The Non Equilibrium Thermodynamics for glassy polymers (NET-GP) approach

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Gas sorption in glassy polymers: a challenging problem

- *The gas solubility in **rubbery or melt** polymers can be predicted based on activity-coefficient or EOS approaches, through the **general thermodynamic** relations for **phase equilibrium** and well established expressions for **fluid state equilibrium free energy** as function of temperature, pressure and composition.*

- *Problems rising when dealing with **glassy polymers**:*
  - *temperature, composition and deformation histories affect the thermodynamic properties of the system*
  - *pseudo-equilibrium conditions rather than true thermodynamic equilibrium are reached by the system*
  - *Lack of reliable expressions for free energy as function of non-equilibrium state variables*

Gas sorption in glassy polymers: dual mode empirical model

$$\boxed{C = k_D p + \frac{C'_H bp}{1 + bp}}$$

✓ *Easy to use,* ***explicit*** *with respect to the concentration*

✓*It depicts a rough but sound picture of gas sorption in glassy matrices*

✓*It correctly describes the relatively* ***high negative sorption enthalpy*** *observed in glassy polymers,* C'_H *can be qualitatively related to physical variables describing out of equilibrium degree*

✓*Empirical in nature, its parameters need to be evaluated* ***for each gas-polymer couple*** *and* ***temperature*** *and are pressure-dependent.*

✓*In some cases it is not qualitatively able to describe the sorption isotherm (ex. Alcohols-PTMSP:* ***sigmoidal sorption****).*

Gas sorption in glassy polymers: predictive models with order parameters

✓*The glassy mixture is a* ***non equilibrium*** *phase, whose properties are derived from a Gibbs free energy expression obtained via* ***statistical thermodynamics****.*

✓*A suitable* ***order parameter****, history dependent, is introduced to define the* ***out of equilibrium*** *degree of the system.*

Wissinger, Paulaitis
(Panayiotou, Vera EOS)

Fractional free volume $\mathbf{f_0}$ *at* T_G *of the mixture; value frozen for all* $T<T_G$*: this model is unable to represent hysteresis, swelling-enhanced sorption (because* f_0 *is constant).*

Barbari, Conforti
(Activity coefficient approach)

Actual fractional number of holes in the mixture per polymer mass, ξ*: does not collapse to an equilibrium expression for the pure polymer; dilation data are always needed for the calculation, even in the low pressure limit.*

NET-GP: assumptions and results

*The **glassy** polymeric phase is*

✓*i) **homogeneous** ii) **isotropic** iii)**amorphous***

✓*The volume relaxation of the polymer follows a **Voigt Model***

✓*The glassy phase reaches an asymptotic **pseudo equilibrium** condition*

- *The polymer density* **(ρ_2) *is an internal state variable*** *for the glassy mixture*

- ***The non equilibrium properties can be related to the equilibrium properties of the mixture**: A under **pseudo-equilibrium** conditions is uniquely related to the **equilibrium** value of A at the same T, V and composition*

- *Correspondingly, the **penetrant chemical potential** can be calculated in the **non equilibrium** glassy mixture.*

- *Phase equilibrium condition requires that the **chemical potential of the penetrant in the external gaseous phase equals the corresponding pseudo equilibrium** value **in the solid phase.** This constraint allows to calculate the pseudo equilibrium solubility of the penetrant in the glassy mixture.*

Choice of ρ_2 as order parameter (1)

- *The polymer density ρ_2 labels the **excess free volume** of the system with respect to the equilibrium value, and depends on the history of the sample: it is equivalent to other order parameters ($\mathbf{f_0}$, ξ).*

- *During sorption, ρ_2 is simply related to the polymer volume **V** (the polymer does not dissolve in the gas $\Rightarrow$ $\mathbf{m_2}$ is constant), which is a macroscopic, directly measurable quantity:*

$$\rho_2 = \mathbf{m_2/V}$$

- *When the volume dilation is negligible, i.e.:*
  - *In the low pressure range, for any penetrant*
  - *In a wide pressure range, for non swelling penetrants*

***the density is equal to that of the dry polymer**:*

For p→0 or for non swelling penetrants : $\rho_2 \approx \rho_2^0$

*(In the other cases, **dilation data** during sorption are needed to calculate ρ_2)*

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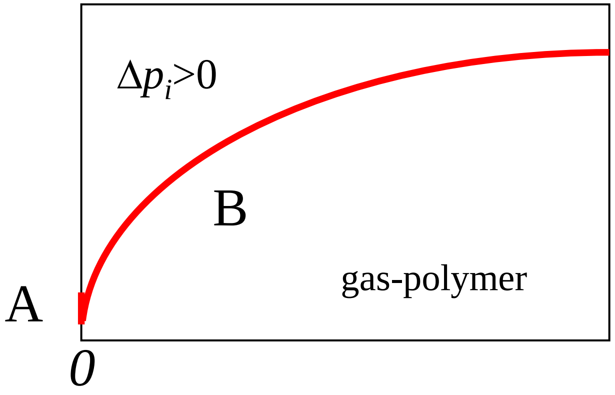
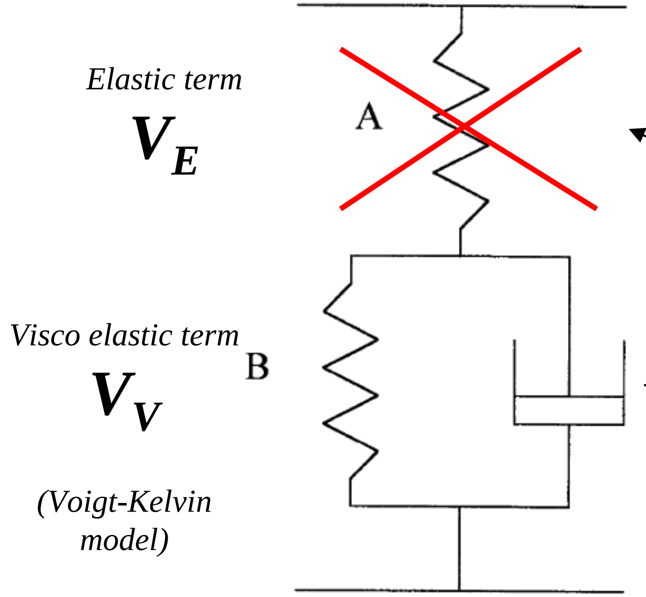
(1): *unless otherwise specified, we will always consider a system formed by a gas (labeled by index 1) and a polymer (labeled by index 2)*

Model for volume relaxation during sorption

During sorption, the situation is similar to the one experienced after a sudden Δp, without sorption. The volume decreases instantaneously due to variation in the total pressure, then starts to increase (viscous part) due to gas sorption inside the matrix, until the viscous response becomes infinitely slow ($V_V \approx V_{V,\infty}$).



$$\boxed{V = V_E + V_V}$$



*We assume that **the prevailing effect is that of swelling,** in view of the high modulus of the glass and relatively low pressure jumps imposed during sorption*

$$V_E \approx \text{const} \Rightarrow \frac{dV}{dt} \approx \frac{dV_V}{dt}$$

$$\frac{dV_V}{dt} = F\left(T, p, V_V, \omega_i\right)$$

ρ_2 internal state variable for glassy mixtures

$$\frac{\mathrm{d}V}{\mathrm{d}t} \approx \frac{\mathrm{d}V_V}{\mathrm{d}t} \equiv H(T, p, \omega_1, V_V) = H(T, p, \omega_1, V - V_E) \quad = F(T, p, \omega_1, V).$$

$$\boxed{\frac{d\rho_2}{dt} = f\left(T, p, \omega_1, \rho_2\right)}$$

By definition, ρ_2 ***is an internal state variable***
for the gas-polymer system during sorption

***1**st **, 2**nd **law** for a **generic** binary **closed** system defined by (**T, p, ρ_2, n$_1$, n$_2$**)*

$$\boxed{\left[\left(\frac{\partial G}{\partial T}\right) + S\right] \cdot \frac{dT}{dt} + \left[\left(\frac{\partial G}{\partial p}\right) - V\right] \cdot \frac{dp}{dt} + \mu_1 \cdot \cancel{\frac{dn_1}{dt}} + \alpha \cdot \frac{d\rho_2}{dt} \le 0}$$

$$\boxed{\frac{dn_1}{dt} = 0}$$ *(mass balance)*

$\forall \frac{dT}{dt}, \frac{dp}{dt}$ *Arbitrarily chosen*

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_{p,\rho_2,n_1,n_2} = -S} \qquad \boxed{\left(\frac{\partial G}{\partial p}\right)_{T,\rho_2,n_1,n_2} = V}$$

$\frac{d\rho_2}{dt}$ *cannot be arbitrarily varied:*

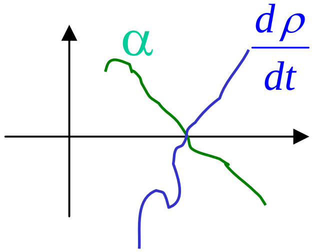
$$\boxed{\alpha \cdot \frac{d\rho_2}{dt} \le 0}$$

$$\left(\alpha \equiv \left(\frac{\partial G}{\partial \rho_2}\right)_{T,p,n_i}\right)$$

ρ_2 internal state variable for glassy mixtures

At equilibrium,
(rubbery polymers) ⇒

$$\frac{d\rho_2}{dt}=0 \qquad \alpha\cdot\frac{d\rho_2}{dt}\le 0$$



Also α must be zero

$$\alpha\equiv\left(\frac{\partial G}{\partial \rho_2}\right)_{T,p,n_i}=0 \;\Rightarrow\; \rho_2\equiv\rho_{2,eq}=\rho_{2,eq}\left(T,p,\omega_i\right) \;\Rightarrow$$

Equation of state

Equilibrium chemical potential →

$$\mu_{1,eq}=\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2}$$

At pseudo equilibrium,
for a glassy mixture:

$$\frac{d\rho_2}{dt}\approx 0$$

but

$$\alpha\equiv\left(\frac{\partial G}{\partial \rho_2}\right)_{T,p,n_i}\neq 0 \qquad \rho_2\neq\rho_{2,eq} \;\Rightarrow$$

EOS does not hold

Pseudo equilibrium chemical potential →

$$\mu_{1,ne}=\left(\frac{\partial G}{\partial n_1}\right)_{T,p,\rho_2,n_2}$$

The value of ρ_2 must be kept constant in the derivation

Extension to the non equilibrium domain: Helmholtz free energy

$$\left[\left(\frac{\partial A}{\partial T}\right)+S\right]\cdot\frac{dT}{dt}+\left(\frac{\partial A}{\partial p}\right)\cdot\frac{dp}{dt}+\left(\frac{\partial A}{\partial n_1}\right)\cdot\cancel{\frac{dn_1}{dt}}+\left[\left(\frac{\partial A}{\partial V}\right)+p\right]\cdot\frac{dV}{dt}\leq 0$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_{p,V,n_1,n_2}=-S}\qquad\boxed{\left(\frac{\partial A}{\partial p}\right)_{T,V,n_1,n_2}=0}$$

$$A_{ne}=A_{ne}\left(T,V,n_1,n_2\right)$$

(2nd law)

A

$$\boxed{\begin{gathered}\hat{A}_{eq}\left(T,\omega_1,\rho_2\right)=\hat{A}_{ne}\left(T,p,\omega_1,\rho_2\right)\\ \hat{G}_{ne}=\hat{A}_{Eq}\left(T,\omega_1,\rho_2\right)+p\hat{V}\ \textbf{ with } p\neq p_{eq}\end{gathered}}$$

At equilibrium: $\frac{dV}{dt}=0$ $\left(\frac{\partial A}{\partial V}\right)=-p_{eq}$ ***E.O.S.***

Extension to the non equilibrium domain: Chemical potential

$$\hat{G}_{ne} = \hat{A}_{Eq}\left(T,\omega_1,\rho_2\right) + p\hat{V} \quad \Rightarrow \quad \boxed{\mu_1^{(GP)} = \left(\frac{\partial m\hat{G}}{\partial m_1}\right)_{T,p,m_2,\rho_2} \equiv \left(\frac{\partial \rho \hat{A}_{Eq}}{\partial \rho_1}\right)_{T,\rho_2}}$$

Non-equilibrium free energy functions can thus be obtained starting from the equations of state associated to the lattice fluid theories, as well as to the tangent hard sphere chain theories

$$\boxed{\mu_{ne}\left(T,p,\omega_1,\rho_2\right) = \mu_{eq}\left(T,\omega_1,\rho_2\right)}$$

The chemical potential expression for glassy phase is different from the usual equilibrium expression:

it must be calculated at the known non-equilibrium value of the polymer density ρ_2

Pseudo equilibrium solubility calculation

1^{st} and 2^{nd} law for an open system:

$$\boxed{\left[\left(\frac{\partial G}{\partial T}\right)+S\right]\cdot\frac{dT}{dt}+\left[\left(\frac{\partial G}{\partial p}\right)-V\right]\cdot\frac{dp}{dt}+\left(\mu_1-\mu_1^{ext}\right)\cdot\frac{dn_1}{dt}+\alpha\cdot\frac{d\rho_2}{dt}\le 0}$$

$$\boxed{\left(\mu_1-\mu_1^{ext}\right)\cdot\frac{dn_1}{dt}+\alpha\cdot\frac{d\rho_2}{dt}\le 0}$$

$\frac{dn_1}{dt}$ Can be arbitrarily varied

At pseudo equilibrium: $\boxed{\frac{dn_1}{dt}=0}$

(mobility of the penetrant is not kinetically hindered as the matrix)

***Pseudo equilibrium condition*:**

$$\boxed{\mu_{1,ne}\left(\,T,\,p,\,\omega_1,\,\rho_2\,\right)\;=\;\mu_1^{ext}\left(\,T,\,p\,\right)}$$

Where $\rho_{2\neq}\,\rho_{2,eq}$

Solubility calculation

Equilibrium :

$$\begin{cases} \boxed{\mu_{1,eq}\left(T, \omega_1, \rho_2 \right) = \mu_1^{ext}\left(T, p\right)} \\ \left(\dfrac{\partial G}{\partial \rho_2}\right)_{T,p,n_i} = 0 \end{cases}$$

Pseudo equilibrium :

$$\begin{cases} \boxed{\mu_{1,ne}\left(T, p, \omega_1, \rho_2 \right) = \mu_1^{ext}\left(T, p \right)} \\ \rho_2 = \rho_{2,\infty} : \dfrac{d\rho_2}{dt} = f\left(T, p, \omega_1, \rho_2\right) \approx 0 \end{cases}$$

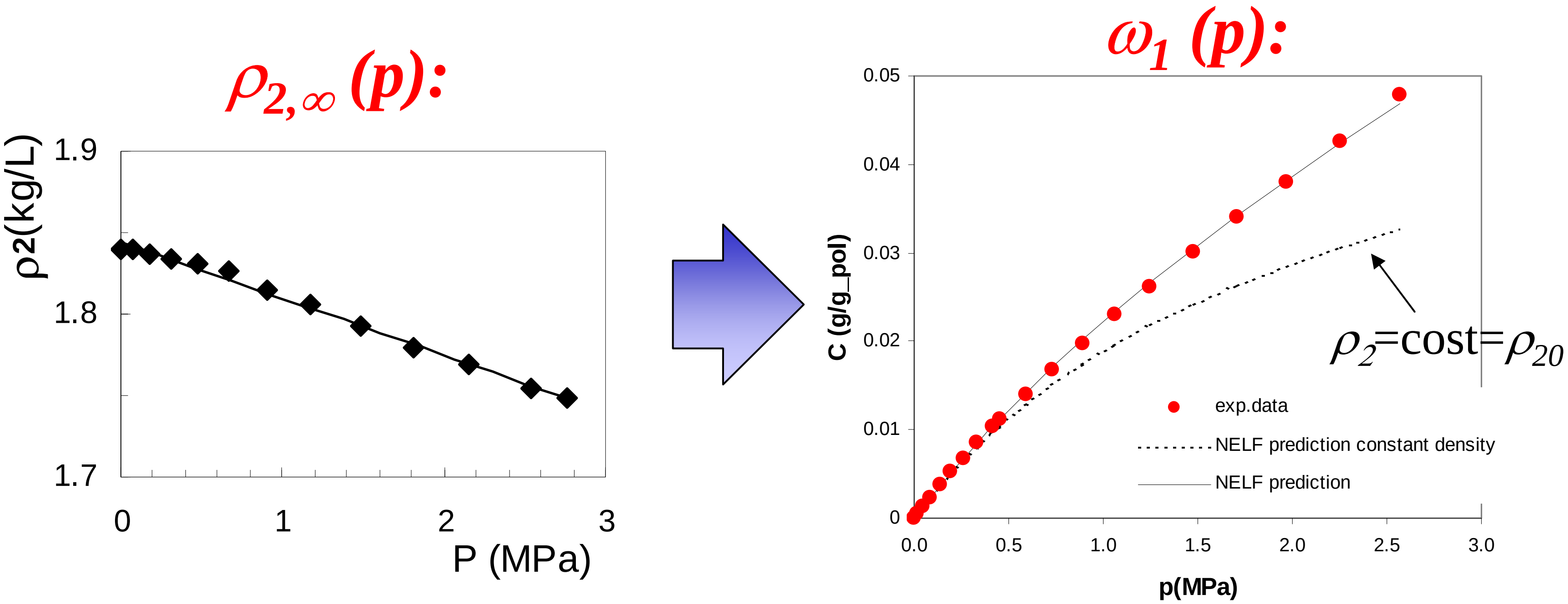
We don't need information on the expression of ***f*** *as long as we can estimate* $\rho_{2,\infty}$ *at given pressure*

In the latest developments, not yet published, it has been demonstrated that the same conclusions are obtained for the relation between non equilibrium and equilibrium properties, even after removing the hypothesis thatthe glassy mixture follows a Voigt type of rheological response

Pseudo equilibrium solubility calculation

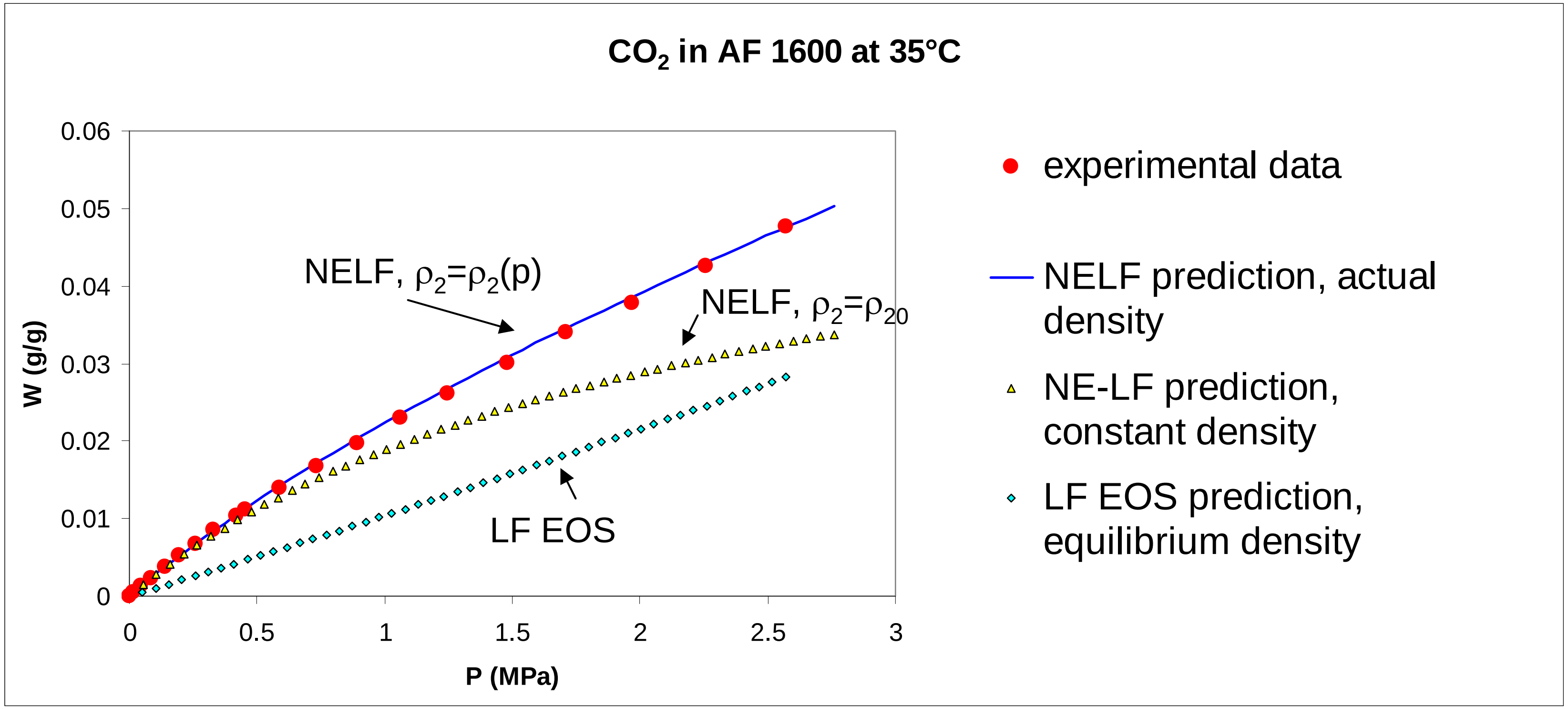
Pseudo equilibrium condition, solved with respect to ω_1

$$\boxed{\overbrace{\mu_{1,ne}\left(T,\,p,\,\omega_1,\,\rho_2\right)}^{\text{Chemical potential in the solid (glassy)phase}} \;=\; \overbrace{\mu_1^{ext}\left(T,\,p\right)}^{\text{Chemical potential in the external gaseous phase}}}$$



System AF1600-CO2 at 35°C
NELF model (Ψ=1)

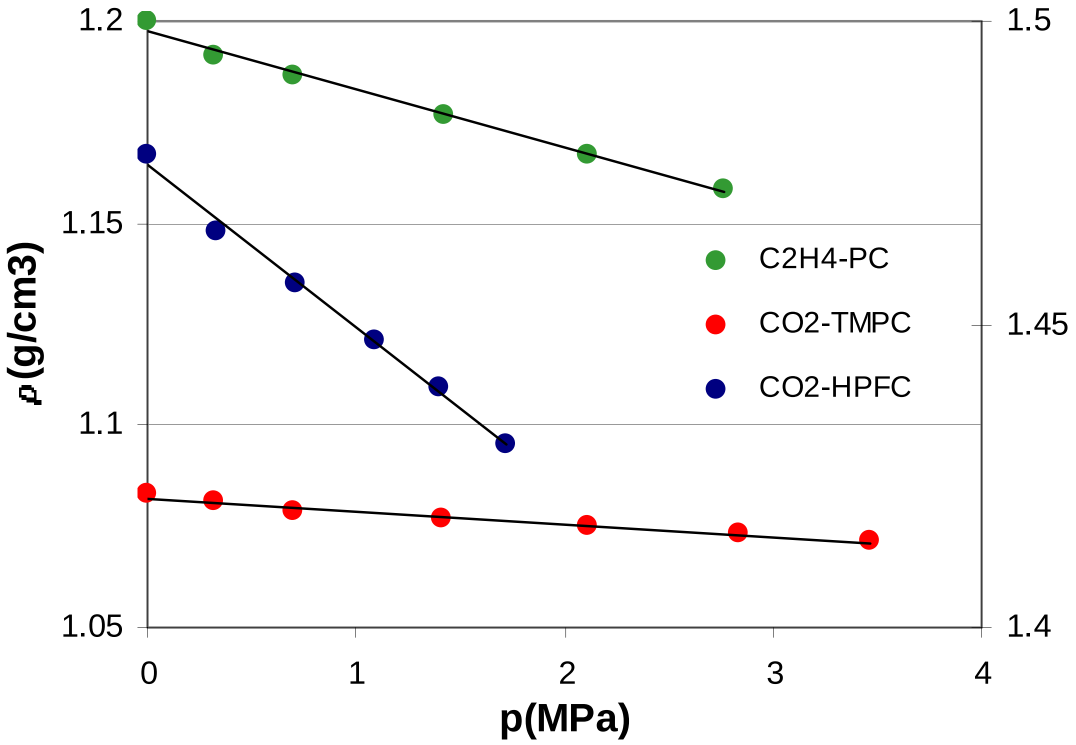
Pseudo equilibrium solubility calculation



CO2	AF1600		
44	1E+30	molar mass	(g/mol)
300	575	charac. temperature	(K)
630	280	charac. pressure	(MPa)
1.515	2.16	charac. density	(K)

Solubility calculation without dilation data

Typical trend of the volume dilation with pressure is linear:



(After Jordan and Koros, 1990)

One can define the
<u>swelling factor</u> k as:

$$\rho_2(p) = \rho_2^0(1-kp)$$

$$\mu_{1,ne}\left(T,\, p,\, \omega_1,\, \rho_2^0\,(1-kp) \right) = \mu_1^{ext}\left(T,\, p \right)$$

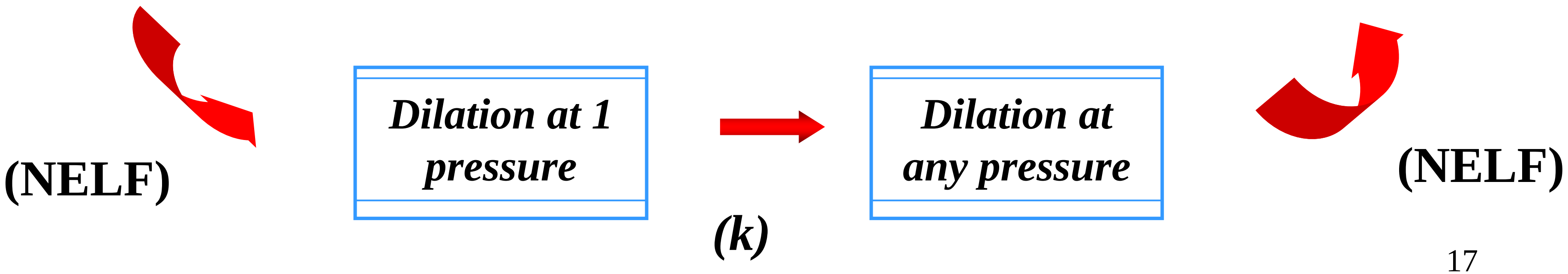
↓

k

Solubility calculation without dilation data

In the <u>absence of dilation data</u>* NELF *can be used as a correlation tool for the entire solubility isotherm based on the solubility at <u>one single pressure</u> through the use of the swelling factor k

ψ = ***1***	⇒***1*** *parameter correlation: k*
ψ = *fitted to one equilibrium data*	⇒***2*** *parameter correlation: k, ψ*



Solubility at 1 pressure

(NELF)

Dilation at 1 pressure

(k)

Dilation at any pressure

(NELF)

Solubility at any pressure

NET-GP general procedure

⇒ *Select an appropriate thermodynamic equilibrium model.*

⇒ ***find the pure component parameters for***

- ***penetrant: use PVT and/or vapor pressure data***
- ***polymer: use PVT data above*** T_g

⇒***the glassy polymer density: must be known***

⇒ ***Calculate penetrant chemical potential and solubility isotherm***

$$\frac{f_1^g}{RT} = c_1 \exp\left(\frac{\mu_{1,ne}^{res}}{RT}\right)$$

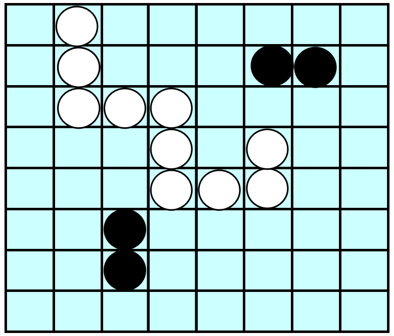
NET-GP main references

1. *Macromolecules* 1996, 29, 7885.
2. *Chem. Eng. Sci*. 1998, 53, 3435-3447.
3. *J. Membrane Sci*. 1998, 147, 73.
4. *ACS Symposium Series* 1999, 733, 179-193.
5. *Ind. Eng. Chem. Res*. 2001, 40, 3027-3037.
6. *Desalination*, v.144, p.73 (2002).
7. *ACS Symposium series*, v.876, p.74 (2004).
8. *ACS Symposium series*, v.876, p.55, (2004)

Equilibrium models:
Lattice Fluid
(LF),
Statistical Associating Fluid Theory
(SAFT),
Perturbed Hard Sphere Chain
(PHSC)

Basics of LF model

“Lattice Fluid” representation of substances



N_0 holes

r_i=number of sites occupied by a molecules of species i

Statistical evaluation of the number of configurations of the lattice with a mean field approximation

Estimate of the energetic interactions between adjacent sites

$$G = RT^{*}\left(\sum_{i=1}^{N} r_i\, n_i\right)\cdot\left\{-\tilde{\rho}+\frac{\tilde{p}}{\tilde{\rho}}+\frac{\tilde{T}}{\tilde{\rho}}\left[\left(1-\tilde{\rho}\right)\ln\left(1-\tilde{\rho}\right)+\tilde{\rho}\sum_{i=1}^{N}\frac{\phi_i}{r_i}\ln\left(\phi_i\,\tilde{\rho}\right)\right]\right\}$$

$\tilde{p} = p / p^{*}$ $\tilde{T} = T / T^{*}$ $\tilde{\rho} = \rho / \rho^{*}$

***r_i**= number of sites per molecule*

***ε^***= Potential energy well depth*

***v^*** = site volume*

***$p^*=\varepsilon^*/v^*$** Characteristic pressure*

***$T^*=\varepsilon^*/k$** Characteristic temperature*

$\rho_i^{*} = \dfrac{M_i}{r_i v_i^{*}}$ *Characteristic density*

LF Equation of state

Characteristic parameters are related to

- T^* ↔ **INTRAmolecular interactions**
- p^* ↔ **INTERmolecular interactions (solubility parameter, compressibility)**
- ρ^* ↔ **crystalline density**

$$\left(\frac{\partial \tilde{G}}{\partial \tilde{v}}\right)_{\tilde{T},\tilde{p}} = 0 \quad \Rightarrow \quad \rho = \rho^*\left\{1-\exp\left[-\left(\frac{\rho}{\rho^*}\right)^2\frac{T^*}{T}-\frac{T^*p}{TP^*}-\left(\frac{\rho}{\rho^*}-\frac{RT^*}{MP^*}\rho\right)\right]\right\}$$

LF EOS

Formally identical for pure substances and for mixtures

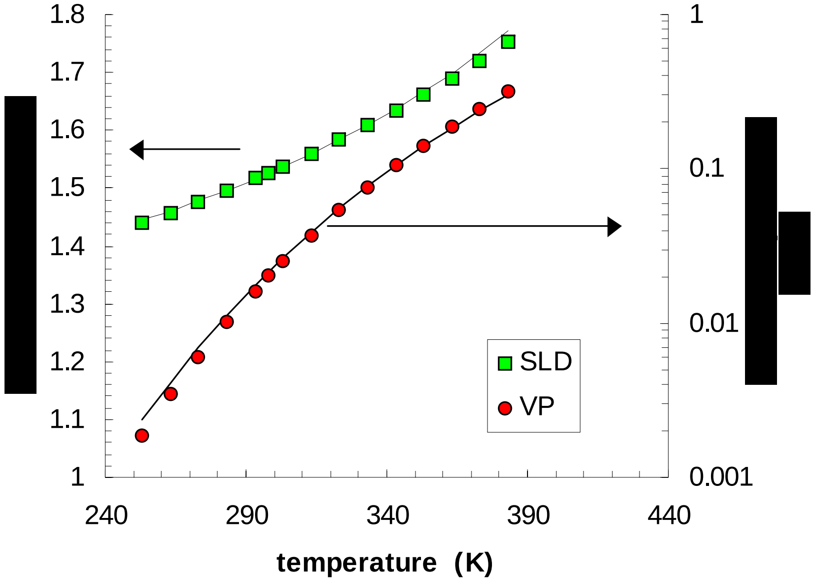
The characteristic parameters can be found in the literature, or estimated by best fitting of:

- *LV equilibrium data or PVT data, for **gases and vapors***

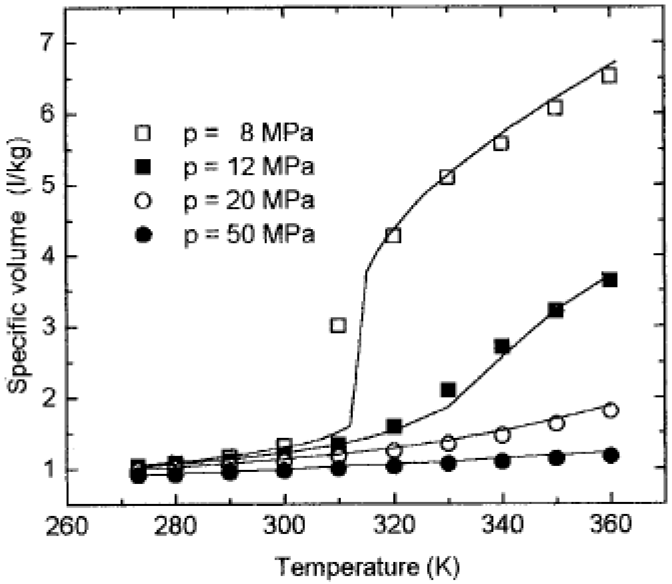
- *PVT data above T_G, for **polymers***

Estimation of LF characteristic parameters for pure gases and vapors

n-C_6 saturated liquid sp.volume and vapor pressure



CO_2 specific volume vs T at various P



n-C_6:

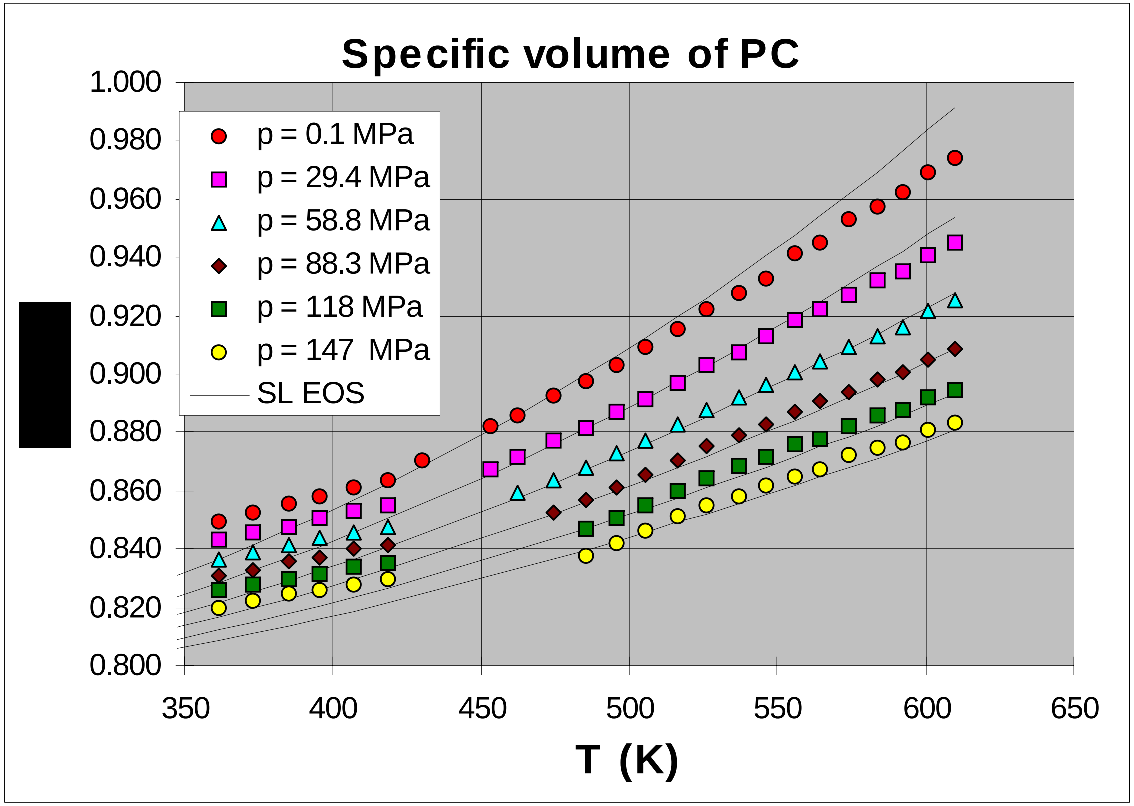
P*	(MPa)	**285**
rho*	(kg/l)	**0.762**
T*	(K)	**490**

CO_2:

P*	(MPa)	**630**
rho*	(kg/l)	**1.515**
T*	(K)	**300**

Estimation of LF characteristic parameters for pure polymers

PVT data above T_G



PC		
bisphenol-A polycarbonate		
T* =	**755**	K
P* =	**534**	Pa
rho* =	**1.275**	kg/l

Some polymers (PTMSP) degrade at $T<T_G$: it is not possible to estimate the LF EOS parameters from the data above T_G!

They can be estimated indirectly via solubility data or with molecular simulation tools

LF model for mixtures: mixing rules

ρ* $\boxed{\frac{1}{\rho^*} = \frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*}}$ **T*** $\boxed{T^* = P^* / \left[\rho^* \left(\frac{P_1^* \omega_1}{T_1^* \rho_1^*} + \frac{P_2^* \omega_2}{\rho_2^* T_2^*} \right) \right]}$ **P*** $\boxed{P^* = \rho^* \left(\frac{P_1^* \omega_1}{\rho_1^*} + \frac{P_2^* \omega_2}{\rho_2^*} + \frac{\omega_1 \omega_2}{\rho_2^* \rho_1^*} \rho^* \left(P_1^* + P_2^* - 2\boldsymbol{P_{12}^*} \right) \right)}$

$$\boxed{\Delta P_{12}^* = P_{11}^* + P_{22}^* - 2\Psi_{12}\sqrt{P_1^* P_2^*}}$$

or:

$$\boxed{P_{12}^* = \Psi_{12}\sqrt{P_1^* P_2^*}}$$

1 binary parameter Ψ_{12} ↔ **gas – polymer interactions**

To be adjusted on **experimental miscibility data**

How do we estimate Ψ <u>without</u> miscibility data ?

<u>1st approx.</u>:

Ψ_{12} **= 1**

$P_{12}^* = \sqrt{P_1^* P_2^*}$

↔

Gas-polymer interactions

=

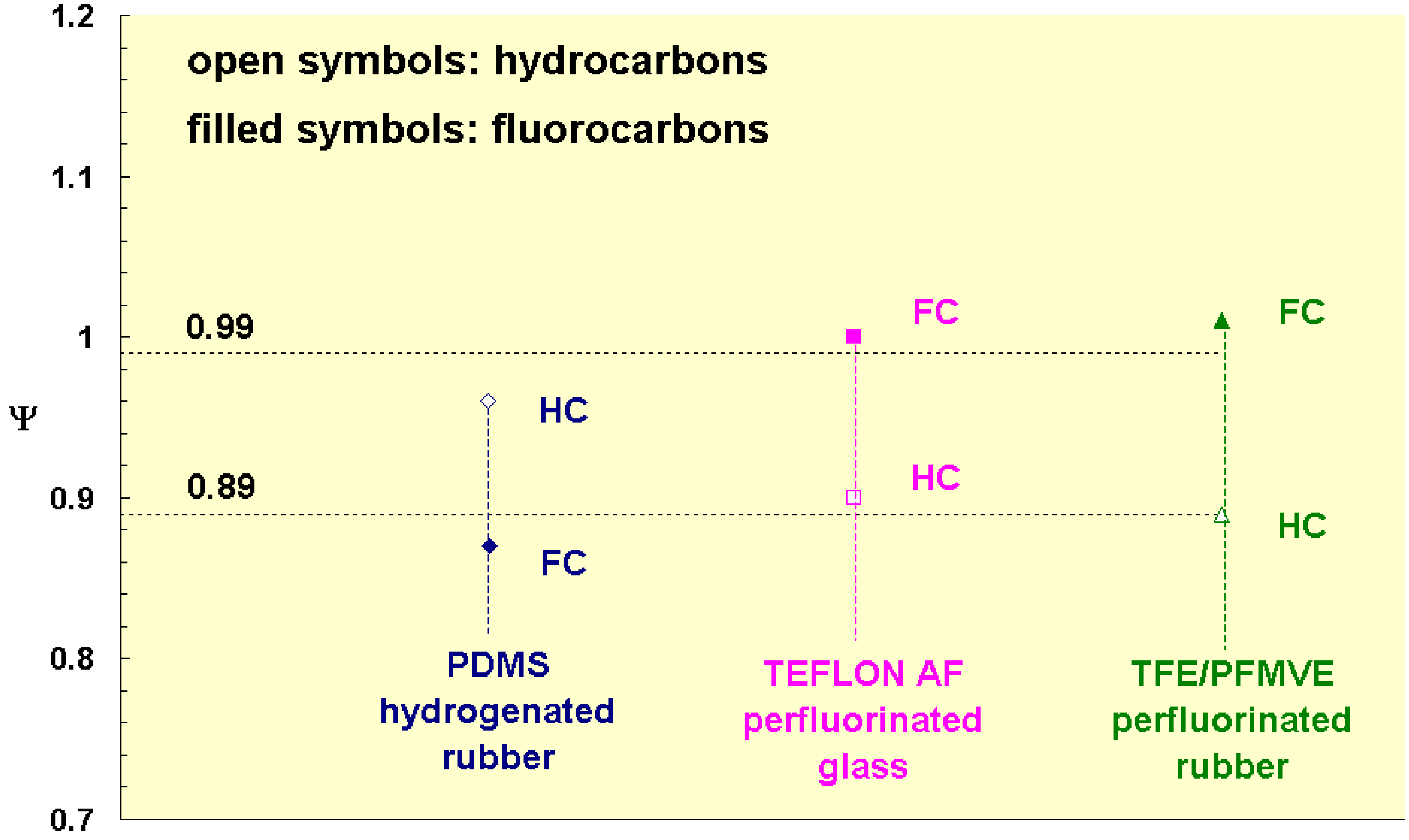
<u>Geometric mean</u> between

gas-gas and

polymer-polymer interactions

Some observations about the mixing rules

It has been observed that the mixing rule, with $\Psi_{12}=1$, is not always appropriate to describe the behavior of mixtures of substances with different functional groups, in particular those involving **fluorocarbons and hydrocarbons**



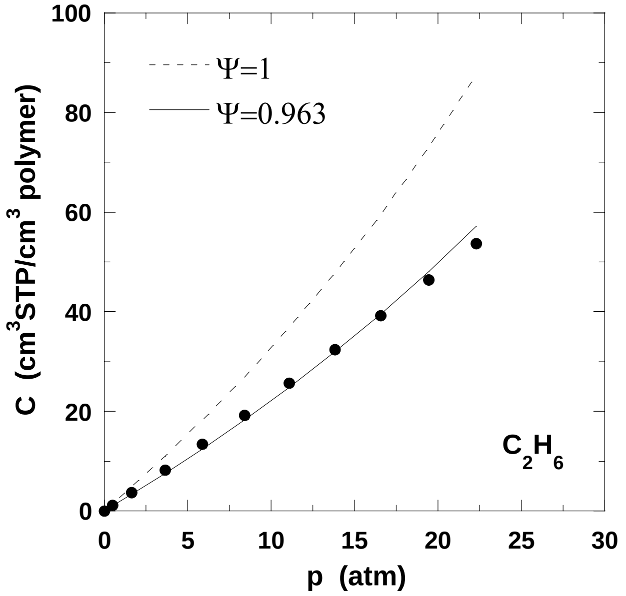
LF EOS for gas sorption in rubbery polymers

$$\tilde{\rho}_1 = 1 - \exp\left[-\frac{\tilde{\rho}_1^2}{\tilde{T}_1} - \frac{\tilde{P}_1}{\tilde{T}_1} - \left(1 - \frac{1}{r_1^0}\right) \cdot \tilde{\rho}_1 \right] \qquad \mathbf{(1)}$$

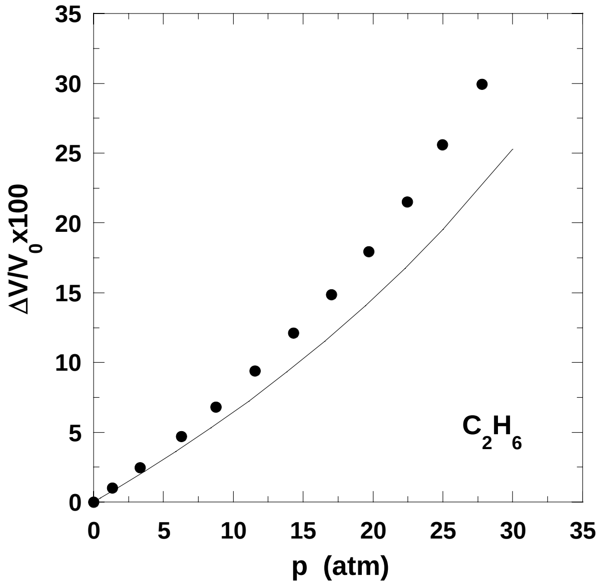
$$\left\{ \begin{array}{l} \tilde{\rho} = 1 - \exp\left[-\frac{\tilde{\rho}^2}{\tilde{T}} - \frac{\tilde{P}}{\tilde{T}} - \left(1 - \frac{\Phi_1}{r_1}\right) \cdot \tilde{\rho} \right] \qquad \mathbf{(2)} \\ \left[-\frac{\tilde{\rho}_1}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \tilde{\rho}_1} + \frac{(1-\tilde{\rho}_1)\ln(1-\tilde{\rho}_1)}{\tilde{\rho}_1} + \frac{\ln \tilde{\rho}_1}{r_1^0} \right] \cdot r_1^0 = \ln \Phi_1 + (1-\Phi_1) + \tilde{\rho} \cdot \frac{M_1}{\rho_1^*} \frac{\Delta P^*}{RT} \cdot (1-\Phi_1)^2 + \left[-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \cdot \tilde{\rho}} + \frac{(1-\tilde{\rho})\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\ln \tilde{\rho}}{r_1} \right] \cdot r_1 \qquad \mathbf{(3)} \end{array} \right.$$

1: EOS for the penetrant
2: EOS for the mixture
3: Phase equilibrium

C_2H_6 in PDMS at 35°C-sorption

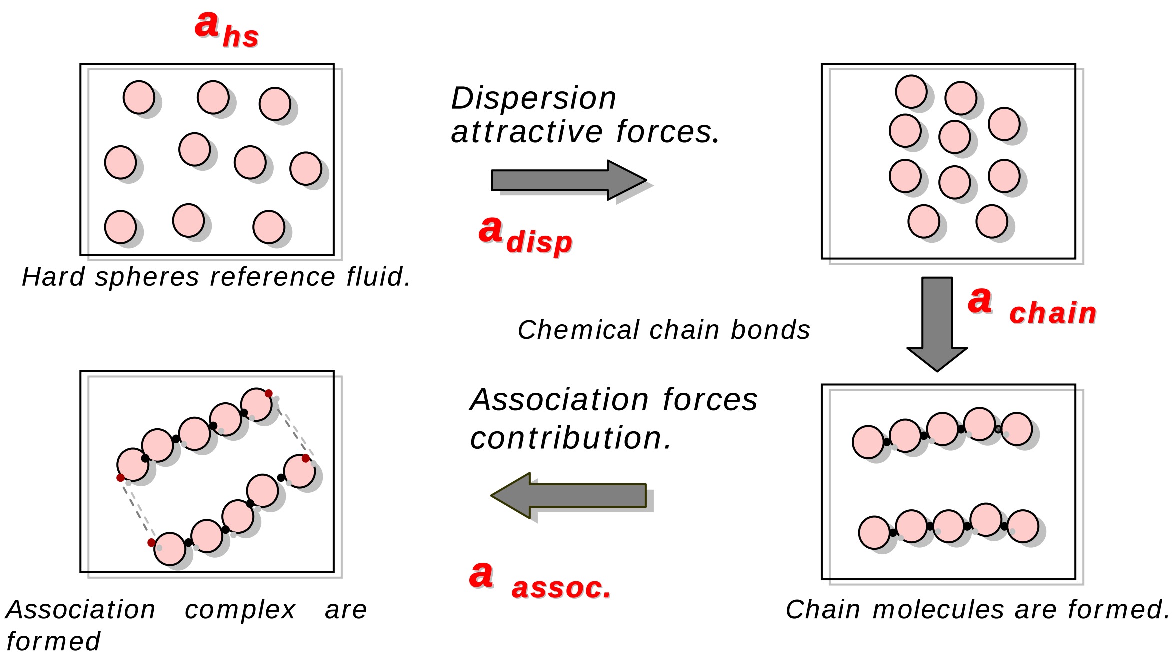


C_2H_6 in PDMS at 35°C-dilation



Basics of SAFT model

Molecules are chains of tangent hard spheres with a fixed mass and a temperature-dependent volume, whose residual Helmholtz free energy can be calculated in an additive way:



a_{hs}

Hard spheres reference fluid.

Dispersion attractive forces.

a_{disp}

a_{chain}

Chemical chain bonds

Chain molecules are formed.

Association forces contribution.

$a_{assoc.}$

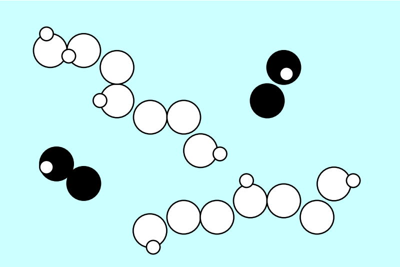
Association complex are formed

$$a^{res} = a(T,V,n) - a^{id}(T,V,n)$$

$$a^{res} = a_{hs} + a_{disp.} + a_{chain} + a_{assoc.}$$

Basics of SAFT model

☞ $a^{res} = (a)_{hs} + (a)_{disp} + (a)_{chain} + (a)_{assoc}$



hard sphere	$(a)_{hs}$	Carnahan & Starling (1969)
dispersion	$(a)_{disp}$	power series fit of square well fluid by Adler (1972)
chain	$(a)_{chain}$	Chapman *et al.* (1990)
association	$(a)_{assoc}$	Chapman *et al.* (1990)

☞ **Pure component parameters**:

⇒ segment diameter	σ	(Å)
⇒ segment mass	m’	(g/mol)
⇒ well depth	ε/k	(K)

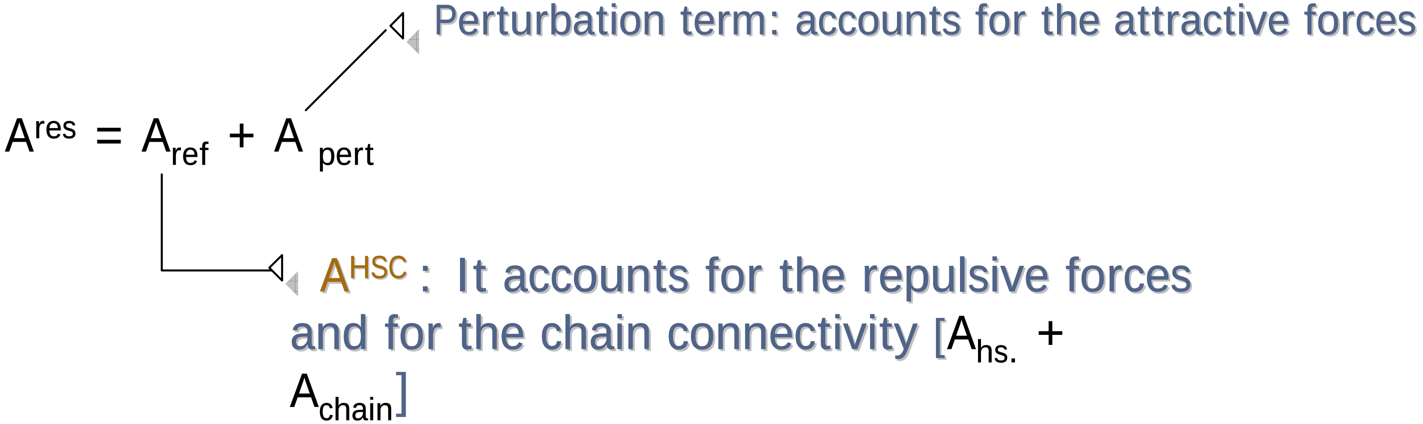
☞ **Binary parameter** k_{ij}

$\varepsilon_{ij} = (\varepsilon_{ii}\, \varepsilon_{jj})^{1/2}\,(1- k_{ij})$

1st order approximation $k_{ij} = 0$

Basics of PHSC model

- In the PHSC EOS the residual Helmholtz free energy is composed of two terms **:**



$A^{res} = A_{ref} + A_{pert}$

Perturbation term: accounts for the attractive forces

A^{HSC} : It accounts for the repulsive forces and for the chain connectivity [$A_{hs.} + A_{chain}$]

- There are no explicit terms for the interactions of associating fluids

Different versions of SAFT and PHSC EOS

- *Within a same theory, there are several versions, differing for the expression used for the terms composing the residual Helmholtz free energy*

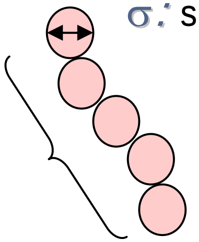
We adopted two versions of each model, so far:

  - ***SAFT** (ot SAFT-HR), by Huang and Radosz (1990)*
    (A_{disp} by Chen-Kreglewsky)
  - ***(PC) SAFT** by Gross and Sadowsky (2001)*
    (A_{disp} from Barker and Henderson perturbation theory)

  - ***PHSC S** simplified (Song et al., 1996)*
    (Van der Waals attractive term)
  - ***PHSC SW** Square well (Hino, Prausnitz, 1997)*
    (perturbation term based on Barker-Henderson theory)

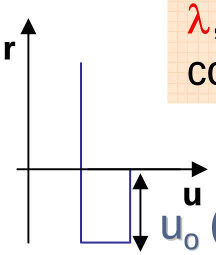
Characteristic parameters of HSC models

- Both models have three characteristic parameters [σ, r, u_o]:



σ: sphere diameter

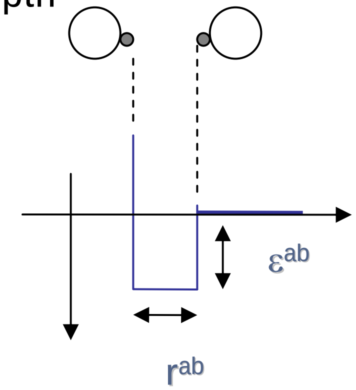
r: number of spheres



u_o (ε) interaction potential well depth

PHSC (square well) has another parameter: λ, the width of the potential well, which is constant among class of substances

- In the case of associating fluids, SAFT models also has:
  - ε^{ab} association energy.
  - $\mathbf{k}^{ab}$ association volume associated to r^{ab}



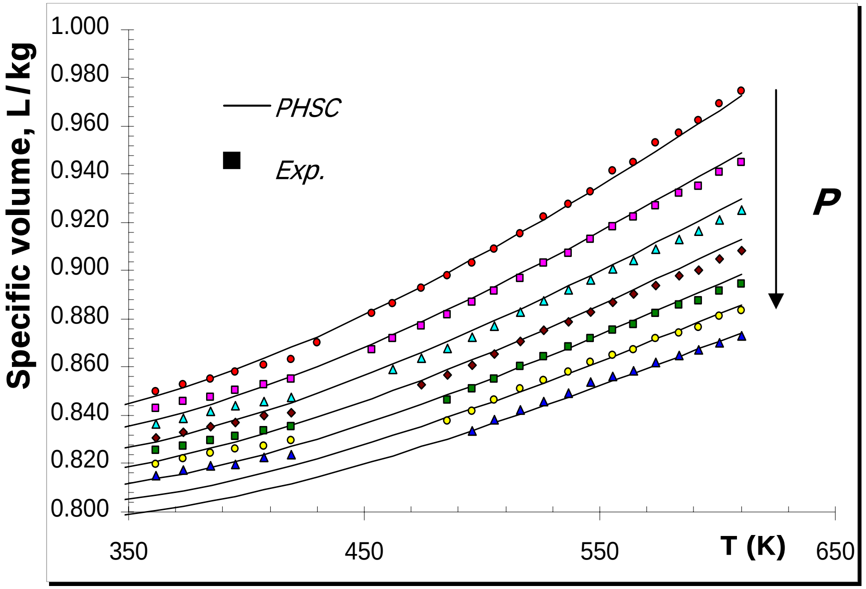
Mixing rules:

- The only adjustable parameter appears in the mixing rules for the dispersion term:

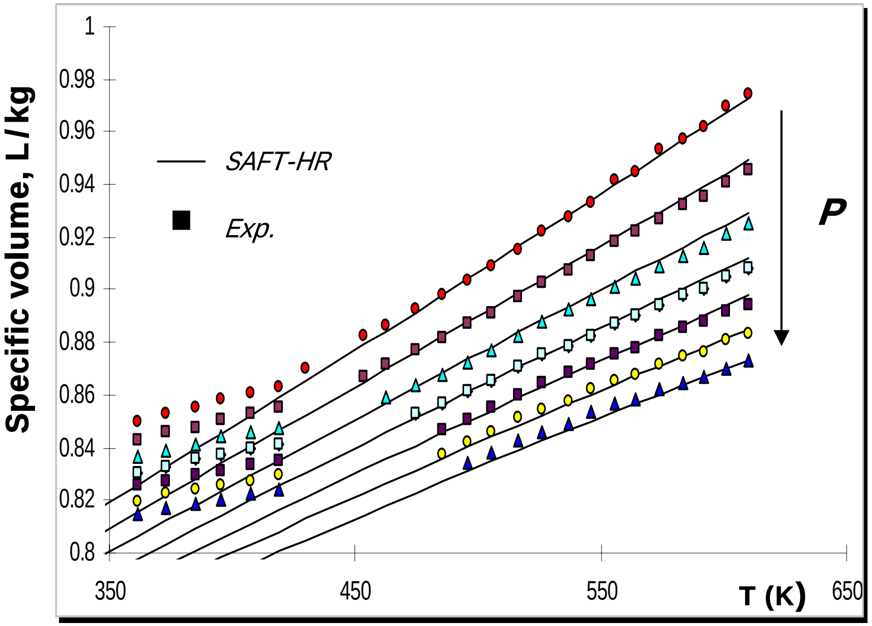
$$u_{ij}^{0} = \left(1 - k_{ij}\right)\sqrt{u_{ii}^{0} \cdot u_{jj}^{0}}$$

Determination of characteristic parameters

Polycarbonate PVT data and PHSC–S EOS



Polycarbonate PVT data and SAFT EOS

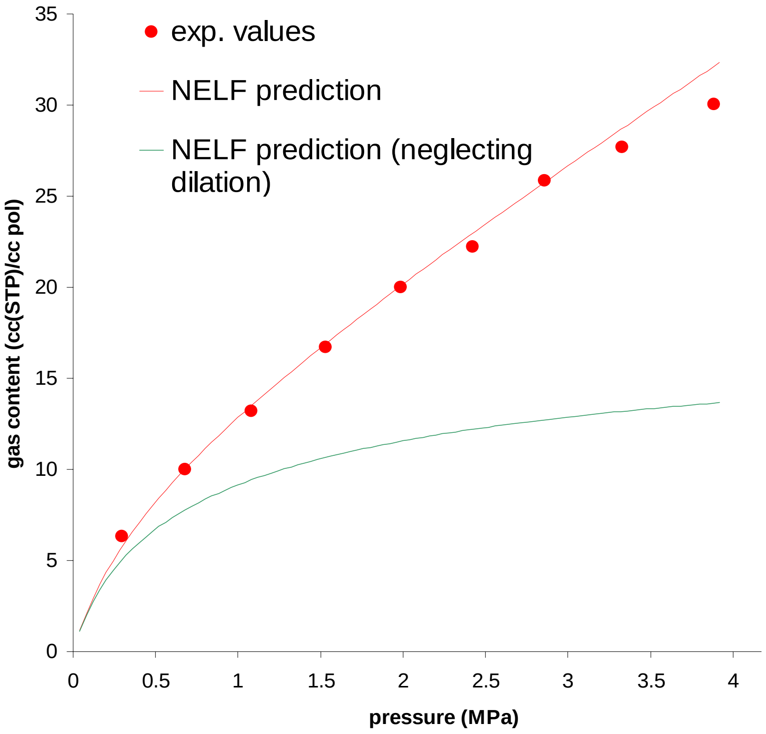


	σ (Å)	MM / r (g/mol)	u_o / k (K)
PHSC-S	**3.707**	**25.74**	**393.0**
SAFT-HR	**3.043**	**25.00**	**371.0**

NET-GP approach: performance, results and comparison with experimental data

NELF predictions (with dilation data)

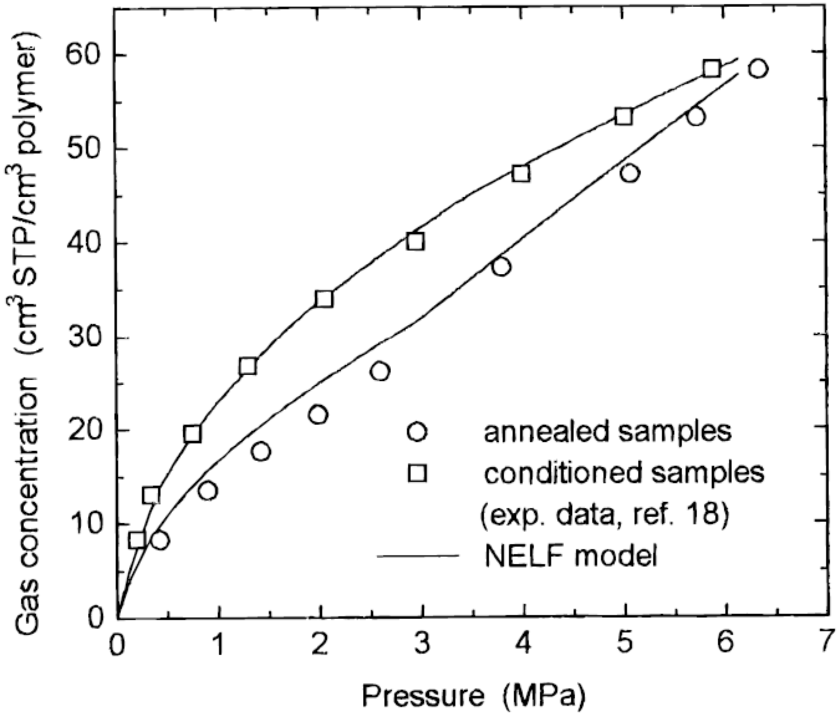
C_2H_4 solubility in PC at 35°C



(data from Fleming and Koros, 1990)

Effect of history

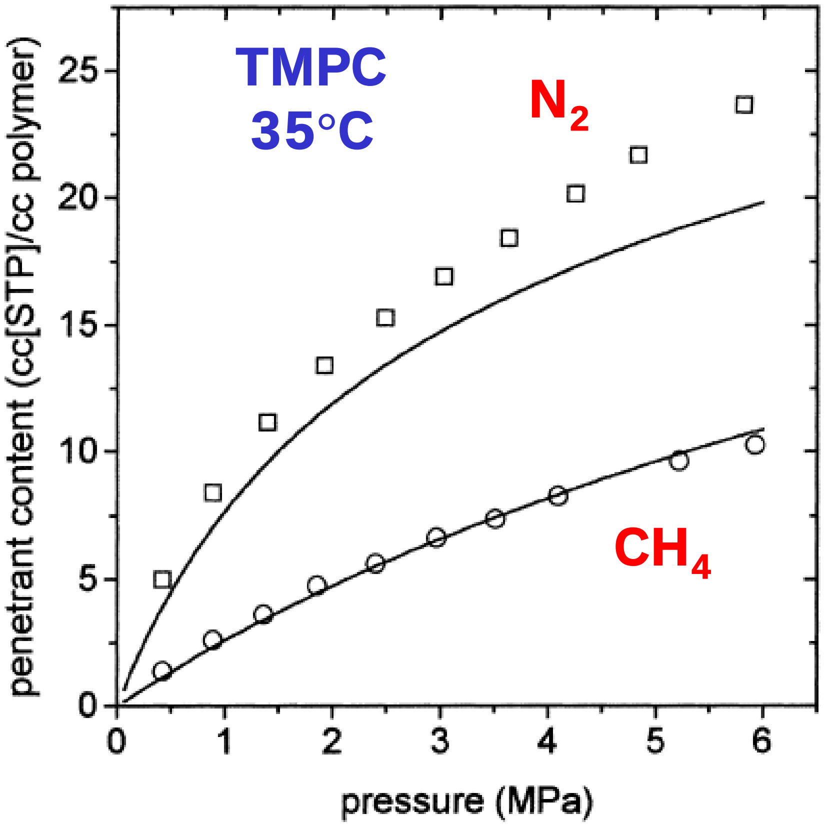
CO_2 solubility in PC at 35 °C



Fleming, G. K.; Koros, W. J.
Macromolecules **1986**, *19*, 2285

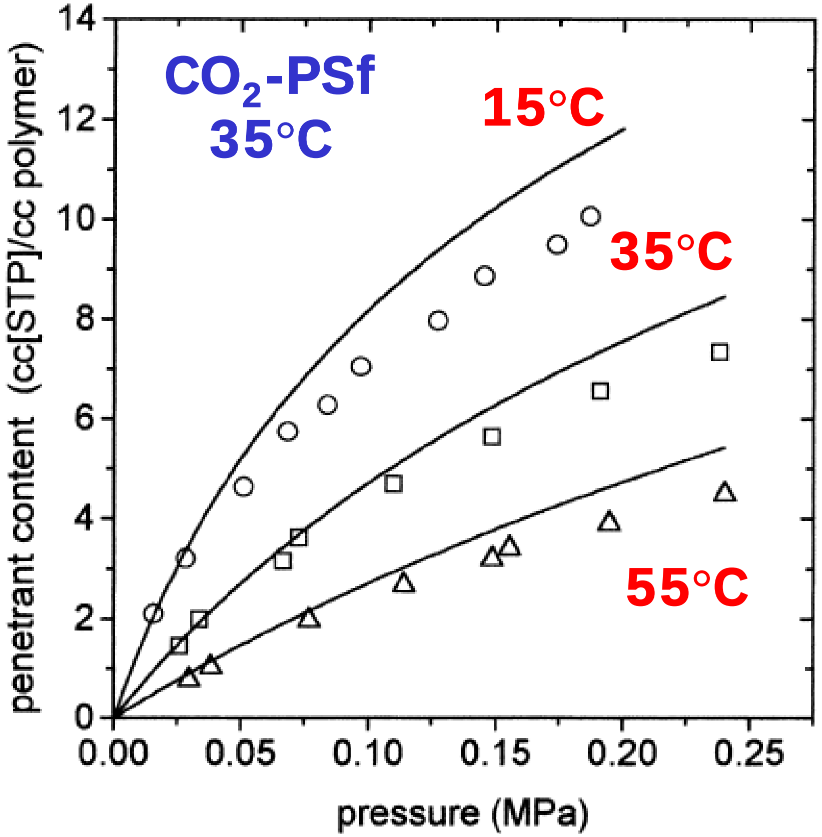
NELF predictions with constant density approx $\rho_2 \approx \rho_2^0$

Non swelling penetrants



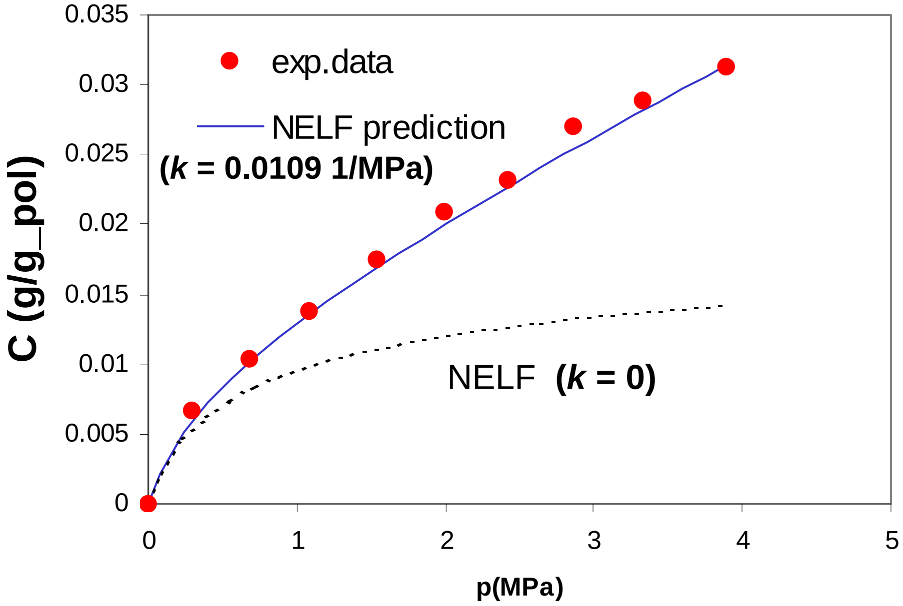
(data from Jordan and Koros)

Swelling penetrants, low pressure



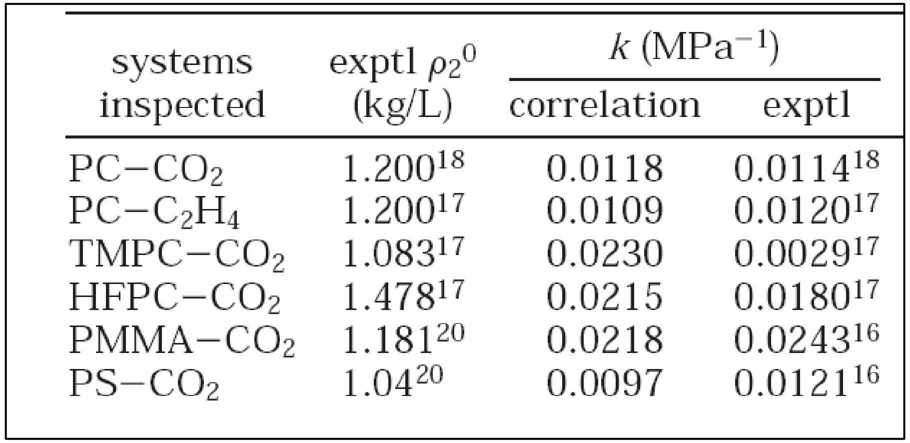
(data from Wang and Kamiya)

NELF correlations (no dilation data)



C_2H_4 in PC at 35°C

(data from Jordan and Koros, 1995)



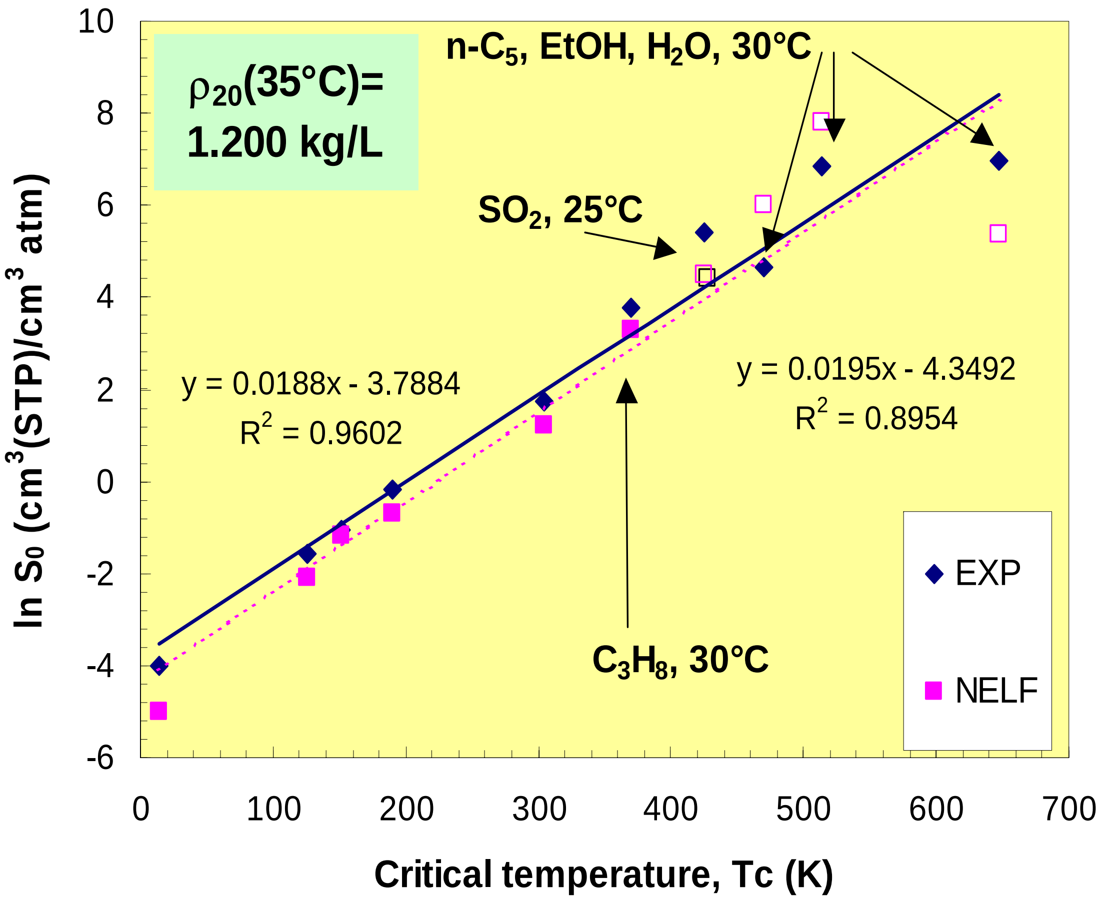
systems inspected	exptl ρ_2^0 (kg/L)	k (MPa^{-1}) correlation	k (MPa^{-1}) exptl
PC−CO_2	1.200[18]	0.0118	0.0114[18]
PC−C_2H_4	1.200[17]	0.0109	0.0120[17]
TMPC−CO_2	1.083[17]	0.0230	0.0029[17]
HFPC−CO_2	1.478[17]	0.0215	0.0180[17]
PMMA−CO_2	1.181[20]	0.0218	0.0243[16]
PS−CO_2	1.04[20]	0.0097	0.0121[16]

The ***swelling coefficient***, ***k***, *estimated in this way, is close to the measured value:*

- ***k*** *is a realistic measure of swelling and not merely an empirical adjustable parameter*
- *This procedure offers a reliable estimate of the dilation isotherm when one sorption datum is available.*

NELF: solubility at infinite dilution vs T_C

$$ln(S_0) = ln\left(\frac{T_{STP}}{P_{STP}T}\right) + r_1^0\left\{\left[1+\left(\frac{v_1^*}{v_2^*}-1\right)\frac{\rho_2^*}{\rho_2^0}\right]ln\left(1-\frac{\rho_2^0}{\rho_2^*}\right)+\left(\frac{v_1^*}{v_2^*}-1\right)+\frac{\rho_2^0}{\rho_2^*}\frac{T_1^*}{T}\frac{2}{P_1^*}\Psi\sqrt{P_1^*P_2^*}\right\}$$



$$S_0 = \lim_{p\to 0}\left(\frac{C}{p}\right)$$

$$ln(S_0) = a + b\cdot T_C$$

NELF: solubility at infinite dilution vs M_W

In the low pressure range, one also has:

$$\boxed{\frac{d}{dr_1^{\circ}}\ln\left[\frac{c_1}{p/p_{vap}}\right]=\ln(v_f)+(1-v_f)\frac{p_2^* v_1^*}{RT}}$$

r_1^0=measure of the chain length

v_f= polymer fract. free volume

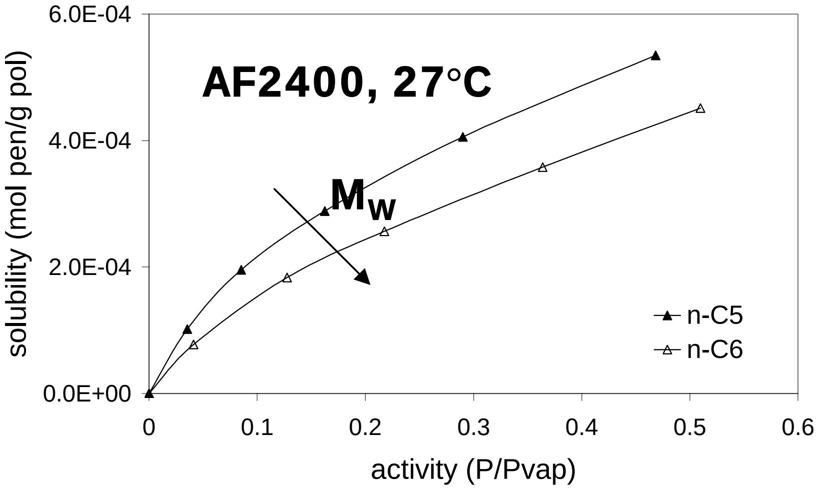
1) *If* $\boldsymbol{v_f}$ *is* ***small****, the r. h. s. of the equation is always* **<** **0***: solubility decreases with increasing* M_W.

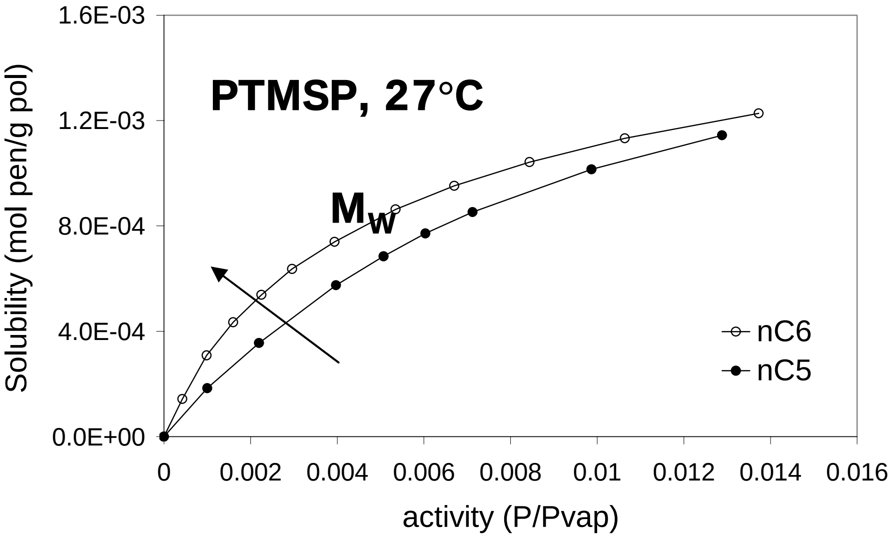
2) *The critical fractional free volume,* $\boldsymbol{v_{fc}}$*, at which the r.h.s.vanishes can exist, depending upon* p_2^*

3) For **small** $\boldsymbol{p_2^*}$ **,** $\mathbf{v_{fc}\rightarrow 1}$ ⇒ even for high $\boldsymbol{v_f}$ *solubility decreases with increasing* M_W

NELF prediction of the correlation between solubility and M_W

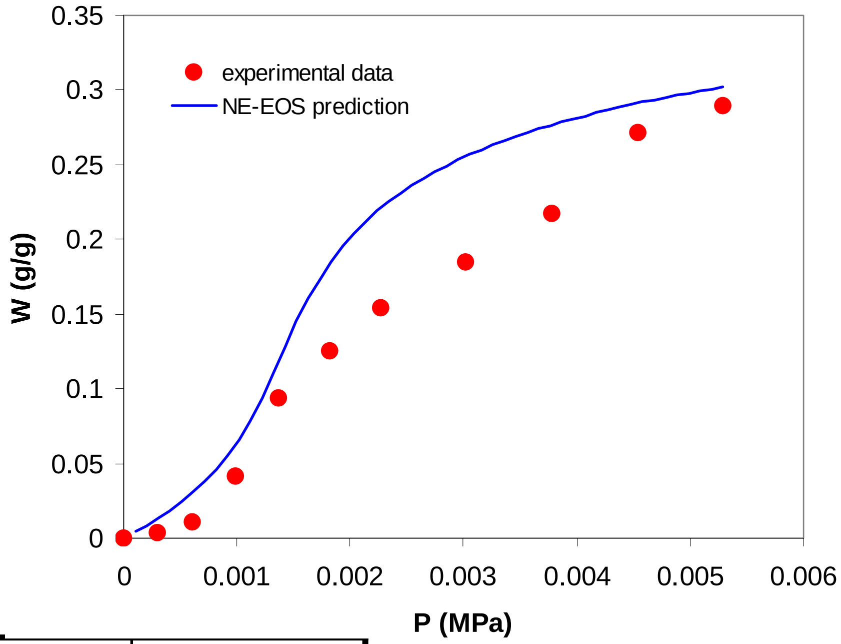
	p_2^* (Mpa)	v_{fc}	v_f
PTMSP	500-600	0.2	0.25-0.30
PTBA 50	500-600	0.2	0.15
AF2400	250-300	→1	0.13-0.18





Sigmoidal isotherms: Alcohols in PTMSP

Ethanol sorption in PTMSP at 25°C



	ρ*(kg/L)	T* (K)	P* (MPa)	ρ_{20} (kg/L)
PTMSP	1.250	515	440	0.74
C_2H_5OH	1.010	432	1065	

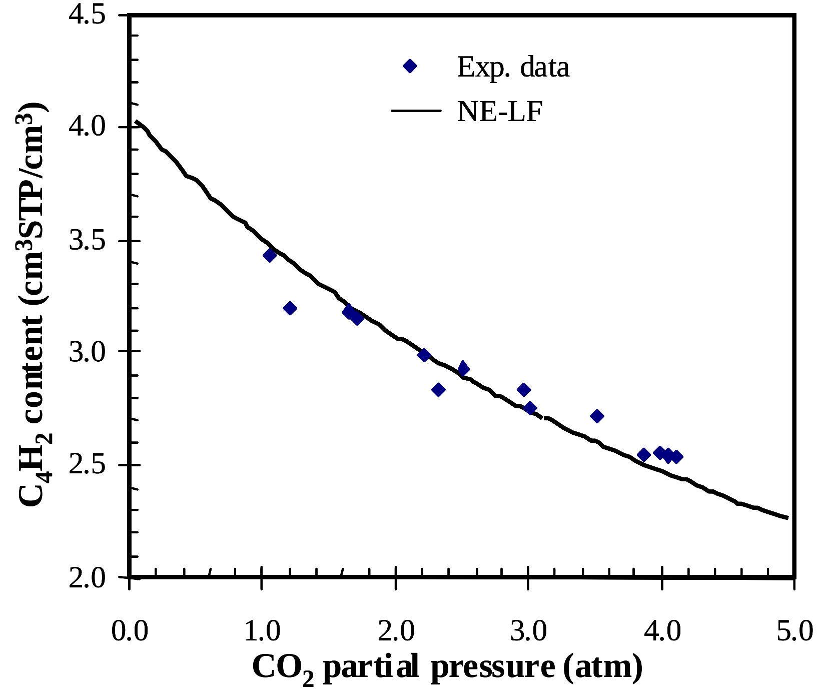
$k_{sw}=k_{12}=0$

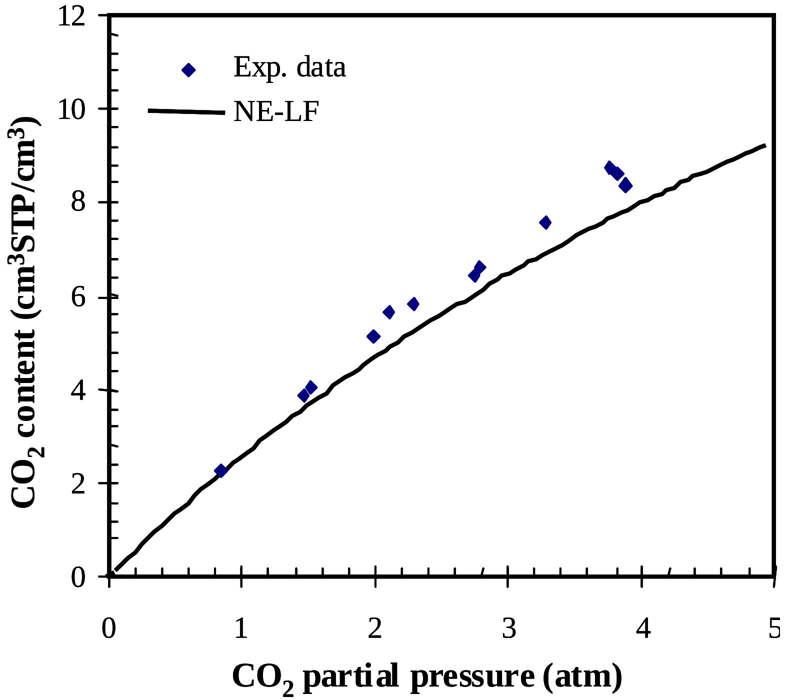
For PTMSP, ρ* is evaluated from experimental data, T* and P* adjusted on the solubility isotherms of alkanes at various temperatures in PTMSP

(data of solubility and pure polymer density from Nakanishi et al.)

NELF prediction of mixed gas sorption

PMMA-C_2H_4-CO_2 mixture at 35°C





C_2H_4 partial pressure = constant= 2.06± 0.08 atm.

- ✓*Default binary parameters for the polymer-penetrant pairs ($k_{12}=k_{13}=0.0$)*
- ✓*Swelling neglected;*
- ✓*VL equilibrium data used for the evaluation of the C_2H_4-CO_2 k_{23} ($k_{23} = 0.024$).*

Data E.S: Sanders, W.J. Koros, H.B. Hopfenberg, V.T. Stannett, *J. Membrane Sci.*, 18, 53 1984

NE-LF prediction of pure gas sorption in blends

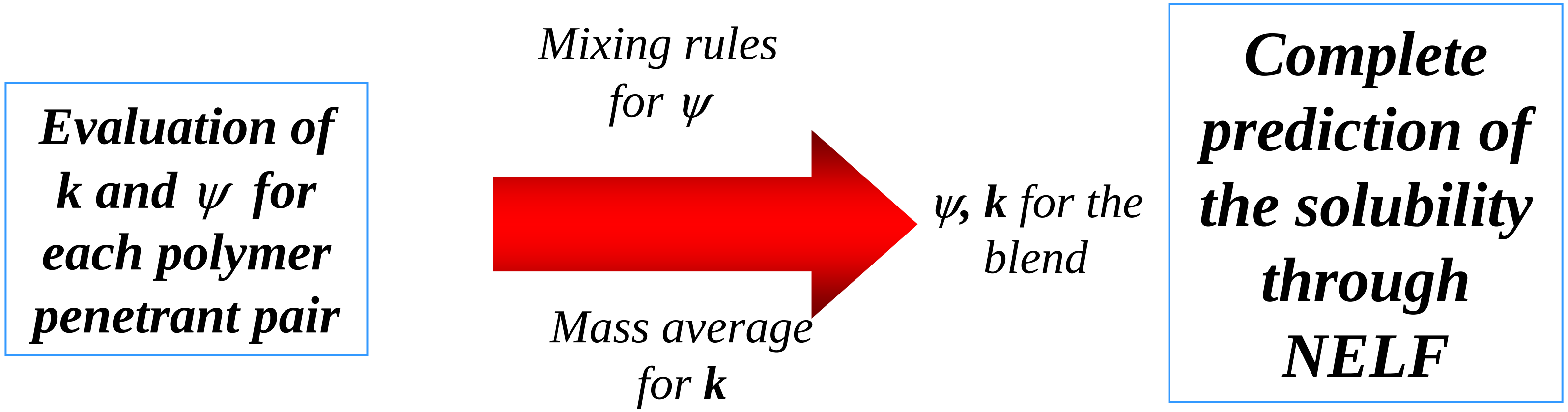
The blend is treated like a pseudo component, mixture of the two homopolymers, and the mixture characteristic parameters calculated accordingly from the pure homopolymers parameters. In particular, for the gas-blend binary parameter:

$$\Delta P^*_{B3} = \frac{\phi_1}{\phi_1+\phi_2}\Delta P^*_{13} + \frac{\phi_2}{\phi_1+\phi_2}\Delta P^*_{23} - \frac{\phi_1\cdot\phi_2}{\phi_1+\phi_2}\Delta P^*_{12}$$

adjusted on the the blend volumetric data or Y=1

adjusted on the solubility of gas in the homopolymers

The swelling coefficient, k_B of the gas in the blend is calculated as the mass average of the swelling parameters of the gas in the two homopolymers.



Evaluation of k and ψ for each polymer penetrant pair

Mixing rules for ψ

*Mass average for **k***

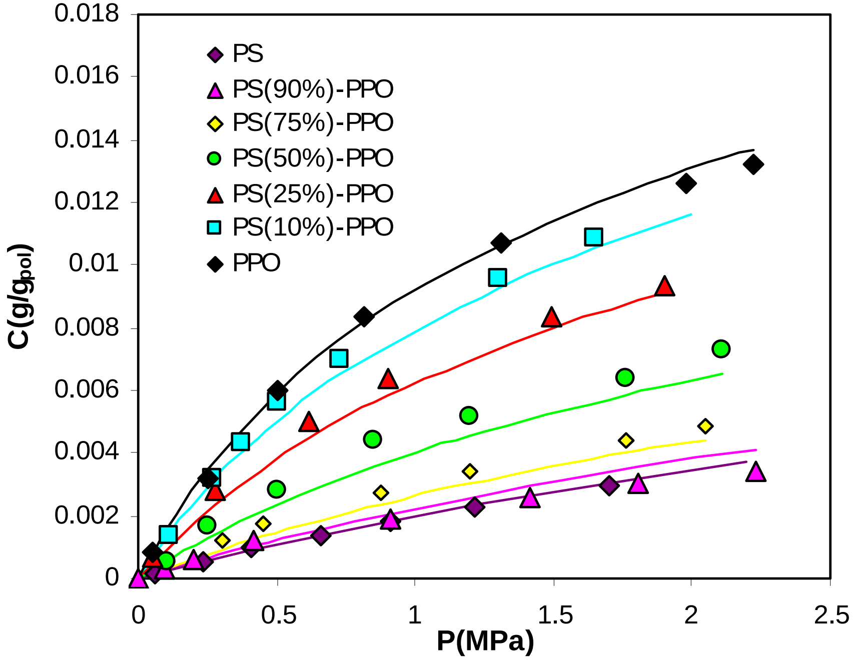
*ψ, **k** for the blend*

Complete prediction of the solubility through NELF

NE-LF prediction of pure gas sorption in blends

CH_4 in PS-PPO at 35°C

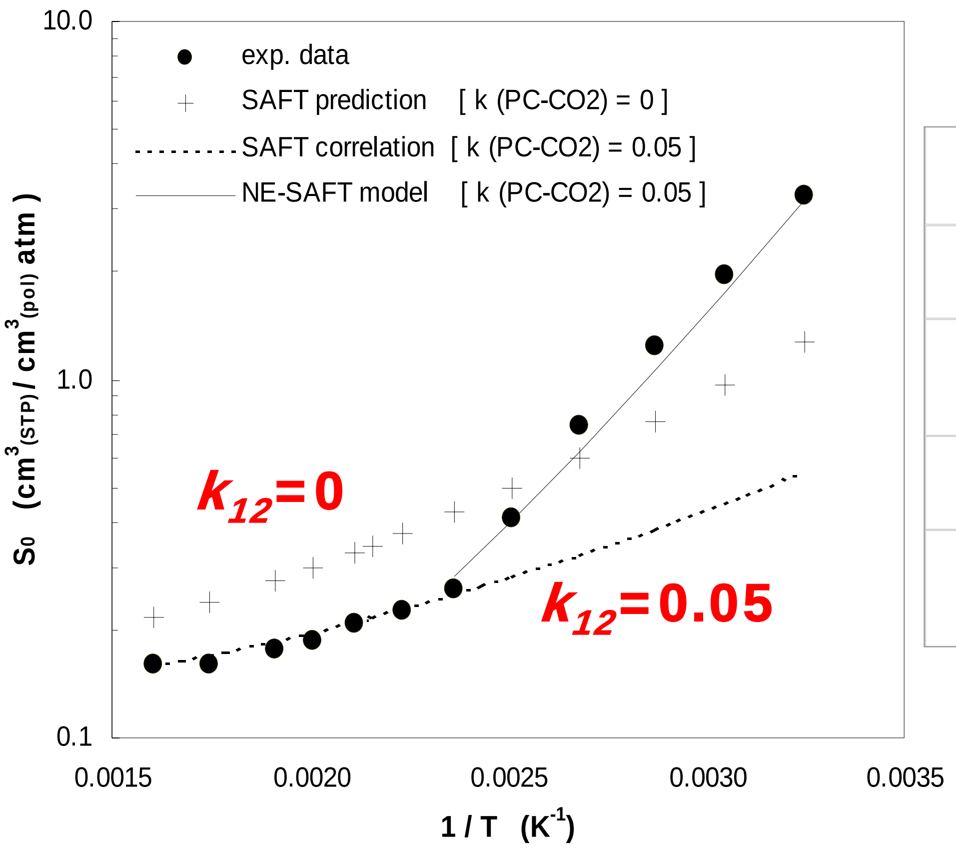
Swelling parameter=0



Y.Maeda, D.R.Paul, *Polymer*, 26, 1985, 2055-2063.

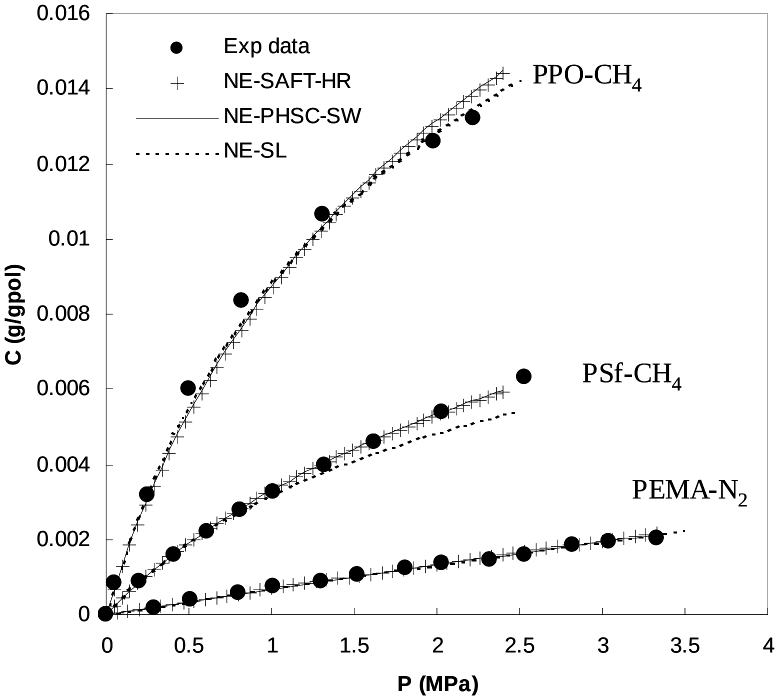
		NELF						
PS				**PPO**			**CH4**	
T*	(K)	**750**	T*	(K)	**3.043**	mol weight		**16.01**
P*	(MPa)	**360**	P*	(MPa)	**25**	T*	(K)	**215**
rho*	(g/cm3)	**1.099**	rho*	(g/cm3)	**371**	P*	(MPa)	**250**
						rho*	(g/cm3)	**0.5**
Kcalc	1/Mpa	**0**	Kcalc	1/Mpa	**0**			
bynary parameter		PS-CH4					**0.9517**	
bynary parameter		PPO-CH4					**1.0931**	

NE-SAFT prediction of infinite dilution solubility across T_G



	PC	CO_2
σ (Å)	3.043	3.171
MW/m(g/mol)	25	31.05
u_0/k (K)	371	216.08

NE-EOS prediction of sorption

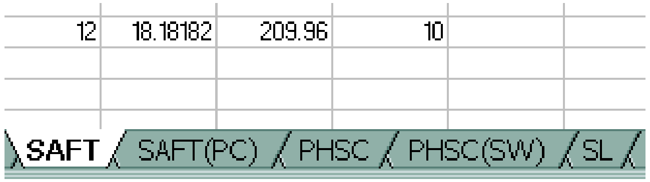


Binary Parameters k_{ij}			
System	**SAFT -HR**	**PHSC-SW**	**SL** (1- Ψ_{ij})
PEMA-N$_2$	0.020	-0.018	0.030
PSf-CH$_4$	-0.015	-0.085	-0.030
PPO-CH$_4$	0.0	-0.085	-0.060

Brief Tutorial

Open file: **model_file_NE** *and save it with the most appropriate name.*

*Check if the pure component parameters for your system, relative to the model that you are going to use (***SL***,* **SAFT***,* **SAFT(PC)***,* **PHSC** *or* **PHSC (SW)***) are in the database. The characteristic parameter for each EOS are put in the homonymous worksheet*



12	18.18182	209.96	10	

Check if in the worksheet named **IG** *there are the molecular weight for the penetrant and the polymer. For the polymer, put* $Mw=10^{\wedge 30}$ *g/mol*

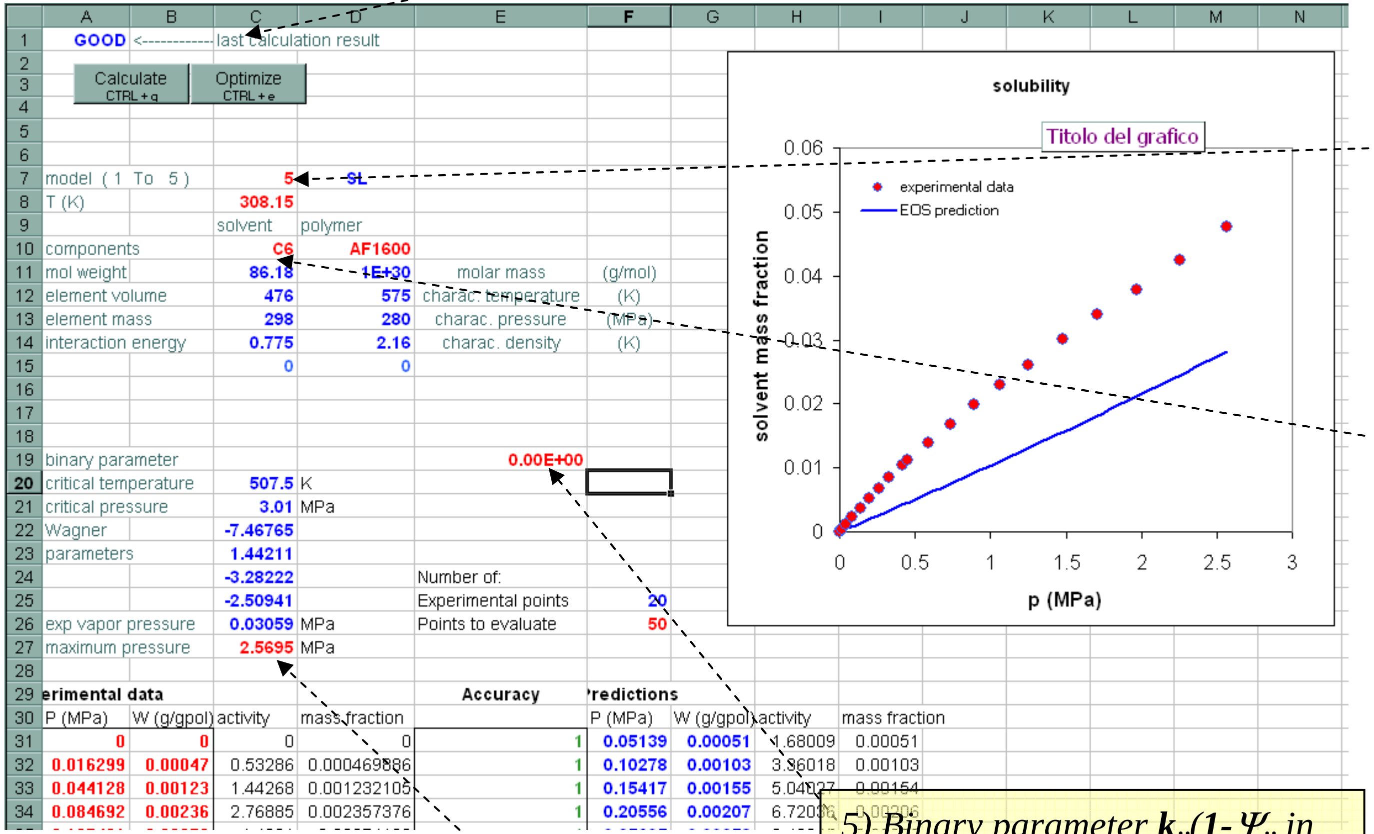
If you found the characteristic parameters and want to perform an equilibrium Solubility calculation, open worksheet named **EQ_SOL**

EQ_SOL: *red cells are to be modified by the user*
Certain cells are protected: you have to remove the protection before modifying them

6) Calculate solubility

1) Choose the EOS that you want to use:
1:SAFT
2: SAFT(PC)
3: PHSC
4: PHSC(SW)
5: SL

2)Choose the name of the components (same name that appears in the database). The system will automatically take the parameters from the database. If you want to test different parameters, you need to insert a new set in the database with a different name: e.g. AF1600-2



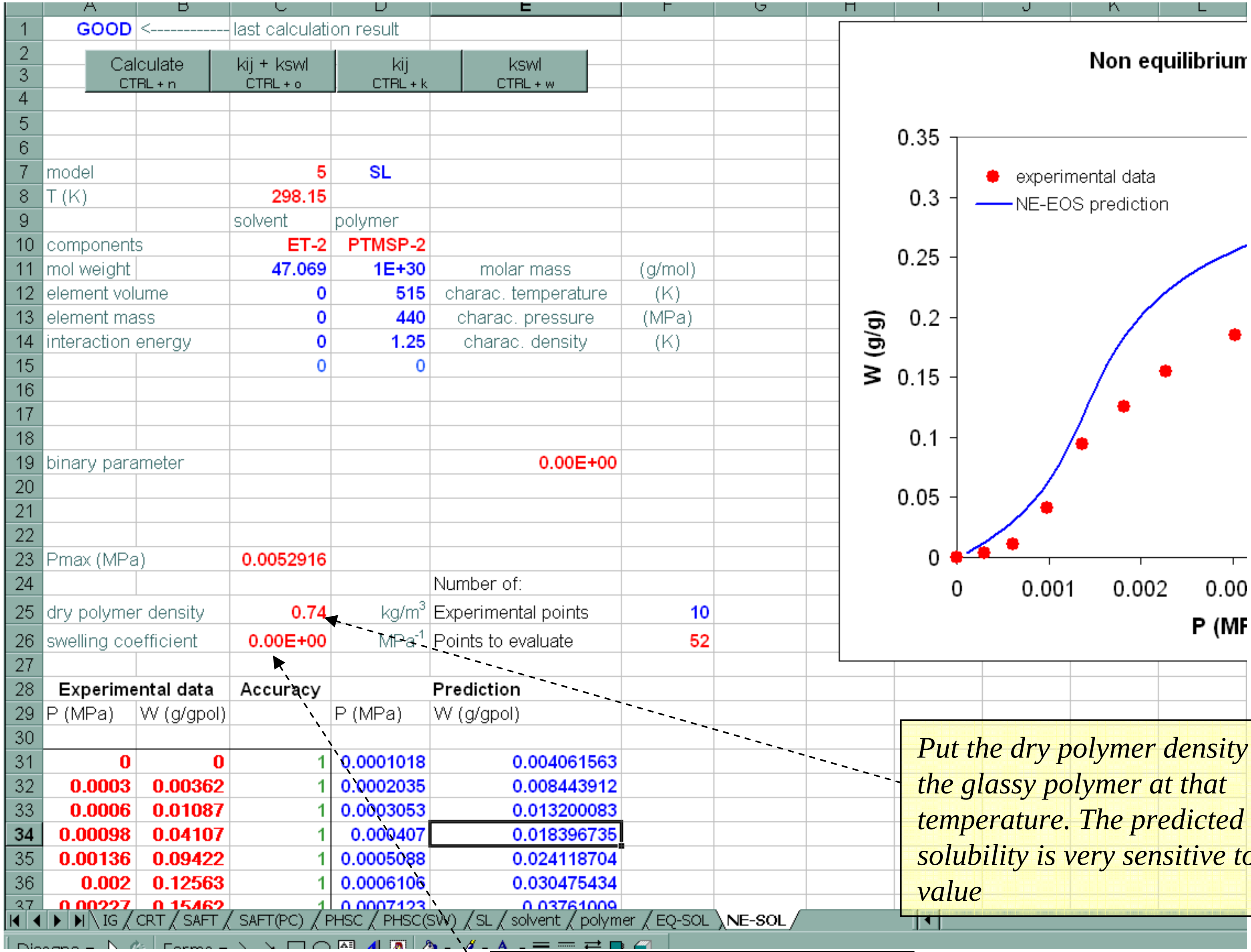
	A	B	C	D	E	F	G	H	I
1	GOOD	<------------	last calculation result						
2									
3									
4									
5									
6									
7	model (1 To 5)		5	SL					
8	T (K)		308.15						
9			solvent	polymer					
10	components		C6	AF1600					
11	mol weight		86.18	1E+30	molar mass	(g/mol)			
12	element volume		476	575	charac. temperature	(K)			
13	element mass		298	280	charac. pressure	(MPa)			
14	interaction energy		0.775	2.16	charac. density	(K)			
15			0	0					
16									
17									
18									
19	binary parameter				0.00E+00				
20	critical temperature		507.5	K					
21	critical pressure		3.01	MPa					
22	Wagner		-7.46765						
23	parameters		1.44211						
24			-3.28222		Number of:				
25			-2.50941		Experimental points	20			
26	exp vapor pressure		0.03059	MPa	Points to evaluate	50			
27	maximum pressure		2.5695	MPa					
28									
29	erimental data				Accuracy	redictions			
30	P (MPa)	W (g/gpol)	activity	mass fraction		P (MPa)	W (g/gpol)	activity	mass fraction
31	0	0	0	0	1	0.05139	0.00051	1.68009	0.00051
32	0.016299	0.00047	0.53286	0.000469886	1	0.10278	0.00103	3.36018	0.00103
33	0.044128	0.00123	1.44268	0.001232105	1	0.15417	0.00155	5.04027	0.00154
34	0.084692	0.00236	2.76885	0.002357376	1	0.20556	0.00207	6.72036	0.00206

3) Put the experimental sorption data

4) Put the maximum experimental pressure

5) Binary parameter $\mathbf{k_{ij}(1-\Psi_{ij}}$ *in SL model): as a first guess put 0, then slightly adjust it (0.1 is a big adjustment: increasing* k_{ij} *will lower the predicted solubility, and viceversa)*

NE_SOL: *same procedure as before plus swelling parameter and dry polymer density*



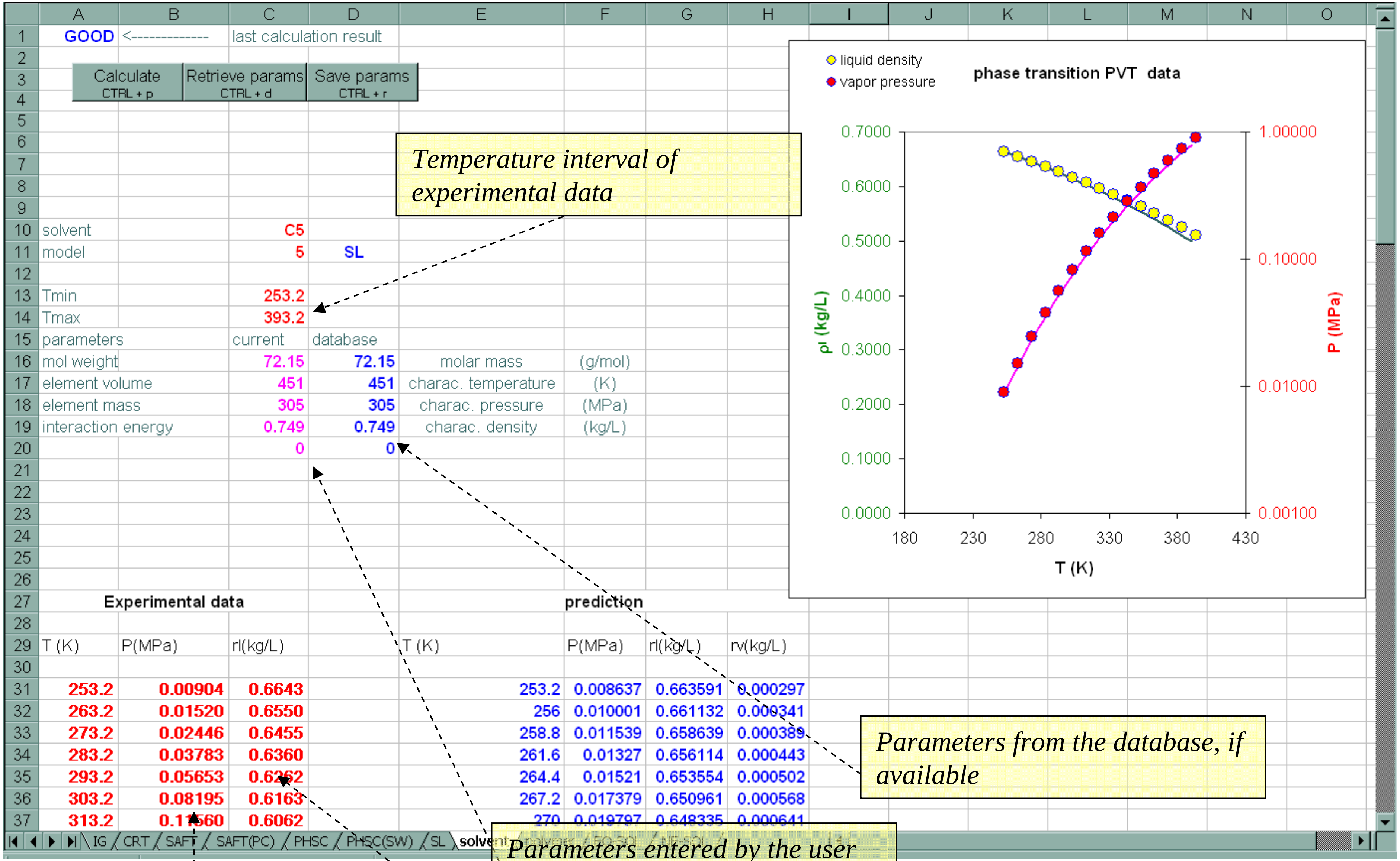
	A	B	C	D	E	F
1	GOOD	<------------	last calculation result			
7	model		5	SL		
8	T (K)		298.15			
9			solvent	polymer		
10	components		ET-2	PTMSP-2		
11	mol weight		47.069	1E+30	molar mass	(g/mol)
12	element volume		0	515	charac. temperature	(K)
13	element mass		0	440	charac. pressure	(MPa)
14	interaction energy		0	1.25	charac. density	(K)
15			0	0		
19	binary parameter				0.00E+00	
23	Pmax (MPa)		0.0052916			
24					Number of:	
25	dry polymer density		0.74	kg/m^3	Experimental points	10
26	swelling coefficient		0.00E+00	MPa^{-1}	Points to evaluate	52
28	Experimental data		Accuracy		Prediction	
29	P (MPa)	W (g/gpol)		P (MPa)	W (g/gpol)	
31	0	0	1	0.0001018	0.004061563	
32	0.0003	0.00362	1	0.0002035	0.008443912	
33	0.0006	0.01087	1	0.0003053	0.013200083	
34	0.00098	0.04107	1	0.000407	0.018396735	
35	0.00136	0.09422	1	0.0005088	0.024118704	
36	0.002	0.12563	1	0.0006106	0.030475434	
37	0.00227	0.15462	1	0.0007123	0.03761009	

Put the dry polymer density of the glassy polymer at that temperature. The predicted solubility is very sensitive to this value

Put the swelling coefficient

✓*If there are no characteristic parameter for the EOS of interest for the penetrant, use worksheet “solvent” with experimental data of vapor pressure and saturated liquid density. The data for some penetrants are in the file* **solvent_data_SL.xls** *file, together with the calculated values with the SL EOS*

✓*If there are no characteristic parameter for the EOS of interest for the polymer, use worksheet “polymer” with experimental data of PVT data above* T_G*. The data for some polymers are in the file* **polymer_data_SL.xls** *file, together with the calculated values with the SL EOS*



GOOD <-------------- last calculation result

solvent	C5			
model	5	SL		
Tmin	253.2			
Tmax	393.2			
parameters	current	database		
mol weight	72.15	72.15	molar mass	(g/mol)
element volume	451	451	charac. temperature	(K)
element mass	305	305	charac. pressure	(MPa)
interaction energy	0.749	0.749	charac. density	(kg/L)
	0	0		

Experimental data — **prediction**

T (K)	P(MPa)	rl(kg/L)	T (K)	P(MPa)	rl(kg/L)	rv(kg/L)
253.2	0.00904	0.6643	253.2	0.008637	0.663591	0.000297
263.2	0.01520	0.6550	256	0.010001	0.661132	0.000341
273.2	0.02446	0.6455	258.8	0.011539	0.658639	0.000389
283.2	0.03783	0.6360	261.6	0.01327	0.656114	0.000443
293.2	0.05653	0.6262	264.4	0.01521	0.653554	0.000502
303.2	0.08195	0.6163	267.2	0.017379	0.650961	0.000568
313.2	0.11560	0.6062	270	0.019797	0.648335	0.000641

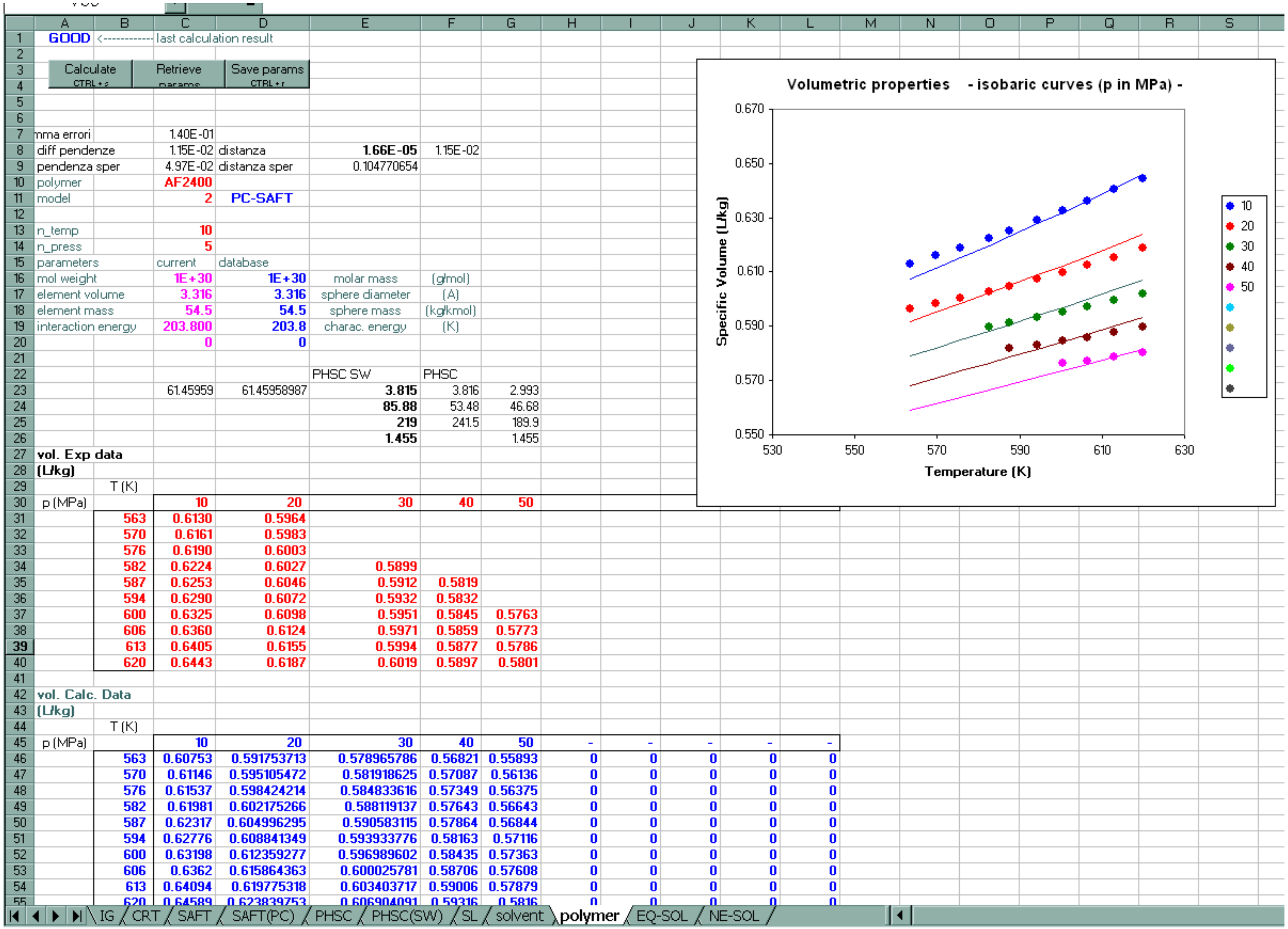
Temperature interval of experimental data

Parameters from the database, if available

Parameters entered by the user and used for the calculation

Exp. Vapor pressure at that T

Exp. Saturated liquid density at that T



	A	B	C	D	E	F	G
1	GOOD	<------------	last calculation result				
2							
3							
4							
5							
6							
7	mma errori		1.40E-01				
8	diff pendenze		1.15E-02	distanza	**1.66E-05**	1.15E-02	
9	pendenza sper		4.97E-02	distanza sper	0.104770654		
10	polymer		**AF2400**				
11	model		**2**	**PC-SAFT**			
12							
13	n_temp		**10**				
14	n_press		**5**				
15	parameters		current	database			
16	mol weight		**1E+30**	**1E+30**	molar mass	(g/mol)	
17	element volume		**3.316**	**3.316**	sphere diameter	(A)	
18	element mass		**54.5**	**54.5**	sphere mass	(kg/kmol)	
19	interaction energy		**203.800**	**203.8**	charac. energy	(K)	
20			**0**	**0**			
21							
22					PHSC SW	PHSC	
23			61.45959	61.45958987	**3.815**	3.816	2.993
24					**85.88**	53.48	46.68
25					**219**	241.5	189.9
26					**1.455**		1.455

vol. Exp data
(L/kg)

		T (K)					
30	p (MPa)		**10**	**20**	**30**	**40**	**50**
31		**563**	**0.6130**	**0.5964**			
32		**570**	**0.6161**	**0.5983**			
33		**576**	**0.6190**	**0.6003**			
34		**582**	**0.6224**	**0.6027**	**0.5899**		
35		**587**	**0.6253**	**0.6046**	**0.5912**	**0.5819**	
36		**594**	**0.6290**	**0.6072**	**0.5932**	**0.5832**	
37		**600**	**0.6325**	**0.6098**	**0.5951**	**0.5845**	**0.5763**
38		**606**	**0.6360**	**0.6124**	**0.5971**	**0.5859**	**0.5773**
39		**613**	**0.6405**	**0.6155**	**0.5994**	**0.5877**	**0.5786**
40		**620**	**0.6443**	**0.6187**	**0.6019**	**0.5897**	**0.5801**

vol. Calc. Data
(L/kg)

		T (K)										
45	p (MPa)		**10**	**20**	**30**	**40**	**50**	**-**	**-**	**-**	**-**	**-**
46		**563**	**0.60753**	**0.591753713**	**0.578965786**	**0.56821**	**0.55893**	**0**	**0**	**0**	**0**	**0**
47		**570**	**0.61146**	**0.595105472**	**0.581918625**	**0.57087**	**0.56136**	**0**	**0**	**0**	**0**	**0**
48		**576**	**0.61537**	**0.598424214**	**0.584833616**	**0.57349**	**0.56375**	**0**	**0**	**0**	**0**	**0**
49		**582**	**0.61981**	**0.602175266**	**0.588119137**	**0.57643**	**0.56643**	**0**	**0**	**0**	**0**	**0**
50		**587**	**0.62317**	**0.604996295**	**0.590583115**	**0.57864**	**0.56844**	**0**	**0**	**0**	**0**	**0**
51		**594**	**0.62776**	**0.608841349**	**0.593933776**	**0.58163**	**0.57116**	**0**	**0**	**0**	**0**	**0**
52		**600**	**0.63198**	**0.612359277**	**0.596989602**	**0.58435**	**0.57363**	**0**	**0**	**0**	**0**	**0**
53		**606**	**0.6362**	**0.615864363**	**0.600025781**	**0.58706**	**0.57608**	**0**	**0**	**0**	**0**	**0**
54		**613**	**0.64094**	**0.619775318**	**0.603403717**	**0.59006**	**0.57879**	**0**	**0**	**0**	**0**	**0**
55		**620**	**0.64589**	**0.623839753**	**0.606904091**	**0.59316**	**0.5816**	**0**	**0**	**0**	**0**	**0**

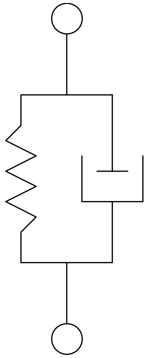
Dankeschön für die Aufmerksamkeit !

Study and modeling of the effect of stress on the diffusion of vapors in glassy polymers

Effect of relaxation processes on gas/vapor solubility in glassy polymers: volume swelling model (VS)

Swelling kinetics of polymeric elements induced by sorption processes

Volume dilation modeled through simple Kelvin-Voigt model for bulk rheology:



$$\frac{1}{\rho_{pol}}\frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$

Example of results from fitting analysis of apparent solubility data in sorption processes driven by volume relaxation phenomena:

n-hexane in PS @ 40°C

sorption process in microspheres

(d ≈ 0.5 μm)

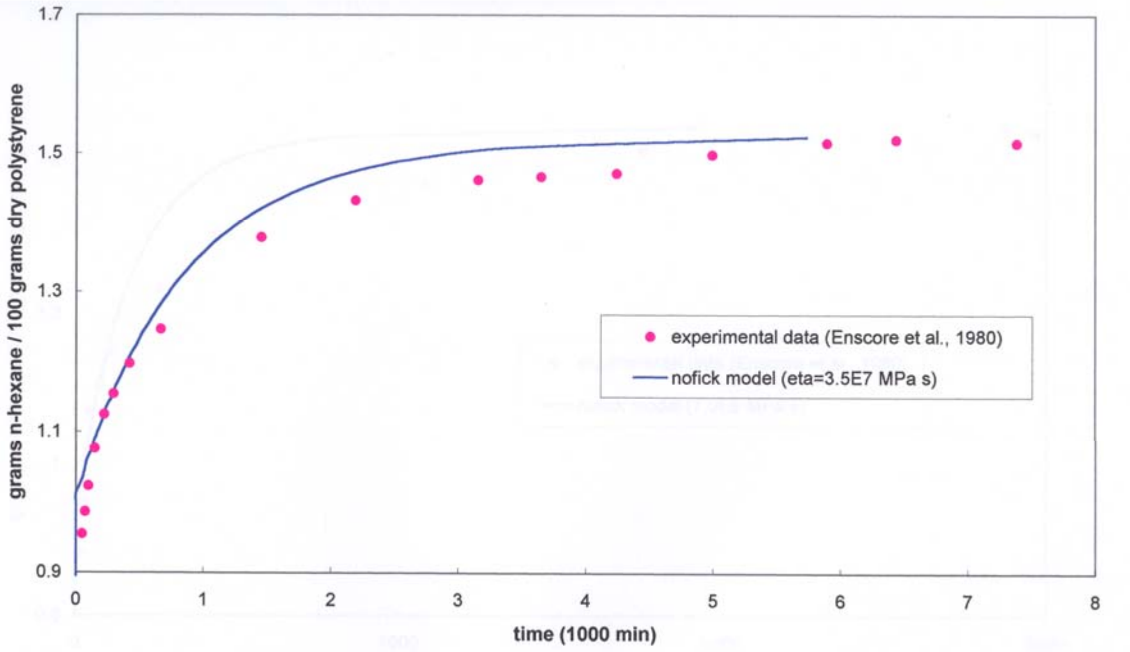
activity jump 0 → 0.1

exp. data from

Enscore, Hopfenberg e

Stannett, 1980

Fitting parameter = bulk viscosity



Mass transport model for gas sorption in glassy polymeric systems with both diffusion and relaxation resistances: case of differential sorption in small characteristic length samples

$$\frac{\partial \rho_{sol}}{\partial t} = \underline{\nabla} \bullet \underline{J}$$

$$\underline{J} = -\mathcal{D}\, \rho_{sol}\, \underline{\nabla} \mu$$

$$\frac{\partial \rho_{pol}}{\partial t} = F$$

Example of simulation results for n-hexane sorption in PS films

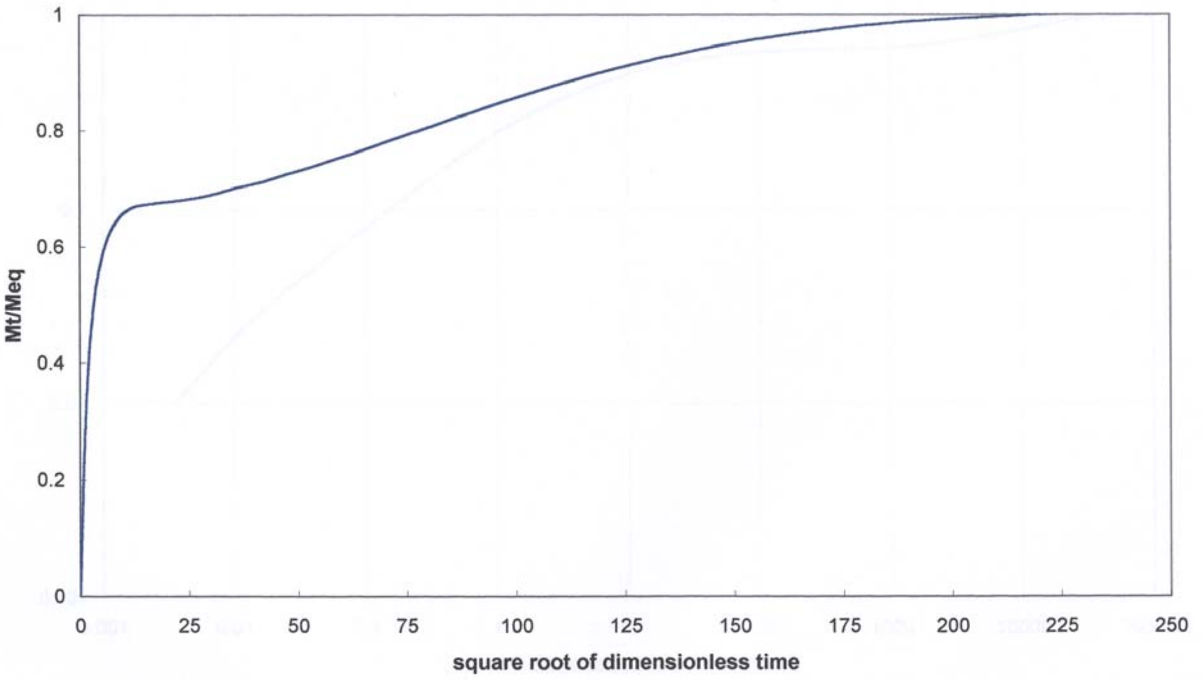
T= 40°C

film thickness = 1 μm

activity jump 0 → 0.1

Diffusion coefficient from Vrentas and Duda Free Volume Theory

Bulk viscosity from analysis of relaxation data



Rate-Type (RT) models for diffusion in polymers

$$\frac{\partial \rho_{sol}}{\partial t} = \underline{\nabla} \bullet \underline{J}$$

$$\tau \frac{\partial \underline{J}}{\partial t} + \underline{J} + \mathcal{D}\rho_{sol}\, \underline{\nabla}\mu = 0$$

$$\frac{\partial \rho_{pol}}{\partial t} = F$$

hyperbolic scheme for mass transport, accounting for a both a relaxation time τ in flux development and a relaxation phenomena in volume swelling of the polymeric element

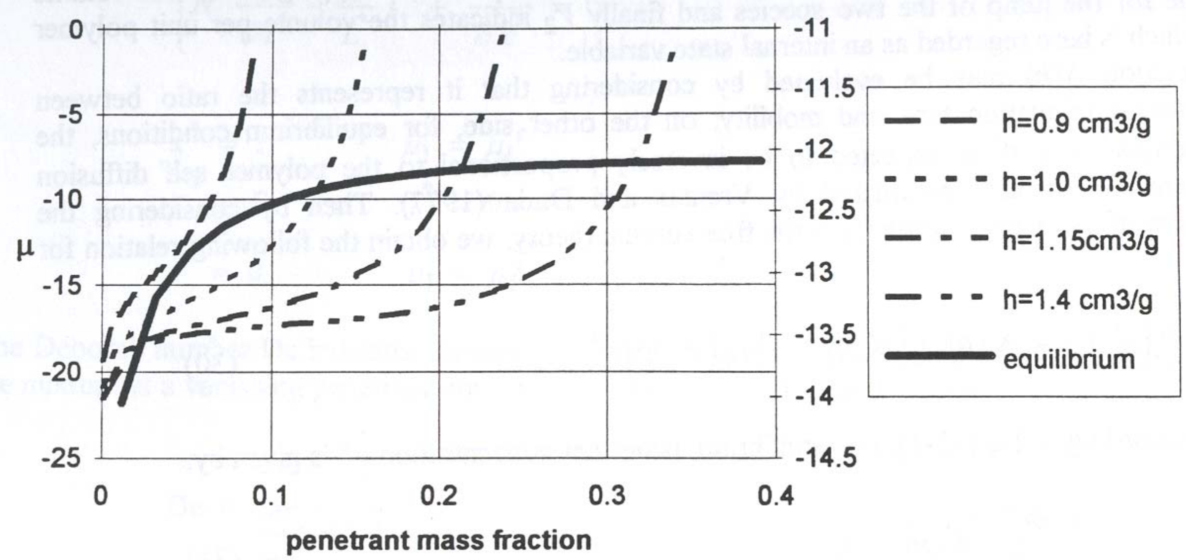
Thermodynamic Analysis for the development of shock concentration waves in the system

Results from the application of 2nd law:

Necessary condition for the formation of shock concentration waves is that:

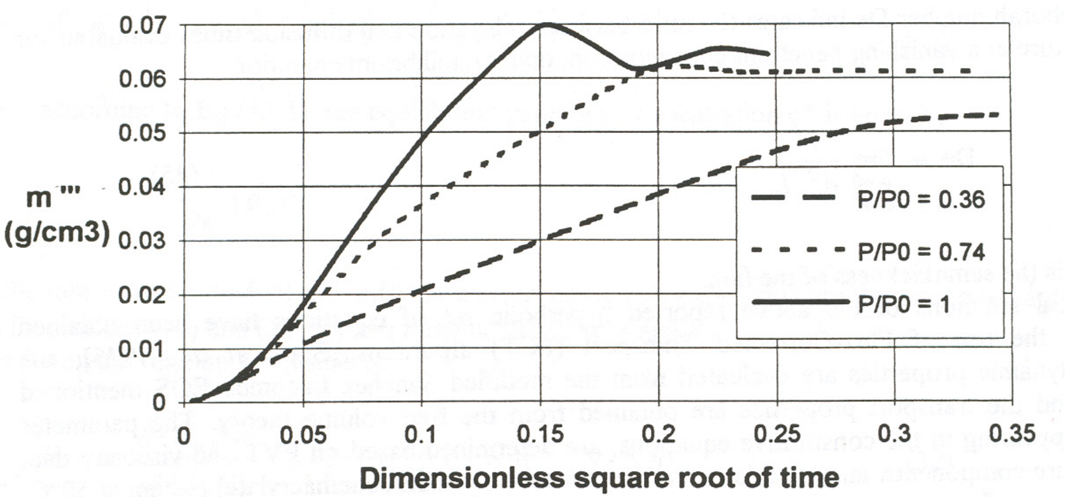
$$\frac{\partial^2 \mu}{\partial \rho_{sol}{}^2} > 0$$

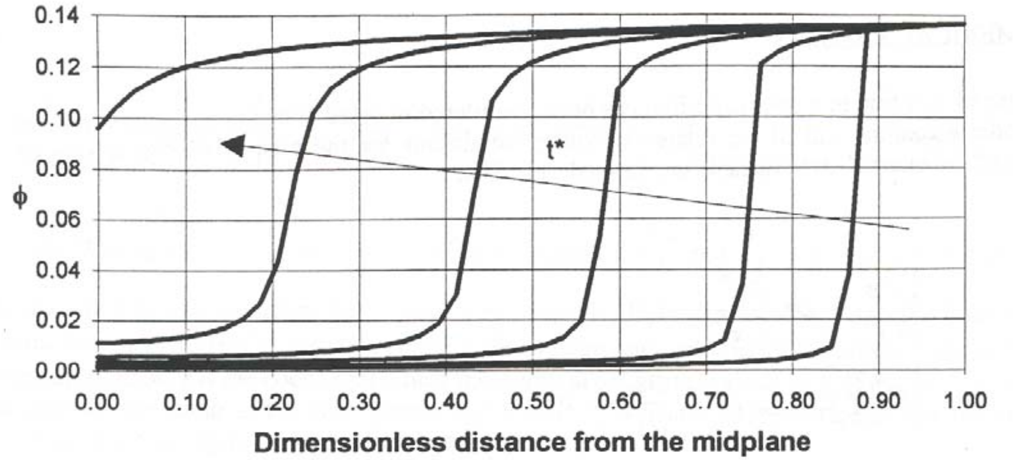
at least in a concentration range



Example of simulation results for RT sorption model: case of negligible volume swelling

Sorption kinetics for the case of ethanol-PMMA system at 30°C ρ_{pol} =1.10 g/cm^3 e diffusivity exponentially increasing function of concentration:
Effect of external solute fugacity





Examples of concentration profiles from simulation of sorption process for ethanol in PMMA (De = 30)