université PARIS-SACLAY

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INRAE AgroParisTech

Migration modeling related to food contact materials: present and future

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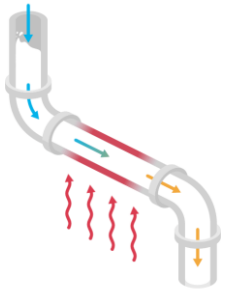
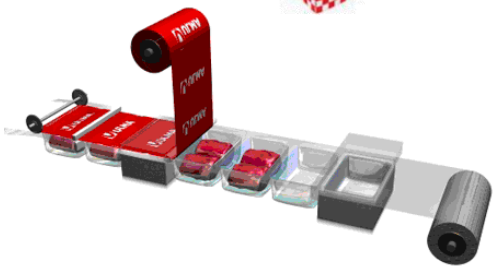
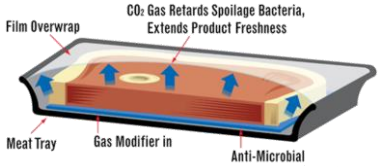
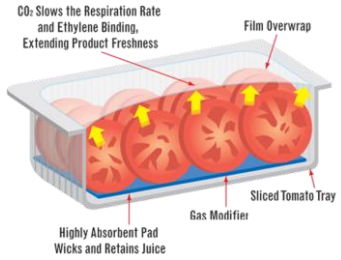
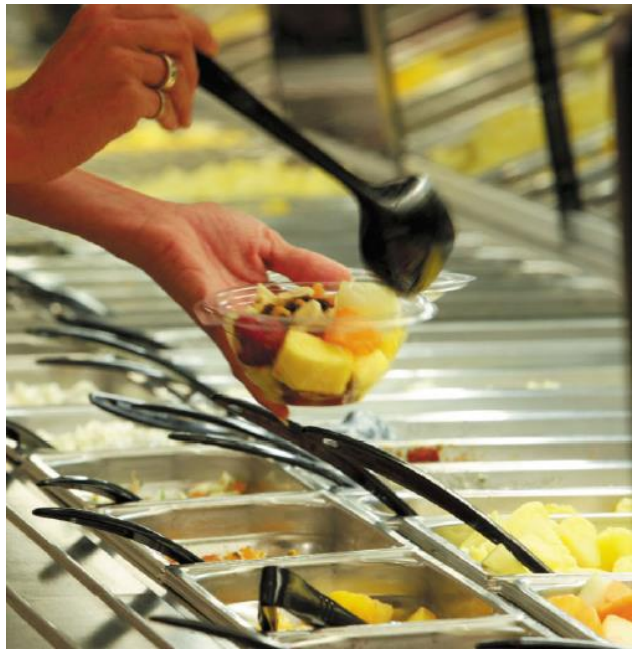


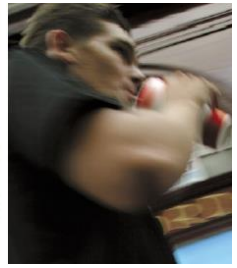
Ultra
High
Temperature



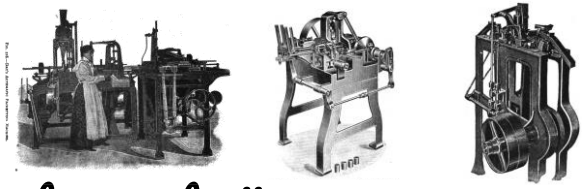








Food inertia: a long history



The 1908 regulation: "...no food substance shall contain any harmful product, chemical..."

L'ART DE CONSERVER,

PENDANT PLUSIEURS ANNÉES,

TOUTES LES SUBSTANCES ANIMALES ET VÉGÉTALES;

Ouvrage soumis au Bureau consultatif des Arts et Manufactures, revêtu de son approbation, et publié sur l'invitation de S. Exc. le Ministre de l'intérieur.

Par APPERT,

Propriétaire à Massy, Département de Seine et Oise, ancien Confiseur et Distillateur, élève de la bouche de la Maison ducale de Christian IV.

« J'ai pensé que votre découverte méritait » un témoignage particulier de la bienveillance » du Gouvernement ».

Lettre de S. Exc. le Ministre de l'intérieur.

A PARIS,

Chez PATRIS et Cie Imprimeurs-Libraires, quai Napoléon, au coin de la rue de la Colombe, N° 4.

1810.

8me Année. — N° 19 — Juillet 1910

LA CONSERVE ALIMENTAIRE

Bulletin mensuel de Vulgarisation Théorique et Pratique de Fabrication

PARAISSANT LE 15 DE CHAQUE MOIS

Rédigé par un groupe de Fabricants-Industriels et de Chefs d'Emplois de cette Industrie

Nicolas APPERT
(1750-1841)

École Nationale D'INDUSTRIE ALIMENTAIRE
Nicolas Appert

COMITÉ DE DIRECTION
Bourse du Commerce
— Paris —

L'idée de la création de cette école dont nous avons été les plus fervents propagandistes vient d'être mise définitivement au point par un groupe de praticiens, de chimistes et d'agronomes distingués qui vont en assurer le fonctionnement.

L'enseignement sera tout à la fois théorique et pratique.

Dans la voie pratique, le Comité de Direction se propose, non pas d'organiser une usine de fabrication de conserves et de produits alimentaires divers, destinée à concurrencer l'industrie libre, mais de créer des laboratoires d'essais et d'enseignement que dirigera un praticien qualifié et où chaque fabricant pourra venir se documenter et concourir aux progrès de la science alimentaire

Les essais théoriques seront dirigés par un technologue éminent, M. Crolbois, chef de laboratoire à l'Institut Pasteur.

Une très large place sera réservée, dans l'enseignement à la question des machines, appareils et ustensiles employés par l'Industrie alimentaire. Un ingénieur diplômé, M. Raymond Monot, des usines de Diétrich, est chargé d'organiser cette partie du programme.

M. Moréal de Brévans, le distingué sous-directeur du laboratoire municipal, a bien voulu se charger de l'enseignement si important de la chimie appliquée à l'alimentation.

Enfin M. Ed. Jacquet, ingénieur-agronome, administrateur de l'école, occupera la chaire de professeur d' « Alimentation Commerciale ».

Ajoutons que notre bulletin transformé en revue bi-mensuelle à laquelle collaboreront désormais les personnalités ci-dessus, devient le Bulletin Officiel de l'Ecole.

En un mot et suivant l'exemple d'autres pays, une Université nouvelle et bien moderne vient de naître en France, celle de l'Industrie Alimentaire. Cette industrie quitte ainsi, définitivement, le domaine empirique pour rentrer dans celui des sciences exactes, où elle avait

200 — LA CONSERVE ALIMENTAIRE

sa place déjà marquée par les exigences et le progrès sans cesse grandissants de la vie contemporaine.

Pour le Comité de Direction :
Aug. Corthay.

Causerie Professionnelle
par Nicolas APPERT

Méfions-nous des Conserves Étrangères

Nous donnons ci-dessous la traduction d'un extrait du passage que M. Hamel consacre à la législation et l'inspection des conserves alimentaires au Canada, dans le traité qu'il publie en ce moment. (Modern practice of canning meats) :

« Comparés avec les règlements qui régissent l'inspection des conserves alimentaires aux Etats-Unis et en Europe, ceux du Canada sont encore à l'état embryonnaire.

Pour protéger les fabricants Canadiens contre la concurrence des Etats-Unis, il était nécessaire de créer une législation, au moins sur le papier.

« Je ne parle pas ici de l'inspection des viandes fraiches qui est soumise à un groupe de savants et de vétérinaires de valeur.

« Mais l'acheteur éclairé de conserves alimentaires quelles qu'elles soient, viandes, poissons, fruits ou légumes est loin d'avoir obtenu la même sécurité.

« Le règlement en date de 1908 qui régit l'inspection des conserves alimentaires nous dit : *Aucune substance alimentaire ne doit contenir de produit nuisible, produits chimiques, colorants ou antiseptiques*, et plus loin on nous dit : *Il sera fourni aux Inspecteurs par les soins du Ministère de l'Agriculture les noms des antiseptiques et colorants inoffensifs dont l'emploi est permis. L'addition de tout autre empêchera le produit de recevoir l'étiquette constatant l'inspection.*

« Nous comprenons bien que les chimistes du Ministère sont là pour condamner tout produit alimentaire où l'analyse révélerait la présence d'un produit chimique dangereux, mais pour ceux qui sont au courant des discussions en cours entre les hygiénistes les plus distingués du monde entier au sujet de la plus ou moins grande nocivité de tel ou tel antiseptique, la satisfaction est maigre.

« Je répète que le fabricant de conserves en boîtes n'a pas besoin d'antiseptiques pour assurer la conservation indéfinie de ses produits. La stérilisation lui suffit.

« Pourquoi donc ne pas faire comprendre au monde entier que les mots « CANADA APPROVED » de l'étiquette signifient absence entière de susbstances nuisibles, aussi bien dans les conserves que dans les viandes fraîches.

« Que si quelques antiseptiques sont considérés comme inoffensifs par le Ministère de l'Agriculture, pourquoi ne pas faire connaître au public comme aux fabricants le nom de ce qui est permis et de ce qui est prohibé?

« Le règlement de 1908 ne prend nullement en considération la qualité de la soudure employée, pas plus que celle de l'acide, et il semble que sur ce point les japonais sont bien en avance sur nous lorsqu'ils donnent les commandes pour leur armée.

« Pour en finir, il semble que des instructions plus complètes auraient été pour le plus grand intérêt du fabricant lui-même, en donnant au public consommateur une garantie parfaite de sécurité. La consommation en aurait été accrue en regagnant la confiance des consommateurs qui sont peu confiants dans les conserves, généralement sans raisons, d'ailleurs. »

G. T. Hamel, ingénieur.

L'auteur faisant une œuvre purement technique et non de polémique est évidemment très modéré. Mais pour qui lit entre les lignes et pour nous qui savons combien sont rares parmi le personnel de l'inspection les gens compétents, toutes les places étant prises par les politiciens, nous ne nous sentons pas rassu-

Assessing migration and exposure to chemicals

Recent history.

1990

https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100BCMB.TXT

EPA 560/5-85-015
September 1990

METHODS FOR ASSESSING EXPOSURE
TO CHEMICAL SUBSTANCES

Volume 11

Methodology for Estimating the Migration of Additives
and Impurities from Polymeric Materials

by

Arthur D. Schwope
and
Rosemary Goydan
Arthur D. Little, Inc.
Cambridge, MA 02140

and

Robert C. Reid
Massachusetts Institute of Technology
Cambridge, MA 02139

EPA Contract No. 68-D9-0166

Project Officer

Thomas Murray
Exposure Evaluation Division
Office of Toxic Substances
Washington, D.C. 20460

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

2005

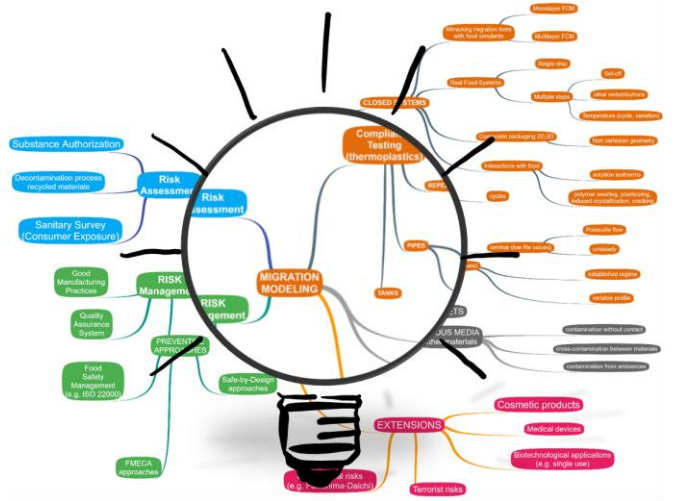
Food Additives and Contaminants, January 2005; 22(1): 73–90

Taylor & Francis
Taylor & Francis Group

Evaluation of migration models that might be used in support of regulations for food-contact plastics

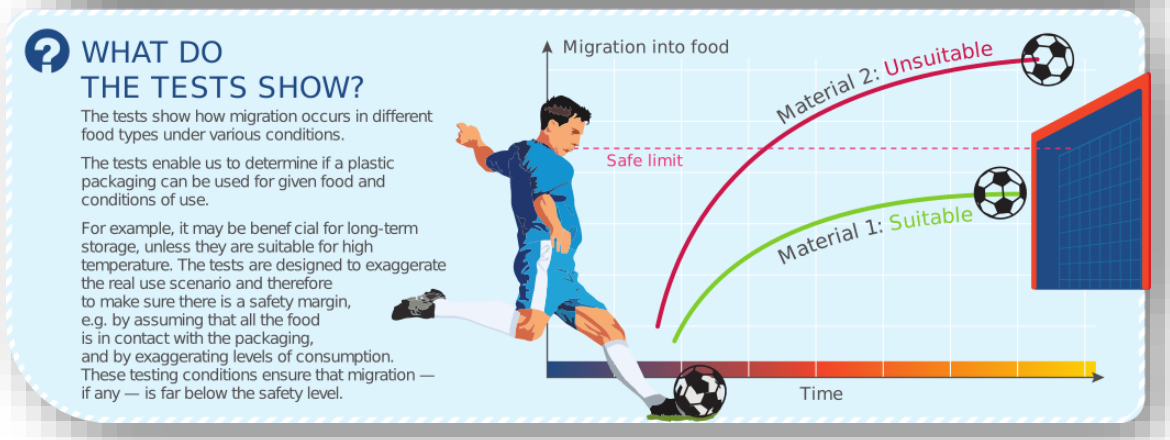
T. BEGLEY[1], L. CASTLE[2], A. FEIGENBAUM[3], R. FRANZ[4], K. HINRICHS[5], T. LICKLY[6], P. MERCEA[7], M. MILANA[8], A. O'BRIEN[9], S. REBRE[10], R. RIJK[11], & O. PIRINGER[7]

[1]*Food & Drug Administration, 5100 Paint Branch Parkway, College Park, MD 20740, USA,* [2]*Central Science Laboratory, Sand Hutton, York Y041 1LZ, UK,* [3]*INRA — CPCB, Moulin de la Housse, F-51697 Reims Cedex 2, France,* [4]*Fraunhofer-Institut IVV, Giggenhauser Straße 35, D-85354 Freising, Germany,* [5]*Cognis GmbH, Henkelstraße 67, D-40551 Dusseldorf, Germany,* [6]*DOW, 1803 Building, Midland, MI 48674, USA,* [7]*Fabes GmbH, Schragenhofstraße 35, D-80992 Munich, Germany,* [8]*Istituto Superiore de Sanita, Viale Regina Elena, 299, I-0161 Rome, Italy,* [9]*PIRA International, Leatherhead KT22 7RU, UK,* [10]*Atofina, Rue Danton 95, F-92300 Levallois-Perret, France, and* [11]*TNO, Utrechtseweg 48, NL-3700 AJ Zeist, the Netherlands*

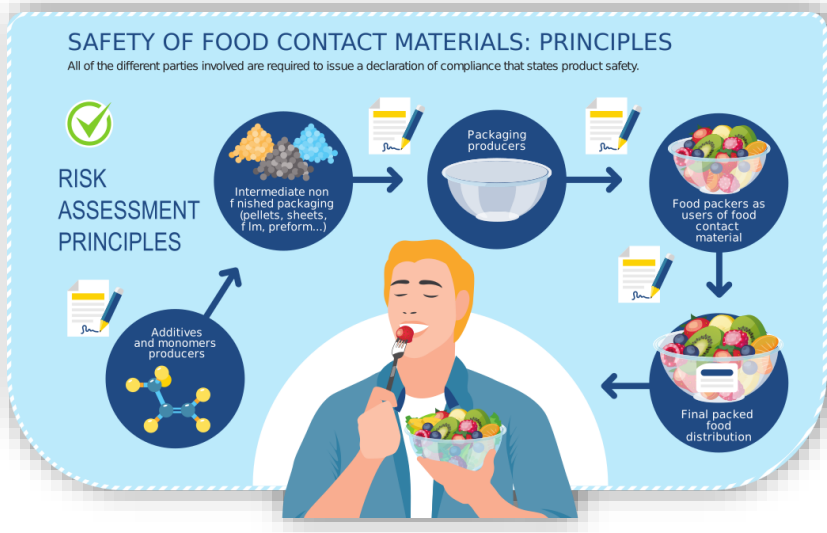


Is migration modeling a trusted science?

EU REGULATION
10/**2011**/EC on plastics



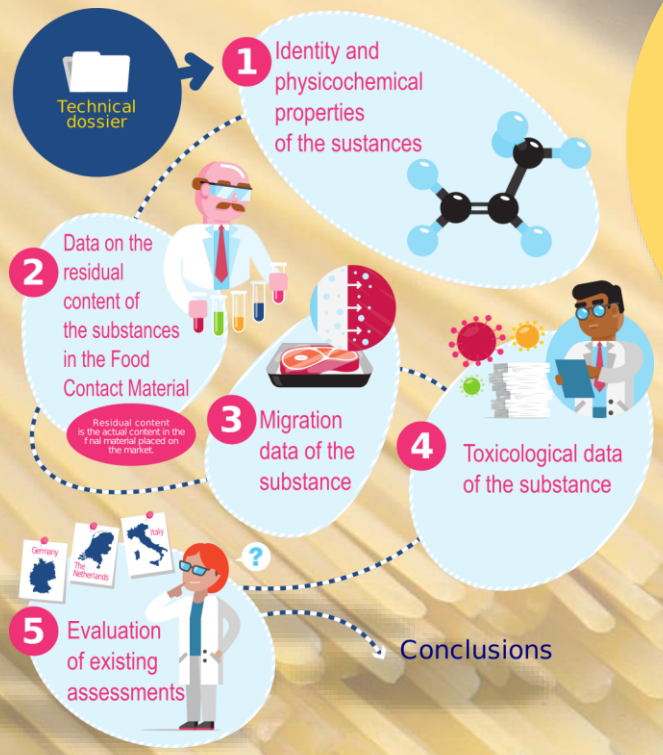
18 As migration testing is complex, costly and time consuming it should be admissible that compliance can be demonstrated also by calculations, including modelling, other analysis, and scientific evidence or reasoning if these render results which are at least as severe as the migration



FDA U.S. FOOD & DRUG ADMINISTRATION

"We have reviewed the proposed recycling process as well as the information you obtained from surrogate testing and migration modeling, which were submitted to demonstrate the capability of the proposed recycling process to remove potential contaminants from PCR-PET.
Based on our review of these data, we have determined that the proposed recycling process, as described in the subject submission, …."

https://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/RecycledPlastics/default.htm



> 60% of ingested Chemicals are coming from Packaging (exposome)

Compliance (contaminations) of 70% of plastics **tested by Modeling**

Contaminations **from non-plastic Materials not considered**

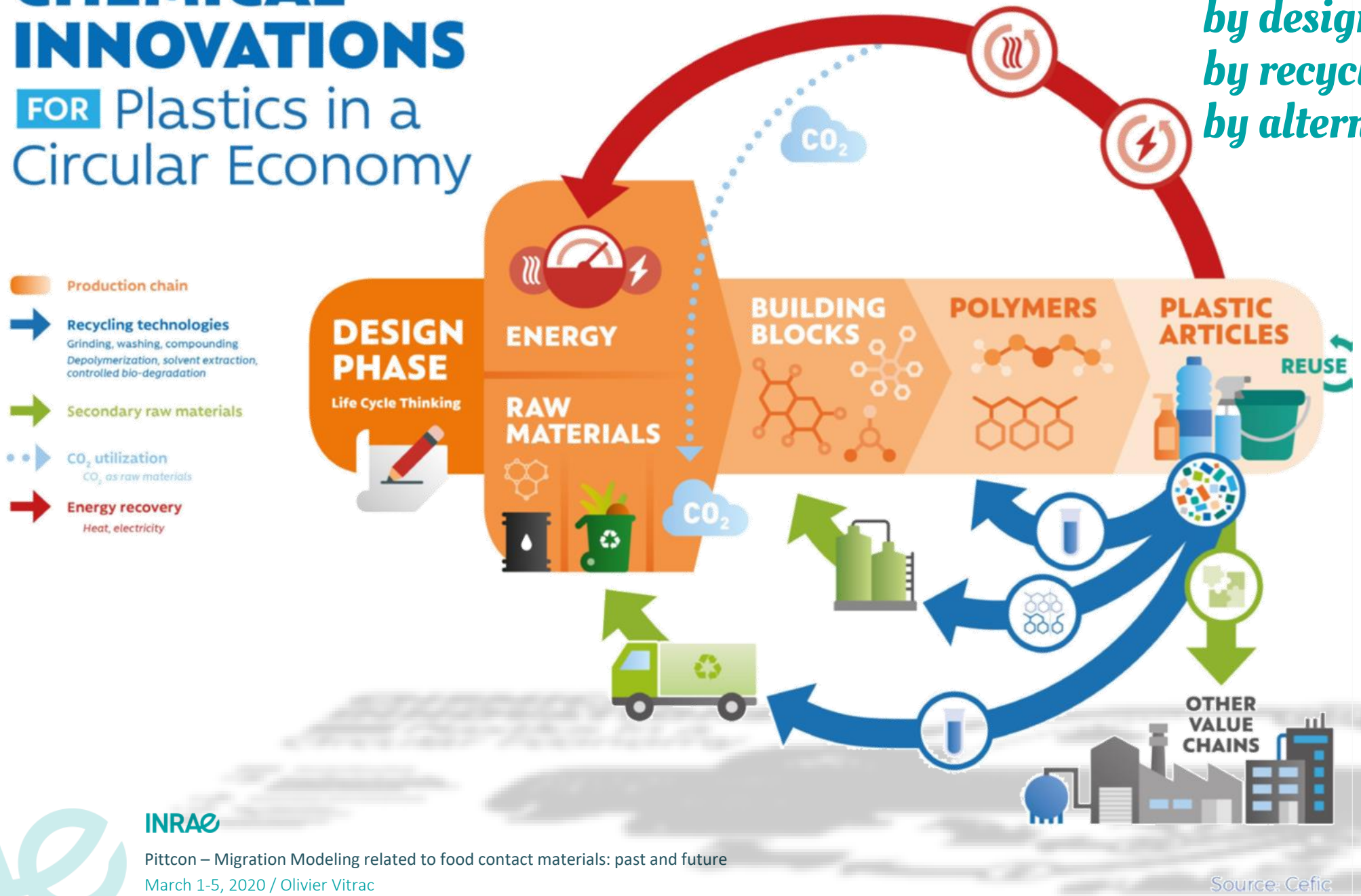
CIRCULAR ECONOMY vs **SAFETY**

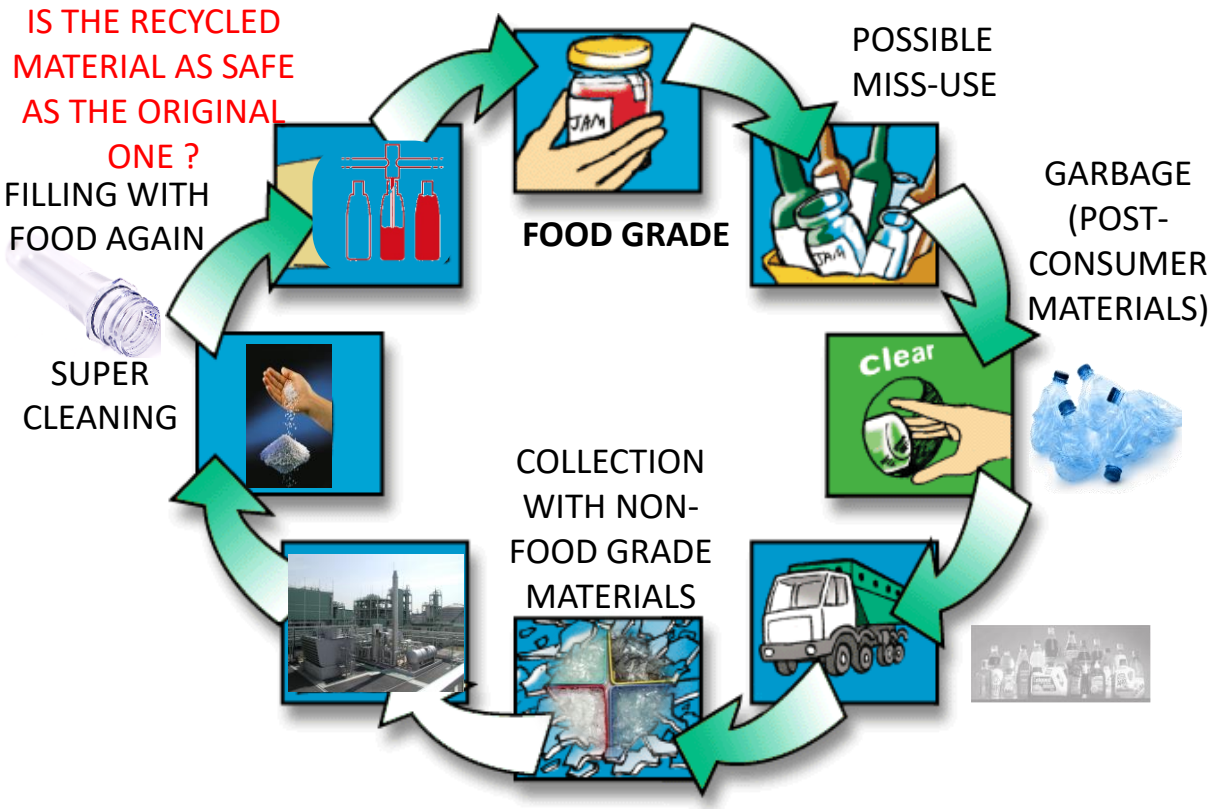
Food Packaging Forum

Workshop "Predicting the safety of food contact articles" - New science and digital opportunities
4 October 2018, Zurich, Switzerland
https://www.foodpackagingforum.org/events/predicting-the-safety-of-food-contact-articles-new-science-and-digital-opportunities

CHEMICAL INNOVATIONS FOR Plastics in a Circular Economy

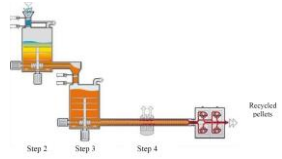
- Circularity
  - by design
  - by recycling
  - by alternative feedstocks





EFSA has issued upward of 140 positive scientific opinions on the safety of processes to recycle plastics for use in food contact material.

ONLY recycled PET is authorized in EU.



500 M€ have been invested in plants capable of converting recycled plastic materials into materials suitable for packaging and food contact applications

In 2014, more than 50% of the recycled PET in Europe was used in food contact applications.

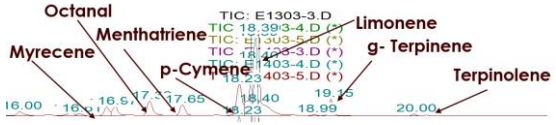
The lack of harmonisation amongst Member States generates legal uncertainty and unnecessary burden for the industry using recycled materials.

It also sets up obstacles for the Circular Economy

Recycling plastics for food contact

REGULATION 282/2008/EC

Misuse issues (post-use contaminations) of Polyethylene terephthalate **(PET)** can be easily handled : glassy polymer, it is mainly contaminated by small contaminants which can be removed by a devolatilization step above T_g



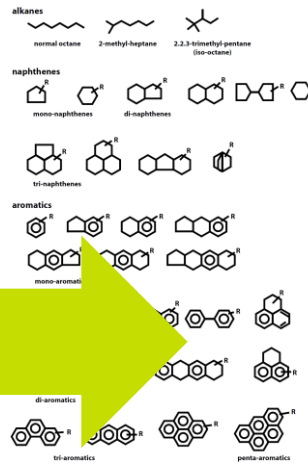
1. Filling and use of HDPE milk bottles
2. Recollection
3. Sorting

Foodgrade HDPE milk bottles

Suitable for Food Contact?

Recycling

Polyolefins are rubber polymers which can be easily contaminated by high molecular weight contaminants after use.



Paper and board contains large amount of residues from printing inks: aromatic (carcinogenic) and aliphatic **mineral oils** can be transferred without contact and lead to cross-contamination between materials

*J. of Chromatography A. 2013;**1293:107-19.***

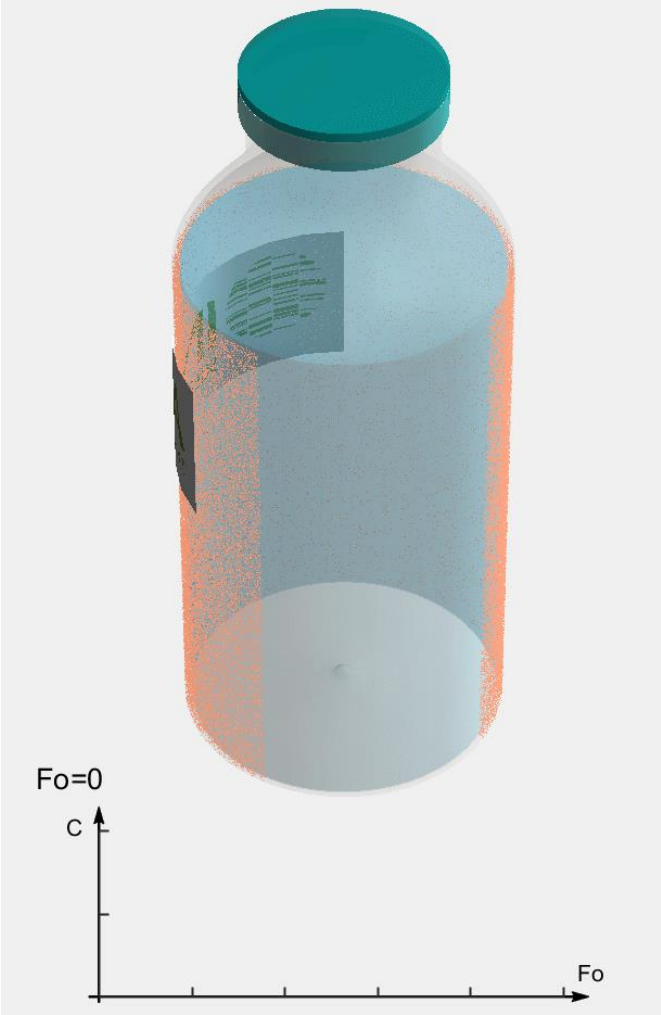
Recycling of PET vs other materials

Recycled PET for food contact is authorized (282/2008/EC)
Recycled polyolefins are authorized only in Germany
Recycled paper and boards is source of recurring crises in EU.

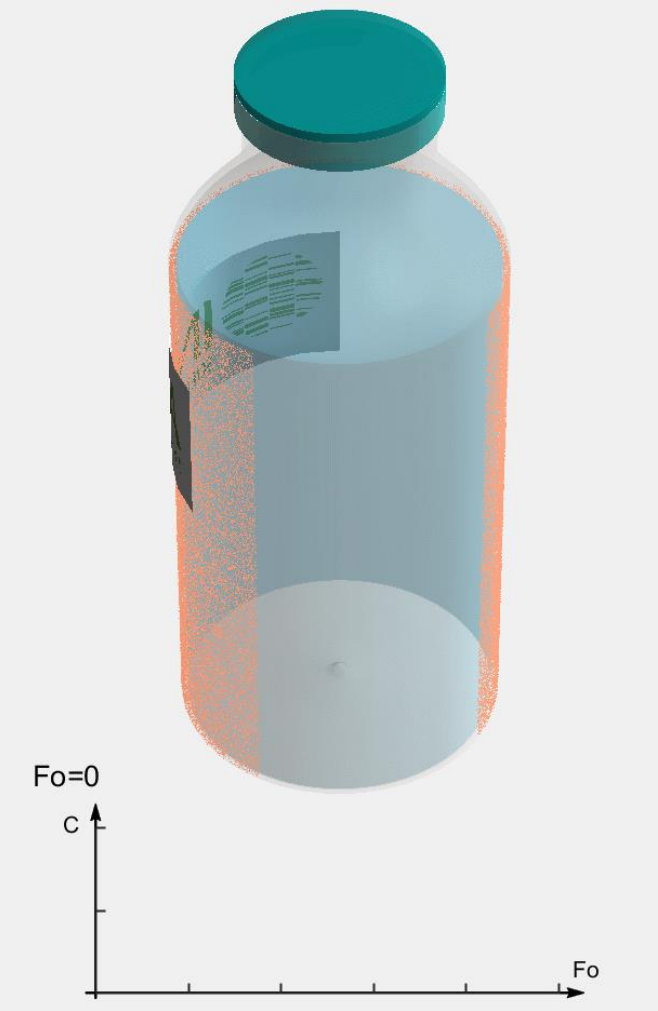
What is migration modeling and how to use it?

$Fo = \frac{D_P t}{l_P^2}$ =dimensionless time; D_P: diffusion coefficient; $K_{i,F/P} = \frac{C_{i,F}^{eq}}{C_{i,P}^{eq}}$: partition coefficient

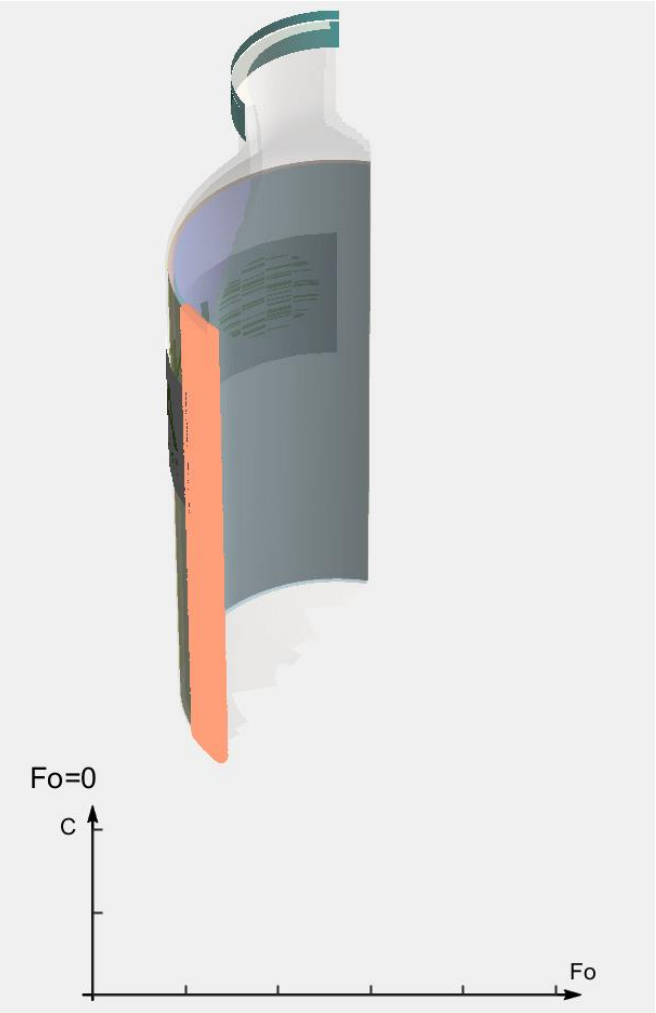
monolayer



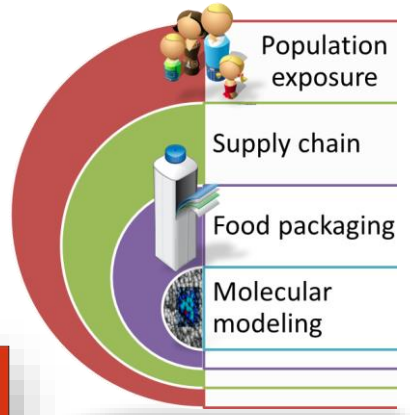
with barrier to diffusion

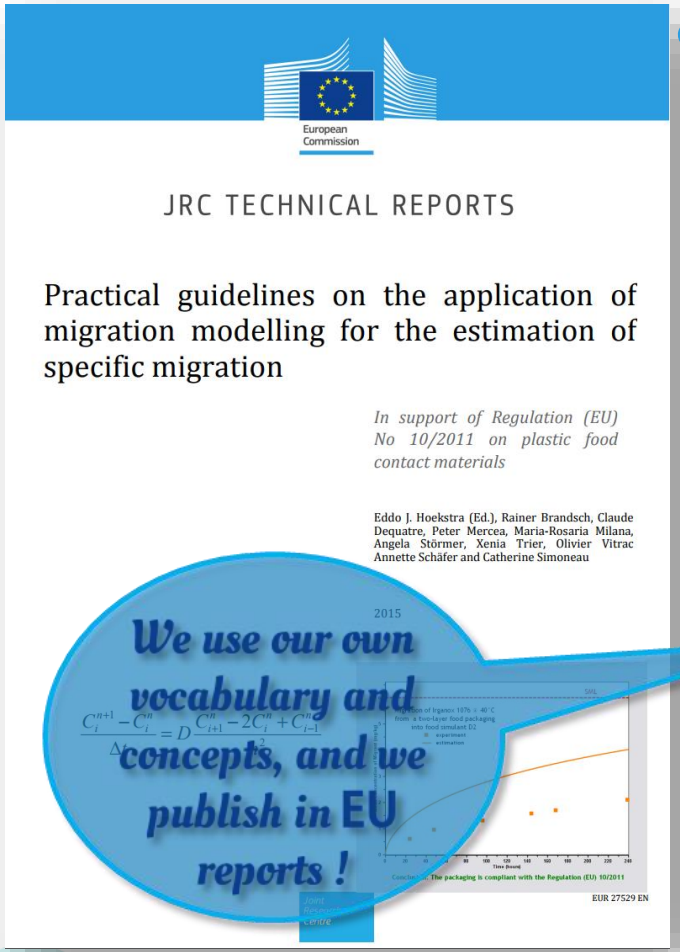


multilayer



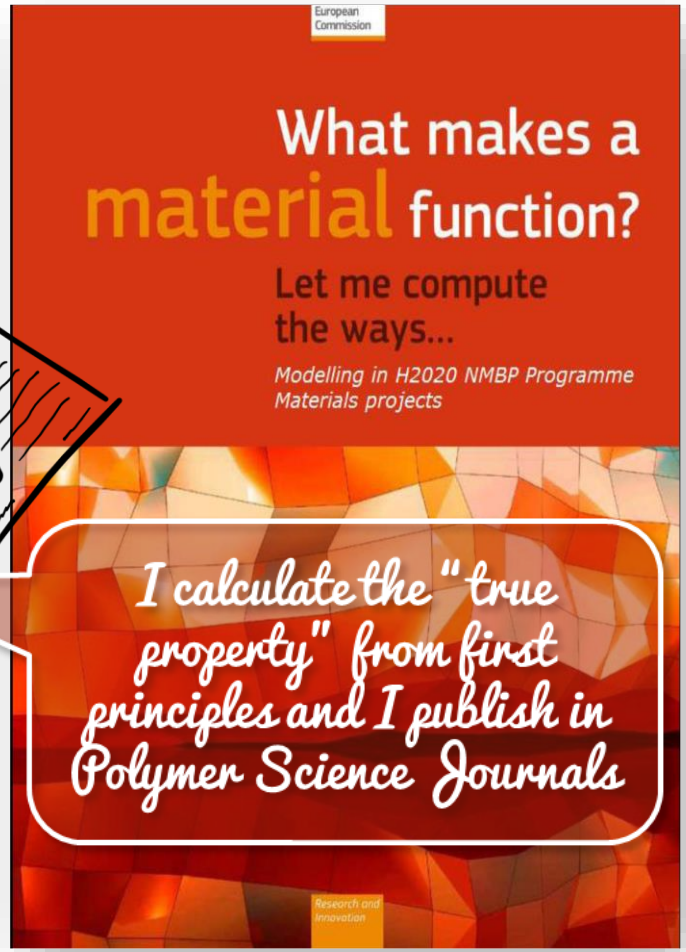
Is migration modeling a trusted science?





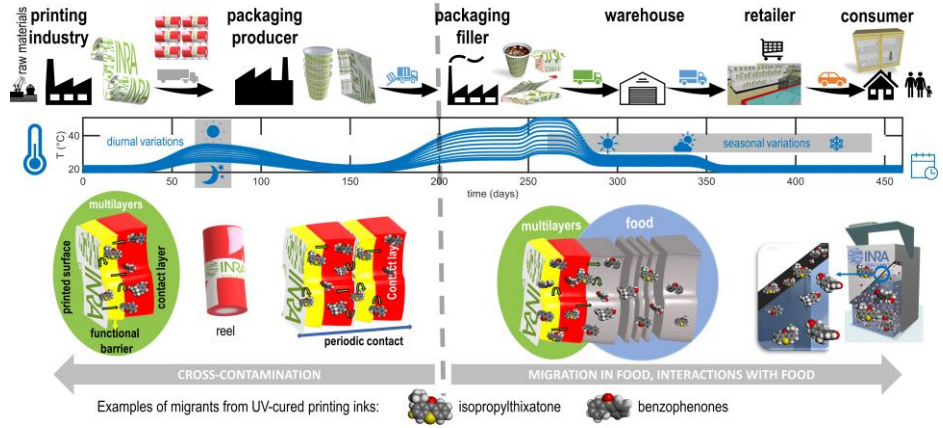
http://publications.jrc.ec.europa.eu/repository/handle/JRC98028

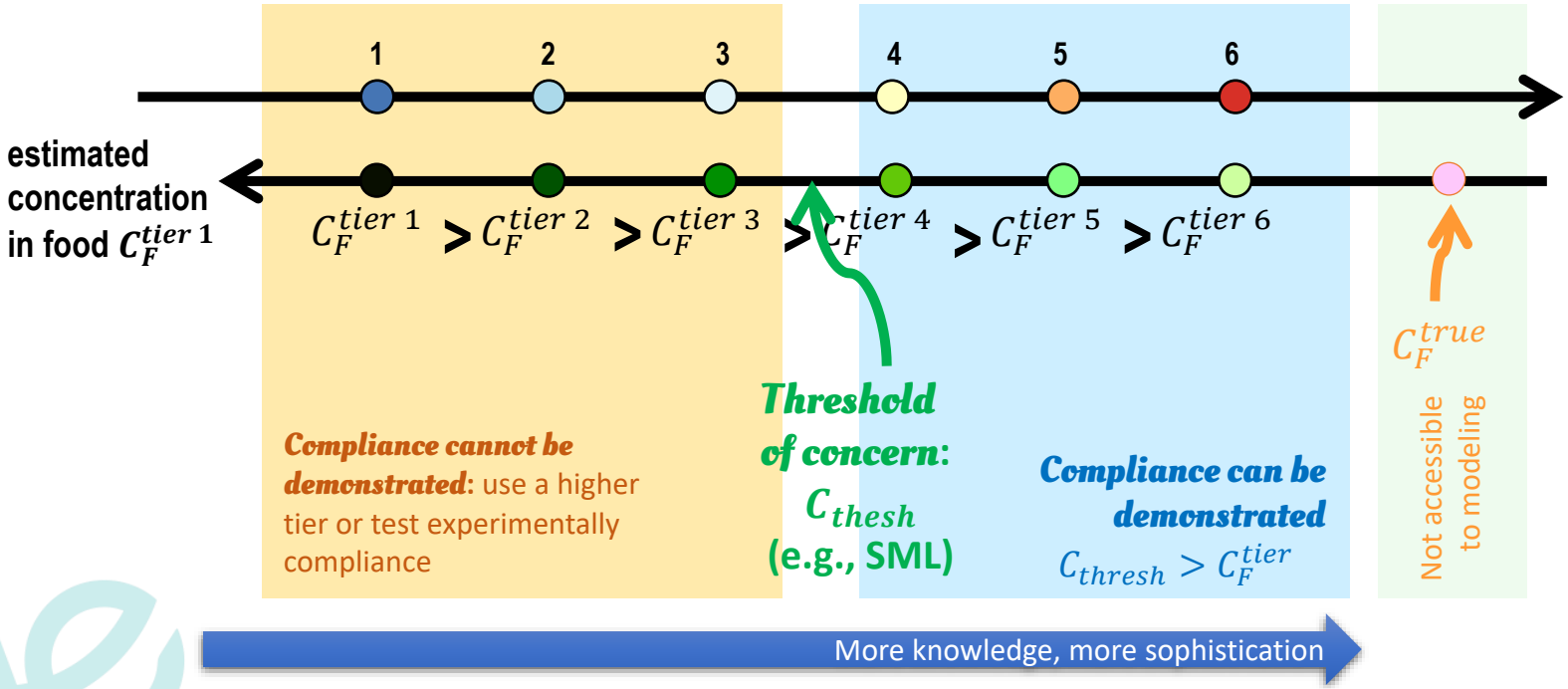
https://publications.europa.eu/en/publication-detail/-/publication/e0845ae1-1b60-11e7-aeb3-01aa75ed71a1

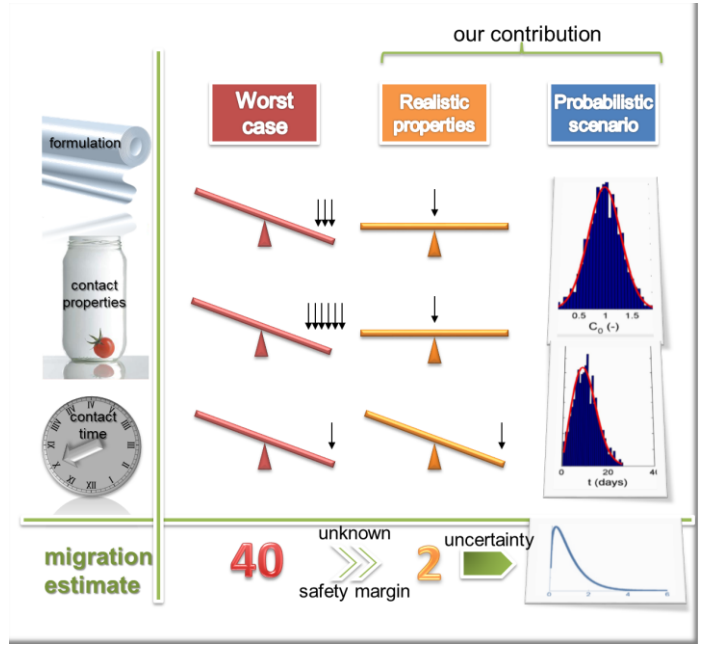


The principles of migration modeling = Tier modeling

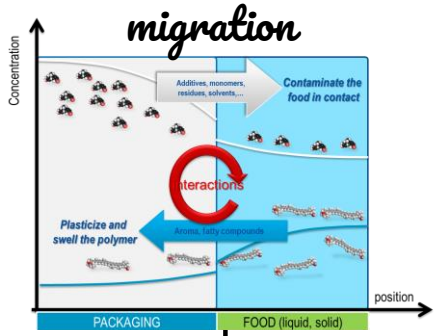
- ***conservatism***: modeling overestimates real migration.
- ***reliability***: mass transfer pathways and substances obey to well-described mechanisms
- ***consistency***: $D_{i,P}$ and $K_{i,F/P}$ are enough known with enough conservatism.
- ***parsimony***: sophisticated and refined scenarios should be considered only when simplified ones fail.
- ***proportionality***: non-compliance cannot be demonstrated by calculation.







Migration pathways where modeling is applied



direct contact

without contact

without food

with food

paper & board

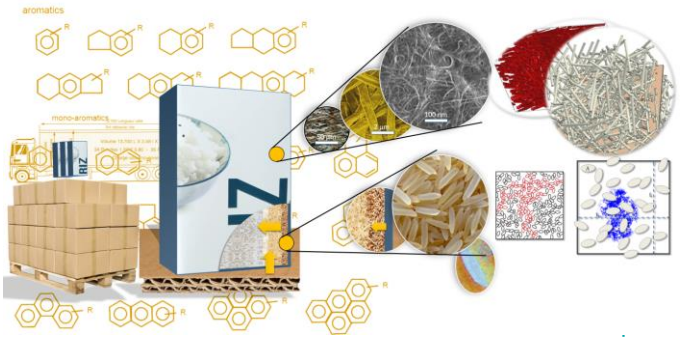
others

heat curing

UV curing

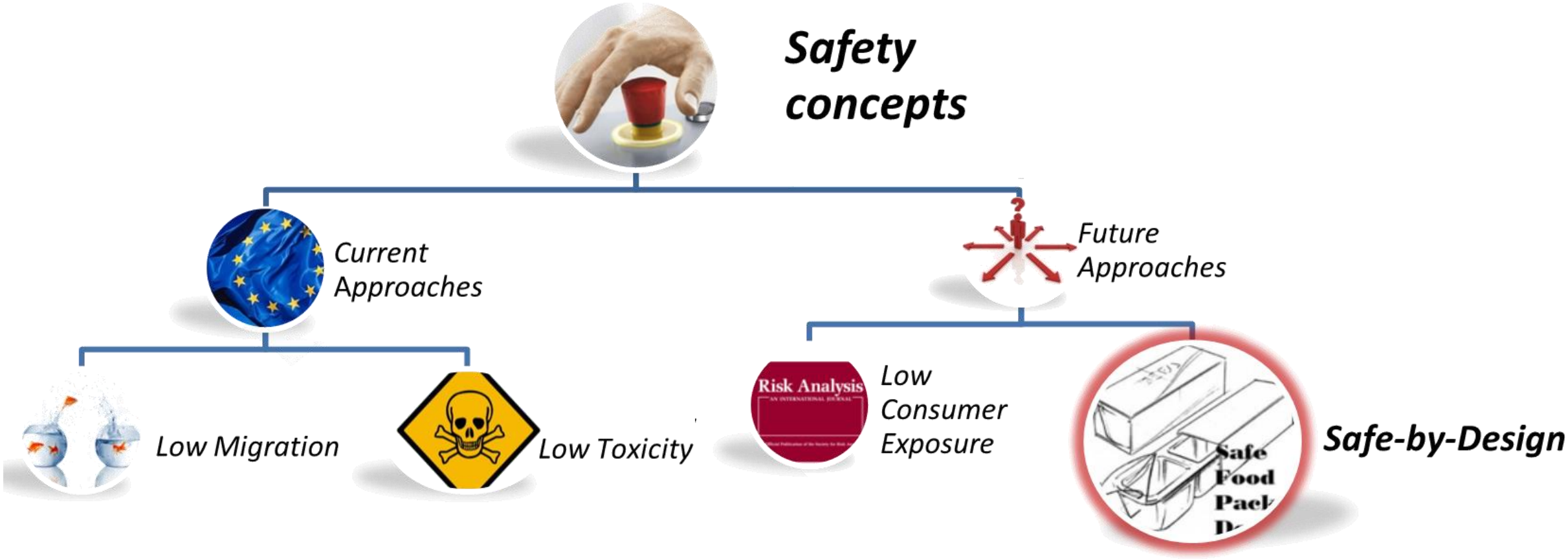
liquid

solid



Preventive approaches

From preventive approaching to integrated engineering

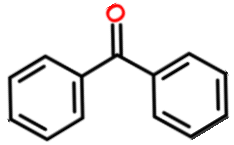


Regulation EC 2023/2006 - Good Manufacturing Practice for materials and articles intended to come in contact with food

+Voluntary approaches & local ordinances

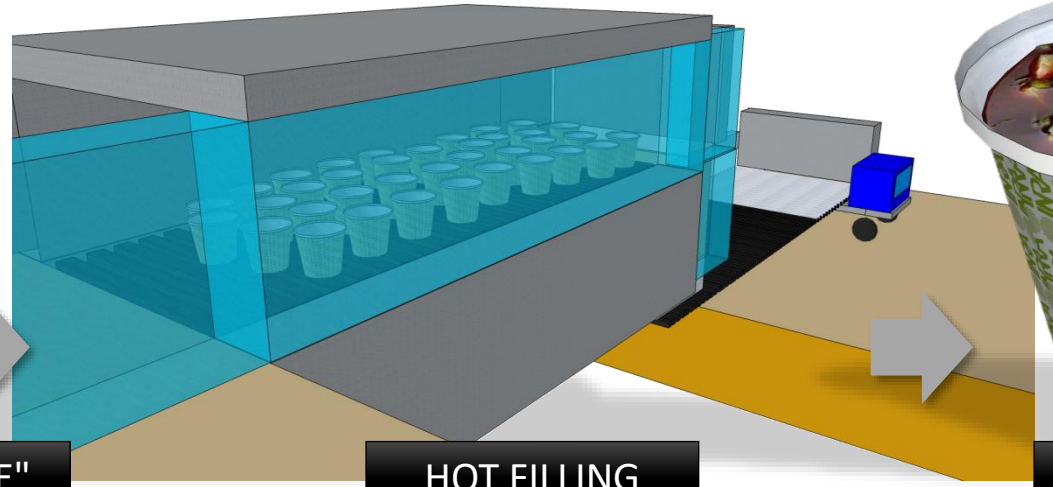
Our recommendations

CHAINED STEPS: where is the critical step?



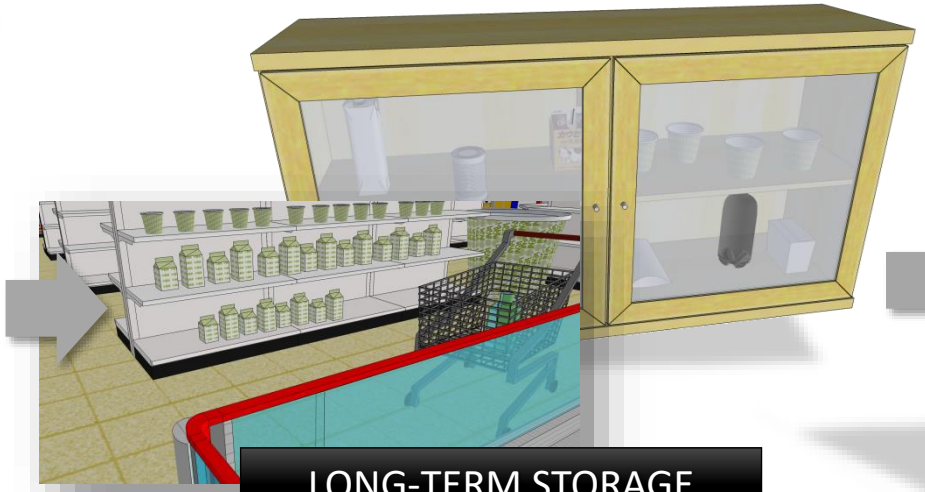
Risk of contamination by a photoiniator in UV-curing printing ink

STORAGE "BEFORE USE"



HOT FILLING

FATTY CONTACT

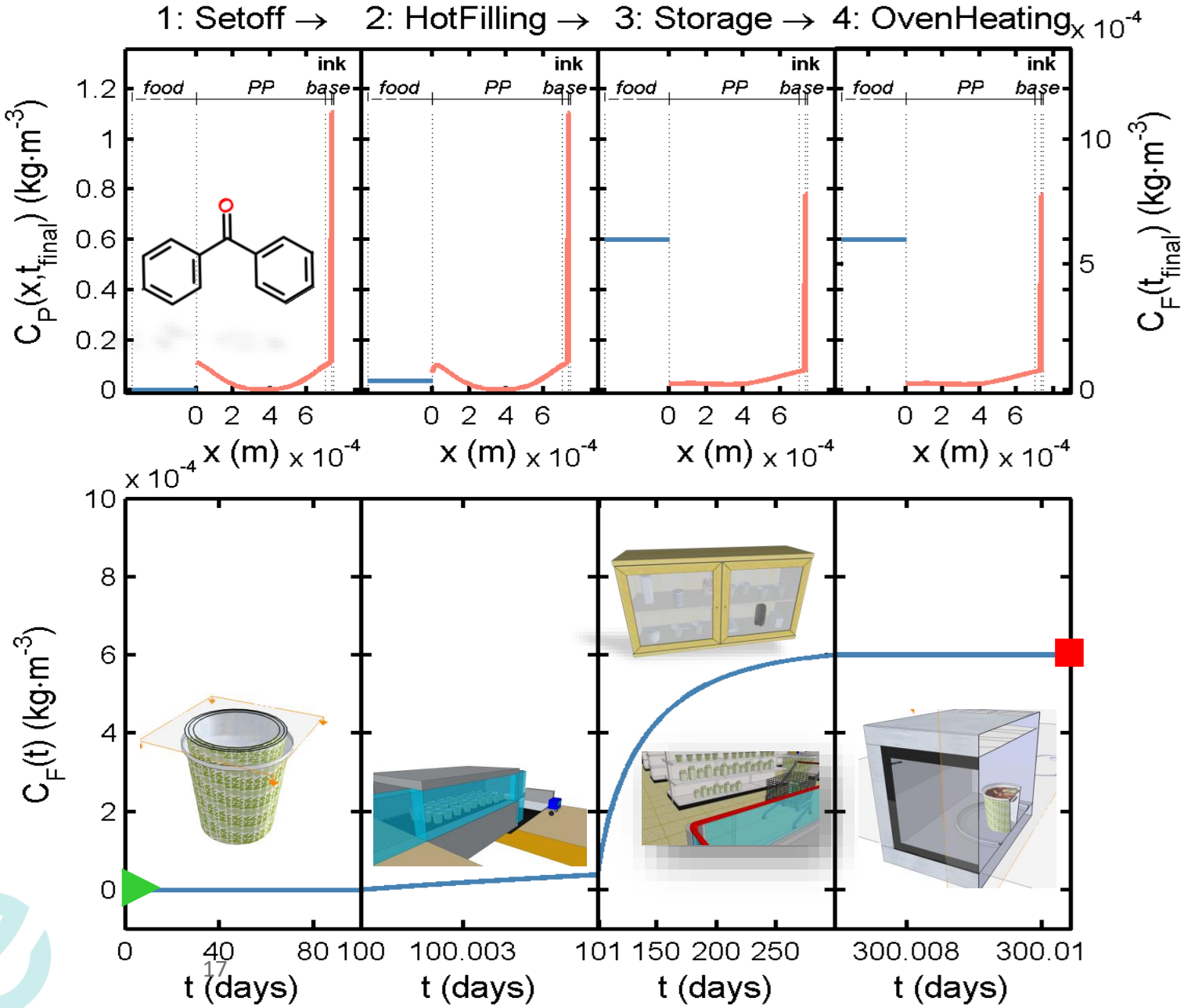


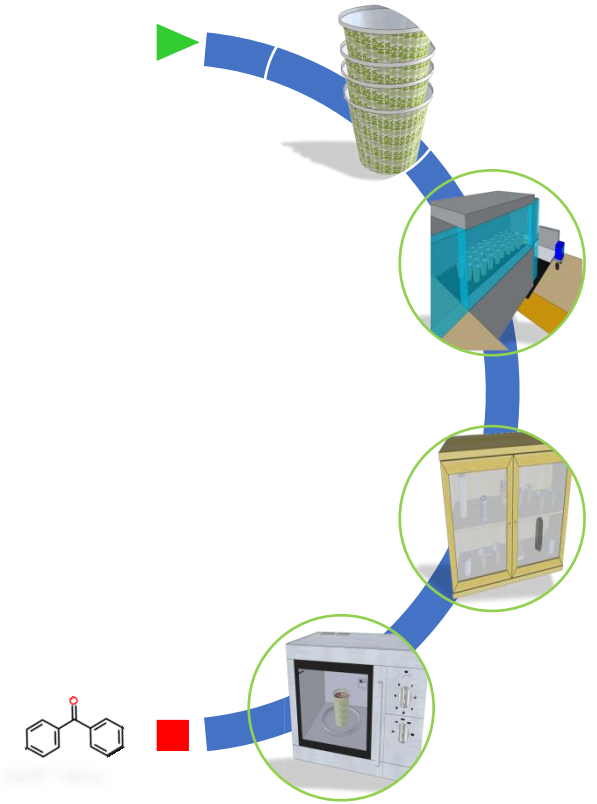
LONG-TERM STORAGE

MICROWAVE OVEN HEATING

CHAINED STEPS

UV-curing printing ink

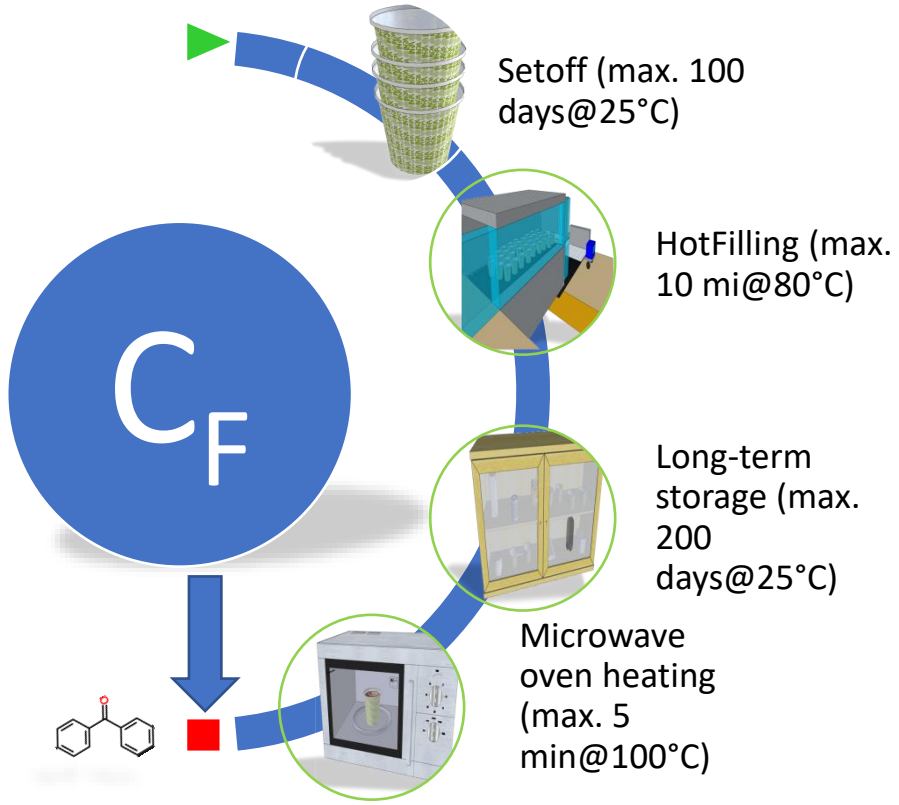


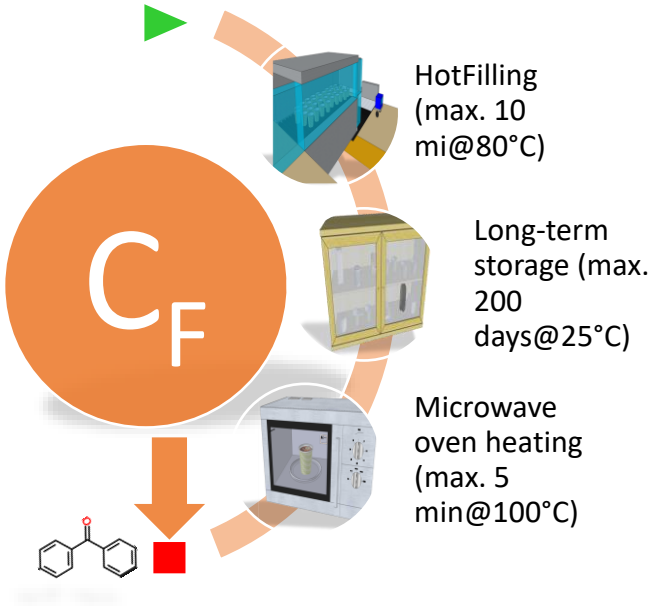


ASSESSING THE SEVERITY OF A SINGLE STEP

CASE OF "SETOFF" STEP

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





comparison with step i alone

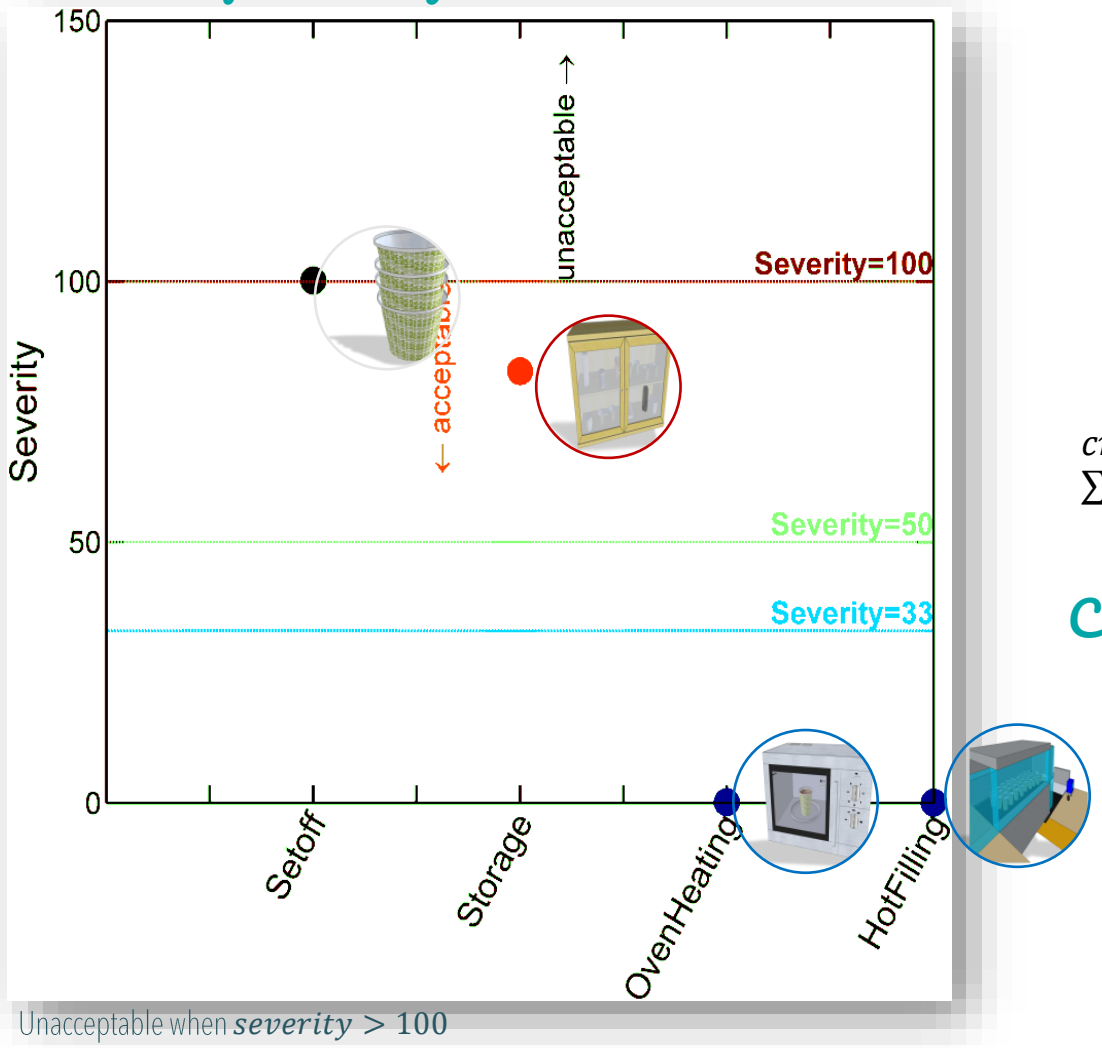
$$\text{Severity}\left(\hat{C}_F(step\,i)\right) = f\left(\max\left(C_{F_M}|_{1\to2\to\cdots\to M} - C_{F_M}|_{1\to2\to\cdots\to M/i}, C_{F_i}|_i\right)\right)$$

comparison with step i removed

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

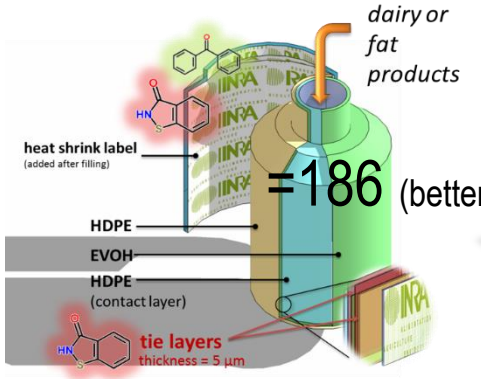
$$severity = 100 \times \frac{C_F}{SML}$$

Critical step (severity scale)



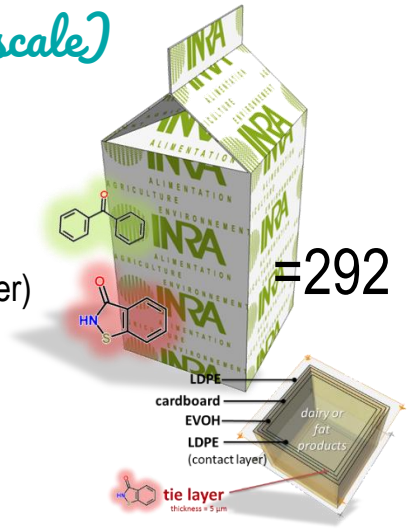
Unacceptable when $severity > 100$

Concurrent design (criticality scale)



=186 (better)

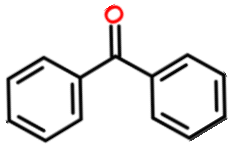
tie layer = EVA



=292

$$criticality = \sum_{all\ components} \sum_{all\ substances} \sum_{all\ modalities} pr(modality) \times severity$$

Critical substance



=115
(almost acceptable)

=124

Failure Mode Effects and Criticality Analysis

Collaborative research project SAFEFOODPACK DESIGN

FMECA « milk for infants stored in a brick »					
Phase	Formulation	Design	Process	Informations	Mechanisms
Inventaire	Formulation	design	Process	Informations	Described mechanisms
Inventaire	• monomers (plastics, adhesives) • catalysts • antioxidants • lubricants • biocides (cardboard, ink) • mineral oil (cardboard) • solvents • photoinitiators • other residus (NIAS)	**two components**: • brick body (4 materials, 5 layers) • cap (two materials incl. the sealing system) **six materials** • LDPE, PP (cap) • aluminum foil • cardboard (origin) • « ink » • « adhesives »	• production, storage, assembly of materials • assembly and storage of components • printing (printing technology, curing/drying….) • storage of empty packaging • aseptic packaging filling (temperature, pretreatment…) • storage and retailing of the bricks filled with milk • conditions of use or storage by the consumer/end-user: chilled, ambient, oven heating? • Consumption-type (bottle feed with direct contact between the mouth and the neck…)	• identity and nature of **materials** in assemblies • **formulation** of materials (substances specifically regulated or not) • **test conditions** used to evaluate the risk of contamination • **conditions of preparation, packaging filling, storage, consumption** of packaged food • communication of **revisions and modifications** in la formulation, design, process and in the final use	• diffusion across layers • set-off • cross-contamination between materials and with the storage ambience • effects of poor drying and curing on printing inks
Hiérarchisation	**Highly concentrated** • antioxidants, lubricants, biocides • mineral oils, photoinitiators • monomers, catalysts, solvents • other residues	**Barrier material** • aluminum foil **Materials acting as reservoir of low molecular weight contaminants** • ink • adhesive **Materials acting as reservoir of high molecular weight of contaminants** • PP, LDPE • paper and board	**steps associated to long-time contact** • storage of materials • storage of components • storage of finished products **steps associated to high temperatures** • aseptic filling • oven heating **steps which may lead to cross-contamination** • storage • printing • assembling / laminating	• **non-documented** or missing information • **accessible information** • **documented** information, which follow each component and materials • **verifiable and auditable information** • **frequency of update** of information : regular, when a change occur, only when the design is modified,...	• mass transfer, which can be **evaluated rapidly from calculations**: from, trough LDPE, PP layers • mass transfer, which can be tested experimentally in a simple manner : set-off • mass transfer, which require a **depth expertise**: cross-contamination, aging

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

Contamination without contact

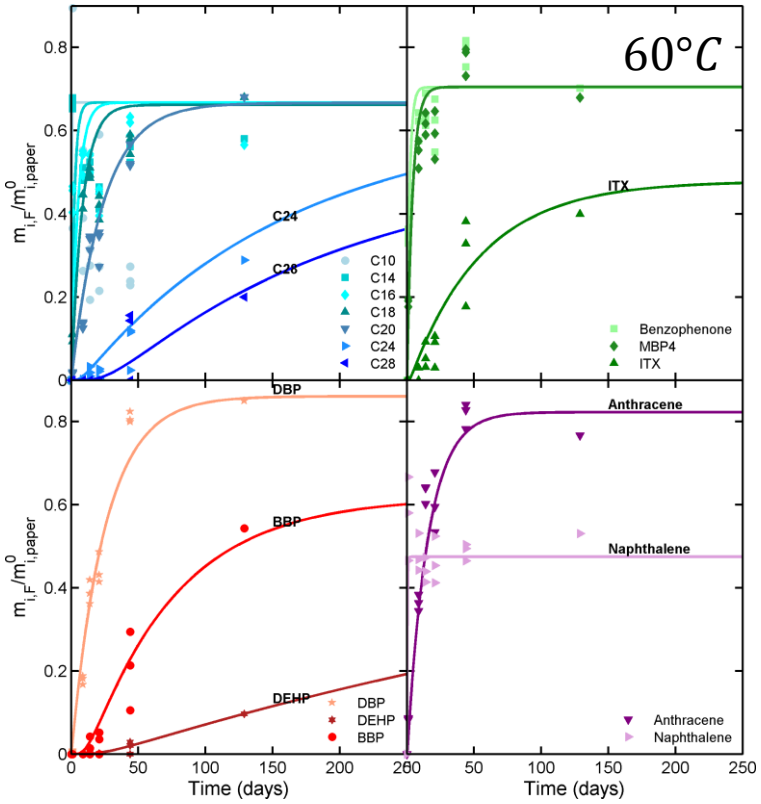
Cross-contamination=Main of NIAS and new (old) routes of contamination

old routes but new issues

CONTAMINATION THROUGH THE GAS PHASE

TENAX packed within a 50 µm thick BOPP bag and exposed to a cardboard material formulated with 15 surrogates

SURROGATES (*i*)
Decane (C10)
Tetradecane (C14)
Hexadecane (C16)
Octadecane (C18)
Eicosane (C20)
Tetracosane (C24)
Octacosane (C28)
Dibutyl phthalate (DBP)
Bis(2-ethylhexyl) phthalate (DEHP)
Benzylbutyl phthalate (BBP)
Benzophenone
4-methyl benzophenone (MBP4)
Isopropyl-9H-thioxanthen-9-one
Anthracene
Naphthalene



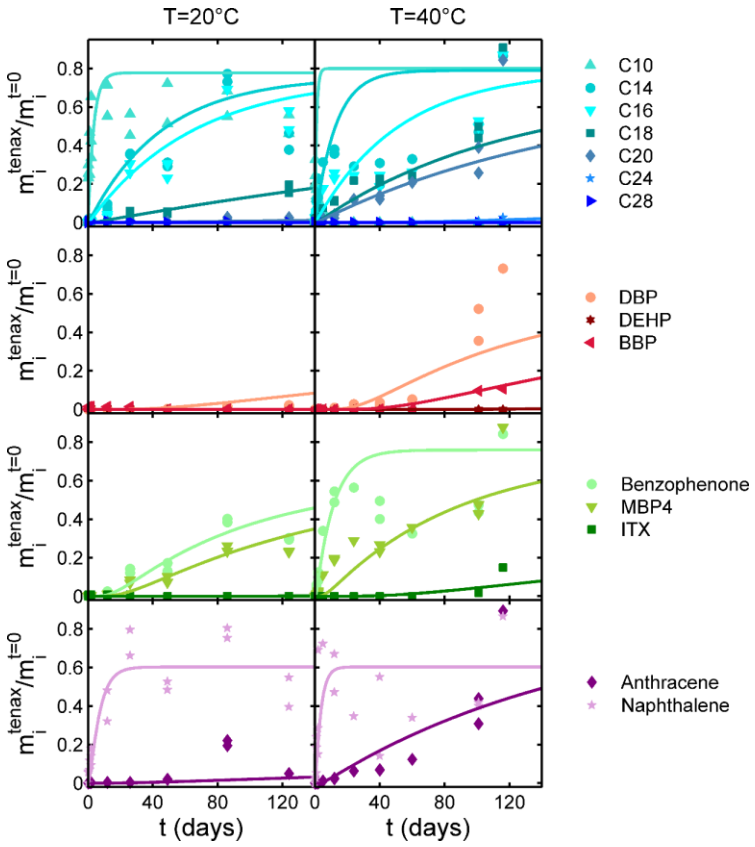
$$\frac{m_{i,F}^{(t)}}{m_{i,P}^{0}} = \frac{V_F}{m_{i,P}^{0}} \int_0^t C_{i,F}^{(t)}\, d\tau$$

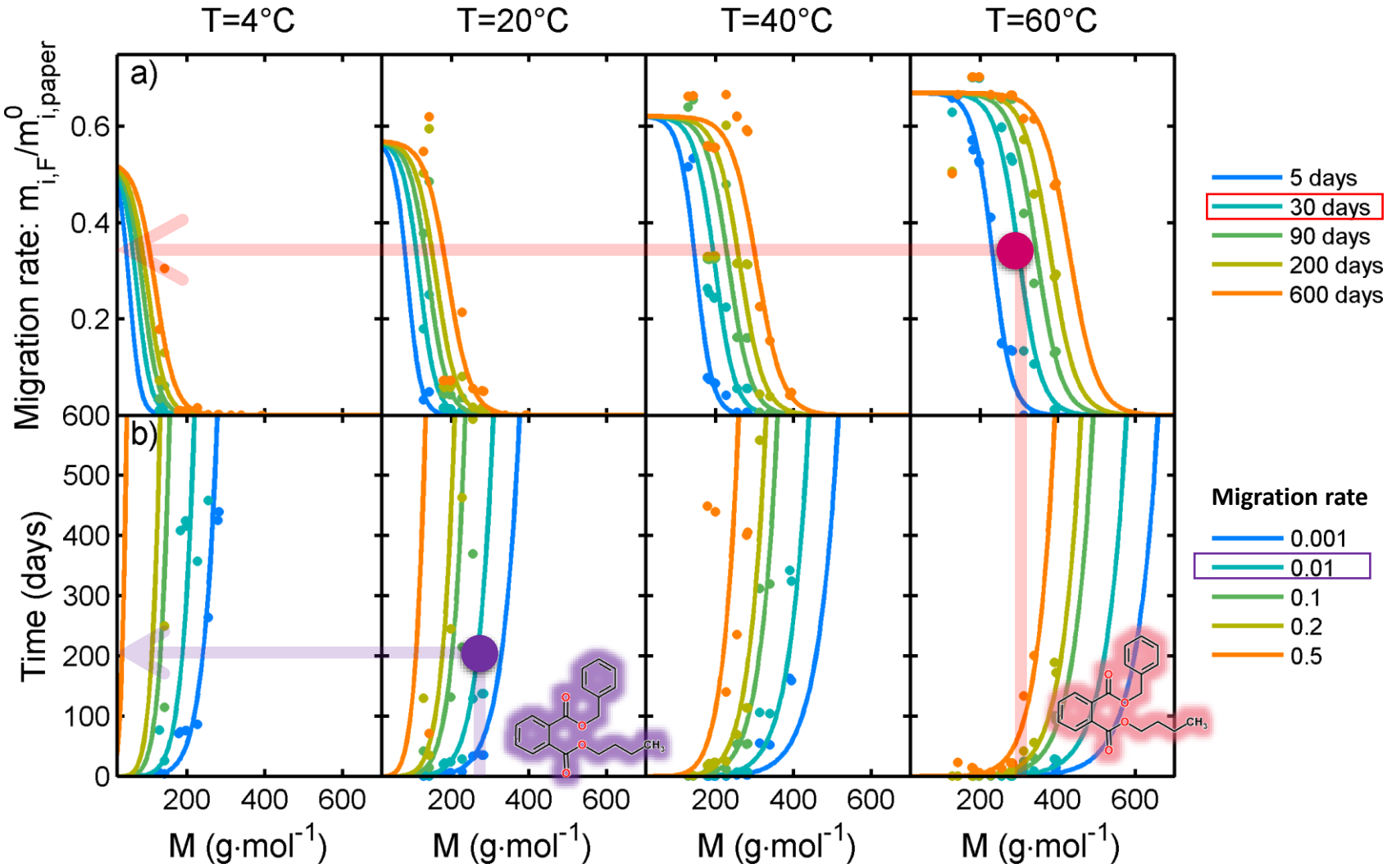
Experimental results at **60°C**, *i*=1…15 → **Detailed modeling** with FMECAengine → $\widehat{C_F}(T, t, i)$ ***i* = 1..15 solutes at any temperature** → **Simplified modeling** Solute independent → $\widetilde{C_F}(T, t, M)$ **simplified at any temperature**

Food Additives and Contaminants. 2017;34:1703-20.

CONTAMINATION TROUGH THE GAS PHASE

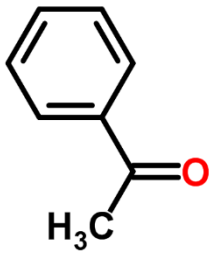
TENAX packed within a 50 µm thick BOPP bag and exposed to a cardboard material formulated with 15 surrogates



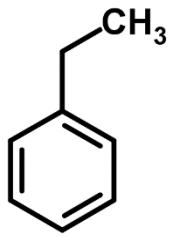


Food Additives and Contaminants. 2017;34:1703-20.

PARTITION COEFFICIENTS WITH AIR




```
>> 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
```

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>> 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 =
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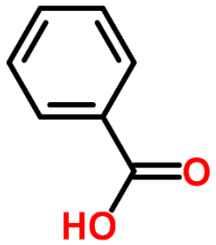
```

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>> FMECAKairP 'benzoic acid'
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LOAD_CHEMISPIDER: updated cache
       238.mat21-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
```
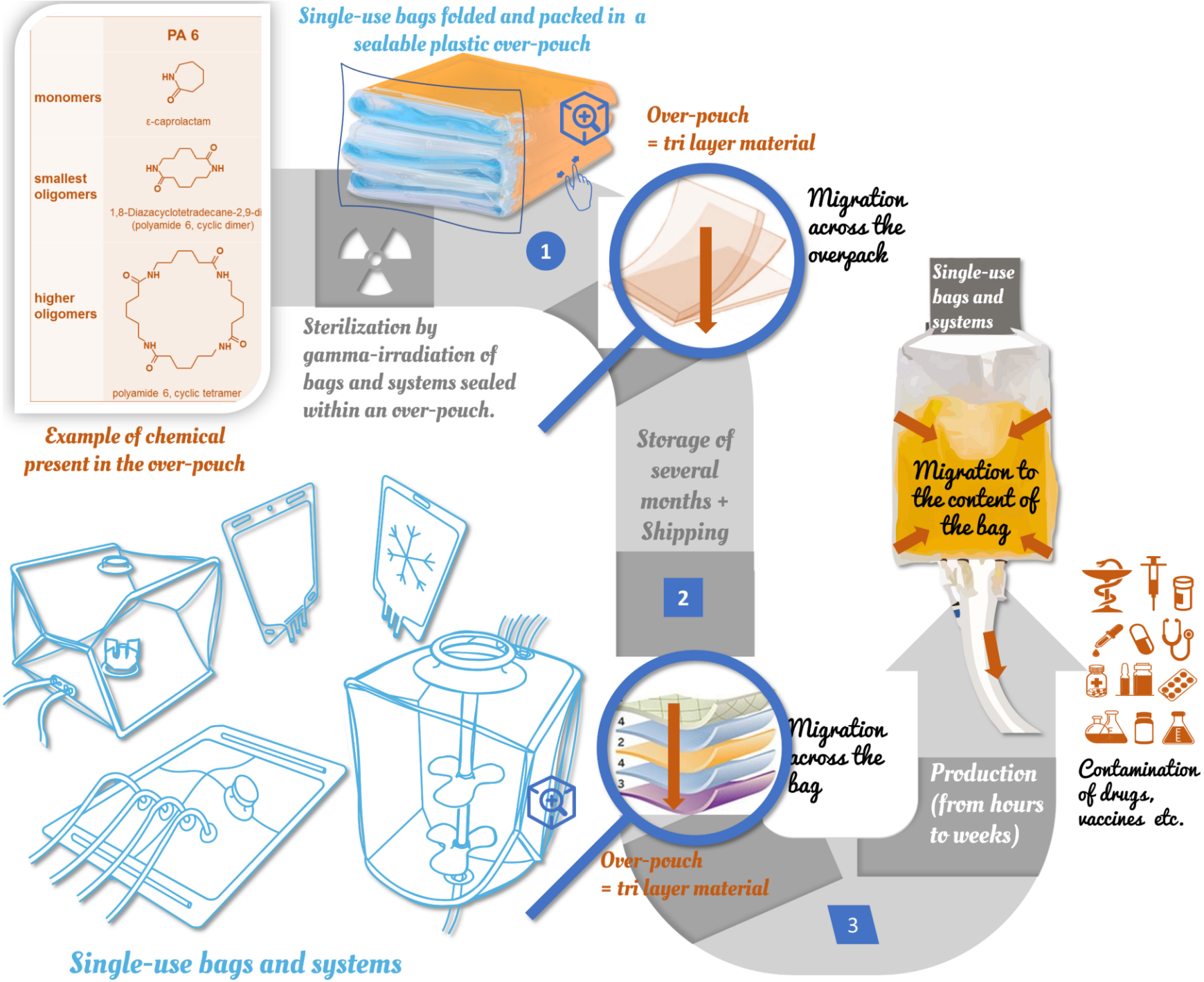
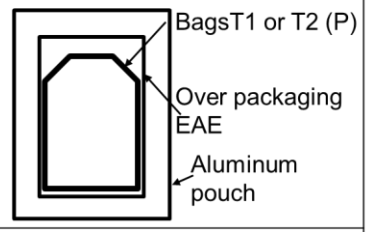

Food Additives and Contaminants 2017, 34 (10), 1703-1720
AIChE Journal 2013, 59, 1183-1212
https://github.com/ovitrac/FMECAengine

Cross-contamination in biotechnological applications



STEP 1
STUDY
"LOADING"



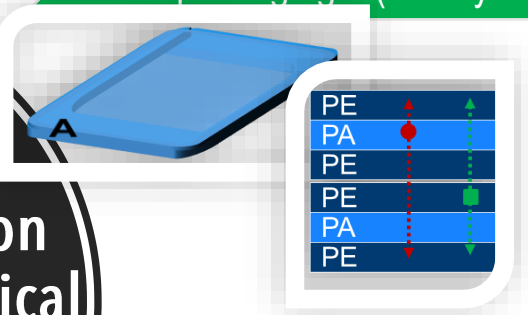
Cross-contamination in biotechnological applications

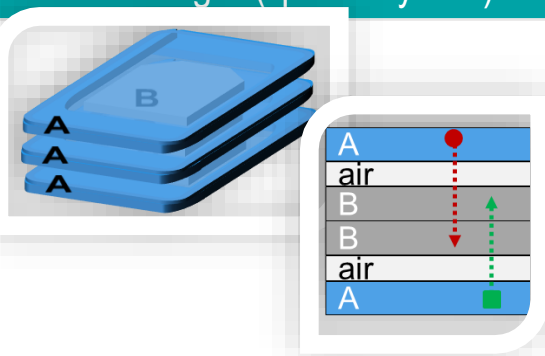
OUR SCOPE

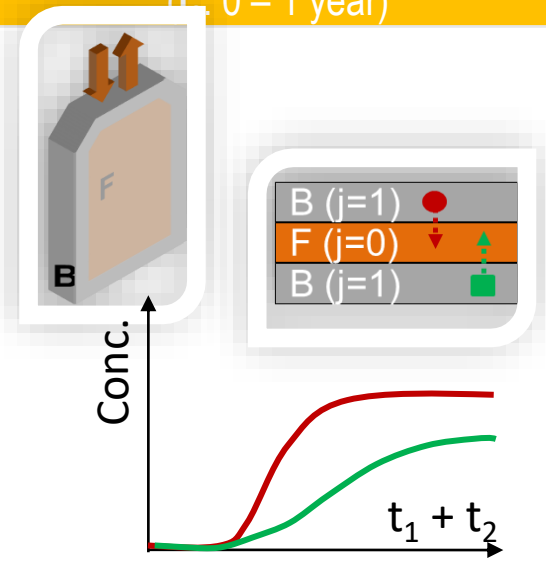
Storage before use of over-packaging A (0 – 1 year)

Storage of over-packaging A and bag B (t_1: 0 – 3 years)

Use of bag B with a liquid F (t_2: 0 – 1 year)





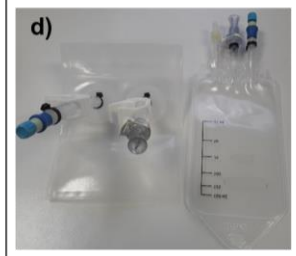


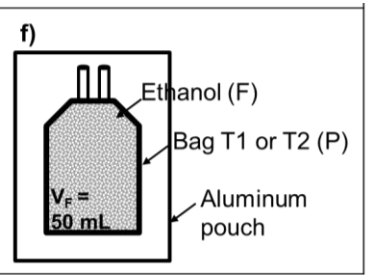
Redistribution of contaminant within the over-packaging

Cross-transfer between over-packaging and bag

Cross-transfer between bag and liquid in use

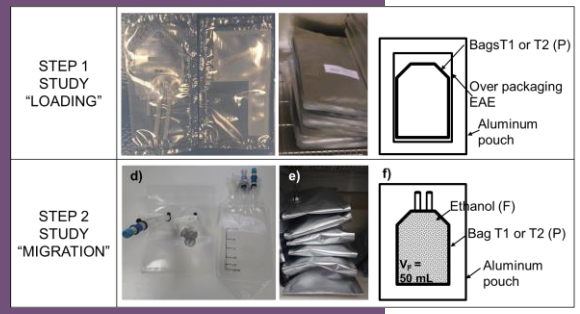
STEP 2
STUDY
"MIGRATION"

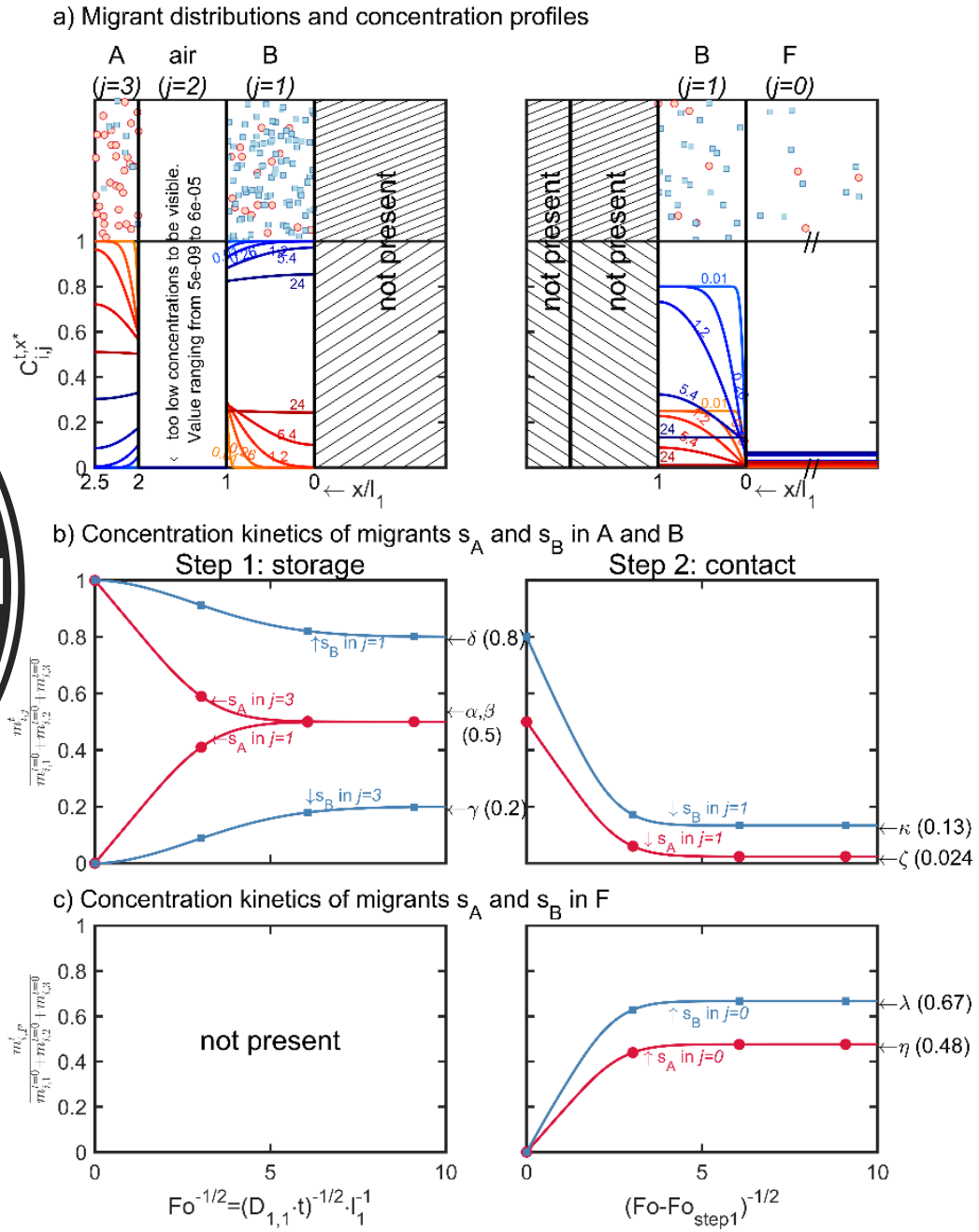


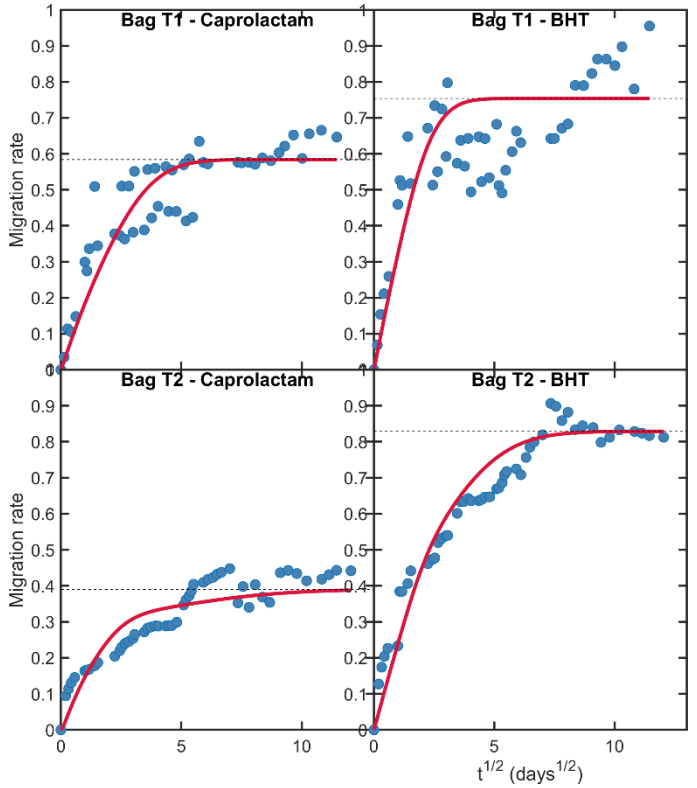


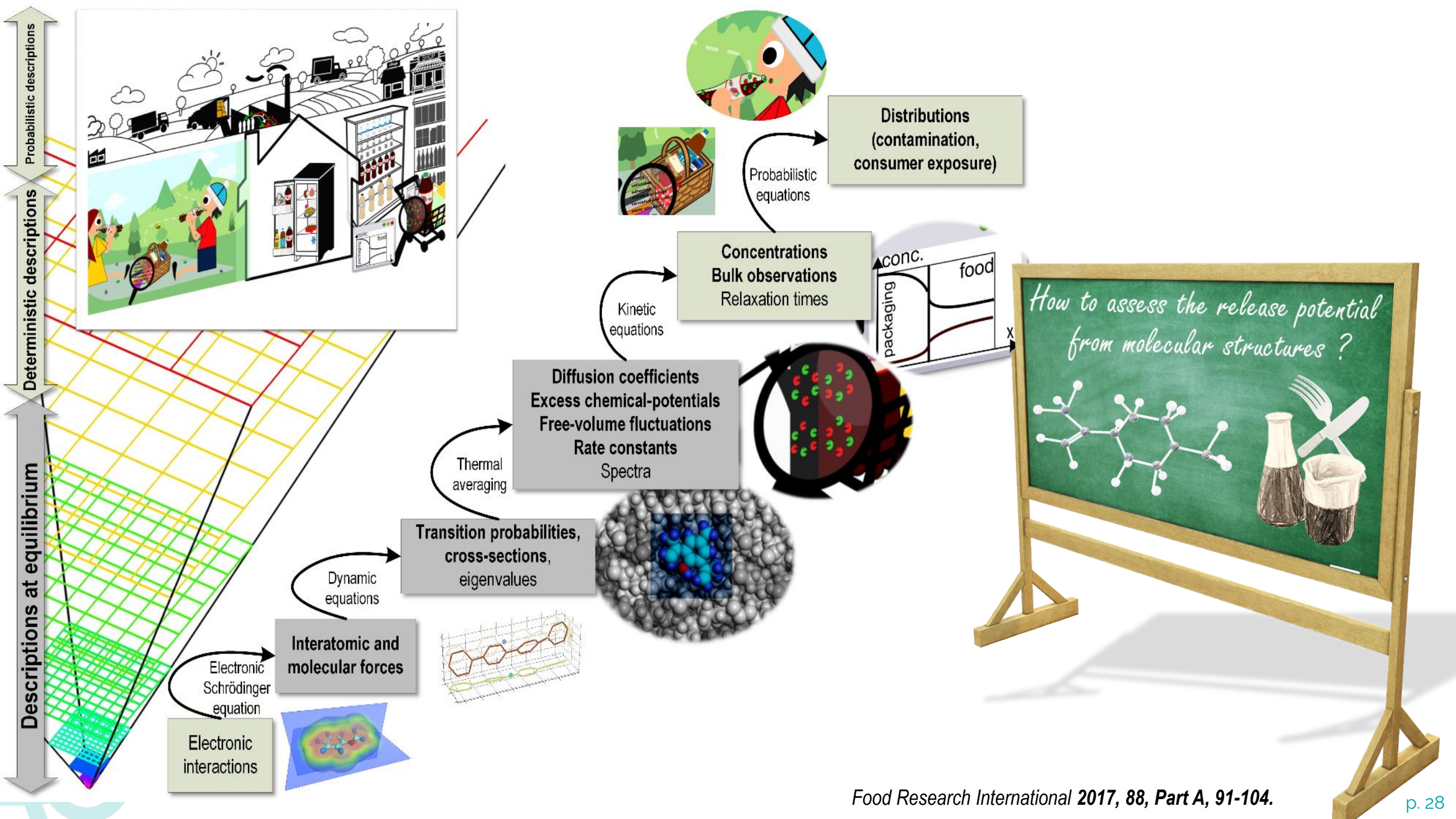
Nguyen P-M, Dorey S, Vitrac O. The Ubiquitous Issue of Cross-Mass Transfer: Applications to Single-Use Systems. *Molecules. 2019;24:3467.*

Cross-contamination in biotechnological applications





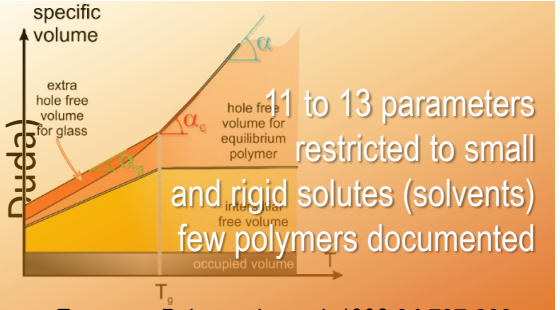
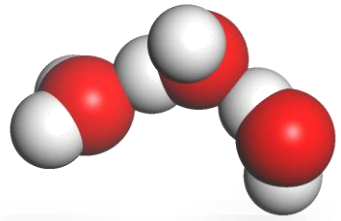
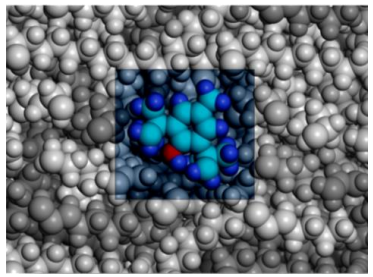
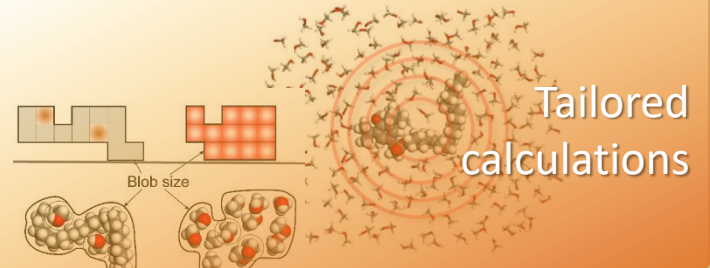


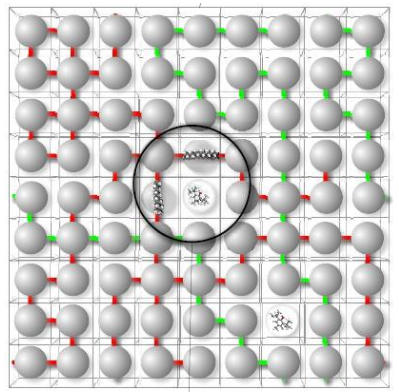


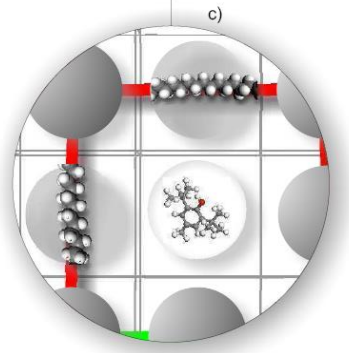
Food Research International ***2017, 88, Part A, 91-104.***

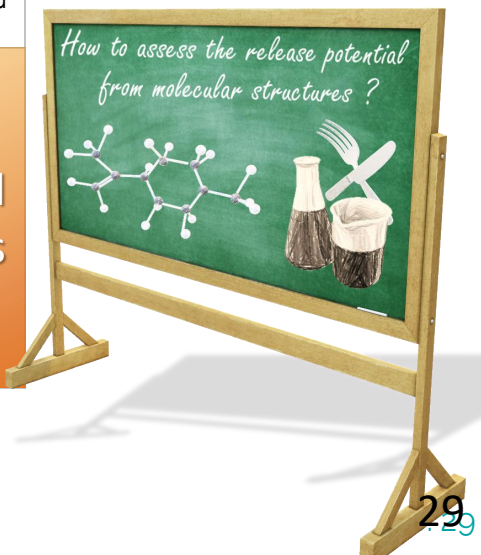
coarse

detailed

	TRANSPORT diffusion coefficients D and their activation E_a	THERMODYNAMICS chemical affinity (Flory-type isotherms)
Worst-case approaches (arbitrary)	For compliance testing (Piringer's equation) *Food Additives and Contaminants. 2005;**22:73-90.***	$K_{F/P} = 1\ or\ 10^{-3}$ JRC Scientific and Technical Reports EUR 27529 EN. Ispra (Italy): European Commission; 2015.
Group contribution methods (fitting)	Decision tree *Journal of Applied Polymer Science. 2006;**101:2167-86.***	UNIQUAC, UNIFAC, Flory—Huggins Prausnitz, Lichtenthaler & de Azevedo. Molecular Thermodynamics of Fluid-Phase Equilibria: Pearson Education; 1998.
Theory from first principles (statistical physics)	Free-volume theory (Vrentas-Duda)  *European Polymer Journal. 1998;**34:797-803.***	Self-association theory  Kontogeorgis & Folas. Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories: Wiley; 2009.
Full atomistic simulation or coarse-grained (no assumptions)	for $D \geq 10^{-14}\ m^2 \cdot s^{-1}$  *Journal of Chemical Physics. 2010;**132:194902.***	 *Industrial & Engineering Chemistry Research. 2010;**49:7263-80.***

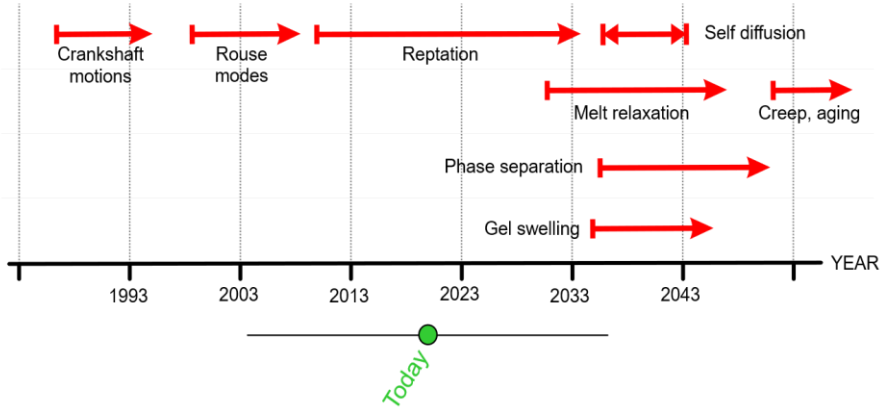


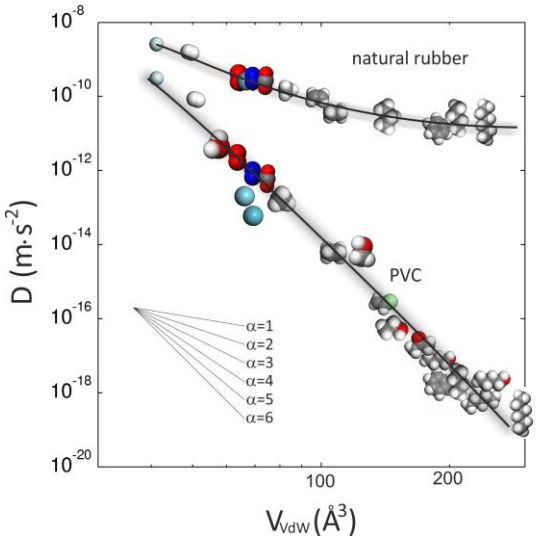




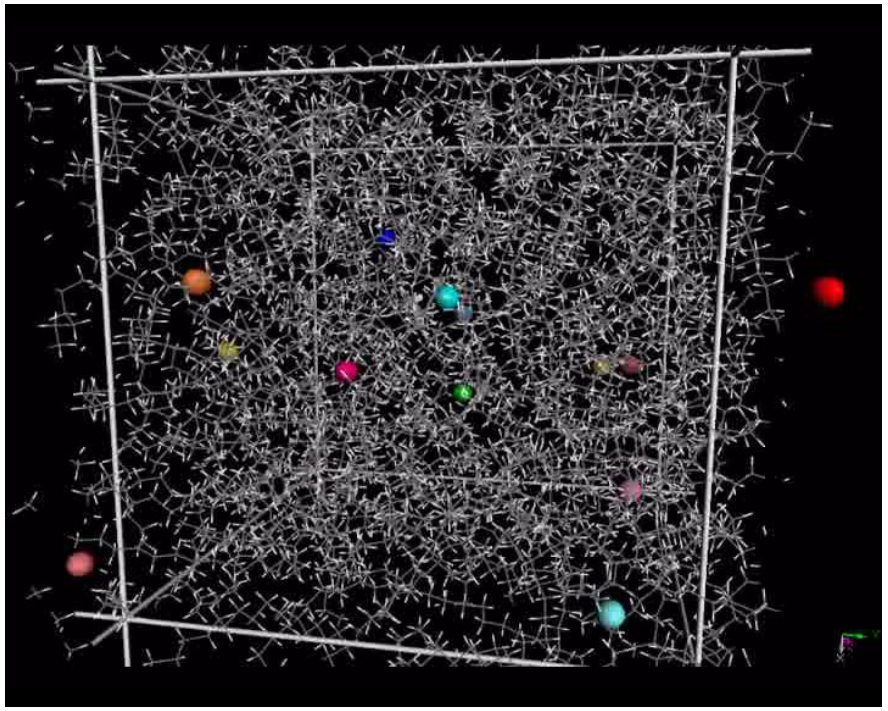
Diffusivities in polymers

Molecular dynamics: 0.5 ns NVT @ 298K

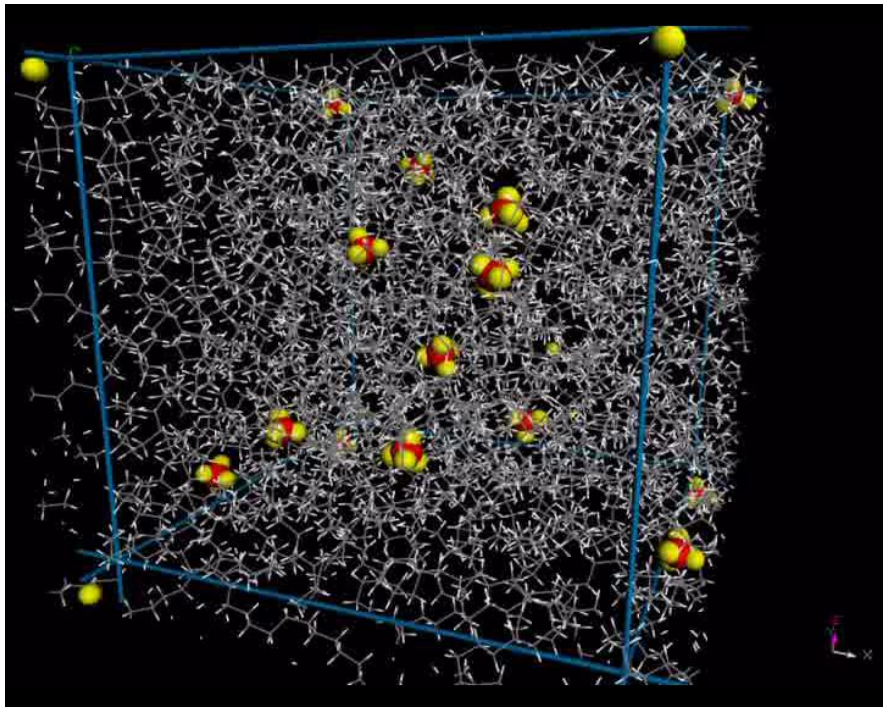




- 10 He

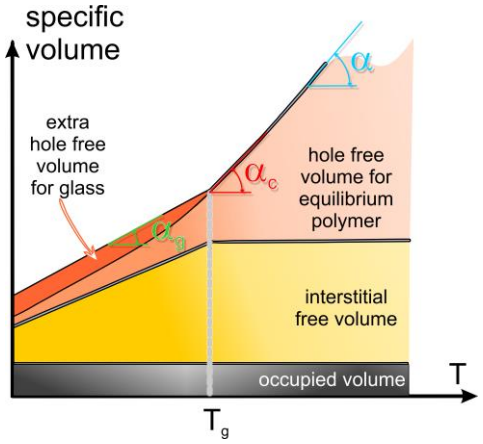


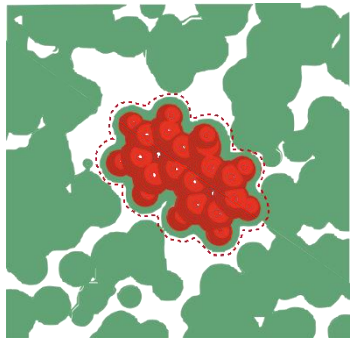
- 10 CH_4

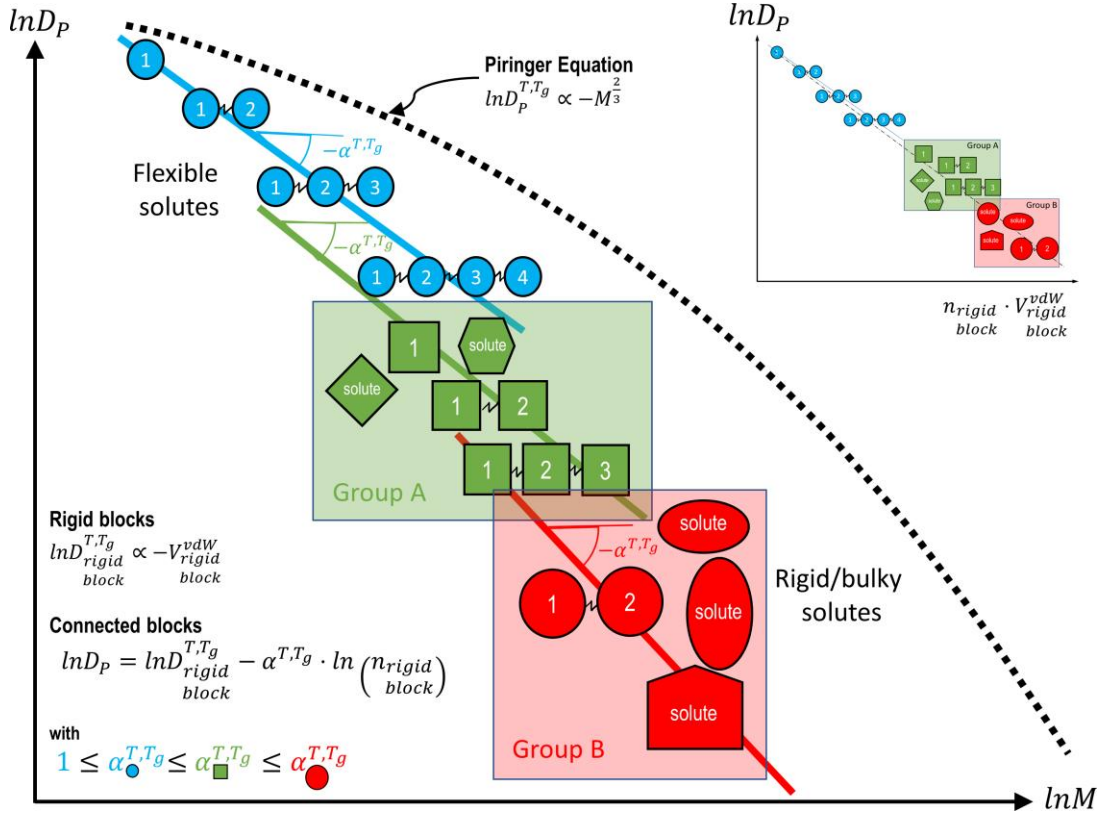


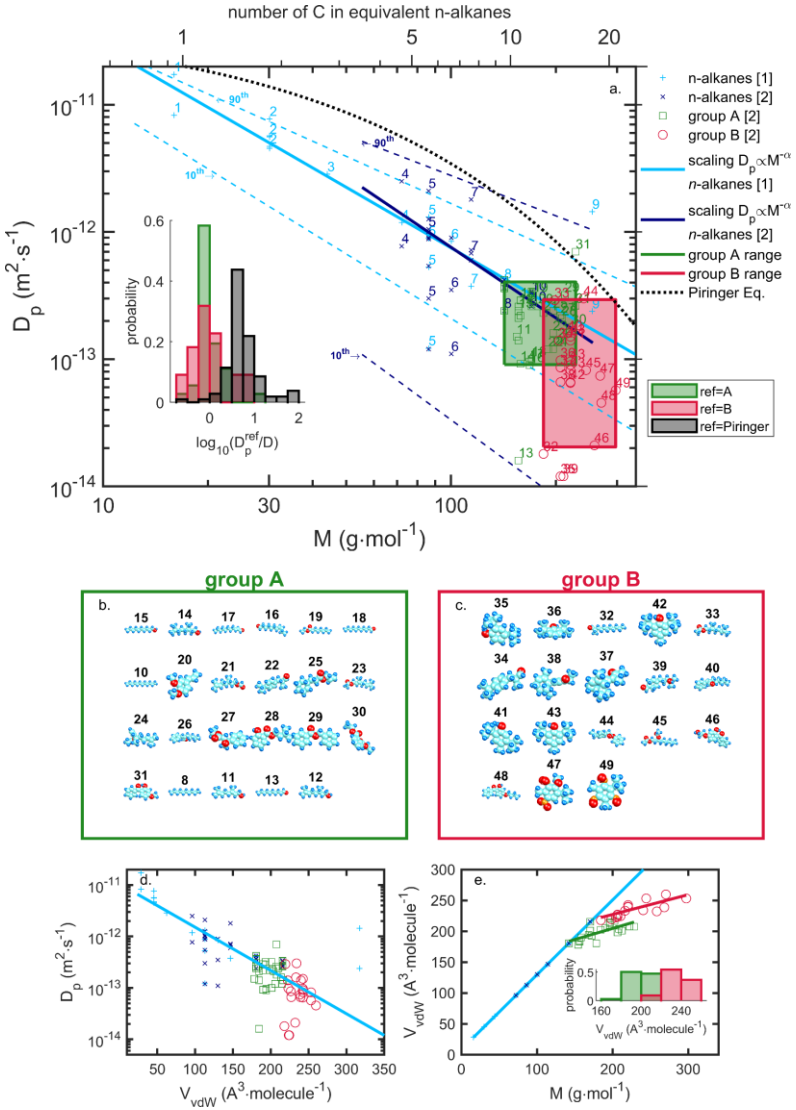
$$D \approx \frac{1}{6}\frac{\partial}{\partial t}\left\langle \left(x_{CM}(t) - x_{CM}(0)\right)^2 \right\rangle$$

Free-volume theory

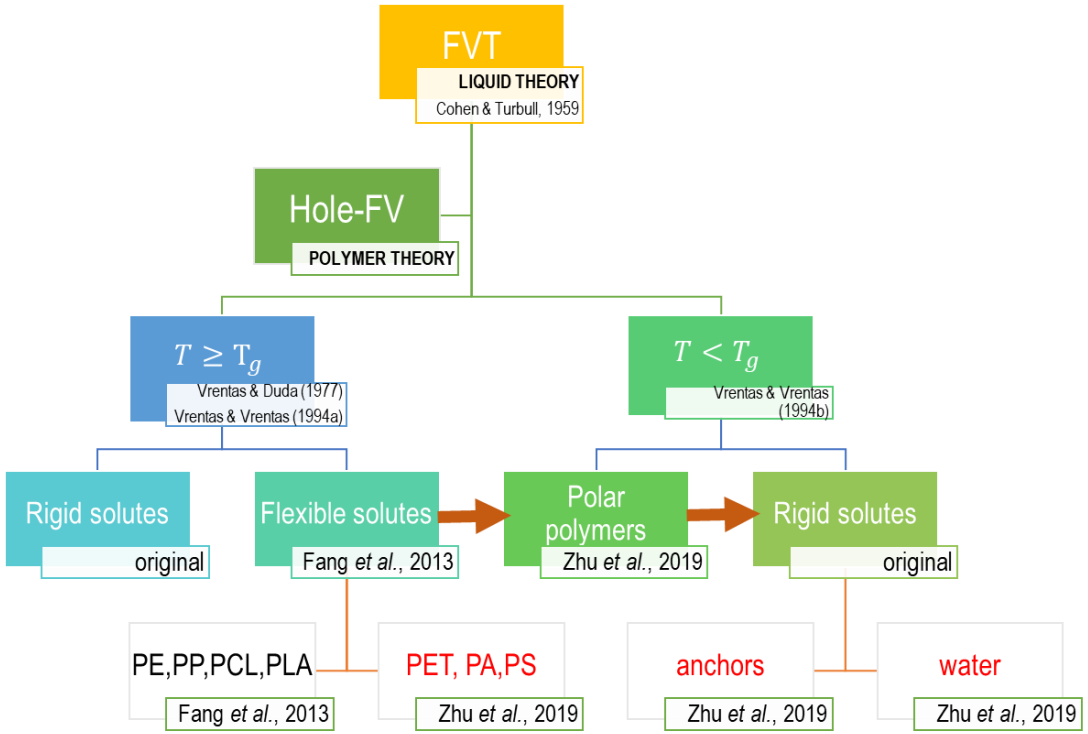


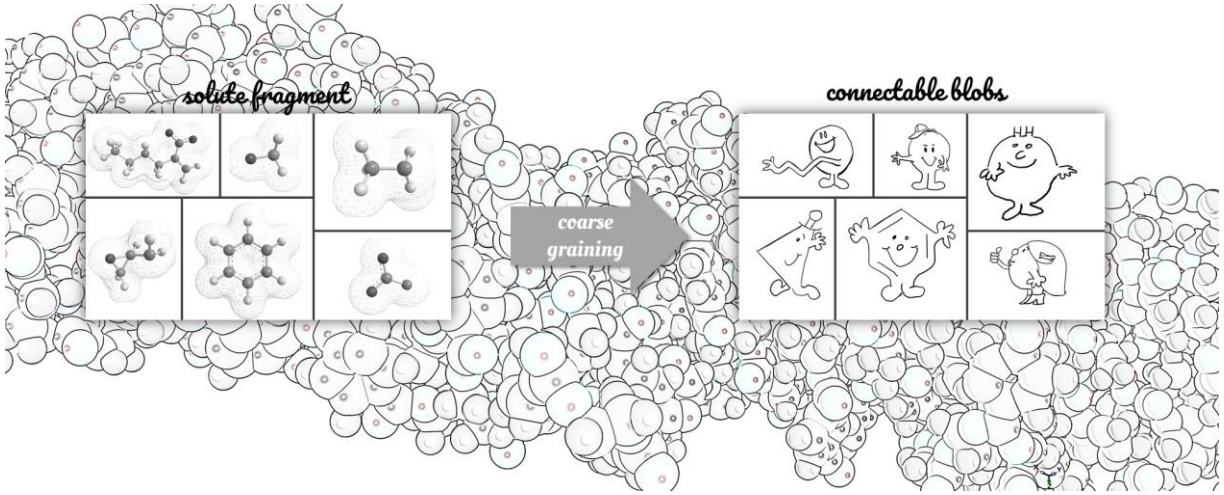






Free-volume theory





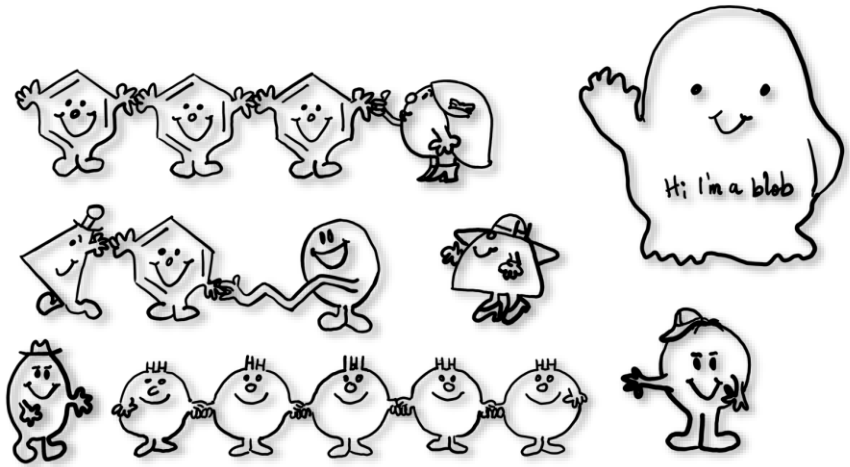
$$D\left(\text{[image]}\right) = 3^{-\alpha} f\left(\text{[image]}\right) f\left(\text{[image]}\right)$$

FV effects (any polymer)

Solute effects (any solute)

$$D(\xi, T, T_g) = D_0(\xi)\exp\left(-\frac{E^*(\xi)}{RT}\right)\exp\left(-\tilde{V}_1^*(\xi)\frac{\alpha_{lin}(T, T_g) + \beta_{lin}}{a_{lin}(T_g)}\right)$$

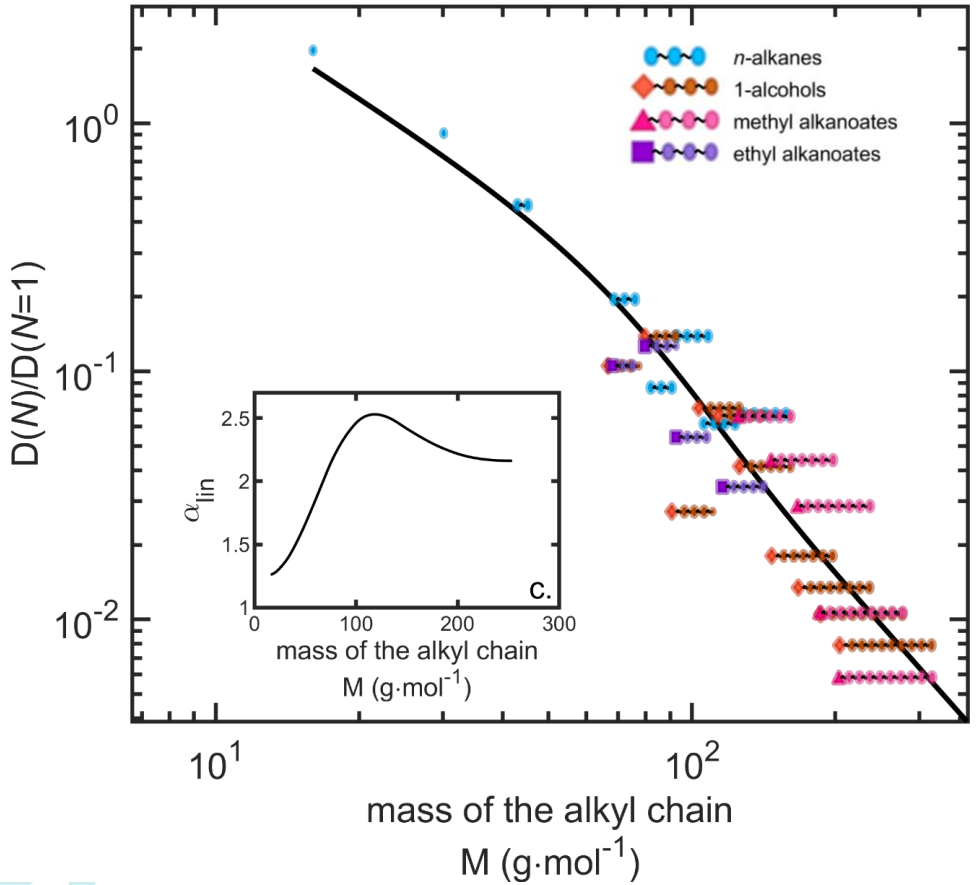
$$\approx D_0(\xi)\exp\left(-\frac{E^*(\xi)}{RT}\right)\exp\left[-\frac{\tilde{V}_1^*(\xi)}{0.24(u + vT_g)}\left(2 + \frac{K_\alpha}{r(T - T_g) + K_\beta}\right)\right]$$

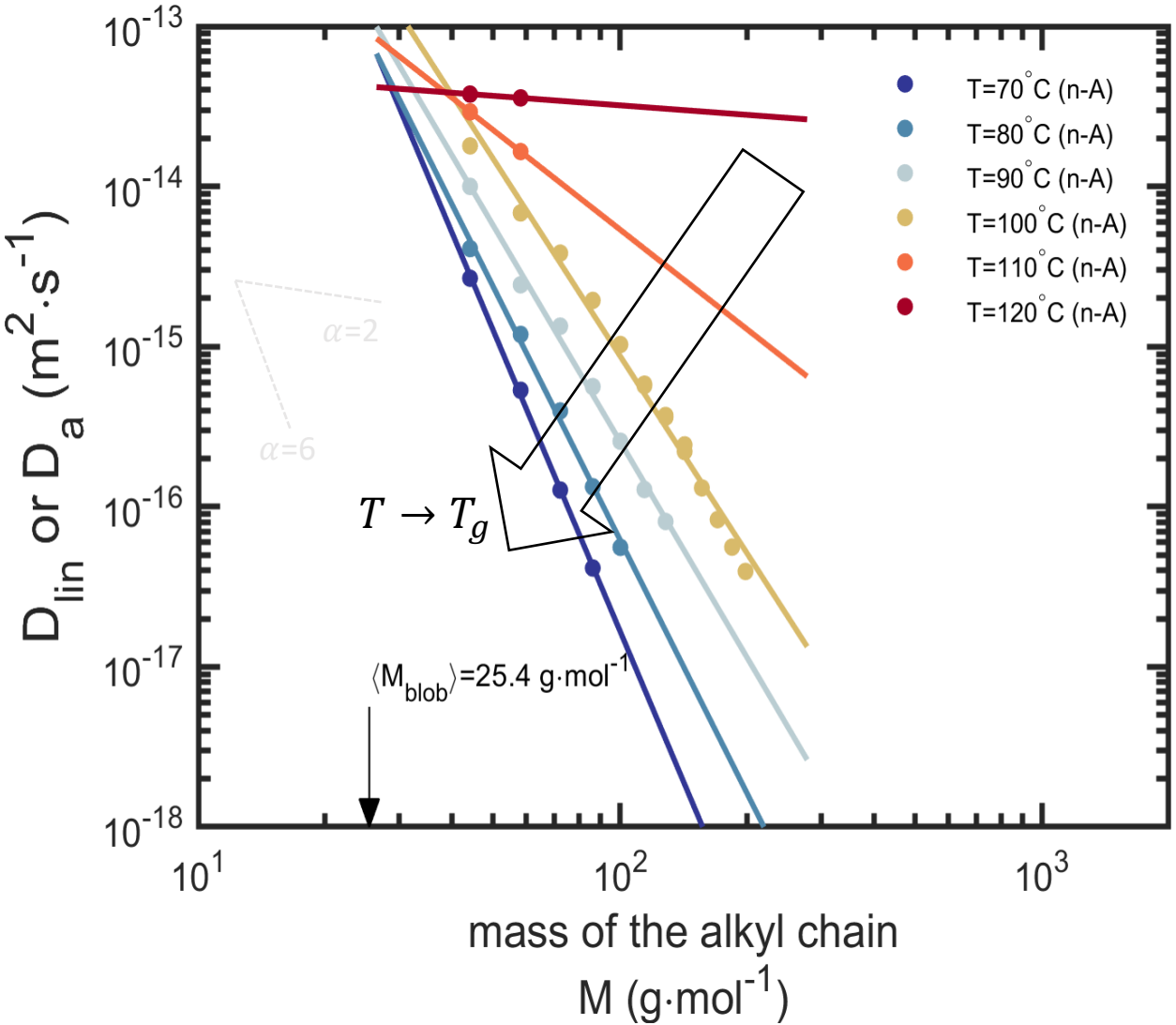


Diffusivities of homologous solutes

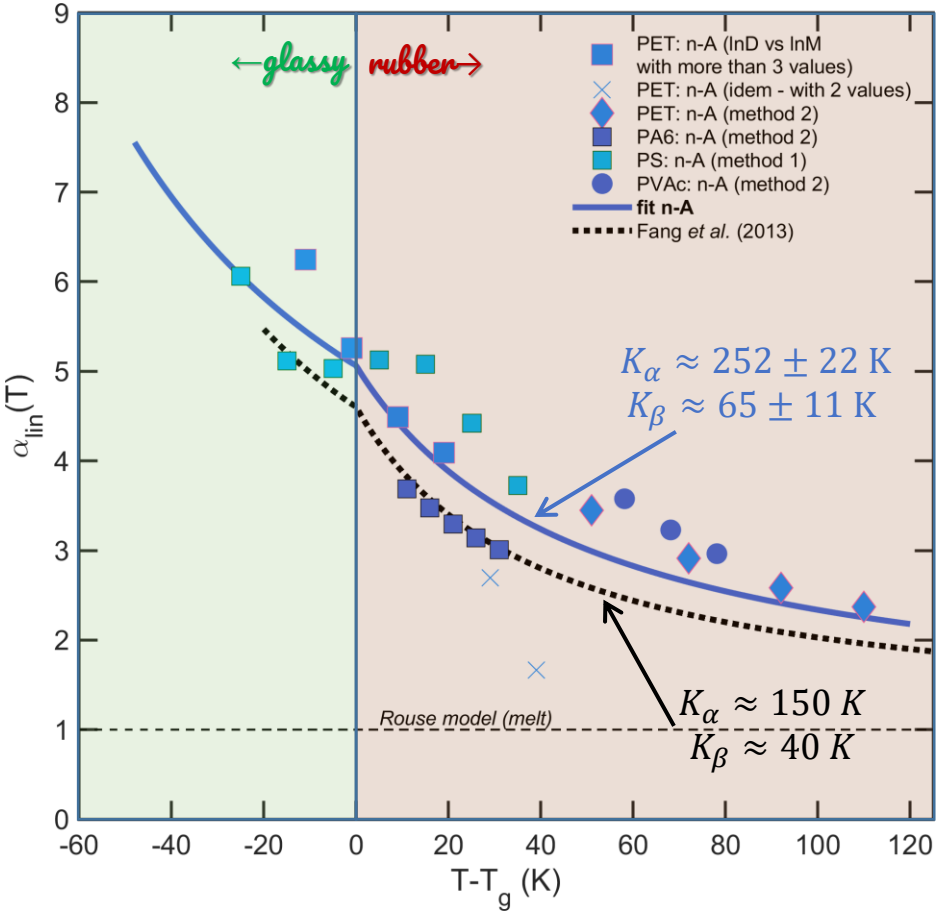
$M = n \cdot M_{blob}$

$$\frac{D_{lin}(M,T)}{D_{lin}(M_{blob},T)} \propto \left(\frac{M}{M_{blob}}\right)^{-\alpha_{lin}(T,T_g)}$$





Universal scaling including for non-documented polymers



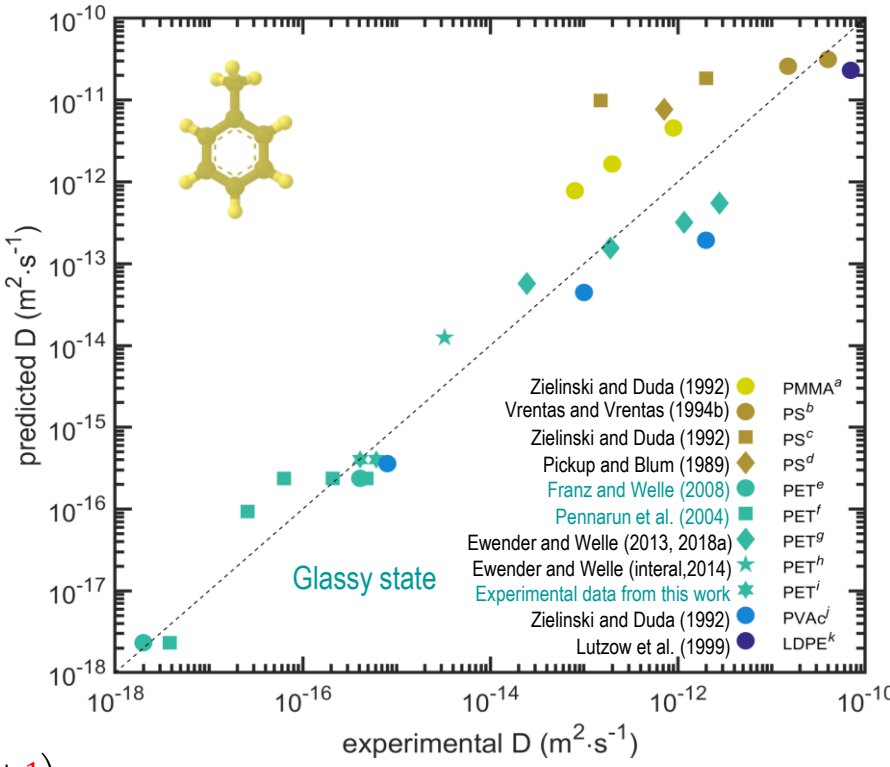
$$\frac{D_{lin}(M,T)}{D_{lin}(M_{blob},T)} \propto \left(\frac{M}{M_{blob}}\right)^{-\alpha_{lin}(T,T_g)}$$

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

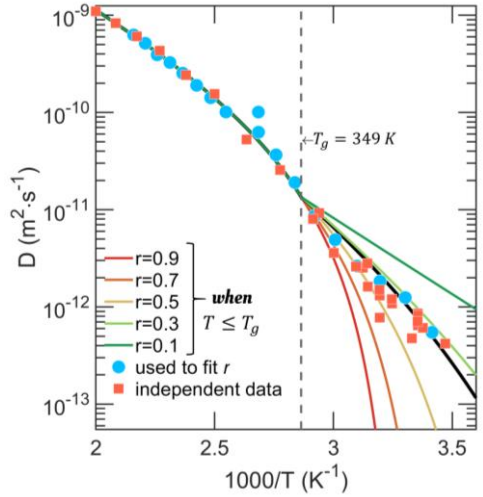
$$with\ r = \begin{cases} 1\ when\ T \geq T_g \\ \frac{\alpha_g}{\alpha_c} \qquad T < T_g \end{cases}$$

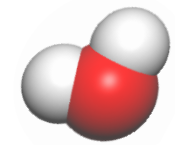
$$D(\xi,T,T_g) = D_0 \exp\left(-\frac{E^*}{RT}\right)\exp\left(-\tilde{V}_1^* \frac{\alpha_{lin}(T,T_g)+1}{0.24}\right)$$

parameter	water	toluene
D_0 (m^2·s^{-1})	2.94·10^{-6}	1.87·10^{-8}
E^* (kJ·mol^{-1})	26.5±2	0
$\tilde{V}_1^*$ (cm^3·g^{-1})	19.3	84.48
r when $T \leq T_g$	0.34±0.03	0.7 (dry)/0.28 (swollen)



Diffusivities of water in amorphous glassy and rubber PET inferred from the scaling of *n*-alkanes (α_{lin}^{T,T_g}) in PET above T_g.



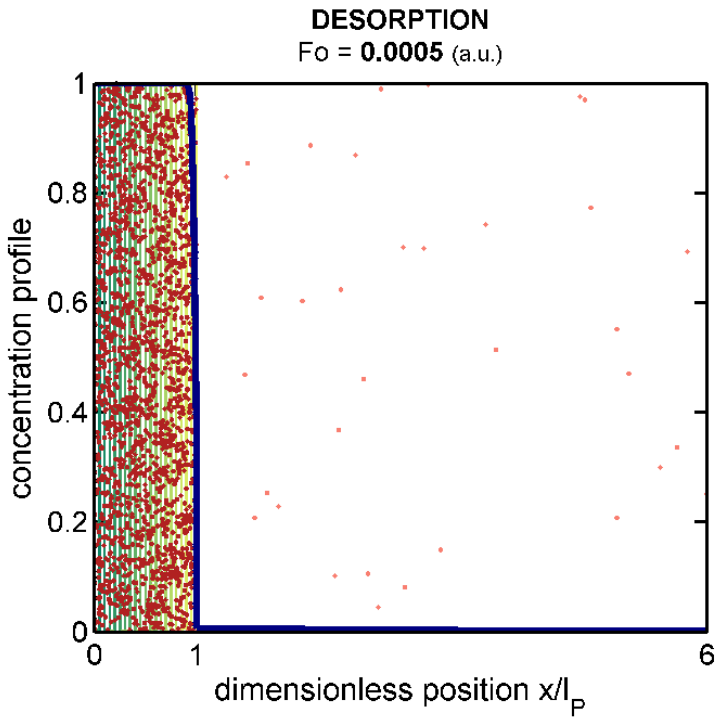


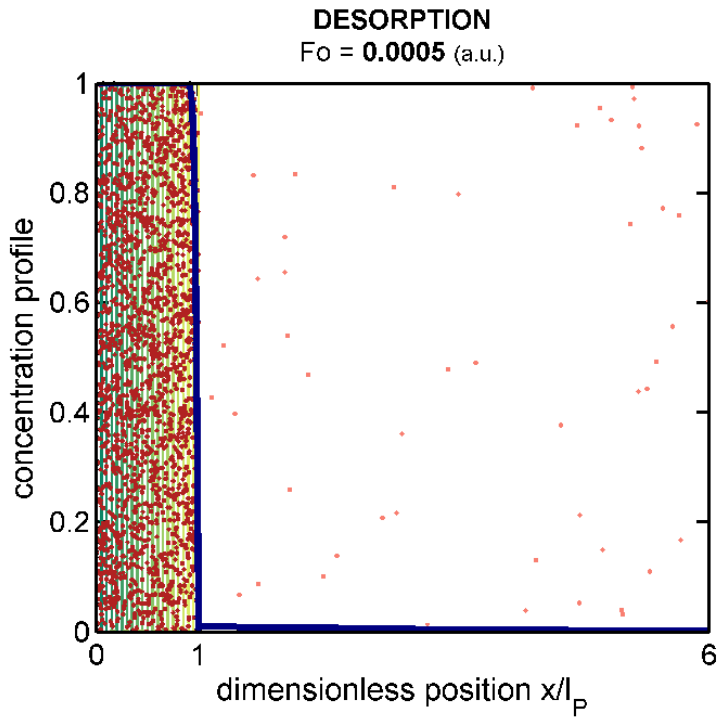
The conventional description of migration

The level of contamination depends essentially on the fatty character of the food in contact

50 × more chemical affinity for P | 50 × more chemical affinity for F

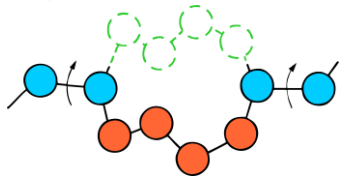
$K_{i,F/P}$ = 1/50 | 50

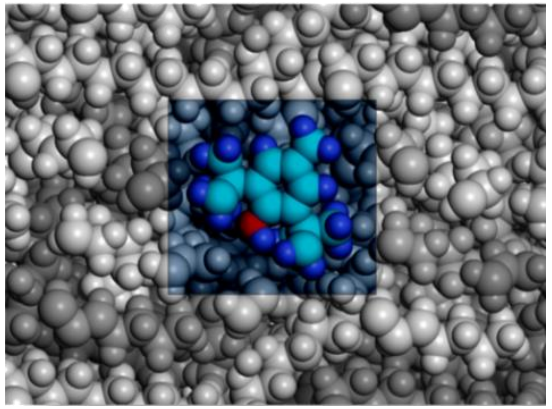




$$K_{i,F/P} = \frac{C_{i,F}^{eq}}{C_{i,P}^{eq}} = \frac{1}{1 - crystallinity} \frac{\gamma_{i,P_{amorphous}}^{v}}{\gamma_{i,F}^{v}}$$

Calculating chemical potentials from an explicit representation of polymer entanglements, liquid structures





0: system state without solute
1: system state with one solute

- **Free energy perturbation:** $exp\left(-\frac{F_1-F_0}{k_BT}\right) = \left\langle exp\left(-\frac{U_1-U_0}{k_BT}\right)\right\rangle$
- **based on Jarsynski's equality:** $exp\left(-\frac{F_1-F_0}{k_BT}\right) = \left\langle exp\left(-\frac{W_{fast}}{k_BT}\right)\right\rangle$
- **Thermodynamic integration** to extended ensembles: $\frac{\partial}{\partial\lambda}F = \left\langle\frac{\partial}{\partial\lambda}U\right\rangle_\lambda$
- **Replica exchange methods** = variant of above but without reaction coordinates (Metropolis algorithm to select likely configurations)
- **Possible biases**: only thermally accessible configurations contribute to exponential averaging

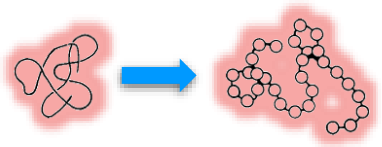
$$K_{i,F/P} = \frac{C_{i,F}^{eq}}{C_{i,P}^{eq}} = \frac{1}{1-crystallinity}\frac{\gamma_{i,P_{amorphous}}^{v}}{\gamma_{i,F}^{v}}$$

Flory theory of amorphous states at equilibrium: implicit representation of polymers

$$\frac{\mu_{i,k}^{excess}}{k_B T} = ln\gamma_{i,k}^{v} = \left(1 - \frac{1}{r_k}\right)\phi_k + \chi_{i,k}^{T}\phi_k^2 \approx \left(1 - \frac{1}{r_k}\right) + \chi_{i,k}^{T} \textbf{ when } \phi_k \to 0$$

lattice approximation (incompressible)

random coil in absence of volume exclusion

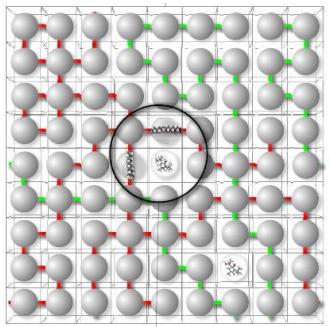


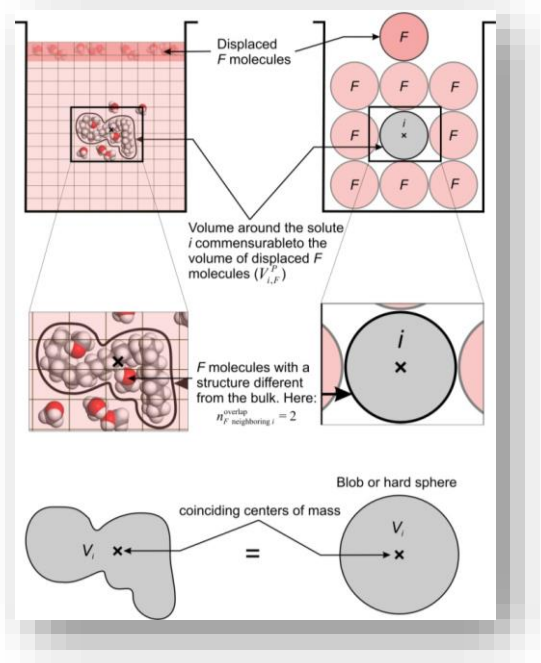
same configuration with excluding volumes

off-lattice approximation (incompressible, atomostic scale)

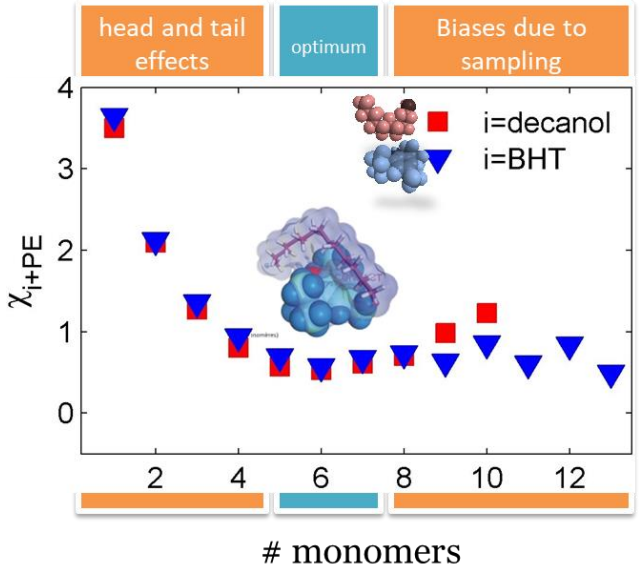
$$2k_B T \chi_{i,k}^{T} = \langle h_{i+k} \rangle_T + \langle h_{k+i} \rangle_T - \langle h_{k+k} \rangle_T - \langle h_{i+i} \rangle_T$$

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

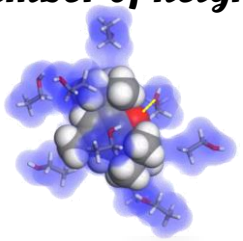




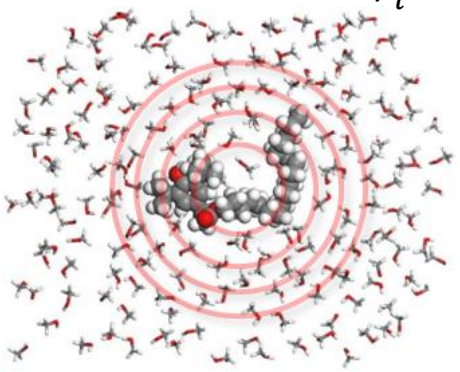
Pair contact energy: $\langle \epsilon_{A+B} \rangle_T$



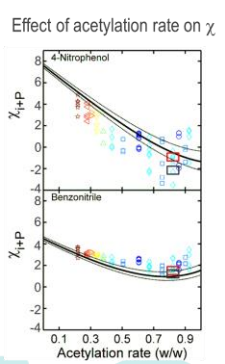
Number of neighbors: $\langle z_{A+B} \rangle$

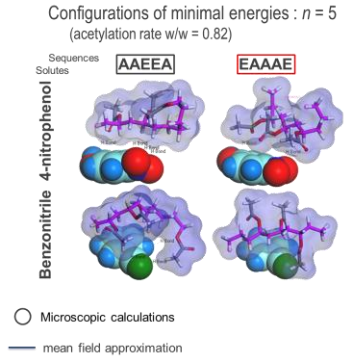


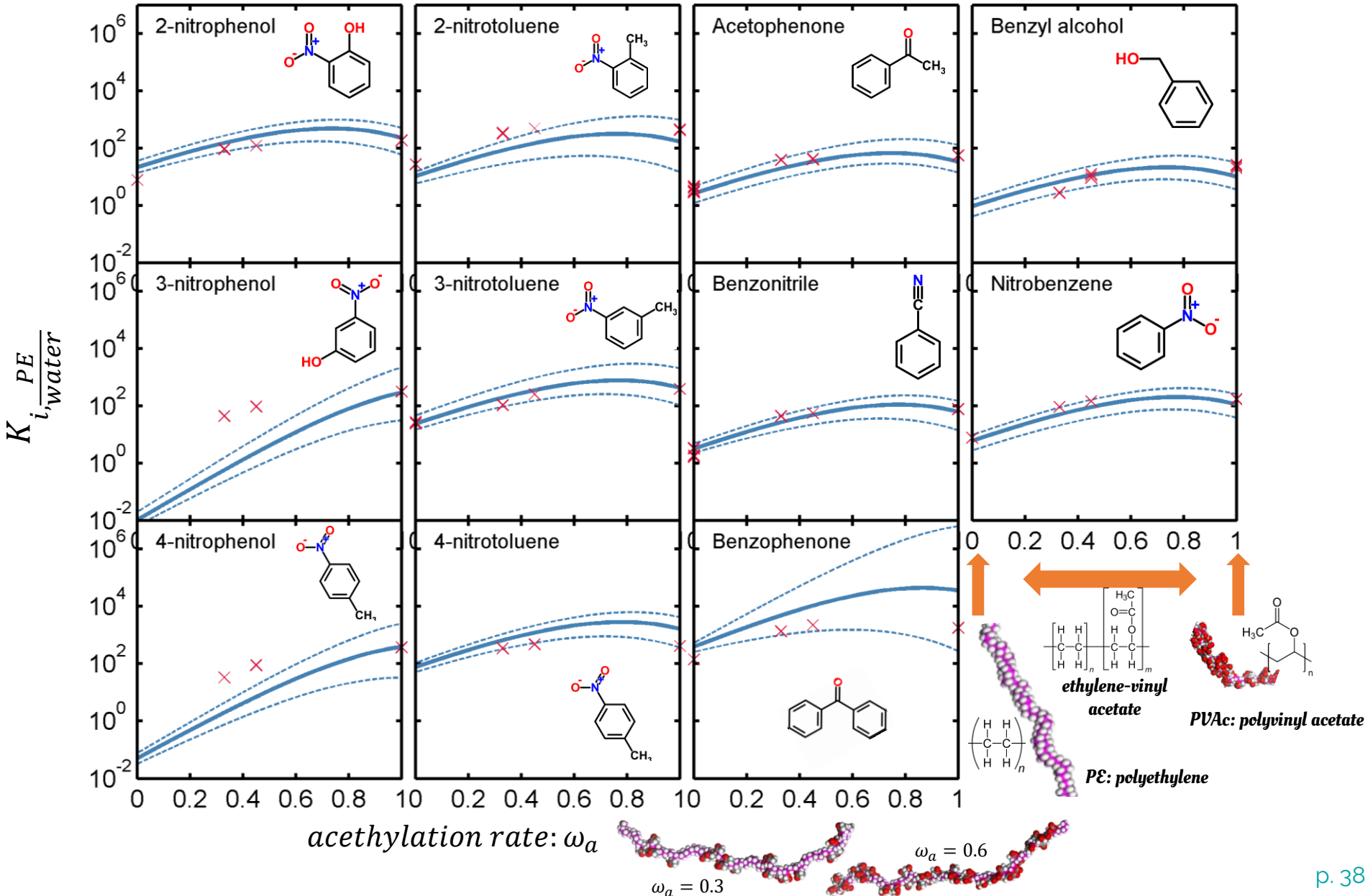
scaling: $r_k = \frac{\overline{V_k}}{\overline{V_i}}$



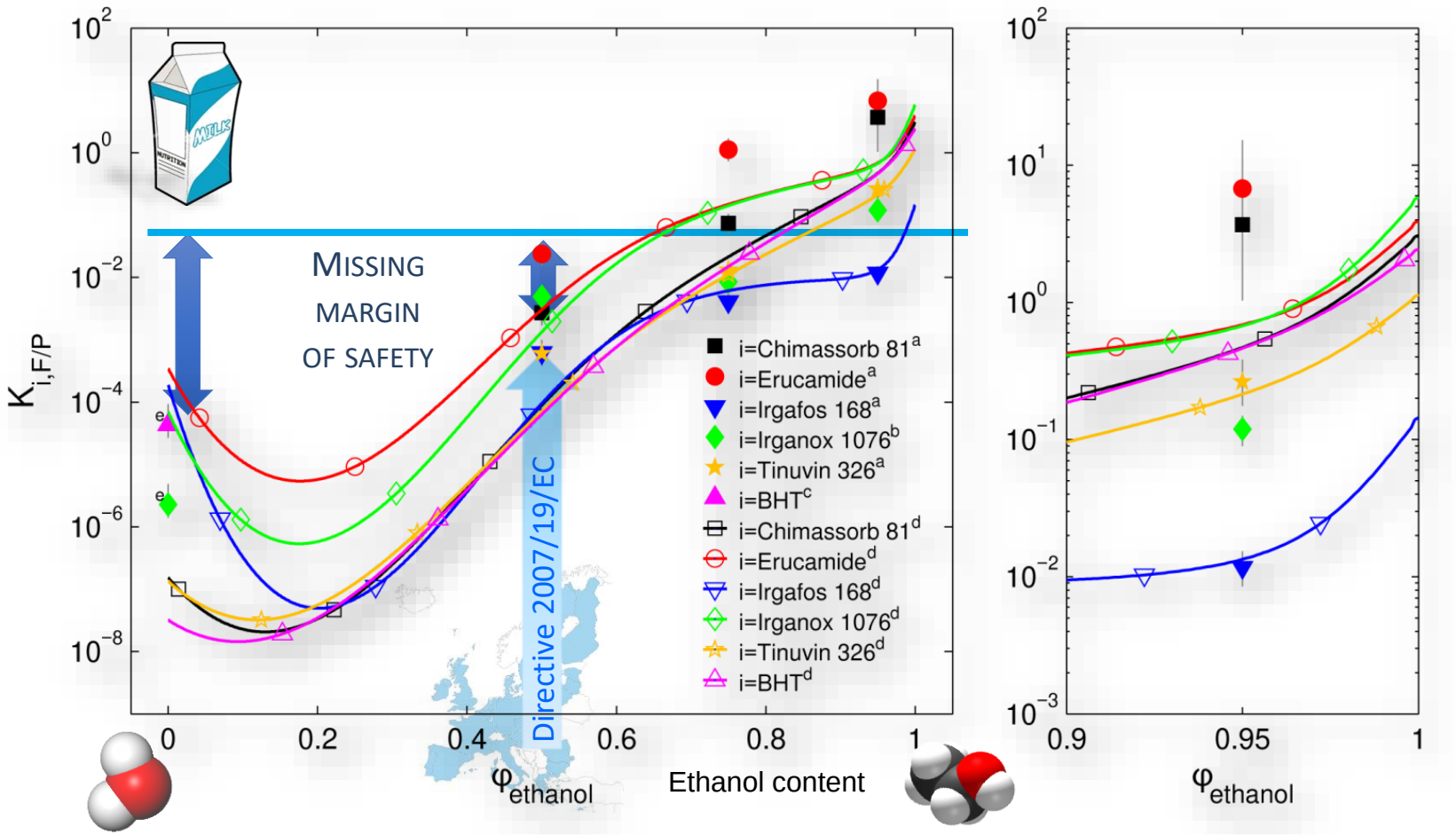
Partition coefficients water-EVA for polar solutes

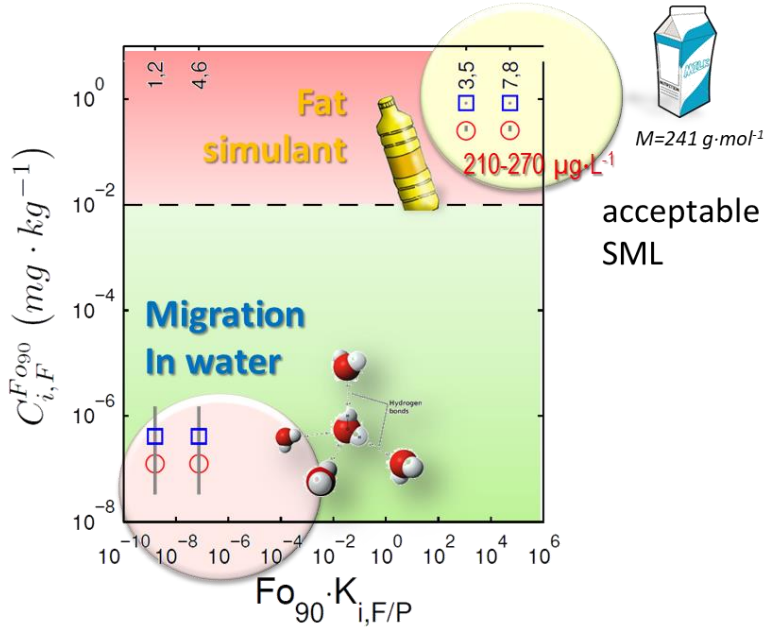






Molecular modeling challenged the choice of food simulants

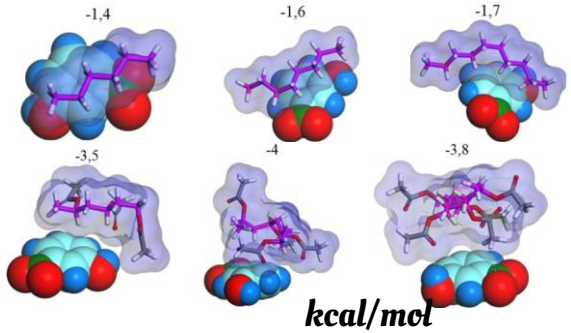


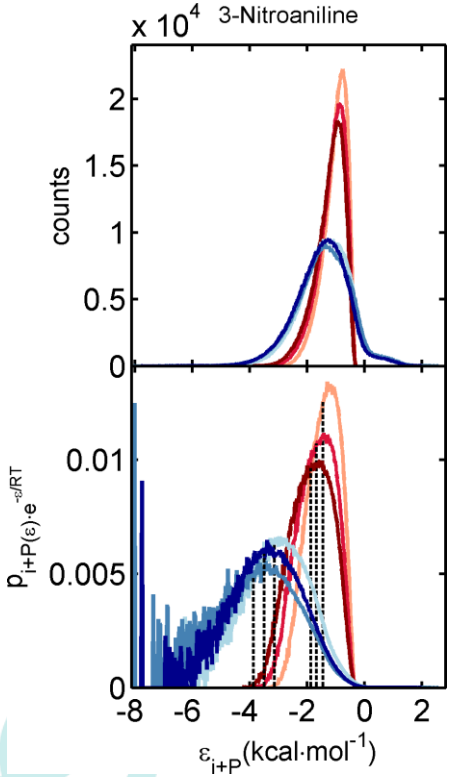


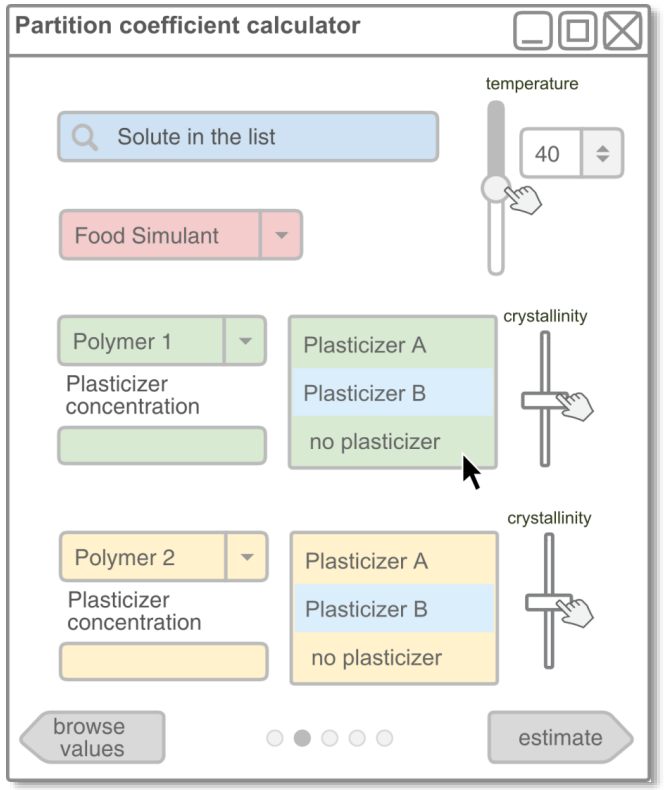
Ind. Eng. Chem. Res. 2010, **49**(16), 7263-7280.
Food Additives and Contaminants, 2009, **26**(12), 1556-1573.

	Date of case	Last change	Reference	Country	
6.	08/09/2005		2005.631	ITALY	food contact materials
RASFF Portal					migration of isopropyl thioxanthone (250 µg/l) from packaging of milk for babies from Spain

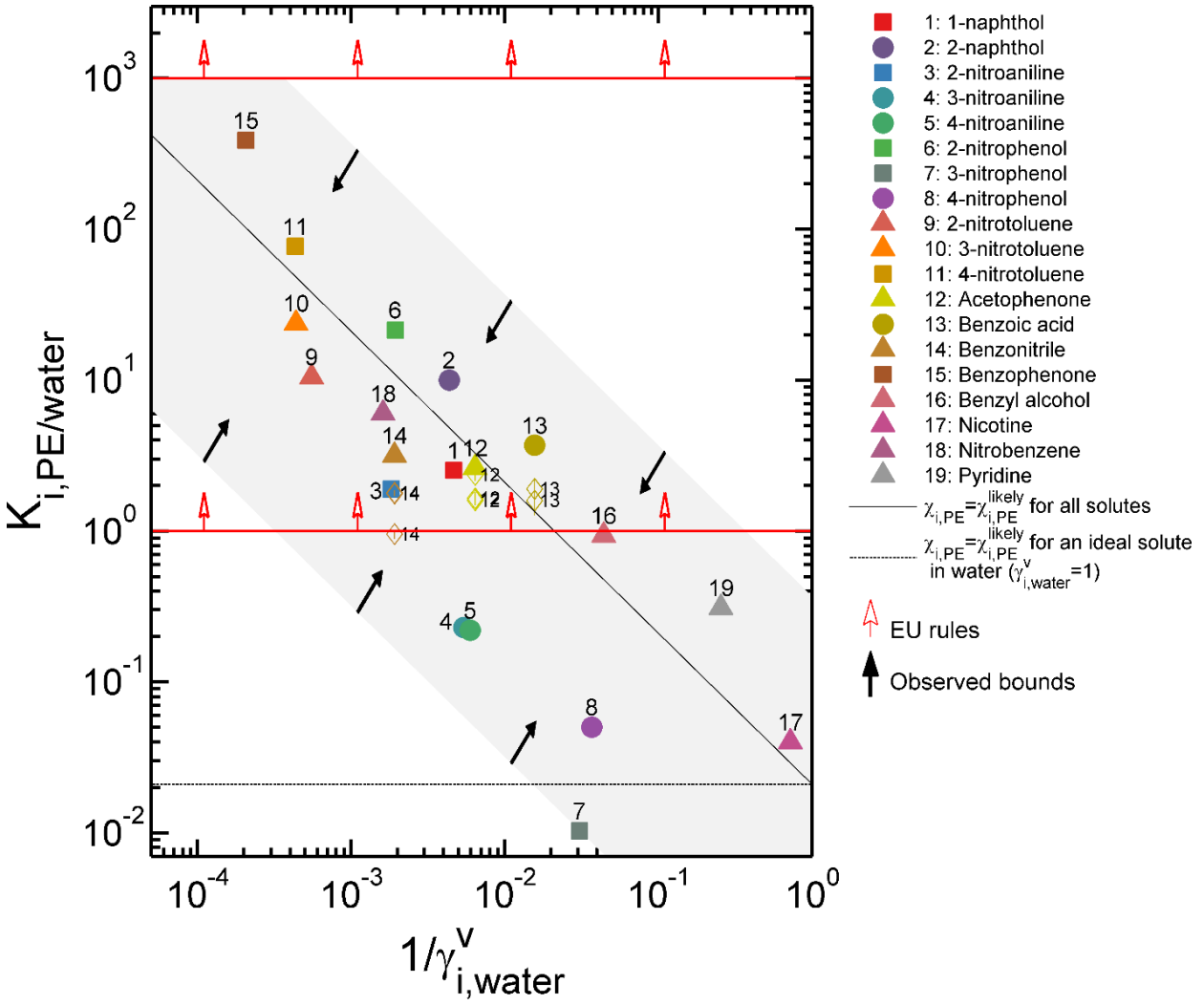
Tailored calculations for IAS and NIAS







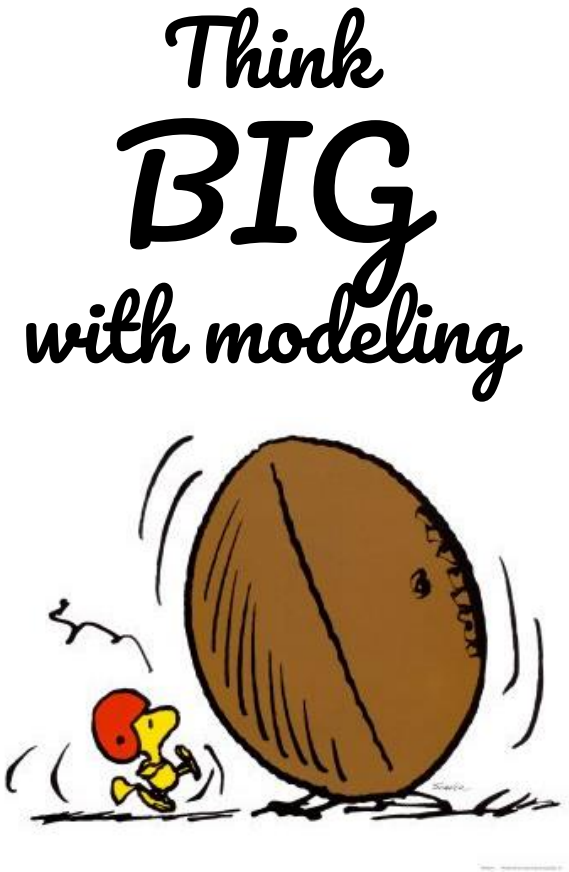
Industrial & Engineering Chemistry Research 2009, 48 (11), 5285-5301.
International Journal of Chemical Reactor Engineering 2010, 8.
Industrial & Engineering Chemistry Research 2010, 49 (16), 7263-7280.
Industrial & Engineering Chemistry Research 2017, 56 (3), 774–787.

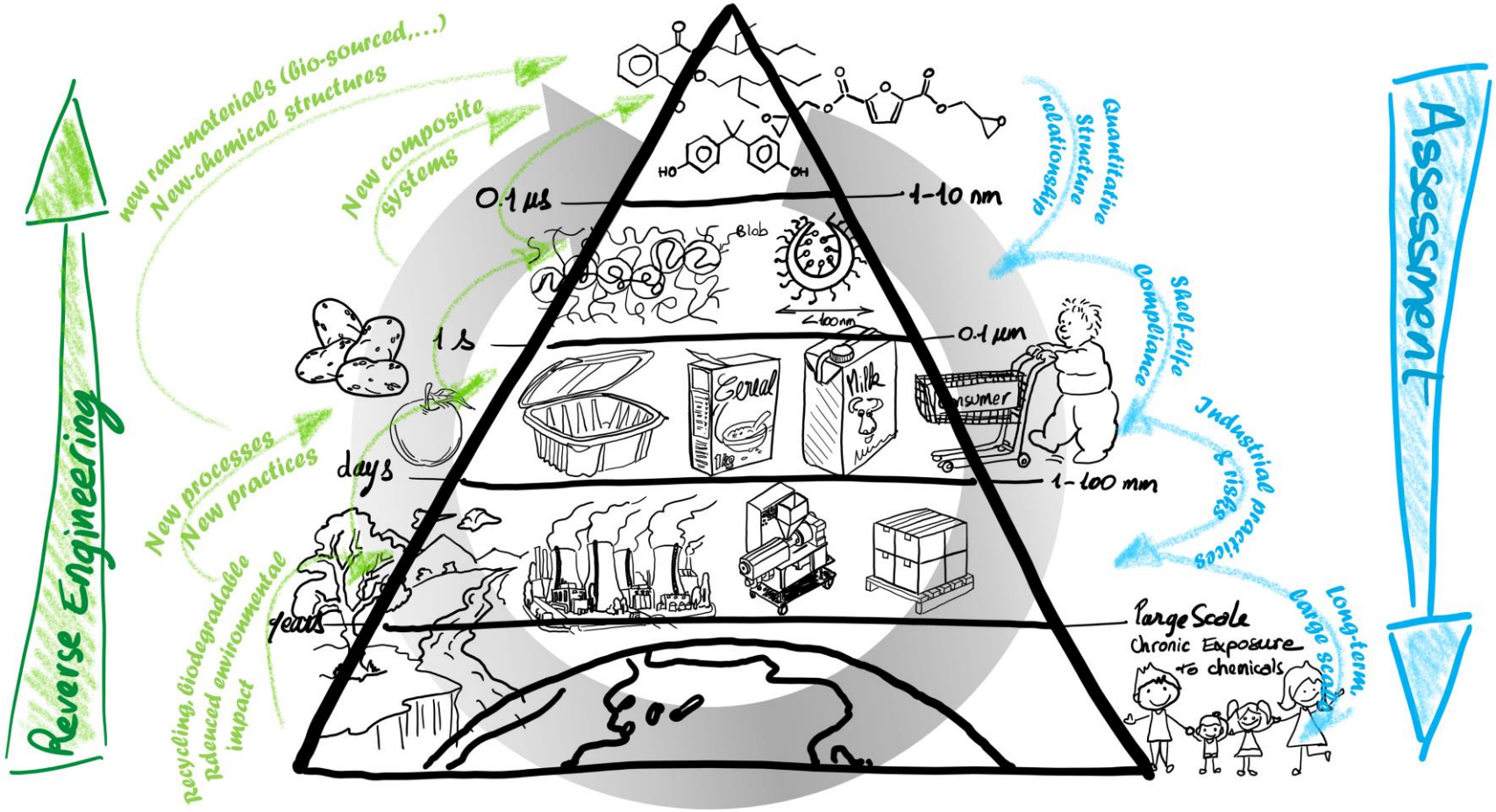


Conclusions & Perspectives

PARIS SMART CITY 2050
Vincent Callebaut Architectures, 2015

Future of modeling = safe-by-design + ecodesign

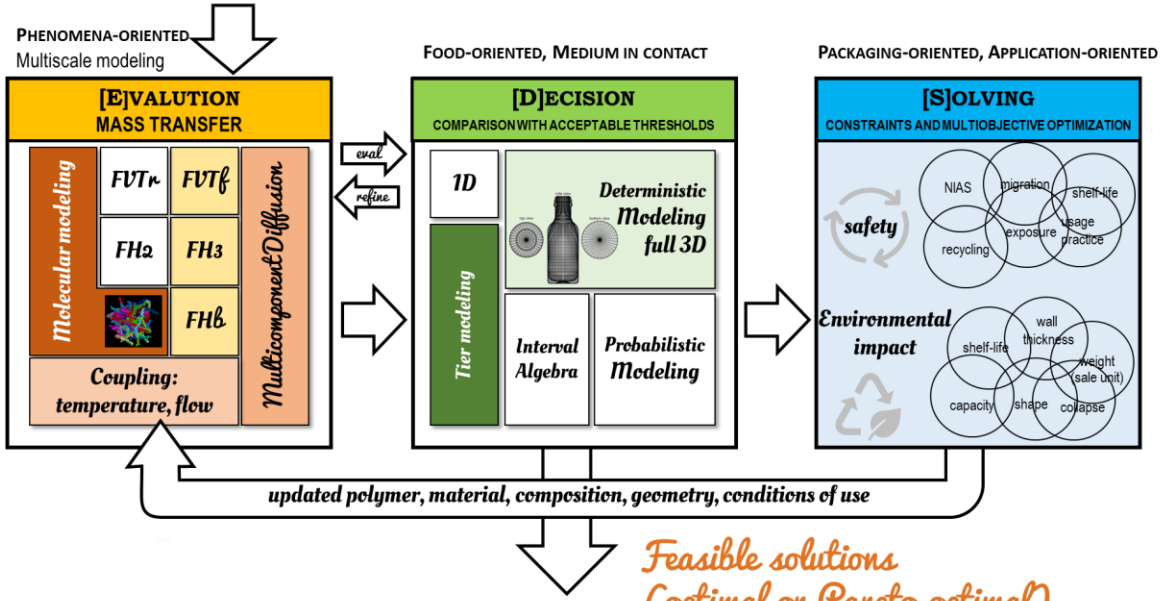




Y. Zhu, B. Guillemat and O. Vitrac, *Frontiers in Chemistry* **2019, 7.**

premises
Market demand, new food products
New regulations (*e.g.*, ban of materials or substances)
Life cycle analysis considerations
First solution from known problem-solving tools (TRIZ, Six Sigma approach, etc.)
Diagnostic from root cause analysis, seek of preventive actions

Our research **Computer-aided drafting**



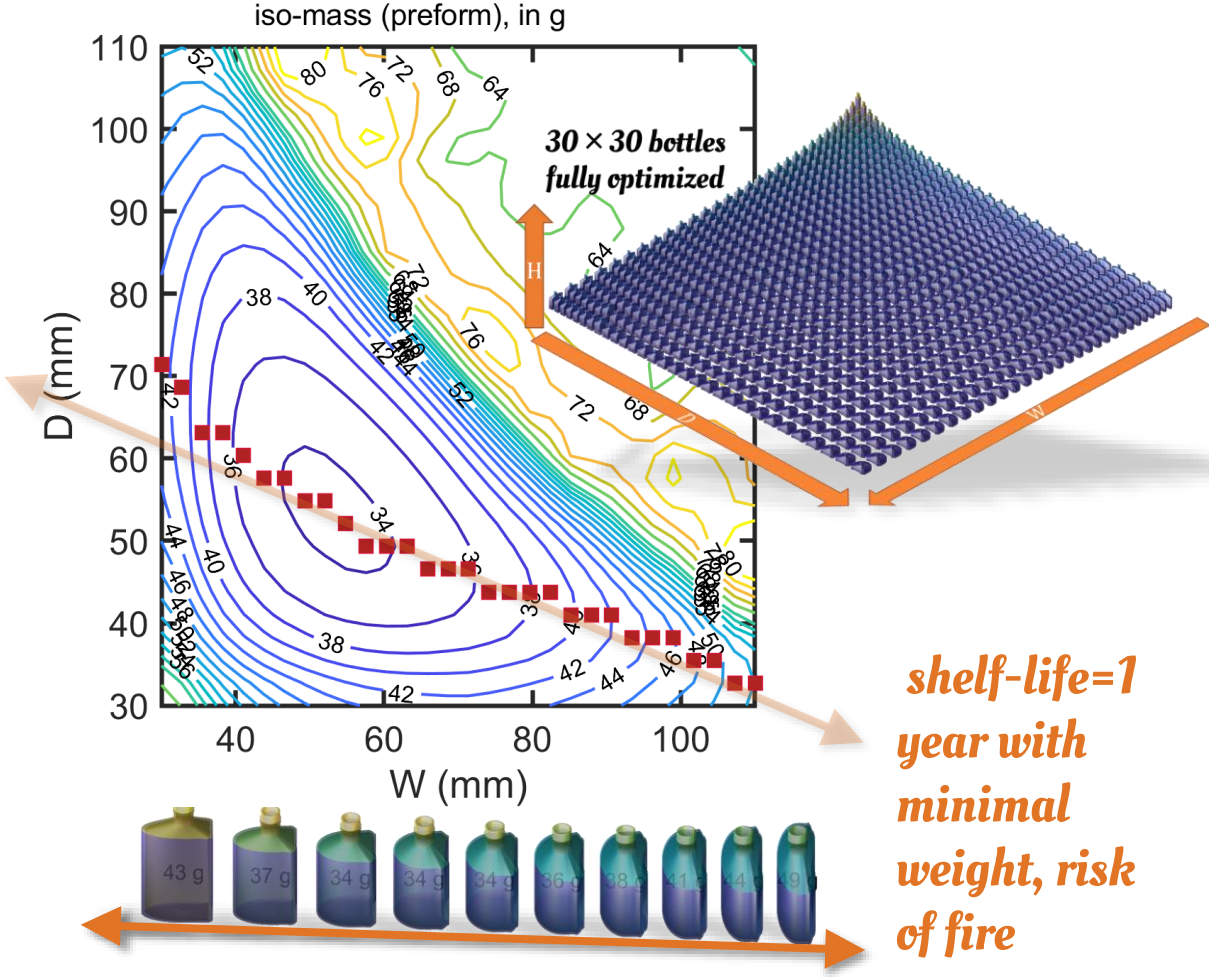
Feasible solutions
(optimal or Pareto-optimal)

FV: hole-free volume theory of diffusion
(*r*=rigid and *f*=flexible solutes)

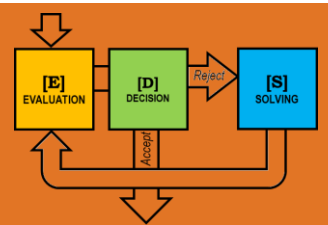
FH: Flory Huggins approximation of chemical affinities and temperature effects
(*2*=binary and *3*=ternary mixturres, *b*= formulation for block polymers)

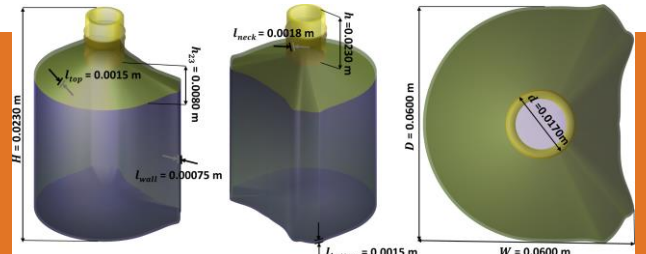
Our research **Rapid prototyping**

applications
Minimized waste, migration risk, optimized shelf-life, optimized process and supply chain
Computer-aided engineering (mechanical resistance) and manufacturing (extrusion-blowing)
Additional validation (e.g., consumer acceptance)
Global environmental footprint
Safe-by-design and eco-design approaches
3D printing, augmented-reality



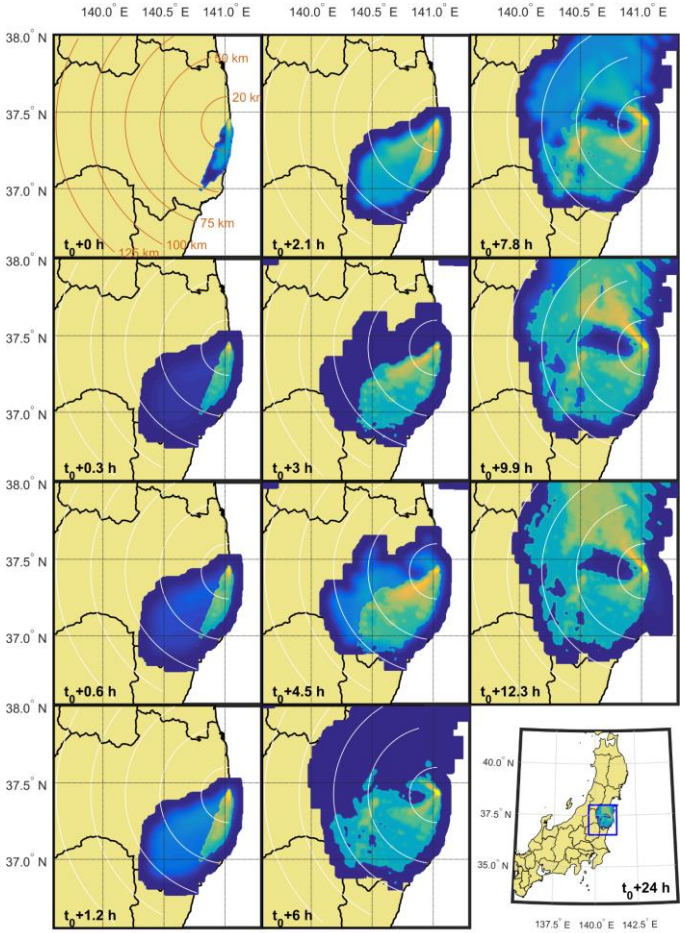
shelf-life=1 year with minimal weight, risk of fire

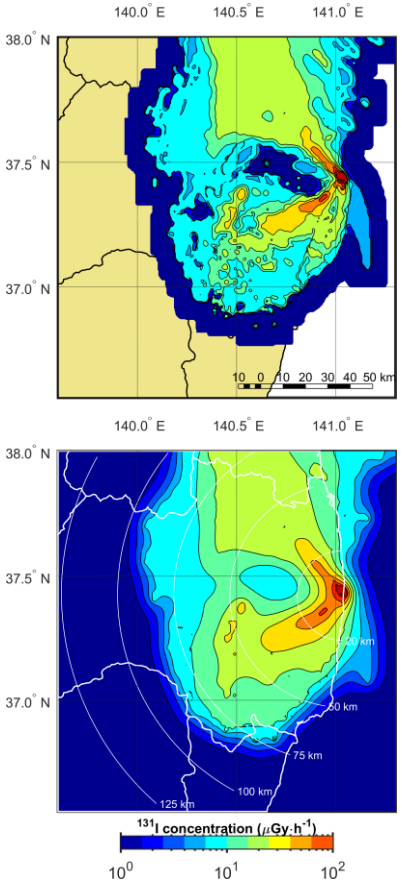


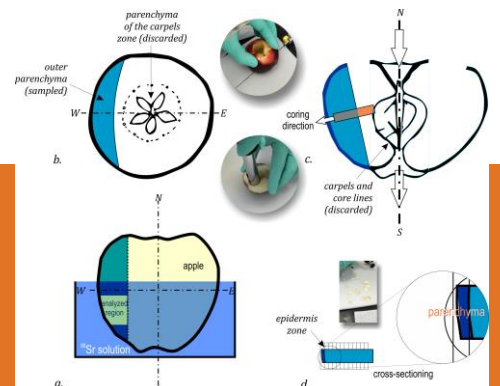


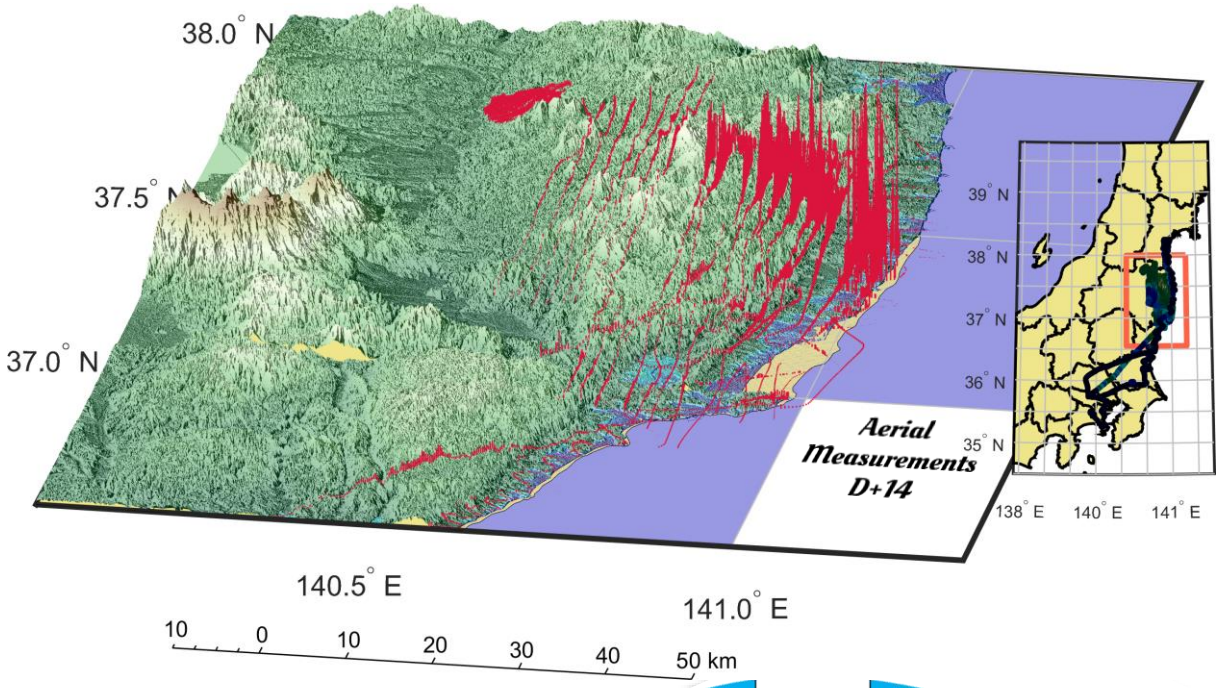
Packaging design

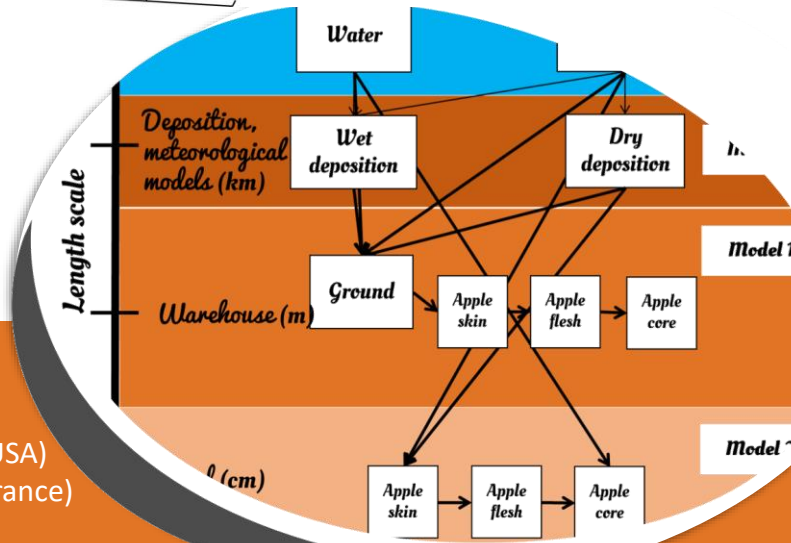
Minatures PET bottles for alcoholic beverages served in planes







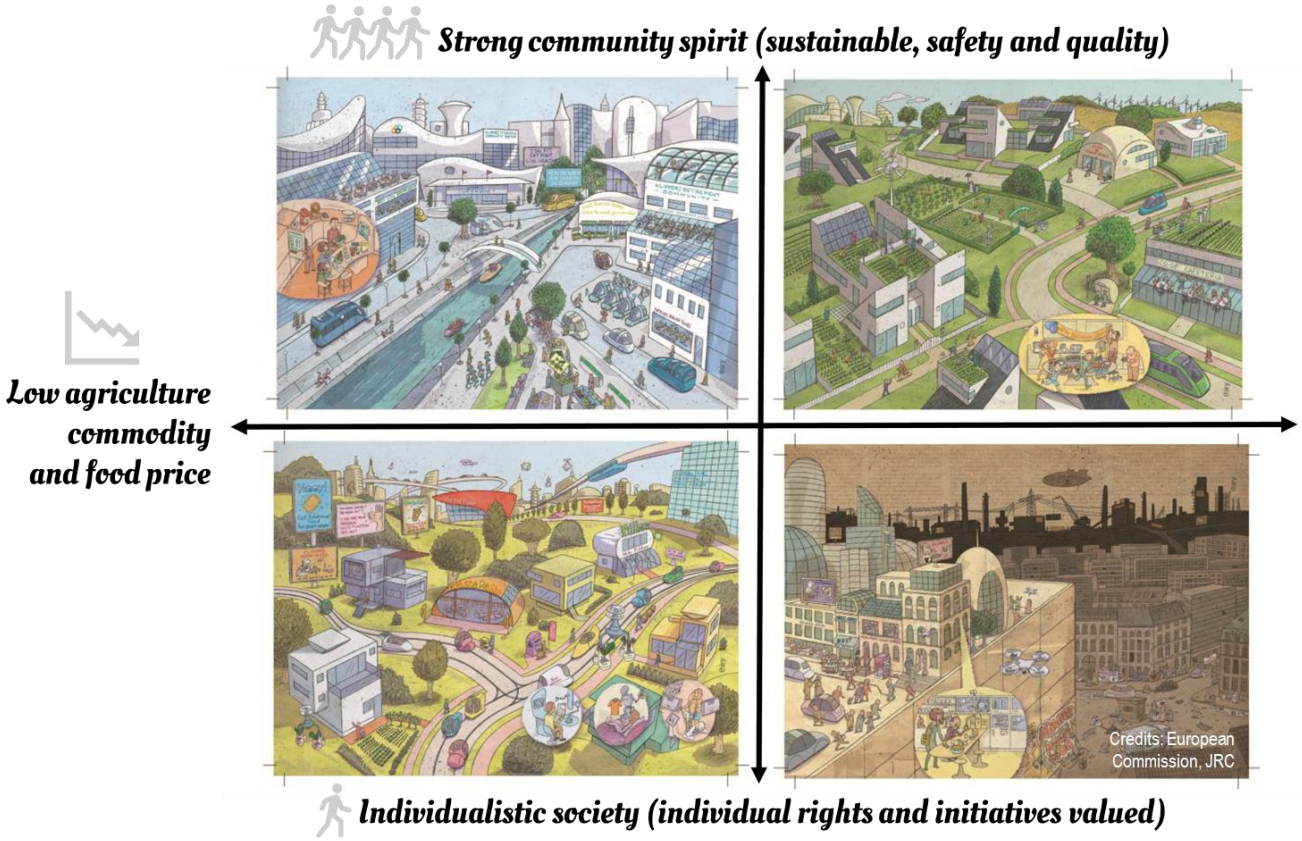


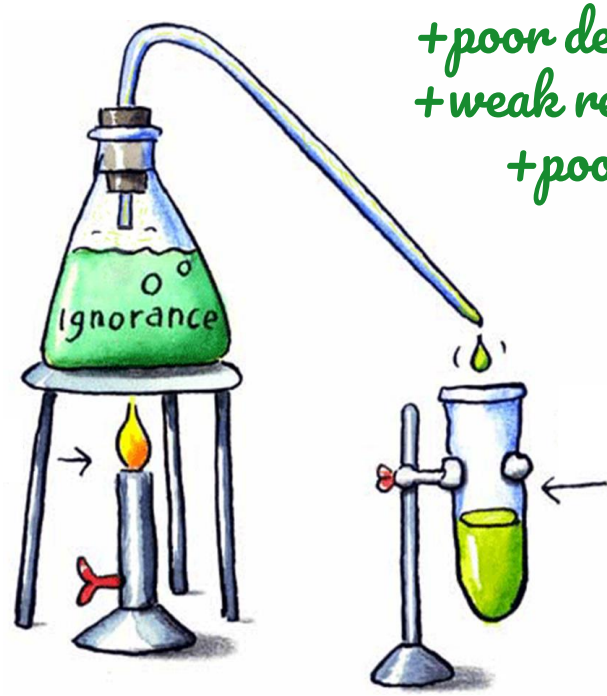


Collaborations

FDA (WEAC, Boston, MA,USA)
IRSN (Fontenay-les-Roses, France)

Let's foresight modeling support public decision

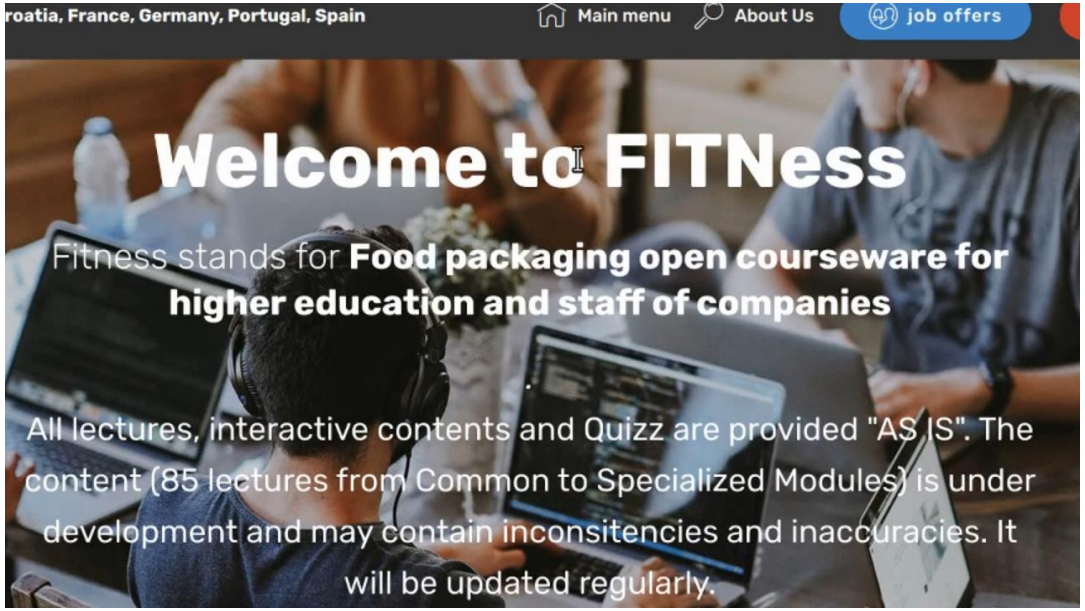


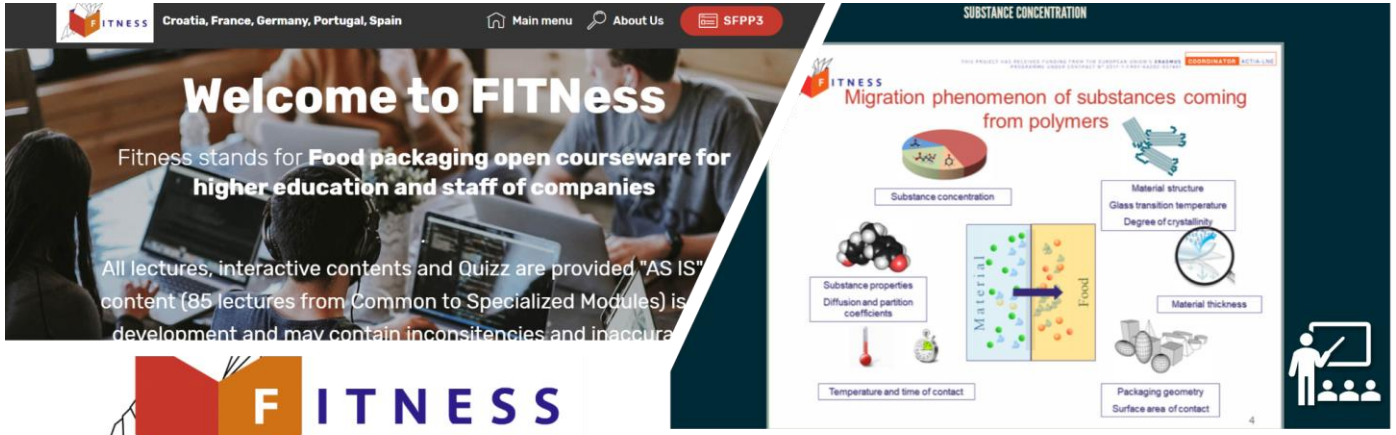


+poor design and GMP
+weak regulation rules
+poor training

=Risk of Contamination + Environmental impact

$$ignorance = \frac{IT}{WHAT\ ABOUT\ IT}$$





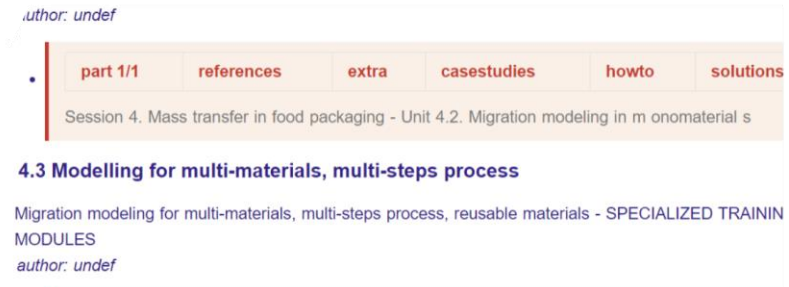
FITNESS

http://fitness.agroparistech.fr

Co-funded by the Erasmus+ Programme of the European Union

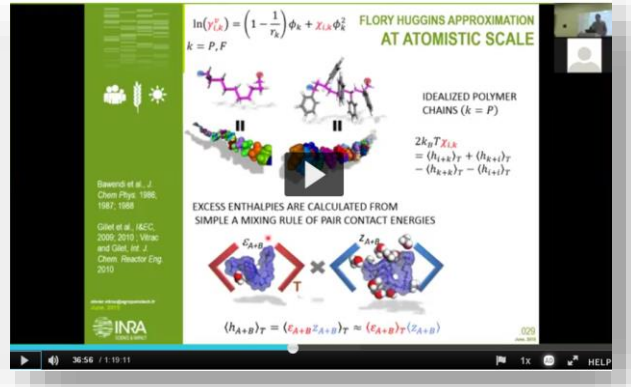
Online lectures

Online lectures
Common modules
1. What is food packaging
1.1 Panorama of food packaging
1.2 Packaging materials and shaping process
1.3 Basic legal framework
2. Properties of food packaging materials
2.1 Thermal, mechanical and barrier properties
3. Packaging and food preservation
3.1 Common physical chemical factors affecting food stability
3.2 Food packaging and shelf life



45

THE SCHOOL OF PACKAGING MICHIGAN STATE UNIVERSITY



- MY LECTURES AT MSU (MI,USA):
  http://www.fshn.msu.edu/events/event/Vitrac
  diffusion
  https://mediaspace.msu.edu/media/dr.+olivier+vitrac+presentsa+diffusion+coefficients+of+organic+solutes+in+polymersa/1_zz20dgt9
  PARTITIONING
  https://mediaspace.msu.edu/media/Dr.+Olivier+Vitrac+presentsA+An+atomistic+Flory-Huggins+formulation+for+the+tailored+prediction+of+activity+and+partition+coefficients/1_uzi6h91k
  SAFETY MANAGEMENT:
  https://mediaspace.msu.edu/media/WorkshopA+Prediction+of+the+migrationA+beyond+conventional+estimates*/1_won1m7aw