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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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[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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THERMODYNAMICS OF MIGRATION IN POLYMERS

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UMR 1145 Food Processing and Engineering

Group Interactions between Materials and Media in Contact

AgroParisTech, 91300 Massy, France

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

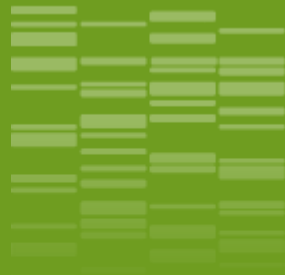




THERMODYNAMICS OF MIGRATION

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**



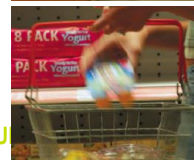
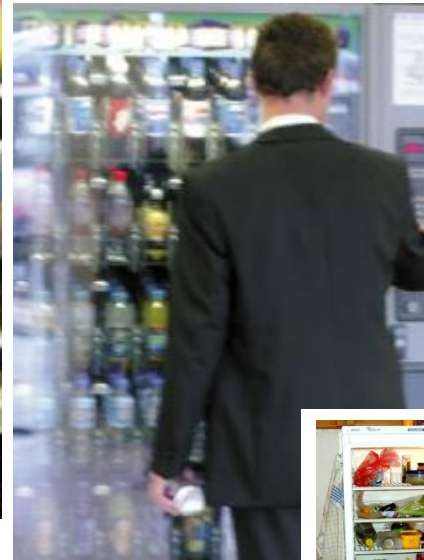
_01

WHAT IS MIGRATION?

DIFFUSION

SORPTION

COUPLED MASS TRANSFER



CONTROVERSY ON THE SAFETY OF PACKAGING MATERIALS

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



Environment:
How Dangerous
Is Plastic?

**Inside
Steve's
Pad**

How Jobs works *by Stephen Fry*
The tale of the tablet *by Lev Grossman*



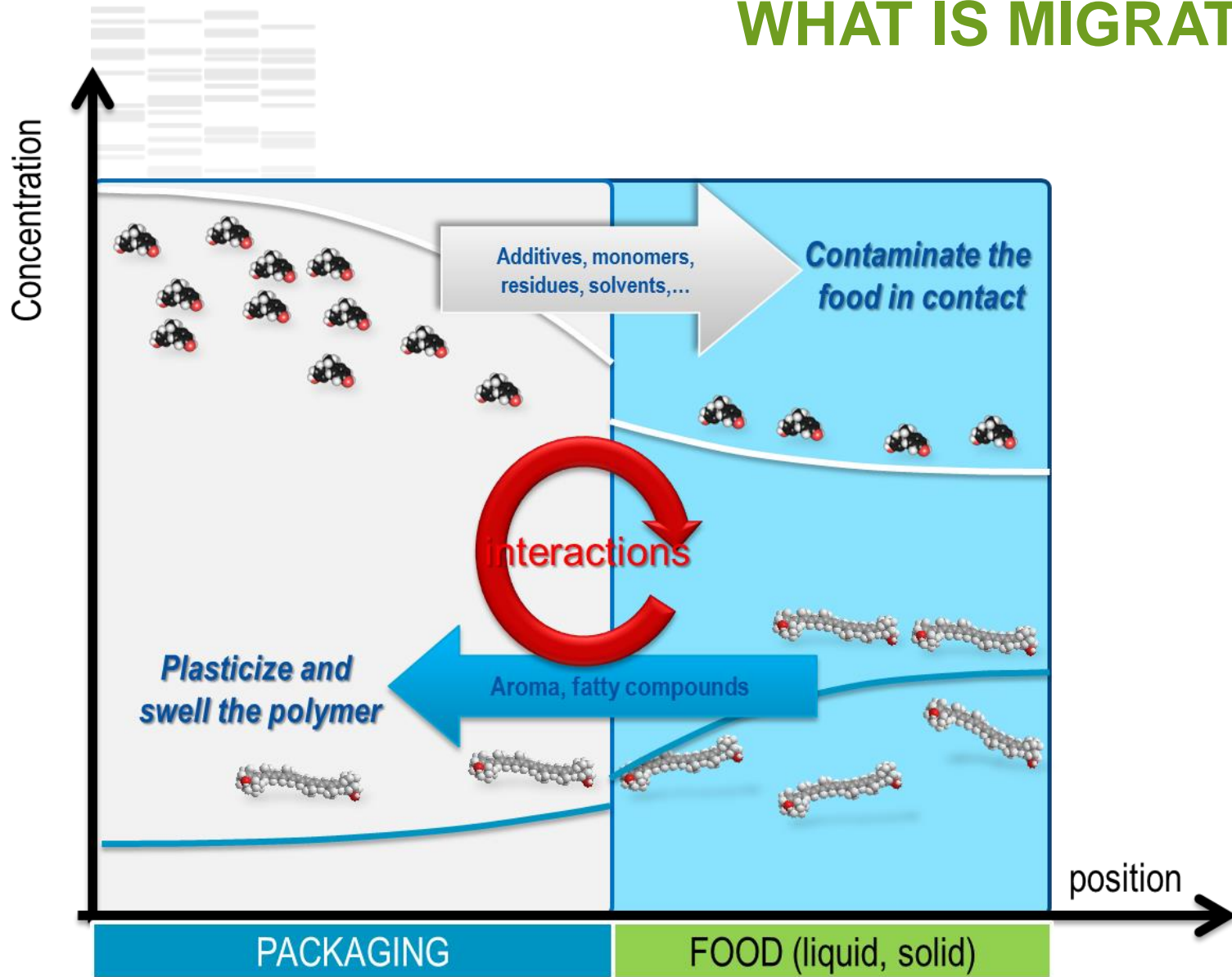
SPECIAL REPORT


The Perils Of Plastic

Chemicals in plastics and other products seem harmless, but mounting evidence links them to health problems—and Washington lacks the power to protect us

BY BRYAN WALSH

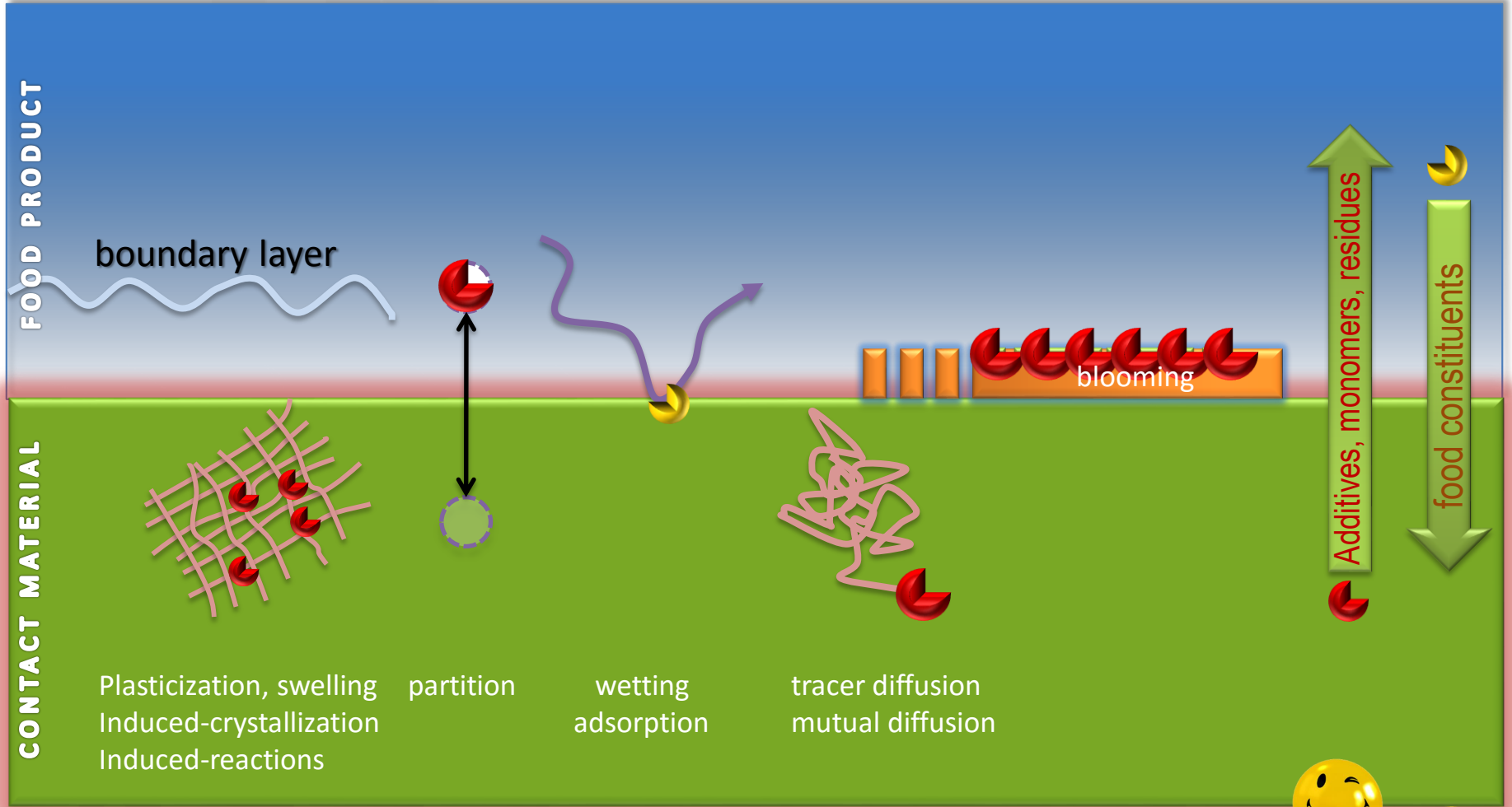
WHAT IS MIGRATION ?



 additive
 food constituent

MIGRATION ISSUES

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





MIGRATION MODELING

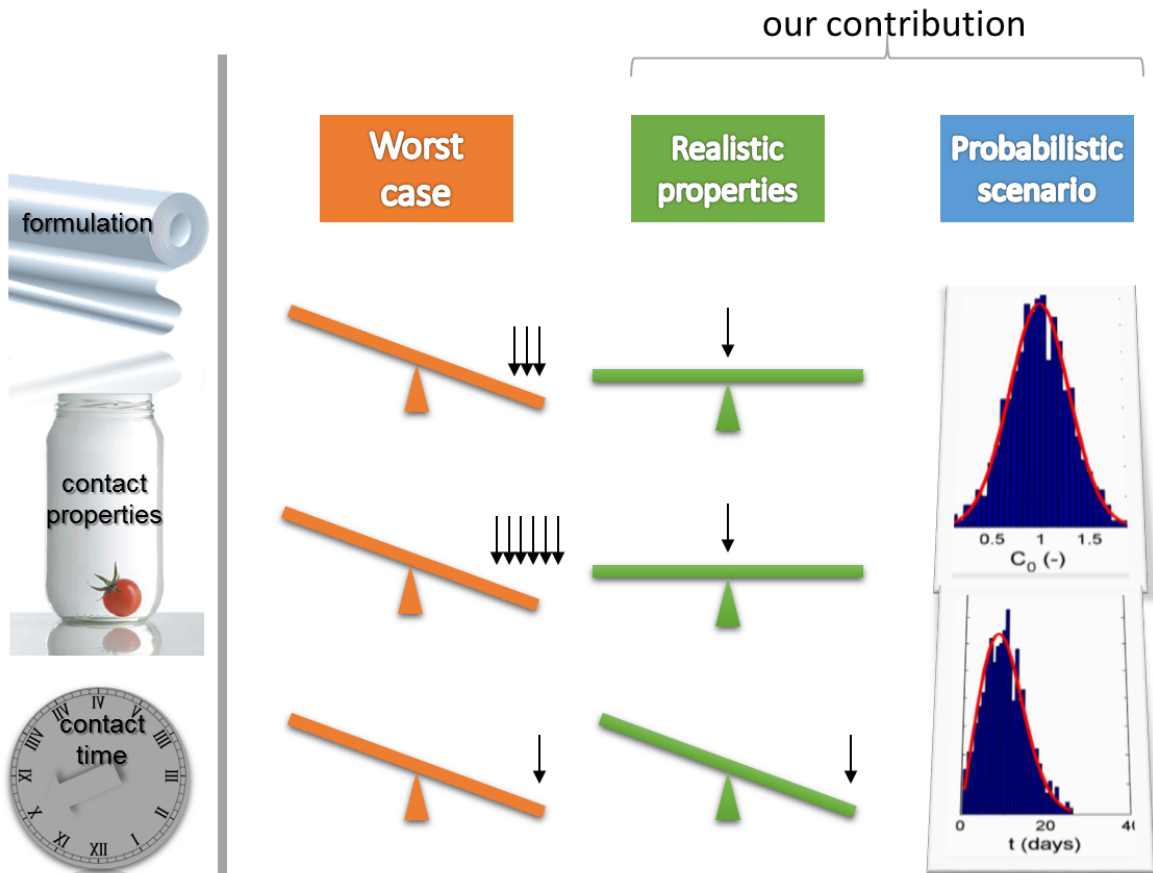
AUTHORIZED/RECOGNIZED IN EU, US, China

At each stage of manufacture, supporting documentation, substantiating the declaration of compliance, should be kept available for the enforcement authorities. Such demonstration of compliance may 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.

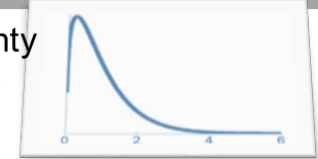
HOW TO OVERESTIMATE MIGRATION

use a tier approach



migration estimate

40 >> 2
 unknown safety margin uncertainty



olivier.vitrac@agroparistech.fr
 Oct 2015



ALL SOFTWARE ARE BUILT ON SIMILAR ASSUMPTIONS

http://modmol.agroparitech.fr/SFPP3/SFPP3_migratives/

SFPP3 client/server DIFFUSION_1DFV2n 🔍 ➔ 🔄

My Information

My user: **demouser** (change user)
My project: **common** (change project)
My database: **common2013a.sfpp3.database.xml**
My Application: **Diffusion_1DFV2n** (change application)

INRA\SFPP3 - 2013-04-18 22:03:53

Archived simulations or templates

acetaldehyde_PET3

Import properties from a previous result file in the current form

Import a concentration profile

Clear all properties in the current form

Search migrants/data: Migrants (M,SML...) Transport Properties

name/IUPAC

Layer selector

<< < > >> 1

Contact conditions

L_FP m³F·m⁻³P

V_F cm³

A_F cm²

rho_F kg·m⁻³ or g·cm⁻³

k_F

Bi

t months

Temperature :

Layer 1

Layer 1

L_P μm

rho_P kg·m⁻³ or g·cm⁻³

K_F/P T

D_P m²·s⁻¹ T

Conc. ppm

Help

Acetaldehyde

Name: Acetaldehyde (Acetic aldehyde; Ethanal; Ethyl aldehyde; CH₃CHO; Acetaldehyd; Aldehyde acetique; Aldeide acetica; NCI-C563...)

CAS: 75-07-0

REF: 10060

InChIKey: IKHGUXGNUITLKF-UHFFFAOYSA-N

Formula: C₂H₄O

M: 44.053 g/mol

SML: 6 ppm

EFSA: Group TDI = 0.1 mg/kg b.w. (calculated as acetaldehyde (including 10060 and 23920))
Toxicity profiles similar to methaldehyde. A 2-year oral rat study and a 3-generation oral rat study including teratogenicity with methamethaldehyde. The reports on nasal carcinogenicity after inhalation were considered without relevance for effects from oral intake of smaller doses, (adopted at 113rd SCF meeting)(17-18 September 1998)
http://europa.eu.int/comm/food/fs/sc/scf/out16_en.html

EU Regulation: +Positive List

Save result as:

Acceptable threshold or specific migration limit ppm

Free

New trends: OPEN-SOURCE codes

<https://github.com/ovitrac/FMECAEngine>



GitHub This repository Search Explore Features Enterprise Blog

ovitrac / FMECAEngine Watch

FMECA software developed in the framework of the project SafeFoodPack Design
<http://modmol.agroparsnfr.fr/SFFPD/>

61 commits 1 branch 0 releases 1 contributor

branch: master FMECAEngine / +

fix for lead_champidre when it used without any existing cache latest commit: e335f6c611

- ovitrac authored 4 days ago
- examples monolayer example update 4 years ago
- production production examples, please change paths to match yours 4 years ago
- Dfluer m Major Update - 10/05/2014 11 months ago
- Dhaleroth m Major Update - 10/05/2014 11 months ago
- Dlrem m Major Update - 10/05/2014 11 months ago
- Dplinger m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECADfluer m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECADplinger m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECAKaliP m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECAEngine_backup_WSLP... FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECAgopolymer m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECAair m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECApdensity m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECAurel m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- FMECAvp m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- MatchingClasngSymbol.m release v0.45 4 years ago
- ModifiedGrainMethod.m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- README first commit 4 years ago
- addax m additional functions to improve/simplify plots 3 years ago
- addzplotub m additional functions to improve/simplify plots 3 years ago
- argcheck m publishing update 3 years ago
- argadm m minor revisions and additions 11 months ago
- arrows m Major Update - 10/05/2014 11 months ago
- autopatch.m Major Update - 10/05/2014 11 months ago
- autopatchname.m Major Update - 10/05/2014 11 months ago
- borderdef.m Major Update - 10/05/2014 11 months ago
- boundedline.m Major Update - 10/05/2014 11 months ago
- buildmarkov m release v0.45 4 years ago
- bykeywords m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- catstruct m release v0.45 4 years ago
- cbraver m minor revisions and additions 11 months ago
- cellcomp m release v0.45 4 years ago
- checkCAS m release v0.45 4 years ago
- checktoolsinstall.m FMECAEngine 0.51 (major update) - though not fully tested 5 days ago
- chemispdir_setup.m release v0.45 4 years ago

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ovitrac / FMECAEngine Watch 1 Star 1 Fork 2

branch: master FMECAEngine / senspatankarC.m

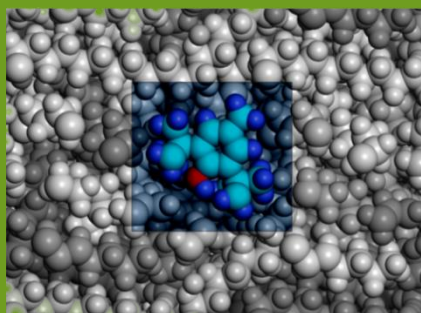
ovitrac on 10 May 2014 Major Update - 10/05/2014
1 contributor

Executable File | 275 lines (252 sloc) | 10.03 kb Raw Blame History

```
1 function res = senspatankarC(F,ploton,dispon)
2 %SENSPATANKAR simulates transfer and reactions through n layers using a modified Patankar Method (see p 45)
3 % the dimensionless formulation is similar to SENSN
4 % all data are normalized according the reference layer or equivalently according to the layer with the lowest D/a value
5 % IT IS THE RESPONSABILITY OF THE USER TO PROVIDE THE APPROPRIATE DIMENSIONLESS NUMBERS
6 % a wrapper used for the online version is available in ../www/home/diffusion_IDFVn.m
7
8 % MS-MATLAB-WEB 1.0 - 25/09/09 - Olivier Vitrac - rev. 05/05/14
9
10 % Revision history
11 % 01/10/07 improve speed
12 % 16/03/09 add restart
13 % 29/04/11 add F.restart.CF
14 % 26/10/11 replace xmesh/xmesh(end) xmesh/F.Irefrc(end) in the interpolation (thanks to Nicolas)
15 % 08/05/14 method = 'pchip' for compatibility with Matlab 2014
16
17 % definitions
18 global timeout
19 timeout = 800; % s
20 % options = odeset('RelTol',1e-4,'AbsTol',1e-4,'Stats','yes','Initialstep',1e-5,'Maxstep',.05,'Maxorder',5);
21 options = odeset('RelTol',1e-4,'AbsTol',1e-4,'Initialstep',1e-8,'Maxstep',.01,'Maxorder',2);
22 Fdefault = struct(...
23     'Bi'           , 1e3,... Biot [hm.LI/D]
24     'k'           , [1 1 1],...[0.5 3 2],... ki, i=1 (layer in contact with the
25     'D'           , [1e-16 1e-14 1e-14 1e-14],... diffusion coefficient
26     'k0'          , 1,... 0 = liquid
27     'l'           , [50 20 10 120]*1e-6,...[50 20 10 120]*1e-6,... m
28     'L'           , 200/1800,... dilution factor (respectively to Iref)
29     'C0'          , [0 500 500 0],... initial concentration in each layer
30     'options'     , options...
31 );
32 %lines to be deleted (0V: 09/04/11, incomplete pieces of code)
33 % 'KR'           , [1 .1 .1 .1],...
```



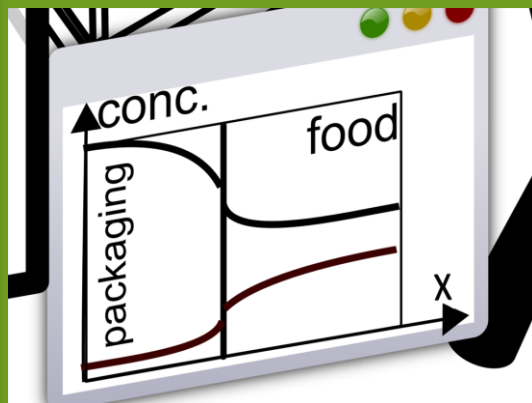
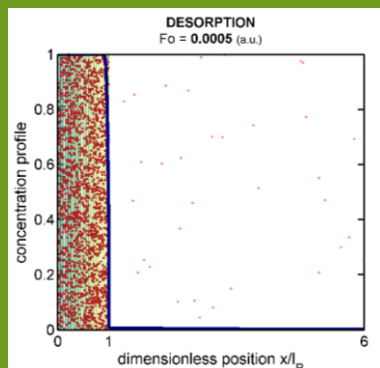
Probabilistic (equilibrium)



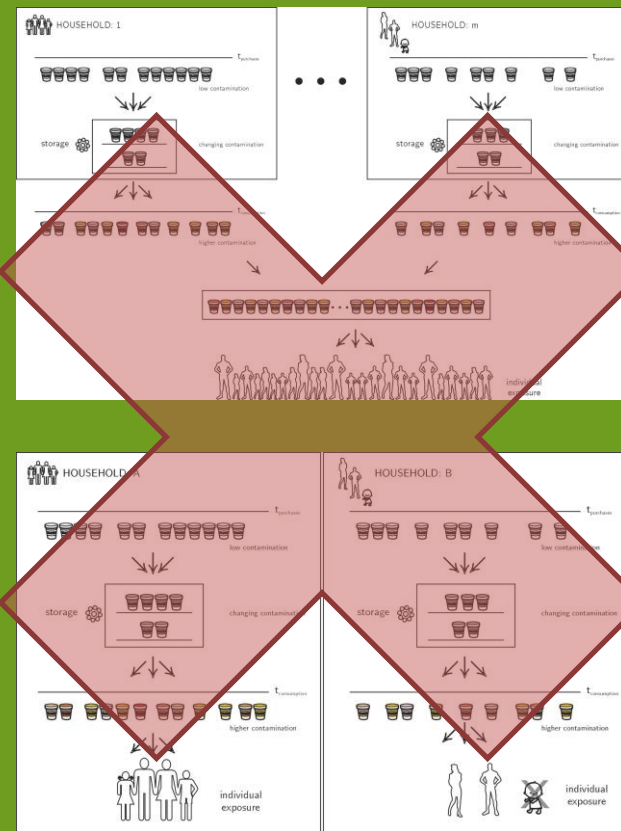
Free energy perturbation

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

Probabilistic/deterministic



Probabilistic (out of equilibrium)



SCALE



_02

DIFFUSION IN POLYMERS

PREDICTING DIFFUSION COEFFICIENTS

Fang X, Vitrac O. *Crit. Rev. Food Sci. Nutr.* (2014). DOI 10.1080/10408398.2013.849654

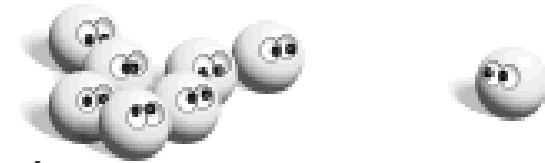
Fang X, et al.. *Macromolecules* (2013) **46** 874-888

Durand M et al. *J. Chem. Phys.* (2010) **132** (19), 194902

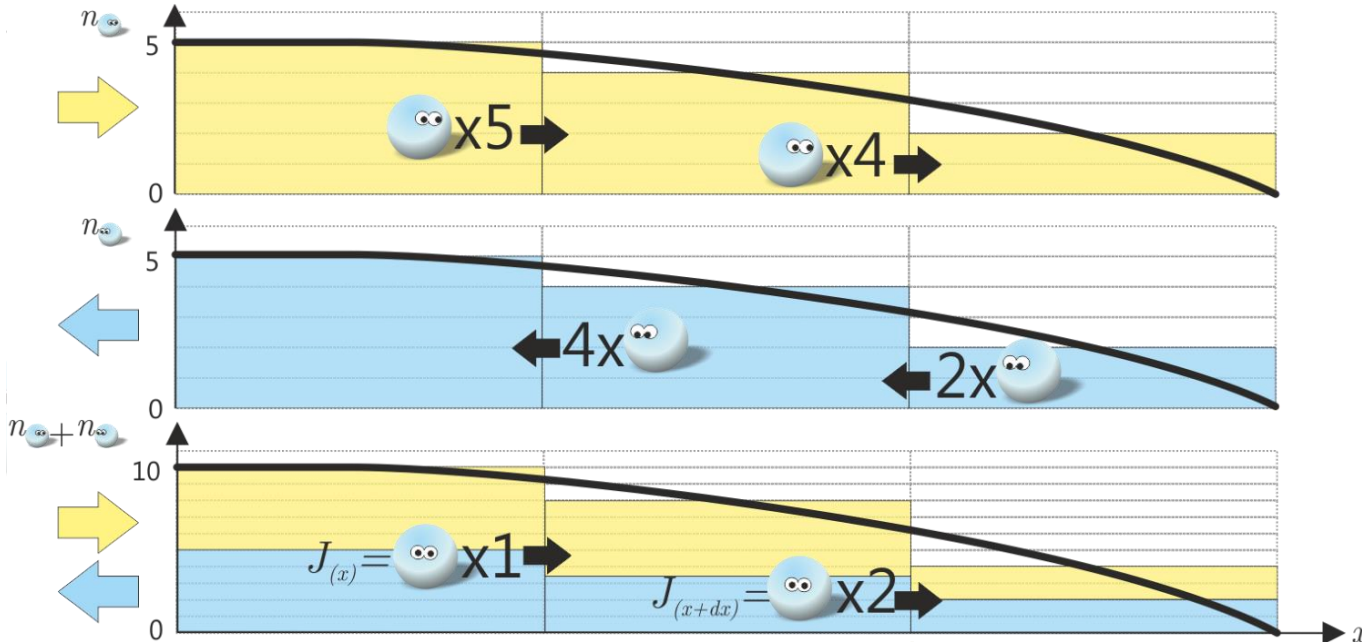
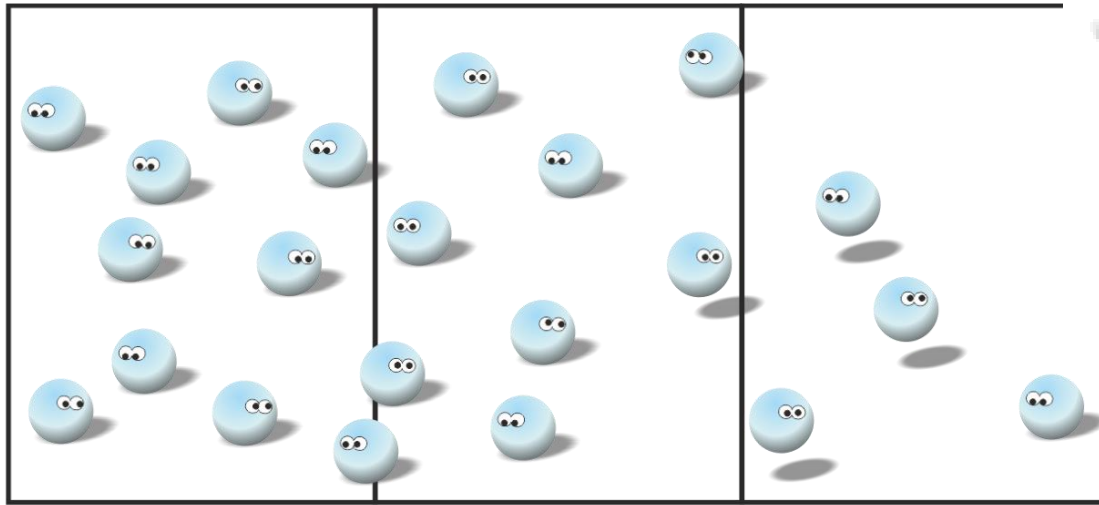
Vitrac O., Hayert M., *Chem. Eng. Sci.* (2007) **62** (9), 2503–2521

Vitrac et al. *J. Appl. Polym Sci.* (2006), **101** 2167-2186

MOLECULAR DIFFUSION



a)

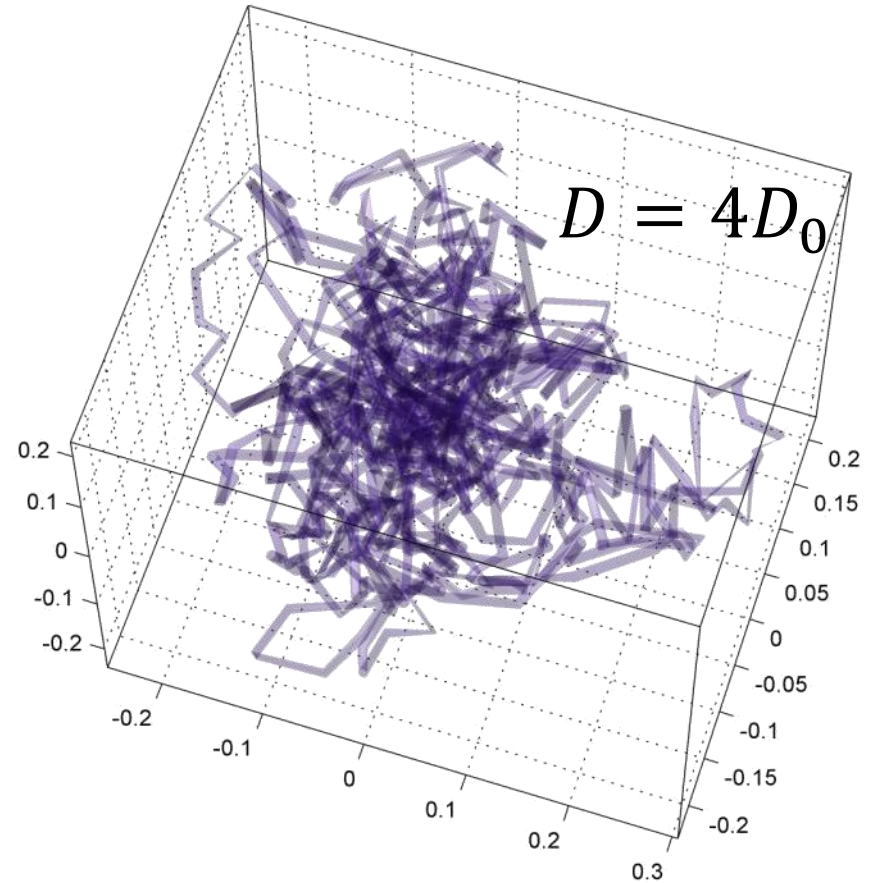
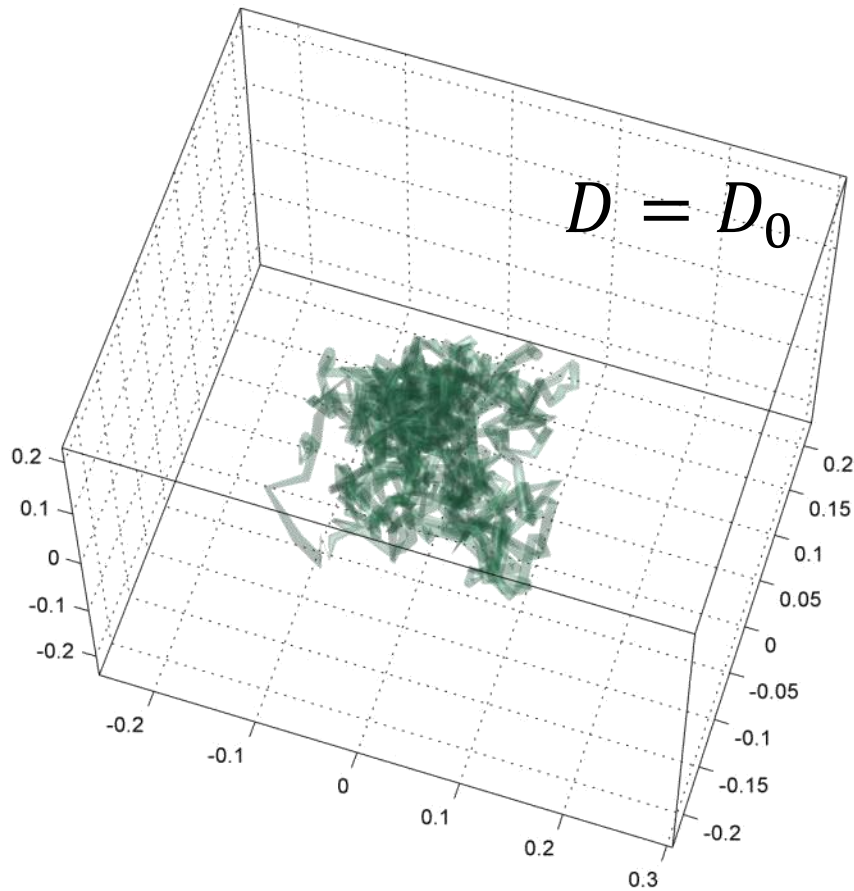


$$\frac{d}{dt} \left(\frac{n_{\text{molecule}}}{V} \right) = \frac{J_{(x)} - J_{(x+dx)}}{dx}$$

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.

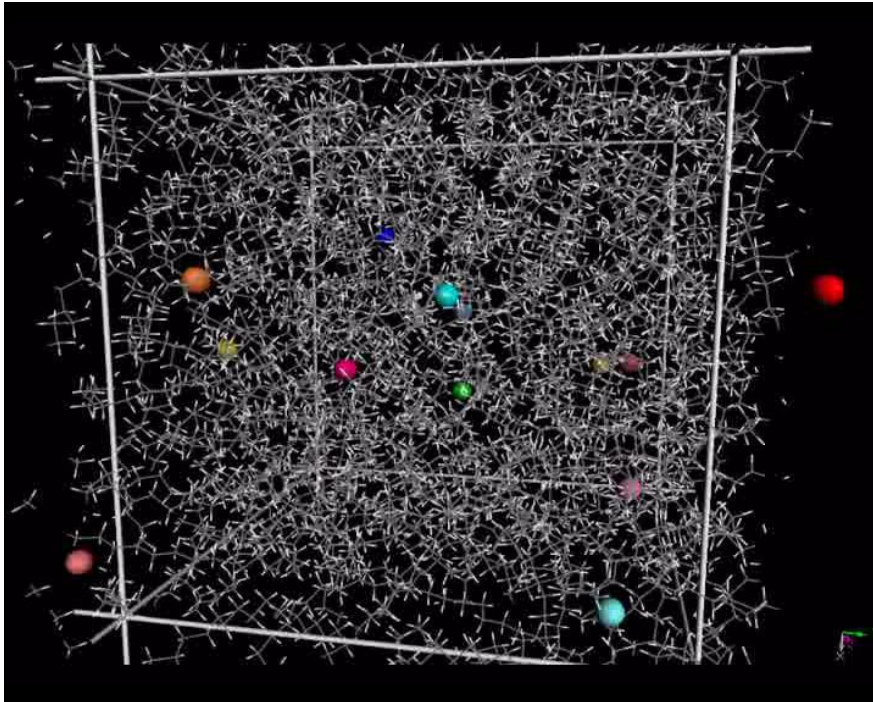
SMALL vs LARGE DIFFUSION COEFFICIENTS (D)



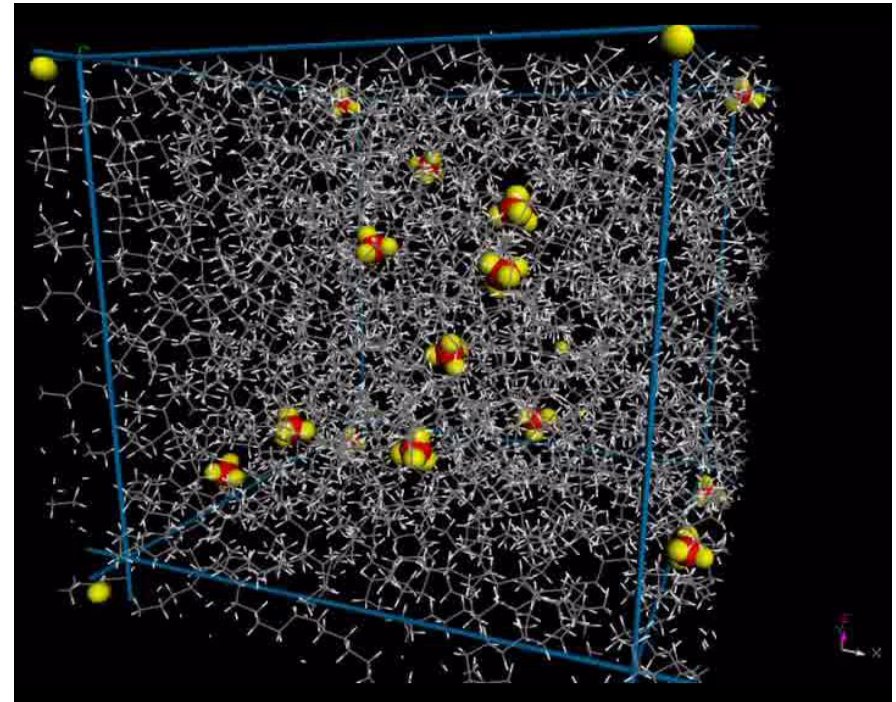
$$D \approx \frac{1}{6} \frac{\partial}{\partial t} \langle (x_{CM}(t) - x_{CM}(0))^2 \rangle$$

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

10 molecules of helium



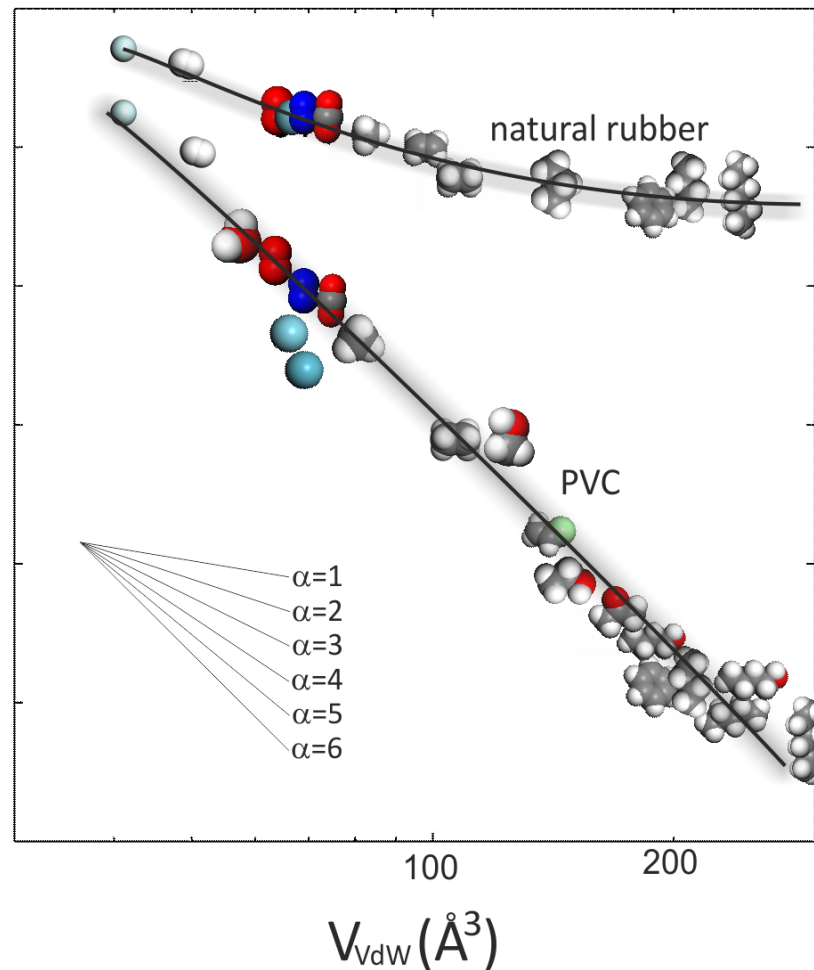
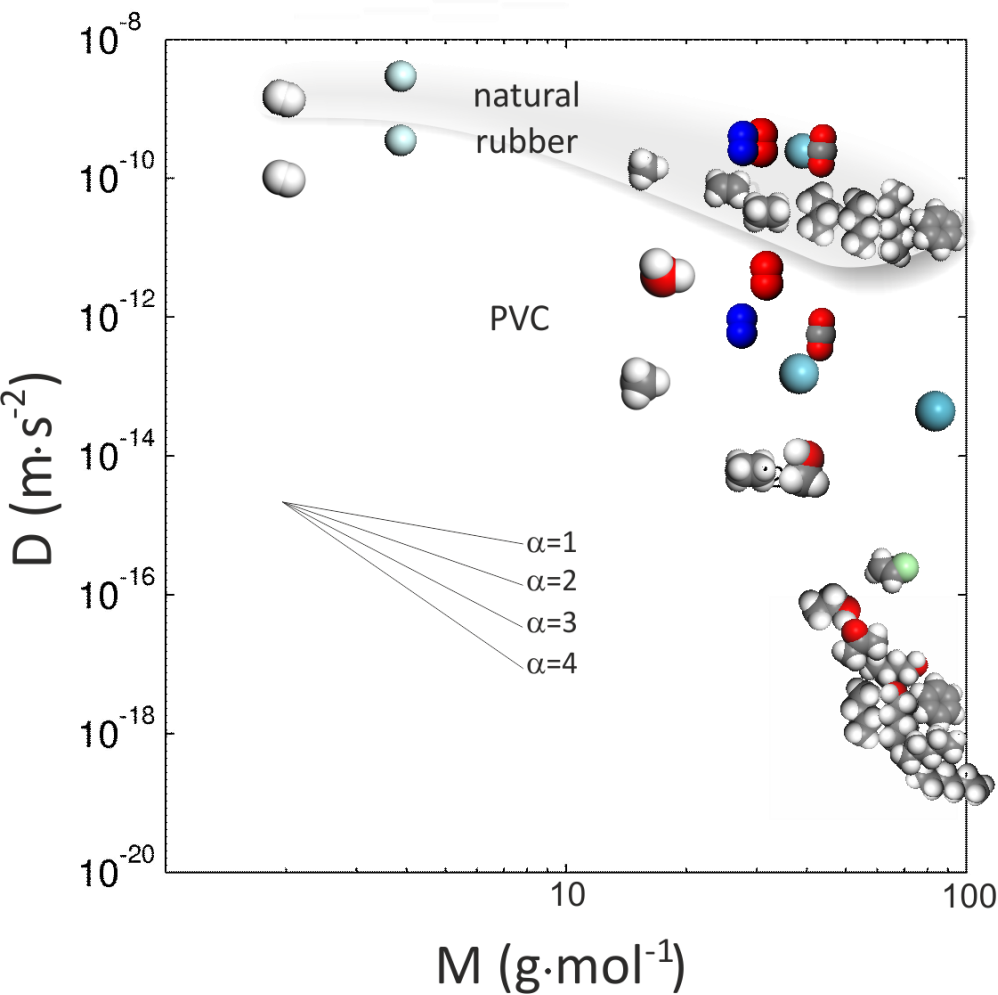
10 molecules of methane



$$D \approx \frac{1}{6} \frac{\partial}{\partial t} \langle (\mathbf{x}_{CM}(t) - \mathbf{x}_{CM}(0))^2 \rangle$$

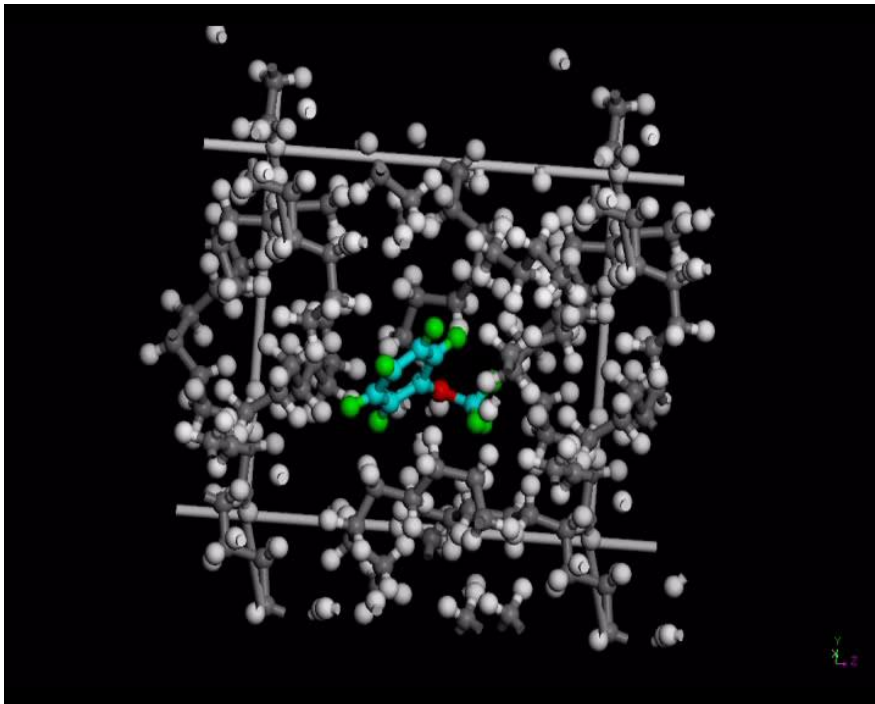
SCALING D WITH SOLUTE SIZE

STIFF DIFFUSANTS



DIFFUSION OF ANISOLE IN POLYETHYLENE (T=298 K)

0.5 ns at 298 K (details)



20 ns full trajectory



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)

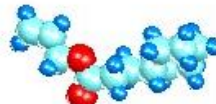
P122



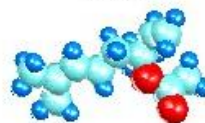
P131



P135



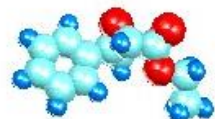
P138



P145



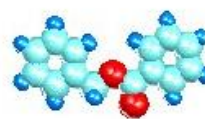
P147



P150



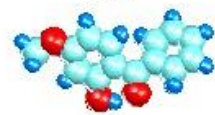
P152



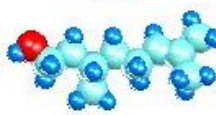
P159



P161



P96



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	Amylcinnamaldehyde 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-amylsalicylate
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	<i>n</i> 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

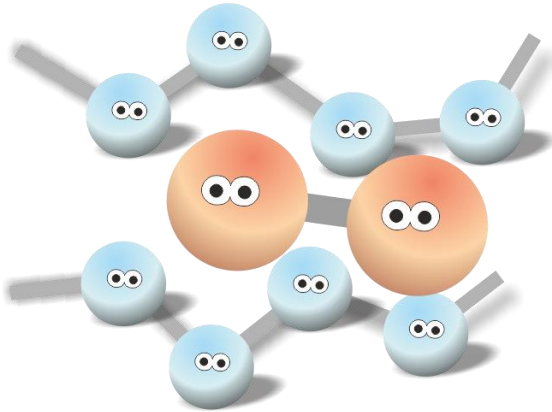
Drobust m2.s-1	stand. dev. m2.s-1	<i>n</i> class size	Dmin m2.s-1	Dmed m2.s-1	Dmax m2.s-1
2.24e-013	1.54e-013	12	1.2e-013	2.3e-013	7e-013

FLEXIBLE DIFFUSANTS

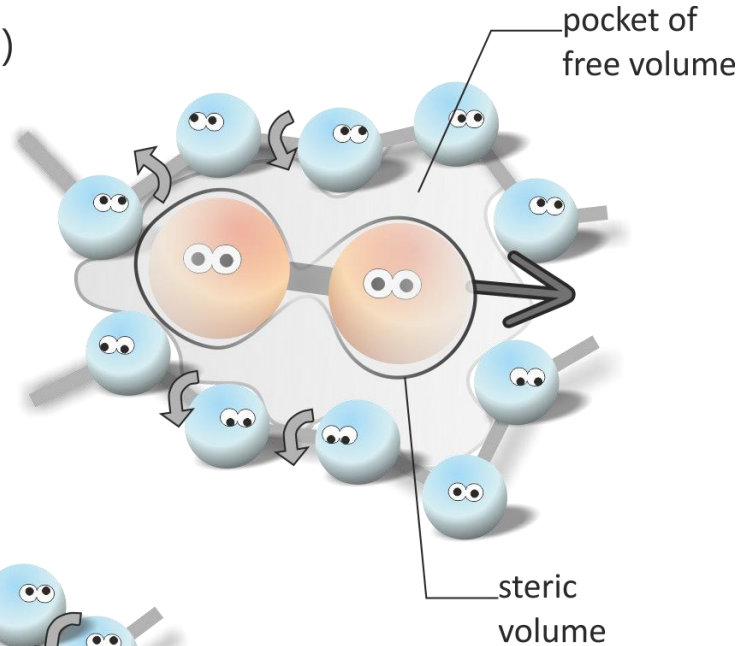
Local and temporary trapping of additive between polymer segments

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

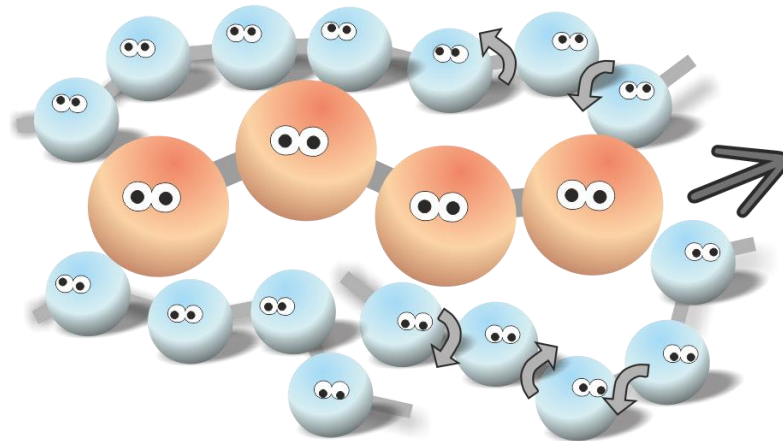
a)



b)



c)

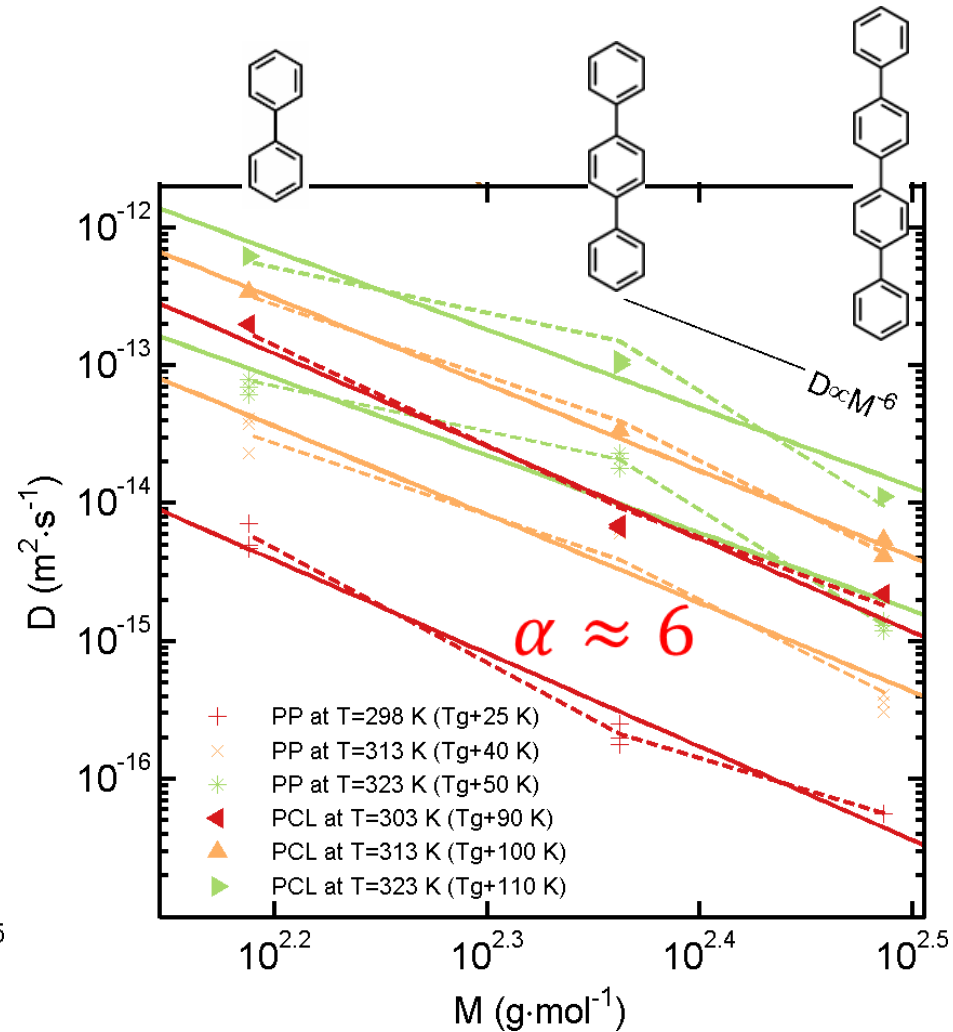
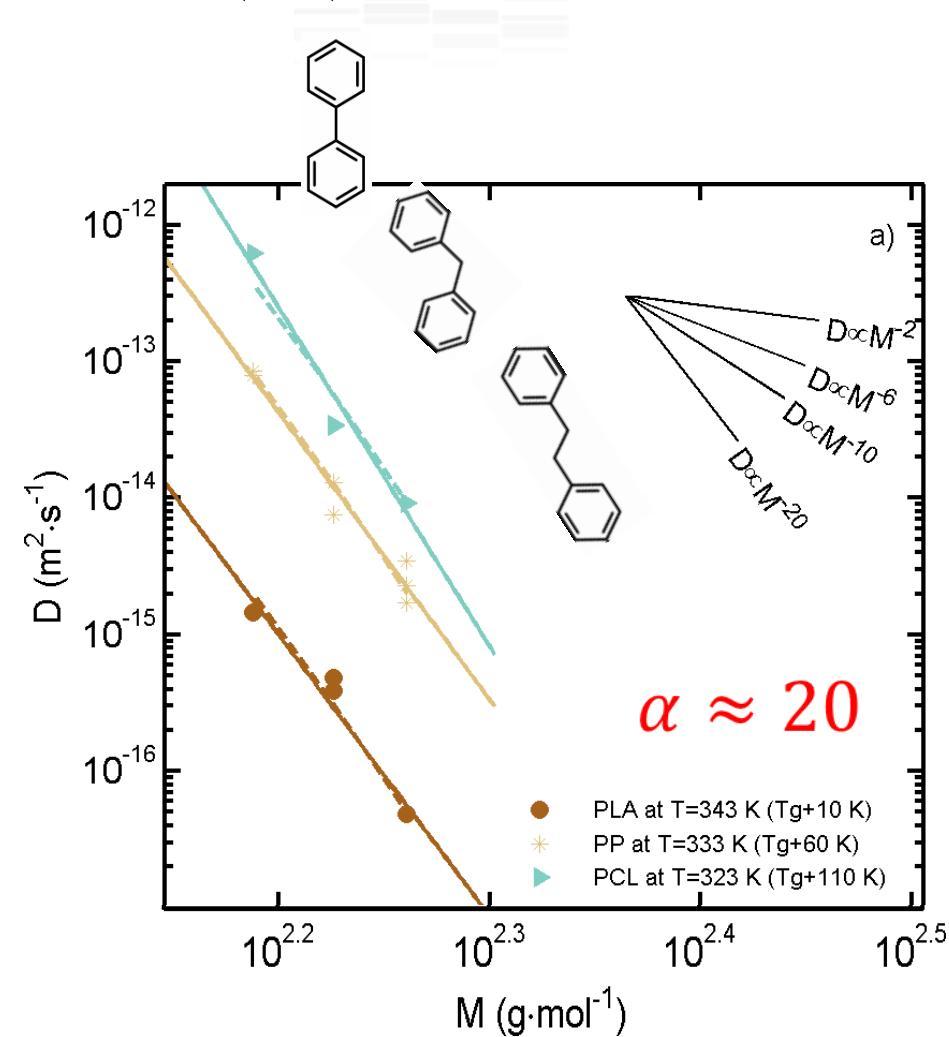


The relative free volume required for the translation of large additives is smaller as displacements of atoms/patterns are more likely not to be correlated together.

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

SCALING EXPONENTS

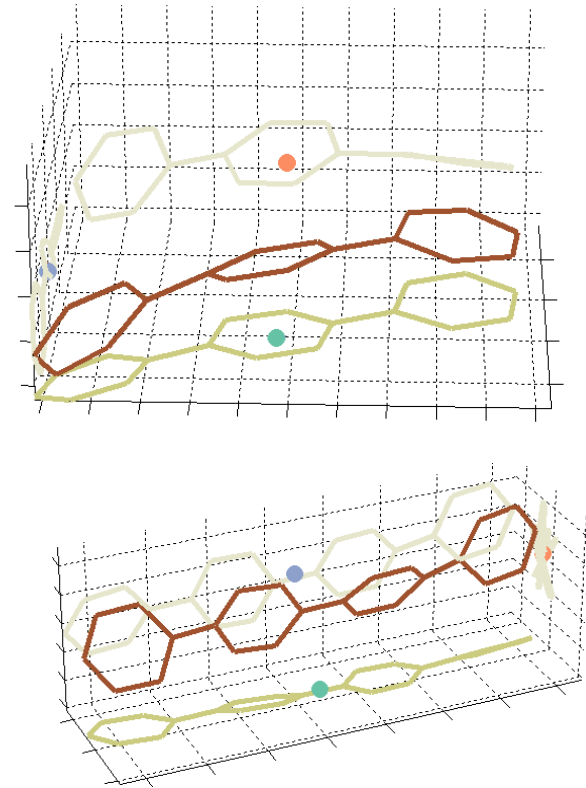
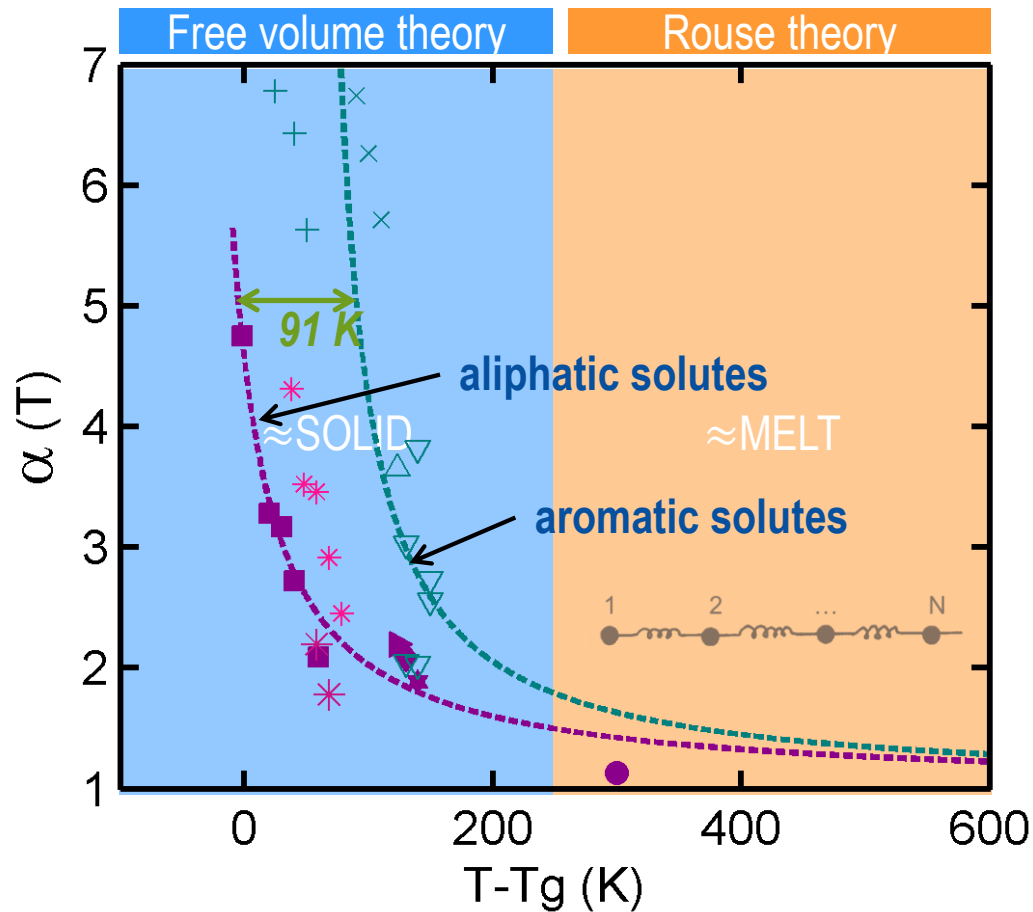
FOR HOMOLEGOUS SERIES OF SUBSTANCES



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

SCALING EXPONENTS

FOR HOMOLEGOUS SERIES OF SUBSTANCES



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

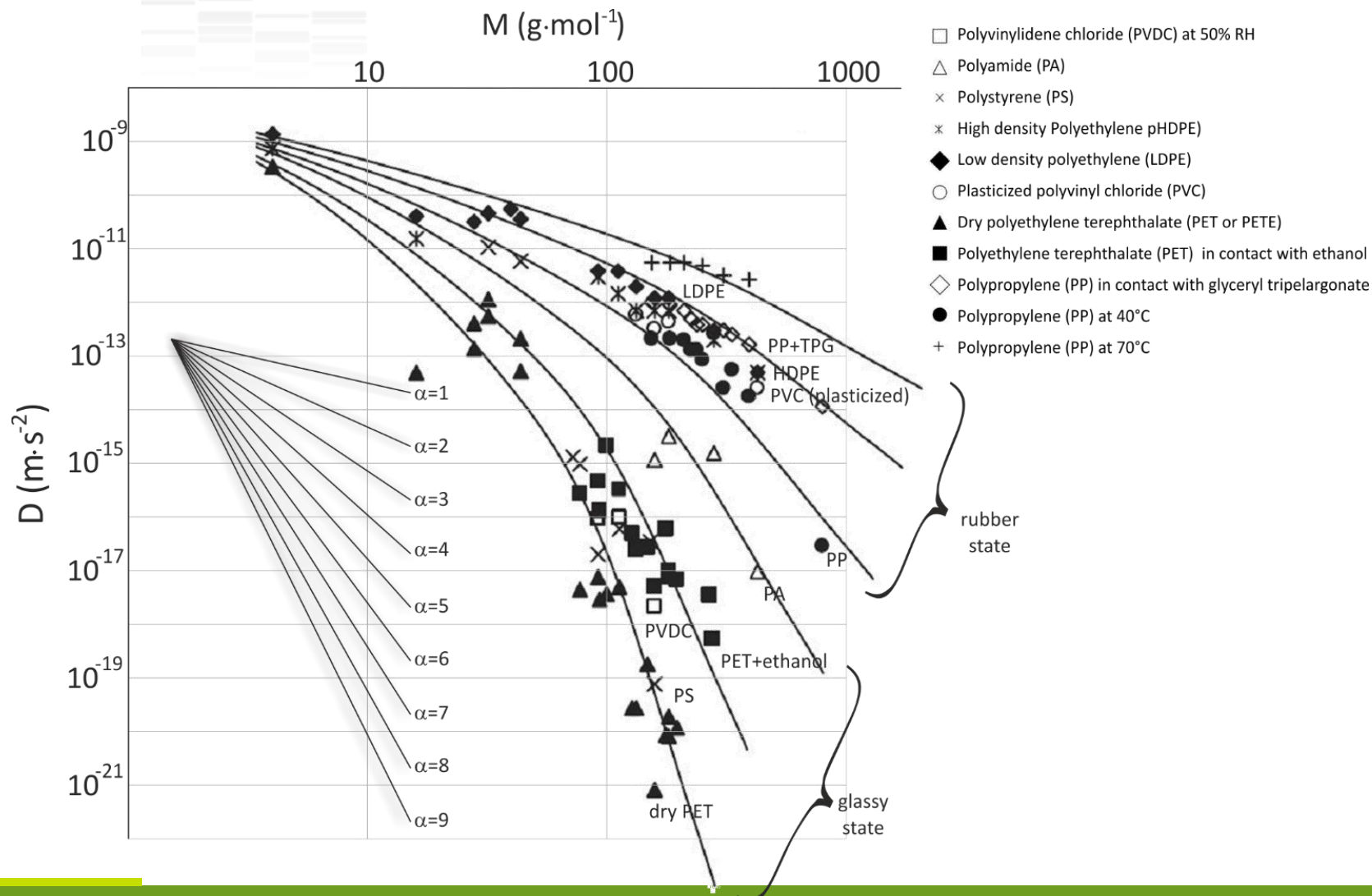
Blob
Shape/size

Formal equivalences between FVT and scaling laws

Rubber polymers: $T > T_g$

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

SCALING EXPONENTS FOR VARIOUS POLYMERS

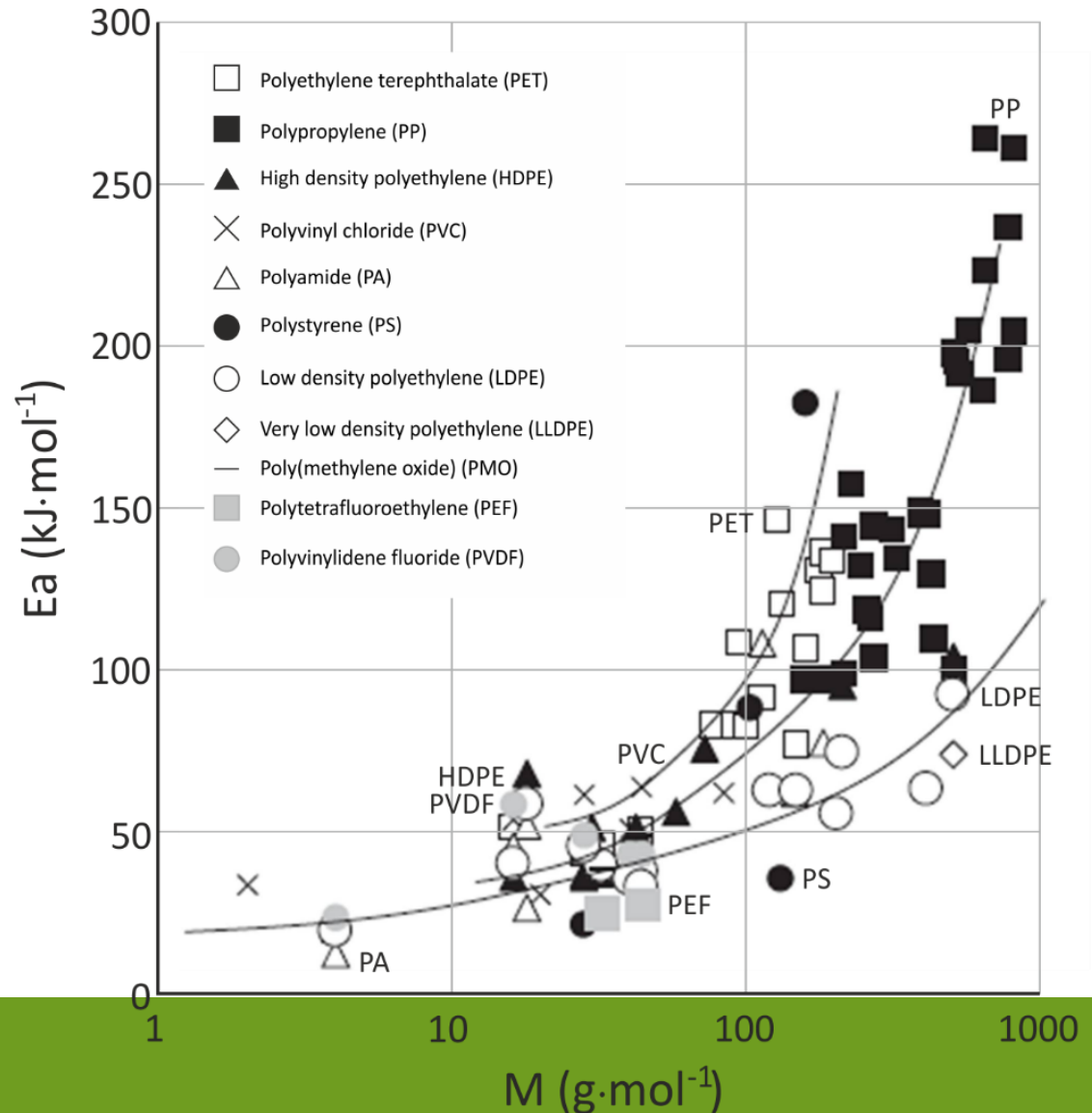


ACTIVATION ENERGY

VARIOUS DIFFUSANTS IN VARIOUS POLYMERS

$$E_a(M) \approx E_a(M_0) + \ln(M/M_0)$$

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.**

EFFECT OF PARTITION COEFFICIENT ON MIGRATION

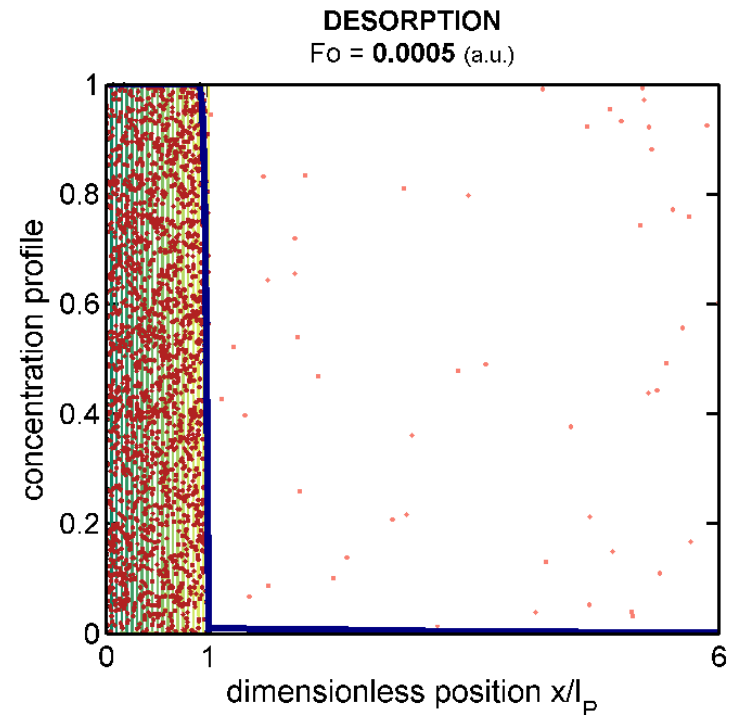
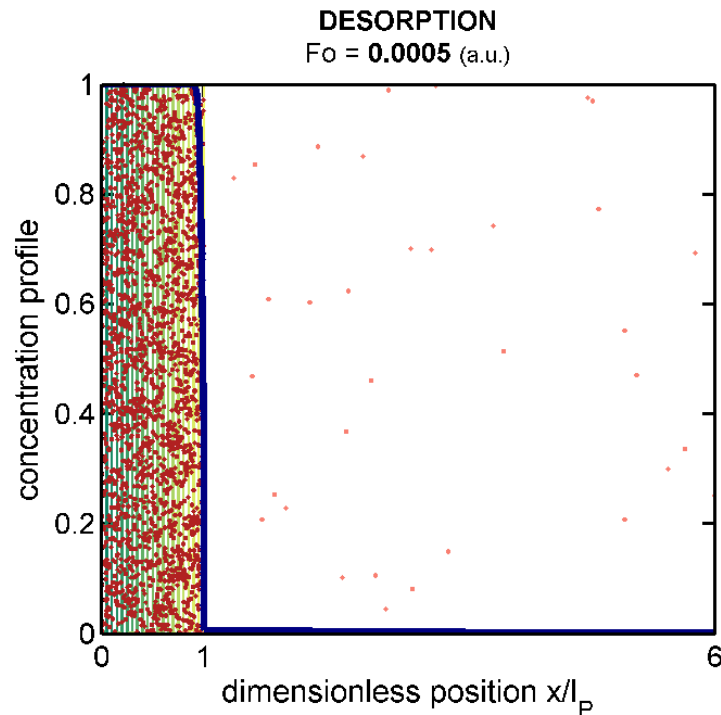
50 times for chemical affinity for P

50 times for chemical affinity for F

$K_{i,F/P} =$

1/50

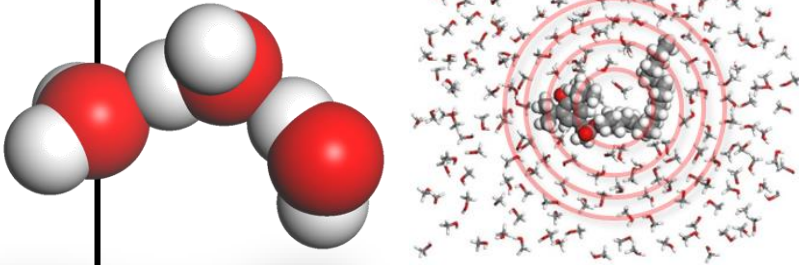
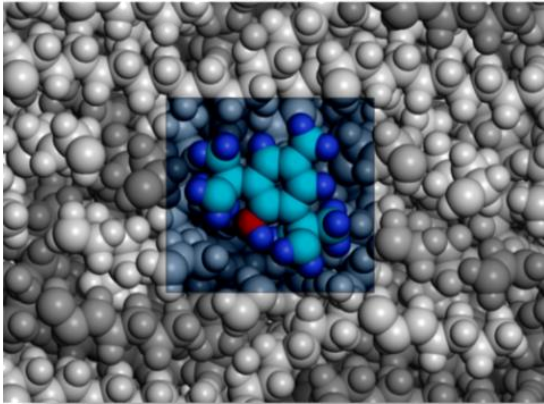
50



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

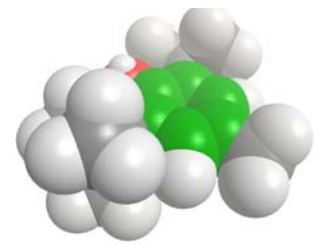
amorphous

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 <u>entangled chains</u> Representation of <u>polymer chains without entanglement</u>

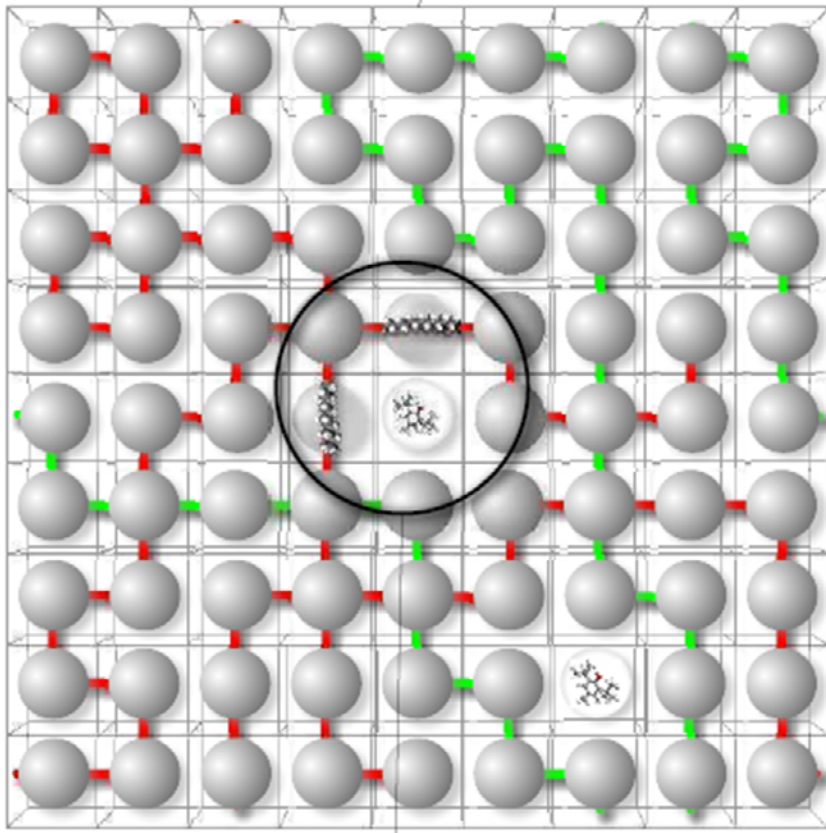


OFF-LATTICE FLORY-HUGGINS FORMULATION OF EXCESS CHEMICAL POTENTIALS IN BINARY BLEND-VOID SYSTEMS



Chemical potential (definition of J. Williard Gibbs)

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



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

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

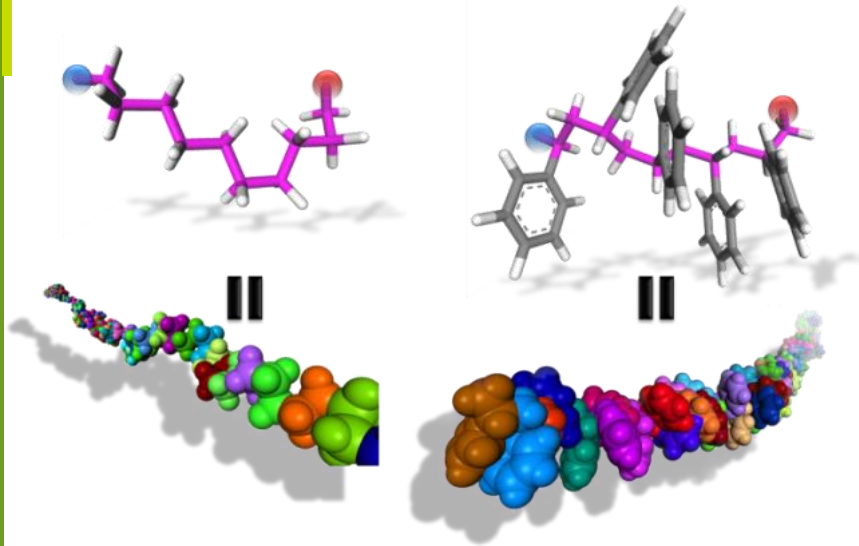
$$\left(1 - \frac{1}{r_k} \right) \cdot \phi_k + \chi_{i,k} \cdot \phi_k^2 \approx \left(1 - \frac{1}{r_k} \right) + \chi_{i,k}$$

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

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

$k = P, F$

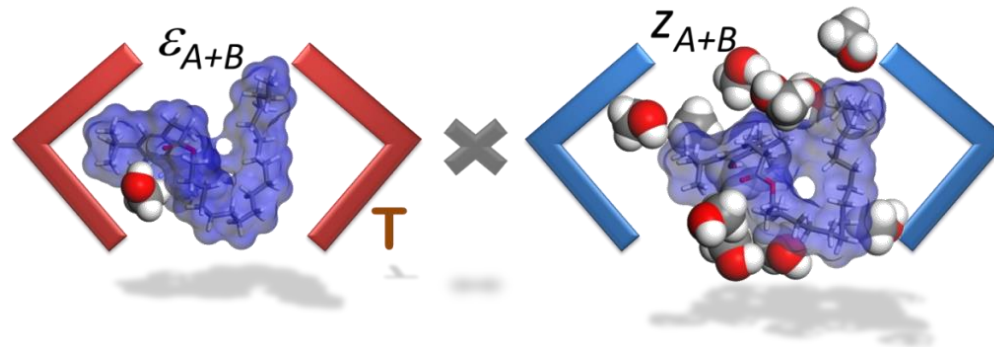
FLORY HUGGINS APPROXIMATION AT ATOMISTIC SCALE



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



$$\langle h_{A+B} \rangle_T = \langle \epsilon_{A+B} z_{A+B} \rangle_T \approx \langle \epsilon_{A+B} \rangle_T \langle z_{A+B} \rangle$$

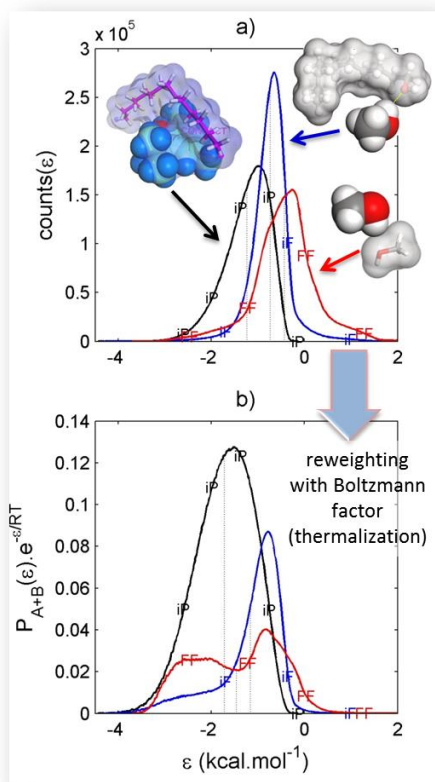
Bawendi et al., *J. Chem Phys.* 1986; 1987; 1988

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

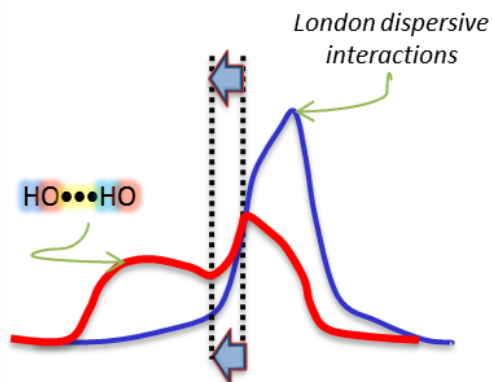
olivier.vitrac@agroparistech.fr
Oct 2015

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

$$\chi_{i,P}^{(n_{i,P}^{\min})} = \frac{\langle h_{i+P}^{n_{i,P}^{\min}} \rangle_T + \langle h_{P+i}^{n_{i,P}^{\min}} \rangle_T - \langle h_{P+P}^{n_{i,P}^{\min}} \rangle_T - \langle h_{i+i} \rangle_T}{2RT}$$

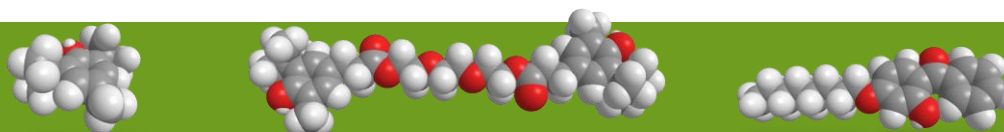
$$n_{i,P}^{\min} = \operatorname{argmin}_{n_P} \left(\chi_{i,P}^{(n_P)} \right)$$

$$\langle h_{j+k} \rangle_T = \langle \varepsilon_{j+k} \rangle_T \langle z_{j+k} \rangle + \beta_{jk}$$

In liquids (denoted F or L)

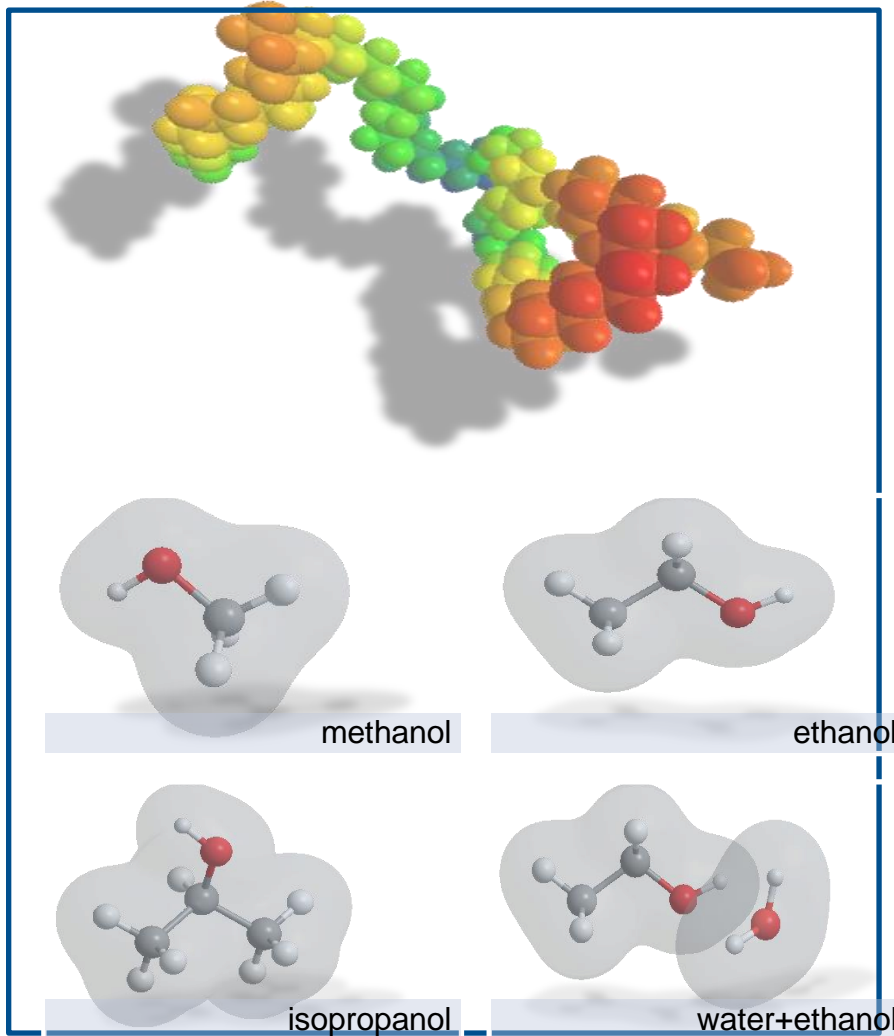
$$\chi_{i,F} = \frac{\langle h_{i+F} \rangle_T + \langle h_{F+i} \rangle_T - \langle h_{F+F} \rangle_T - \langle h_{i+i} \rangle_T}{2RT}$$

$$\text{For water: } \langle h_{F+F} \rangle_T = 4 \langle \varepsilon_{A+B} \rangle_T \langle z_{A+B} \rangle$$



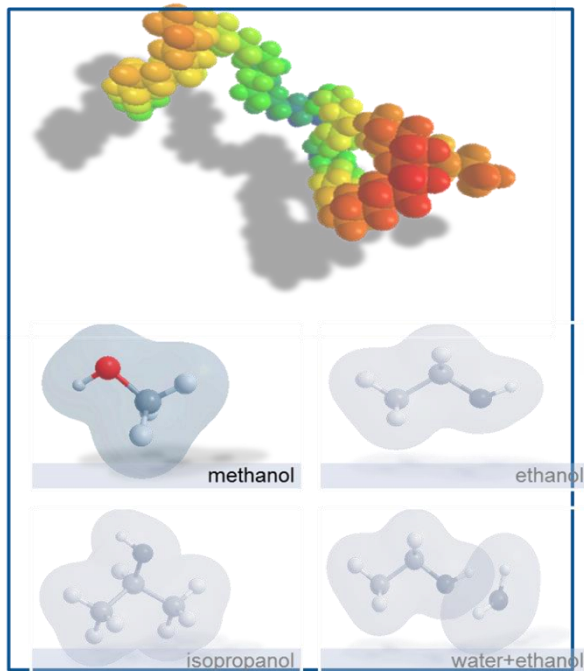
FIRST COMPARISONS BETWEEN DIRECT CALCULATIONS AND EXPERIMENTS (no fit) – 45 SOLUTES

Polyethylene in contact with

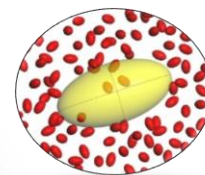
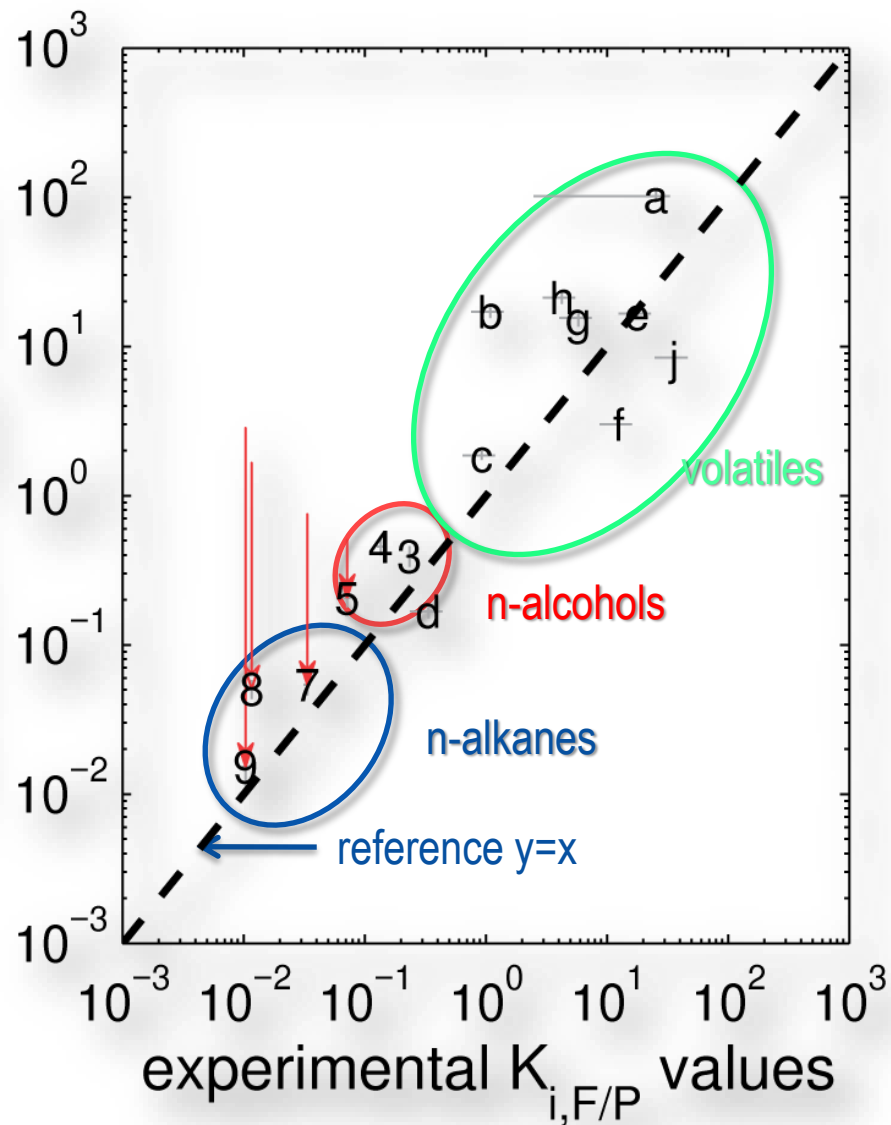


Alkanes	Alcohols	Volatiles	Plastics additives
decane	decanol	camphor	BHT
undecane	undecanol	diphenyl oxide	chimassorb 81
dodecane	dodecanol	diphenylmethane	Erucamide
tridecane	tridecanol	d-limonene	Irganox 1076
tetradecane	tetradecanol	dl-menthol	Irganox 1035
pentadecane	pentadecanol	eugenol	Irganox 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-POLYETHYLENE PARTITIONING

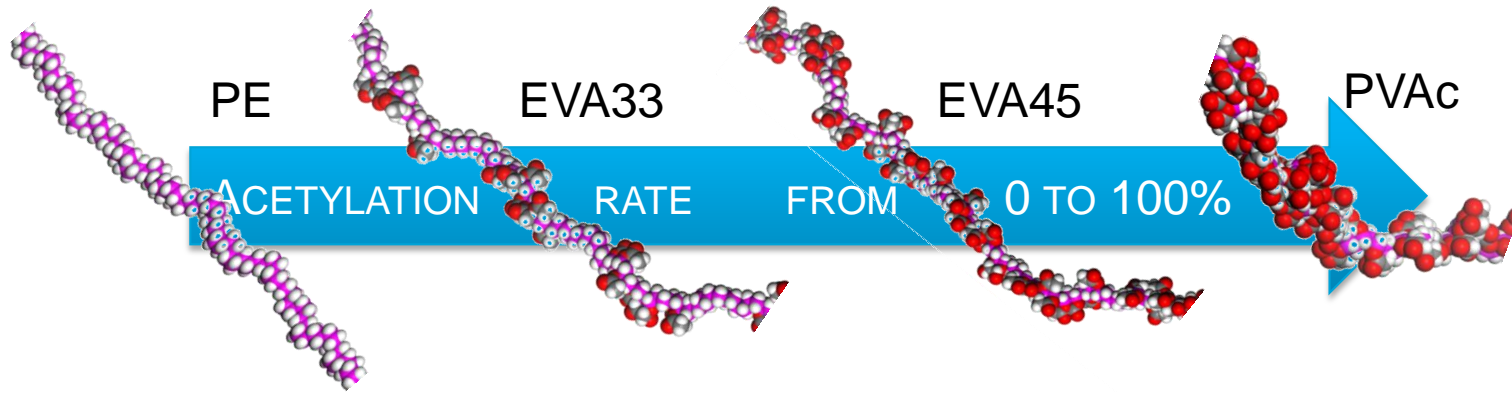


calculated $K_{i,F/P}$ values



Effect of overlapping F molecules

EXTENSION TO COPOLYMERS (ethylene vinyl acetate)

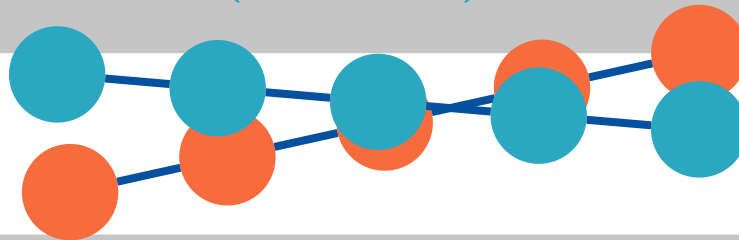


APOLAR

POLARITY++

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

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



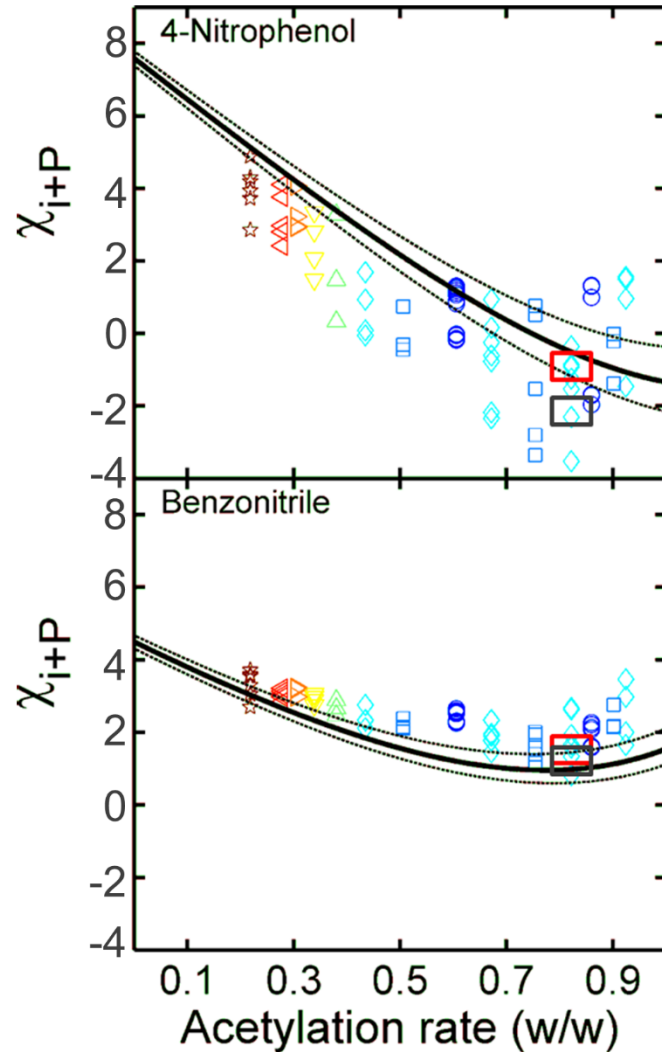
Microscopic approach (binary : $i + copolymer$) : sampling of all possible isomers



COMPARISON BETWEEN THE MICROSCOPIC AND MEAN FIELD APPROXIMATION

Effect of acetylation rate on χ_{i+P}

Configurations of minimal energies : $n = 5$
(acetylation rate $w/w = 0.82$)

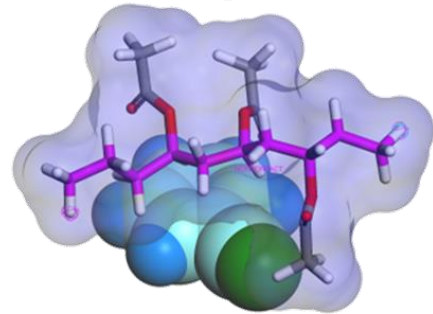
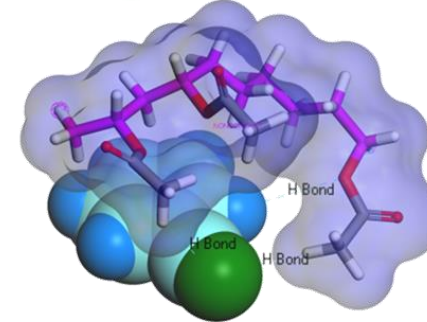
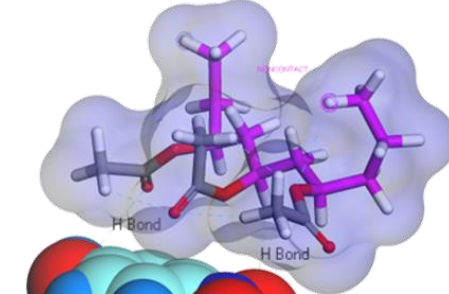
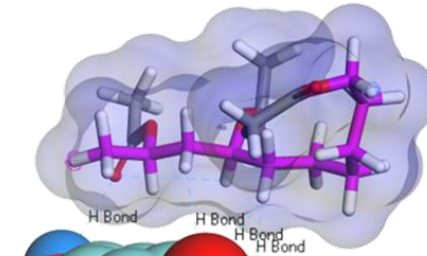


Sequences
Solutes

AAEEA

EAAAE

Benzonitrile
4-nitrophenol

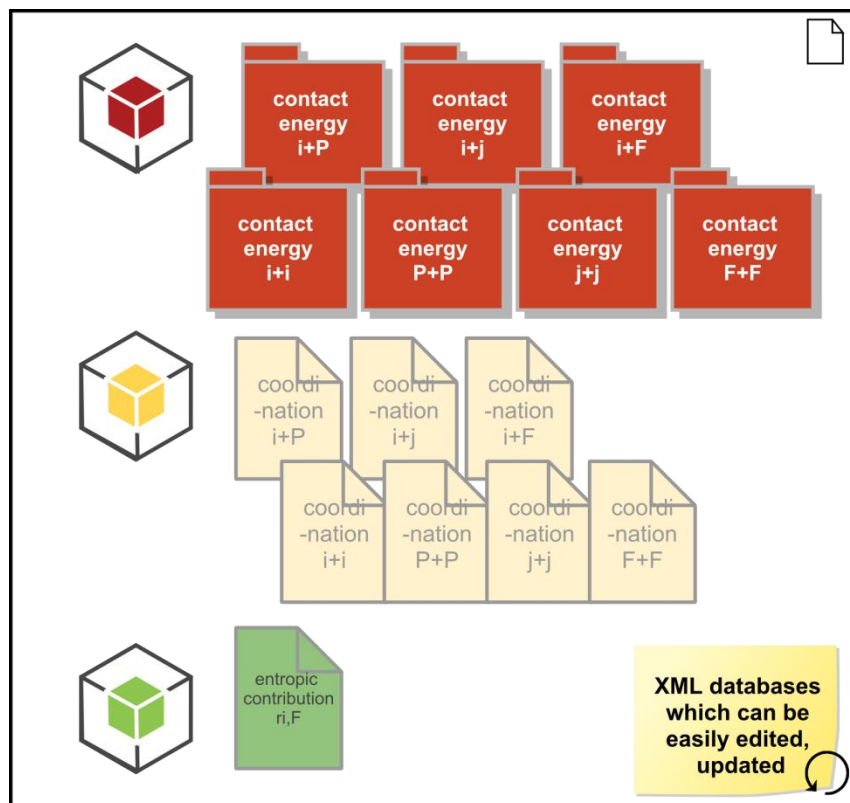


○ Microscopic calculations

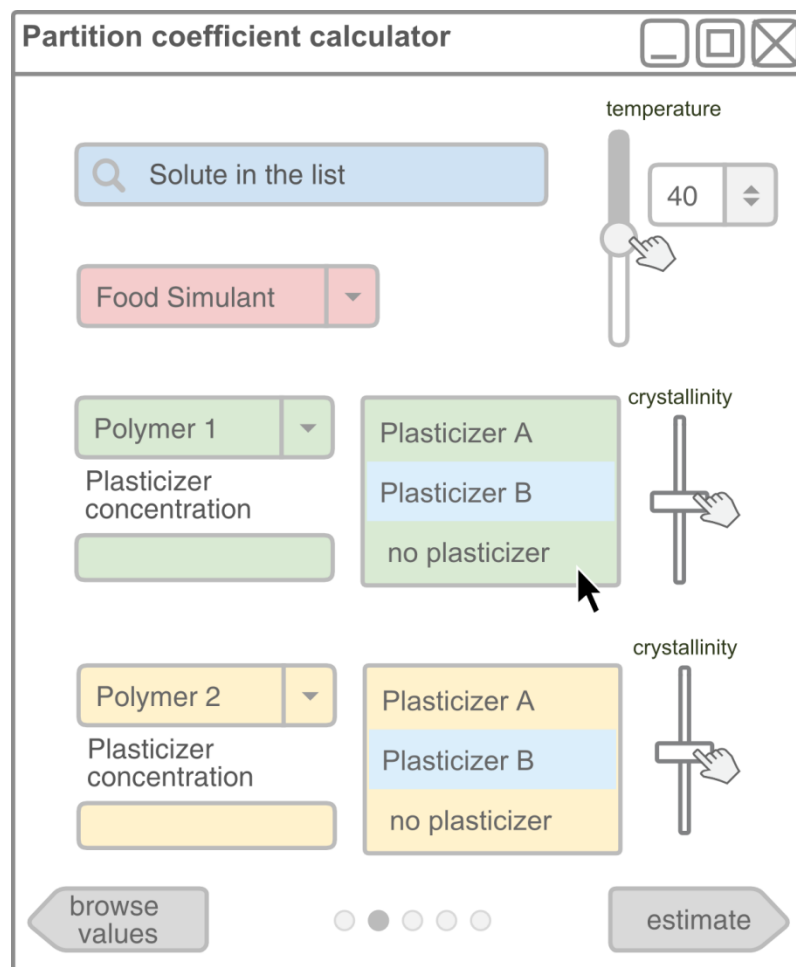
— mean field approximation

MOLECULAR RESULTS INTEGRATED WITHIN A “SMALL” SOFTWARE

Databases of results
calculated at molecular scale



Small “real-time” software



$i =$



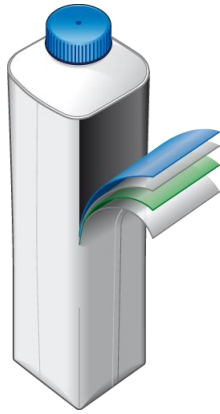
_04

PREVENTIVE APPROACHES OF THE CONTAMINATION

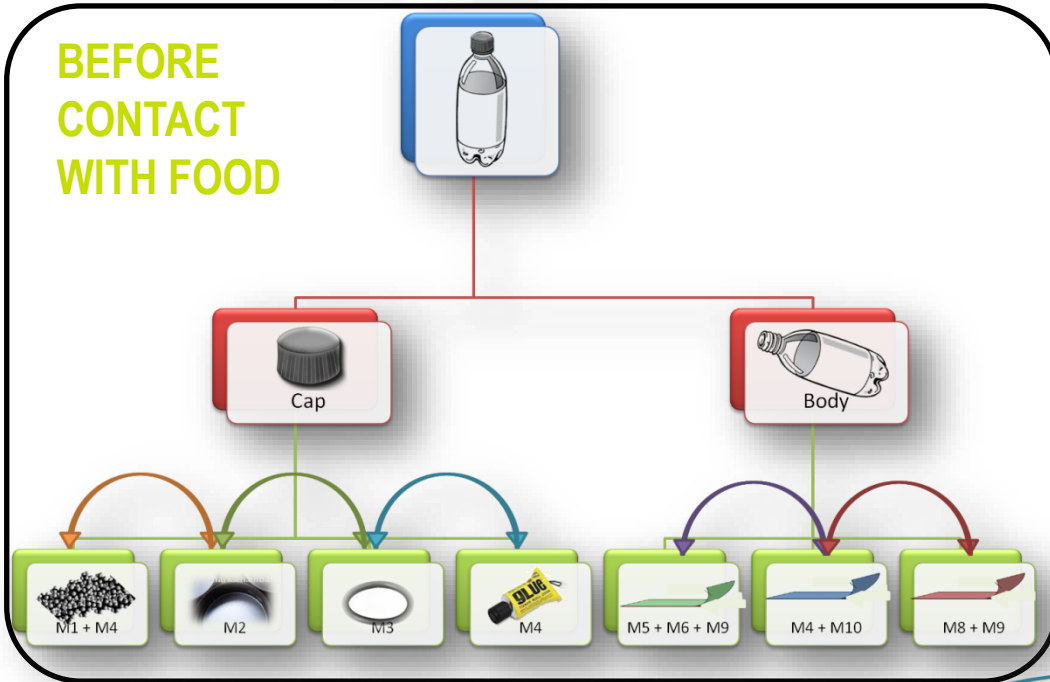
FMECA APPROACHES

- 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).

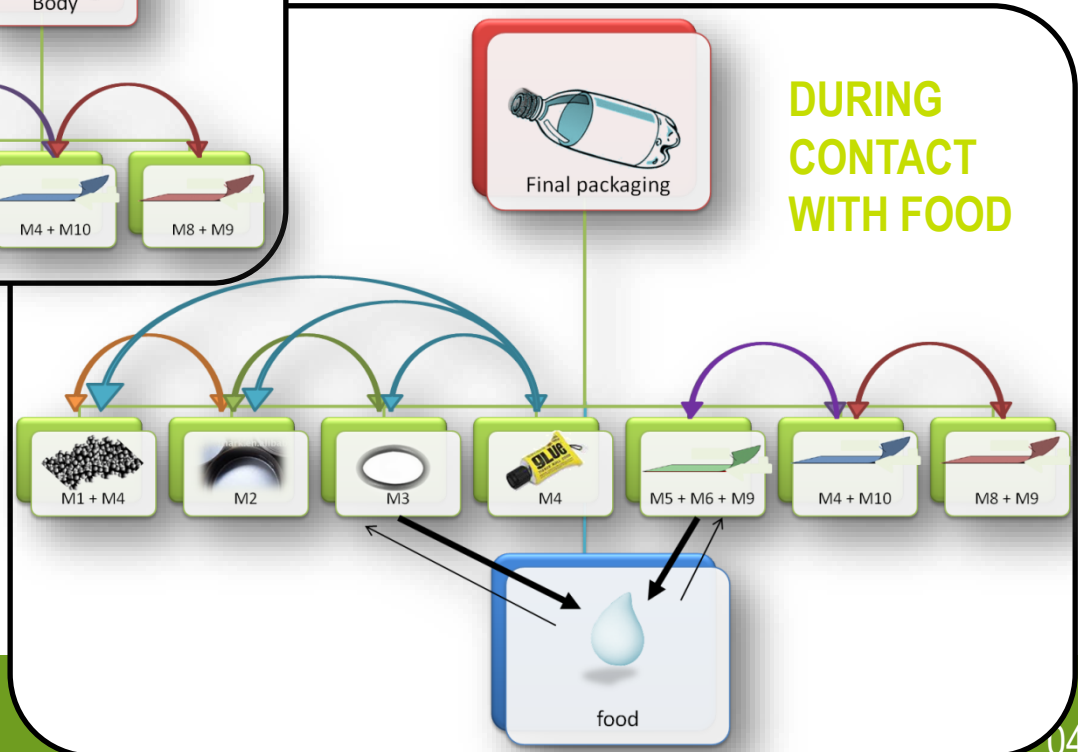
CROSSED-MASS TRANSFER BETWEEN MATERIALS



BEFORE CONTACT WITH FOOD



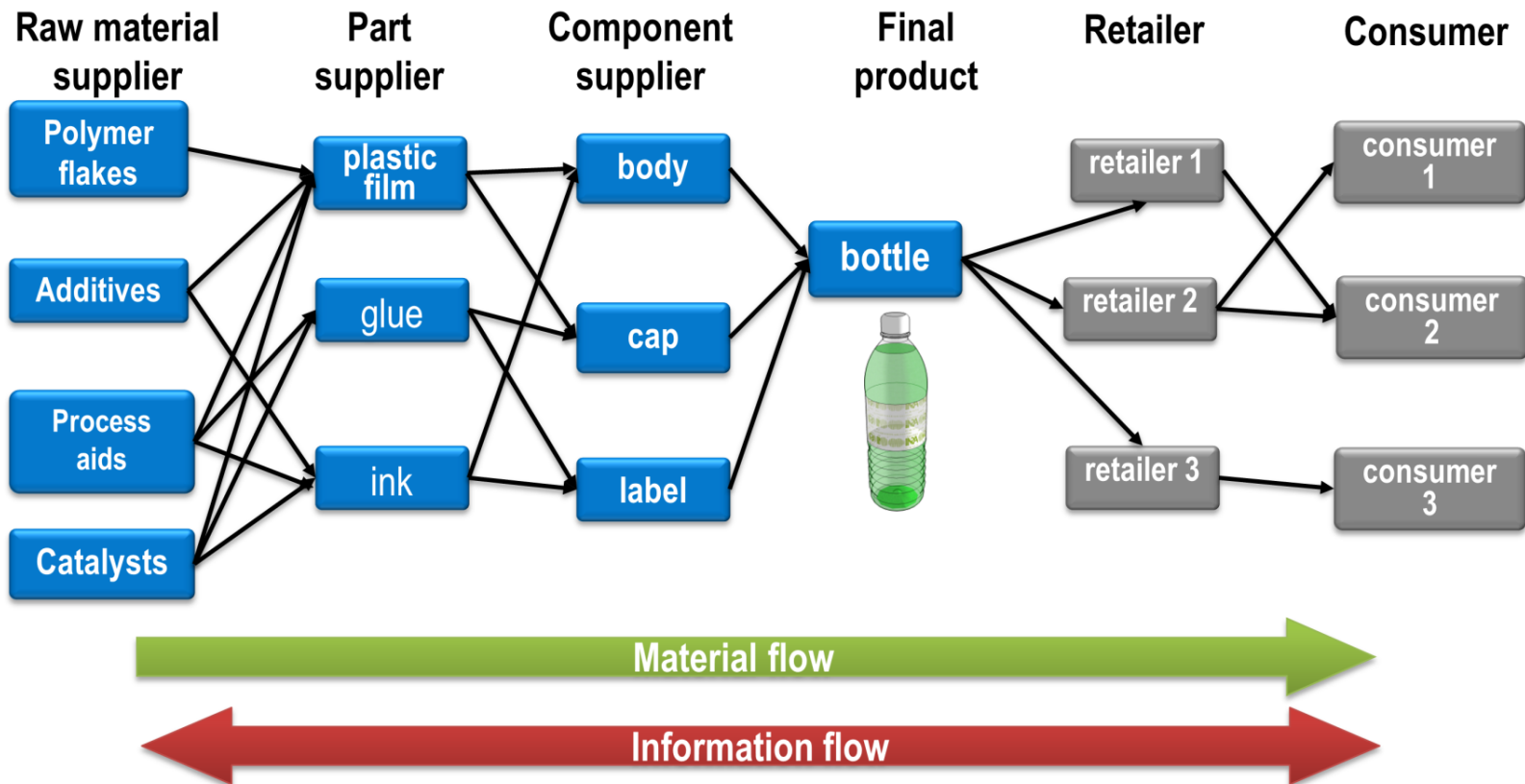
DURING CONTACT WITH FOOD





TOWARDS NEW CONCEPTS

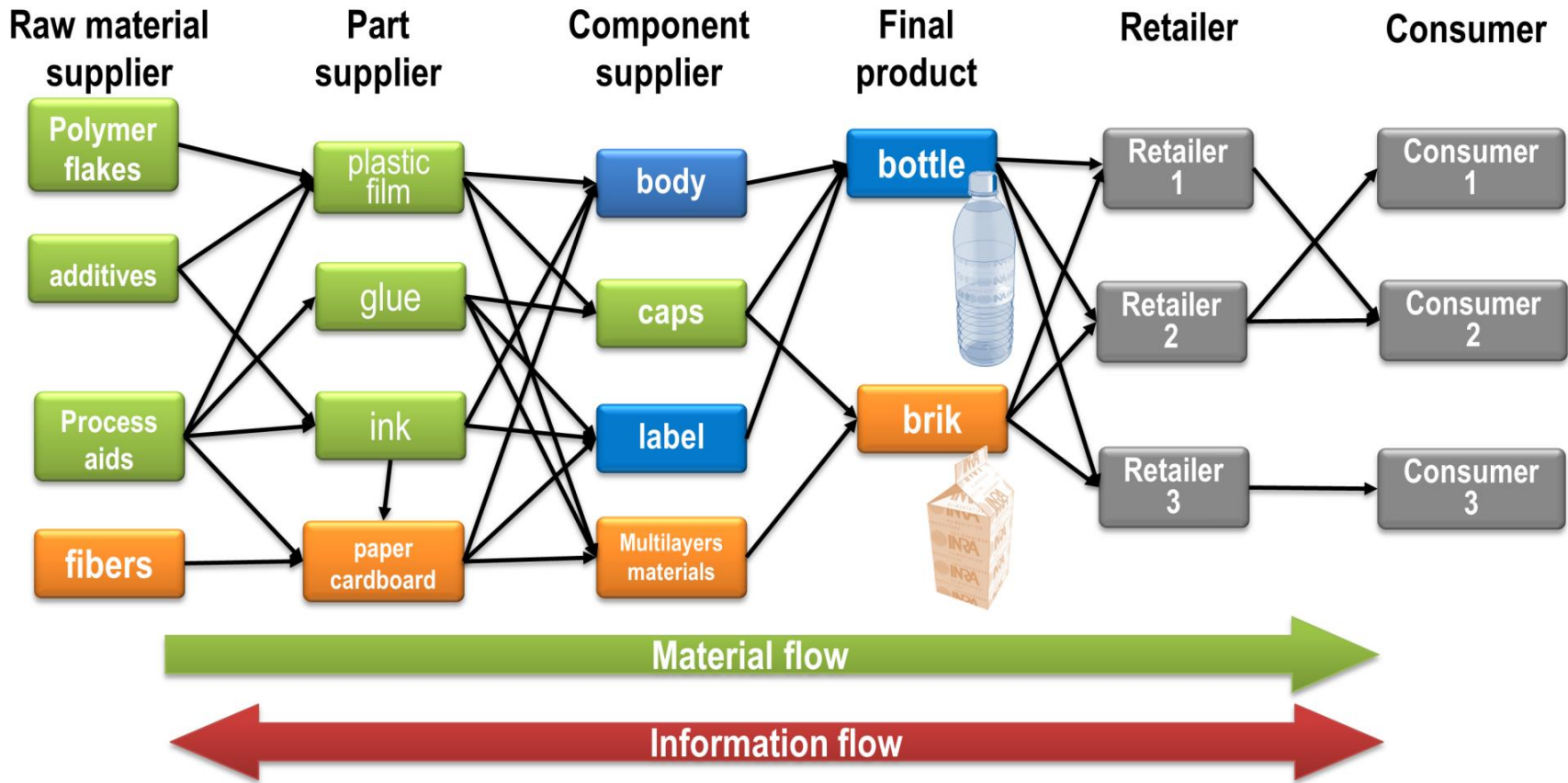
DEVELOPING COOPERATION BETWEEN STAKEHOLDERS





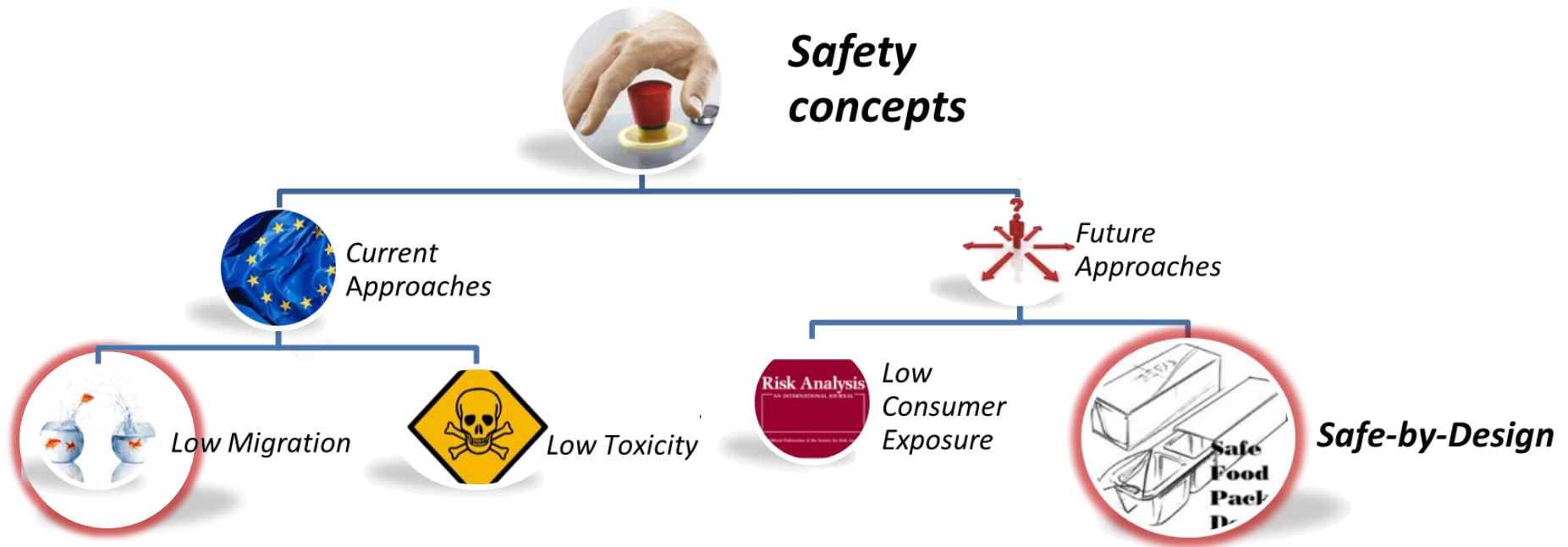
TOWARDS NEW CONCEPTS

DEVELOPING COOPERATION BETWEEN STAKEHOLDERS



TOWARDS NEW CONCEPTS

PREVENTIVE APPROACHES OF FOOD SAFETY



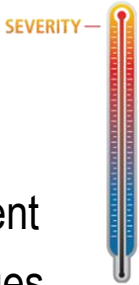
17 groups of materials listed in Annex 1 of regulation 1935/2004/EC are still not covered by specific measures. They must be produced according to **Good Manufacturing Practices** (Regulation 2023/2006/EC) incl. 3 pillars: quality assurance system, quality control system, documentation.

Failure Mode Effects Criticality Analysis

LOGICAL STEPS

- ❖ List of components and functions
- ❖ Failure = migration mode tree
- ❖ **Severity** = $f(C_F)$

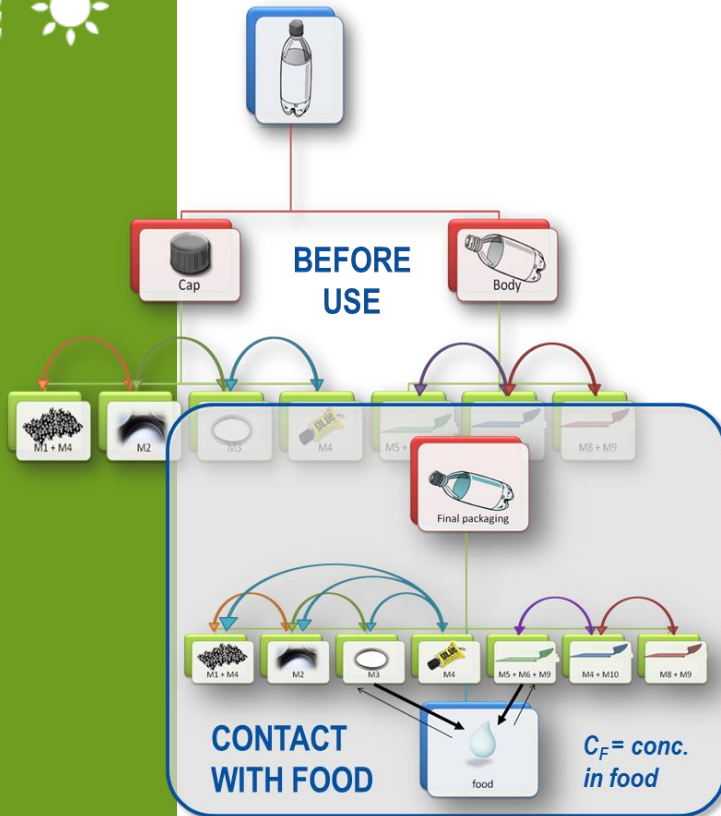
- Dimensionless scale
- Normalized by toxicological data
- Substance and material independent
- Linear to C_F for acceptable C_F values and non-linear beyond



❖ Criticality ranking

- by component
- by substance
- by process or storage step
- Comparative designs

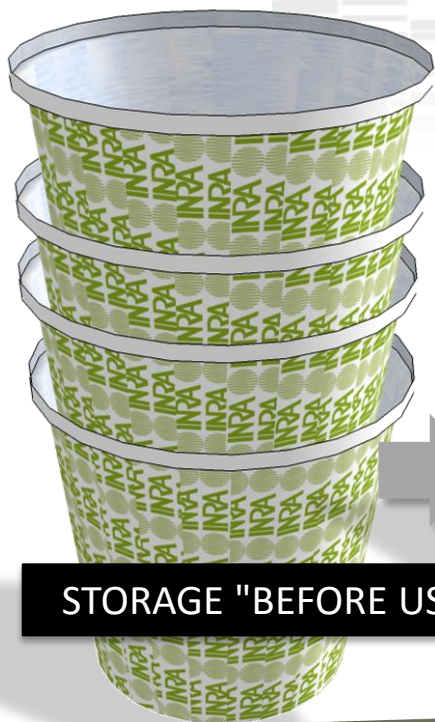
❖ Ensuring **detectability** via calculations and simulation



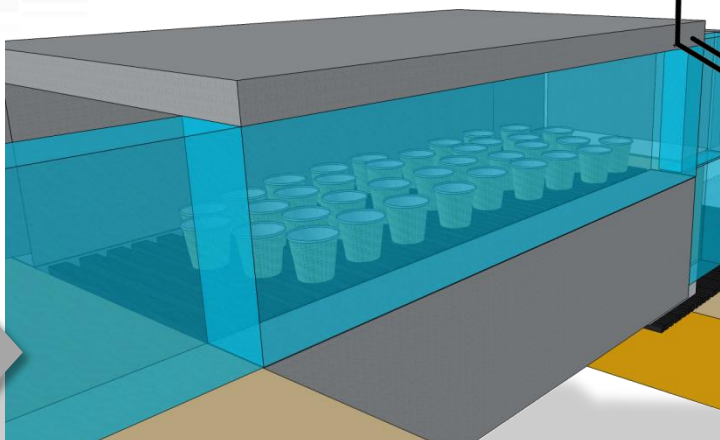
Nguyen *et al.* 2013, AIChE J.

READY TO EAT "CHINESE SOUP"

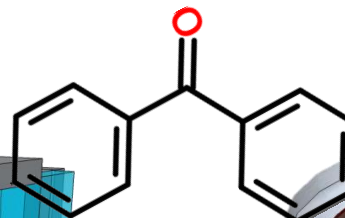
CHAINED STEPS



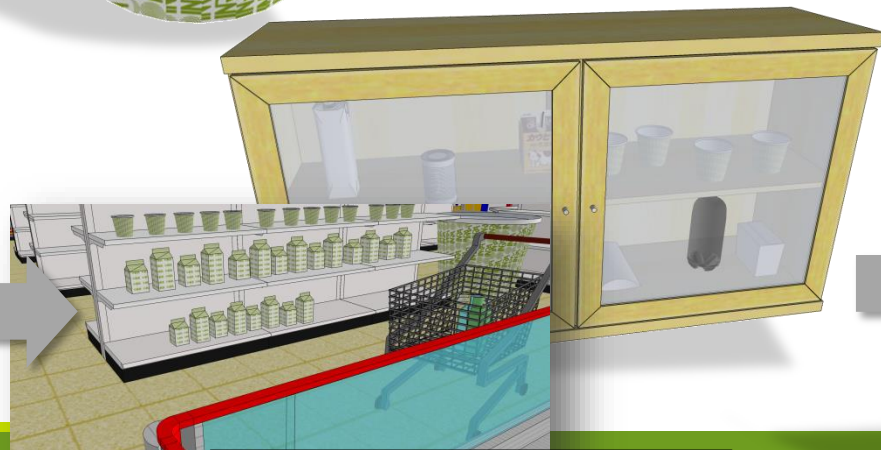
STORAGE "BEFORE USE"



HOT FILLING



FATTY CONTACT



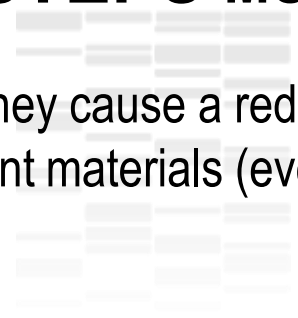
LONG-TERM STORAGE



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"

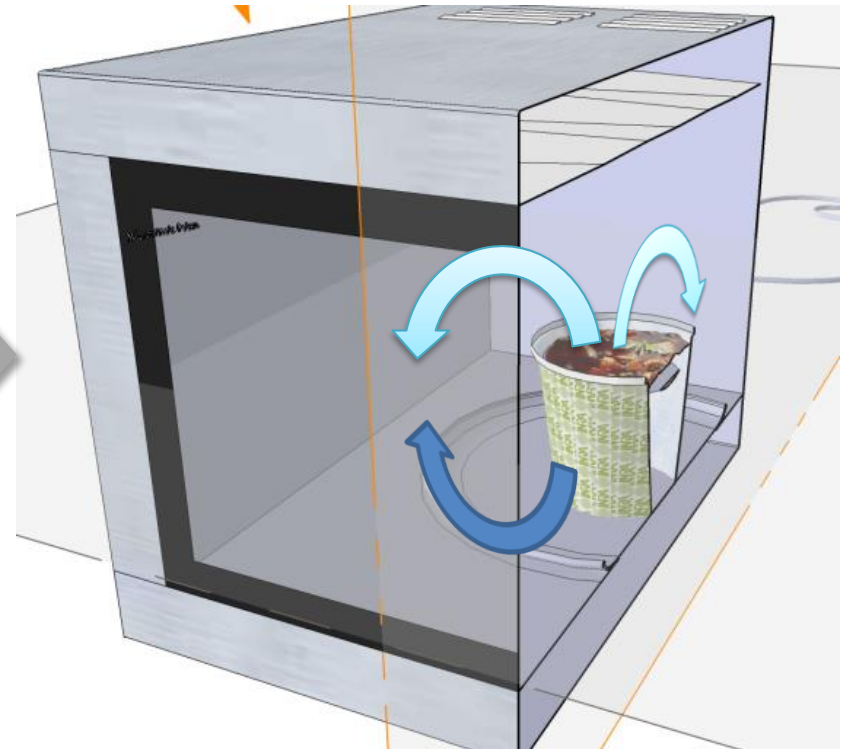
CROSS-MASS TRANSFER BETWEEN
INTERNAL AND EXTERNAL SURFACES

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



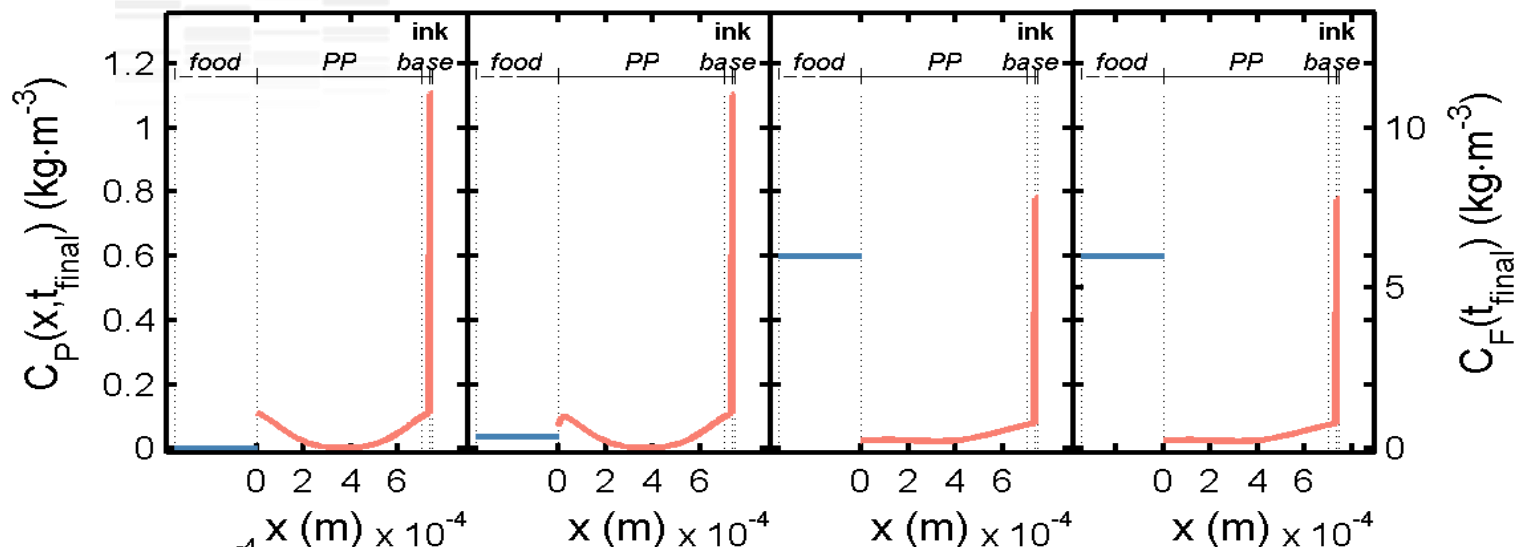
MICROWAVE HEATING



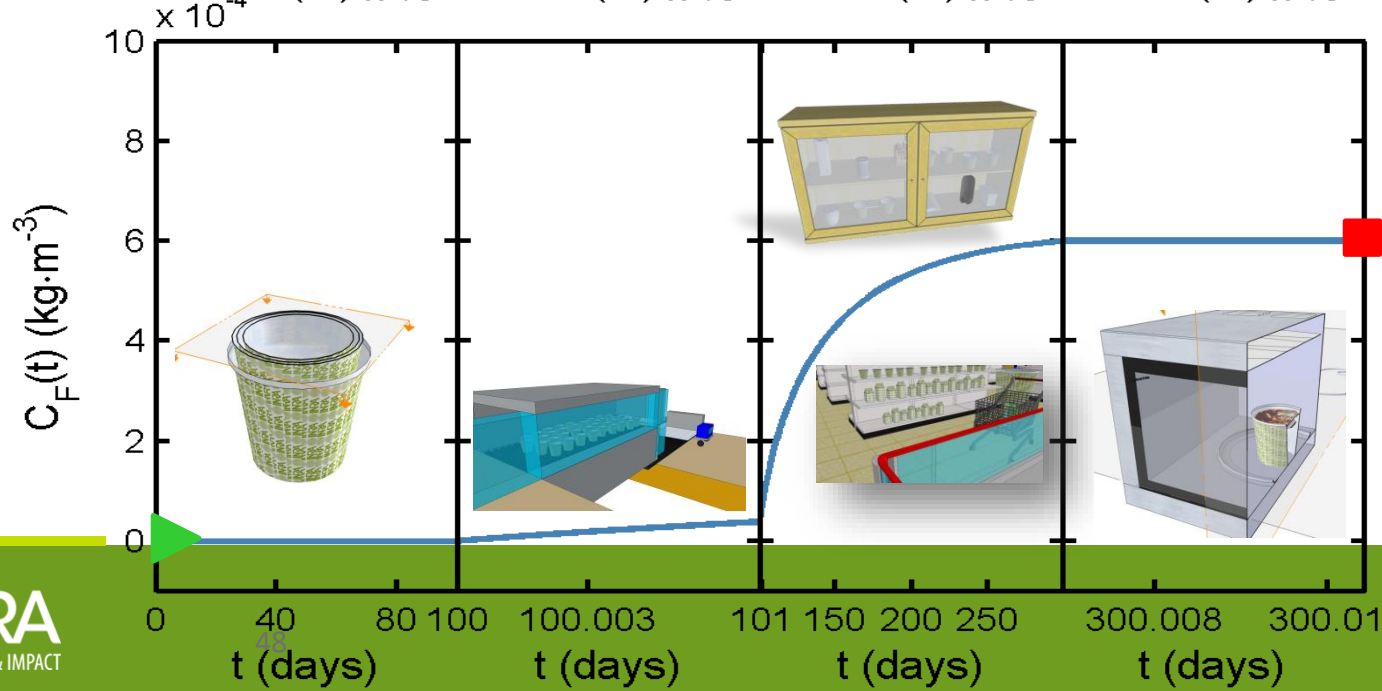
TRANSFER IN VAPOR PHASE
+STEAM EXTRACTION

CHAINED STEPS

1: Setoff → 2: HotFilling → 3: Storage → 4: OvenHeating $\times 10^{-4}$

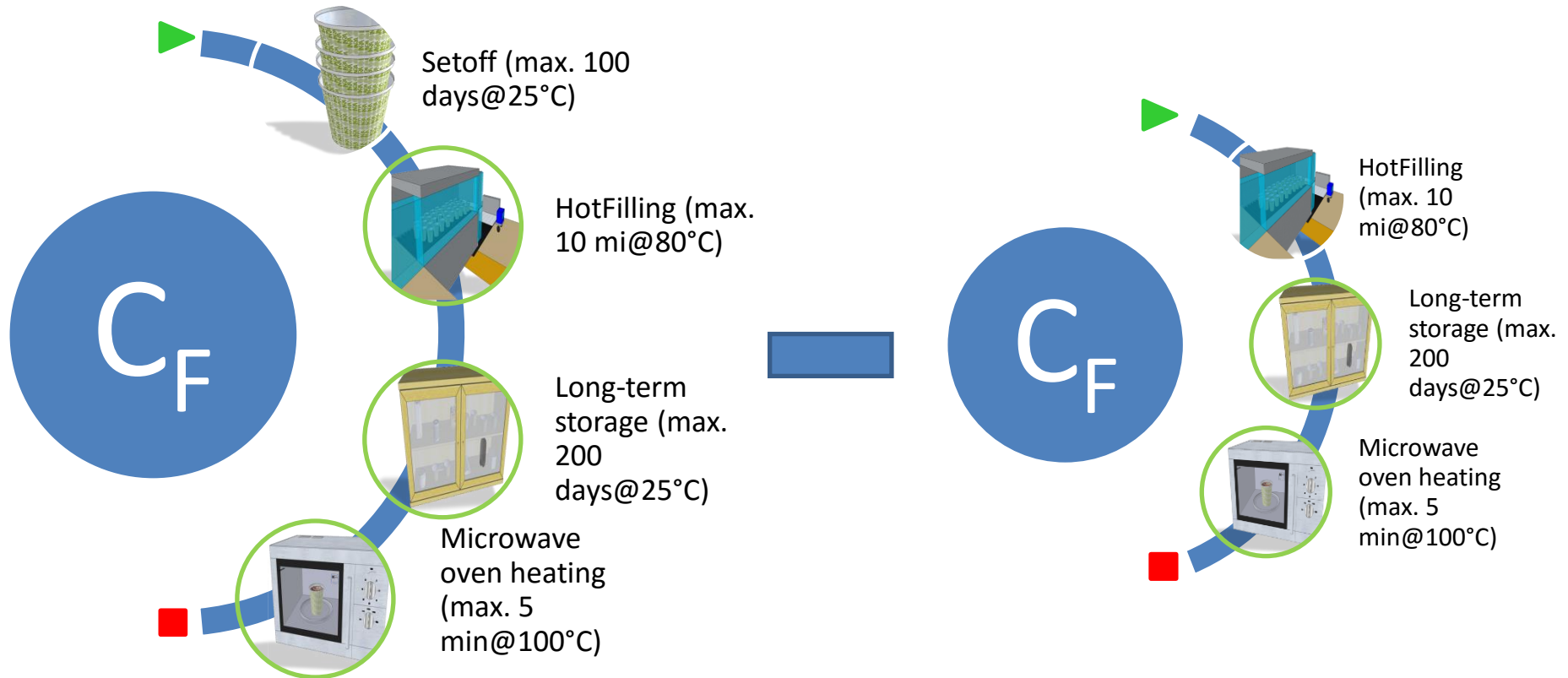


$C_F(t_{\text{final}})$ (kg·m⁻³)



ASSESSING THE SEVERITY OF A SINGLE STEP

CASE OF "SETOFF" STEP

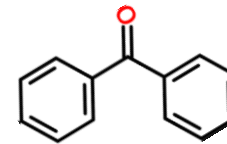
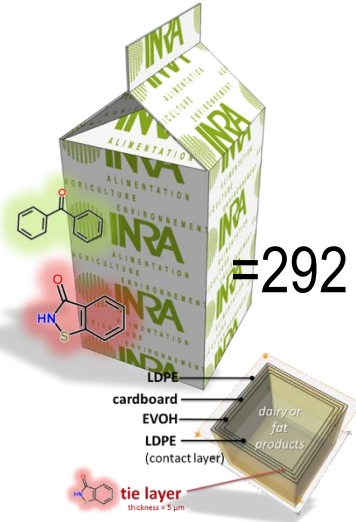
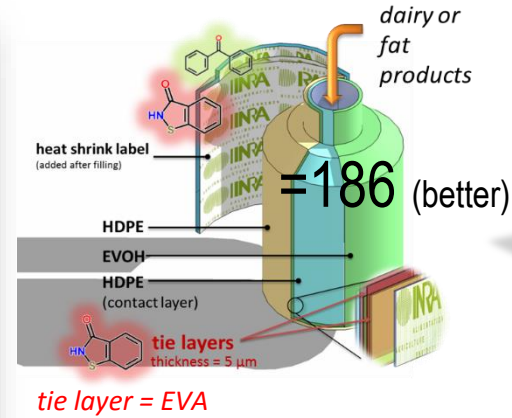
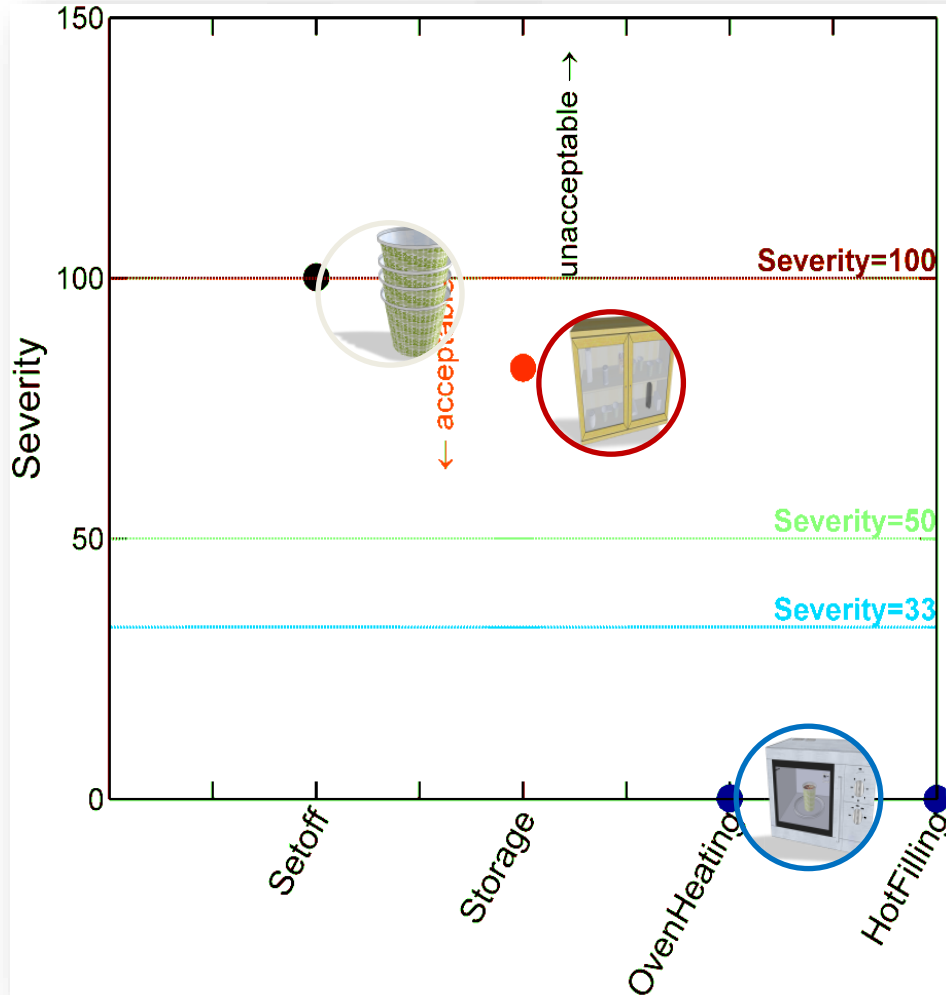


Full methodology described in *AIChE J.* 2013, **59**(4), 1183-1212

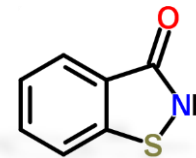
$$\text{Severity}(\hat{C}_F(\text{step } i)) = f \left[\max \left[\underbrace{C_{F_M} |_{1 \rightarrow 2 \rightarrow \dots \rightarrow M} - C_{F_M} |_{1 \rightarrow 2 \rightarrow \dots \rightarrow M/i}}_{\text{comparison with step } i \text{ removed}}, C_{F_i} |_i \right] \right]_{\text{step } i \text{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

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

CASE OF "SETOFF" STEP



=115
(almost acceptable)



=124

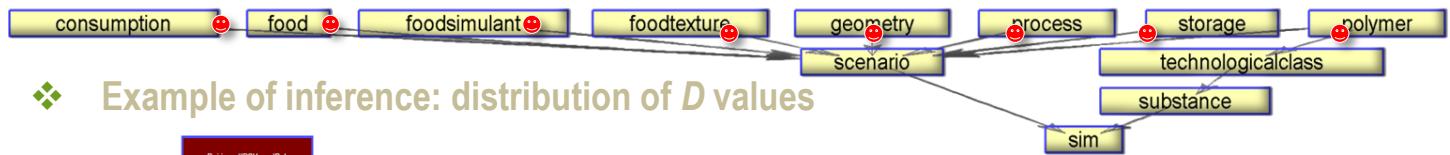
AUTOMATIC GENERATION OF MIGRATION SCENARIOS

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



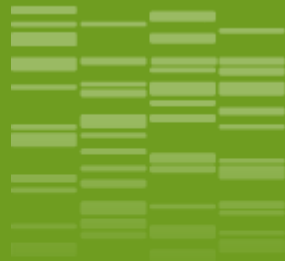
- ❖ Example of inference: distribution of *D* values

The diagram illustrates the inference process for *D* values distribution. It starts with a root node: `Danger([PSYogurtPot; scenario: id->polymer; r([PSYogurtPot; ce; no: id->polymer; po; lymer: acronym->compo; sillon; substance: te; ch; ologicalclass--M]; [PSYogurtPot; so; ma; no: id->temperature; storage: id->tempe; rature])`. This node branches into three intermediate nodes: `PSYogurtPot; scenario: id->polymer`, `PSYogurtPot; scenario: id->polymer; ce; no: id->temperature; rature: id->temperatu; re`, and `87 values (1.48e-024e4.19e-020e2.41e-018)`. The first node further branches into `1 value (PS)` and `PS polymer: acronym->composition; subst; itar: techn; ologicalclass--M`. The second node branches into `chilled storage: id->temperature` and `87 values (79.9e421e2.29e+003)`. The third node branches into `87 values (79.9e421e2.29e+003)` and `1 value (7)`. The `87 values (79.9e421e2.29e+003)` node further branches into `87 values (79.9e421e2.29e+003)` and `87 values (79.9e421e2.29e+003)`. The final output is a distribution of *D* values, shown as a histogram.

Visual elements include:

- Pot PS**: A blue box with a white trash can icon containing a recycling symbol.
- Substances::additives**: A blue box with a molecular structure icon.
- Molecular Mass**: A blue box with a histogram icon.
- Diffusion coefficient overestimated via the Piringer's Formula**: A blue box with a histogram icon.

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



Ignorance

Miss-conception



- Education
- Training
- Research

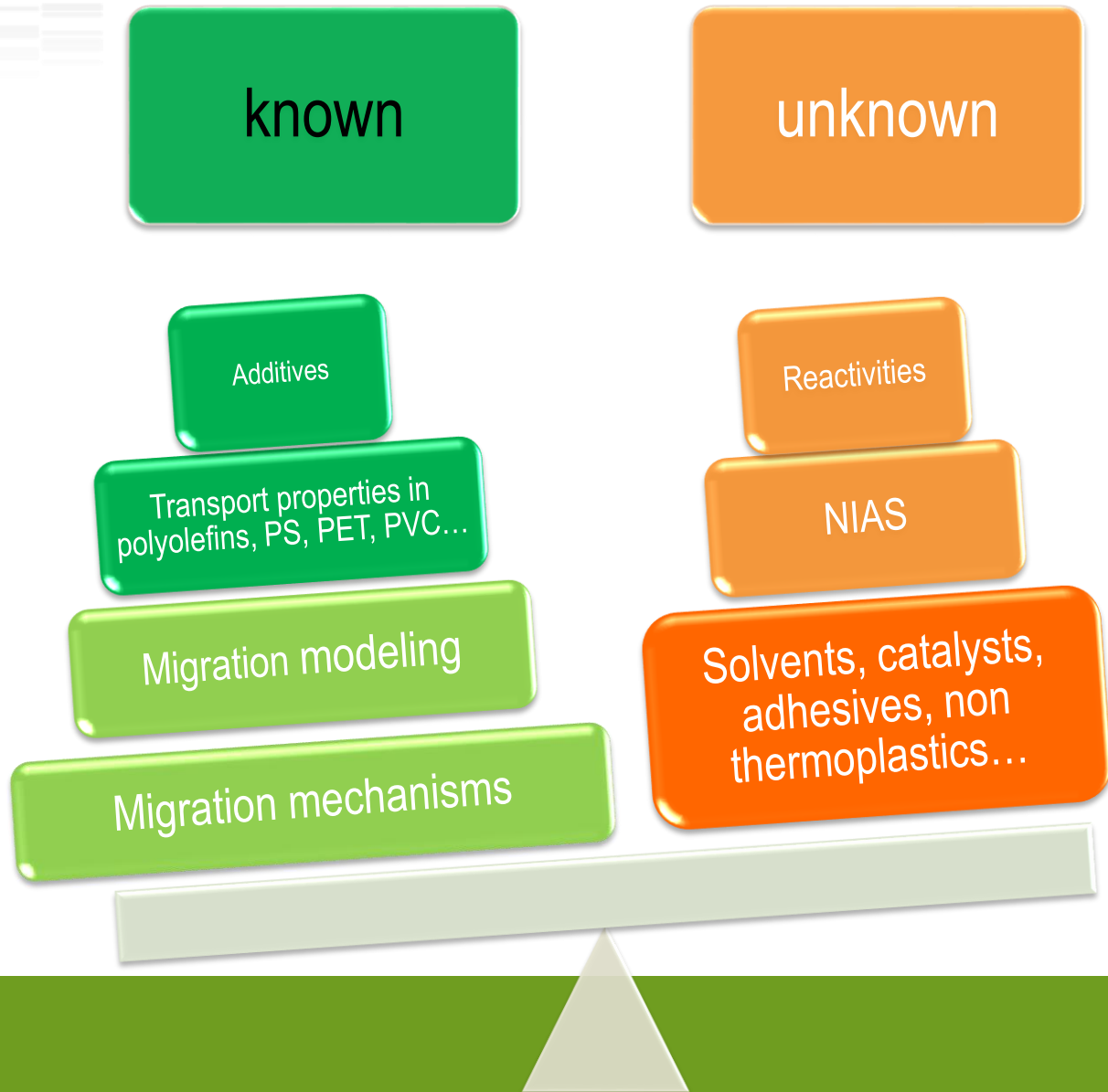
_05

COMPLEMENTARY TOOLS AND PROSPECTS

overview

MIGRATION MODELING

STATE OF THE ART



BLIND QUANTITATIVE DEFORULATION

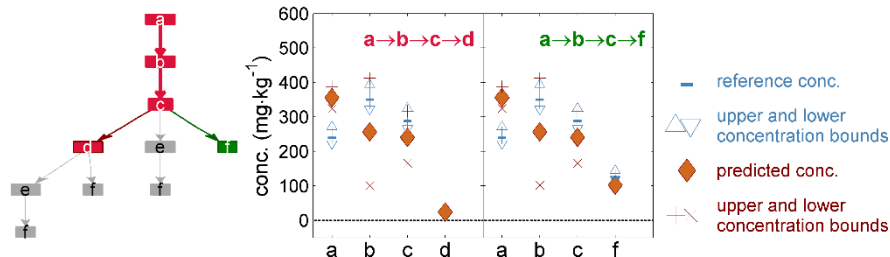
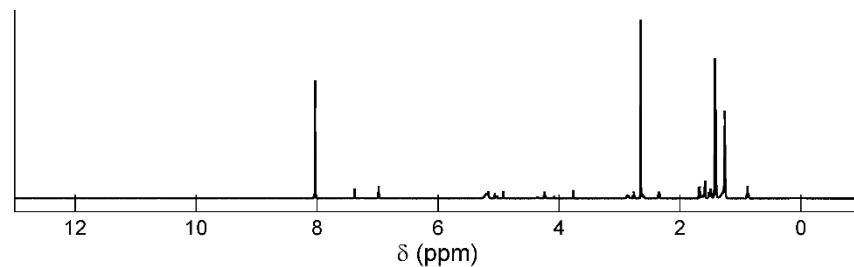
<https://github.com/ovitrac/SFPDnmrspec>

Example:
real PP

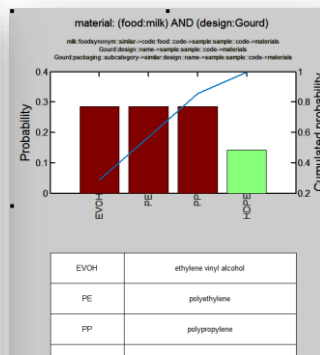
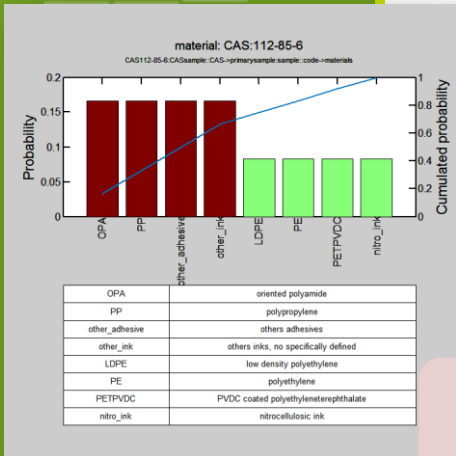
Present	Class	Likely substances	ρ
x	C07	a: Irganox 3114	0.95
x	C11	b: Irganox 1035	0.83
x	C14	c: Stearic acid	0.82
	C12	d: Irganox PS802	0.76
	C12	e: Irganox PS800	0.74
x	C12	f: Irganox 1010	0.66

The screenshot displays the SFPDnmrspec - v 0.1 software interface. It includes a 'Deformation parameters' section with various input fields, a 'Project name' field, and a 'Mixture spectrum' selection. A table of results is visible, listing classes and likely substances with their respective correlation coefficients (ρ) and likely concentrations. The interface also features logos for partner institutions like ANR, INRA, and ANIA.

Class	Likely substances	ρ	Number of scenarios	Likely conc. (mg kg ⁻¹)
C07	a: Diethyleneglycol	0.98	3	2.7e+03 at 7e+03
C03	b: Dibutylsebacate	0.32	4	6.4e+02 at 3e+03
C04	c: Eucamide	0.31	3	1.5e+03 at 6e+03
C03	d: Stearic acid	0.28	2	5.2e+03 at
C04	e: Oleamide	0.27	1	1 at



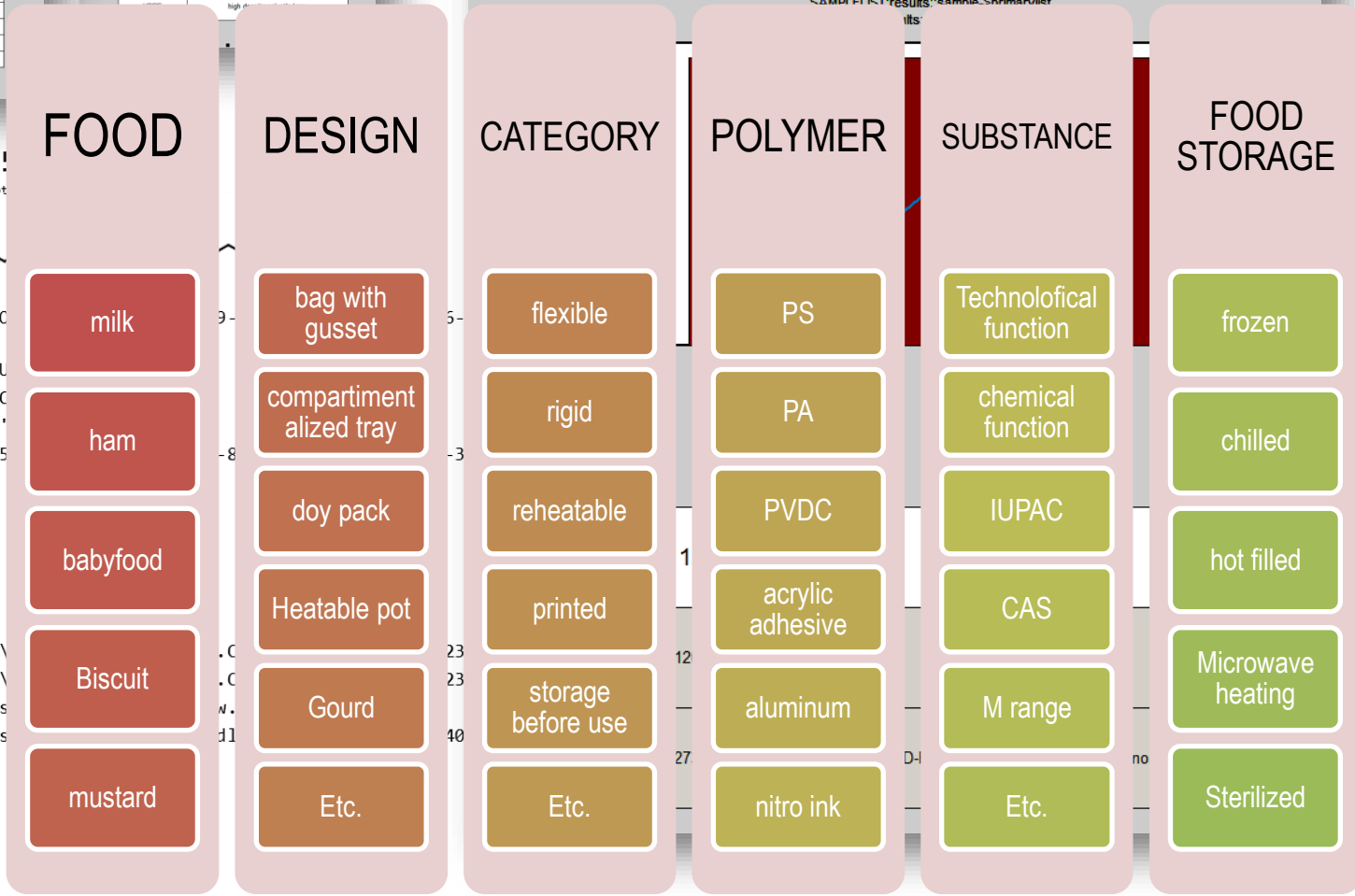
EXPERT SYSTEM



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

H-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
SAMPLEFIRSTresults::sample->primarylist



```
>> load_chemspider 112-85-6
CHEMSPIDER reuses cached data for '112-85-6' (date=21-sept-2015)
```

```
ans =
CCCCCCCCCCCCCCCCCCCC(=O)O
CSID: 7923
InChI: 'InChI=1S/C22H44O2/C22H44O2/c1-22H,1H3,(H,23,24)O'
InChIKey: 'UKMSUNONTOPOIO-UHFFFAOYSA-N'
SMILES: 'CCCCCCCCCCCCCCCCCCCC(=O)O'
Name: 'Docosanoic acid'
CAS: {'112-85-6' '165-85-8'}
Synonyms: {1x68 cell}
QuickMass: [1x1 struct]
quickproperties: [1x1 struct]
Properties: [1x1 struct]
UserProperties: [8x1 struct]
EPI: [1x1 struct]
Thumbnail: 'C:\Data\Olivier\112-85-6.png'
structure: 'C:\Data\Olivier\112-85-6.png'
url: 'http://www.chemspider.com/chemspider.nsf/0/112-85-6'
urlstructure: 'http://www.chemspider.com/chemspider.nsf/0/112-85-6'
links: [1x1 struct]
```

olivier.vitrac@agroparistech.fr
Oct 2015



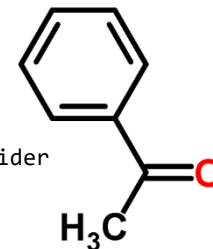
EXAMPLES OF GENERATION OF TRANSPORT PROPERTIES FOR VOLATILE CONTAMINANTS

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)
```

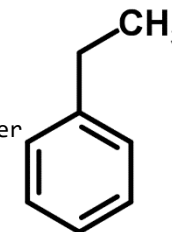
```
ans =
      9.1995e-06
```



>> 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)
```

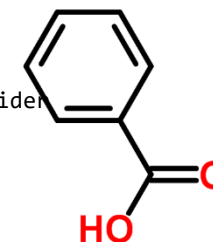
```
ans =
      2.2485e-04
```



>> 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
```



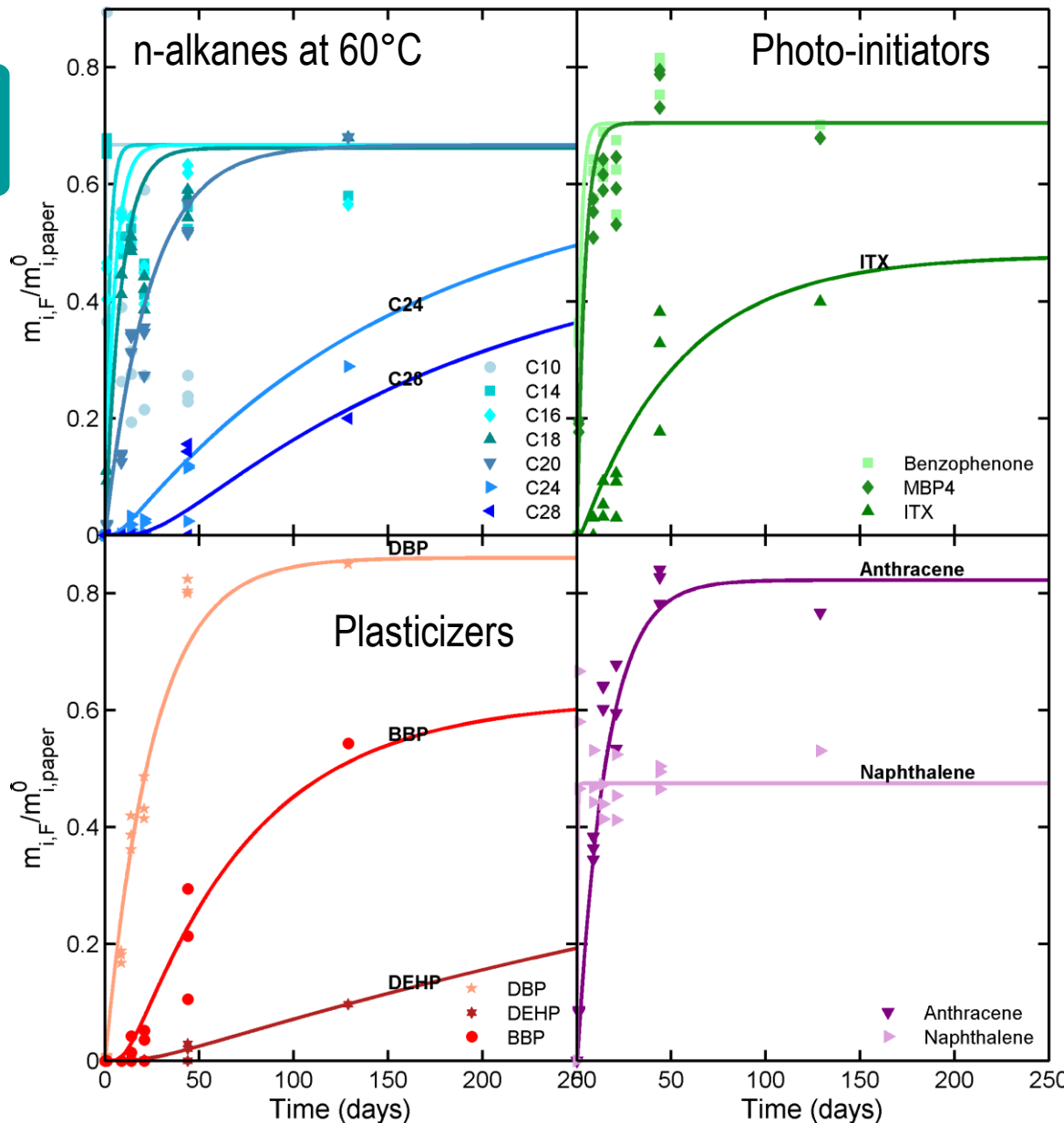
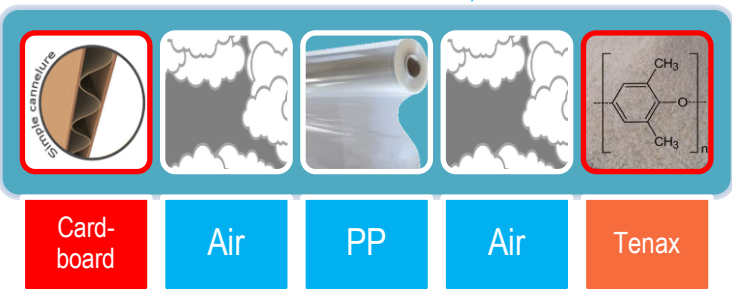
PREDICTIONS vs EXPERIMENTS

Experimental results
15 solutes

Detailed modeling
with FMECAengine

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

0 to 120 days



Thank you



Merci
Danke
Thank You
ขอบคุณค่ะ
Terima kasih
Dhanyavad
Kam sah hamnida
Xièxie
Gracias
Vielen dank
ευχαριστώ

FOOD, ENERGY & ENVIRONMENT



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	<i>Conference Center, Room 100, School of Packaging</i>
30th June (Tuesday) 2:00pm- 3:00pm	An atomistic Flory-Huggins formulation for the tailored prediction of activity and partition coefficients	<i>The Ternes Outreach Center, Room 120, School of Packaging Registration required</i>
1st July (Wednesday) 2:00pm- 4:00pm	Workshop: Prediction of the migration: beyond conventional estimates*	<i>The Ternes Outreach Center, Room 120, School of Packaging Registration required</i>