

## COSMO-based models: fundamentals and tools

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May, 2024

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## The Complexity of Liquid Mixtures\*

- The precise description of even nonelectrolyte liquids at low pressures remains an enduring challenge
- Polar compounds interact differently than nonpolar compounds
- Associating compounds introduce another layer of complexity
- With aqueous mixtures, the intricacy further intensifies

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## Classical activity coefficient models

Wilson: Grant M. Wilson. “Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing”. In: *J. Am. Chem. Soc.* 86.2 (Jan. 1964), pp. 127–130

NRTL: Henri Renon and JM Prausnitz. “Local compositions in thermodynamic excess functions for liquid mixtures”. In: *AIChE J.* 14.1 (1968), pp. 135–144

UNIQUAC: Denis S. Abrams and John M Prausnitz. “Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems”. In: *AIChE J.* 21.1 (Jan. 1975), pp. 116–128

UNIFAC: Aage Fredenslund, Russell L. Jones, and John M. Prausnitz. “Group-contribution estimation of activity coefficients in nonideal liquid mixtures”. In: *AIChE J.* 21.6 (Nov. 1975), pp. 1086–1099



## Classical activity coefficient models and quasi-chemical theory

- What is less known is that these common semi-empirical models used today (Wilson, NRTL, UNIQUAC, and UNIFAC) originate from the *quasi-chemical* treatment of Guggenheim\*
- The quasi-chemical treatment assumes molecular interactions are pairwise and can be seen as chemical reactions:



- An then, as usual:

$$\frac{[AB]^2}{[AA][BB]} = K(T) = \exp\left(\frac{-2w}{zkT}\right)$$

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## More about the quasi-chemical theory

- For each pair of compounds there would be a nonlinear equation:

$$\frac{[AB]^2}{[AA][BB]} = K(T) = \exp\left(\frac{-2w}{zkT}\right)$$

- These nonlinear equations have to be combined with mass balance equations to solve for all quantities
- There is need to define a coordination number  $z$
- The interaction energy  $w$  has to be fitted with mixture data
- The method was later extended to functional groups and even formulated in terms of surface area fractions in C Panayiotou and J.H. Vera. "The quasi-chemical approach for non-randomness in liquid mixtures. Expressions for local surfaces and local compositions with an application to polymer solutions". In: *Fluid Phase Equilib.* 5.1-2 (Jan. 1980), pp. 55–80





## More about the quasi-chemical theory

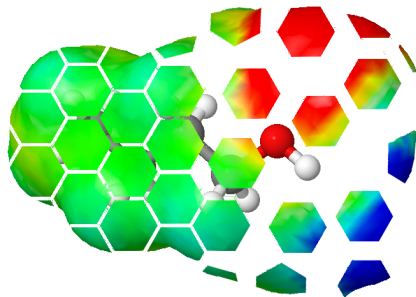
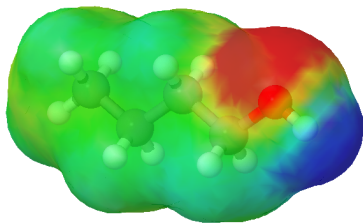
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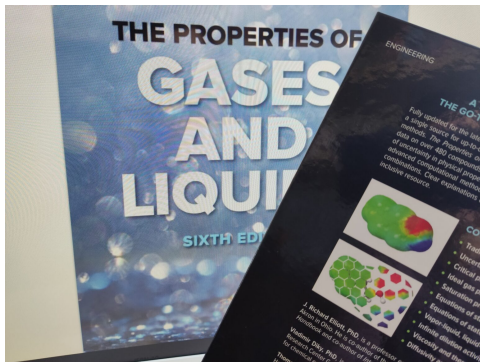
## Quasi-chemical theory with small segments\*



- The quasi-chemical equations can be applied for the interaction between small surface segments: this results in the COSMO-RS or COSMO-SAC models
- \*Rafael de P. Soares and Paula B. Staudt. "Beyond activity coefficients with pairwise interacting surface (COSMO-type) models". In: *Fluid Phase Equilib.* 564 (2023)



## Quasi-chemical theory equivalence with COSMO-RS/SAC

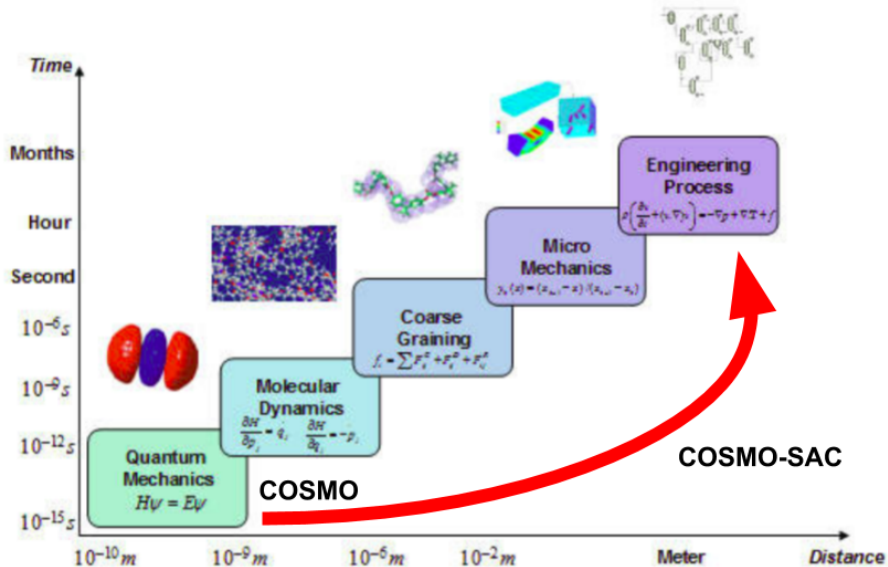


- In J.R. Elliott et al. *The Properties of Gases and Liquids, Sixth Edition*. McGraw-Hill Education, 2023, COSMO-RS/SAC models as referred as Small Segment QuasiChemical Theory (SS-QCT), deeming them “essentially equivalent”
- In our recent work we have used the term “modern quasi-chemical”\*

\*Rafael de P. Soares and Paula B. Staudt. “Unraveling order and entropy with modern quasi-chemical models”. In: *Fluid Phase Equilib.* 583 (2024), p. 114113

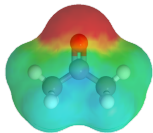
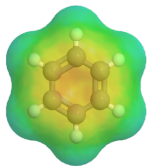


# Multi-scale modelling and COSMO-based models



# COSMO method (solutes alone) vs COSMO-RS/SAC

- The COSMO\* method was originally developed for the computation of solvation effects
- Belongs to the class of dielectric continuum models



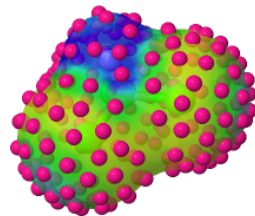
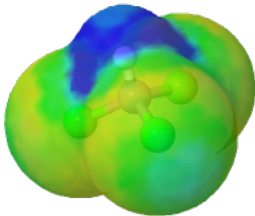
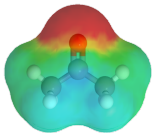
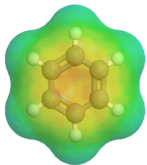
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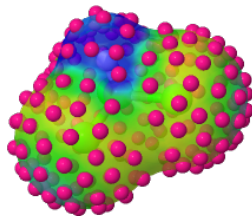
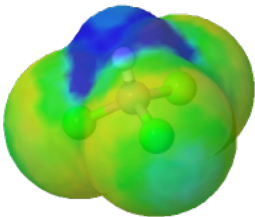
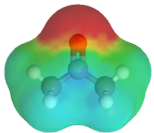
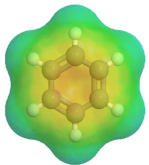


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- Induced charge densities are computed by quantum chemistry packages (time consuming) and then stored in a database (e.g. LVPP sigma-profile database<sup>†</sup> <http://github.com/lvpp/sigma>)



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# JCOSMO and LVPP sigma-profile database

The screenshot displays the JCSMO software interface. The main window is titled "JCSMO" and has a menu bar with "File" and "Help". Below the menu bar is a "Configuration" section with a "Model" dropdown set to "COSMO-SAC-HB2 (GAMESS)". A list of configuration parameters is visible on the left, including "Sigma profile", "Energetic term", and "Charts".

In the center, there is a "Selected Compounds" table:

Compound	Multiplier
ACETONE	1.0
CHLOROFORM	1.0

To the right of the table is a search box containing "chlorof" and a list of search results: "CHLOROFORM", "DICHLOROFLUOROMETHANE", "ETHYL\_CHLOROFORMATE", and "TRICHLOROFLUOROMETHANE". Buttons for "Add", "Remove", "View Surfaces", and "View Pie Plot" are located to the right of the search results.

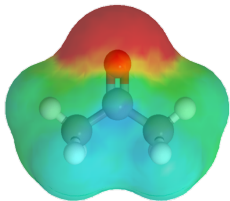
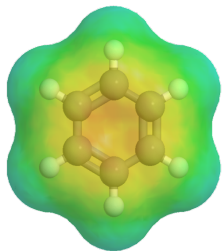
A "Surface Viewer" window is overlaid on the main interface. It contains two 3D surface plots. The left plot is for "ACETONE (85.95 Å<sup>3</sup>, 102.04 Å<sup>2</sup>)" and the right plot is for "CHLOROFORM (104.67 Å<sup>3</sup>, 116.11 Å<sup>2</sup>)". Below the plots is a slider for "Opacity" ranging from "Opaque" to "Translucent". A "Close" button is located at the bottom right of the window. At the bottom of the Surface Viewer window, there is a formula:  $\ln \gamma_1^w : \ln \gamma_2^w \mid \gamma_1^w : \gamma_2^w$ .

On the right side of the main interface, there is a "Temp. [K]" input field with the value "298" and a "Calculate" button. Below this is a large empty plot area.

Download at <https://ufrgs.br/lvpp>



# COSMO-RS – Surface contacting theory (mixtures)



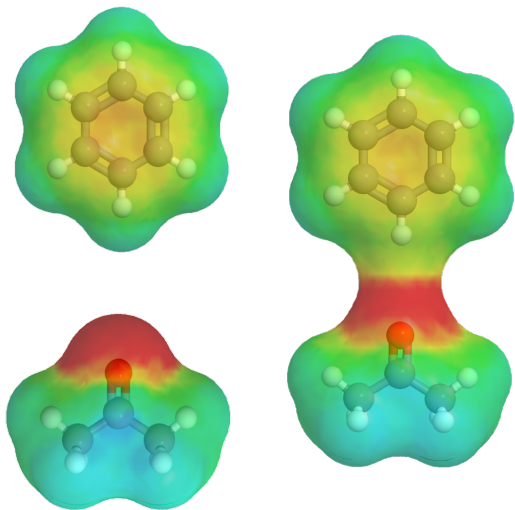
- In the COSMO-RS\* methods we rely on COSMO computations with the molecules surrounded by a **perfect conductor**
- Based on these *pure* substance computations, the mixture behavior is predicted ( $\gamma_i$ ,  $\mu_i$ )
- The COSMO-SAC† formulation follows the same idea
- For every contact between segments  $m$  and  $n$  there is an energy change  $E_{m,n}$
- There are many possible contacts in solution

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\*Andreas Klamt. In: *The J. of Phys. Chem.* 99.7 (1995), pp. 2224–2235

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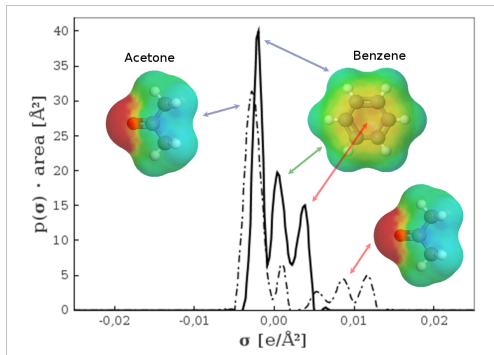


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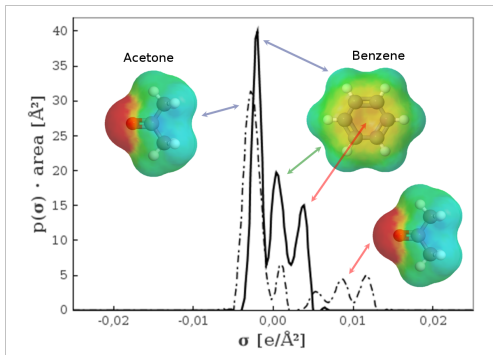
# Sigma profile – $p(\sigma)$



- For a statistical thermodynamics treatment (without using MD or MC), the 3D apparent surface charges are projected into a simple histogram
- These **pure compound** distributions, known as *sigma profiles* –  $p(\sigma)$ , are the basis for computing  $\gamma_i$  or  $\mu_i$  in **mixture**

- “It is always desirable to express the properties of a solution in terms that can be calculated completely from the properties of the pure components.” – J. M. Prausnitz. *Molecular thermodynamics of fluid-phase equilibria*. Third. Prentice-Hall, 1999.

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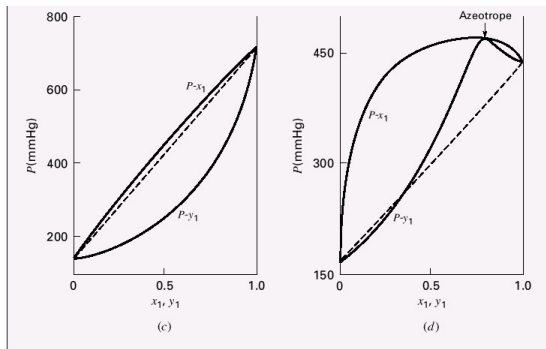
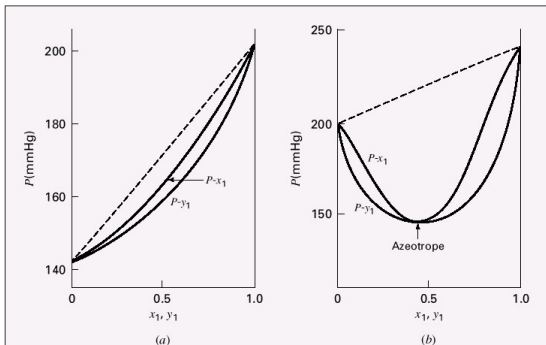


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# Why some mixtures behave so differently?

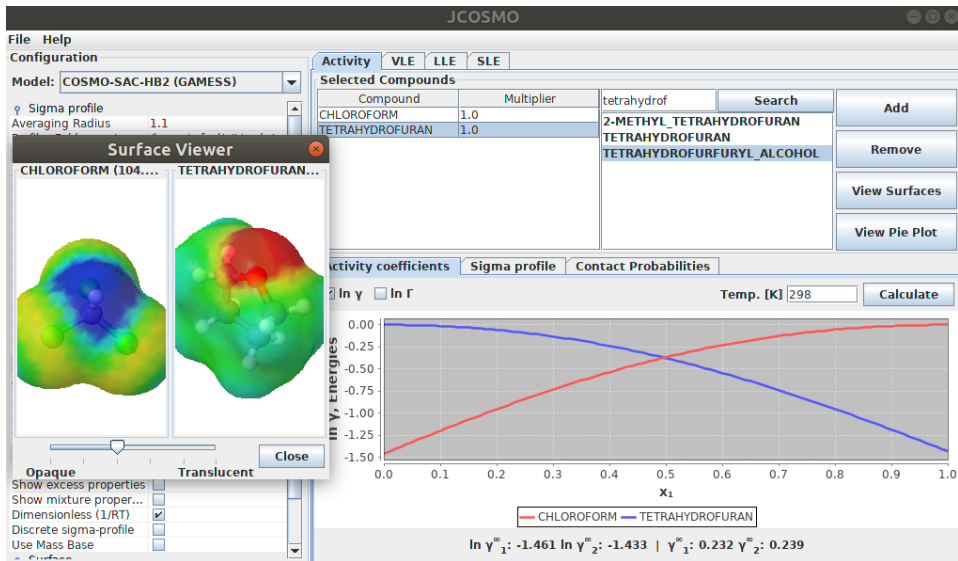
- Why some molecules *like* so much each other?
- Some seem to not care and some actually *dislike* each other.



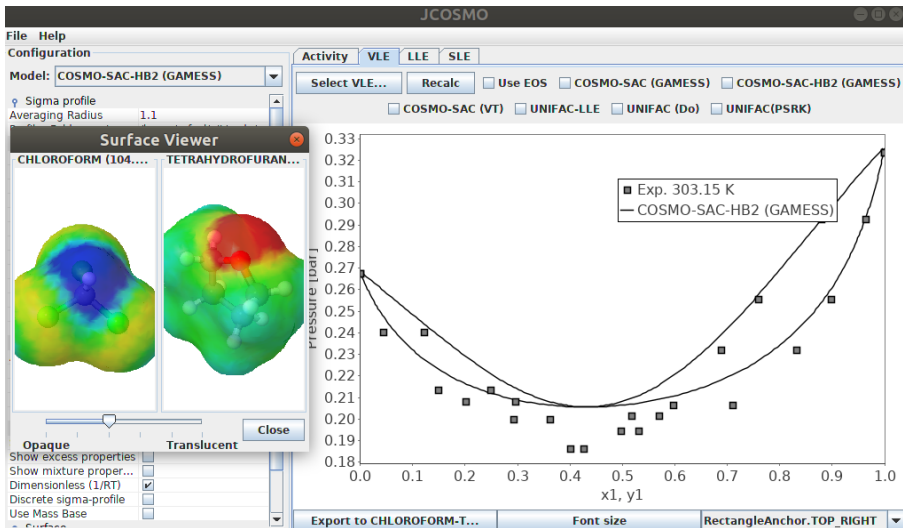
**Figure 10.8:**  $P_{xy}$  diagrams at constant  $T$ : (a) tetrahydrofuran(1)/carbon tetrachloride(2) at 30°C; (b) chloroform(1)/tetrahydrofuran(2) at 30°C; (c) furan(1)/carbon tetrachloride(2) at 30°C; (d) ethanol(1)/toluene(2) at 65°C. Dashed lines:  $P_x$  relation for Raoult's law.

Figure from J.M. Smith, H.C. Van Ness, and M. Abbott. *Introduction to Chemical Engineering Thermodynamics*. McGraw-Hill Education, 2005. ISBN: 9780073104454.

# Example of negative deviation from Raoult's law

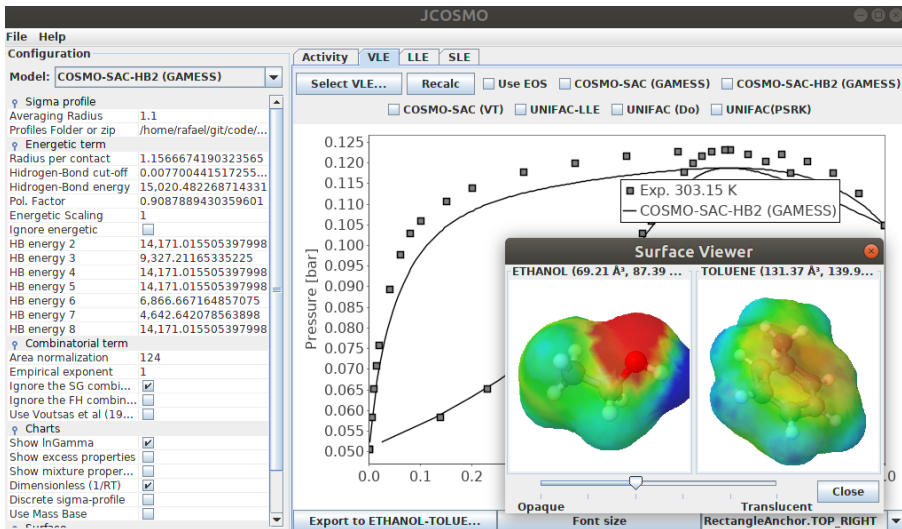


# Example of negative deviations from Raoult's law



Experimental data from Horacio N. Sólamo and Ana C. Gomez Marigliano. In: *J. of Sol. Chem.* 22.10 (Oct. 1993), pp. 951–962

# Example of positive deviations from Raoult's law



Experimental data from Stanley M. Byer, Richard E. Gibbs, and Hendrick C. Van Ness. In: *AIChE Journal* 19.2 (1973), pp. 245–251



## Tools for creation of apparent surface charge densities

- **Avogadro**: an advanced molecule editor and visualizer, <https://avogadro.cc/>
- **GAMESS**: General Atomic and Molecular Electronic Structure System, <https://www.msg.chem.iastate.edu/gamess/>
- **COSMO patch for GAMESS**: procedure to enable sigma-profile outputs with GAMESS, .gout files, <https://github.com/lvpp/sigma/tree/master/GAMESS>
- **Sigma-LVPP**: LVPP sigma-profile database, <https://github.com/lvpp/sigma>



## The Goal of Statistical Thermodynamics

- The goal of statistical thermodynamics is to predict macroscopic properties using microscopic (molecular) information
- For instance, the pressure we measure is an average over many, many molecular collisions
- We could calculate all trajectories (position and velocity) of each molecule in the system and derive any macroscopic property
- However, we cannot compute the  $10^{24}$  molecule-wall collisions per second for each square centimeter of surface for a gas at standard conditions\*
- Clearly, we need to simplify that ...

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\*Stanley I. Sandler. *An Introduction to Applied Statistical Thermodynamics*. John Wiley & Sons, 2010, p. 360. ISBN: 9780470913475



## The Postulates of Statistical Mechanics\*

- The first postulate:

**All microstates that have the same energy are equally probable**, given they have the same number of particles and system volume

- The second postulate:

The (long) time average of **any mechanical property in a real macroscopic system is equal to the average value of that property over all the microscopic states** of the system, each state weighted with its probability of occurrence, provided that the microscopic states replicate the thermodynamic state and environment of the actual system.

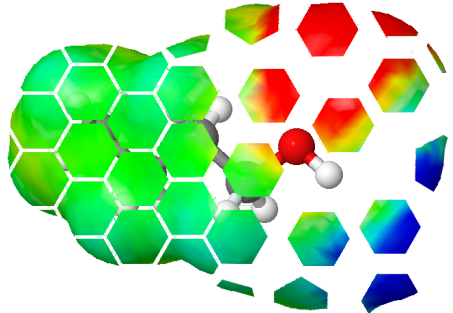
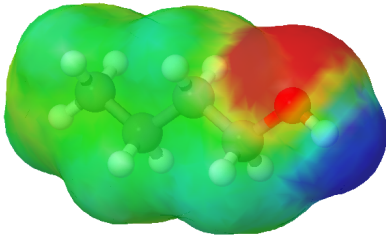
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## Pairwise Interacting Surface Segment Models

- Each molecule consists in a molecular shaped cavity
- These cavities consist in many *segments* of identical area  $Q_{eff}^*$

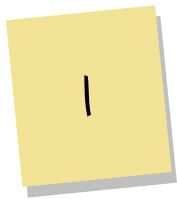


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## An extremely Simple Fluid - The Sticky Fluid

- Assume we have a fluid consisting in 2 *sticky* (post-it) notes

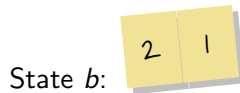
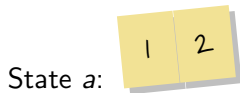


- In this fluid the *notes* don't exist alone, only in pairs
- If order is important, how many possible states do we have?



## An extremely Simple Fluid - The Sticky Fluid

- For two segments,  $N = 2$ , and the number of pairs per state is  $N_p = 1$



- What should be the probability of finding the system on each of these states?



## The Boltzmann Energy Distribution

- If all states of equal energy should be equally probable, what should be the probabilities of states of different energy?
- It is possible to show that the probability of occurrence of a microstate  $i$  with energy  $E_i$  is\*:

$$p_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{\Psi_i}{\mathcal{Z}(N, V, \beta)} \quad (1)$$

where  $j$  is over all possible states;  $\mathcal{Z}(N, V, \beta)$  is the canonical partition function, with  $\beta = 1/kT$  (positive) so that a state of higher energy has a lower probability of occurrence; and  $\Psi_i$  is the Boltzmann factor of the state  $i$ .

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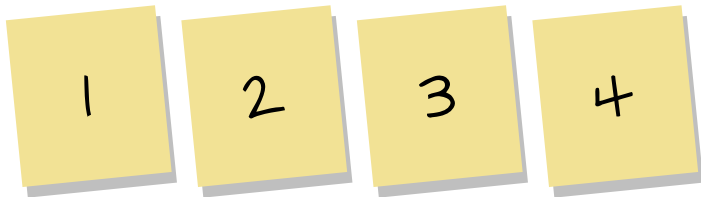
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## Sticky Fluid Probabilities and Internal Energy

- Back to our sticky fluid, *segments* don't exist alone, only in pairs
- For the case we have 4 segments,  $N = 4$



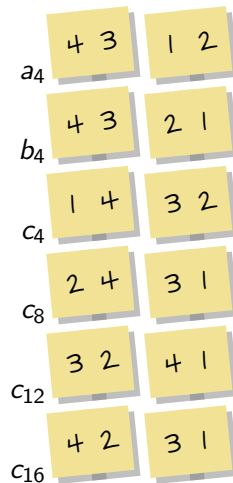
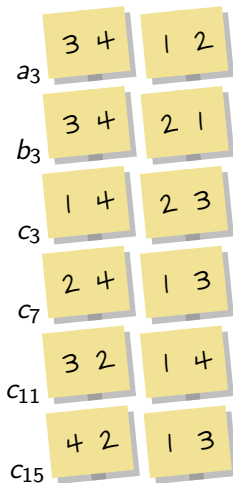
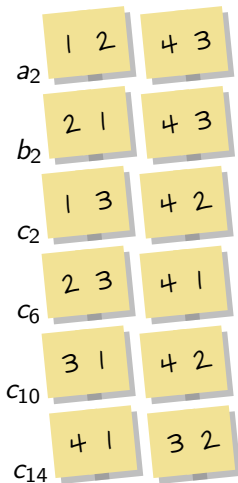
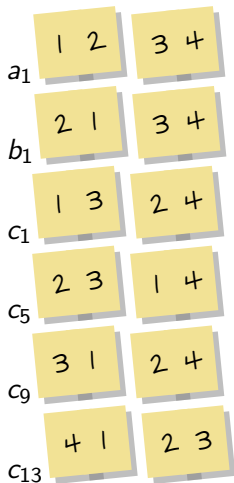
- The number of pairs per state is  $N_p = 2$ , how many different states should we have?

Check <https://github.com/lvpp/pysac/blob/main/notebook/microstates.ipynb>.



# Sticky Fluid, listing all states

- For  $N = 4$ , we have  $N! = 4! = 24$  different states with two pairs each,  $N_p = 2$



## Sticky Fluid Probabilities and Internal Energy

- List the  $N! = 24$  different states in a spreadsheet
- Assume  $\beta = 1$  and that the energy of pair 1-2 is  $u_{12} = 1 \cdot 2 = 2$ , of pair 3-4 is  $u_{34} = 3 \cdot 4 = 12$  and so on
- For each state, compute the total energy (sum of the energy formation for the two pairs), Boltzmann factor, and probability of occurrence (or fraction of time)
- What would be the macroscopic (average) internal energy for this system?
- What if the temperature increases:  $\beta = 1/2$ ,  $\beta = 1/10$ , ...



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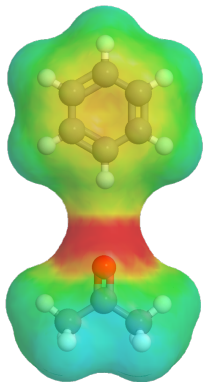


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## COSMO-RS\* – Surface contacting theory



- Assume each molecule consists in several *sticky notes*, *patches*, or surface segments
- In solution, these segments should all be in pair contact
- For each surface pair contact, there is an energy associated
- This results in different behavior for different substances in solution
- We could try to enumerate all possible microstates, calculate their probabilities, and derive all properties from there. But this gets overwhelming as the number of segments grows ( $N!$  microstates) ...

\*Andreas Klamt. In: *The J. of Phys. Chem.* 99.7 (1995), pp. 2224–2235



## Pair contact probabilities

- In the case of a completely random distribution (also known as the *zeroth approximation*\*), the pair contact probability should be simply:

$$\theta_{mn}^0 = \Theta_m \Theta_n \quad (2)$$

where  $\Theta_m$  is the area fraction of the segment type  $m$ .

- For the general case, the pair contact probability is<sup>†</sup>:

$$\theta_{mn} = \Theta_m \Gamma_m \Theta_n \Gamma_n \Psi_{mn} \quad (3)$$

where  $\Gamma_m$  is the *activity coefficient* of the segment.

\*E A Guggenheim. *Mixtures*. Clarendon Press, 1952

<sup>†</sup>Rafael de P. Soares and Paula B. Staudt. "Beyond activity coefficients with pairwise interacting surface (COSMO-type) models". In: *Fluid Phase Equilib.* 564 (2023)





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## Activity coefficients and the self-consistency equation

- If we sum the pair probability over all segments of a given type:

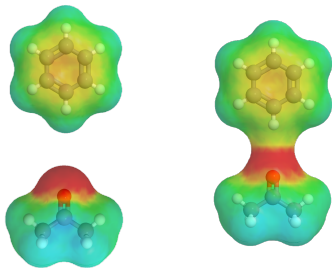
$$\sum_n \theta_{mn} = \Theta_m = \sum_n \Theta_m \Gamma_m \Theta_n \Gamma_n \Psi_{mn} \quad (4)$$

- Then we can divide both sides by  $\Theta_m \Gamma_m$  and rearrange to get:

$$\Gamma_m = \left[ \sum_n \Theta_n \Gamma_n \Psi_{mn} \right]^{-1} \quad (5)$$

- This equation is known as the “self-consistency” equation in COSMO-RS and COSMO-SAC models. Some important notes:
  - The activity coefficient of a given segment  $m$  depend on all other  $n$
  - This is a system of equations that need to be solved numerically, unlike classical (explicit) models like Wilson, NRTL, UNIQUAC, UNIFAC, ...

# Surface contacting theory – interaction energy



- The COSMO-SAC\* interaction energy is given

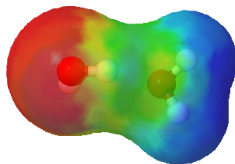
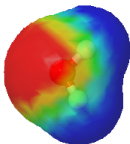
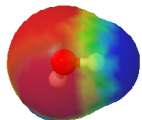
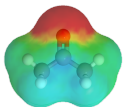
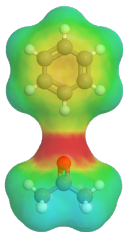
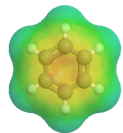
$$\text{by: } u_{mn} = \underbrace{\frac{\alpha' (\sigma_m + \sigma_n)^2}{2}}_{\text{electrostatic}}$$

---

\*ST Lin and S.I. Sandler. In: *Ind. Eng. Chem. Res.* 41.5 (2002), pp. 899–913

†S. J. Grabowski. In: *The J. of Phys. Chem. A* 105.47 (2001), pp. 10739–10746

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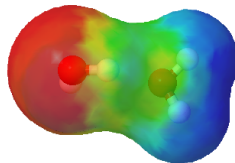
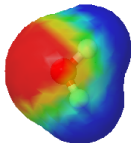
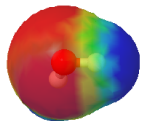
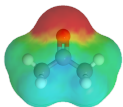
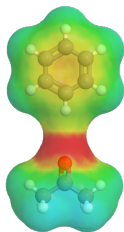
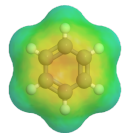
$$u_{mn} = \underbrace{\frac{\alpha' (\sigma_m + \sigma_n)^2}{2}}_{\text{electrostatic}} - \underbrace{\frac{u_{m,n}^{\text{HB}}}{2}}_{\text{hydrogen bond}}$$

- For strong HB, the distance of the bond is shorter than the sum of the van der Waals radii†

\*ST Lin and S.I. Sandler. In: *Ind. Eng. Chem. Res.* 41.5 (2002), pp. 899–913

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- For strong HB, the distance of the bond is shorter than the sum of the van der Waals radii†
- It is usually assumed that dispersion mostly cancels out for excess properties

\*ST Lin and S.I. Sandler. In: *Ind. Eng. Chem. Res.* 41.5 (2002), pp. 899–913

†S. J. Grabowski. In: *The J. of Phys. Chem. A* 105.47 (2001), pp. 10739–10746

# COSMO-SAC formulation for activity coefficients

- Based on segment activity coefficients computed in a pure fluid  $\Gamma_m^i$  and in solution  $\Gamma_m^s$ , the activity coefficient of a substance  $i$  given by:

$$\ln \gamma_i^{res} = \sum_{m \in i} \nu_m^i (\ln \Gamma_m^s - \ln \Gamma_m^i) \quad (6)$$

$$\nu_m^i = \frac{Q_m^i}{Q_{eff}} \quad (7)$$

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res} \quad (8)$$

with  $\ln \gamma_i^{comb}$  given by Flory-Huggins or Staverman-Guggenheim. For more details please check:

- ST Lin and S.I. Sandler. In: *Ind. Eng. Chem. Res.* 41.5 (2002), pp. 899–913
- Renan Pereira Gerber. “NOVO MODELO DE COEFICIENTE DE ATIVIDADE: F-SAC”. UFRGS, 2012
- F. Ferrarini et al. In: *AIChE Journal* 64.9 (2018), pp. 3443–3455
- Luiz F. K. Possani and Rafael de P. Soares. In: *Braz. J. of Chem. Eng.* 36 (Mar. 2019), pp. 587–598

## Vapor-Liquid equilibria at low pressure

By default modified Raoult's Law is assumed

$$P y_i = x_i \gamma_i P_i^{sat}$$

Raoult Law

Considering vapor phase as an ideal gas and the liquid as an ideal solution ( $\gamma_i = 1$ ):

$$P y_i = x_i P_i^{sat}$$



## Vapor-Liquid equilibrium at high-pressure

- For a mixture of  $i$  components in vapor-liquid equilibrium:

$$\hat{f}_i^v = \hat{f}_i^l$$

- Using fugacity coefficients to describe non-idealities ( $\hat{f}_i = P y_i \hat{\phi}_i$ ):

$$P y_i \hat{\phi}_i^v = P x_i \hat{\phi}_i^l$$

- $\phi - \phi$  Method:

$$y_i \hat{\phi}_i^v = x_i \hat{\phi}_i^l$$

- Where  $\hat{\phi}_i$  is computed by SRK-MC coupled with COSMO-SAC by the SCMR\* mixing rule

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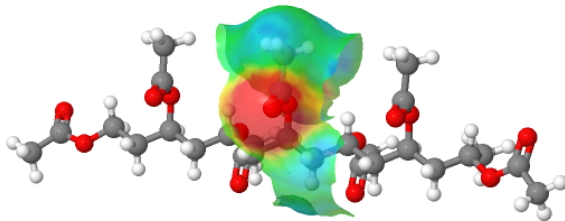
\*P.B. Staudt and R.P. Soares. In: *Fluid Phase Equilib.* 334 (Nov. 2012), pp. 76–88





## Polymer VLE

- Polymers are represented by their repeating unit, extracted from an oligomer\*:



- Within JCOSMO set the multiplier for polymer compounds or supply the polymer average molecular weight so it can be calculated

\*Paula B. Staudt et al. In: *Fluid Phase Equilib.* 472 (2018), pp. 75–84



## Liquid-Liquid Equilibrium – Qualitative

- Two phase split is usually a consequence of **positive deviations** from the Raoult's law
- Positive (and substantial) values for  $g^E$  have to be present
- For instance, when using the 1 parameter Margules model, a two phase split will only occur if the model parameter is  $A = \ln \gamma_i^\infty \geq 2$  or  $g^E/RT \geq 0,5$  in its maximum point

Check it yourself with a few cases

Using JCOSMO, (COSMO-SAC-HB2 model) to plot  $g^E/RT$  for the following mixtures water/ethanol, water/*n*-butanol e water/*n*-hexane at 298 K. Discuss your findings.



## Liquid-Liquid Equilibrium

- Considering two liquids ( $\alpha$  and  $\beta$ ) in equilibrium:

$$\hat{f}_i^\alpha = \hat{f}_i^\beta$$

- and  $\hat{f}_i = x_i \gamma_i f_i$ :

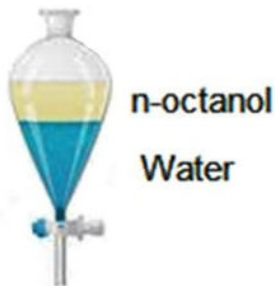
$$x_i^\alpha \gamma_i^\alpha f_i = x_i^\beta \gamma_i^\beta f_i$$

- Finally:

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta$$



## Octanol/water partition coefficient: $K_{OW}$



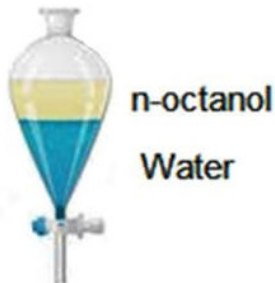
- At ambient temperature and pressure, water and 1-octanol are partially miscible: octanol-rich (72.5 mol % 1-octanol) and water-rich (99.99 mol % water)
- 1-octanol is a good surrogate for the lipids in aquatic and animal biota
- $K_{OW}$  has wide applications in biological, pharmaceutical, and environmental studies\*

$$K_{OW} = \frac{C_i^{OR}}{C_i^{WR}} = 0.148 \frac{\gamma_i^{WR, \infty}}{\gamma_i^{OR, \infty}}$$

\*Shiang-Tai Lin and Stanley I. Sandler. In: *Ind. Eng. Chem. Res.* 38.10 (Oct. 1999), pp. 4081–4091. DOI: 10.1021/ie990391u



## Octanol/water partition coefficient: $K_{OW}$



- Prediction with COSMO-SAC:

$$K_{OW} = \frac{C_i^{OR}}{C_i^{WR}} = 0.148 \frac{\gamma_i^{WR,\infty}}{\gamma_i^{OR,\infty}}$$

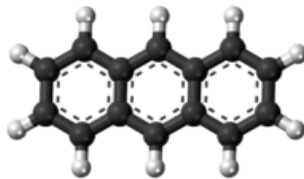
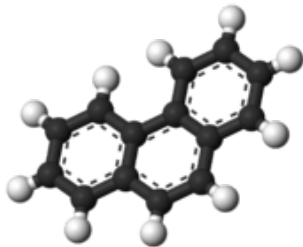
- Experimental values for  $\log_{10} K_{OW}^*$ :
  - acetone: -0.24
  - chloroform: 1.90
  - benzene: 2.15
  - isobutane: 2.76
  - heptane: 4.66

\*Shiang-Tai Lin and Stanley I. Sandler. In: *Ind. Eng. Chem. Res.* 38.10 (Oct. 1999), pp. 4081-4091. DOI: 10.1021/ie990391u



## Solid-liquid Equilibrium

- When analyzing SLE, solid properties are as important as molecular interactions
- For instance, phenanthrene e anthracene solubilities in benzene at 25 °C:
  - phenanthrene: 20,7 % mol,  $T_f = 100\text{ }^\circ\text{C}$
  - anthracene: 0,81 % mol,  $T_f = 217\text{ }^\circ\text{C}$



## Solubility - SLE

- In solid-liquid equilibrium:

$$\hat{f}_i^s = \hat{f}_i^l$$

- Considering a pure solid (species 1, solute) in equilibrium with a liquid (solvent):

$$f_1^s = \hat{f}_1^l$$



## Solubility - SLE

- ESL:

$$f_1^s = \hat{f}_1^l$$

- considering  $\hat{f}_1^l = x_1 \gamma_1 f_1^l$

$$f_1^s = x_1 \gamma_1 f_1^l$$

$$\frac{f_1^s}{f_1^l} = x_1 \gamma_1 \quad \ln \left( \frac{f_1^s}{f_1^l} \right) = \ln(x_1 \gamma_1)$$





## Solubility - SLE

- From fugacity definition:

$$g_1^s - g_1^l = RT \ln \left( \frac{f_1^s}{f_1^l} \right) \quad g_1^s - g_1^l = -\Delta g_{fus}$$

- recalling:  $g = h - Ts$ :

$$\ln(x_1 \gamma_1) = -\frac{\Delta g_{fus}}{RT} \quad \ln(x_1 \gamma_1) = -\frac{\Delta h_{fus}}{RT} + \frac{\Delta s_{fus}}{R}$$

- being  $\Delta h_{fus}$  and  $\Delta s_{fus}$  evaluated at  $T_f$ .



## Solubility - SLE

- To determine  $\Delta h_{fus}$  and  $\Delta s_{fus}$  at equilibrium temperature  $T$ :

$$\Delta h_{fus,T} = \Delta h_{fus,T_f} + \int_{T_f}^T \Delta C_p^{fus} dT$$

$$\Delta s_{fus,T} = \Delta s_{fus,T_f} + \int_{T_f}^T \frac{\Delta C_p^{fus}}{T} dT$$

- since  $\Delta g_{fus,T_f} = 0$ :

$$\Delta s_{fus,T} = \frac{\Delta h_{fus,T_f}}{T_f} + \int_{T_f}^T \frac{\Delta C_p^{fus}}{T} dT$$



## Solubility - SLE

- Considering  $\Delta C_p^{fus}$  temperature independent:

$$\ln(x_1\gamma_1) = -\frac{\Delta h_{fus,T_f}}{R} \left[ \frac{1}{T} - \frac{1}{T_f} \right] - \frac{\Delta C_p^{fus}}{R} \left[ 1 - \frac{T_f}{T} - \ln \left( \frac{T}{T_f} \right) \right]$$

- Usually  $\Delta C_p^{fus}$  is small and sometimes unknown and so the SLE equation is simplified:

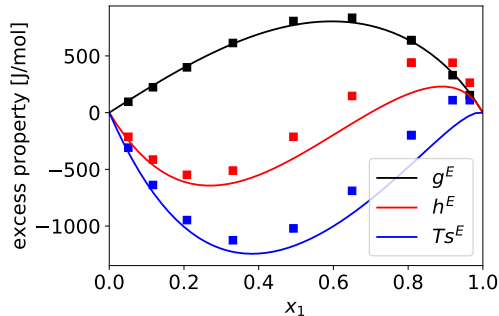
$$\ln(x_1\gamma_1) = \frac{\Delta h_{fus,T_f}}{R} \left[ \frac{1}{T_f} - \frac{1}{T} \right]$$

- Where  $x_1$  is the solute molar fraction in the liquid phase (solubility).



## Chloroform/methanol system

- This is a very complex system with s-shaped excess enthalpy and entropy
- The ESD-MEM2 model (SAFT-like) can describe the VLE, but was unable to fit the excess enthalpy (and hence entropy)\*
- COSMO-SAC and F-SAC can represent well all excess properties†



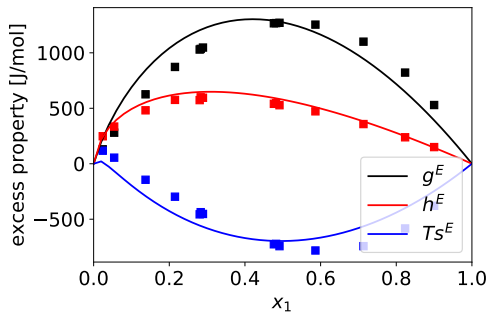
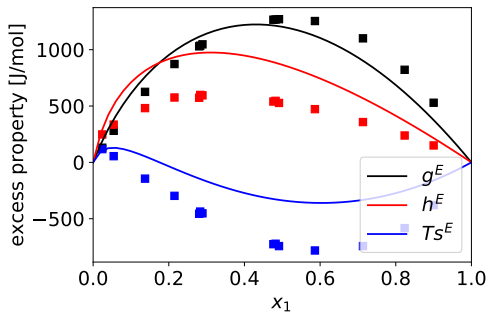
\* J. Richard Elliott. In: *J. Chem. Eng. Data* (2023)

† Rafael de P. Soares and Paula B. Staudt. "Unraveling order and entropy with modern quasi-chemical models". In: *Fluid Phase Equilib.* 583 (2024), p. 114113



## *n*-butanol/*n*-hexane system\*

- Again a complicated system, with s-shaped excess entropy. Left figure is with original F-SAC parameters, right with HB energy changed. Reduced or increased?



\*Rafael de P. Soares and Paula B. Staudt. "Unraveling order and entropy with modern quasi-chemical models". In: *Fluid Phase Equilib.* 583 (2024), p. 114113



## Comparison with classical activity models

### COSMO-based models

- Requires the numerical solution of systems of equations
- Universal parameters and per compound sigma-profile (quantum chemistry)
- Exact statistical thermodynamic solution but approximate interaction energies

### Classical models

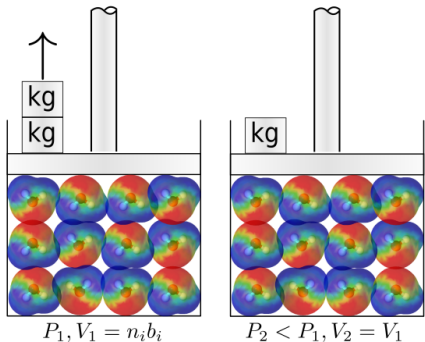
- Direct formulas for the activity, no numerical solution needed
- Parameters adjusted for each pair of compounds or pair of functional groups
- Approximate statistical thermodynamic and adjusted interaction energies



## Model for liquid phases only?



COSMO surface for water,  
its core volume  $b_i$  is constant



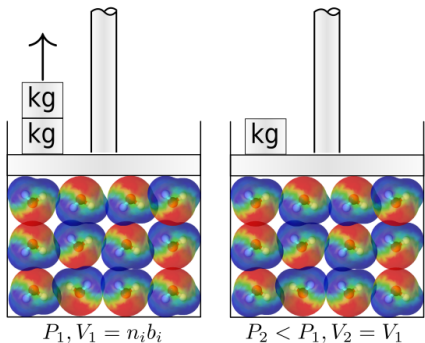
- The *real* solution should not contain the perfect conductor surrounding the molecules
- For every contact between molecules, the conductor is partially excluded
- Thus, all surface segments should be in *pairwise* contact
- Hence there is no *free volume* and  $V = n_i b_i$



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COSMO surface for water,  
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- For every contact between molecules, the conductor is partially excluded
- Thus, **all** surface segments should be in *pairwise* contact
- Hence there is no *free volume* and  $V = n_i b_i$





# EOS combined with COSMO-RS/SAC

- **NRCOSMO\***: combination of COSMO with the so called non-random hydrogen-bonding (NRHB) equation of state
- **$\sigma$ -MTC<sup>†</sup>**: an extension of the Mattedi-Tavares-Castier equation which combines the sigma-profile from COSMO computations with the generalized van der Waals theory
- **Cubic EOS + MR + COSMO-SAC:**
  - PR+WS+COSMO-SAC<sup>‡</sup>
  - PR+SCMR+COSMO-SAC<sup>§</sup>
  - PR+mSCMR+COSMO-SAC<sup>¶</sup>
  - ...
- All methods need some *bridge* to couple COSMO with the EOS

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\*C. Panayiotou. In: *Pure and Applied Chemistry* 83.6 (Jan. 2011), pp. 1221–1242

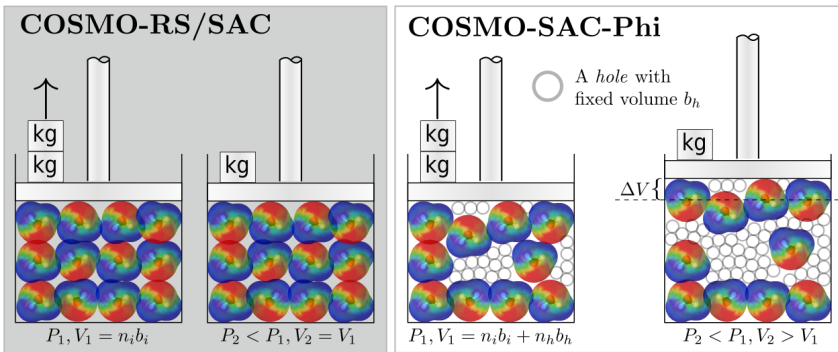
†C.T.O.G. Costa, F.W. Tavares, and A.R. Secchi. In: *Fluid Phase Equilib.* 409 (Feb. 2016), pp. 472–481

‡MT Lee and ST Lin. In: *Fluid Phase Equilib.* 254.1-2 (June 2007), pp. 28–34

§P.B. Staudt and R.P. Soares. In: *Fluid Phase Equilib.* 334 (Nov. 2012), pp. 76–88

¶LH Wang, CM Hsieh, and ST Lin. In: *Ind. Eng. Chem. Res.* 57.31 (June 2018), pp. 10628–10639

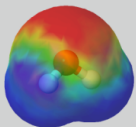
# COSMO-SAC-Phi\*: seamless extension



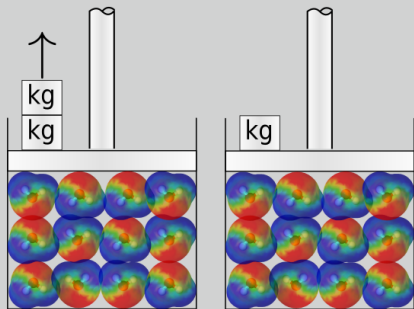
- By this *pseudo-mixture*, COSMO-RS, COSMO-SAC, or F-SAC can be used to compute  $\mu_i$  and  $\mu_h$  as long as we know the number of molecules and holes

# COSMO-SAC-Phi: seamless extension

## COSMO-RS/SAC



COSMO surface for water,  
its core volume  $b_i$  is constant



$$P_1, V_1 = n_i b_i$$

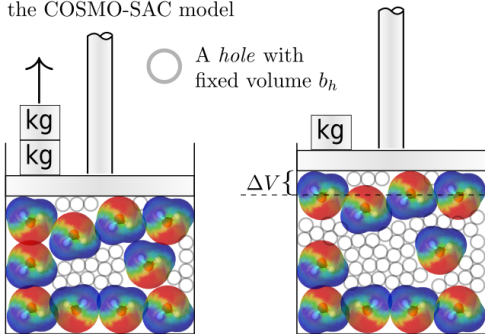
$$P_2 < P_1, V_2 = V_1$$

Incompressible liquids,  
no empty spaces are allowed

## COSMO-SAC-Phi

$$P = \underbrace{P_R}_{\text{repulsion}} + \underbrace{P_A}_{\text{attraction}} \quad P_A = - \left( \frac{\partial A^r}{\partial V} \right)_{T, \mathbf{n}} = - \frac{\tilde{\mu}_h^r}{b_h}$$

$\tilde{\mu}_h^r$  is the *hole* residual chemical potential in the *pseudo-mixture* (molecules + *holes*) computed by the COSMO-SAC model

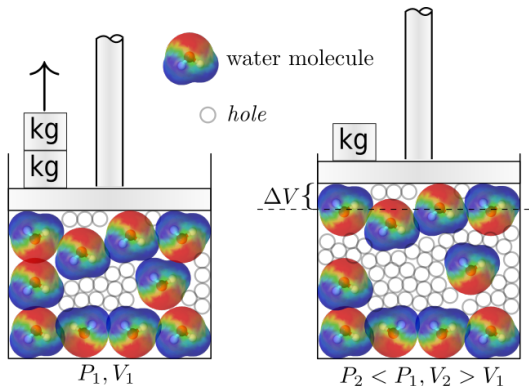


$$P_1, V_1 = n_i b_i + n_h b_h$$

$$P_2 < P_1, V_2 > V_1$$

Compressible fluids, volume can change  
by adding or removing *holes* of fixed volume

## COSMO-SAC-Phi assumptions and equations

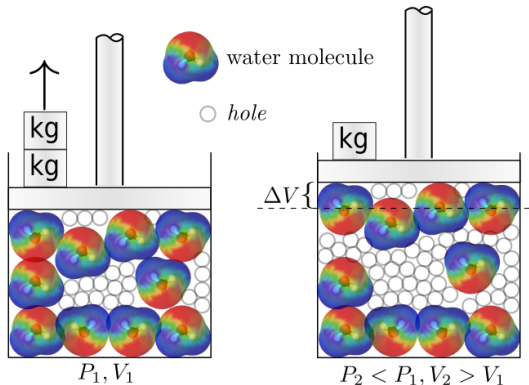


- The *real* mixture is described by  $\mathbf{n} = [n_1, n_2, \dots, n_i, \dots, n_N]$
- The pseudo-mixture is described by  $\tilde{\mathbf{n}} = [\mathbf{n}, n_h]$
- No empty spaces (other than holes)  
 $V = \sum_i n_i b_i + n_h b_h$
- For given  $(T, V, \mathbf{n})$ :  
 $n_h = \frac{1}{b_h} (V - \sum_i n_i b_i)$

- What should be the shape of a *hole*? Probably not a sphere, otherwise we will have empty spaces.



## COSMO-SAC-Phi assumptions and equations

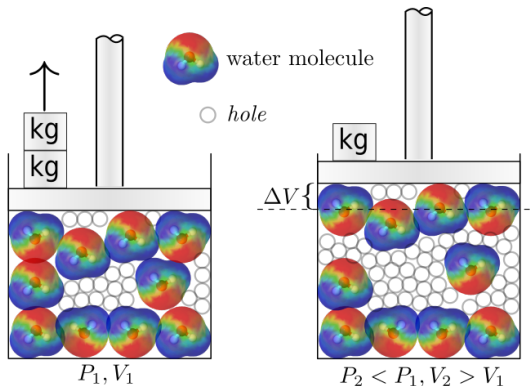


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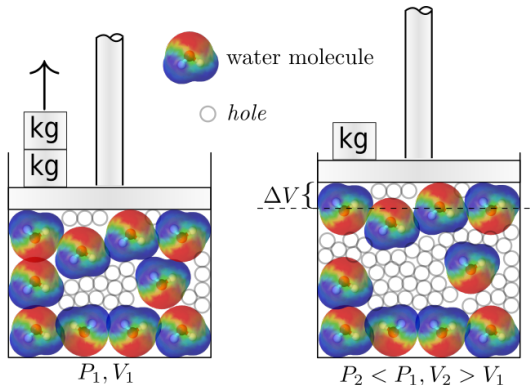


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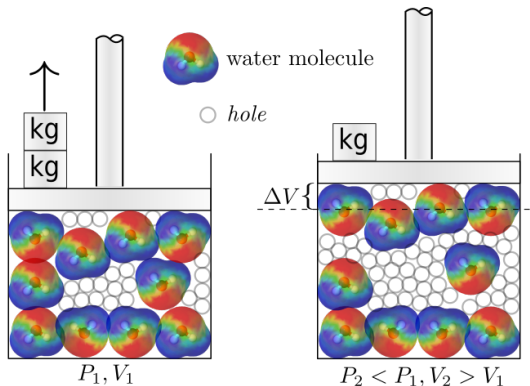
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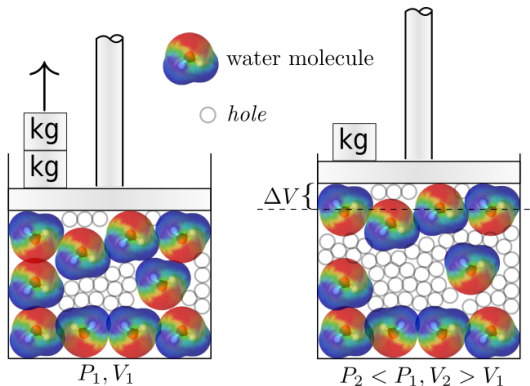
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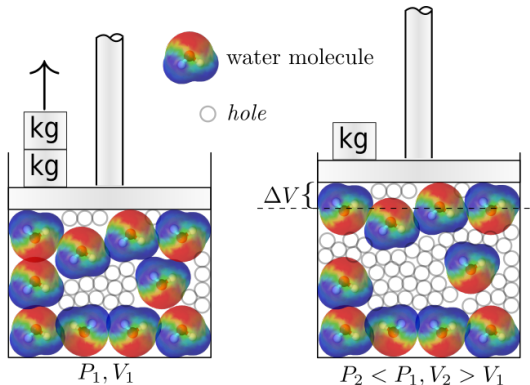
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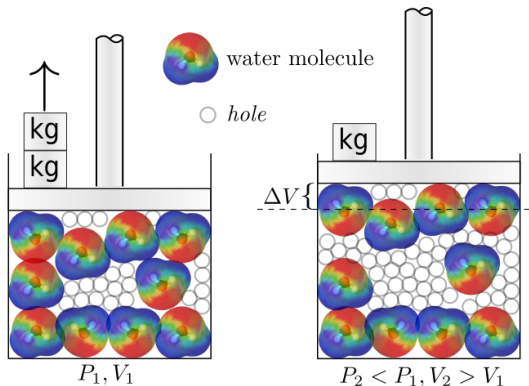


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## COSMO-SAC-Phi: Ideal Gas reference



- In order to replace the reference to an Ideal Gas (IG), simply apply the  $V \rightarrow \infty$  limit
- Alternatively put the compound *infinitely diluted* in holes

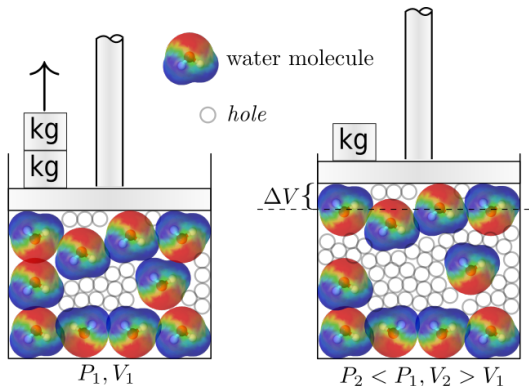
• With the *pseudo-mixture* this is simple, just make:

$$\tilde{\mathbf{n}}^{\text{IG}} = [\mathbf{n} = \mathbf{0}, n_h = 1] = [0, 0, \dots, 1]$$

• With residual properties defined, we can compute not only pressure, but fugacity



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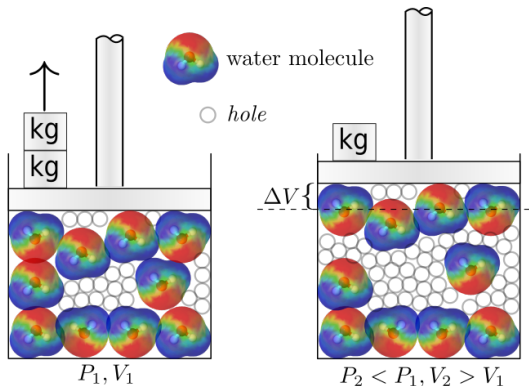
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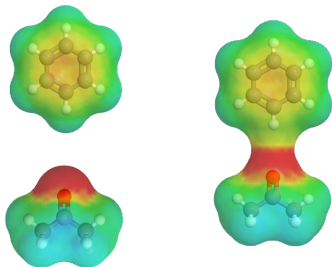
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# Surface contacting theory – interaction energy



- The COSMO-SAC\* interaction energy is given

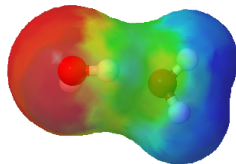
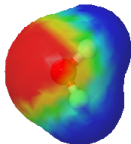
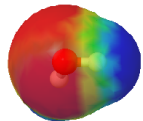
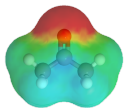
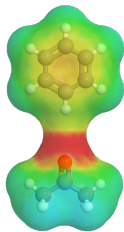
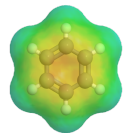
$$\text{by: } \Delta W_{mn} = \underbrace{\frac{\alpha' (\sigma_m + \sigma_n)^2}{2}}_{\text{electrostatic}}$$

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\*ST Lin and S.I. Sandler. In: *Ind. Eng. Chem. Res.* 41.5 (2002), pp. 899–913

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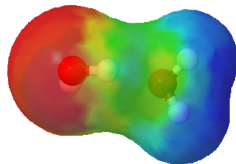
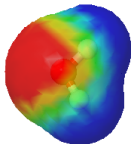
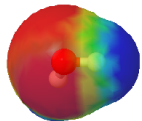
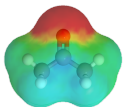
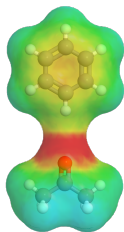
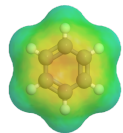
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- For strong HB, the distance of the bond is shorter than the sum of the van der Waals radii†

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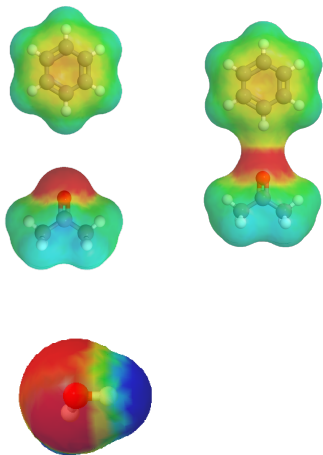
- For strong HB, the distance of the bond is shorter than the sum of the van der Waals radii†
- It is usually assumed that dispersion mostly cancels out for excess properties

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# Surface contacting theory – dispersion



- For an EOS we need a dispersion contribution\*:

$$\Delta W_{m,n} = \underbrace{\frac{\alpha' (\sigma_m + \sigma_n)^2}{2}}_{\text{electrostatic}} - \frac{E_{m,n}^{\text{HB}}}{2} - \frac{E_{m,n}^{\text{Disp}}}{2}$$

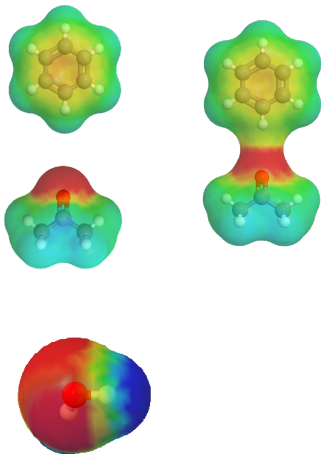
- With per compound dispersion parameters:

$$E_{m,n}^{\text{Disp}} = \sqrt{\delta_m \delta_n}$$

$$\delta_m = \delta_m^0 (1 - \exp(-\delta_m^T / T))$$



# Surface contacting theory – dispersion



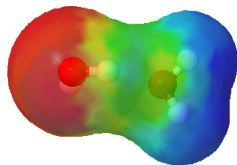
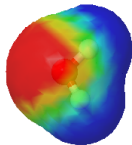
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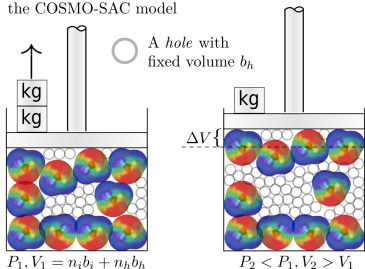


# COSMO-SAC-Phi: implementation

## COSMO-SAC-Phi

$$P = \underbrace{P_R}_{\text{repulsion}} + \underbrace{P_A}_{\text{attraction}} \quad P_A = - \left( \frac{\partial A^r}{\partial V} \right)_{T, \mathbf{n}} = - \frac{\tilde{\mu}_h^r}{b_h}$$

$\tilde{\mu}_h^r$  is the *hole* residual chemical potential in the *pseudo-mixture* (molecules + *holes*) computed by the COSMO-SAC model



Compressible fluids, volume can change by adding or removing *holes* of fixed volume

- Repulsive pressure by a simple hard sphere model
- $\sigma$ -profiles from the open source LVPP sigma-profile
- GMHB1808 COSMO-SAC parametrization

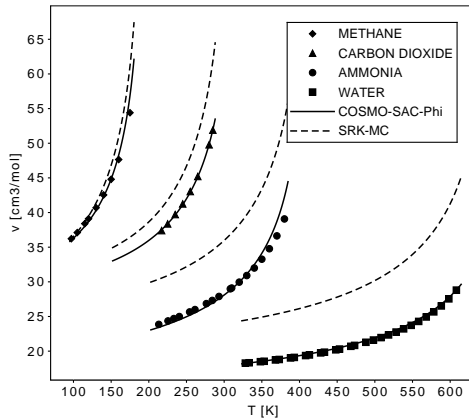
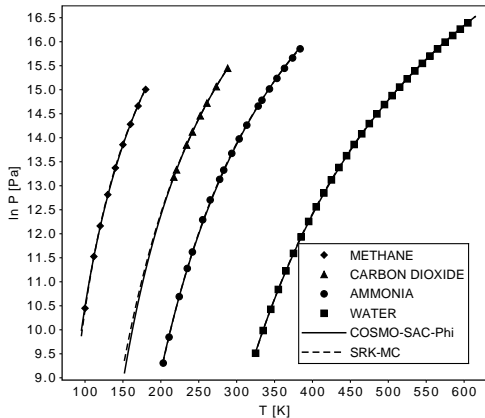
Freely available at <http://github.com/lvpp/sigma>

- Per compound parameters:  
 $b_i, \delta_i^0, \delta_i^T, \text{ and } b_{h,i}$



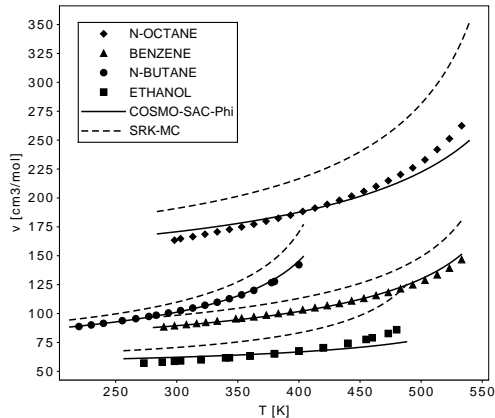
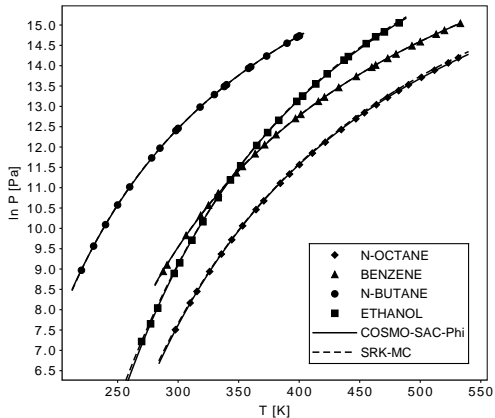
# Pure compound saturation pressure and liquid volume

	COSMOSAC-PHI		SRK-MC	
	Pressure	Volume	Pressure	Volume
Average deviation (%)	1.15	1.63	1.64	15.48



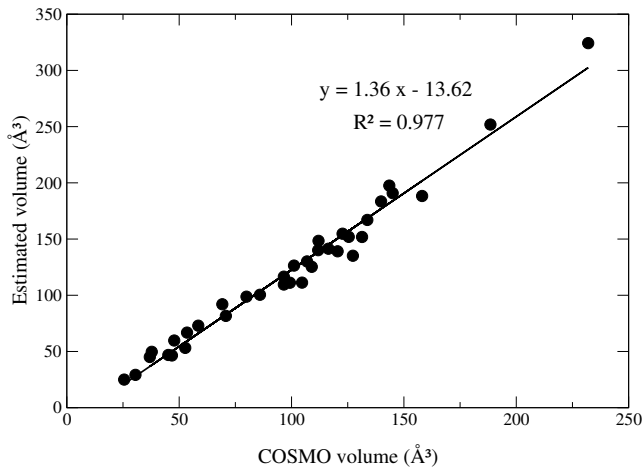
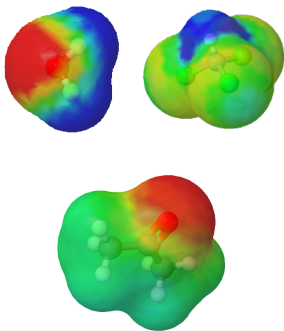
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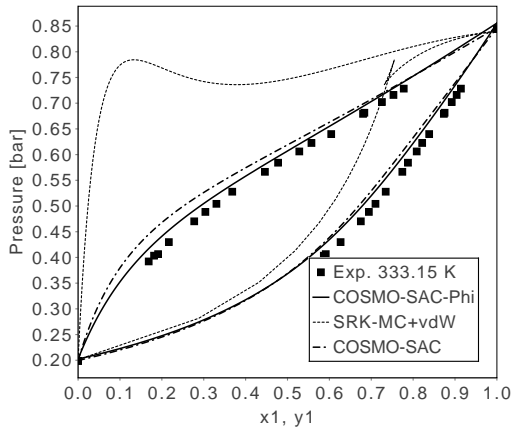
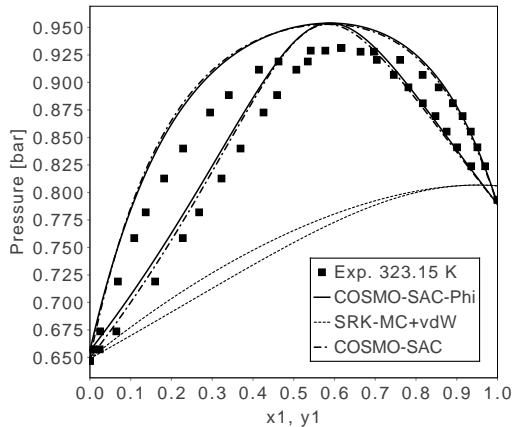


# Reducing the number of parameters

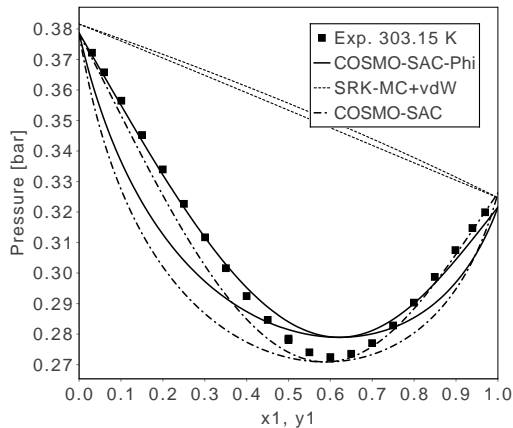
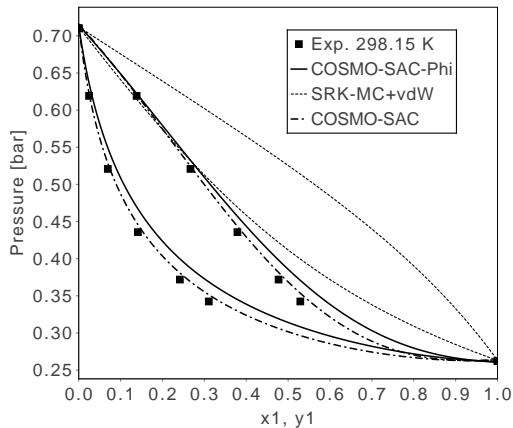
- Correlation between COSMO volume and estimated volume  $b_i$



## Low pressure VLE predictions (no BIPs)

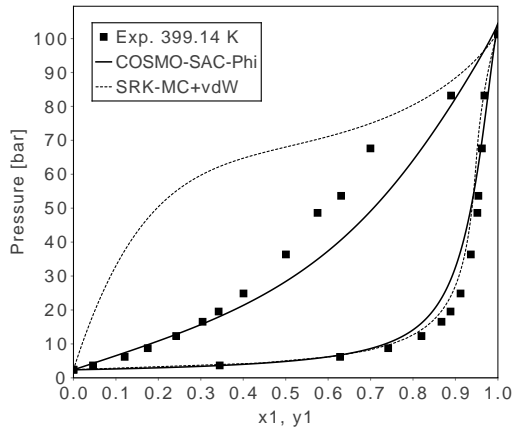
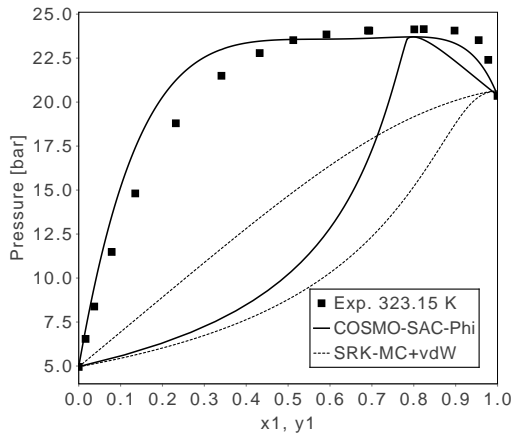


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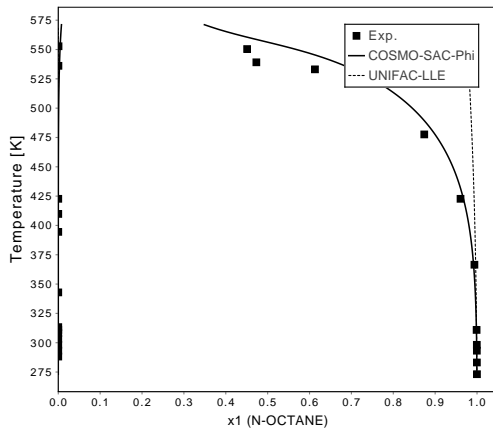
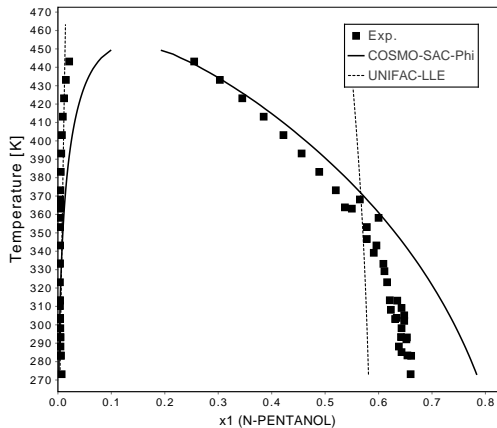




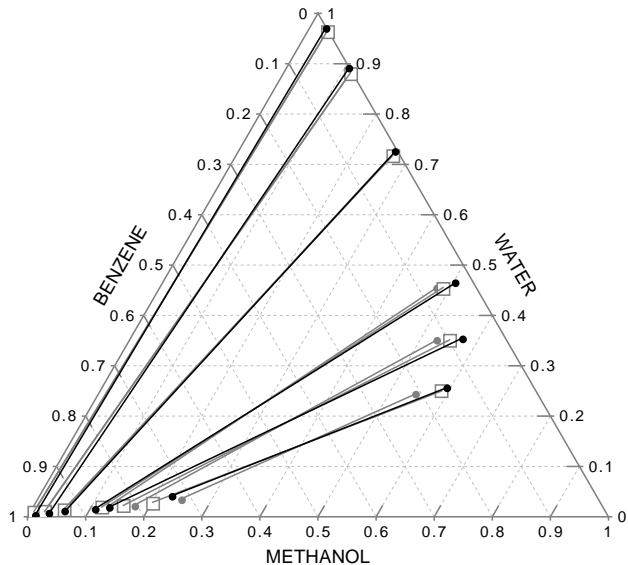
## High pressure VLE predictions (no BIPs)



## LLE predictions

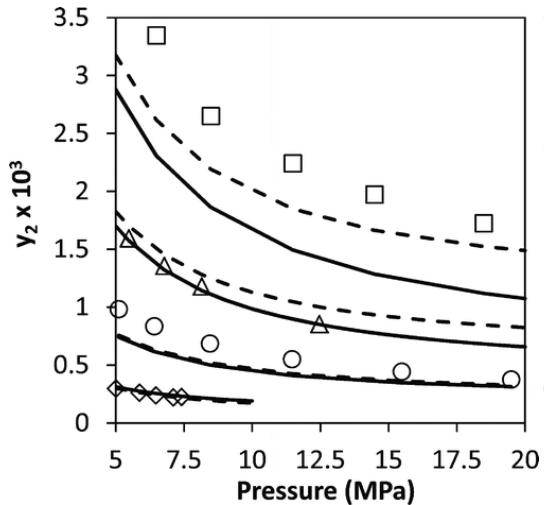


# Ternary LLE prediction

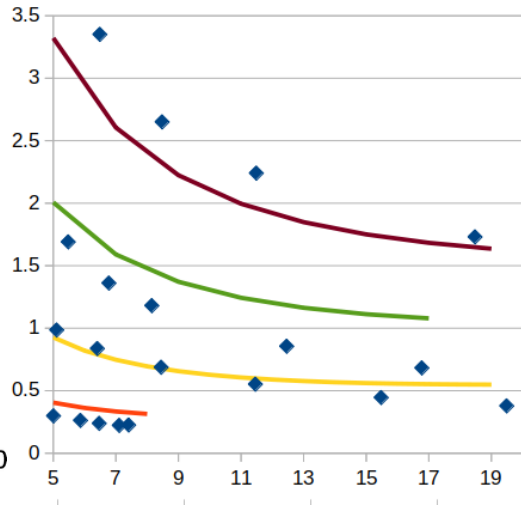


● Exp. Data, 303.2 K □ COSMO-SAC-Phi ● UNIFAC-LLE

# Gas related systems\*

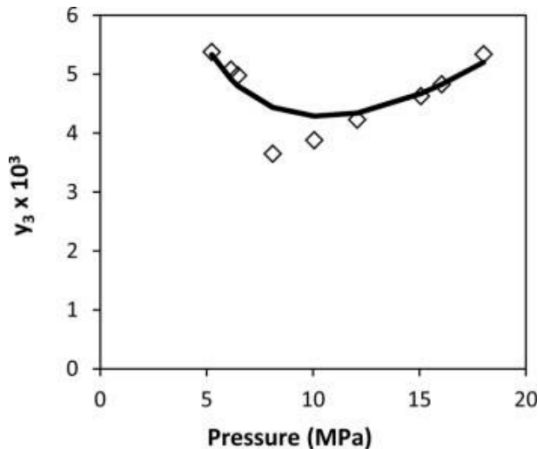


(i) methane/water, CPA+BIP (solid) and GERG-WATER+T-BIP (dashed)

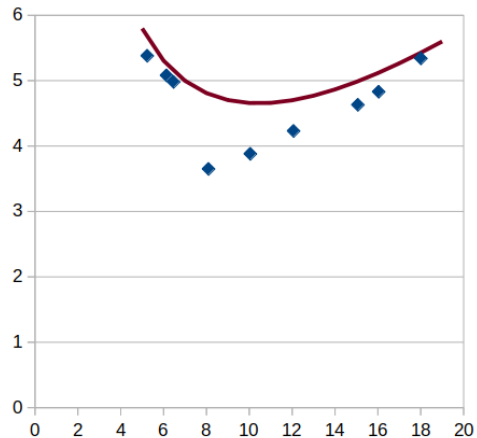


(j) COSMO-SAC-Phi predictions

# Gas related systems\*



(k) methanol in gas phase, CPA+BIP (solid)



(l) COSMO-SAC-Phi predictions

\*Michael Frost et al. In: *J. of Chem. Eng. Data* 59.4 (Apr. 2014), pp. 961–967

## COMO-SAC-Phi: current state and possible improvements

- COSMO-SAC can be seamlessly extended to capture pressure effects by the addition of free-volume (holes)
- There is no need to define a lattice, coordination number, or association scheme
- The proof of concept required pure compound parameters for volume and dispersion
- Pure compound saturation pressure and volume could be correlated with less than 2% average error
- Mixture VLE and LLE were predicted with a good accuracy for several different substances, kinds of deviations and pressures
- Future work:
  - The current repulsive contribution should be improved
  - Solid surfaces can be explicitly considered (test the model for adsorption and confined fluids)
  - ...



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# Thank you!

- The LVPP sigma-profile database is freely available at <https://github.com/lvpp/sigma>
- Our homepage: <https://ufrgs.br/lvpp>
- Contact: [rafael.pelegrini@ufrgs.br](mailto:rafael.pelegrini@ufrgs.br), [paula.staudt@ufrgs.br](mailto:paula.staudt@ufrgs.br)

- Special thanks:

