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Thermodynamics of migration in polymers: Can contamination from materials in contact be predicted, controlled and possibly avoided?

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Phuong Nguyen

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[1] AIChE Journal 2005, 51 (4), 1080-1095. [2] AIChE Journal 2013, 59 (4), 1183-1212. [3] J. Chem. Phys. 2010, 132(19): 194902 [4] Crit. Rev. Food Sci. Nutrition 2015, doi: 10.1080/10408398.2013.849654. [5] I&EC 2009, 48 (11), 5285-5301. [6] I&EC 2010, 49 (16), 7263-7280. [7] Int. J. Chem. React. Eng. 2010, 8. [8] J. Polym. Sci. Part B: Polym. Phys. 2014, 52 (19), 1252-1258. [9] Nguyen, P.-M.; Guiga, W.; Dkhissi, A.; Vitrac, O., submitted to I&EC. [10] Macromol. 2013, 46 (3), 874-888. [11] J. Appl. Polym. Sci. 2006, 101 (4), 2167-2186. [12] J. Appl. Polym. Sci. 2010, DOI: 10.1002/app.32950. [13] I&EC 2015, 54 (10), 2667-2681.

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Single-Use Technologies
Bridging Polymer Science to Biotechnology Applications
Oct 18-21, 2015 - Leesburg, VA, USA

THERMODYNAMICS OF MIGRATION IN POLYMERS

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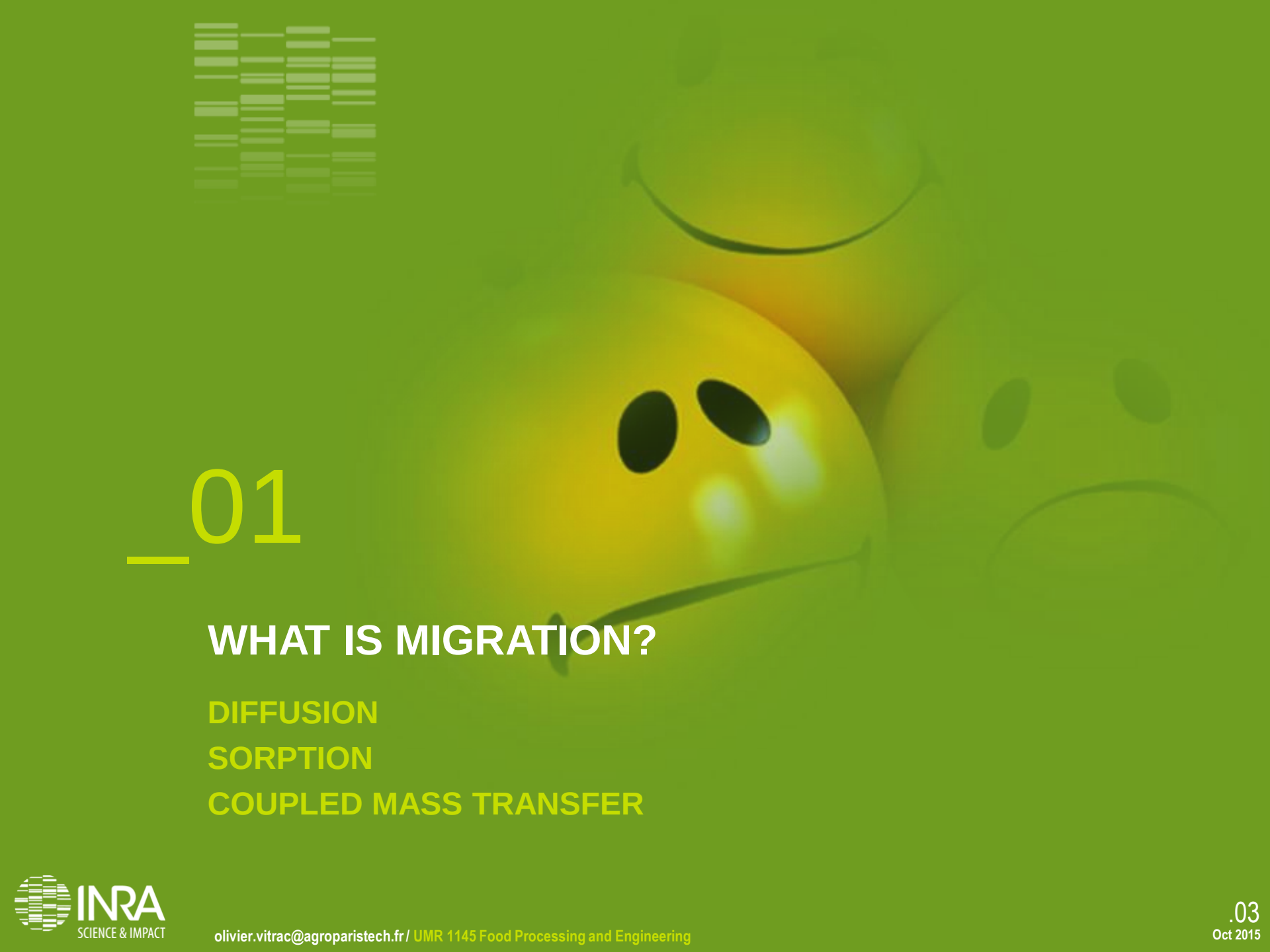
http://modmol.agroparistech.fr , http://www.inra.fr

THERMODYNAMICS OF MIGRATION

CAN CONTAMINATION FROM MATERIALS IN CONTACT BE PREDICTED, CONTROLLED AND POSSIBLY AVOIDED?

- _01 WHAT IS MIGRATION?
- _02 DIFFUSION AND DIFFUSION COEFFICIENTS
- _03 CHEMICAL AFFINITY… MOLECULAR PREDICTIONS
- _04 PREVENTIVE APPROACHES
- _05 COMPLEMENTARY TOOLS AND PROSPECTS



_01

WHAT IS MIGRATION?

DIFFUSION

SORPTION

COUPLED MASS TRANSFER













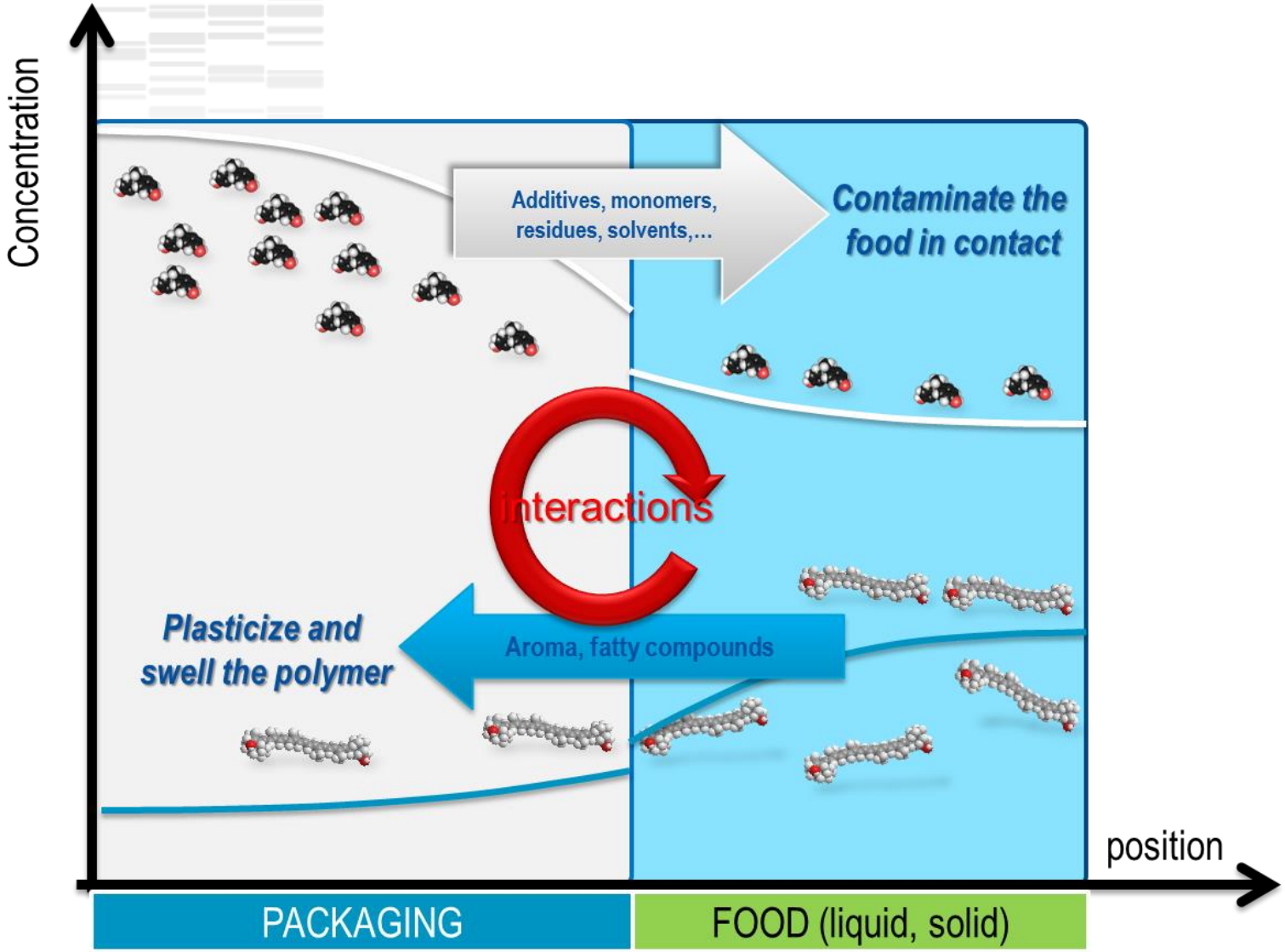




CONTROVERSY ON THE SAFETY OF PACKAGING MATERIALS

Time, 2010, April 12, 30-36. (7 pages !)

WHAT IS MIGRATION ?

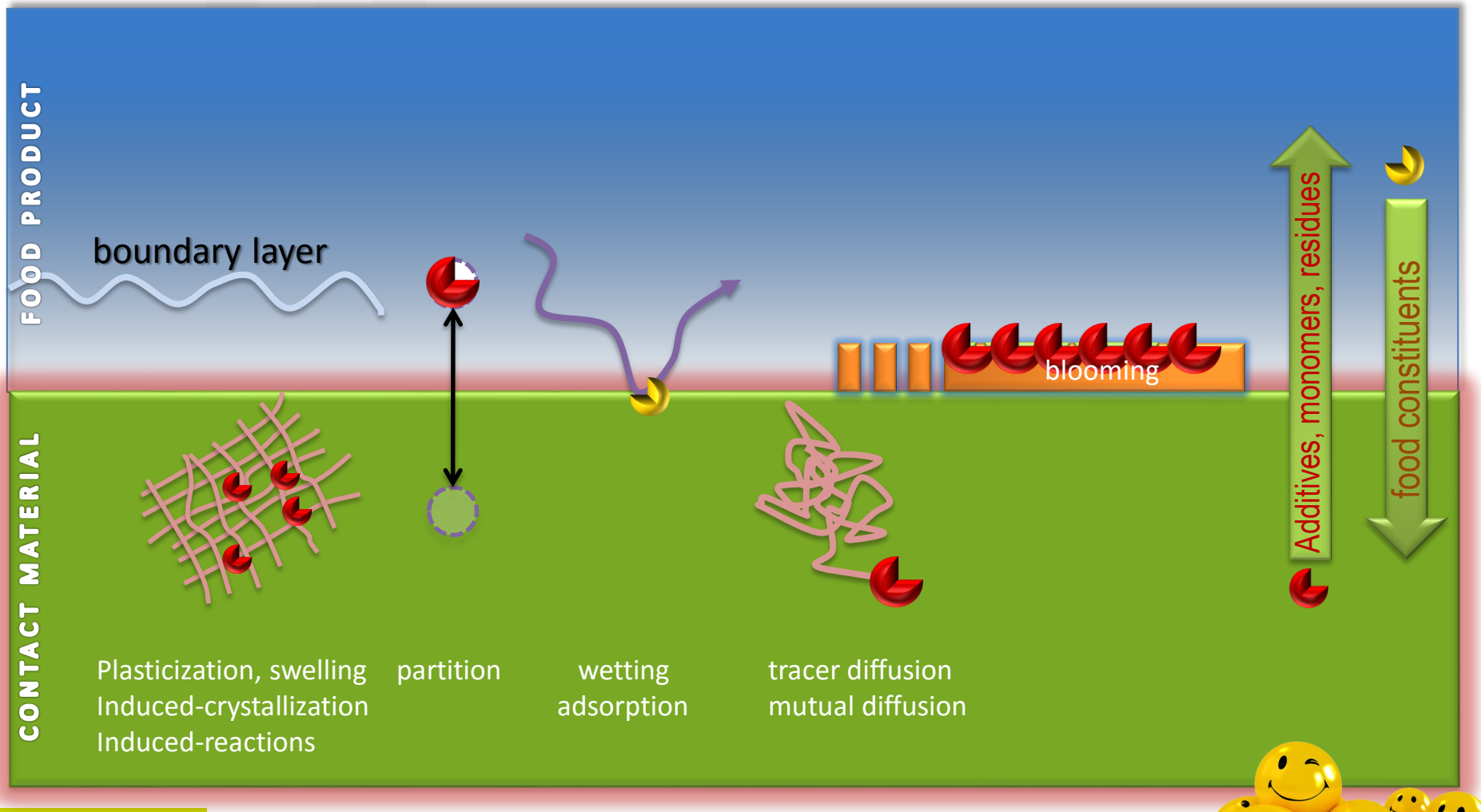


additive

food constituent

MIGRATION ISSUES

= VARIOUS CROSSED MASS TRANSFER FROM THE MATERIAL AND THE MEDIUM IN CONTACT



MIGRATION MODELING

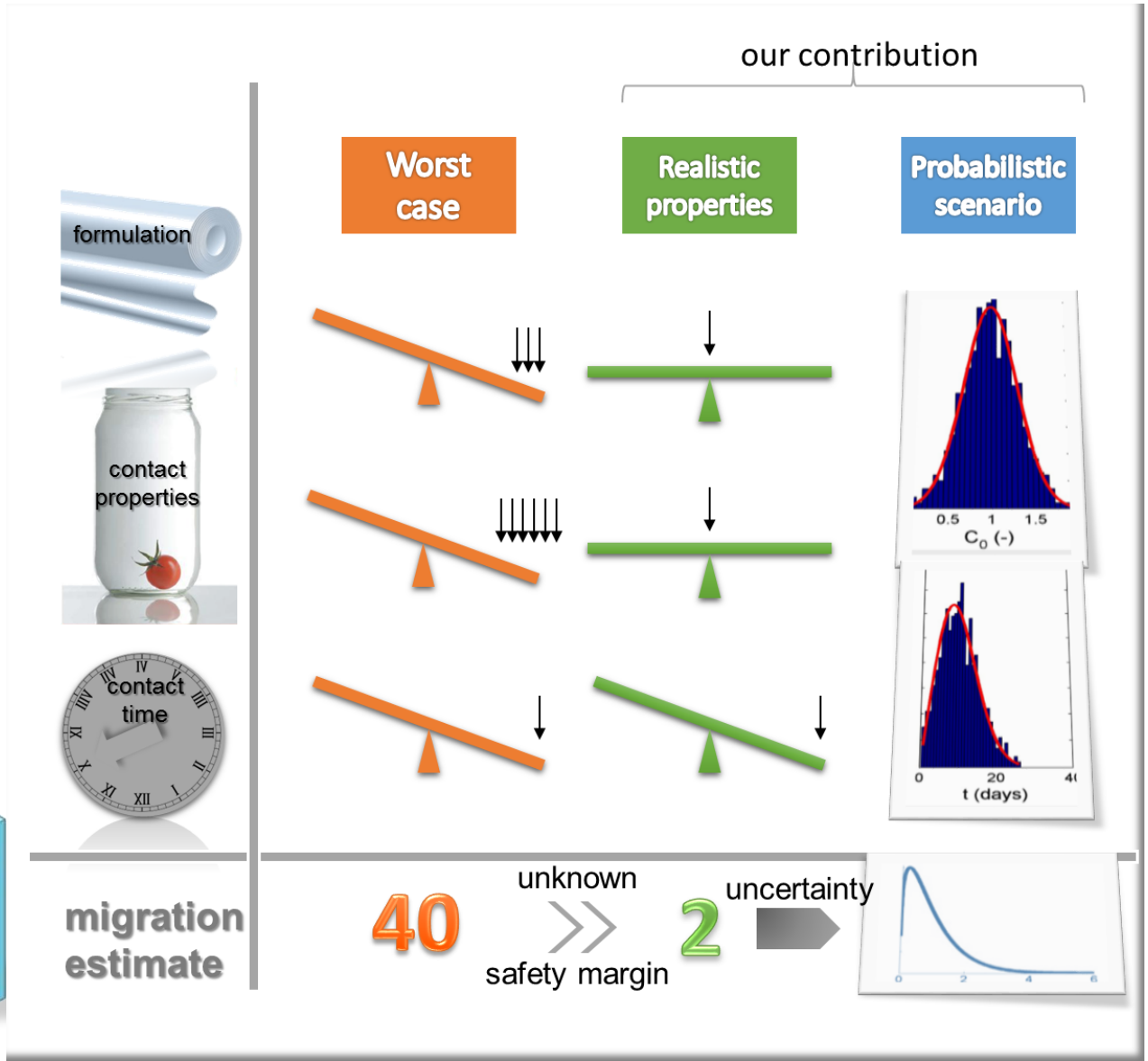
AUTHORIZED/RECOGNIZED IN EU, US, China

At each stage of manufacture, supporting documentation, substantiating the declaration of compliance, should be kept available for the enforcement authorities. Such demonstration of compliance July be based on migration testing. As migration testing is complex, costly and time consuming it should be admissible that compliance can be demonstrated also by calculations, including modelling, other analysis, and scientific evidence or reasoning if these render results which are at least as severe as the migration testing. Test results should be regarded as valid as long as formulations and processing conditions remain constant as part of a quality assurance system.

[…]the migration potential can be calculated based on the residual content of the substance in the material or article applying generally recognised diffusion models based on scientific evidence that are constructed such as to overestimate real migration.

HOW TO OVERESTIMATE MIGRATION

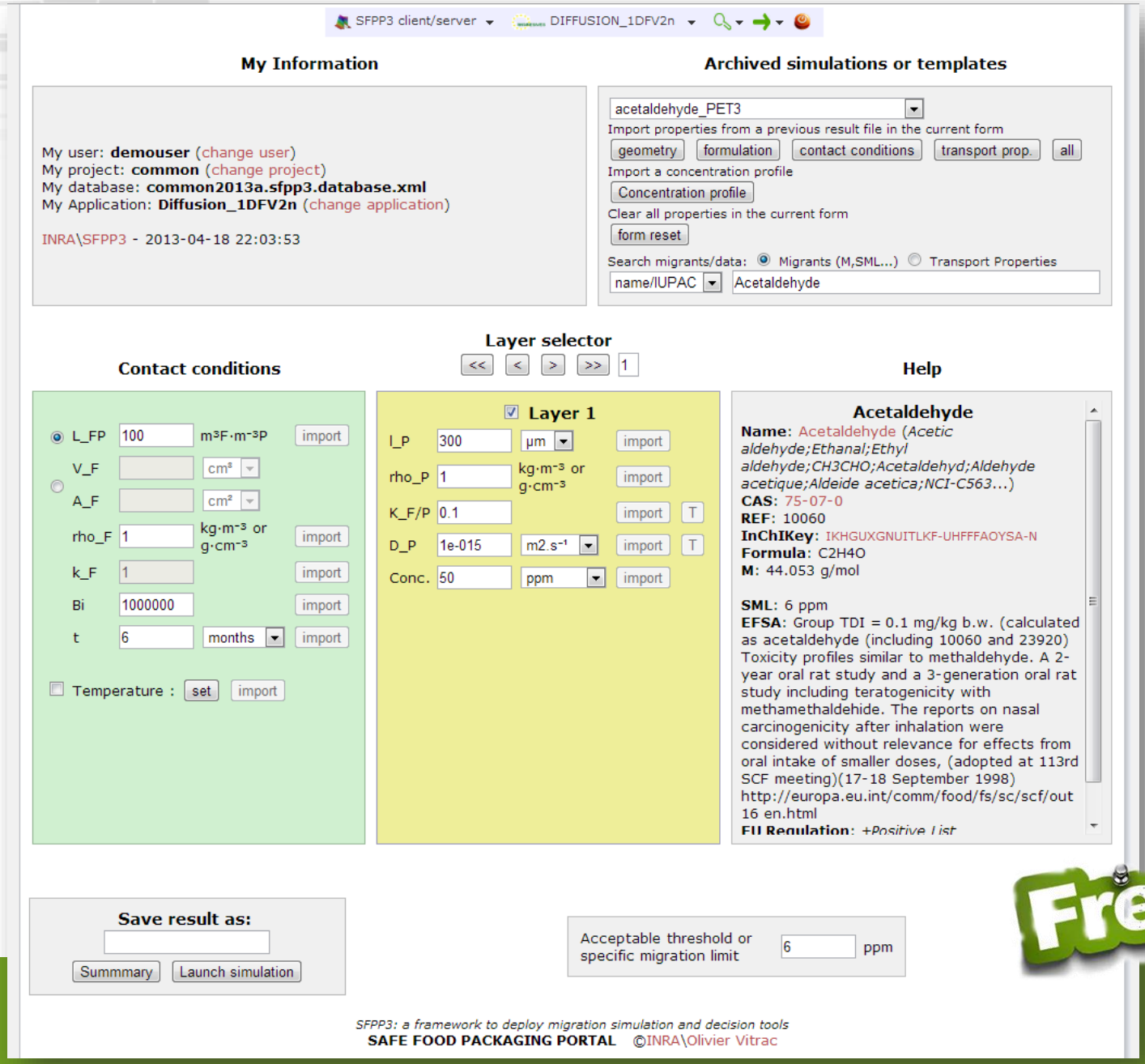
use a tier approach



olivier.vitrac@agroparistech.fr

Oct 2015

ALL SOFTWARE ARE BUILT ON SIMILAR ASSUMPTIONS

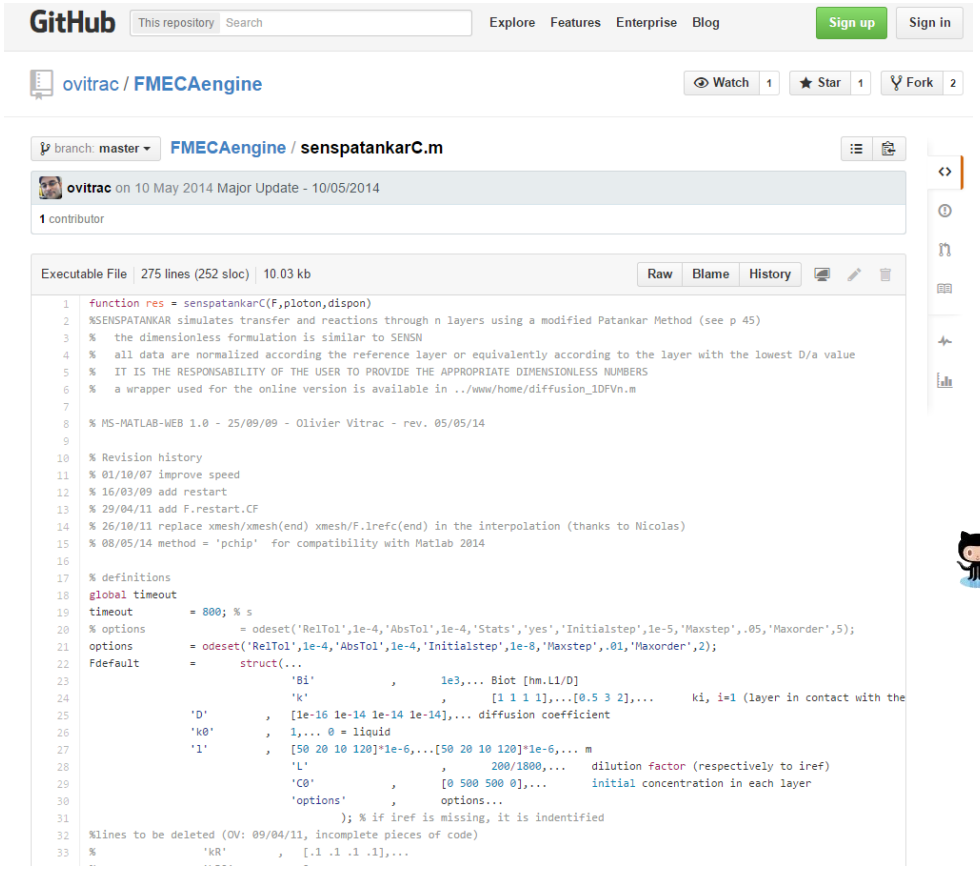


Free

http://modmol.agroparistech.fr/SFPP3/SFPP3_migresives/

New trends: OPEN-SOURCE codes

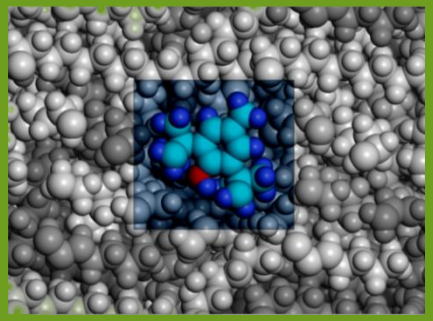
https://github.com/ovitrac/FMECAengine



Probabilistic (equilibrium)

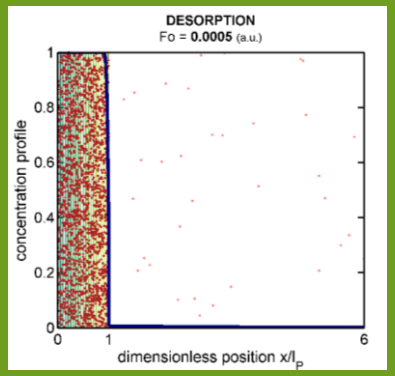
Probablistic/deterministic

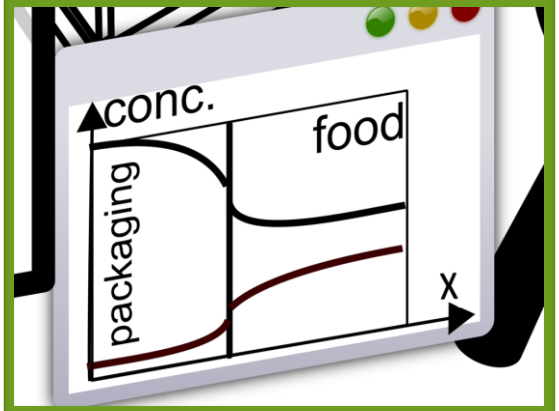
Probabilistic (out of equilibrium)

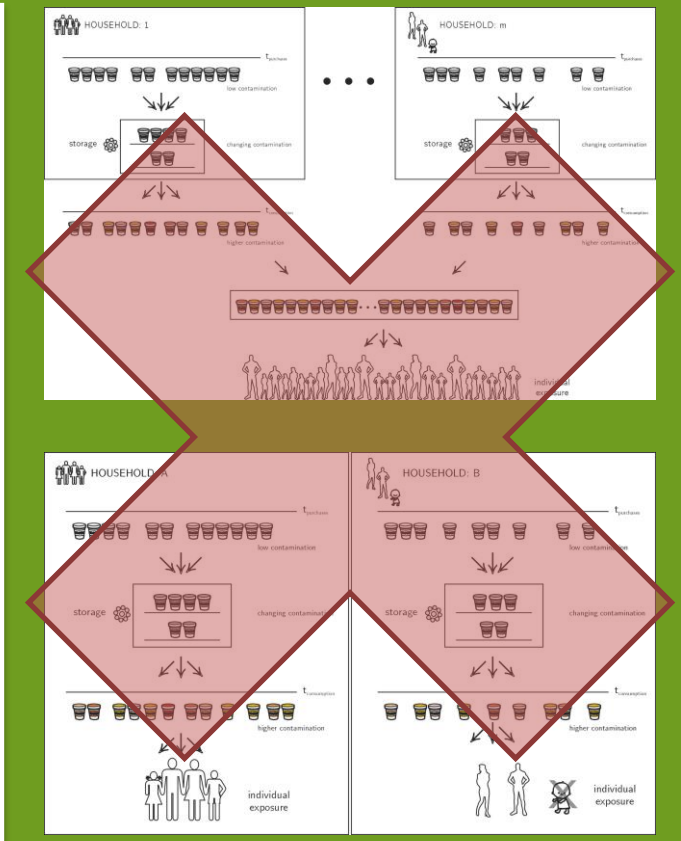


Free energy perturbation

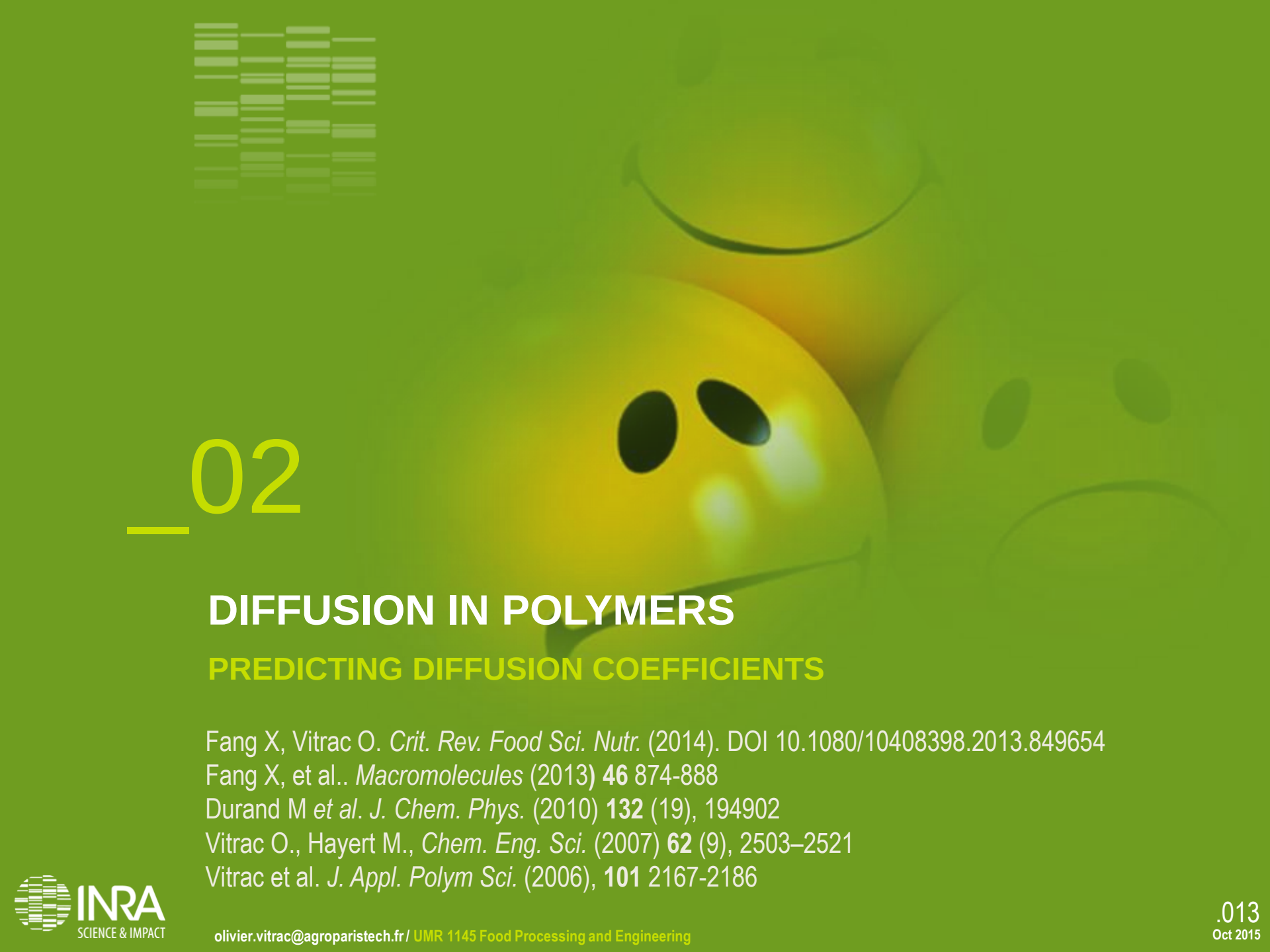
$$\exp\left(-\frac{F_1 - F_0}{k_B T}\right) = \left\langle \exp\left(-\frac{U_1 - U_0}{k_B T}\right)\right\rangle$$







SCALE



_02

DIFFUSION IN POLYMERS

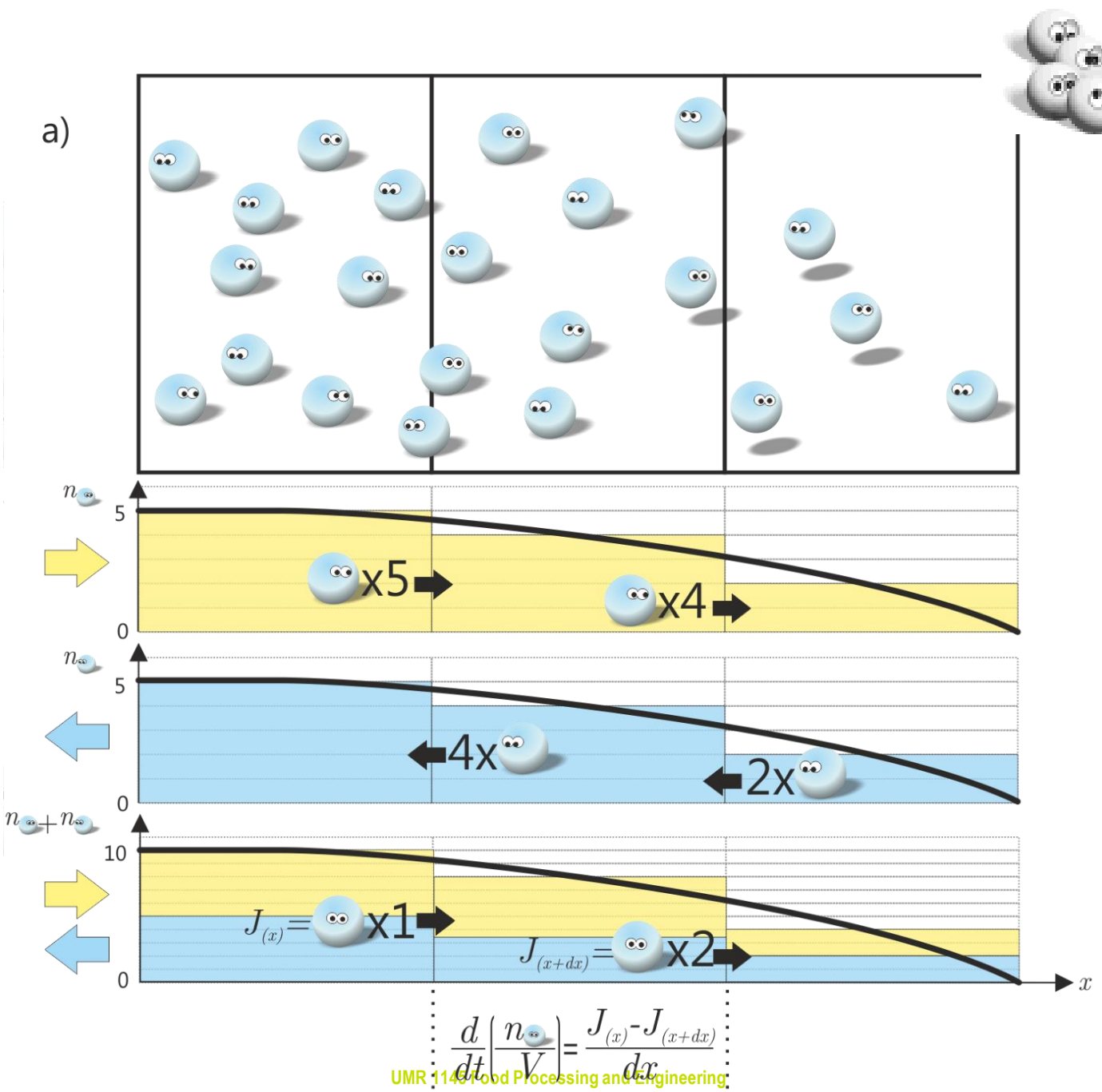
PREDICTING DIFFUSION COEFFICIENTS

Fang X, Vitrac O. *Crit. Rev. Food Sci. Nutr.* (2014). DOI 10.1080/10408398.2013.849654
Fang X, et al.. *Macromolecules* (2013) **46** 874-888
Durand M *et al. J. Chem. Phys.* (2010) **132** (19), 194902
Vitrac O., Hayert M., *Chem. Eng. Sci.* (2007) **62** (9), 2503–2521
Vitrac et al. *J. Appl. Polym Sci.* (2006), **101** 2167-2186

INRA SCIENCE & IMPACT

olivier.vitrac@agroparistech.fr / UMR 1145 Food Processing and Engineering

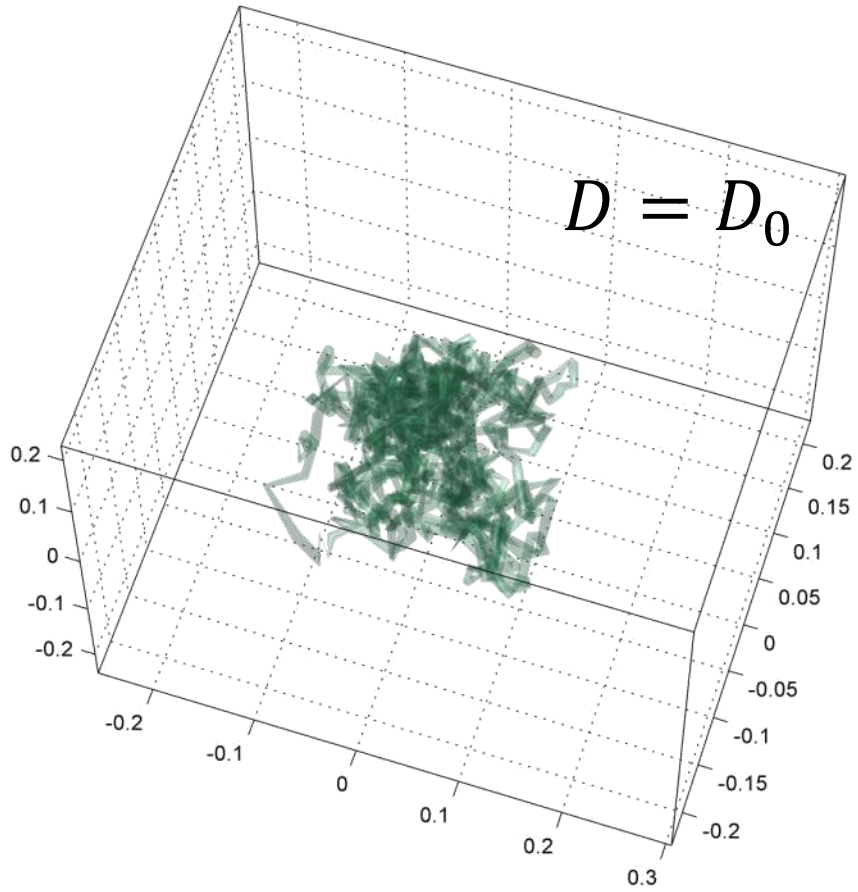
MOLECULAR DIFFUSION

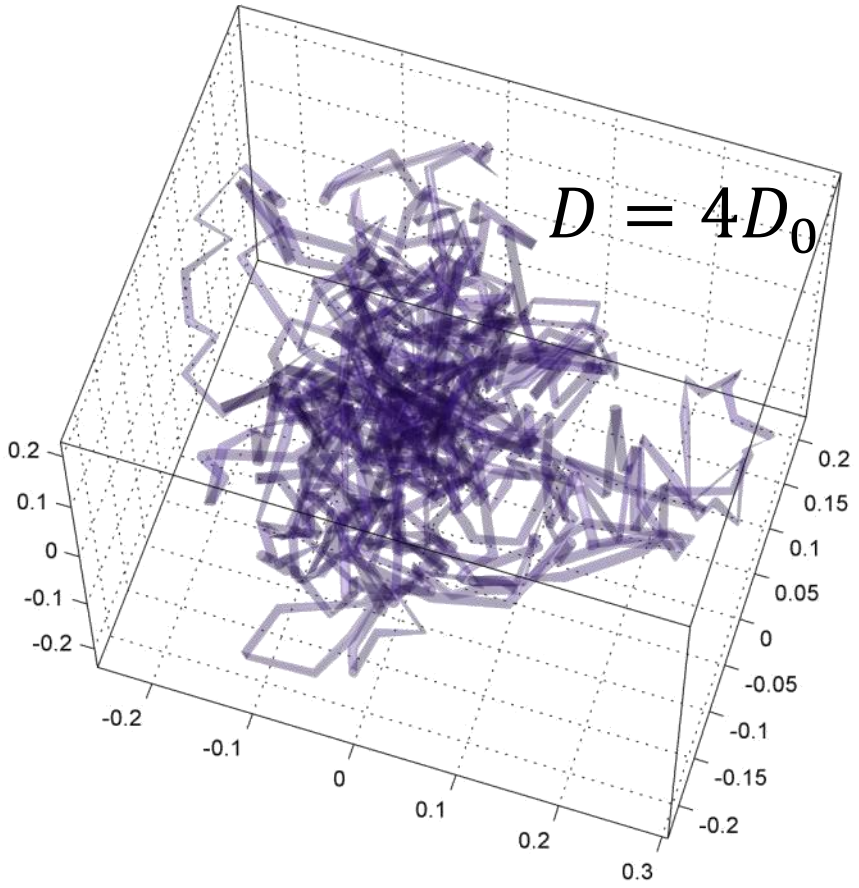


Molecules are represented as jumping beads. They have equal probabilities to hop to left and right directions.

The direction of the next hop at microscopic scale is indicated by the direction towards beads are staring.

SMALL vs LARGE DIFFUSION COEFFICIENTS (D)

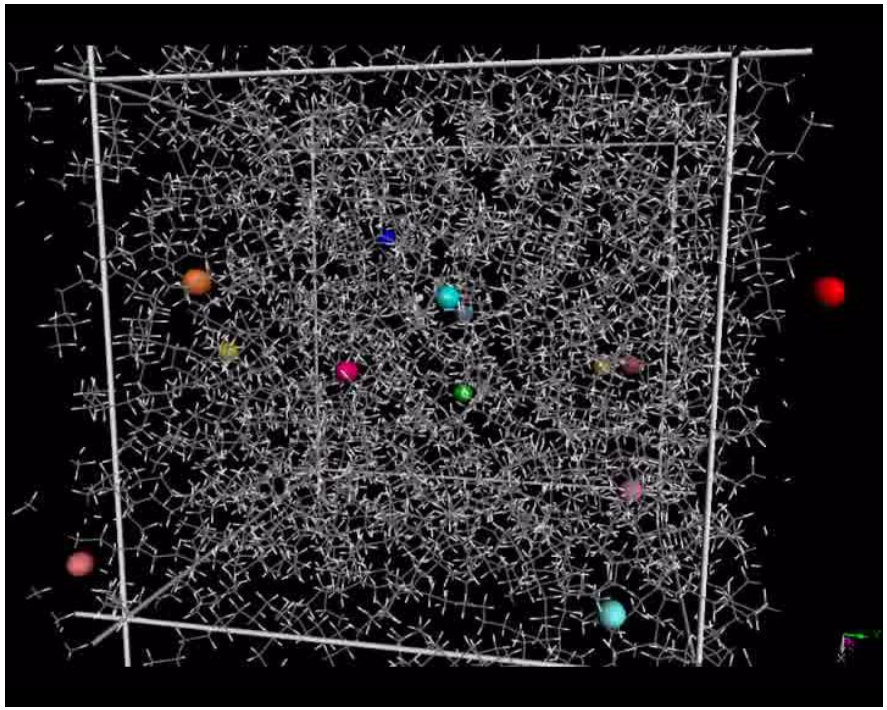




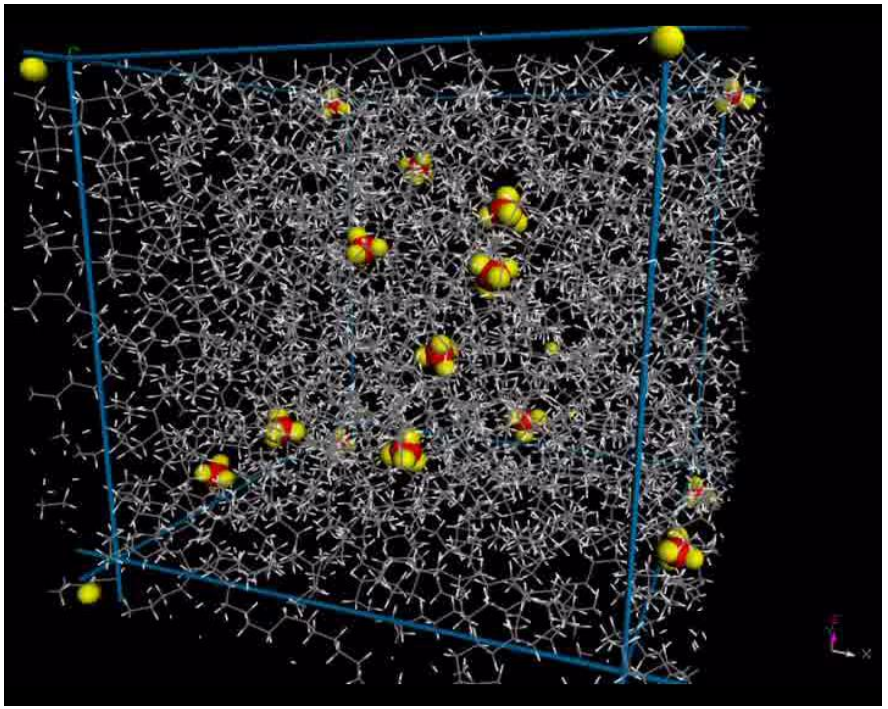
$$\mathrm{D} \approx \frac{1}{6}\frac{\partial}{\partial t}\langle \left(\boldsymbol{x_{CM}}(t) - \boldsymbol{x_{CM}}(0)\right)^2 \rangle$$

DIFFUSION IN POLYETHYLENE (0.5 NS SIMULATION, T=298 K)

10 molecules of helium



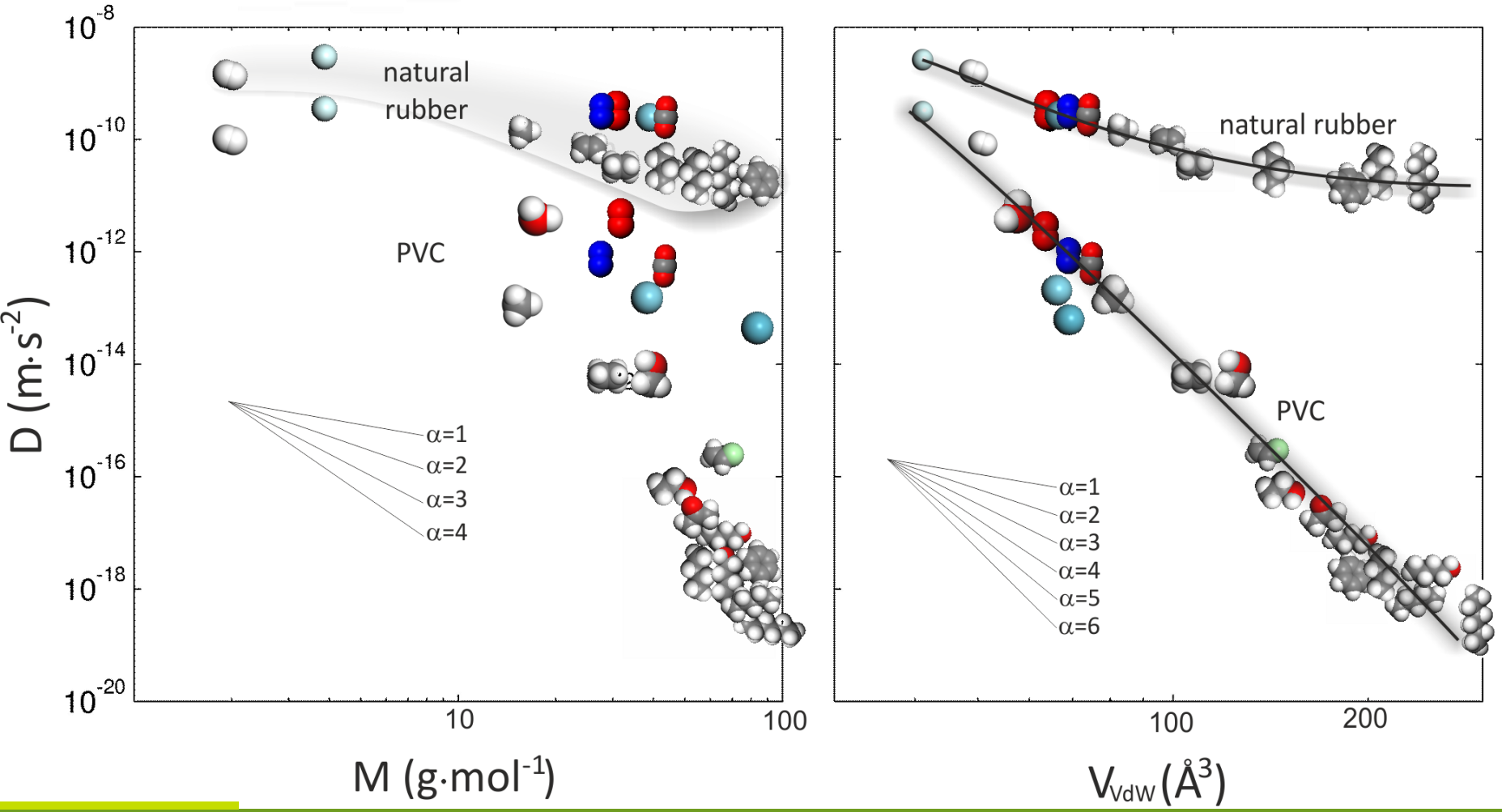
10 molecules of methane



$$D \approx \frac{1}{6}\frac{\partial}{\partial t}\langle \left(\boldsymbol{x_{CM}}(t) - \boldsymbol{x_{CM}}(0)\right)^2 \rangle$$

SCALING D WITH SOLUTE SIZE

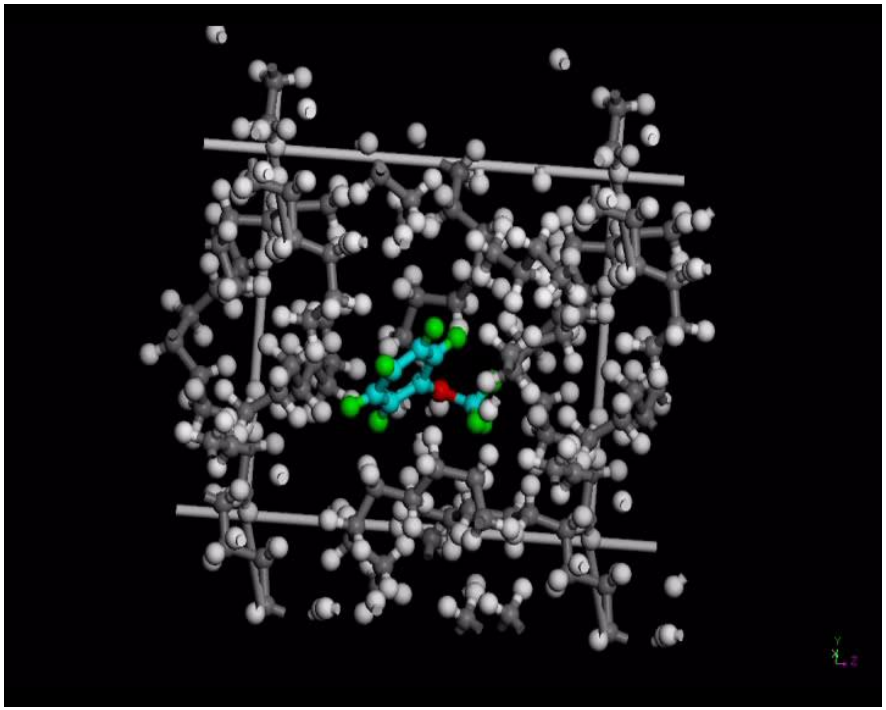
STIFF DIFFUSANTS



From: A. R. Berens, Pure Appl. Chem., **1981**, 53, 365

DIFFUSION OF ANISOLE IN POLYETHYLENE (T=298 K)

0.5 ns at 298 K (details)



20 ns full trajectory

QSPR-MS version 1.0

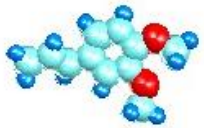
Molecule: **P161**
"2-Hydroxy-4-methoxybenzophenone (Chimassorb 90)"
CAS# **131-57-7**

Polymer: **LDPE 23°C**

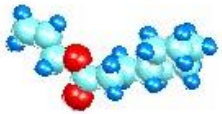
class size: **11**

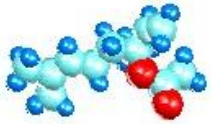
Similar 3D structures for *D* prediction

(pruning level: **20**)

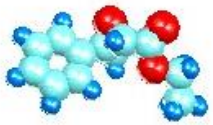
P122 

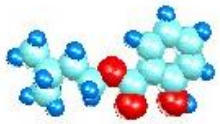
P131 

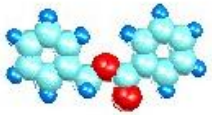
P135 

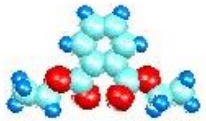
P138 

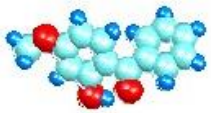
P145 

P147 

P150 

P152 

P159 

P161 

P96 

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List of molecules in the current class

code	formula	M g.mol-1	CAS #	chemical name
P122	C11 H14 O2	178	93-16-3	2-Methoxy-4-propenylanisol (Methylisoeugenol)
P131	C13 H18 O1	190	103-95-7	2-Methyl-3-(4-isopropyl)phenylpropanal (Cyclamen aldehyde)
P135	C12 H20 O2	196	2705-87-5	Allyl-3-cyclohexylpropionate
P138	C12 H20 O2	196	115-95-7	3,7-Dimethyl-1,6-octadien-3-ylacetate (Linalylacetate)
P145	C14 H18 O1	202	122-40-7	Amylcinnamicaldehyde or 2-Phenylmethylene-heptanal
P147	C12 H14 O3	206	77-83-8	3-Methyl-3-phenylglycidate (Aldehyde C16)
P150	C12 H16 O3	208	NaN	Iso-amylsalicilate
P152	C14 H12 O2	212	120-51-4	Benzylbenzoate
P159	C12 H14 O4	222	84-66-2	Diethylphthalate (DEP)
P161	C14 H12 O3	228	131-57-7	2-Hydroxy-4-methoxybenzophenone (Chimassorb 90)
P96	C10 H20 O1	156	106-22-9	3,7-Dimethyl-6-octen-1-ol (Citronellol)

summarized 3D molecular information

prop 3D	min value	median value	max value
M	**156**	**202**	**228**
VdW volume	**180**	**206**	**217**
Gyration radius	**3.54**	**3.9**	**4.11**
Inertial along z	**261**	**383**	**449**
Inertial along x	**28.2**	**61.9**	**103**
Section xy	**48.4**	**65.1**	**76.8**
Section yz	**23.1**	**30.9**	**75.4**
Dipolar moment	**1.23**	**2.99**	**4.2**
Flexion	**2.59**	**4.46**	**6.24**

D robust statistics

Drobust m2.s-1	stand. dev. m2.s-1	*n* *class size*	Dmin m2.s-1	Dmed m2.s-1	Dmax m2.s-1
2.24e-013	**1.54e-013**	12	1.2e-013	**2.3e-013**	7e-013

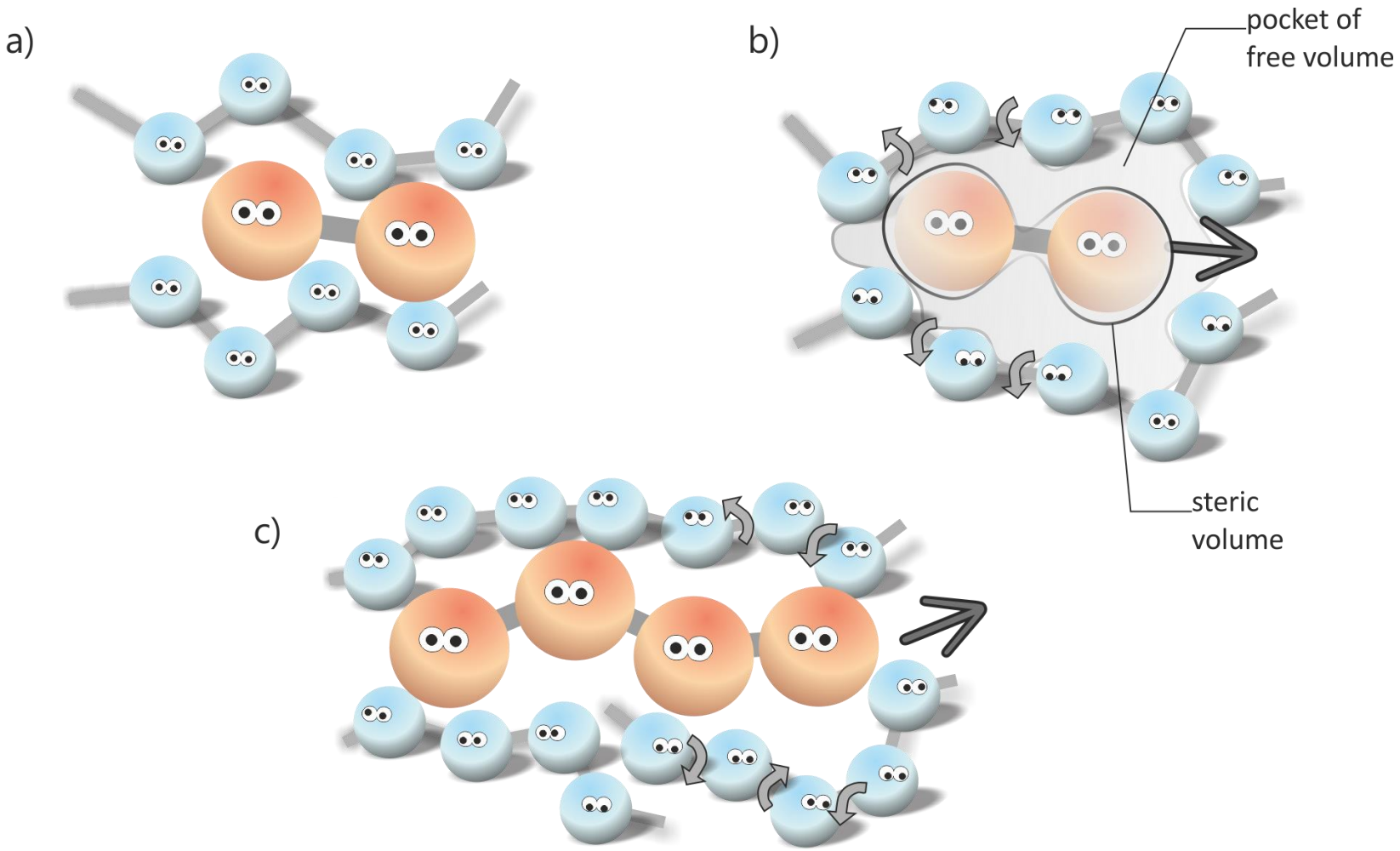
D robust statistics

Drobust m2.s-1	stand. dev. m2.s-1	*n* *class size*	Dmin m2.s-1	Dmed m2.s-1	Dmax m2.s-1
2.24e-013	**1.54e-013**	12	1.2e-013	**2.3e-013**	7e-013

FLEXIBLE DIFFUSANTS

Local and temporary trapping of additive between polymer segments

Additive translation controlled by the relaxation of polymer itself and by the rate of creation of free volumes.

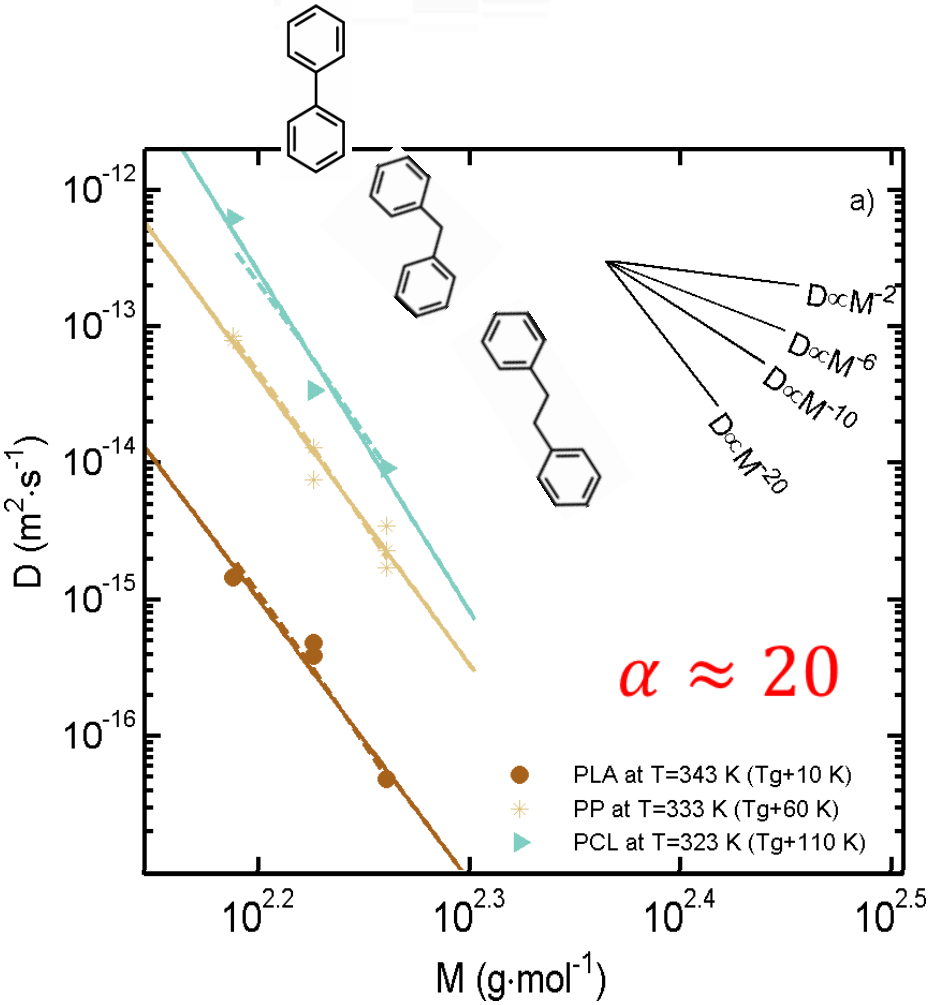


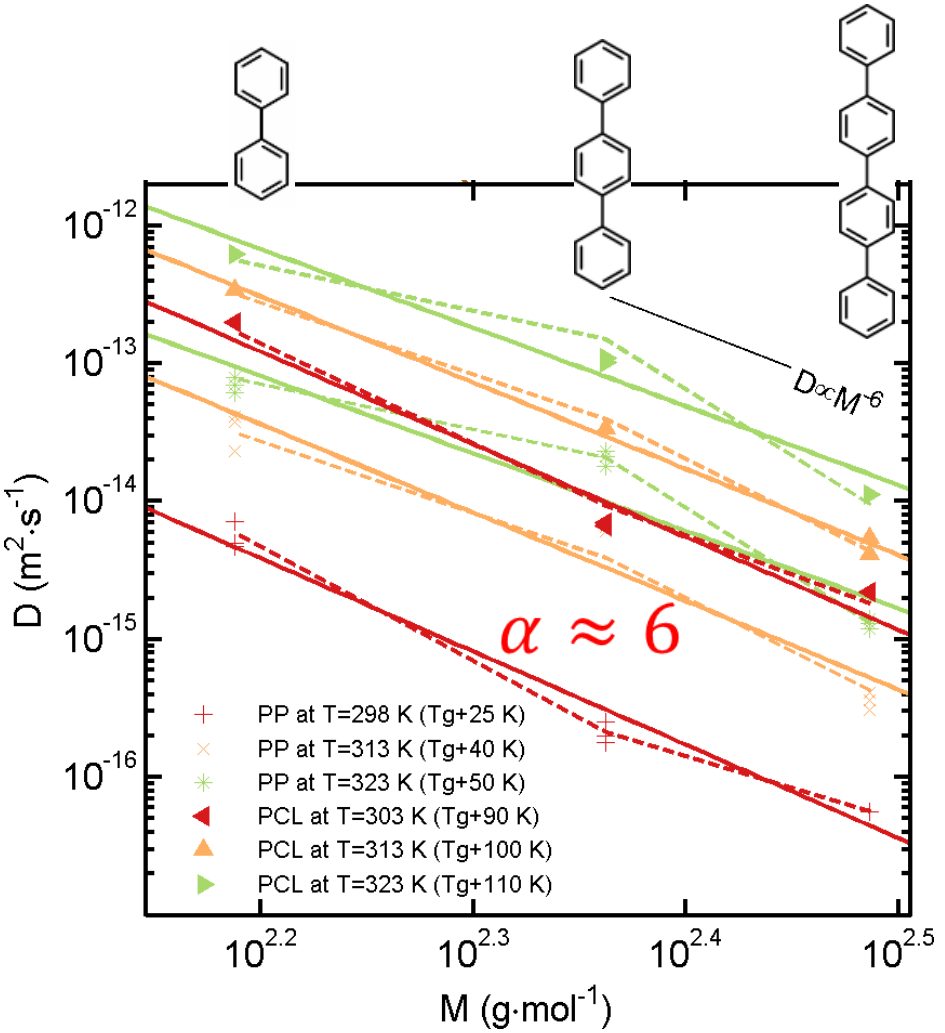
The relative free volume required for the translation of large additives is smaller as displacements of atoms/patterns are more likely not to be correlated together.

$$\frac{D}{D_0} \propto \left(\frac{M}{M_0}\right)^{-\alpha(T,T_g)}$$

SCALING EXPONENTS

FOR HOMOLEGOUS SERIES OF SUBSTANCES

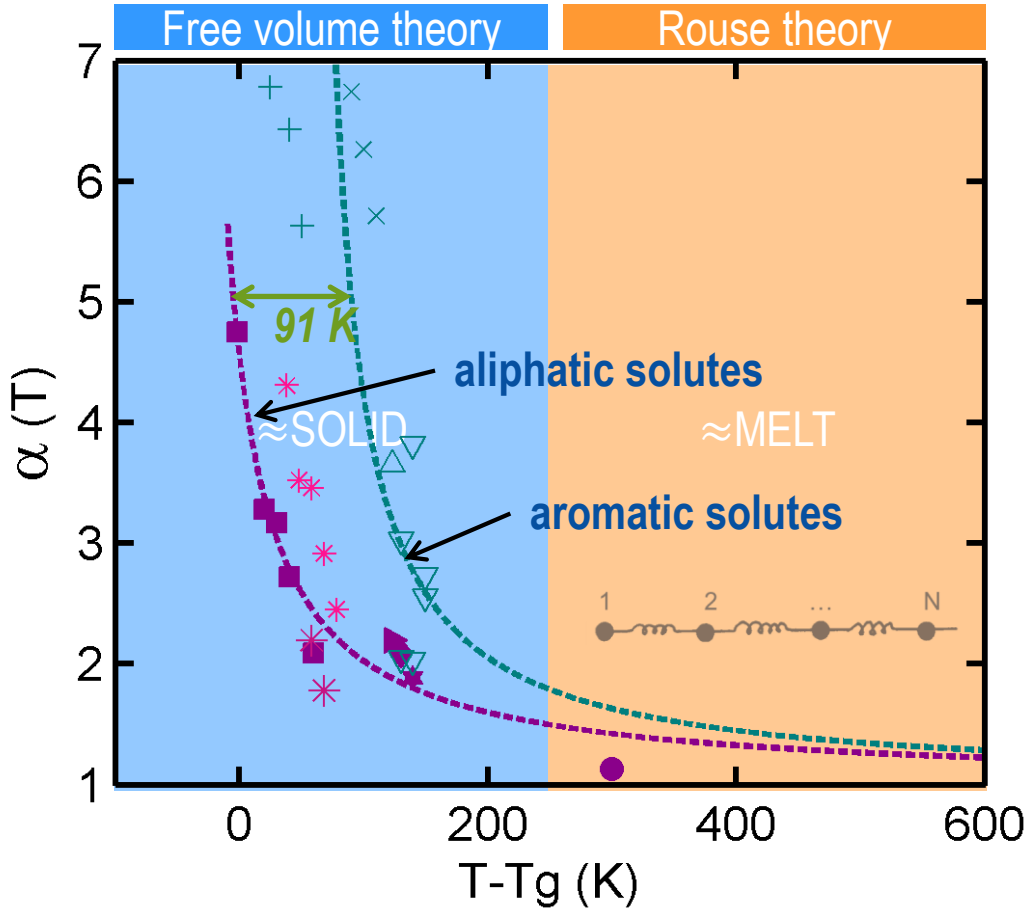


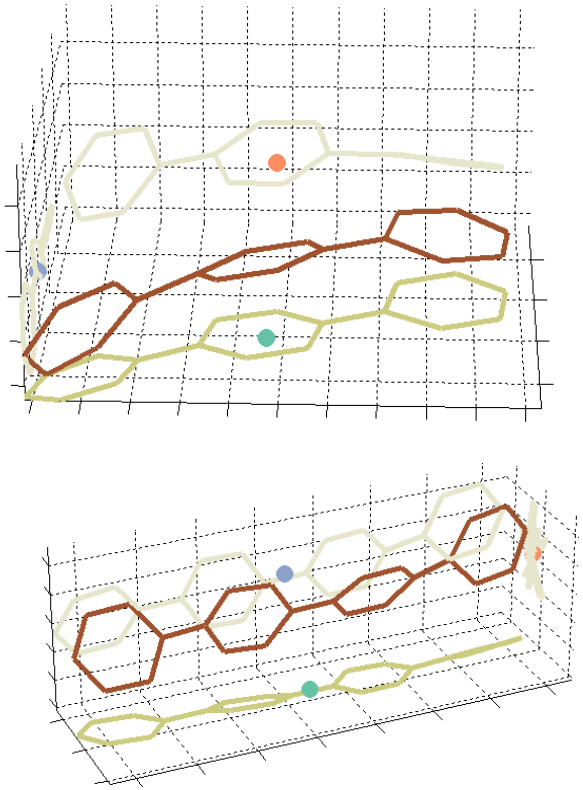


$$\frac{D}{D_0} \propto \left(\frac{M}{M_0}\right)^{-\alpha(T,T_g)}$$

SCALING EXPONENTS

FOR HOMOLEGOUS SERIES OF SUBSTANCES





$$\alpha(T,Tg) = 1 + \frac{K_\alpha}{T - Tg + K_\beta}$$

Blob Shape/size

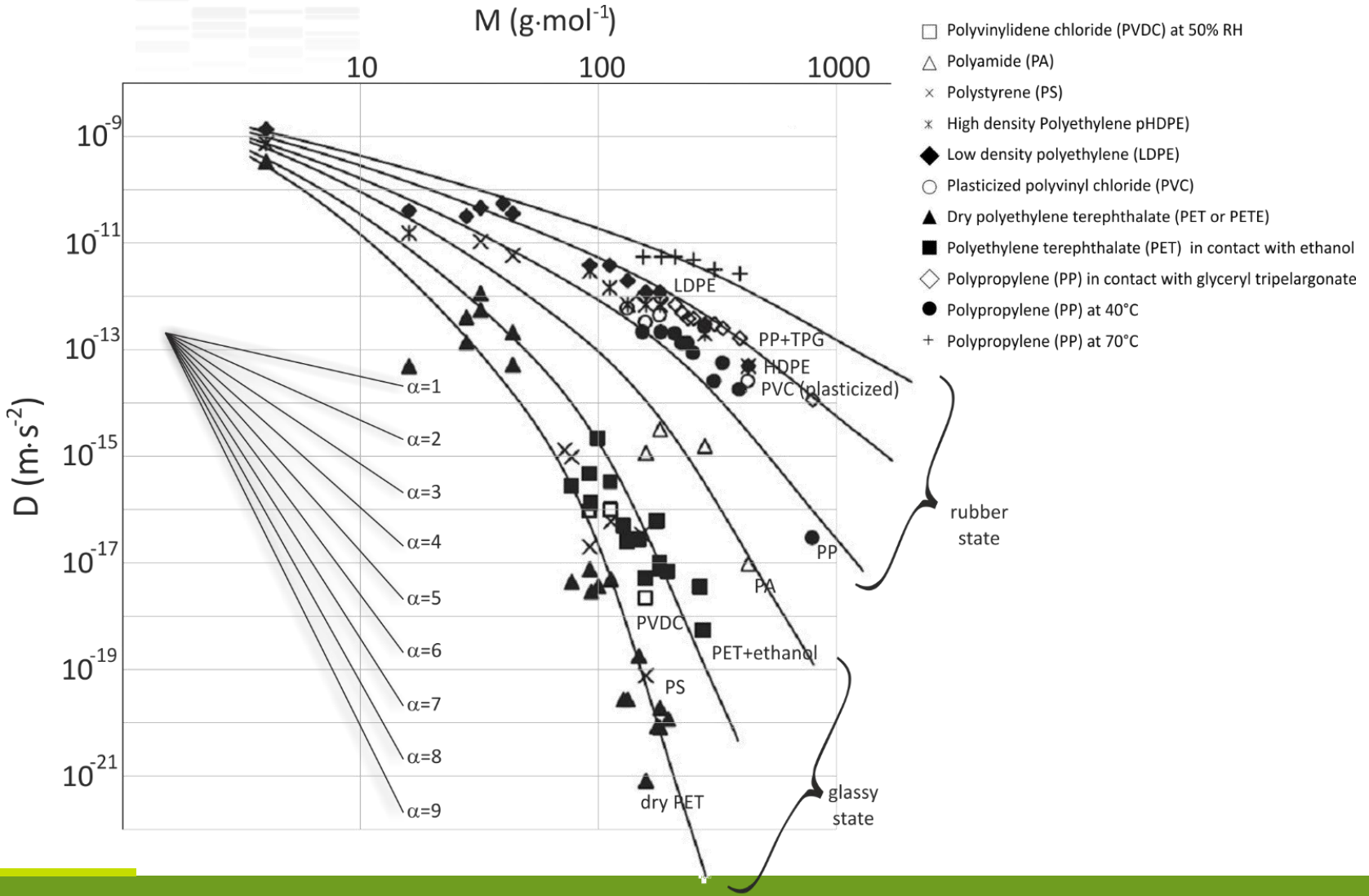
Formal equivalences between FVT and scaling laws

Rubber polymers: $T > T_g$

	Scaling law (Eq. (19))	*Free-volume theory (Eq. (22))*
Relative diffusant effects	$\ln\left(\frac{M}{M_0}\right)$	$0.24(\xi-\xi_0)$
Scaling exponent $\alpha(T,Tg)$	$1+\frac{K_\alpha}{T-T_g+K_\beta}$	$0.24\frac{\gamma}{K_{12}}\frac{\hat{V}_P^*}{K_{22}+T-T_g}$ K_{12}, K_{22} are polymer free-volume parameters.
Relative activation energy $Ea(M,T)-Ea(M_0,T)=$ $Ea(\xi,T)-Ea(\xi_0,T)=$ $\frac{\partial \ln\frac{D(M,T)}{D(M_0,T)}}{\partial 1/T}=$	$\mathrm{K}_\alpha\frac{RT^2}{\left(T-T_g+\mathrm{K}_\beta\right)^2}\ln\frac{M}{M_0}$	$\underbrace{E^*(\xi)-E^*(\xi_0)}_{\to 0}$ $+(\xi-\xi_0)\frac{\gamma\bar{V}_P^*}{\mathrm{K}_{12}}\frac{RT^2}{\left(K_{22}+T-T_g\right)^2}$

SCALING EXPONENTS

FOR VARIOUS POLYMERS

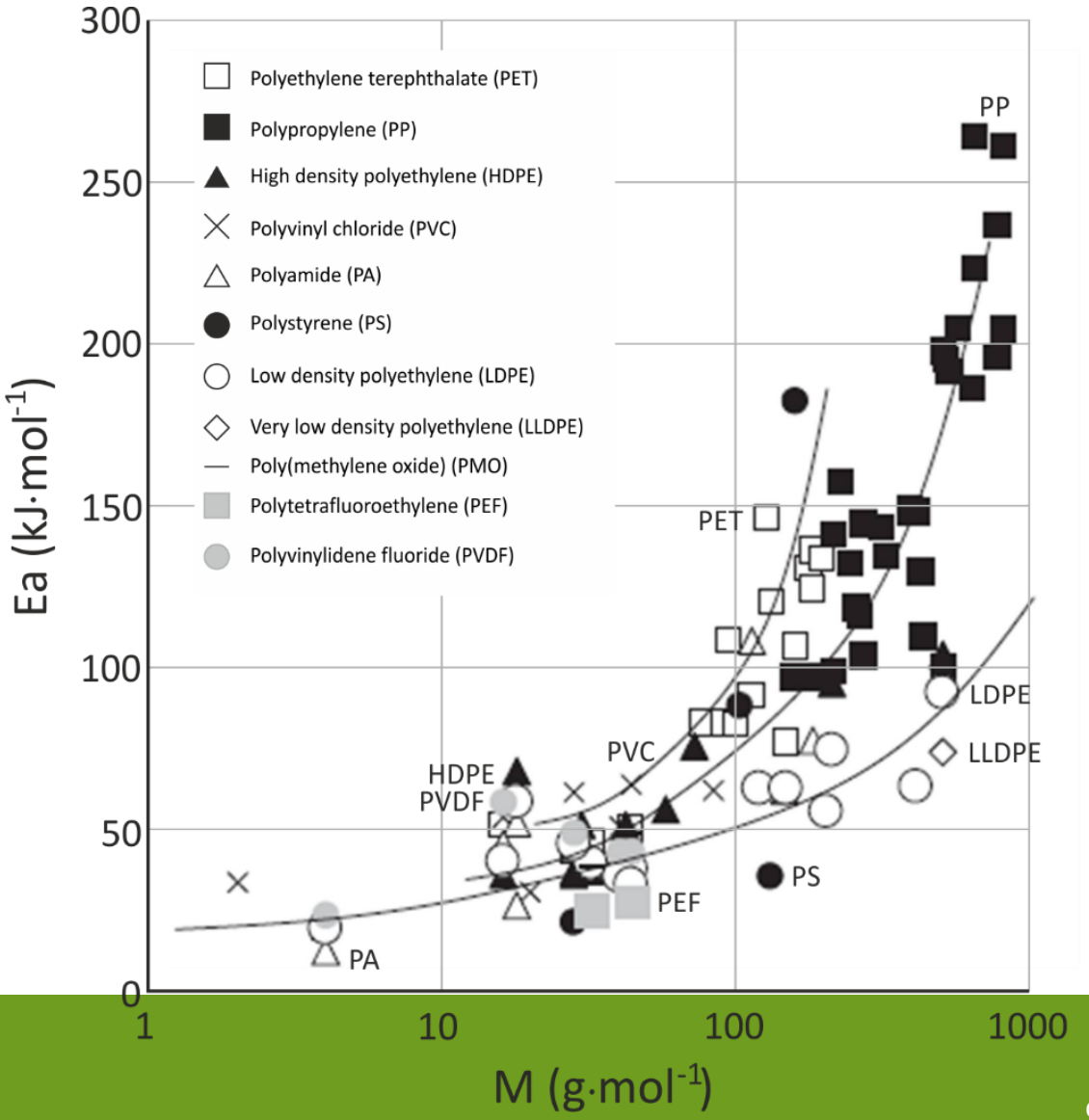


Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac)
http://www.tandfonline.com/doi/full/10.1080/10408398.2013.849654

ACTIVATION ENERGY

VARIOUS DIFFUSANTS IN VARIOUS POLYMERS

$$\mathrm{Ea}(M) \approx \mathrm{Ea}(M_0) + ln(M/M_0)$$



Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac)
http://www.tandfonline.com/doi/full/10.1080/10408398.2013.849654

03

CHEMICAL AFFINITY
PARTITION COEFFICIENTS
HEAT OF SORPTION

HOW MOLECULAR MODELING CAN PREDICT THEM?

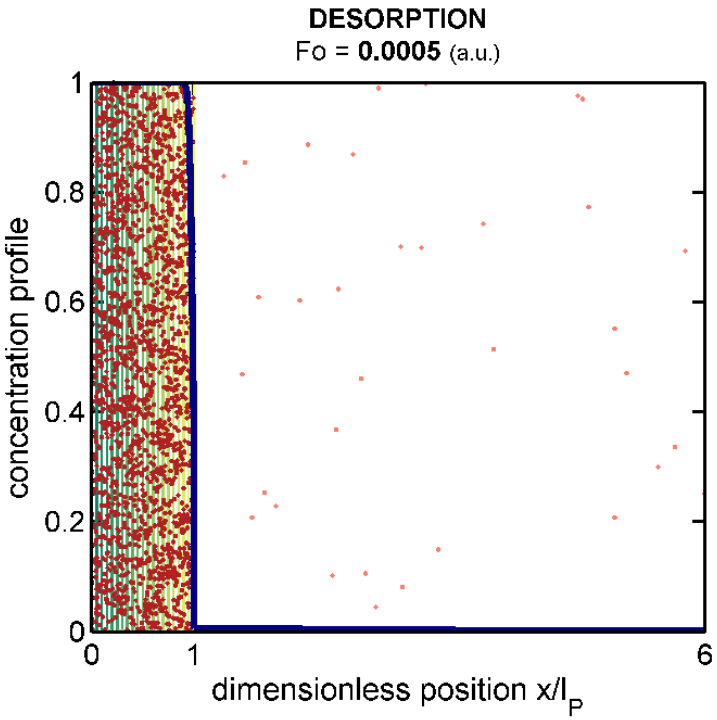
Industrial & Engineering Chemistry Research. **2009**;48(11):5285-5301.
Int. J. Chem. React. Eng. **2010**;8.
Industrial & Engineering Chemistry Research. **2010**;49(16):7263-728
Polym. Sci. Part B: Polymer Physics, **2014**, 52(19), 1252–1258
Nguyen P-M, Guiga W, Dkhissi A, Vitrac O. *submitted to I&EC*. **2015**.

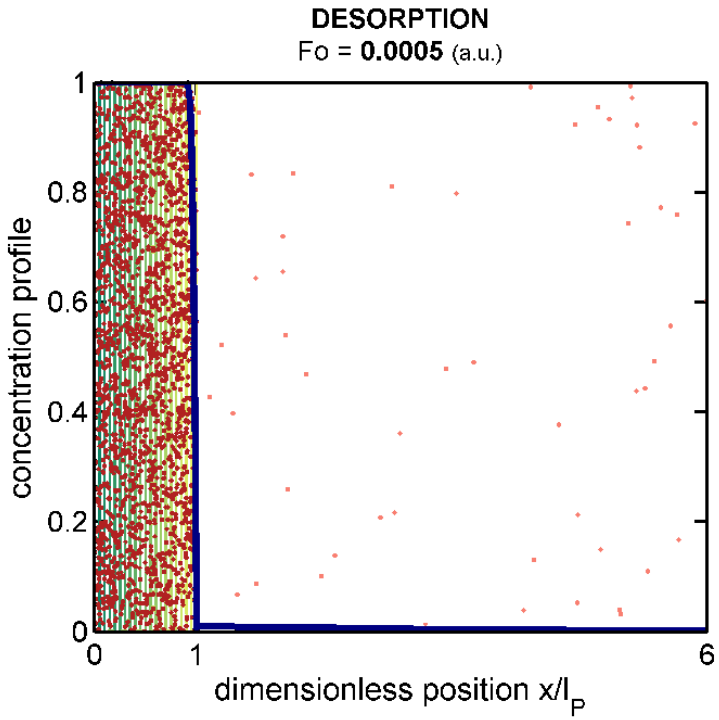
INRA
SCIENCE & IMPACT

EFFECT OF PARTITION COEFFICIENT ON MIGRATION

50 times for chemical affinity for P | 50 times for chemical affinity for F

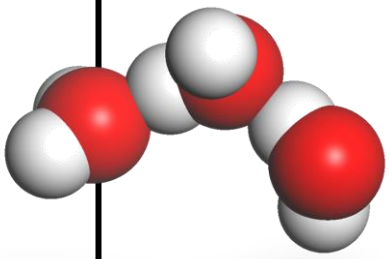
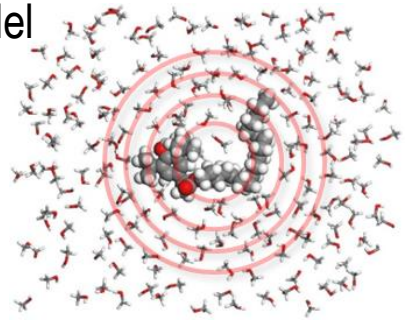
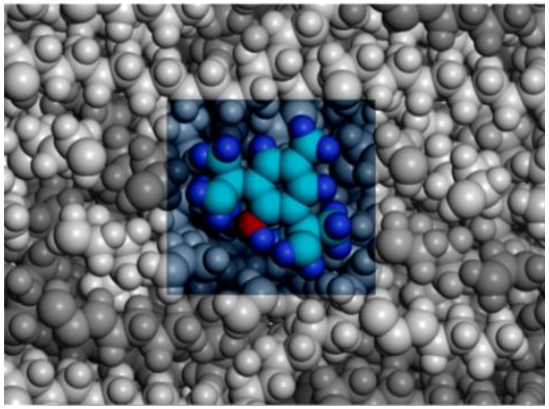
$K_{i,F/P}$ = **1/50** | **50**





$$K_{i,F/P} = \frac{C_{i,F}^{eq}}{C_{i,P}^{eq}} = \frac{1}{1 - crystallinity} \frac{\gamma_{i,P}^{v}{}_{amorphous}}{\gamma_{i,F}^{v}}$$

MANY METHODS AVAILABLE

Class	Models
Group contribution	UNIQUAC, UNIFAC, NRTL
Associative model  	SAFT, PRISM Optimized for polar and liquid phase (De Anda et al Pol. Eng. & Sci., 2011)
Molecular modelling at atomistic scale 	Explicit representation of entangled chains
	Representation of polymer chains without entanglement

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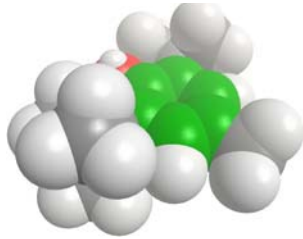
Oct 2015

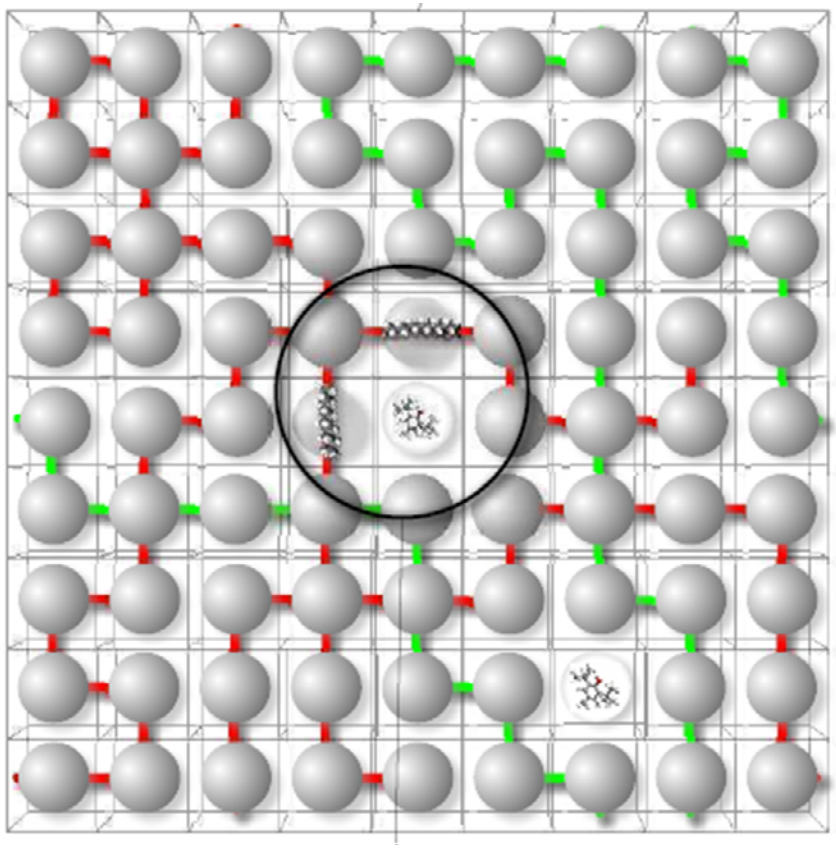
INRA SCIENCE & IMPACT

Off-Lattice Flory-Huggins Formulation of Excess Chemical Potentials in Binary Blend-void Systems



Chemical potential (definition of J. Willard Gibbs)

$$\mu_{i,k} = \left(\frac{\partial G_{i+k}}{\partial n_i}\right)_{P,T,i\neq \mathrm{j}} = \mu_i^0 + RTlna_i = \mu_i^0 + RTln\phi_i + RTln\gamma_{i,k}^v = \mu_i^0 + \mu_i^{id} + \mu_{i,k}^{excess}$$



Flory expression at infinite dilution in *k*=P or in *k*=F

$$\frac{\left\{\mu_{i,k}^{excess}\right\}_{k=P,F}}{k_B \cdot T} = \ln \gamma_{i,k}^v =$$

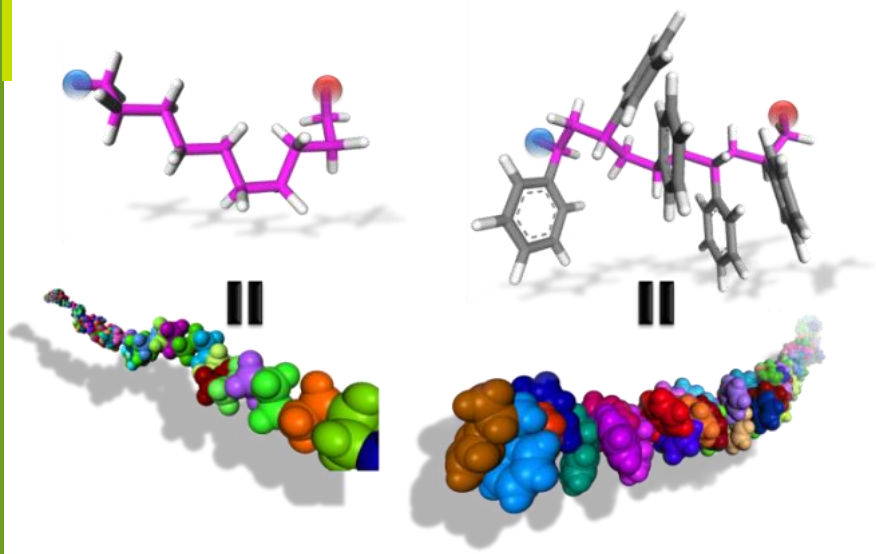
$$\left(1-\frac{1}{r_k}\right)\cdot\phi_k + \chi_{i,k}\cdot\phi_k^2 \approx \left(1-\frac{1}{r_k}\right) + \chi_{i,k}$$

$$2k_BT\chi_{i,k} = \langle h_{i+k}\rangle_T + \langle h_{k+i}\rangle_T - \langle h_{k+k}\rangle_T - \langle h_{i+i}\rangle_T$$

FLORY HUGGINS APPROXIMATION AT ATOMISTIC SCALE

$$\ln(\gamma_{i,k}^{v}) = \left(1 - \frac{1}{r_k}\right)\phi_k + \chi_{i,k}\phi_k^2$$

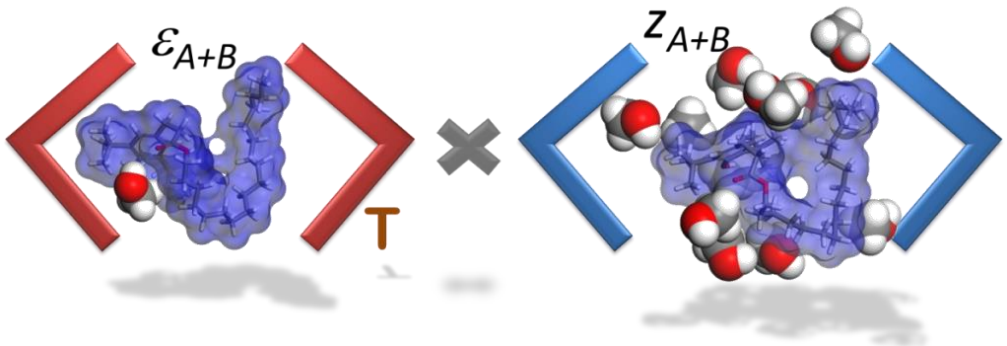
$$k = P, F$$



IDEALIZED POLYMER CHAINS ($k = P$)

$$2k_B T \chi_{i,k} = \langle h_{i+k}\rangle_T + \langle h_{k+i}\rangle_T - \langle h_{k+k}\rangle_T - \langle h_{i+i}\rangle_T$$

EXCESS ENTHALPIES ARE CALCULATED FROM SIMPLE A MIXING RULE OF PAIR CONTACT ENERGIES



$$\langle h_{A+B}\rangle_T = \langle \mathcal{E}_{A+B} Z_{A+B}\rangle_T \approx \langle \mathcal{E}_{A+B}\rangle_T \langle Z_{A+B}\rangle$$

Bawendi et al., *J. Chem Phys*. 1986; 1987; 1988

Gillet et al., *I&EC*, 2009; 2010 ; Vitrac and Gilet, *Int. J. Chem. Reactor Eng*. 2010

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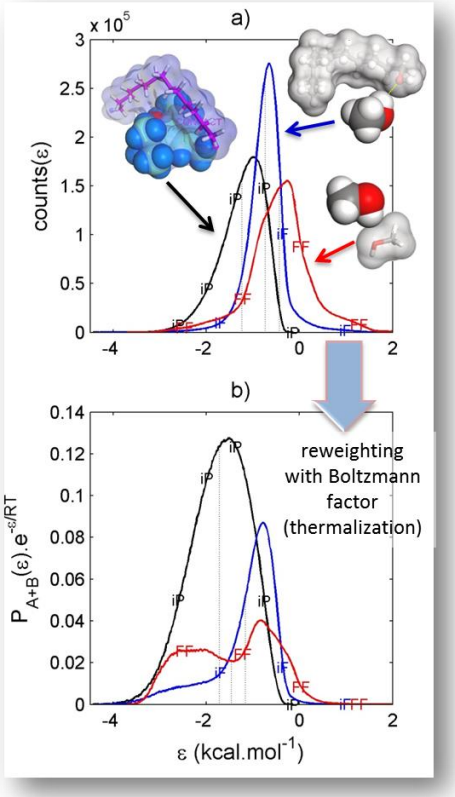
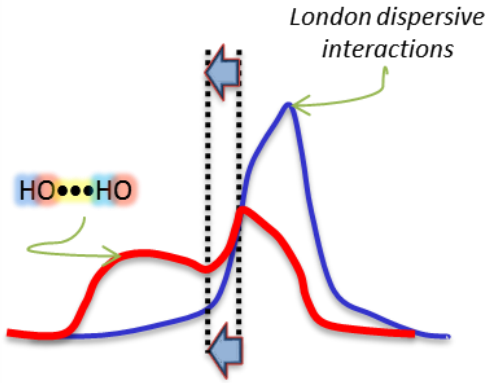
INRA SCIENCE & IMPACT

DETAILS OF THE ENERGY SAMPLING PROCEDURE

Pair contact energies



$$\langle \varepsilon_{A+B} \rangle_T = \frac{\int_{-\infty}^{+\infty} \varepsilon pr(\varepsilon) \exp\left(-\frac{\varepsilon}{RT}\right) d\varepsilon}{\int_{-\infty}^{+\infty} pr(\varepsilon) \exp\left(-\frac{\varepsilon}{RT}\right) d\varepsilon}$$



Excess enthalpies

Homopolymers

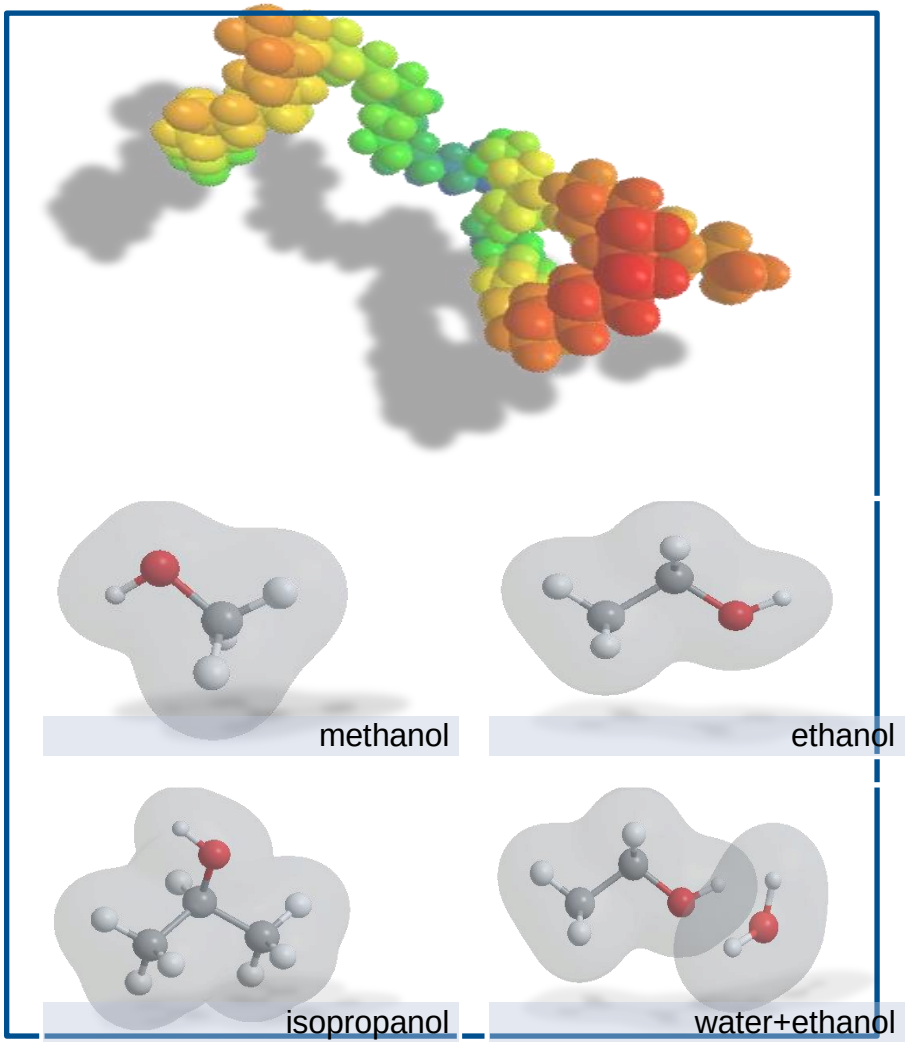
- $\chi_{i,P}^{\left(n_{i,P}^{\min}\right)} = \frac{\langle h_{i+P}^{n_{i,P}^{\min}} \rangle_T + \langle h_{P+i}^{n_{i,P}^{\min}} \rangle_T - \langle h_{P+P}^{n_{i,P}^{\min}} \rangle_T - \langle h_{i+i} \rangle_T}{2RT}$
- $n_{i,P}^{\min} = \underset{n_P}{\operatorname{argmin}} \left(\chi_{i,P}^{(n_P)} \right)$
- $\langle h_{j+k} \rangle_T = \langle \epsilon_{j+k} \rangle_T \langle z_{j+k} \rangle + \beta_{jk}$

In liquids (denoted F ou L)

- $\chi_{i,F} = \frac{\langle h_{i+F} \rangle_T + \langle h_{F+i} \rangle_T - \langle h_{F+F} \rangle_T - \langle h_{i+i} \rangle_T}{2RT}$
- For water: $\langle h_{F+F} \rangle_T = 4 \langle \varepsilon_{A+B} \rangle_T \langle z_{A+B} \rangle$

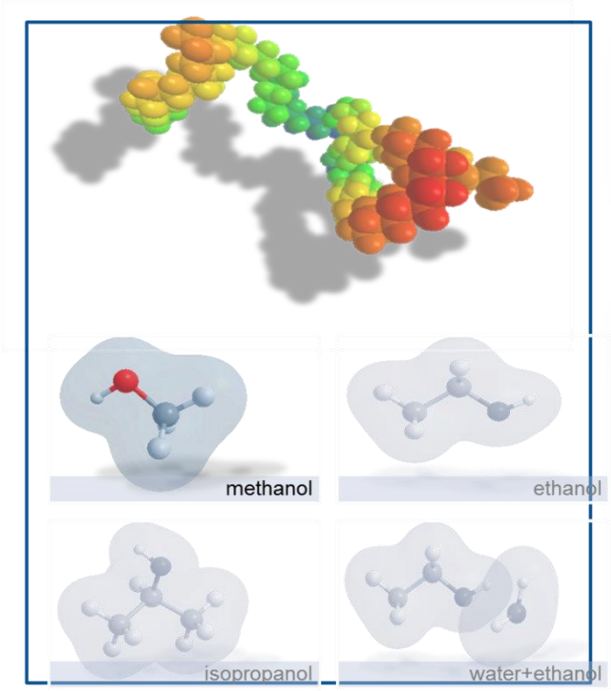
FIRST COMPARISONS BETWEEN DIRECT CALUCLATIONS AND EXPERIMENTS (no fit) – 45 SOLUTES

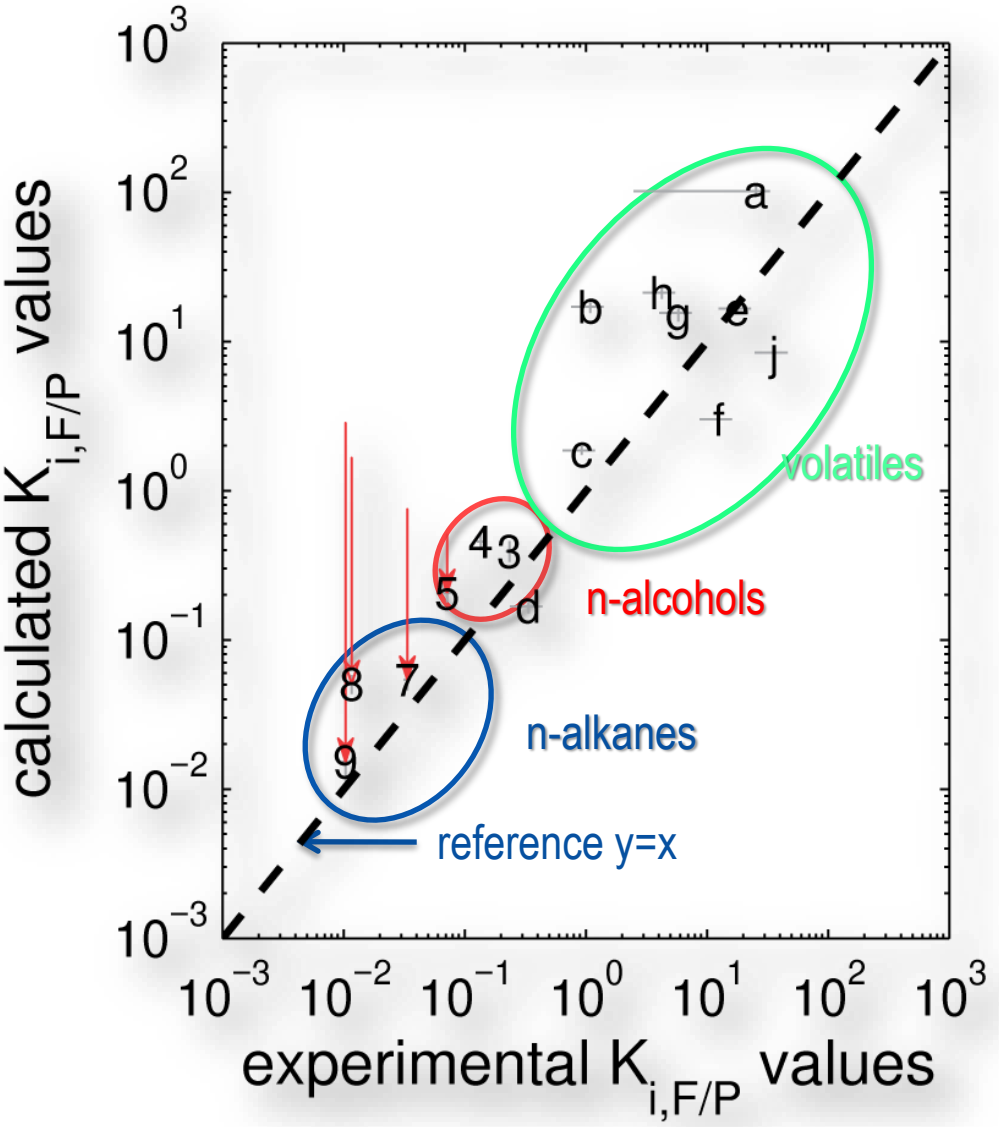
Polyethylene in contact with

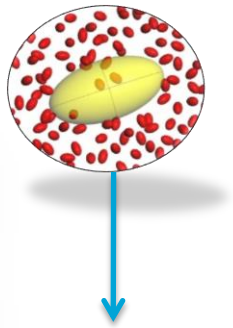


Alkanes	Alcohols	Volatiles	Plastics additives
decane	decanol	camphor	BHT
undecane	undecanol	diphenyl oxide	chimassorb 81
dodecane	dodecanol	diphenylmethane	Erucamide
tridecane	tridecanol	d-limonene	Irganox 1076
tetradecane	tetradecanol	dl-menthol	Irganox 1035
pentadecane	pentadecanol	eugenol	Irganox 245
hexadecane	hexadecanol	isoamyl acetate	Irgafos 168
heptadecane	heptadecanol	linalyl acetate	Irganox 3114
octadecane	octadecanol	phenylethyl alcohol	Irganox ps802
nonadecane	nonadecanol		stearic acid
eicosane	eicosanol		Tinuvin 326
docosane			
tetracosane			
octacosane			

METHANOL-POLYETHYLNE PARTITIONING

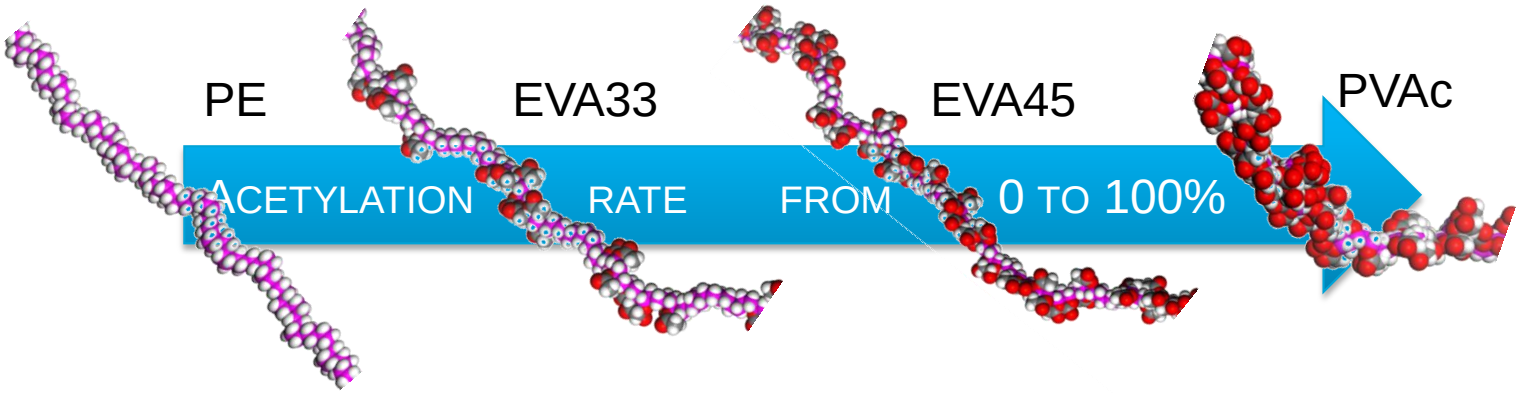






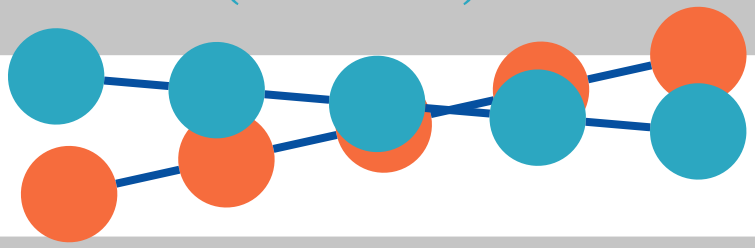
Effect of overlapping F molecules

EXTENSION TO COPOLYMERS (ethylene vinyl acetate)



Mean field approximation (Flory-Huggins ternary : *i* + PE + PVAc)

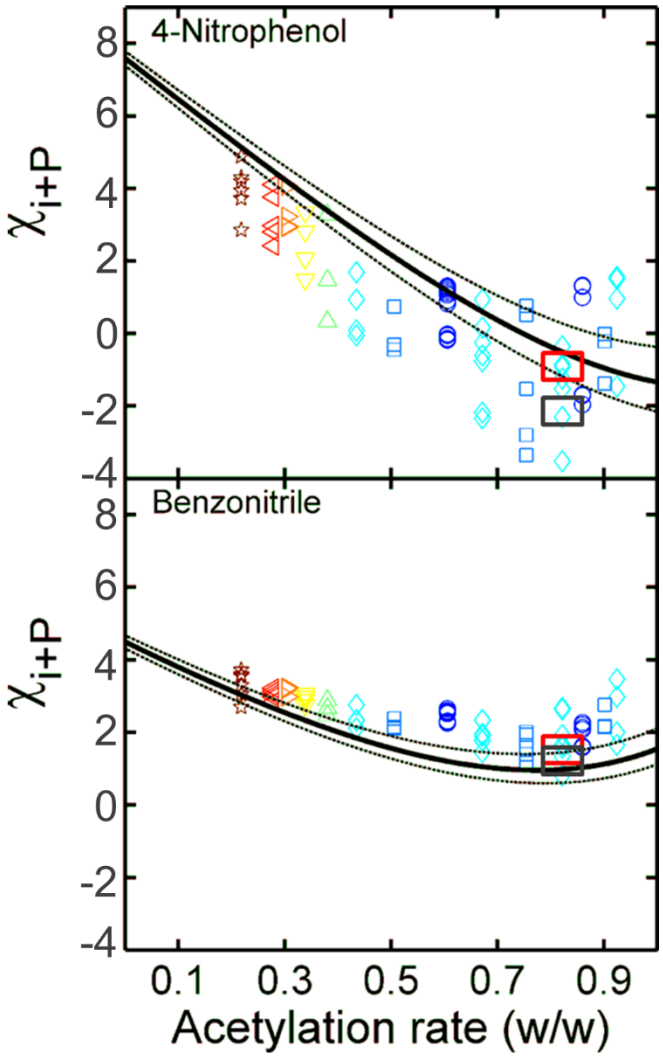
$$\chi_{i,EVA}^{(w_{VA})} = \chi_{i,PVAc}\phi_{VA}^{(w_{VA})} + \chi_{i,PE}\left(1-\phi_{VA}^{(w_{VA})}\right) - \chi_{PVAc,PE}\phi_{VA}^{(w_{VA})}\left(1-\phi_{VA}^{(w_{VA})}\right)$$



Microscopic approach (binary : *i* + copolymer) : sampling of all possible isomers

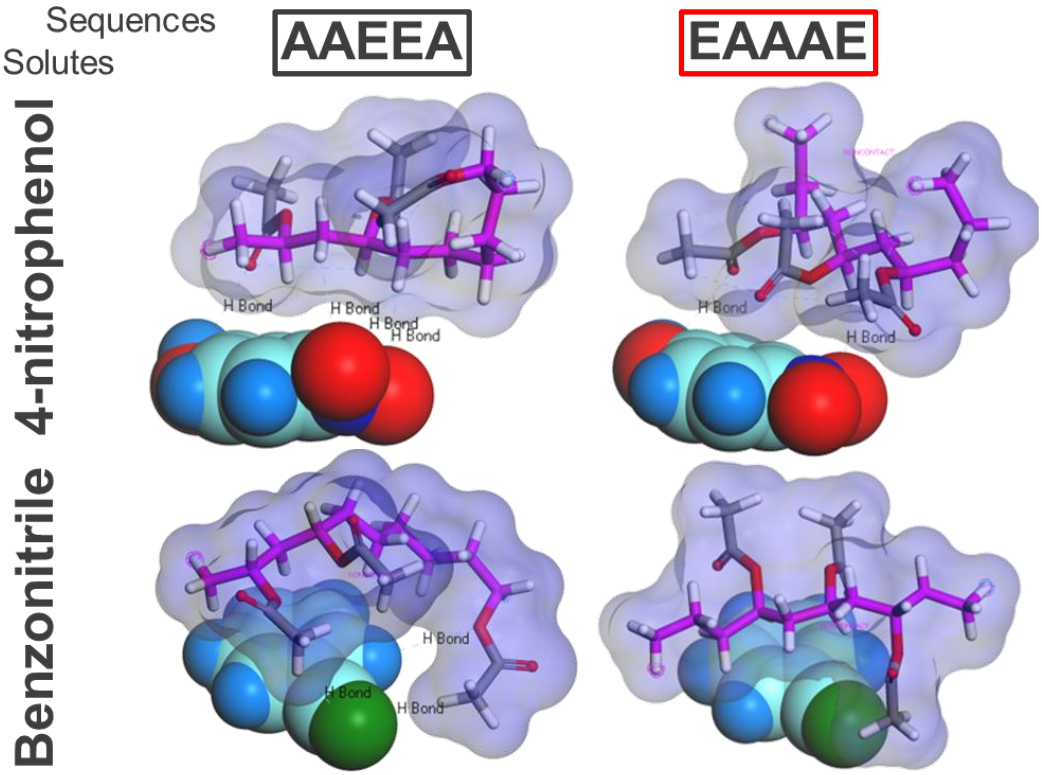
COMPARISON BETWEEN THE MICROSCOPIC AND MEAN FIELD APPROXIMATION

Effect of acetylation rate on χ



Configurations of minimal energies : n = 5

(acetylation rate w/w = 0.82)

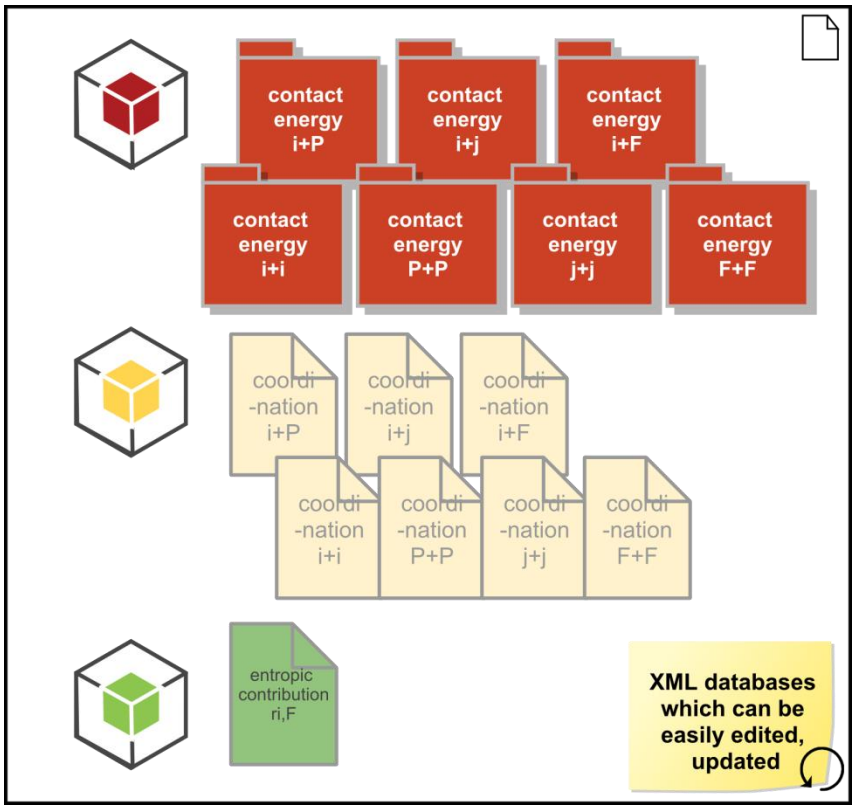


Microscopic calculations

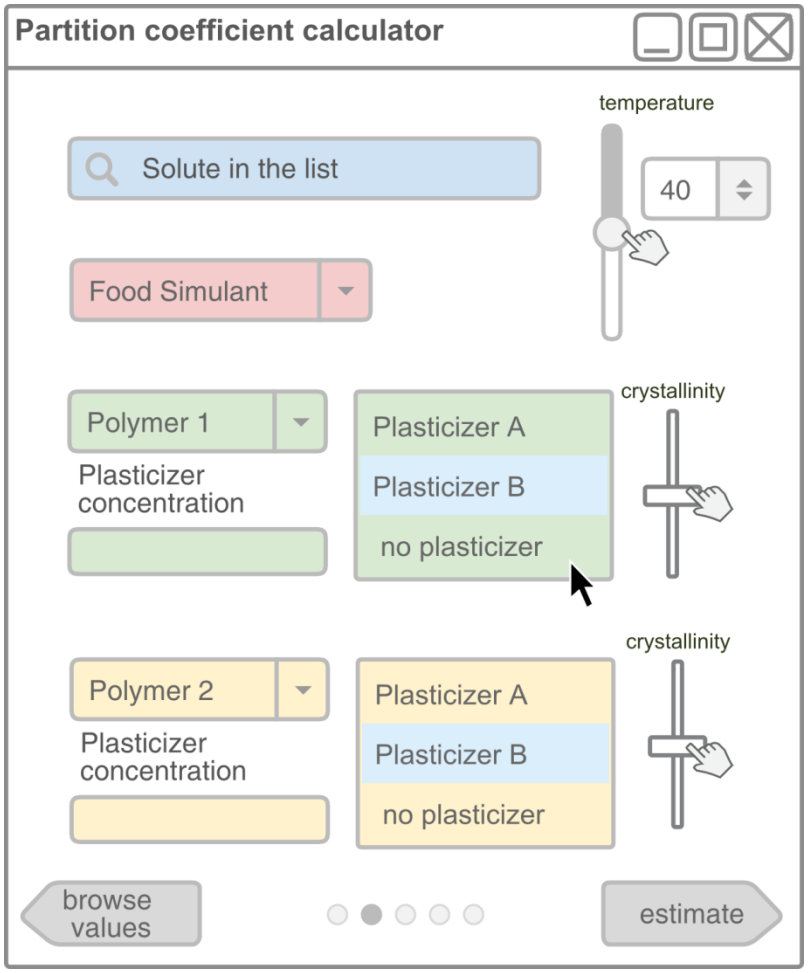
mean field approximation

MOLECULAR RESULTS INTEGRATED WITHIN A "SMALL" SOFTWARE

Databases of results calculated at *molecular scale*



Small "real-time" software



$i =$ 

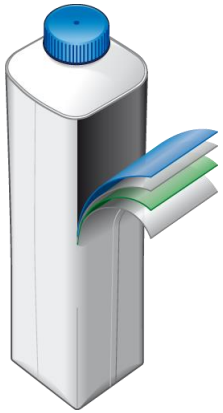
_04

PREVENTIVE APPROACHES OF THE CONTAMINATION

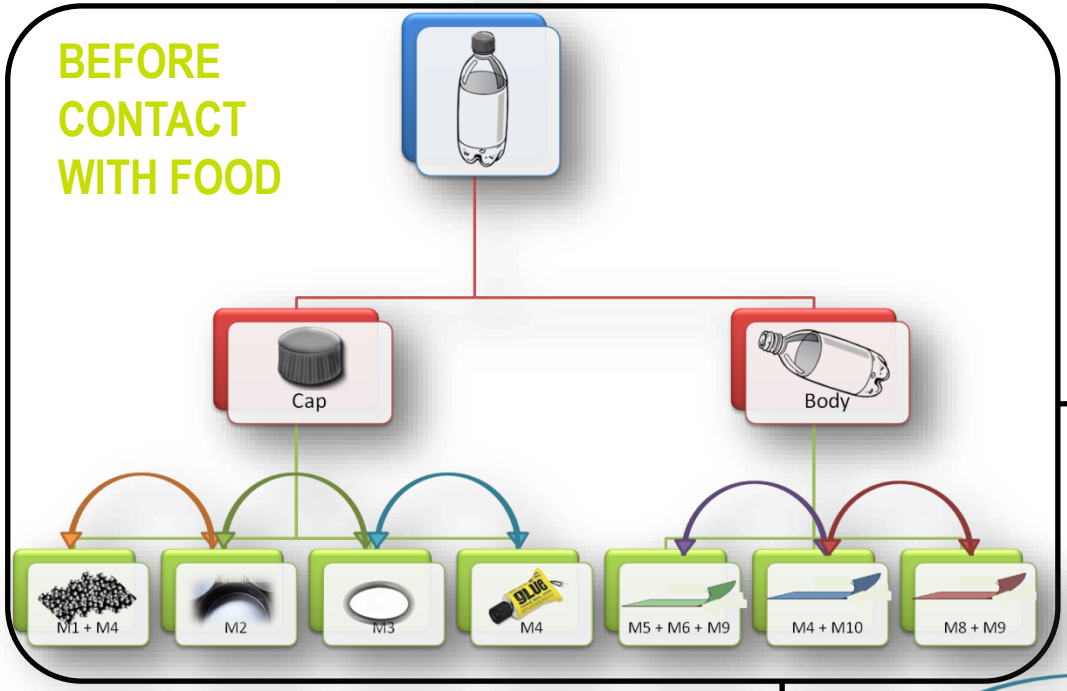
FMECA APPROACHES

AIChE Journal **59, 1183 (2013).**
Chemical Engineering Science **99, 2 (2013).**
Journal of Applied Polymer Science **119, 1492 (2011).**
Food Additives and Contaminants **26, 1556, (2009).**
Food Additives and Contaminants **24, 194 (2007).**
Food Additives and Contaminants **24, 75 (2007).**
Industrial & Engineering Chemistry Research **45, 7941 (2006).**
AIChE Journal **51, 1080 (2005).**
Food Additives and Contaminants **22, 956 (2005).**

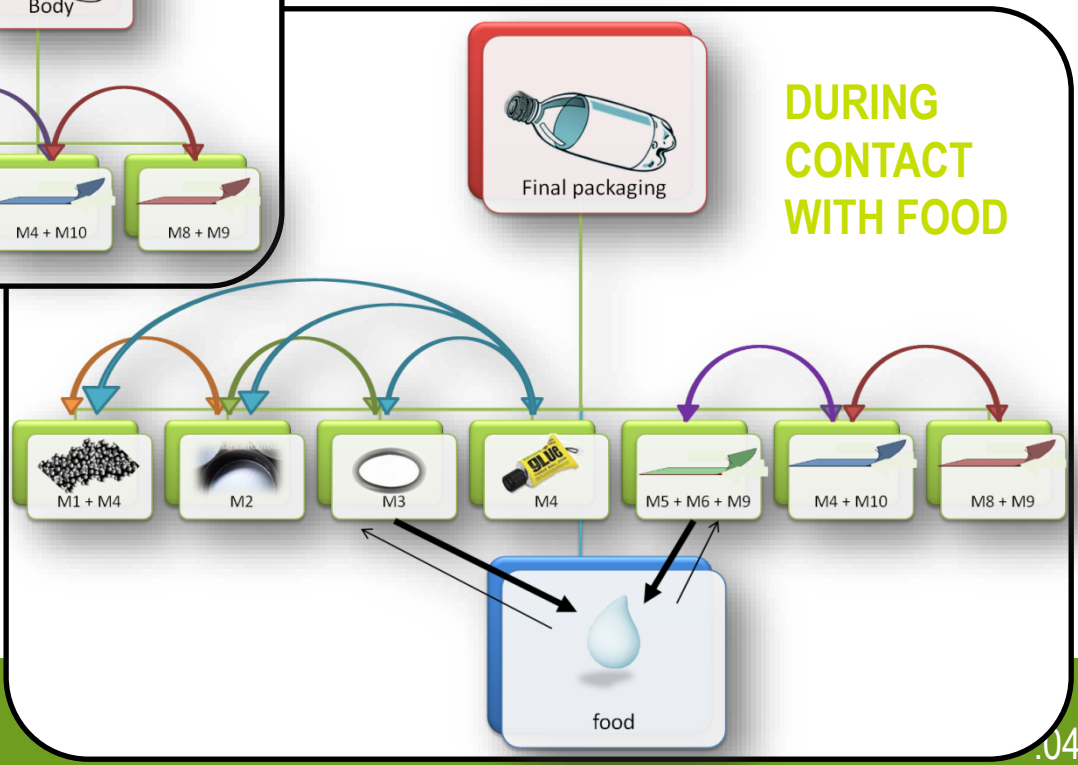
CROSSED-MASS TRANSFER BETWEEN MATERIALS



BEFORE CONTACT WITH FOOD

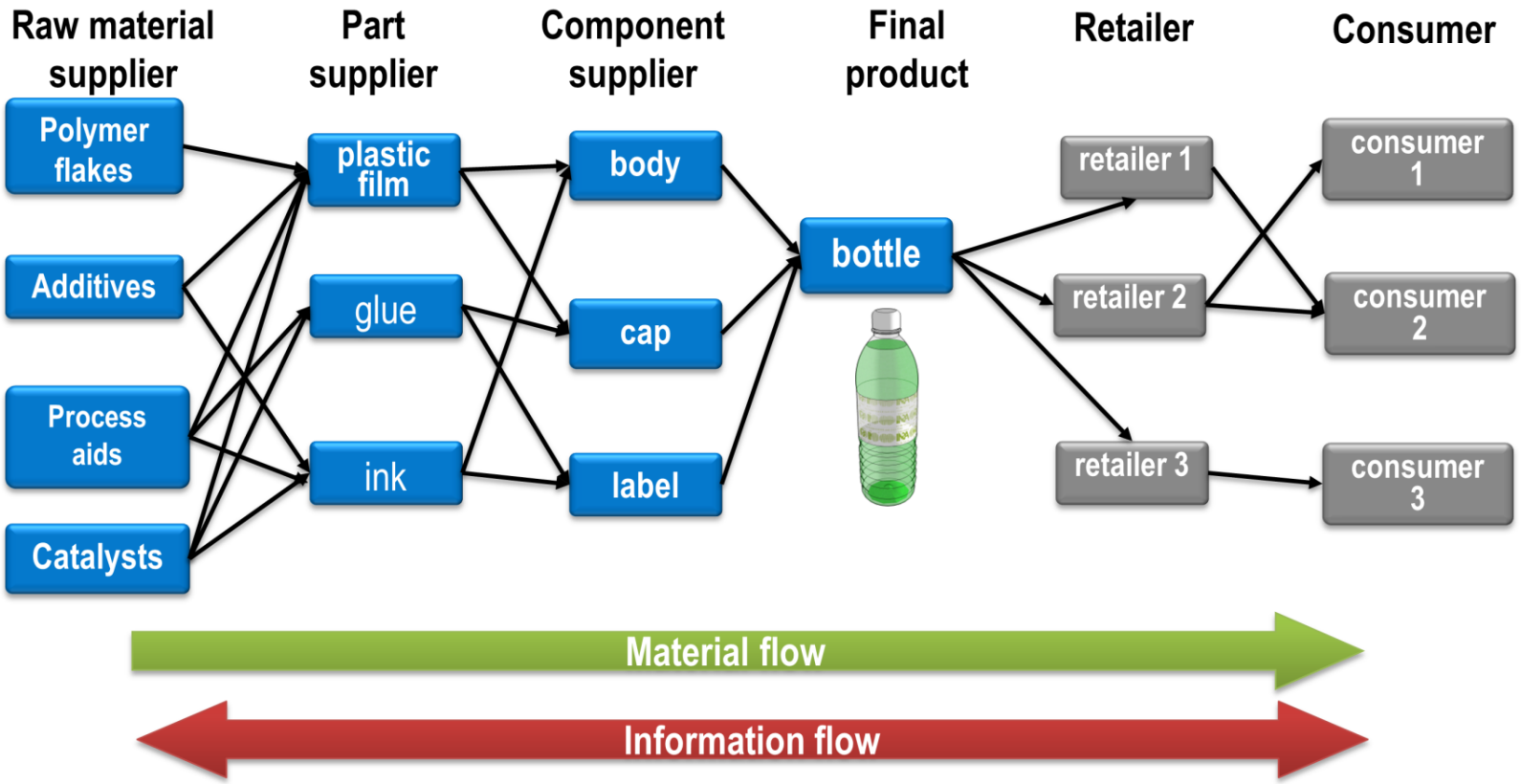


DURING CONTACT WITH FOOD



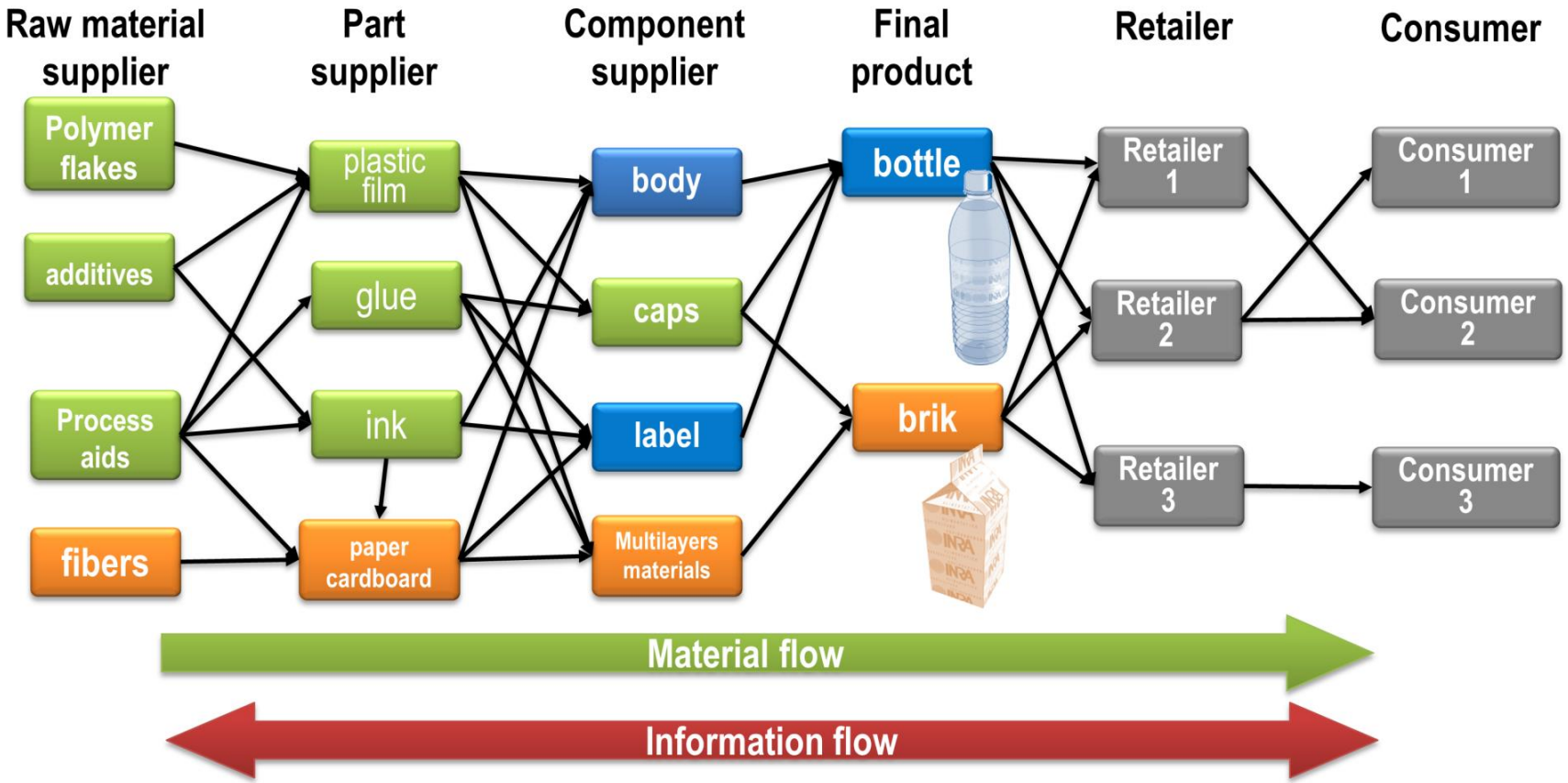
TOWARDS NEW CONCEPTS

DEVELOPING COOPERATION BETWEEN STAKEHOLDERS



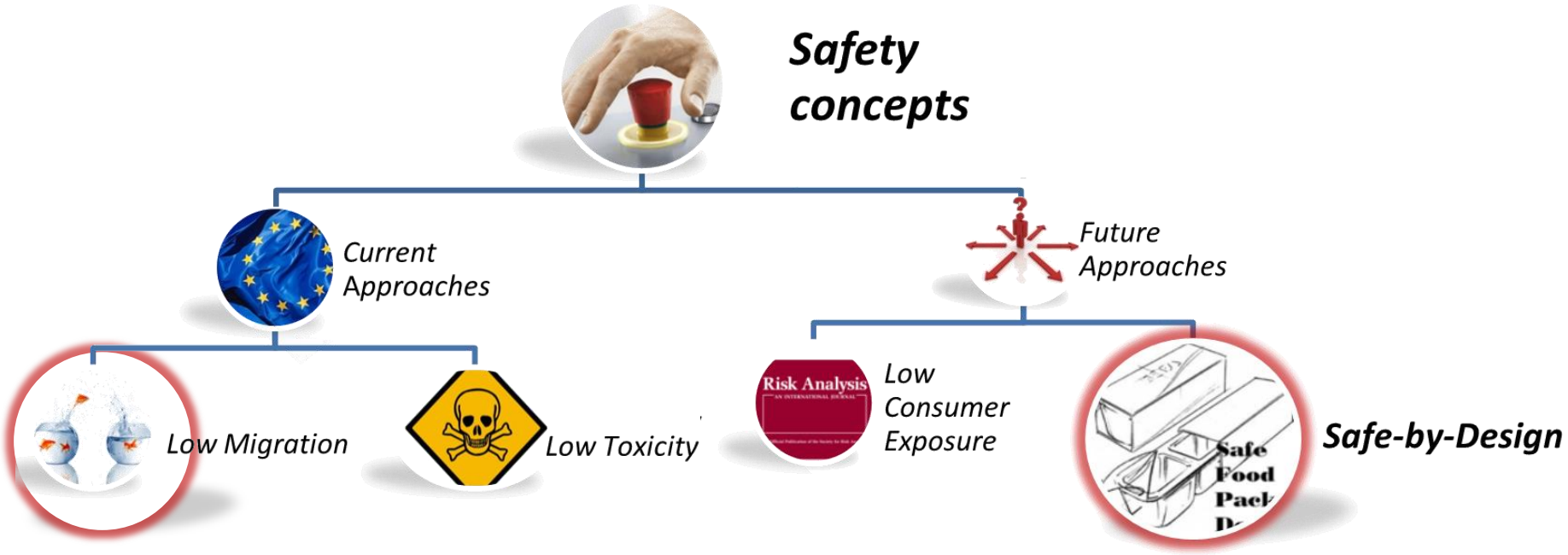
TOWARDS NEW CONCEPTS

DEVELOPING COOPERATION BETWEEN STAKEHOLDERS



TOWARDS NEW CONCEPTS

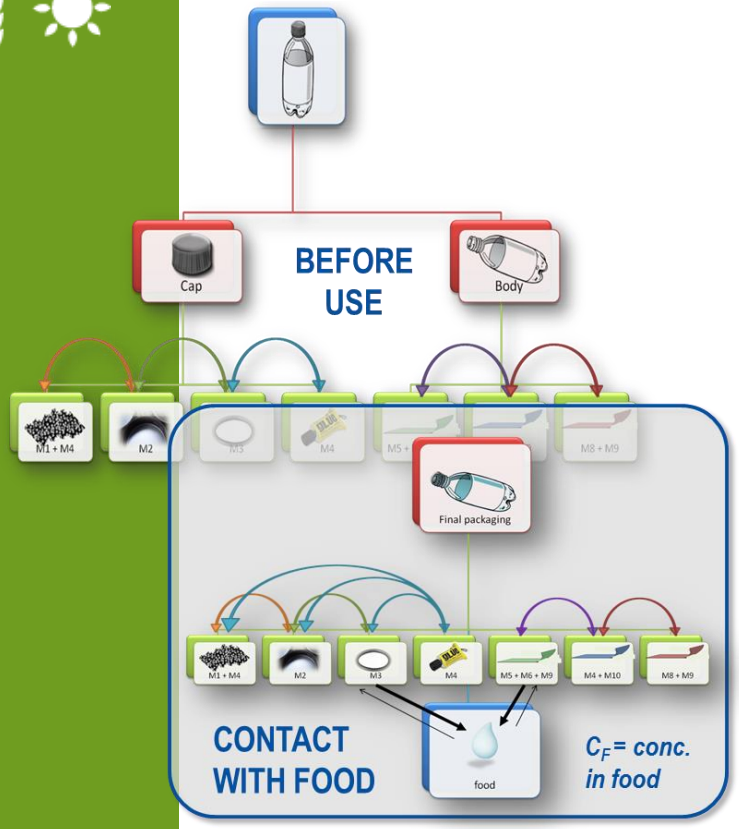
PREVENTIVE APPROACHES OF FOOD SAFETY



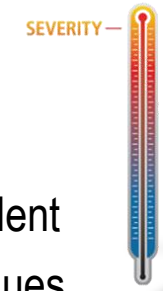
17 groups of materials listed in Annex 1 of regulation 1935/2004/EC are still not covered by specific measures.
They must be produced according to **Good Manufacturing Practices** (Regulation 2023/2006/EC)
incl. 3 pillars: quality assurance system, quality control system, documentation.

Failure Mode Effects Criticality Analysis

LOGICAL STEPS



- List of components and functions
- Failure = migration mode tree
- **Severity** = $f(C_F)$
  - Dimensionless scale
  - Normalized by toxicological data
  - Substance and material independent
  - Linear to C_F for acceptable C_F values and non-linear beyond



- **Criticality ranking**
  - by component
  - by substance
  - by process or storage step
  - Comparative designs
- Ensuring **detectability** via calculations and simulation

Nguyen *et al*. 2013, AIChE J.

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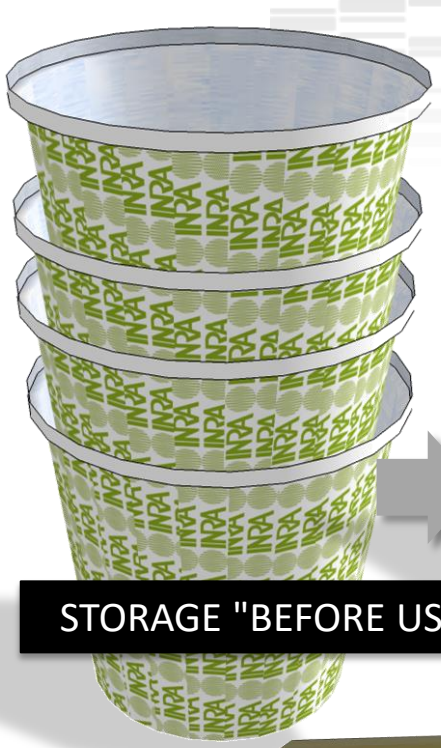
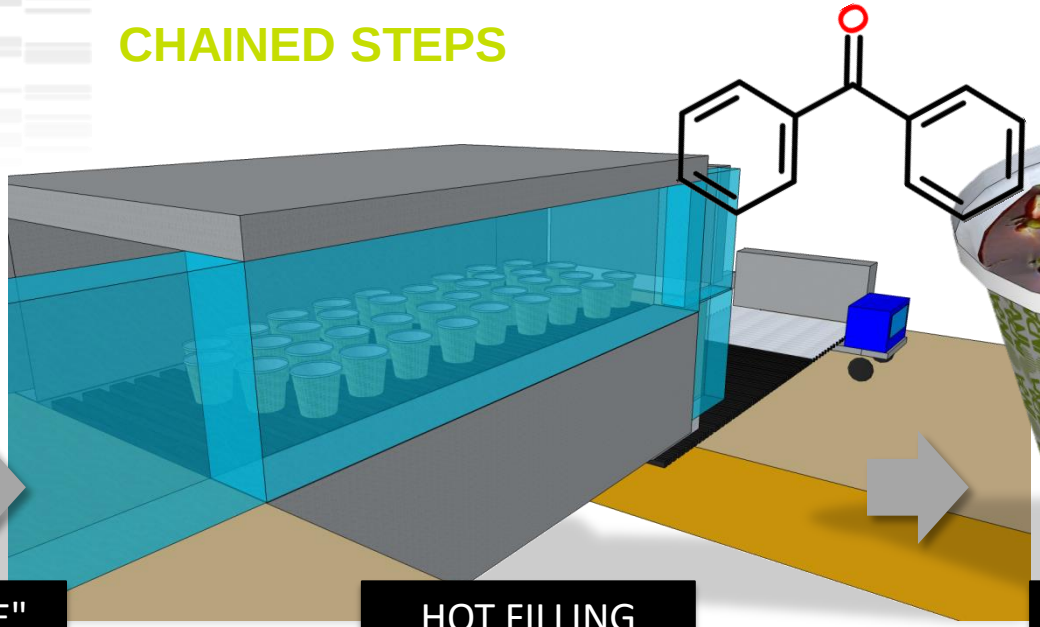
READY TO EAT “CHINESE SOUP”

CHAINED STEPS

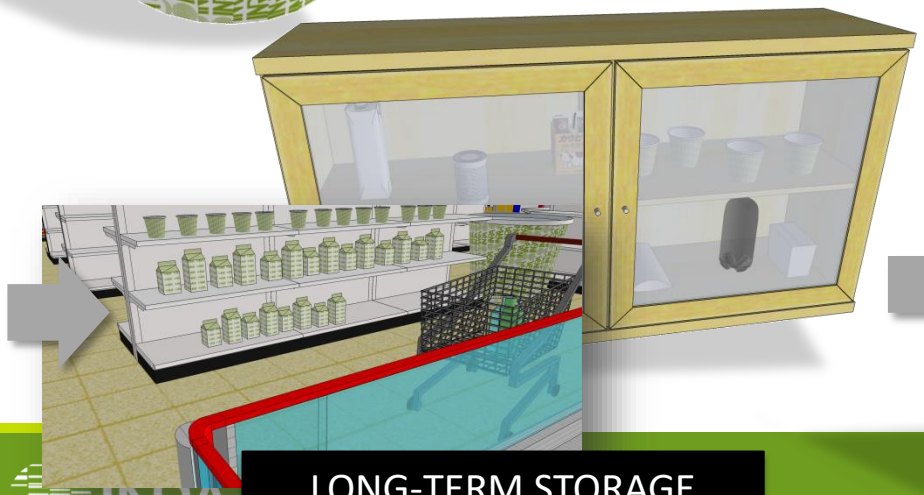


STORAGE "BEFORE USE"



HOT FILLING

FATTY CONTACT



LONG-TERM STORAGE

MICROWAVE OVEN HEATING

ALL STEPS MUST BE INCLUDED IN THE ANALYSIS

As soon they cause a redistribution of packaging constituents through the different materials (even without food contact).

"SETOFF"

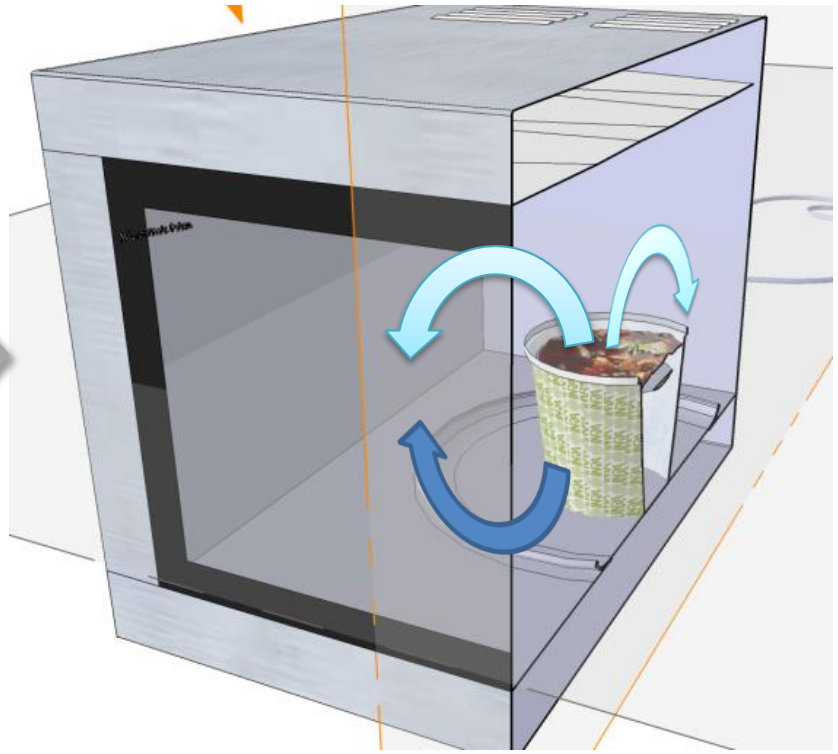
STORAGE "BEFORE USE"

CROSS-MASS TRANSFER BETWEEN INTERNAL AND EXTERNAL SURFACES

ALL STEPS MUST BE INCLUDED IN THE ANALYSIS

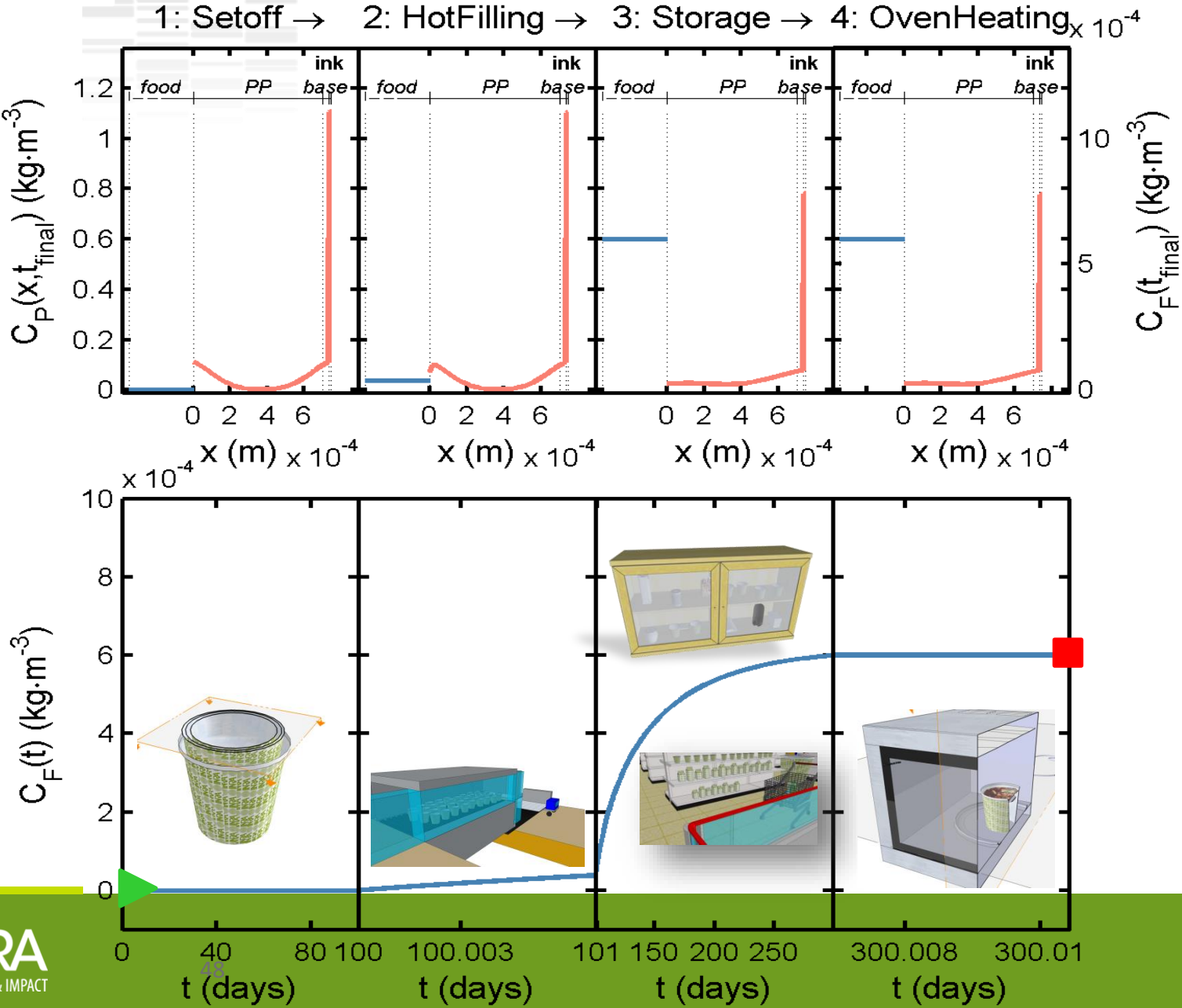
Mass transfer in the gas phase cannot be neglected during curing, long-term storage and oven heating

MICROWAVE HEATING



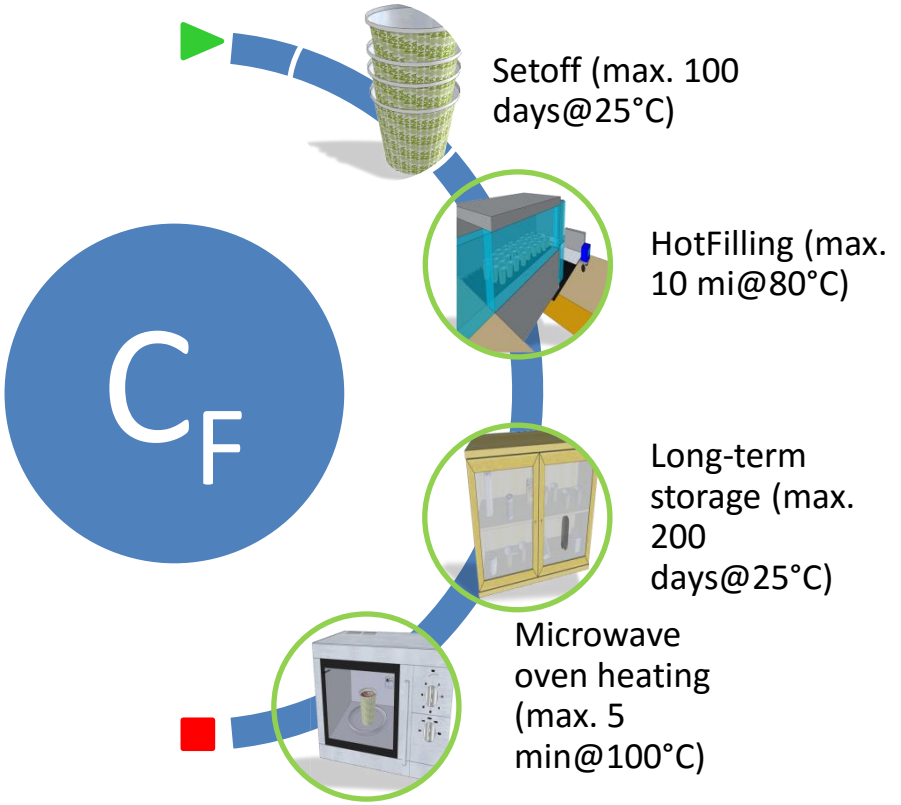
TRANSFER IN VAPOR PHASE
+STEAM EXTRACTION

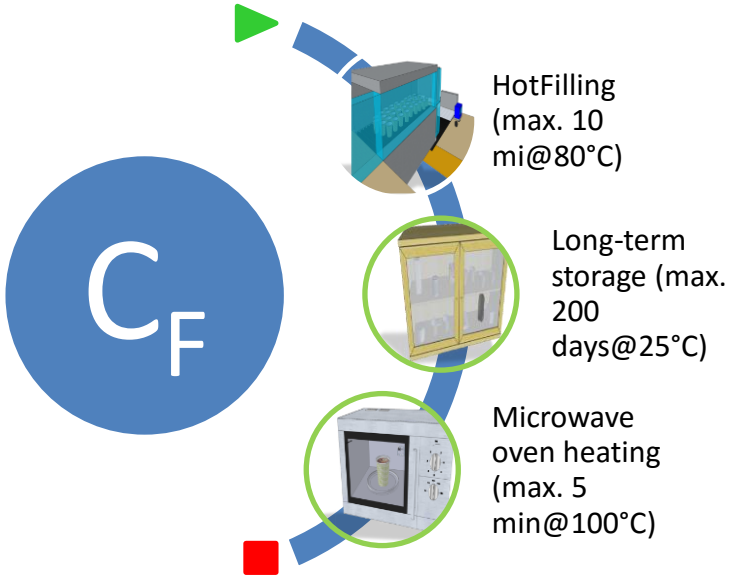
CHAINED STEPS



ASSESSING THE SEVERITY OF A SINGLE STEP

CASE OF "SETOFF" STEP



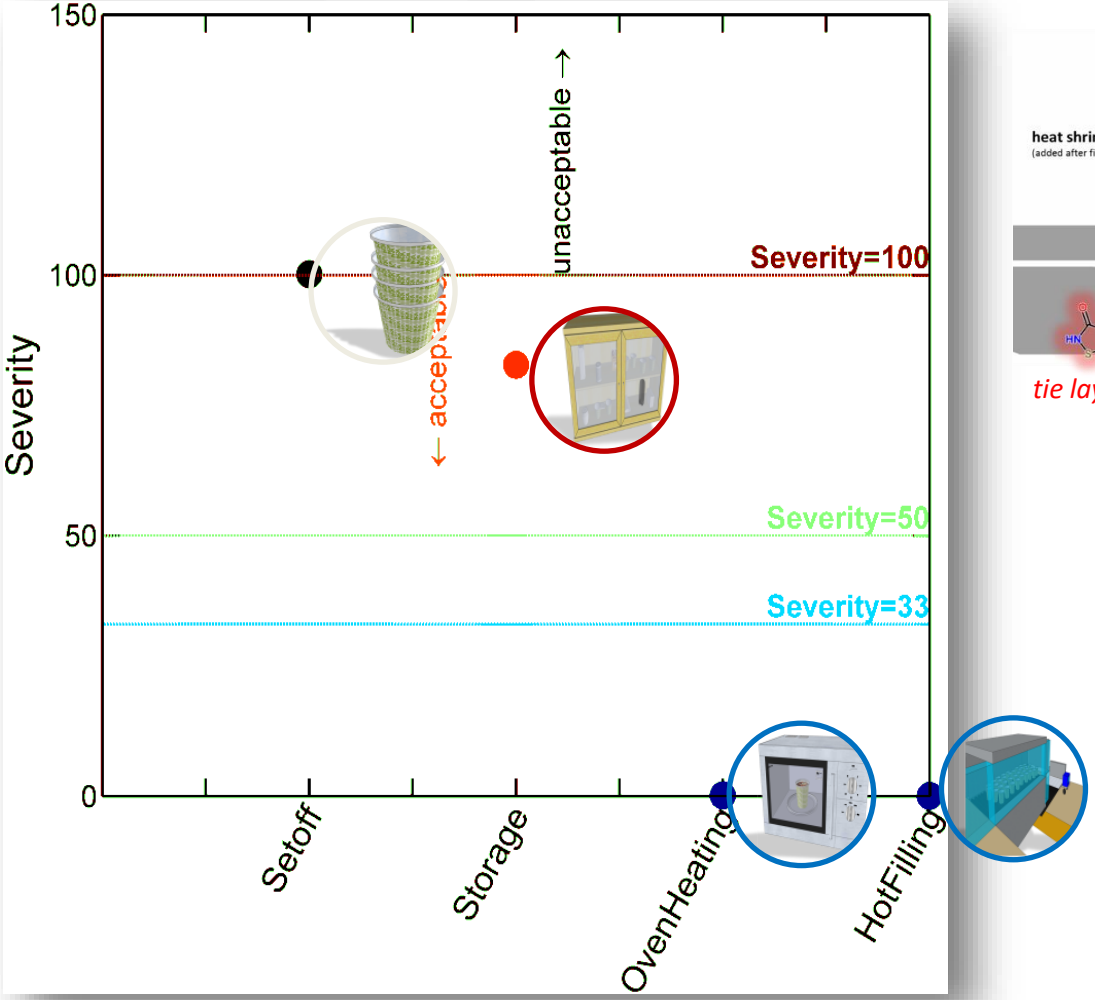


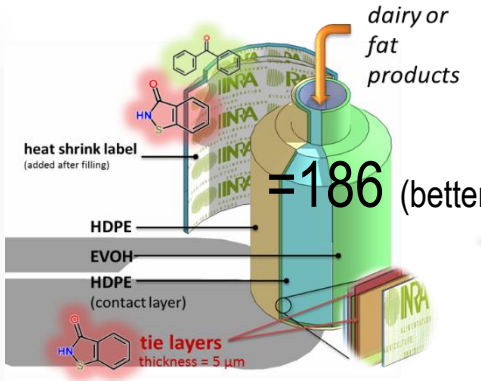
Full methodology described in *AIChE J.* 2013, **59**(4), 1183-1212

$$\text{Severity}\left(\hat{C}_F\left(\text{step}\,i\right)\right) = f\left[\max\left(\underbrace{C_{F_M}\big|_{1\to 2\to\cdots\to M} - C_{F_M}\big|_{1\to 2\to\cdots\to M/i}}_{\text{comparison with step } i \text{ removed}}, \underbrace{C_{F_i}\big|_i}_{\text{step } i \text{ alone}}\right)\right]$$

COMPARING THE SEVERITY OF A SEVERAL STEPS, PACKAGING DESIGNS, SUBSTANCES…

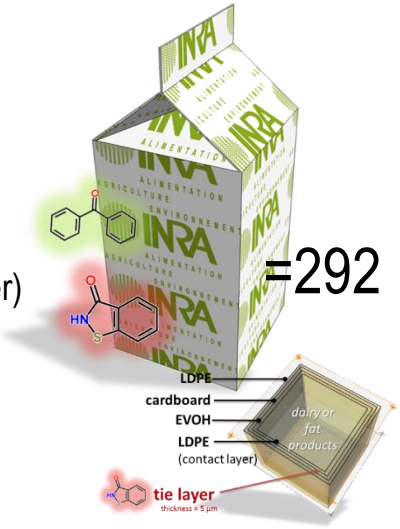
CASE OF "SETOFF" STEP



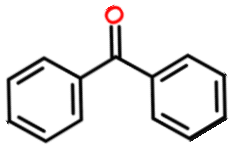


=186 (better)

tie layer = EVA



=292



=115
(almost acceptable)

=124

Full methodology described in *AIChE J.* 2013, **59**(4), 1183-1212

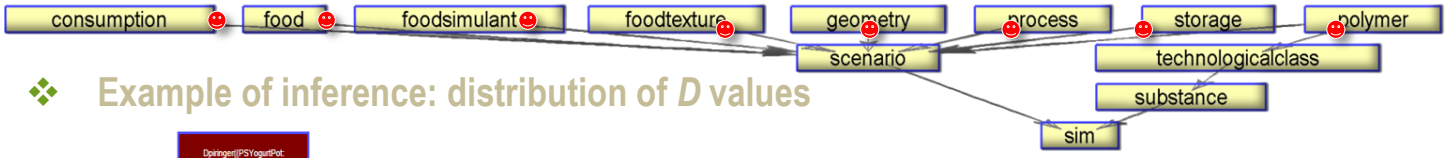
AUTOMATIC GENERATION OF MIGRATION SCENARIOS

id	parent	geometry	polymer	food	foodsimulant	foodtexture	step	temperature	comment
LDPEYogurtBottle		smallbottle	LDPE	yogurt	ethanol50	liquid	storage	chilled	*pot of yogurt*
HDPEOilCap		cap	HDPE	oil	fatty	liquid	storage	ambient	*oil bottle cap*
PPDrinkGoblet		gobletPP	PP	hotdrink	ethanol50;fatty	liquid	consumption	hot	*coffee goblet*
PPButterContainer		container	PP	butter	fatty	semisolid	storage	chilled	*butter container*
PPCreamPot		container	PP	cream	fatty	semisolid	storage	chilled	*pot of cream*
PPDrinkStraw		straw	PP	yogurt	ethanol50	liquid	consumption	ambient	*straw*
PSYogurtPot		pot	PS	yogurt	ethanol50	semisolid	storage	chilled	*pot of yogurt*
PSDrinkGoblet		gobletPS	PS	hotdrink	ethanol50;fatty	liquid	consumption	hot	*coffee goblet*
PVCSauceLid		gasket	pPVC	sauce	fatty	liquid	process	sterilization	*cover gasket*
PVCSauceLid2	PVCSauceLid		pPVC	sauce	fatty	liquid	storage	ambient	

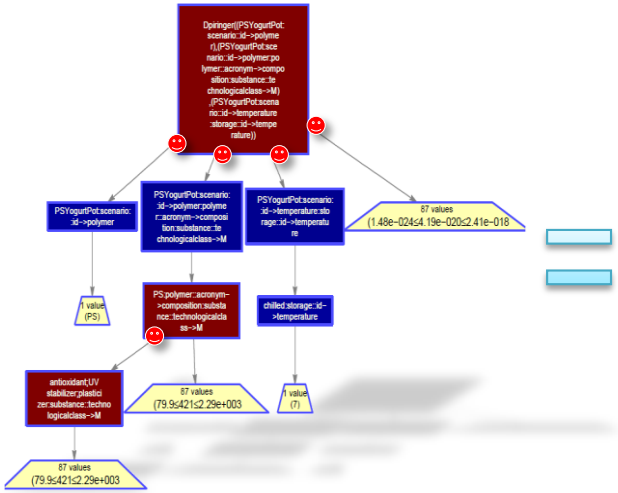
- 9 packaged food products purchased on the French market in 2011
- Geometry and materials were determined

id	parent	geometry	polymer	food	foodsimulant	foodtexture	step	temperature	comment
PSYogurtPot		pot	PS	yogurt	ethanol50	semisolid	storage	chilled	*pot of yogurt*

- Simulation scenarios were automatically generated via an expert system

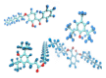


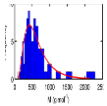
- Example of inference: distribution of *D* values



Pot PS

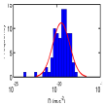
Substances::additives





Molecular Mass

Diffusion coefficient overestimated via the Piringer's Formula



3 scenarios based on 5th, 50th,95th percentiles

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Oct 2015

INRA SCIENCE & IMPACT

Ignorance

Miss-conception

- Education
- Training
- Research

_05

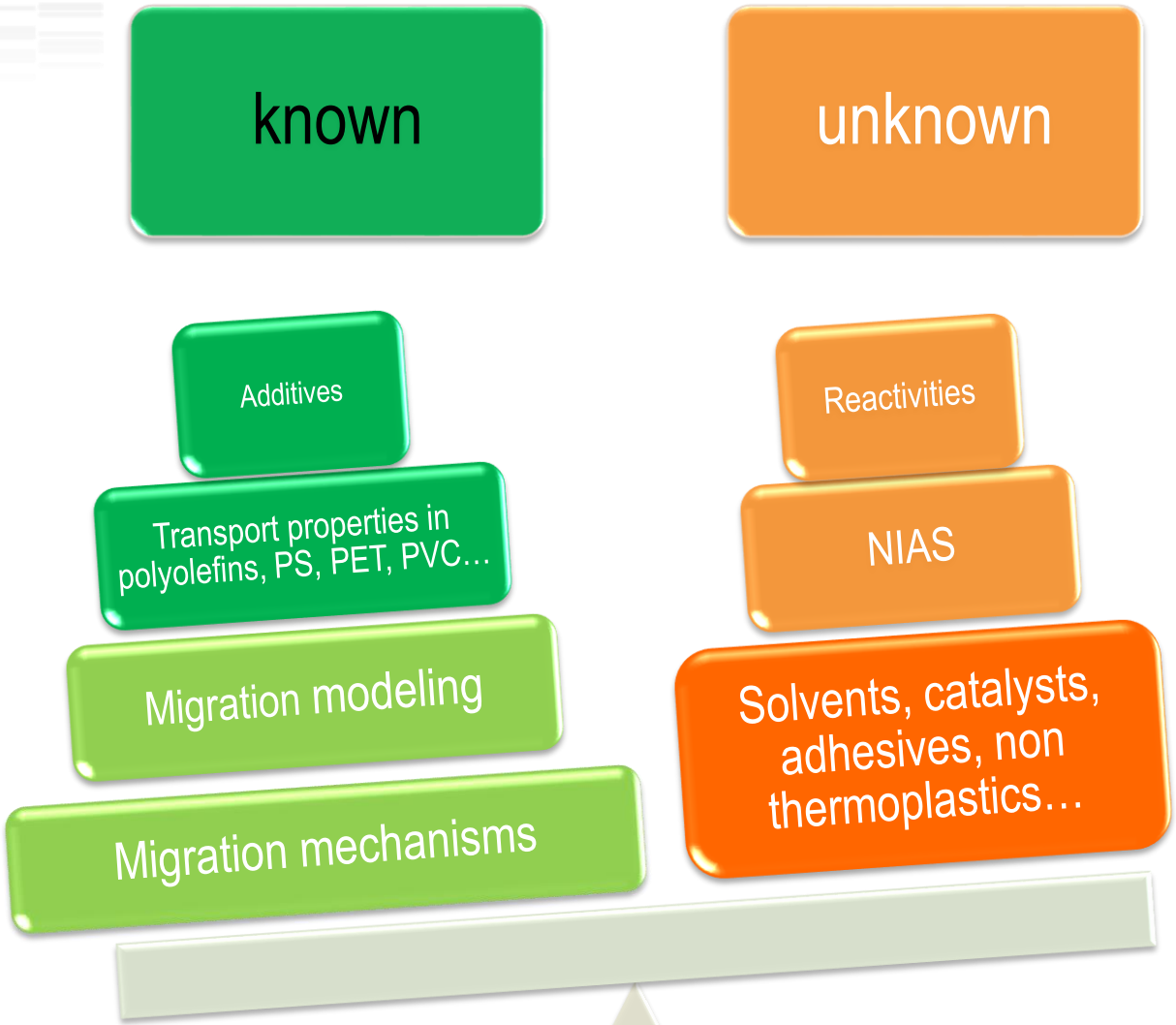
COMPLEMENTARY TOOLS AND PROSPECTS

overview

MIGRATION MODELING

STATE OF THE ART

RESEARCH EFFORT

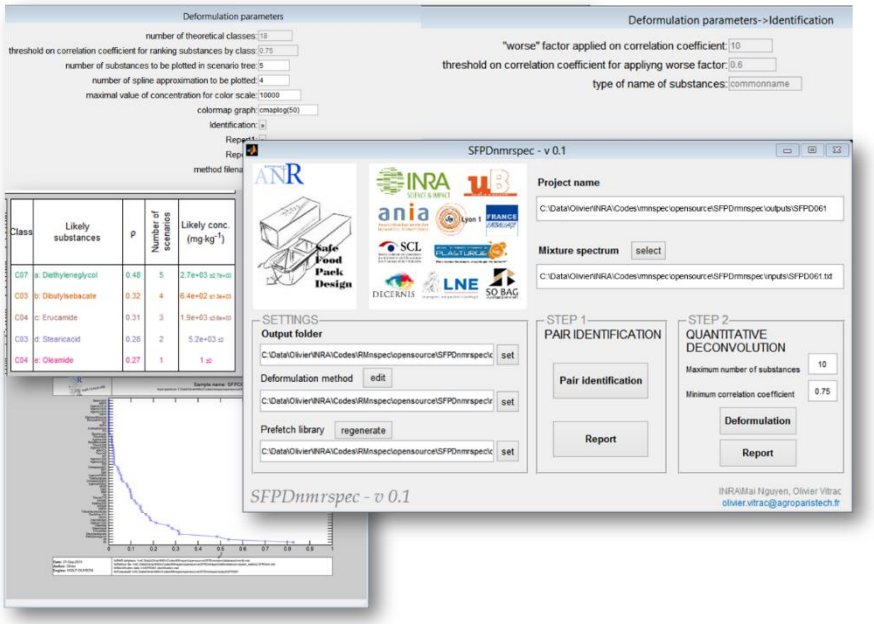


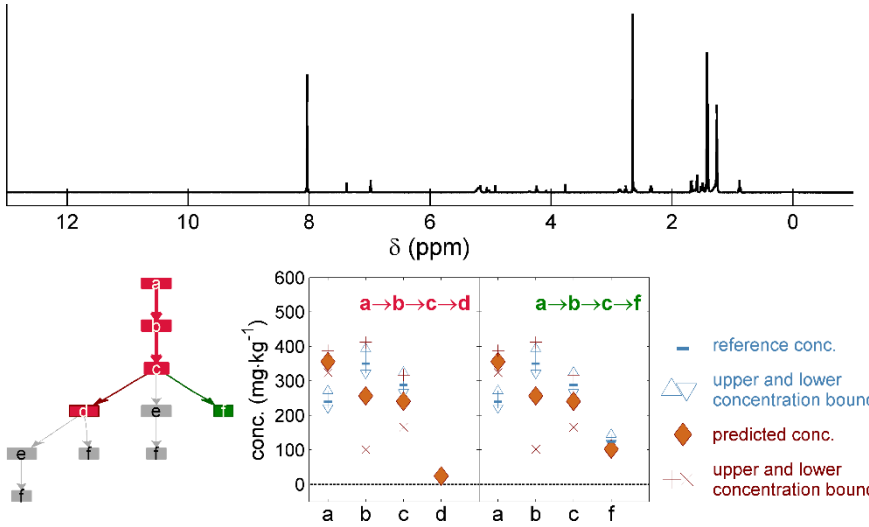
BLIND QUANTITATIVE DEFORULATION

https://github.com/ovitrac/SFPDnmrspec

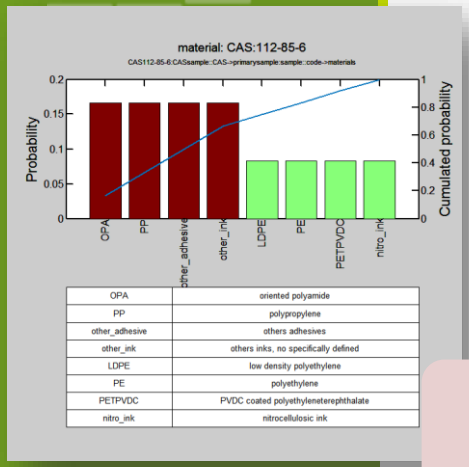
Example: real PP

Present	Class	Likely substances	ρ
x	C07	a: Irganox 3114	0.95
x	C11	b: Irganox 1035	0.83
x	C14	c: Stearic acid	0.82
	C12	d: Irganox PS802	0.76
	C12	e: Irganox PS800	0.74
x	C12	f: Irganox 1010	0.66

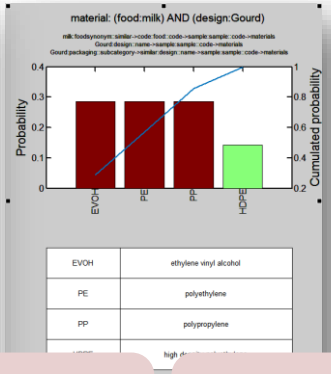




EXPERT SYSTEM



OPA	oriented polyamide
PP	polypropylene
other_adhesive	others adhesives
other_ink	others inks, no specifically defined
LDPE	low density polyethylene
PE	polyethylene
PETPVDC	PVDC coated polyethyleneterephthalate
nitro_ink	nitrocellulosic ink



EVOH	ethylene vinyl alcohol
PE	polyethylene
PP	polypropylene

substance: (substance:@volatiles)
AND (polymer:PS)
AND (storagebeforeuse:stack)

-1;CAS110-98-5;CAS10303-64-7;CAS111-41-1;CAS107-88-0;CAS111-87-5;CAS115-77-5;CAS120-47-8;CAS120-80-9;CAS122-95-2;CAS123-6
PS:polymer::code->primarylist
stack:storagebeforeuse::name->sample
SAMPLELIST:results::sample->primarylist

```
>> load_chemspider 112-8
CHEMSPIDER reuses cached data for '112-85-6' (date=21-sept

ans =

            CSID: 7923
           InChI: 'InChI=1S/C22H44O
21H2,1H3,(H,23,24)'
        InChIKey: 'UKMSUNONTOPOIO-U
          SMILES: 'CCCCCCCCCCCCCCCC
            Name: 'Docosanoic acid'
             CAS: {'112-85-6'   '165
        Synonyms: {1x68 cell}
       QuickMass: [1x1 struct]
  quickproperties: [1x1 struct]
      Properties: [1x1 struct]
  UserProperties: [8x1 struct]
             EPI: [1x1 struct]
       Thumbnail: 'C:\Data\Olivier\
       structure: 'C:\Data\Olivier\
             url: 'http://www.chems
   urlstructure: 'http://www.chems
           links: [1x1 struct]
```

FOOD	DESIGN	CATEGORY	POLYMER	SUBSTANCE	FOOD STORAGE
milk	bag with gusset	flexible	PS	Technolofical function	frozen
ham	compartiment alized tray	rigid	PA	chemical function	chilled
babyfood	doy pack	reheatable	PVDC	IUPAC	hot filled
Biscuit	Heatable pot	printed	acrylic adhesive	CAS	Microwave heating
mustard	Gourd	storage before use	aluminum	M range	Sterilized
	Etc.	Etc.	nitro ink	Etc.	

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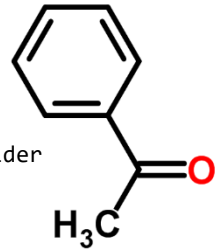
Oct 2015

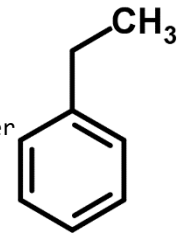
INRA SCIENCE & IMPACT

EXAMPLES OF GENERATION OF TRANSPORT PROPERTIES FOR VOLATILE CONTAMINANTS

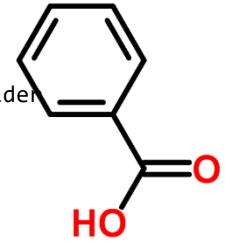
- **ROUGH ESTIMATES OF A AIR/POLYMER PARTITION COEFFICIENTS**




```
>> FMECAKairP acetophenone
LOAD_CHEMSPIDER          extraction of ChemSpiderID=7132 ('acetophenone') completed in 10.26 s
LOAD_CHEMISPIDER: updated cache
             7132.mat      21-sept.-2015 21:37:19      77.6 kBytes   C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'acetophenone' (date=21-sept.-2015 21:37:19)
ans =
   9.1995e-06
```




```
>> FMECAKairP ethylbenzene
LOAD_CHEMSPIDER          extraction of ChemSpiderID=7219 ('ethylbenzene') completed in 11.9 s
LOAD_CHEMISPIDER: updated cache
             7219.mat      21-sept.-2015 21:42:34      107.1 kBytes   C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'ethylbenzene' (date=21-sept.-2015 21:42:34)
ans =
   2.2485e-04
```




```
>> FMECAKairP 'benzoic acid'
LOAD_CHEMSPIDER          extraction of ChemSpiderID=238 ('benzoic acid') completed in 5.746 s
LOAD_CHEMISPIDER: updated cache
             238.mat       21-sept.-2015 21:45:01      41.2 kBytes   C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'benzoic acid' (date=21-sept.-2015 21:45:01)
ans =
   1.3674e-08
```

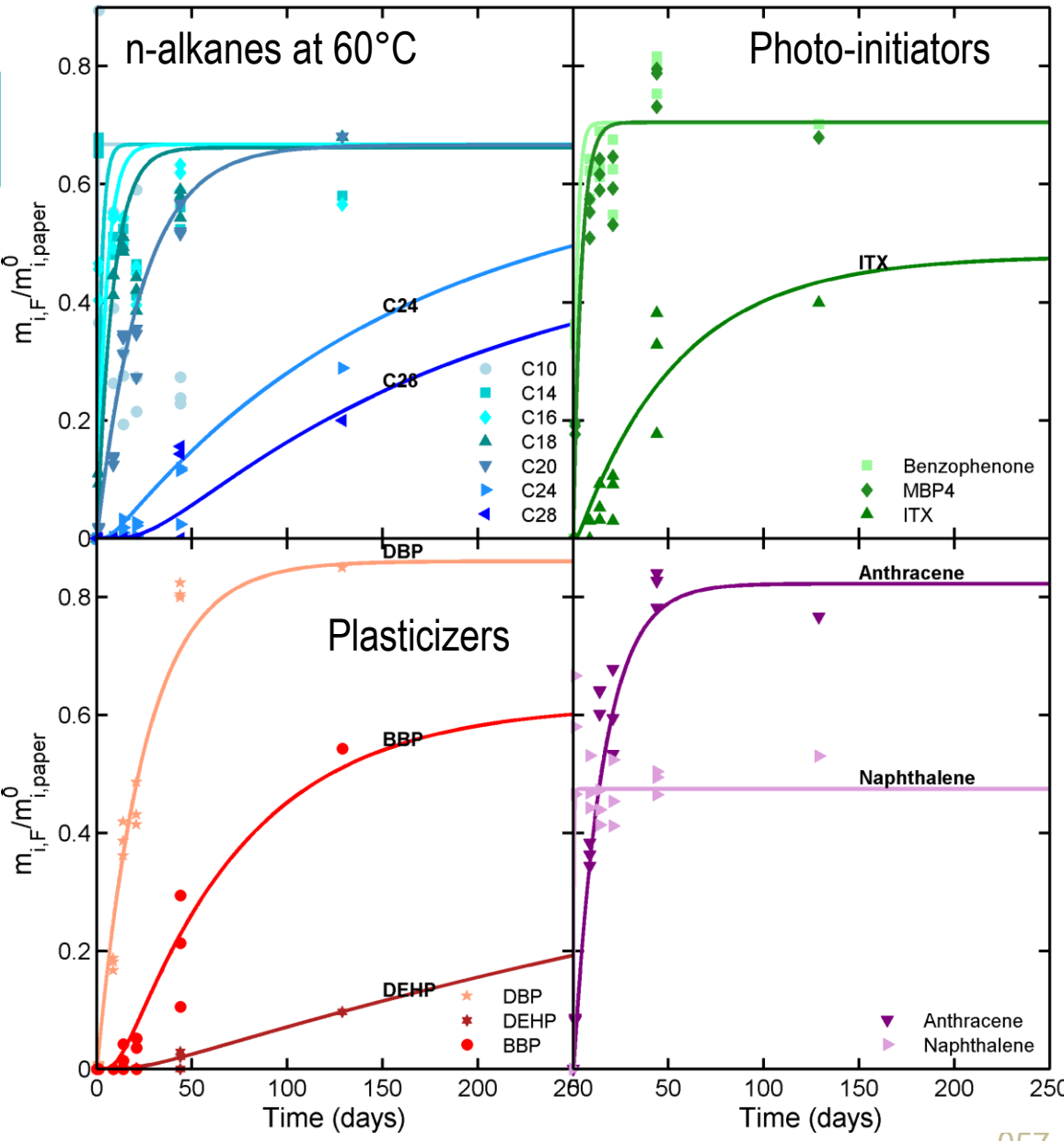
PREDICTIONS vs EXPERIMENTS

Nguyen *et al*. 2014, submitted to I&EC, FAC

Experimental results 15 solutes → **Detailed modeling** with FMECAengine

$$\frac{m_{i,F}^{(t)}}{m_{i,P}^{0}} = \frac{V_F}{m_{i,P}^{0}} \int_0^t C_{i,F}^{(t)}\, d\tau$$

0 to 120 days



https://github.com/ovitrac/FMECAengine

Thank you

Merci

Danke

Thank You

ขอบคุณค่ะ

Terima kasih

Dhanyavad

Kam sah hamnida

Xièxie

Gracias

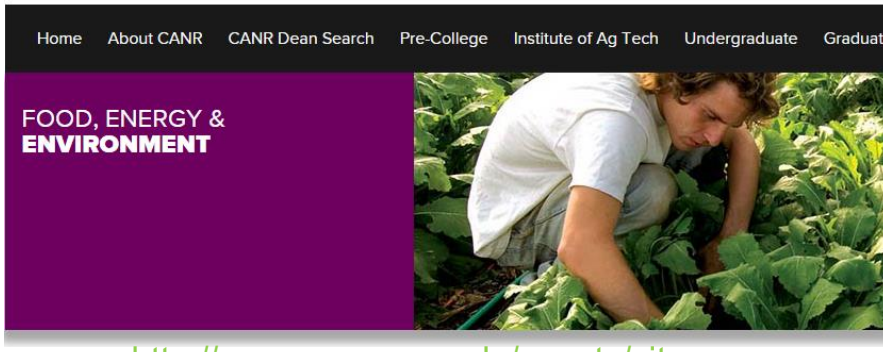
Vielen dank

ευχαριστώ

MICHIGAN STATE UNIVERSITY

COLLEGE OF
AGRICULTURE & NATURAL RESOURCES

Dr. Olivier Vitrac lectures and workshops



Date: July 1, 2015
Location: School of Packaging, MSU

LECTURES ABOUT

"PREDICTION OF MASS TRANSFER IN POLYMERS"

by OLIVIER VITRAC, Ph.D.

INRA, FRANCE

http://www.canr.msu.edu/events/vitrac
http://www.packaging.msu.edu/industry_testing_services/downloadable_presentations

When	Presentation	Where
29th June (Monday) *10:00am-11:00am*	**Diffusion coefficients of organic solutes in polymers: new perspectives of prediction**	*Conference Center, Room 100, School of Packaging*
30th June (Tuesday) 2:00pm-3:00pm	**An atomistic Flory-Huggins formulation for the tailored prediction of activity and partition coefficients**	*The Ternes Outreach Center, Room 120, School of Packaging* *Registration required*
1st July (Wednesday) 2:00pm-4:00pm	**Workshop: Prediction of the migration: beyond conventional estimates***	*The Ternes Outreach Center, Room 120, School of Packaging* *Registration required*