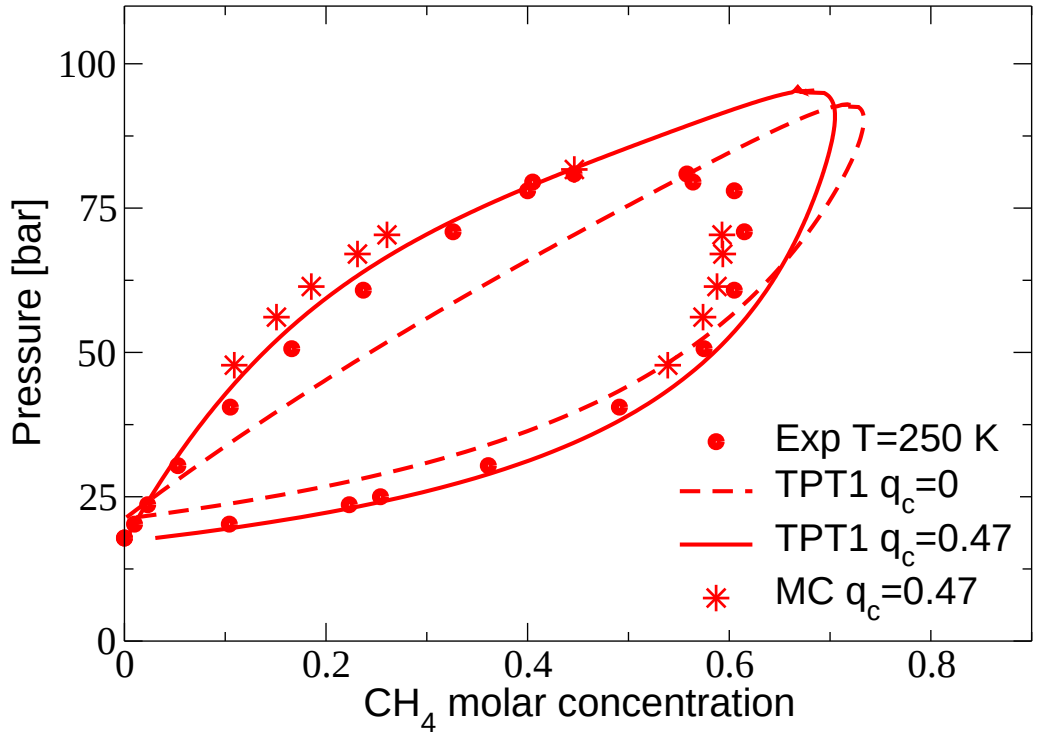


QUADRUPOLAR MIXTURES

J. Chem. Phys., accepted

MONOMER MIXTURES (CH_4 + CO_2)

using: *i*) simple LJ (q_c=0), and *ii*) q_c=0.47 (the adjusted value)

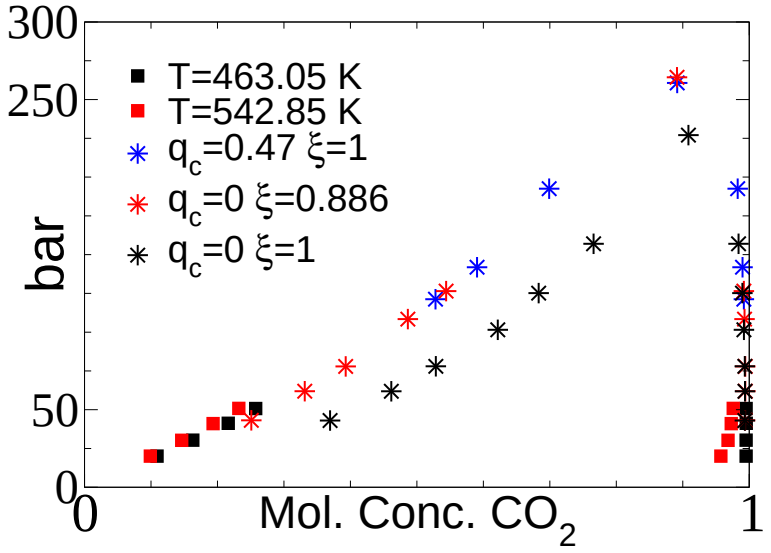


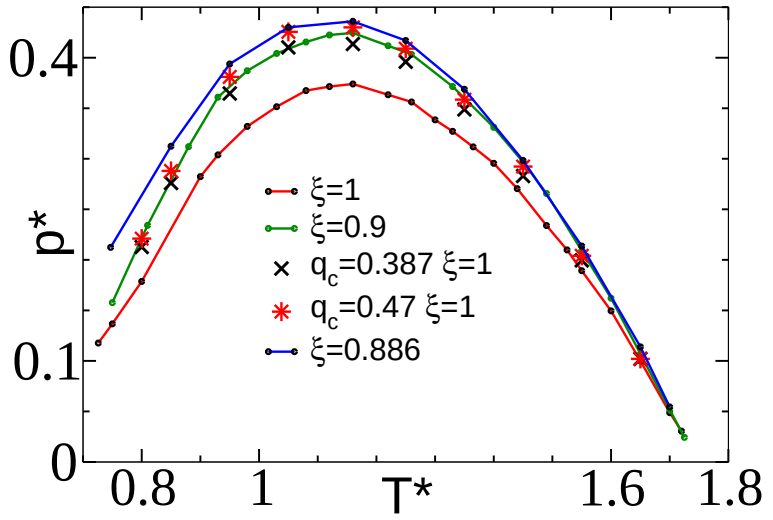
Note: mean-field theories such as TPT1-MSA overestimate the critical pressure and thus predict too large two-phase loops (can be improved by MC)

MIXTURES: $CO_2 + C_{16}H_{34}$

(P. Virnau et al. JCP **121**, 2169)

- (left) Isotherm: $\star$ are MC results (T=486 K), ■ ■ exp. results
  (right) Critical line: the full line are previous MC with $\xi \leq 1$





  - Note the nice agreement with experiments at low T

  - The results with $q_c > 0$ ($\xi = 1$) agree with previous simulations in which $\xi < 1$ has been tuned (reminder $\epsilon_{sp} = \xi\sqrt{\epsilon_s \epsilon_p}$)

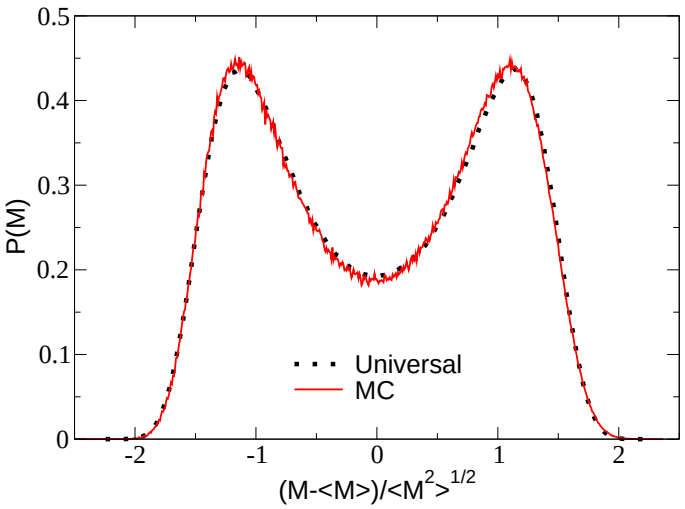
DETERMINING THE CRITICAL POINT

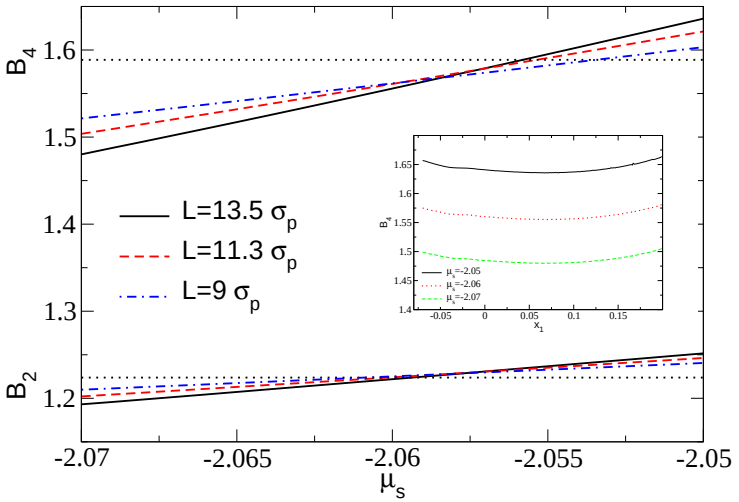
- Order parameter (neglecting pressure mixing, M. Fisher)

$$\mathcal{M} = N_p + x_1 \cdot N_s + x_2 \cdot E_{\text{tot}}$$

- x_1, x_2 (like μ_s and μ_p), tuned in order to get the best agreement between $P(\mathcal{M})$ and the universal Ising plot (N. Wilding)

- FSS analysis with x_1 determined minimizing the cumulants ($x_2 \approx 0$)



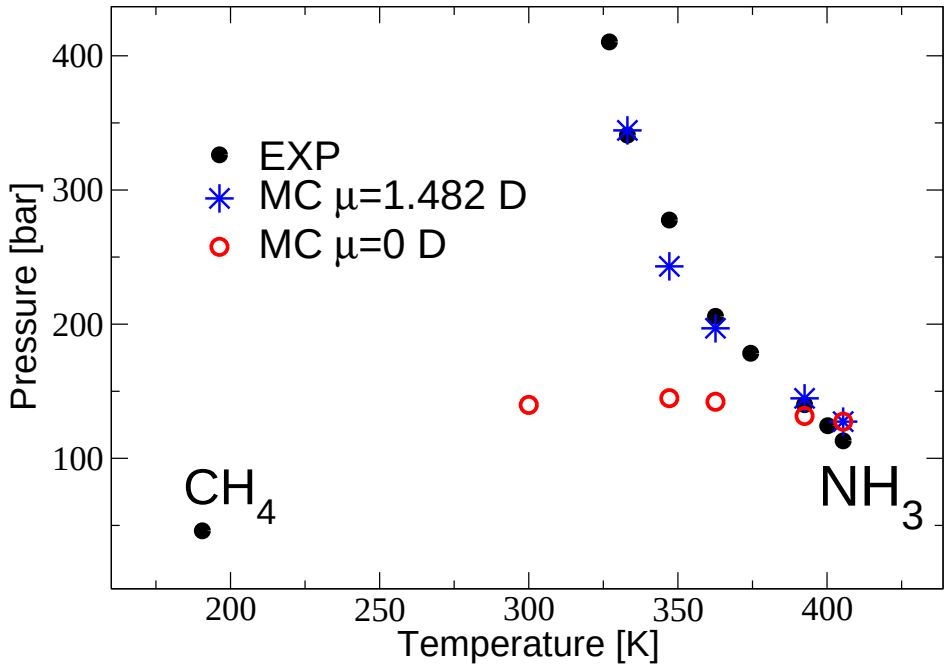


DIPOLAR MIXTURES

Phys. Chem. Chem. Phys., submitted

MONOMER MIXTURE $CH_4 + NH_3$

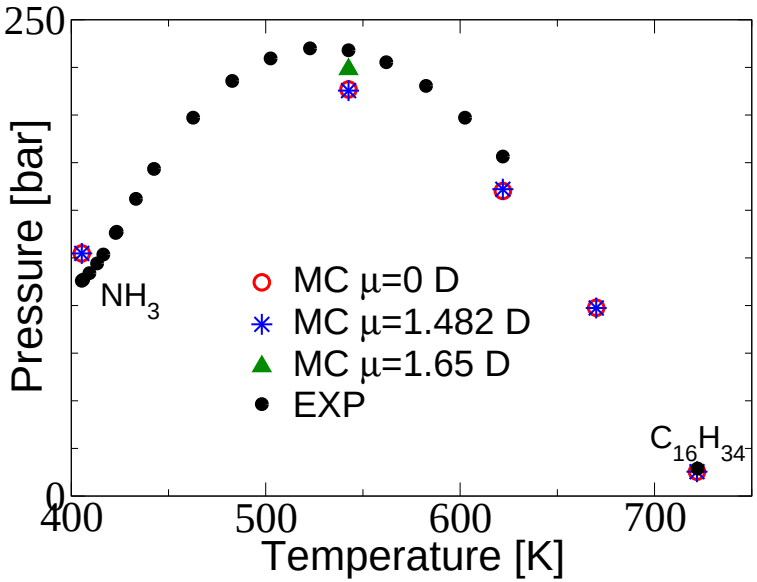
- Critical line

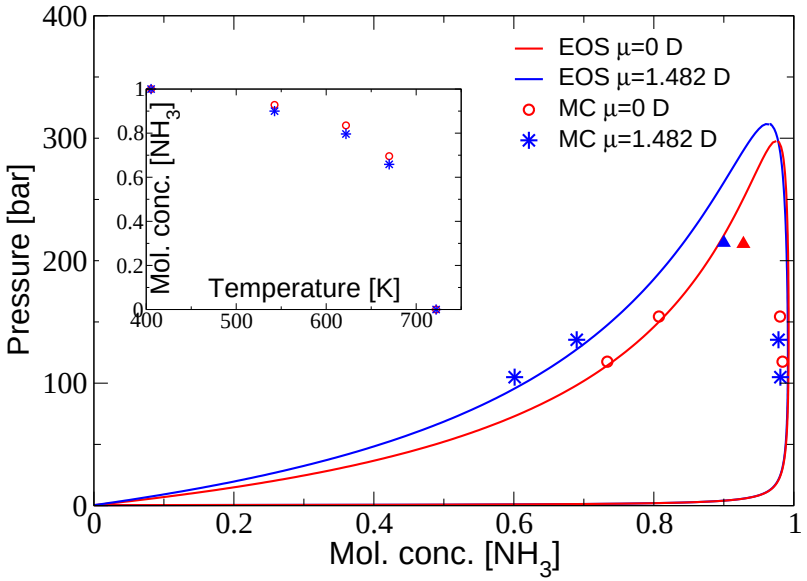


- The new model can reproduce *i*) the proper type of phase diagram and *ii*) quantitative significant data

$NH_3+C_{16}H_{34}$

- Critical line and an isothermal slice (for $NH_3+C_{16}H_{34}$)





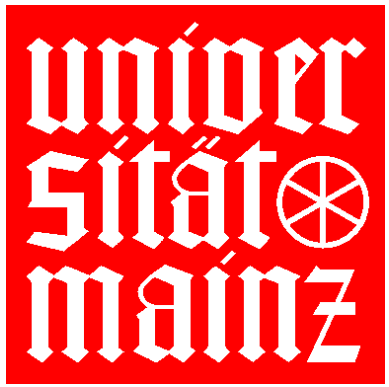
- Agreement with experiment not yet perfect

CONCLUSIONS

- We have introduced two CGm for dipolar and quadrupolar solvents
- The models are highly portable and can be immediately derived for a given solvents (without additional efforts)
- Phase diagrams of the pure substances are in good agreement with experiments (even if compared with atomistic models)
- Using simple combining rules, mixture phase diagrams are nicely in agreement with experiments
- Residual discrepancies are comparable with apolar systems ones

ACKNOWLEDGEMENTS

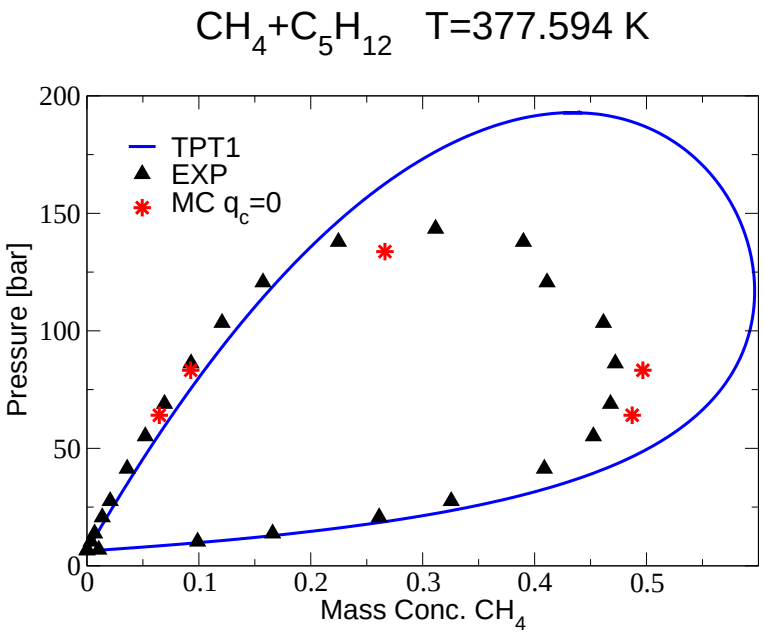
- BASF AG (Ludwigshafen) for financial support
- NIC (Jülich) and (ZDV Mainz) for CPU time
- F.Heilmann, J.Horbach, E.Müller, H.Weiss for discussions

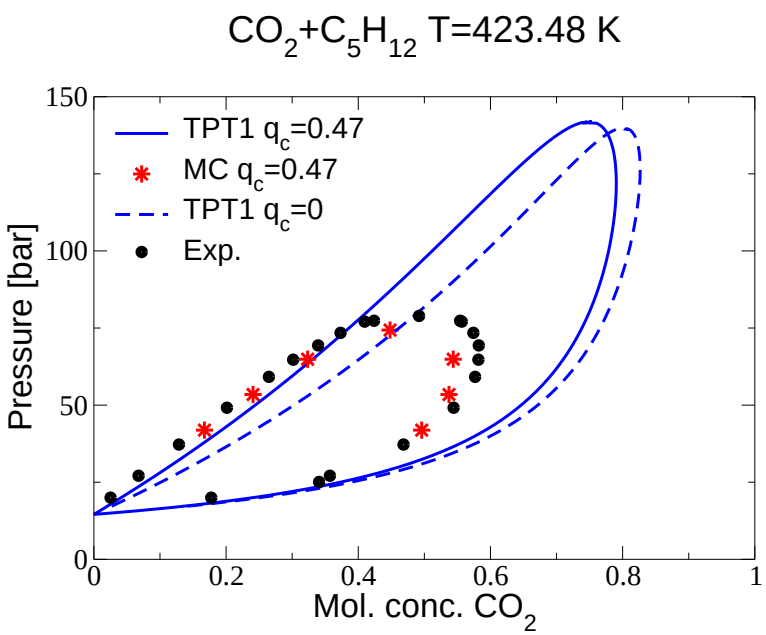


END

END

POLYMER MIXTURES: first examples

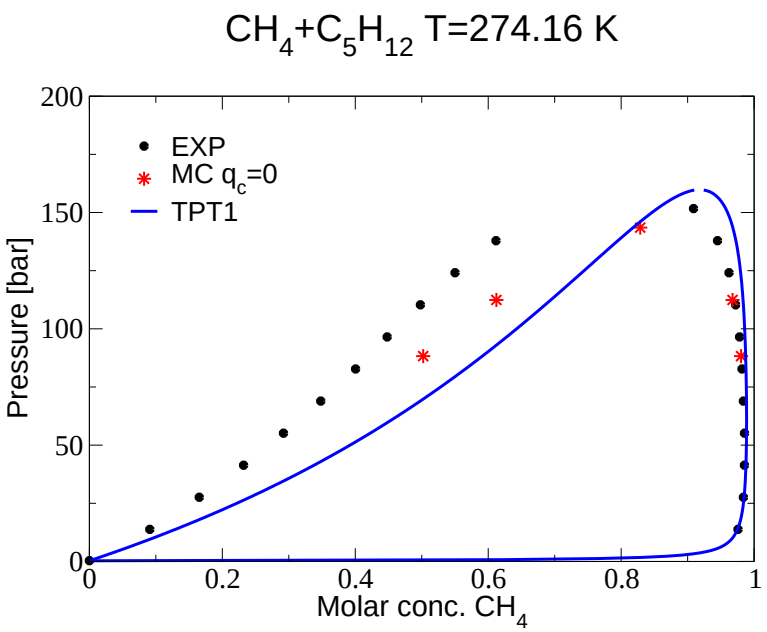


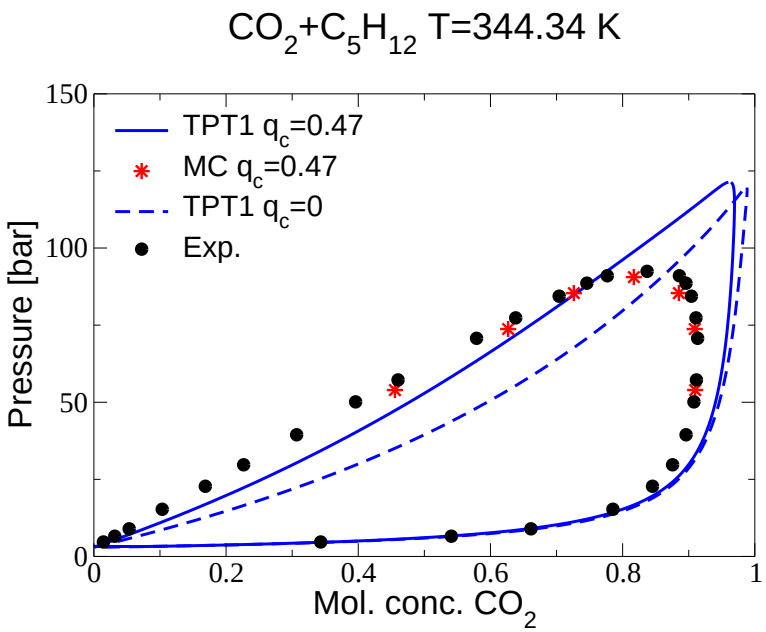


- TPT1 cannot reproduce the critical region (being a Mean-Field theory)

- At lower temperature the agreement seems to be worse (quality of the CGm?)

POLYMER MIXTURES: first examples

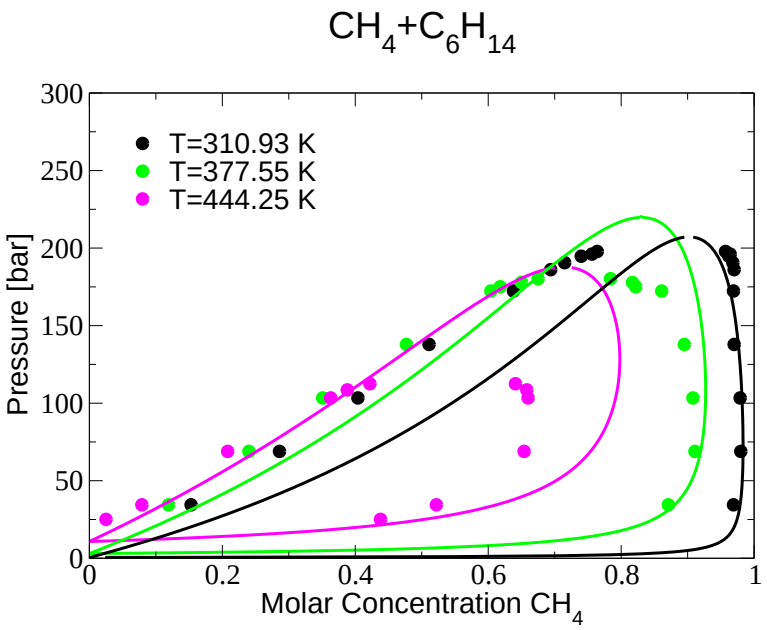


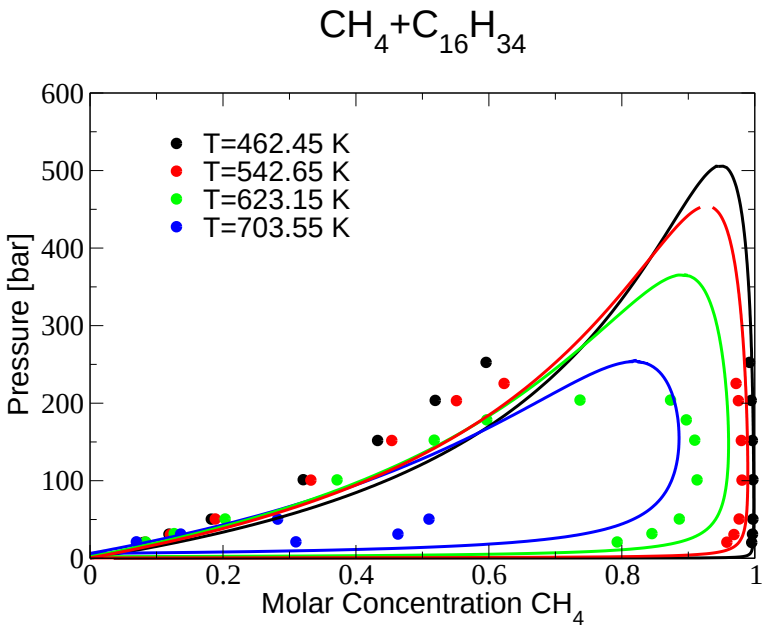


- TPT1 cannot reproduce the critical region (being a Mean-Field theory)

- At lower temperature the agreement seems to be worse (quality of the CGm?)

MIXTURES: other apolar cases TPT1

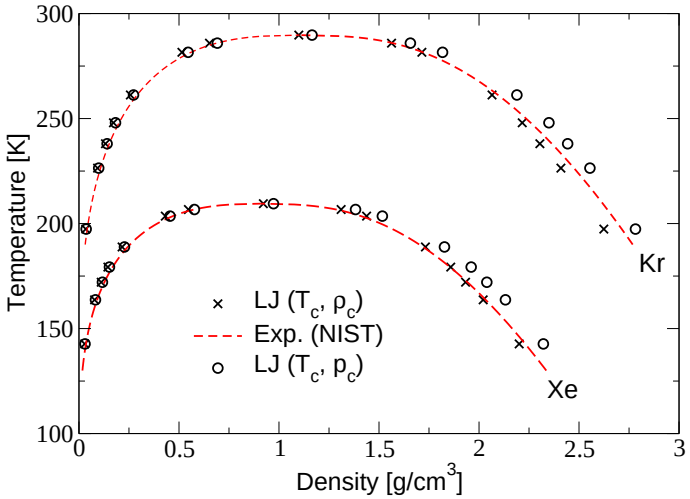


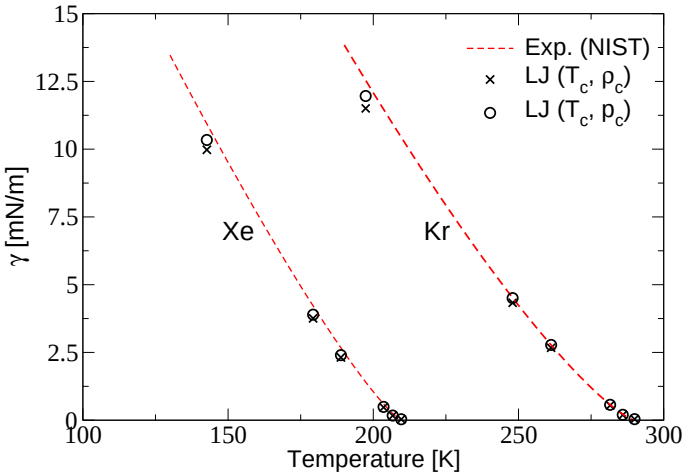


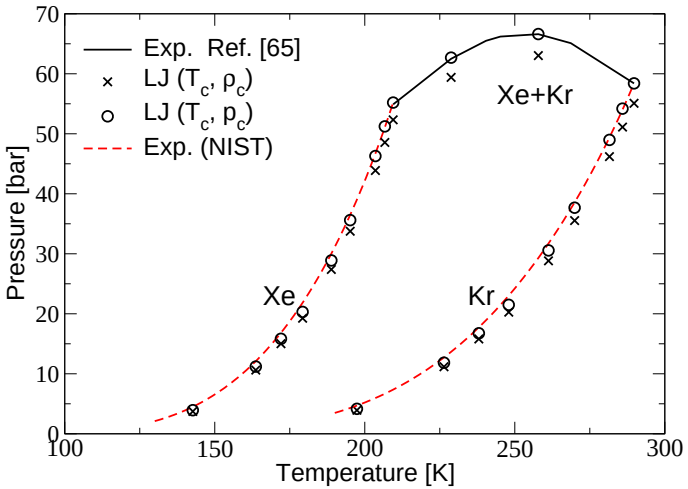
- We confirm the previous scenario in which discrepancies are bigger

- We have to investigate the low temperature (high pressure) discrepancies with MC simulations (in progress!)

A SIMPLER CASE (Xe + Kr)



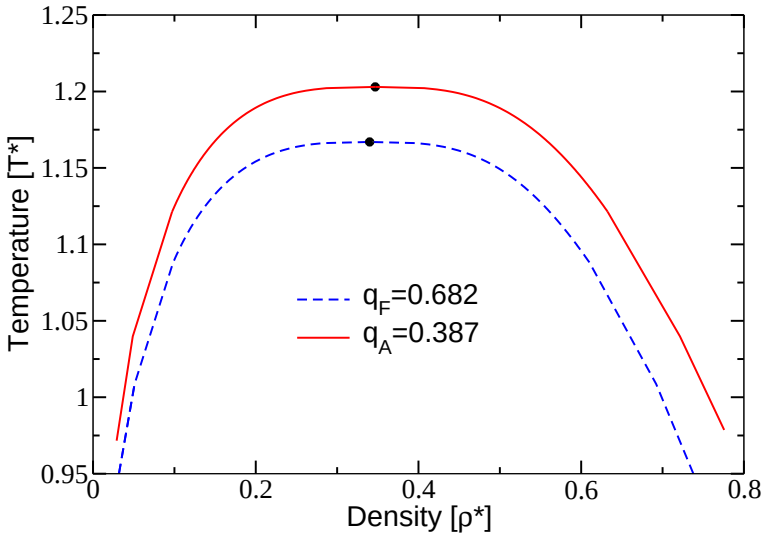


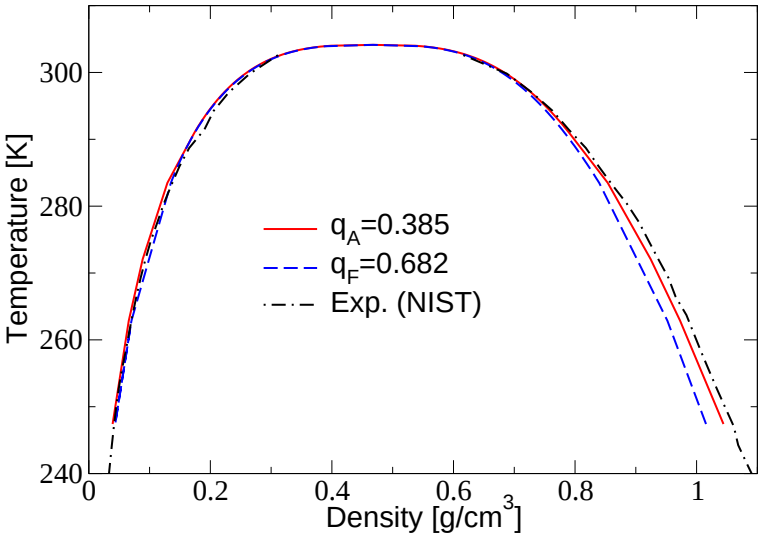


ANGLE-DEPENDENT POTENTIALS

Does the not-averaged model work even better? No (B. M. Mognetti et al. Phys. Rev. E **77**, 041506)

- (left) Same ϵ_s, σ_s, and Q





- (right) Same T_c, ρ_c, and Q

$\Rightarrow$ We learn *i*) the importance of fixing the CP and *ii*) we are encouraged to use the averaged model

TPT1-MSA EQUATION OF STATES

- Strategy: to know how good is the EOS and where can be used

- Previous project: TPT1-MSA (L. G. MacDowell et al. JCP **113**, 419; JCP **117**, 6360)

  – Potential mapped onto two Yukawa potentials [$\mathcal{Y}_1(r)$, $\mathcal{Y}_2$(r)] which allow us to compute $g(r)$ and the thermodynamics (Y. Tang et al. JCP **99**, 9828; FPE **134**, 21)

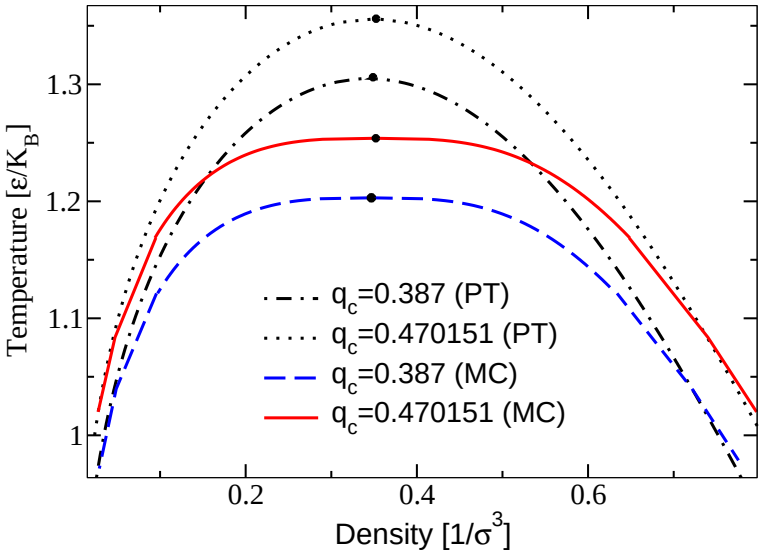
- We generalize the previous considerations using two more Yukawa tails to fit the quadrupolar part of the potential

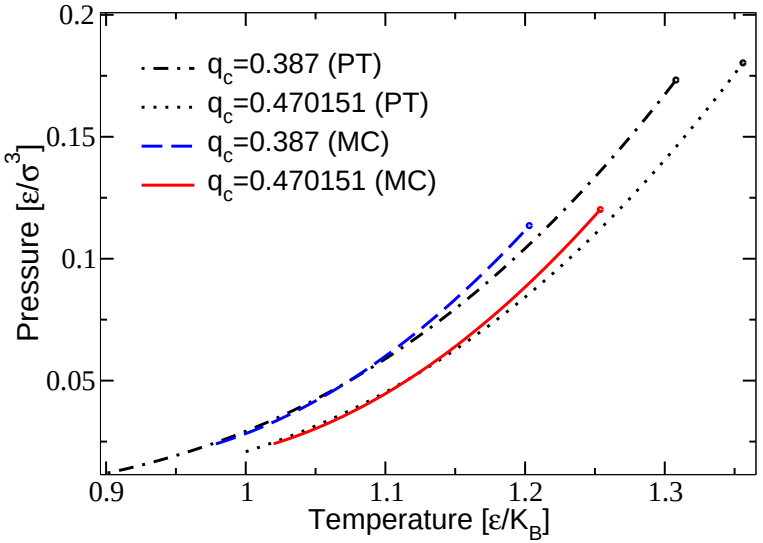
$$V_{q_c}^{(\mathrm{A})}(r) = \begin{cases} d_{\mathrm{HS}}(q_c, T) & , \quad r < r_0 \\ \Big(\mathcal{Y}_1(r) + \mathcal{Y}_2(r)\Big) - \frac{7}{20} q_c \frac{T_c}{T} \Big(\mathcal{Y}_3(r) + \mathcal{Y}_4(r)\Big) & , \quad r > r_0 \end{cases}$$

plus proper one fluid approximation for q_c in the mixtures

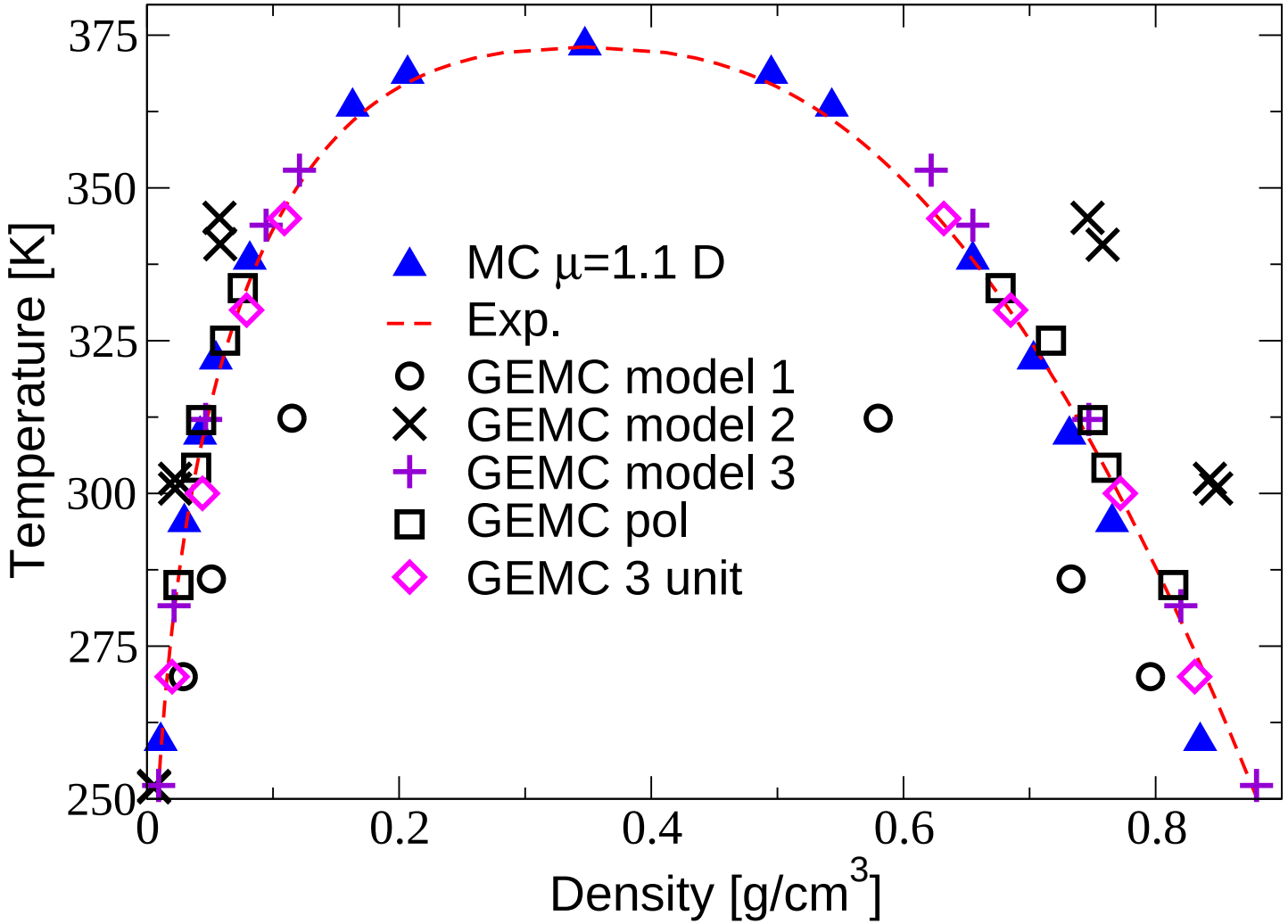
MC vs. MSA-TPT1 EOS

Pure substances. Nice agreement far from the critical point.

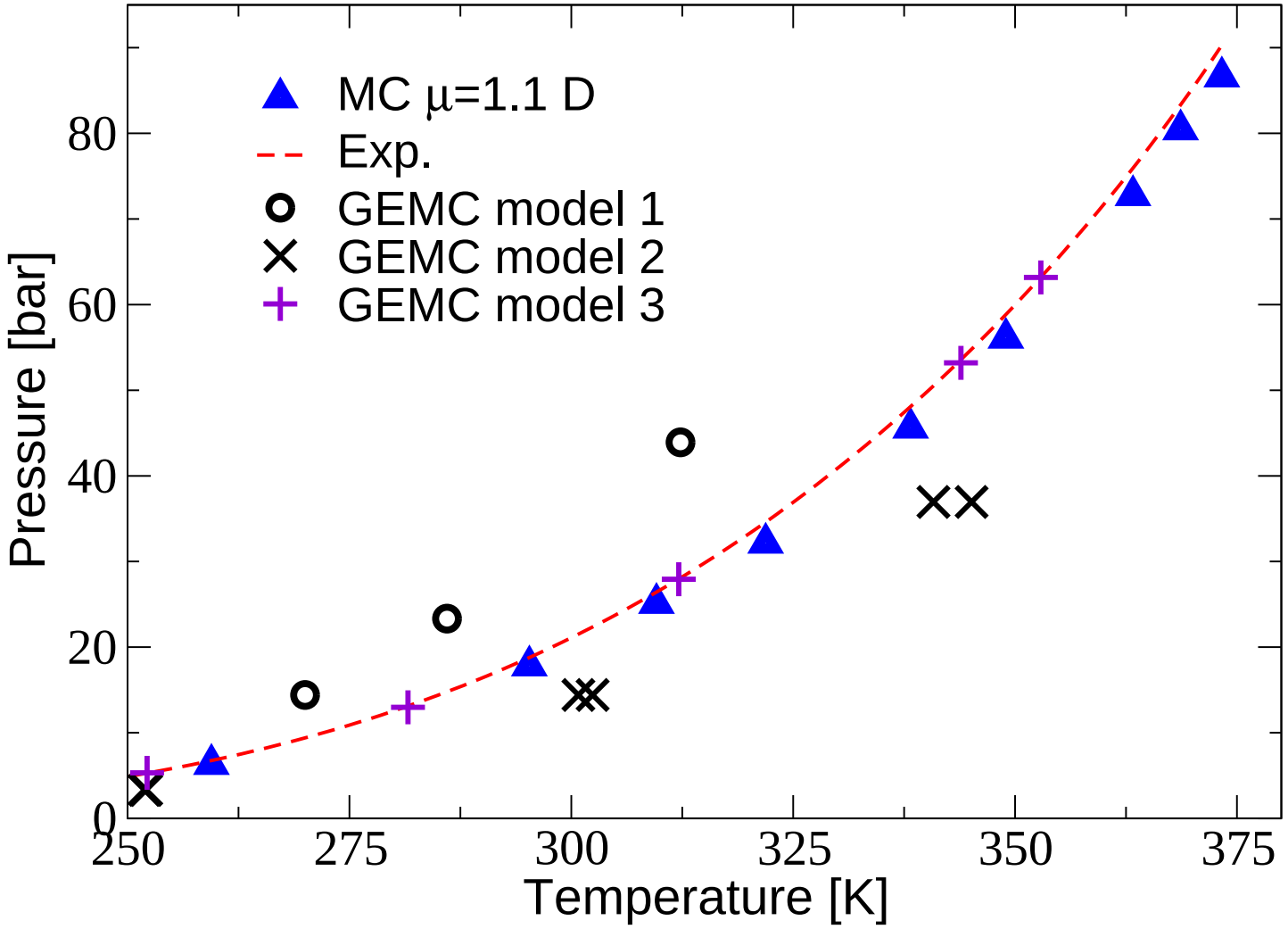




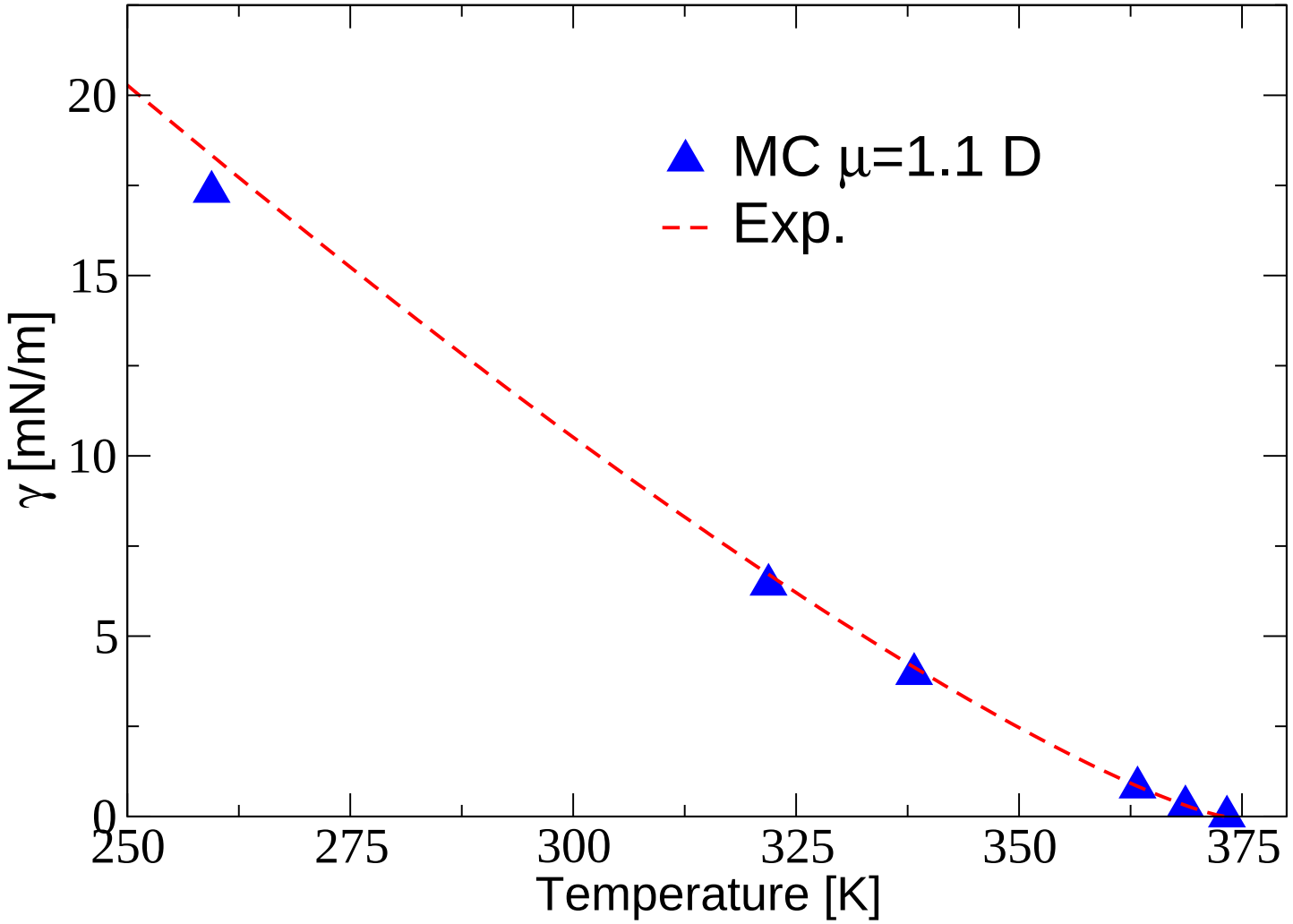
H_2S: μ_{exp}=1.1D (λ_c=0.023)



H_2S: μ_{exp}=1.1D (λ_c=0.023)



H_2S: μ_{exp}=1.1D (λ_c=0.023)



REMAPPING $V^{(A,D)}$ in V^{LJ}

- $V^{(\mathrm{A,D})} = 4\epsilon_s[(\frac{\sigma_s}{r})^{12} - (1+\lambda)(\frac{\sigma_s}{r})^{6}] = 4\tilde{\epsilon}_s[(\frac{\tilde{\sigma}_s}{r})^{12} - (\frac{\tilde{\sigma}_s}{r})^{6}]$

  $\tilde{\epsilon}_s = \epsilon_s\,(1+\lambda_c T_c/T)^2 \qquad\qquad \tilde{\sigma}_s{}^6 = \sigma_s{}^6/(1+\lambda_c T_c/T)$

  - We cut and shift (at $2{\cdot}\tilde{\sigma}_s{}^{7/6}$) the effective LJ $\Rightarrow$ ϵ_s and σ_s rescaled by proper known factors

- Having a set of simulation results for the cut and shifted LJ potential $\{T_i^*,\, \rho_{i,g}^*,\, \rho_{i,l}^*,\, p_i^*,\, \gamma_i^*\}$ (and knowing ϵ_s and σ_s)

  - The physical temperature T_i must satisfy the following relation

$$T_i = \frac{\tilde{\epsilon}_s T_i^*}{k_B} = \frac{T_i^*}{k_B}\epsilon_s(1+\lambda_c\frac{T_c}{T_i})^2$$

  - Knowing T_i one can compute $\tilde{\epsilon}_s$ and $\tilde{\sigma}_s$ and mapping all the simulation quantities in physical unit (using standard formula)

FIXING THE CGm, DIPOLAR MODEL

- At the critical point $T = T_c$ the mapped LJ potential must be equal to the LJ interaction of the apolar model $\tilde{\epsilon}_s(T_c) = \epsilon_0$ $\tilde{\sigma}_s(T_c) = \sigma_0$

- Using the mapping formula $\epsilon_s \to \tilde{\epsilon}_s$, $\sigma_s \to \tilde{\sigma}_s$ at the critical point

$$\frac{\epsilon_s}{\epsilon_0} = \frac{1}{(1+\lambda_c)^2} \qquad \frac{{\sigma_s}^6}{{\sigma_0}^6} = (1+\lambda_c)$$

and using the expression $\lambda_c = \lambda_{c0}(\epsilon_0/\epsilon_s)(\sigma_0/\sigma_s)^6$ we finally conclude

$$\frac{\epsilon_s}{\epsilon_0} = (1-\lambda_{c0})^2 \qquad \frac{{\sigma_s}^6}{{\sigma_0}^6} = \frac{1}{(1-\lambda_{c0})} \qquad \lambda_c = \frac{\lambda_{c0}}{1-\lambda_{c0}}$$

Notice that for $\lambda_{c0} \to 1$ the mechanism break down (also in the quadrupolar case?)

- Alternatively use $T_c(\lambda_c)/T_c(0) = (1+\lambda_c)^2$ and $\rho_c(\lambda_c)/\rho_c(0) = \sqrt{1+\lambda_c}$ in the previous slide

ON THE USE OF MAGNIFIED VALUES FOR μ

- Is it only our problem? No

	μ_{phys}/D	μ_{opt}/D our CGm	μ_{opt}/D SM FPE **220**, 1
NH_3	1.482	1.482	-
H_2S	1.1	1.1	1.64
CCl_2O	1.17	2	3.035
N_2O	0.166	1.25	1.76
C_6H_5Cl	1.7	3.5	-

- We use optimal dipolar moments magnified by the same order of magnitude of the SM potential

- Possible explanations
  - Magnification related to polarizable effects
  - Point-like approximation is not good

MONOMER MIXTURES (CH_4 + C_6H_6)

using: *i*) simple LJ (Q=0), *ii*) the experimental value Q=12 DÅ, and *iii*) the adjusted one Q=13 DÅ