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### Predicting Diffusion Coefficients of Chemicals in and through Packaging Materials

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# ACCEPTED MANUSCRIPT

## Predicting diffusion coefficients of chemicals in and through packaging materials

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Most of the physicochemical properties in polymers such as activity and partition coefficients, diffusion coefficients and their activation with temperature are accessible to direct calculations from first principles. Such predictions are particularly relevant for food packaging as they can be used (1) to demonstrate the compliance or safety of numerous polymer materials and of their constitutive substances (*e.g.* additives, residues...), when they are used: as containers, coatings, sealants, gaskets, printing inks, etc. (2) or to predict the indirect contamination of food by pollutants (*e.g.* from recycled polymers, storage ambiance...) (3) or to assess the plasticization of materials in contact by food constituents (*e.g.* fat matter, aroma...). This review article summarizes the classical and last mechanistic descriptions of diffusion in polymers and discusses the reliability of semi-empirical approaches used for compliance testing both in EU and US. It is concluded that simulation of diffusion in or through polymers is not limited to worst-case assumptions but could also be applied to real cases for risk assessment, designing packaging with low leaching risk or to synthesize plastic additives with low diffusion rates.

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Keywords: diffusion, packaging, mathematical modeling, molecular modeling, migration

## 1 Introduction

The evolution of our urban lifestyles (takeout food, portioned packaging food, ready-to-eat food or microwaved food...) inevitably leads to a lot of concerns not only of sustainability impacts of packaging (Lewis *et al.*, 2010) but also of packaging food safety involving an increase of the surface area of the materials in contact with food and consequently to a repeated exposure to chemical substances leached by these materials (Delmaar *et al.*, 2005; van Leeuwen and Vermeire, 2007; Halden, 2010). Even if food contact materials are not the only source of exposure, such a chronic exposure starts from the first stages of life: during fetal life with the food ingested by the mother (Ranjit *et al.*, 2010) and baby foods (Muncke, 2011). The exposure related to ubiquitous substances (*i.e.* highly frequent in food) depends on the considered substance or family, its frequency of occurrence, the time and temperature of contact between the food and its packaging (Vitrac and Hayert, 2005, 2007a; Vitrac and Leblanc, 2007; Poças *et al.*, 2010) and in a less extent additional physicochemical factors such as pH and ozone content, which were found significant for the migration of bisphenol A (Mercea, 2009). Calculation methods for assessing consumer exposure of chemicals from packaging materials have been reviewed by Poças and Hogg (2007). They attract nowadays more and more attention due to the high concern for the contamination of packaged food product by endocrine disruptors (Vandenberg *et al.*, 2009; Wagner and Oehlmann, 2009; Tacker, 2011; Batra, 2011; du Yeon *et al.*, 2012) or cocktail of substances (Muncke, 2009; Zeliger, 2011). As a result, packaging materials are involved in strong scientific controversies propagated by evocative titles or editorials in both magazine and scientific literature such as: "How dangerous is Plastic" in Time Magazine of April 12, 2010 (Walsh, 2010); "...the drinking water left in a hot car can cause

breast cancer" in Nature Reviews Endocrinology of May, 2010 (Heath, 2010). Two controversies have found large echoes in the scientific literature: the contamination of drinking water stored in polyethylene terephthalate bottles (Bach *et al.*, 2012) and the role of packaging on the exposure to bisphenol A (Vandenberg *et al.*, 2009; Goetz *et al.*, 2010; Sharpe, 2010; Siva, 2012). Without necessarily similar audience, many surveys tend to incriminate almost all available materials in the market including: plastics (Wittassek and Angerer, 2008; Felix *et al.*, 2008; Guart *et al.*, 2011; Bach *et al.*, 2012; Kappenstein *et al.*, 2012), can coatings (Poole *et al.*, 2004), paper and board (D'Hollander *et al.*, 2010; Vollmer *et al.*, 2011). These experimental studies are macroscopic and usually neglect the physicochemical details and the conditions, where the amounts transferred to the food are significant. Such phenomena have been reviewed by Lau and Wong (2000), Piringer and Baner (2000, 2008), Helmroth *et al.* (2002a), Arvanitoyannis and Bosnea (2004), Poças *et al.* (2008). They all conclude on the key role of diffusion and its activation on migration of organic substances (*e.g.* additives, polymer residues) and mineral substances (*e.g.* catalyst residues) (Fordham *et al.*, 1995; Kawamura *et al.*, 2009; Welle and Franz, 2010; Haldimann *et al.*, 2012). Diffusion mechanisms in solid polymers have been discussed in several reference textbooks (Mehrer, 2010; Neogi, 1996; Stastna and De Kee, 1995; Vieth, 1991) and reviews. They tend however to focus either on the diffusion of gas molecules in polymers (Alexander Stern, 1994; Klopffer and Flaconnecche, 2001) or large molecules in gels (Masaro and Zhu, 1999). Hence, there is a general opinion according to: diffusion coefficients of additive-like molecules could not be predicted accurately (page 156 of Cussler (2009)) or related to the chemical structures of the diffusants (page 135 of Piringer and Baner (2008)). The practical consequence is that migration modeling concepts used to check the compliance of food

contact materials or for evaluating consumer exposure to packaging substances rely on models (Helmroth *et al.*, 2002a; Begley *et al.*, 2005) disconnected from the progress gained in the field of Polymer Science or more broadly in Chemical Engineering over the last decade. The question is all the more relevant than it could be expected that the same science might be used to design low migration materials assemblies and to assess the safety of materials (Vitrac and Hayert, 2007a; Nguyen *et al.*, 2013). For complementary properties, such as partition coefficients (Tehrany and Desobry, 2004) and their activation with temperature, it has been demonstrated that both molecular dynamics (Hess *et al.*, 2008; Hess and van der Vegt, 2008; Özal *et al.*, 2008; Boulougouris, 2010, 2011; De Angelis *et al.*, 2010) and advanced molecular simulation techniques (Gillet *et al.*, 2009a, 2010; Vitrac and Gillet, 2010) enable tailored and accurate estimations of partition coefficients of additive and polymer residues in rubber and glassy polymers (Lipscomb, 1990) without requiring any fitting procedure or experimental data. Similar trends have been obtained for diffusion coefficients, by simulating hundreds of configurations with coarse-grained molecular dynamics (Durand *et al.*, 2010) and by bridging free-volume theories for small and rigid solutes with the theory of flexible solutes in solid polymers (Fang *et al.*, 2013).

This review aims at filling the gap between disciplines to encourage a more critical use of physical models of diffusion rather than empirical approaches to extend the applications where migration modeling can be used for decision making (Brandsch *et al.*, 2002; Arvanitoyannis and Bosnea, 2004; Vergnaud and Rosca, 2006; Vitrac and Hayert, 2007a ; Gillet *et al.*, 2009b). Such contributions could be also thought to be used to assess consumer exposure to arbitrary substances whatever the availability of contamination data and to develop safe materials. In

particular, the concepts of homologies which enable to extrapolate the diffusion coefficient of from one molecule to a close one or from a polymer to another one are detailed in depth beyond early attempts by Reynier *et al.* (2001a), Reynier *et al.* (2001b) and Vitrac *et al.* (2006).

## 2 The concepts of “generally recognized diffusion models” in legal US and EU systems

US and EU manage the risk of contamination of food by packaging substances by two closely related concepts but with different application modalities: “food contact substance notifications” under the US law and “inert food contact materials” principles in EU regulations.

According to US law, only the regulatory status of the components of a food contact material is tested and not the whole material itself. Under section 409(h)(2)(C) of the Federal Food, Drug, and Cosmetic Act (CFR, 2011) , a “food contact substance” is defined as a special (*i.e.*, indirect (Till *et al.*, 1987)) food additive “intended for use as a component of materials used in manufacturing, packing, packaging, transporting, or holding food if such use is not intended to have any technical effect in such food”. Coatings, plastics, paper, adhesives, as well as colorants, antimicrobials and antioxidants found in packaging fall into this category (Shanklin and Sánchez, 2005). Any substance, which was not generally considered as safe (GRAS) in food (CFR, 2012a) or in food packaging (CFR, 2012b) and not subjected to any Threshold of Regulation Exemption (CFR, 2012c; Munro *et al.*, 2002), must be listed in the inventory of effective food contact substance (FDA, 2012b), which includes 952 substances at the beginning of 2013 or listed in the CFR parts 174-181. If the substance does not fulfill any of the previous criteria because the substance is not listed and must be used for a different intended use, a notification must be

submitted. The notification stepwise process (FDA, 2012a) authorizes diffusion modeling as a substitute of experimental migration testing or to extrapolate the data at a different temperature as soon as a “predictable migration-time behavior (*e.g.* Fickian diffusion)” has been established. An example cited: “migration for two hours of retorting at 121°C can be estimated and added to migration after 238 hours at 40°C”. Without citing it, the reasoning assumes several properties or approximations. Firstly, that the transferred amount is invariant with the product  $Dt$  or  $\sqrt{Dt}$  (see Eq. 4.18 of Crank’s book (Crank, 1979) and section 3.1.4), where  $D$  is the diffusion coefficient and  $t$  is contact time. Secondly, it assumes an Arrhenius behavior over the whole range of temperature between 40°C and 121°C with activation energy of *ca.* 60 kJ·mol<sup>-1</sup> ( $\approx 8.31 \times 10^{-3} \ln(238/2) / (\frac{1}{273+40} - \frac{1}{273+121})$ ). Is it true for every polymer? Even if the glass transition temperature is crossed? Even if the material is closer to its melting point/flow threshold than its glass transition temperature? For any migrant regardless its size, geometry and flexibility? Similar extrapolations are used in US system to assess the safety of recycled materials. In this case, surrogates are used to simulate the misuse of materials before recycling (FDA, 2006). They should include: a volatile polar organic substance, a volatile non-polar organic substance, a non-volatile polar organic substance, a non-volatile non-polar organic substance, and a heavy-metal salt. As reported in Appendix 1 of (FDA, 2006), most of the  $D$  values used in numeric challenge tests originate also from mathematical models with a goal of extrapolating  $D$  values from one molecule to a next one. The safety of packaging for irradiated foods (Paquette Kristina, 2004) and of so-called “functional barriers” (see section 3.1.4) for both food (FDA, 2006, 2007) and drug (MAPP 5015.5, 2011) applications are supported by very similar arguments.

The EU regulation system uses in a very similar fashion the concept of migration rate or diffusion rate. Article 3 of the EU framework regulation 1935/2004/EC (EC, 2004) defines a so-called “inert packaging” as “manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could endanger human health...”. Migration modeling is a legal concept introduced in EU, initially via the article 14 of the Directive 72/2002/EC (EC, 2002a): “For certain types of plastics the availability of generally recognized diffusion models based on experimental data allows the estimation of the migration level of a substance under certain conditions, therefore avoiding complex, costly and time-consuming testing”. The concept has been reformulated in the Regulation 10/2011/EC: “generally recognized diffusion models based on scientific evidence that are constructed such as to overestimate real migration.” In other words, the estimation of diffusion parameters (*e.g.* diffusion coefficient, activation energies) and partitioning is assumed to be conservative and not the real values. But, How conservative are they? Is it safe to extrapolate the behavior from a small molecule to a large one? From low temperatures to higher temperatures? In EU, the results of the project SMT-CT98-7513(EC, 2002b) and published as a collective work by Begley *et al.* (2005) is usually chosen as reference (Poças *et al.*, 2008), whereas the Food and Drug administration (FDA, 2006) recommends earlier or alternative versions of these models (Baner *et al.*, 1996; Limm and Hollifield, 1996).

The sources of diffusion coefficients and activation energies are scarce and underline the needs of reliable models in absence of a generic database of diffusion coefficients. A bibliometric analysis ([ISI Web of Knowledge v5.9, Thomson Reuters, USA – on Feb 3<sup>rd</sup>, 2013]) shows that the number of specific studies of diffusion coefficients in polymers is in particularly

low regarding the importance of the task (*e.g.* number of substances and polymers): it is usually thought that between 5000 and 8000 different substances would enter into the composition of food contact materials with 885 substances for the sole positive list of additives and monomers for plastics in EU (EC, 2011, 2012a, b). Since 1979, 86 articles have been published in Macromolecules – the first journal in Polymer Science by its number citations –with “Diffusion Coefficient” in the title (over a total of 774 with “Diffusion” in the title). The collected effort tended to be reported to less specialized journals such as Food Additives and Contaminants, which has reported diffusion coefficient values in 45 articles, since 1990. The concept of “generally recognized diffusion model” is even more difficult to establish. The 90<sup>th</sup> edition of CRC Handbook of Chemistry and Physics (Lide, 2009) reports diffusion coefficients in gases, liquids and semi-conductors but none for polymers. The Physical Properties of Polymers Handbook (Mark, 2007) and The Polymer Data Handbook (Mark, 1999) report only diffusion coefficients of gases. Only the 4<sup>th</sup> edition of the Polymer Handbook (Brandrup *et al.*, 1999) includes some diffusion coefficients for organic compounds but without inferring any generic rules to extrapolate to other substances and polymers.

### 3 Some generalities about diffusion

#### 3.1 *Mass transfer from and to food packaging materials*

In most of the cases, the reality of leaching of substances by materials in contact into food cannot be observed by naked eyes. Migrating substances are indeed usually colorless, odorless and tasteless. Even with analytical methods, identifying an unknown chemical among all the food constituents is a cumbersome task (Himmelsbach *et al.*, 2009; Silva *et al.*, 2006;

Simal-Gandara *et al.*, 2002). By contrast, the reverse process is easier to highlight. In the everyday life, we shall have already noticed that transparent plastic tableware and containers can be easily tainted by food pigments, or their surface properties can be affected by oily contact. For both transfer from or to food packaging materials, diffusional transport is involved.

### *3.1.1 Sorption of food constituent into food packaging: first observation of the reality of diffusion*

A change of refraction index associated to the sorption of decane, simulating an oily contact, in polystyrene is presented in Fig. 1 based on the observations of Morrissey and Vesely (2000) but also described by Feigenbaum *et al.*, (1991). A moving migration front separates an outer region with polystyrene swollen by decane and a dry region, where the polymer remains at glassy state ( $T < T_g$  with a glass transition temperature  $T_g$  of ca. 95 °C). From a physicochemical point of view, the depicted sorption involves a complex transport mechanism combining the solute concentration gradient and the gradient of elastic stresses as detailed in (Del Nobile *et al.*, 1994; Lipscomb, 1990; Mensitieri *et al.*, 1991; Miller-Chou and Koenig, 2003).

### *3.1.2 Cross mass transfer in multicomponent food packaging systems*

Main migrants from packaging materials reported in the literature fall into two categories (Brimer and Skaanild, 2011; Crompton, 2007; Deshpande, 2002; Rahman, 2007):

1. Intentionally added substances known as additives to aid processing or end-service (life-time, mechanical properties...), including antioxidants, antiblocking agents, antifungal agents, bactericidal agents, brighteners and whiteners, colorants, expanding agents,

impact improvers, ultraviolet protective agents and ultraviolet degradation inhibitors, printing ink adhesives, gas barrier packaging oxygen scavengers, antisplit agents, antistatic agents, heat and light stabilizers, melt strength improvers, plasticizers, lubricants and slip agents, pigments, fillers, mold release agents, and fungicides.

2. Polymerization residues, including monomers, oligomers (with a molecular weight of up to 200), catalysts (mainly metallic salts and organic peroxides), solvents, emulsifiers and wetting agents, raw material impurities, plant contaminants, inhibitors, decomposition and side reaction products.

Apart of plasticizers, additives are usually hindered and bulky substances with relatively low diffusion coefficients, well-known primary distribution in packaging assemblies and initial concentrations typically lower than  $0.005 \text{ kg}\cdot\text{kg}^{-1}$ . Liquid plasticizers (Patrick and Limited, 2005) are by contrast small and low branched molecules used in high concentration (above  $0.1 \text{ kg}\cdot\text{kg}^{-1}$ ) with a much higher migration power. They tend to be ubiquitous not only in cling films but also in printing ink, adhesives, sealing closures, etc. Residues exhibit much broader chemical structures and migration behaviors: polymer degradation products, incomplete cross-linking reaction products, polymerization catalysts and initiators in curing reactions, processing aids such as solvents and surface agents... The occurrence of such substances and their migration routes are far less documented. According to (Deshpande, 2002), the more volatile gaseous monomers, *e.g.* ethylene, propylene, and vinyl chloride, usually decrease in concentration with time, but very low levels may persist in the finished product almost indefinitely. Styrene and acrylonitrile residues are generally the most difficult to remove.

Typical migrants with molecular weight ranging from 100 to 2300 g·mol<sup>-1</sup> are listed in Table 1. As detailed in Nguyen *et al.* (2013), recent crises such as those involving printing ink residues arose from an insufficient description and understanding of diffusional transport along the packaging and recycling supply chain. Ink components can be redistributed during the storage of films before contact (Nguyen *et al.*, 2013) or be present in recycled paper and board fibers and permeate across the primary packaging and contact layers (Biedermann *et al.*, 2011). In simple words, the list of possible contaminants is neither limited to the components of the layer in contact nor to the primary packaging.

Possible migrants which are not in contact with food need to diffuse before contaminating the food. More generally, diffusion is the limiting mechanism as soon as the concentration profile in the any layer (in direct contact or not with food) is not uniform. The identified sources and routes of all transfers are reported in Table 2; possible couplings due to cross-transfer are sketched in Fig. 2 in agreement with the more general discussion found in Vergnaud and Rosca, (2006). Activation of desorption of packaging constituents into food due to plasticization of the contact layer by food constituents (see Fig. 1) is poorly described the literature and very often referred as “oil extraction” (Helmroth *et al.*, 2002b; Riquet *et al.*, 1998). It is, however, underlined that not only triacylglycerols but many hydrophobic food constituents such as the aroma can also be absorbed in layers in contact (Ducruet *et al.*, 2007).

### 3.1.3 Mass transfer controlled by diffusion in the packaging materials

As reviewed by Wijmans and Baker (1995) “The solution-diffusion model has emerged over the past 20 years as the most widely accepted explanation of transport” in membrane

separation and more generally across dense polymers. This model must not be confused with other models, such as the “pore-flow model”, in which migrants are transferred by “pressure-driven convective flow through tiny pores”. This last model applies, for example, for papers and boards but not for plastics and thermosets.

For plastics, the generalization solution-diffusion model is also well accepted for multilayers and multi-materials as justified in Poças *et al.*, (2008); Roduit *et al.*, (2005); Tosa *et al.*, (2008) and in Nguyen *et al.*, (2013); Vitrac and Hayert, (2007a), respectively. For each packaging component, diffusion is controlled by a diffusion coefficient  $D$  (S.I. unit  $\text{m}^2 \cdot \text{s}^{-1}$ ). The main assumptions are summarized in Fig. 3. Between the food and the layer in contact and between packaging components, a partitioning coefficient, as reviewed by Tehrany and Desobry, (2004), controls the distribution of migrants between materials. On food side, mass diffusion combined with advection may also occur. Mass transfer resistances on the food side have been reported both in liquids (Goujot and Vitrac, 2013; Vitrac and Hayert, 2006; Vitrac *et al.*, 2007) and in “solid” food such as meat (Sanches Silva *et al.*, 2010; Sanches Silva *et al.*, 2007) and cheese (Cruz *et al.*, 2008). Concentration profiles of several chemicals in different food products have been reported during the EU project “Migrosure” (Franz and Simoneau, 2008). The corresponding mathematical modeling of mass transfer through the packaging and food has been formulated almost in its modern form by Reid *et al.*, (1980) and reformulated with several simplifications in several reviews (Helmroth *et al.*, 2002a; Lau and Wong, 2000; Poças *et al.*, 2008) and in more general terms by Rahman (2007) (see Table 40.2). They all acknowledge that the profiles and kinetics fit within the general diffusional and boundary equations discussed earlier by Crank (1979). In the field of food contact materials, the first mathematic models have

been described by Reid *et al.* (1980) and subsequently by Chatwin and Katan (1989). The authors showed in particular that the migration process could be satisfactorily simplified as a one-dimensional mass transfer problem from a contact material, with a total thickness  $l_P$ , to a food system, with a finite volume, denoted  $V_F$ . The key features are: i) to keep the real contact surface area,  $A$ , between the material and the food and consequently the same dilution ratio  $Al_P/V_F$ ; and ii) to reproduce the difference in solute chemical affinity between the food and the plastic in contact with a proper choice of the partition coefficient,  $K_{F/P}$ . Without increasing significantly the mathematical complexity, a boundary layer approximation can be used to account for the existence of an additional mass transfer resistance on the food side governed by a mass transfer coefficient,  $h$  with SI units in  $\text{m}\cdot\text{s}^{-1}$  (Reid *et al.*, 1980; Vergnaud, 1998; Vitrac and Hayert, 2005, 2006; Goujot and Vitrac, 2013). Experimental values have been tabulated by (Vitrac *et al.*, 2007) and can be incorporated within a dimensionless mass Biot number:  $Bi=h l_P/D$ . In the simplest case of monolayer materials with constant and uniform properties, the set of transport and conservation equations corresponding to Fig. 3 is given by:

$$\begin{cases} \frac{\partial c_{(x,t)}}{\partial t} = D \frac{\partial^2 c_{(x,t)}}{\partial x^2} \\ j|_{x=l_p}^{(t)} = -D \frac{\partial c}{\partial x}|_{x=l_p}^{(t)} = h(K_{F/P}c_{(x=l_p,t)} - c_F); \frac{\partial c}{\partial x}|_{j=0}^{t>0} = 0 \\ C_F^{(t)} = C_F^{(t=0)} + \frac{A}{V_F} \int_0^t j|_{x=l_p}^{(\tau)} d\tau \end{cases} \quad (1)$$

where  $c_{(x,t)}$  is the local concentration in packaging layer in contact. For uniform initial concentration profiles, approximate and exact analytical solutions to the set (1) can be found in Sagiv, (2001, 2002); Vitrac and Hayert, (2006); Goujot and Vitrac, (2013). It is important to note

that these references use a dimensionless form of Eq. (1), involving  $Bi$ , a dimensionless time or Fourier number  $Fo=Dt/l_p^2$ , a dilution ratio  $L=Al_p/V_F$

### 3.1.4 The concept of functional barrier

The concept of functional barrier is broadly used by the packaging community without clear definition (Widen, 1998). Article 3 of Regulation 10/2011/EC (EC, 2011) defines it as “a barrier consisting of one or more layers of any type of material which ensures that the final material or article complies with Article 3 of Regulation (EC) No 1935/2004”. In more general terms, it could be defined as a barrier layer inducing a significant delay in the permeation of migrants as reproduced in Fig. 4. When the barrier layer consists of one single layer of thickness  $l_{FB}$  and associated with a diffusion coefficient  $D_{FB}$ , the delay is given by Eq. of 4.25 in book of Crank (1979):

$$t_{delay} = \frac{l_{FB}^2}{6D_{FB}} \quad (2)$$

Glass and aluminum foil are considered absolute barriers and associated to infinite lag time. Polyesters (Bayer, 2002; Pennarun *et al.*, 2004a; Pennarun *et al.*, 2004b), amorphous silicate deposits (Fei *et al.*, 2012) have been proposed as significant functional barriers. Their use including virgin PET has been more particularly suggested for preventing recycled PET to be in direct contact with food (Begley and Hollifield, 1993; Crockett and Sumar, 1996; Triantafyllou *et al.*, 2002; Feigenbaum *et al.*, 2005; Dole *et al.*, 2006b; Cruz *et al.*, 2011). Polymer materials combining a functional barrier has been also proposed to prevent food contamination by various contact materials, including: irradiated polymers (Sadler *et al.*, 2001), materials incorporating nanoparticles (Alfadul and Elneshwy, 2010), printed materials (Fiselier

and Grob, 2012; Johns *et al.*, 2000; Piergiovanni *et al.*, 1999). The extension of transport equations (1) to materials incorporating a functional barrier is given in Laoubi and Vergnaud, (1996).

### 3.2 *Molecular diffusion*

#### 3.2.1 *A macroscopic definition*

The term “diffusion” by itself is the process by which matter is transported from one part of a system to another as a result of random molecular motions of the center-of-mass of molecules (Crank, 1979). The process may cover very different realities: bulk diffusion in gas, liquids or solids, Knudsen diffusion inside pores, surface, surface diffusion, capillary condensation, molecular sieving... (Cussler, 2009; Krishna and Wesselingh, 1997). Molecular diffusion is the general term for a mass transfer in the bulk (*i.e.* far from walls) in absence of external forces and consequently due to the sole effect of the thermal motion of all molecules and atoms. On earth, these conditions are difficult to fulfill in fluids due to some residual advection terms generated by gravity and better verified in solids (Brogioli and Vailati, 2000). Tracer diffusion and self-diffusion are the two special cases of spontaneous mixing of molecules, where diffusion occurs in absence of a significant composition gradient (or chemical potential gradient). This type of diffusion can be followed using isotopic tracers. The tracer diffusion is usually assumed to be identical to self-diffusion (assuming no significant isotopic effect) and takes place under thermodynamical equilibrium (Masaro and Zhu, 1999). By contrast, mutual diffusion or chemical diffusion occurs in a presence of a concentration gradient or more generally in presence of a chemical potential gradient (Wesselingh and Krishna, 2006). The

diffusion coefficients for these two types of diffusion processes are generally different because the diffusion coefficient for chemical diffusion is binary and it includes the effects due to the correlations between the displacements of the different diffusing species (Vignes, 1966).

The apparent paradox associated to a net mass flux along direction  $x$ ,  $J(x)$ , in presence of a sparse gradient, is removed by noting that such a flux must be proportional to the difference between the average molar velocity of the considered molecules,  $u$ , and of the mass reference frame,  $u_0$ , along  $x$  (Wesselingh and Krishna, 2006):

$$J(x) = c(u - u_0) = -D \frac{\partial c}{\partial x} \Big|_{(x)} \quad (3)$$

The superiority of this representation arises because it is also defined in presence of one single migrant. In this case,  $u$  and  $u_0$  are time-averaged instead of population averaged and  $J$  is a stokesian flux (Keffer *et al.*, 2004). Although such results may look obvious to many readers, they remain a very active research area (Mu *et al.*, 2009), in particular to express  $u$  with the local properties of the polymer bulk or in presence of nanocharges, see some examples in Masaro and Zhu, (1999); Keffer *et al.*, (2004); Choudalakis and Gotsis, (2009); Arora and Padua, (2010); Mu *et al.*, (2010); Spearot *et al.*, (2012); Janes and Durning, (2013). The first concepts emerged with two papers among five that A. Einstein wrote in 1905 identified today as, “the year that changes the face of physics” (Stachel, 2005). As quoted by Einstein himself, the first “paper is a determination of the true sizes of atoms from the diffusion and viscosity of dilute solutions of neutral substances”; the second “proves that, on the assumption of the molecular [kinetic] theory of heat, bodies of the order of magnitude of 1/1000 mm, suspended in liquids, must already perform an observable random movement that is produced by thermal motion”.

### 3.2.2 A microscopic definition

Since the works of A. Einstein, the reality of the molecules is not a subject of debate (Psilios, 2011). The description of the random walks of migrants in polymers is exemplified in Fig. 5 as one-dimensional mass transport. The discrete hopping mechanism but continuous in time is consistent with the kinetic Monte-Carlo simulations proposed in high dimensions by Vitrac and Hayert (2007a) for diffusants much larger than polymer voids in polymers, such as plastic additives. Below a critical time scale, large comparatively to the vibration of atoms, diffusants appear trapped. Beyond, a sufficient reordering of the whole diffusant-polymer system enables independent displacements of the center-of-mass, denoted CM, of the diffusant. In absence of correlated displacements of CM, the motion is called Brownian (Hanggi and Marchesoni, 2005) and is controlled by the self-similar skewed trajectories. These derivations lead to express the diffusion coefficient,  $D$ , as the product of a hopping frequency,  $v_{(t)}$ , and squared hopping length,  $l_{(t)}$ , (Vitrac and Hayert, 2007a):

$$\lim_{t \rightarrow \infty} D_{(t)} = \lim_{t \rightarrow \infty} \frac{1}{2d} l_{(t)}^2 v_{(t)} \quad (4)$$

where  $d$  is the number of dimensions (*i.e.*  $d$  is 3 in 3D). It is very important to note the analogy of Eq. (4) and Eq. (2) used for functional barriers ( $d=3$  in this case as migrants are not confined along a line).

### 3.2.3 Trace diffusion and random walks

On time scales longer than molecular trapping times, the results of Einstein, Smoluchowsky, Langevin and Perrin (Haw, 2002) enable to relate to the time dependence of the motions of a single additive type substance to Fickian diffusion used in system (1). Einstein

turned the macroscopic diffusion problem into a probabilistic description by noting that the evolution of the spatial distribution  $p_{(x,t)}$  of a single particle can be predicted by the second equation of Fick (Einstein, 1905b):

$$\frac{\partial p_{(x,t)}}{\partial t} = D \frac{\partial^2 p_{(x,t)}}{\partial x^2} \text{ with } p_{(x,t=0)} = \delta(x) \quad (5)$$

where  $\delta(x)$  is the delta or Dirac function with  $\delta(x=0)=1$  and 0 elsewhere. For an infinite one-dimensional mass transfer problem, multiplying the left hand side of Equation (5) by  $x^2$  and integrating them by parts yields the mean-square-displacement (MSD) of the diffusant:

$$\int_{-\infty}^{+\infty} \frac{\partial p_{(x,t)}}{\partial t} x^2 dx = \frac{\partial}{\partial t} \int_{-\infty}^{+\infty} p_{(x,t)} x^2 dx = \frac{\partial}{\partial t} \langle x^2 \rangle \quad (6)$$

By noticing that  $\int_{-\infty}^{+\infty} \frac{\partial}{\partial x} \left( x^2 \frac{\partial p_{(x,t)}}{\partial x} \right) dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} (xp_{(x,t)}) dx = 0$  for any odd integrand and that

mass balance enforces  $\int_{-\infty}^{+\infty} p_{(x,t)} dx = 1$ , a similar treatment to the right hand side of Eq. (5) leads to

a constant:

$$\begin{aligned} \int_{-\infty}^{+\infty} \left( x^2 D \frac{\partial^2 p_{(x,t)}}{\partial x^2} \right) dx &= D \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} \left( x^2 \frac{\partial p_{(x,t)}}{\partial x} \right) dx - D \int_{-\infty}^{+\infty} \left( \frac{\partial x^2}{\partial x} \frac{\partial p_{(x,t)}}{\partial x} \right) dx = 0 - 2D \int_{-\infty}^{+\infty} \left( x \frac{\partial p_{(x,t)}}{\partial x} \right) dx \\ &= -2D \left( \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} (xp_{(x,t)}) dx - \int_{-\infty}^{+\infty} p_{(x,t)} dx \right) = 2D \end{aligned} \quad (7)$$

Equating (6) and (7) demonstrate that the variance of the position of a diffusant centred around of 0 will increase linearly with time as illustrated on simulations depicted in Fig. 6. This property is used to derive diffusion coefficients in polymers from molecular dynamics

simulations including  $N_{\text{diffusants}}$  according to the generalized Einstein relationship (Durand *et al.*, 2010; Keffer *et al.*, 2004; Li *et al.*, 1997):

$$\begin{aligned}
 D &= \frac{1}{6N_{\text{diffusants}}} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_{i=1}^{N_{\text{diffusants}}} [r_i^{\text{CM}}(t) - r_i^{\text{CM}}(0)]^2 \right\rangle \\
 &= \frac{1}{6N_{\text{diffusants}}} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_{\text{diffusants}}} g_{\text{CM}}(t) \\
 &\approx \frac{1}{6N_{\text{diffusants}}} \lim_{t \rightarrow \infty} \frac{g_{\text{CM}}(t)}{t}
 \end{aligned} \tag{8}$$

where  $r_i^{\text{CM}}(t)$  is the position of the center-of-mass of the  $i^{\text{th}}$  diffusant. The ensemble averaged operator  $\langle \rangle$  is applied to all possible reference positions of CM  $r_i^{\text{CM}}(0)$ . According to Eq. (3), it is important to notice that the positions are corrected from a possible drift of the center-of-mass of the whole system.

### 3.2.4 Mutual diffusion

When the concentration of diffusant is large (*e.g.* plasticizer or solvent), the flux of diffusant may disturb the local composition of the binary mixture which may in return affect the interactions with surrounding force. In this case, it is preferable to relate the diffusant concentration gradient  $\partial c / \partial x$  to its corresponding chemical potential gradient  $\partial \mu / \partial x$  (Krishna and Wesselingh, 1997). By expressing chemical potentials in polymers with volume fractions as recommended in Gillet *et al.*, (2009a, 2010) instead of molar fractions, the intuitive approach of Vignes (1966), reviewed by Hsu and Chen, (1998); Nauman and He, (2001), leads to Eqs. (9) and (10):

$$\frac{\partial \mu}{\partial x} = \frac{\partial \mu}{\partial \phi} \frac{\partial \phi}{\partial x} = RT \frac{\partial \ln(\gamma\phi)}{\partial \phi} \frac{\partial \phi}{\partial x} = \frac{RT}{c} \left[ \frac{\partial \ln(\gamma)}{\partial \ln(\phi)} + 1 \right] \frac{\partial c}{\partial x} = \Gamma \frac{RT}{c} \frac{\partial c}{\partial x} \quad (9)$$

where  $\gamma$  is the diffusant activity coefficient respectively to its volume fraction  $\phi$ .  $T$  is the absolute temperature,  $R$  is gas constant,  $\Gamma$  is the thermodynamic factor that controls the deviation from ideality:  $\Gamma$  is a thermodynamic correction factor depending strongly on the local composition and equal to 1 when the polymer-diffusant mixture is ideal, that is when the solute-polymer obeys to Henry's law. Substituting Eq. (9) in Eq. (3) gives a new definition of the net flux:

$$J(x) = -D_{MS} \frac{c}{RT} \frac{\partial \mu}{\partial x} \Big|_{(x)} = -D\Gamma^{-1} \frac{\partial c}{\partial x} \Big|_{(x)} \quad (10)$$

where  $D_{MS}$  is the Maxell-Stefan diffusivity (Curtiss and Bird, 1996; Krishna and Wesselingh, 1997). Several expressions generalizing  $D = \Gamma D_{MS}$  have been proposed for diffusant-polymer mixtures, they are all derived from Darken equation (Sunderrajan *et al.*, 1996).

As already exemplified in Fig. 1, the absorption of the release of substances can modify the relaxation of polymer chains. When mass transfer causes the glass transition to be crossed or approached, major deviations to a Fickian behavior (pure self-similar random walk on several time and length scales) can occur as reported experimentally in Callaghan and Pinder, (1984); Vrentas *et al.*, (1986); Saby-Dubreuil *et al.*, (2001); Dubreuil *et al.*, (2003); Mueller *et al.*, (2012). Consistent descriptions of such transports in technological contexts are proposed by Narasimhan and Peppas (1996).

### 3.3 *Diffusion in thermoplastic and elastomers*

Thermoplastics and elastomers are polymeric materials possibly compounded with additives and charges (Brydson, 1999). Their differences are very subtle: the first one flows in melts when temperature is increased and are used as fibers or containers, whereas elastomer is defined as a polymer which displays rubber-like elasticity (IUPAC, 2007) with primary uses as adhesives or sealants. From a chemical point of view, elastomers are usually polymers cross-linked during a curing step (McKeen, 2008). Such concepts are now extended via physical crosslinking to thermoplastic elastomers (Costa *et al.*, 2010) which combine segments with low glass transition temperature, denoted  $T_g$ , and with crystalline segments or rigid segments with high  $T_g$ .

Below their melting point at solid state, polymer materials consist of entangled chains, whose organization is not completely random (Crawshaw and Windle, 2003; Lakes, 1993). Fig. 7 exemplifies such a hierarchized in high density polyethylene at different scales of observation. The resulting broad dispersion of chain segmental motions in time and space has been investigated by molecular dynamics simulation at atomistic scale (Kotelyanskii and Theodorou, 2004) and coarse-grained scale gathering one or several monomers in one single bead or blob (Vettorel *et al.*, 2007). It is usually considered that diffusion in semi-crystalline polymers occurs exclusively in the amorphous phase of the polymer as reviewed by Hedenqvist and Gedde (1996) and experimentally tested by Van Alsten *et al.*, (1995). Although spherulites depicted in Fig. 7 are argued to be impenetrable, several multi-scale simulations showed that diffusion spreads through defects in spherulites (Mattozzi *et al.*, 2006; Nilsson *et al.*, 2009) and in interphases between crystallites (Zhu *et al.*, 2001). The possible invasion of large crystalline structures by

diffusants would explain the apparent homogeneity of diffusion concentration profiles in most of semi-crystalline polymers. As a result, beyond critical time and space scales, diffusion appears homogeneous in space and linear theory of diffusion with a uniform diffusion coefficient (see Eq. (1)) is fulfilled.

According to temperature and  $T_g$ , the amplitude and frequency of segmental motions can vary in a dramatic extent between rubbery materials ( $T > T_g$ ), with time scales between  $10^{-13}$  s and  $10^{-3}$  s, and glassy materials ( $T < T_g$ ) where they reach  $10^3$  s and beyond (Barrat *et al.*, 2010). The different cooperative chain segmental displacements from glassy to molten state are sketched in Fig. 8. As detailed by Baschnagel *et al.*, (2004) from simulations at different scales and illustrated in Fig. 14, only crankshaft motions exist below  $T_g$  and can contribute to diffusion. Above  $T_g$ , local polymer relaxations are combined with large segmental motions between entanglements and restrictions, offering large fluctuations of free volumes (see section 5). Finally, above the polymer melting point,  $T_m$ , the chain can translate along its full length.

Higher densities in glassy materials combined with extremely low renewal rates of free volumes cause diffusion coefficients to be several lower decades in glassy polymers than in rubber ones. Fig. 9 illustrates the scaling of  $D$  for two extreme polymers: natural rubber and glassy polyvinyl chloride (PVC), thought as likely upper and lower envelopes of diffusion coefficients met in plastics and substances with molecular weights ( $M$ ) lower than  $200 \text{ g}\cdot\text{mol}^{-1}$ . The ratio of  $D$  in rubber to PVC increases exponentially with the volume of the diffusant (see section 5 for more details) for He ( $M=4 \text{ g}\cdot\text{mol}^{-1}$ ), methane ( $M=16 \text{ g}\cdot\text{mol}^{-1}$ ) and Hexane ( $M=86 \text{ g}\cdot\text{mol}^{-1}$ ) are ca. 10,  $10^4$  and  $10^7$  respectively. The difference in translation mechanism between glassy and rubber polymers is further illustrated in Fig. 14.

## 4 Scaling laws and friction models

The molecular weight  $M$  is one of the main molecular descriptors to predict an order of magnitude of  $D$ . This section presents the main scaling laws  $D \propto M^\alpha$  associated to the tracer diffusion or self-diffusion in condensed phases and the polymer matrices. These scaling laws are first introduced from theoretical considerations and compared with experimental values.

### 4.1 Overview

#### 4.1.1 Hydrodynamic theory of diffusion

Firstly Einstein (Einstein, 1905a, b; Einstein and Fürth, 1956) and subsequently Langevin (Langevin, 1908; Lemons and Gythiel, 1997) proposed and extended a likewise interpretation of the Brownian motion. By assuming that acceleration of contribution is short-lived, Einstein showed that the driving force,  $f$ , which Langevin showed to be random with white spectrum, should be equated by a drag force proportional to the displacement velocity of the diffusant:  $\zeta_0(u-u_0)$ , with  $\zeta_0$  a molar friction coefficient. By noting that the work associated to this force is also the work to insert the diffusant in the matrix (Krishna and Wesselingh, 1997),  $f$  can be expressed in the form (see Eqs. (3) and (10)):

$$f = -\frac{\partial \mu_{(x)}}{\partial x} = \zeta_0(u-u_0) = \zeta_0 \frac{J_{(x)}}{c_{(x)}} = -\overbrace{\zeta_0 \frac{D\Gamma^{-1}}{RT}}^{\equiv 1} \frac{\partial \mu_{(x)}}{\partial x} \quad (11)$$

By identification, one gets a first mechanistic description of  $D$ , known as Einstein relationship:

$$D = \Gamma \frac{RT}{\zeta_0} \quad (12)$$

For a spherical substance of radius  $R_H$  diffusing in a medium of viscosity  $\eta$ , the Stokes formula with sticks boundary conditions predicts  $\zeta_0 = 6\pi\eta R_H$  (6 is replaced by 4 with a slip boundary condition instead (Kirkwood and Riseman, 1948)). For non-spherical substances,  $R_H$  is called hydrodynamic radius and its value depends not only on the shape but also mechanism of translation. For instance, for an aromatic ring of diameter  $R_\phi$ ,  $\zeta_0$  is expected to vary between  $\frac{32}{3}\eta R_\phi$  and  $16\eta R_\phi$  according to the ring translates edge on (likeliest) or face on (unlikely), respectively. The value averaged over all orientations is  $12\eta R_\phi$  (Berg, 1993).

For a flexible substance including  $N$  similar heavy atoms or sub-units (*e.g.* methylene group in  $n$ -alkanes), so-called blobs,  $R_H$  could be thought proportional to the gyration radius  $\left(\frac{1}{N} \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{CM})^2\right)^{\frac{1}{2}}$ , where  $\{\mathbf{r}_i\}_{i=1..N}$  and  $\mathbf{r}_{CM}$  are the position vectors of blobs and of center-of-mass (CM) respectively. The positions depend however on the conformations of the substance so that only the scaling law as:  $R_H \propto N^\alpha$  can be easily derived (Yamakawa, 1971), with  $\alpha$  depending on the diffusant flexibility. For  $N$  compact beads, one expects  $\alpha \approx 1/3$  whereas, for a linear and sufficiently long molecule, 1/2 and 3/5 are expected in a theta (*i.e.* random coils configurations) and good solvent (*i.e.* stretched configurations), respectively (Teraoka, 2002). It is important to notice that such descriptions prevent  $\alpha$  from exceeding a value of 1. The Kirkwood-Riseman theory (Kirkwood and Riseman, 1948) offers further insight by calculating explicitly the total friction coefficient, which simplifies for a bead-spring model as (Pastor and Karplus, 1988):

$$\zeta_t = \eta \frac{6\pi\sigma}{1 + \frac{\sigma}{N} \sum_{i,j=1..N, i \neq j} \left\langle \left( \|\mathbf{r}_i - \mathbf{r}_j\| \right)^{-1} \right\rangle} N \quad (13)$$

where  $\sigma$  is the effective radius of a blob, assumed to be all identical.  $\|\mathbf{r}_i - \mathbf{r}_j\|$  is the distance between blobs.

#### 4.1.2 Theoretical composition laws for diffusants consisting in $N$ repeated patterns

For a linear and flexible solute consisting of  $N$  repeated patterns (also called blobs), it is relevant to express  $D$  as a scaling law with  $N$  or equivalently with  $M$ :

$$\frac{D(T)}{D_0(T)} = \left( \frac{M}{M_0} \right)^{-\alpha(T)} \quad (14)$$

where  $M_0$  and  $D_0$  are the molecular weight and diffusion coefficients of reference molecule. The values of  $\alpha$  for typical mechanisms of diffusion are reported in Table 3.

When the displacements of all  $N$  blobs are homogenous in time with a growing mean-square-displacement (msd) denoted  $g(t)$ , the msd of the center-of-mass (CM) is inferred from the covariance of the averaged displacements of all blobs (Fang *et al.*, 2013):

$$g_{CM}(t) = \frac{1}{N^2} \left( \sum_{i=1}^N g(t) + 2 \sum_{i,j: i < j} C_{i,j}(t) g(t) \right) = \left( \frac{1}{N} + \frac{2}{N^2} \sum_{i,j: i < j} C_{i,j}(t) \right) g(t) \quad (15)$$

By neglecting torsional constraints, only the  $N-1$  correlations between the displacements of connected blobs are significant and Eq. (15) becomes:

$$g_{CM}(t) = \frac{g(t)}{N} + 2 \frac{N-1}{N^2} C_{connect}^{(t)} g(t) \quad (16)$$

wherein  $C_{connect}^{(t)}$  is the normalized correlation between the displacements of two connected blobs.

Replacing Eq. (16) in Eq. (8) leads to a definition of  $D$  close to the one proposed by Kirkwood and Riseman (1948). In the latter,  $D$  is combined to be the sum of two contributions:

- i) A composition law for  $N$  blobs equivalent to  $\frac{g(t)}{N}$  in Eq. (16) and named after Rouse work (Prince E. Rouse, 1953), and corresponding to  $\alpha=1$  in Eq. (14).
- ii) An additional effect due to weak interactions between blobs generalizing the Derjaguin's approximation between two spherical particles (Derjaguin, 1934).

Replacing  $\zeta_0$  in Eq. (12) by  $\zeta$ , defined in Eq. (13), one gets Eq. (17) for an ideal system ( $F=1$ ) (Edwards *et al.*, 1981):

$$D = \lim_{t \rightarrow \infty} \frac{g_{CM}(t)}{6t} = D_{rouse} + D_{hydrodynamics} = \frac{RT}{N\zeta_0} + \frac{RT}{6\pi\eta} \frac{\sum_{i,j=1..N,i \neq j} \langle (\mathbf{r}_i - \mathbf{r}_j)^{-1} \rangle}{N^2} \quad (17)$$

The concept of hydrodynamic interactions is derived from colloidal theories (Liang *et al.*, 2007) and assume that the linear solute is a collection of colloidal particles diffusing in an incompressible solvent continuum. Such assumption is known to be well verified for polymers in melt or linear diffusants dissolved in a solvent consisting of much smaller molecules (Masaro and Zhu, 1999), but it is questionable for short migrants in interactions with long and entangled polymer chains where renewal rates of free volumes are much slower. According to Fang *et al.* (2013), long-lived contacts tend to dominate so that the coupling between correlated displacements of blobs can be neglected (*i.e.* no effect of the square dependence) and so that  $\alpha$  can be considered equal to unity.

Scaling of  $D$  as  $\alpha=1$  (Rouse theory) has been initially proposed in diluted solutions (Prince E. Rouse, 1953), and has been subsequently generalized to concentrated media (Ferry *et*

*al.*, 1955). This theory is the most likely for linear solutes which are not entangled with the polymer. In practice, it is well verified for both self- (*e.g.* *n*-alkane or *n*-alcohols diffusing among other alkanes) and trace diffusion (*e.g.* *n*-alkanes in polyethylene) as soon as the static and dynamic properties of the host can be considered independent from the length of the considered diffusants. For self-diffusion, free volume effects have to be corrected (as the density of the host change with  $M$ ) to get  $\alpha = 1$  (Harmandaris *et al.*, 2002; Meerwall *et al.*, 1998), if not the monomeric friction coefficients,  $\zeta_0$  is found to vary with diffusant length (Rhee *et al.*, 1977; Wong *et al.*, 1970). For trace diffusion coefficients,  $\alpha=1$  is found in polyethylene melts without any subsequent correction as the density of the host is constant at constant temperature. Similar results for self and trace  $D$  have been systematically investigated by coarse-grained molecular dynamics simulation by Durand *et al.* (2010) with a generic flexible model in the temperature range, 1.3Tg and 4Tg. However, it is emphasized that  $\alpha$  values much larger than 1 have been reported by (Kwan *et al.*, 2003; Vitrac *et al.*, 2007) in solid polymers. The breakdown of the Rouse model near  $T_g$  has been suggested by Plazek *et al.* (1993) but resisted to correct explanations since recent years.

For large molecules ( $N \gg 30$ ), values greater than 1, ranging between 2 and 2.4 are proposed by reptation theory (Lodge, 1999), but it would be misleading to envision such mechanisms to substances with molecular masses ranging between  $10^2$  and  $10^3$  g·mol<sup>-1</sup> as their gyration radii are much smaller than the typical entanglement length of polymer segments (Fang *et al.*, 2013). Indeed, reptation mechanisms should be envisioned as a special case of Rouse relaxation where the translational displacements are enabled only along the contour of the molecule. The relaxation of Rouse model in curvilinear frame and its back projected in the

laboratory reference frame has been exactly calculated by De Gennes (1971) and is known to be the main factor responsible for an increase of  $\alpha$  from 1 to 2 for self-diffusion of polymer chains.

#### **4.2 Experimental data of diffusion coefficients in solid polymers**

Comparatively to diffusion in liquids or polymer melts, diffusion coefficients in solid polymers exhibit a broader range over several decades (Cussler, 2009; Fang *et al.*, 2013; Vitrac *et al.*, 2006), which are associated to a large spectrum of size and shape dependences, but with  $\alpha$  values strictly larger than 1.

##### **4.2.1 Linear substances**

In solid polymers, above the glass transition temperature of the polymer but below its melting point (or threshold of flow in the amorphous polymer), it has been proposed that the deviation to Rouse theory (*i.e.*  $\alpha > 1$ ) could be associated to a mixture of short and long-lived contacts with the polymer. For linear solutes, the following scaling of  $D$  has been theoretically based on double relaxation mode of blobs displacements:

$$\frac{g_{CM}(t)}{6D_0 t} = \frac{1}{\underbrace{\frac{2^N - 1}{2^{N-1} - 1}}_{N^{\Delta\alpha}} N} \frac{1}{C(t)} \quad (18)$$

where  $C(t)$  is the cumulated pair correlations between the displacements of all particles in the system to enable the translation of one single blob.

Experimentally, two strategies have been used to assess the deviation of  $\alpha$  to unity:

- i) measurement of  $D$  values of homologous series in the same conditions (*e.g.* same

polymer, same temperature, same method...) applied in Kwan *et al.*, (2003); Vitrac *et al.*, (2007); Fang *et al.*, (2013).

- ii) massive collections of  $D$  values of different substances from literatures as applied in (Vitrac *et al.*, 2006).

Both approaches are illustrated in Fig. 9 and Fig. 10 respectively. Fig. 10 provides  $\alpha$  value of  $n$ -alkanes in low density polyethylene far above  $T_g$ . The given experimental data confirm a strong dependence of molecular mass larger than 1 and approximately equal to 2 for linear  $n$ -alkanes ( $n=12..18$ ) and non-monotonously increase with the molecular weight. For branched alkanes ( $M=10..10^{3.2}$  g·mol<sup>-1</sup>), the reported  $\alpha$  values in Fig 10c) vary from 1 to 3.

#### 4.2.2 Additive type substances

For additive-type molecules, an homologous series of substance is difficult to establish (Hatzigrigoriou *et al.*, 2010; Pinte *et al.*, 2010; Pinte *et al.*, 2008). Scaling of  $D$  can be inferred only from the collection on a large set of data of  $D$  with  $M$ . The reported  $D$  values of additive-like molecules varying several decades in both rubbery and glassy states are demonstrated in Fig. 11. Scaling exponent  $\alpha$  increases again more rapidly with molecular weight in glassy polymer than in rubbery polymer.

#### 4.2.3 Combined effect of $T$ , $T_g$ and geometry

Recently, the discrepancy between  $\alpha$  values in melts (e.g.  $\alpha=1$  in polyethylene melt at 453K as shown by von Meerwall *et al.* (2007)) and in solid polymer (Vitrac *et al.*, 2007) has been explained, as the consequence of the temperature dependence of  $\alpha$  with polymer density.

Indeed thermoplastics are highly thermo-expandable above  $T_g$ . For aliphatic polymers above its  $T_g$ , plasticized or not, the following  $T-T_g$  dependence has been proposed for  $\alpha$ :

$$\alpha(T, T_g) = 1 + \Delta\alpha(T - T_g) = 1 + \frac{K_\alpha}{T - T_g + K_\beta} \quad (19)$$

where  $K_\alpha$  and  $K_\beta$  are temperature-equivalent parameters.  $K_\alpha$  is almost constant and  $K_\beta$  depends on the solutes series.

This dependence is illustrated on Fig. 12 for both linear and aromatic solutes series (Fang *et al.*, 2013). Presented diffusants are almost homologous and gathered in different polymers far above its  $T_g$ . For each series,  $D$  values are scaled as a power law of  $M$  (ranging between 70 and  $10^3$  g·mol<sup>-1</sup>), whose exponents are much greater than unity and tend to decrease when temperature is increasing. By fitting collected  $\alpha$  values versus  $T-T_g$  as described in Eq. (19), Fang *et al.* (2013) gets the scaling of diffusion behaviors of linear and aromatic solutes appear separated by a temperature shift of 91K.

## 5 Free-volume theories

### 5.1 Common assumptions

As quoted by Vrentas and Duda (1977), although the free-volume model of molecular transport is based on an oversimplified view of the detailed molecular processes, there exists a significant amount of evidence that such theories can be used to predict diffusion coefficients in liquids and polymeric materials (Hedenqvist *et al.*, 1996; Jain *et al.*, 1975). Free-volume theories rely on a common assumption that free volumes in amorphous systems can be decomposed

between interstitial free volume distributed almost uniformly around the considered substance and discontinuous distribution of holes (*i.e.* pocket of voids) as shown in Fig. 13 on a cross-section of a simulated polymer including a dissolved rigid aromatic diffusant. The free volume itself can be determined experimentally by positron annihilation lifetime spectroscopy (PALS) (Consolati and Quasso, 2001) or indirectly by following the approach of (Vrentas and Duda, 1977). According to Cohen and Turnbull (1959) and following earlier derivations by Doolittle (1951) for viscosity, it is thought that the redistribution of the energy of the interstitial free volume is so large that only the reorganization of free volume holes can be involved in the translation of diffusants. Both types of voids around diffusants are illustrated in Fig. 13. In liquids, Frenkel (Frenkel, 1955) describes similarly the transport of holes as a consequence of the displacements of all molecules in the mixture: one molecule occupying the hole next to it while leaving a similar hole at its initial position. The incompressibility of atoms compensates therefore instantaneously any increase in size of a hole by an opposite diminution of another hole.

The major assumption in Cohen and Turnbull (1959) theory is that the redistribution of holes does not require any change of the energy of the host+diffusant system (*i.e.* no significant free energy barrier to cross). At first sight, one important consequence should be that diffusion in polymers should not be activated by temperature. This conclusion would however be misleading as the static and dynamic properties of the polymers are also affected by temperature. The volume fraction of holes and their renewal rate is indeed higher at higher temperature, so that diffusion appears activated by temperature as the sole consequence of the thermal expansion of the liquid or of the rubber polymer. The interpretation of Cohen and Turnbull (1959) remains in

essence statistical. The diffusant translates when any amount of hole free volumes larger than a critical value, denoted  $\hat{V}^*$  appears. By noting  $D(v)$  the theoretical diffusion coefficient expected for a hole volume  $v$  occurring with a probability  $p(v)$ , the measurable diffusion coefficient is defined as the average over all possibilities of hole volumes larger than  $\hat{V}^*$ :

$$D(\hat{V}^*) = \int_{\hat{V}^*}^{+\infty} p(v) D(v) dv \quad (20)$$

Equivalently,  $p(v)$  must be seen as the limit probability distribution of the number of attempts of moving any atom (Bernouilli trials) before the first translation occurs. As the geometric distribution converges to the exponential one, it comes that  $p(v)$  is exponentially distributed and Eq. (20) becomes after integration (see Eu (2006) for a detailed demonstration and discussion):

$$D(T) = D_0 \exp(-\gamma \hat{V}^* / \hat{V}_{FH}(T)) \quad (21)$$

where  $D_0$  is a pre-exponential factor proportional to the section of the cage that is related to the geometry of the diffusant itself,  $\gamma$  is an overlap factor (ranged between  $1/2$  and  $1$ ) introduced because the same free volume is available to more than one diffusant.

$\hat{V}_{FH}(T)$  is the average hole free volume per molecule in the host. As  $\hat{V}^*$  is related to the diffusing species and could be thought roughly proportional to the volume of the diffusant. According to Fig. 9, this approximation is acceptable for short diffusants in elastomers far above  $T_g$  but not in glassy polymers. In the latter,  $\hat{V}^*$  is read to be proportional to  $6 \ln V_{VdW}$  instead, where  $V_{VdW}$  is the Van-der-Waals volume of the diffusing substance.

Additional sophistications are required to explicit the effect of temperature on  $\hat{V}_{FH}$  above and below  $T_g$  and to enable fractional jumps (translation much smaller than the size of the solute). Finally, the theory of free-volume theory which does not incorporate free energy barrier considerations (see Vitrac and Hayert (2007b)) must be extended to account the mixture of long and short-lived contacts between the solute and the surrounding polymer (Fang *et al.*, 2013).

## 5.2 Vrentas and Duda theory for rigid solutes

The Vrentas and Duda model extended iteratively Eq. (21) to polymer-solvent mixtures (Eq. (22)) through several papers (Vrentas and Duda, 1977; Vrentas *et al.*, 1985a; Vrentas *et al.*, 1985b). The general equation of Vrentas and Duda is more general than Eq. (21) and covers mutual diffusion. Since trace diffusion is a special case of mutual diffusion, it can be simplified as Eq. (22) for diffusant jumping as a single blob:

$$D = D_0 \exp\left(-\frac{E^*}{RT}\right) \exp\left(-\xi \frac{\gamma \hat{V}_P^*}{\hat{V}_{FH}}\right) \quad (22)$$

where  $\xi \hat{V}_P^*$  replaces  $\hat{V}^*$  in Eq. (21). The parameter  $\xi$  lumps all diffusant characteristics (volume, geometry,...); it is defined in the original formulation as the ratio of critical molar volume of diffusant jumping unit to critical molar volume of polymer jumping unit. The jumping unit is the elemental fragment of the diffusant or polymer involved in the translation.  $\hat{V}_P^*$  is a polymer dependent parameter with a meaning of the specific hole free volume of polymer required for a jump.  $\hat{V}_{FH}$  relates to the polymer thermal expansion property defined as the average hole free volume per gram of mixture and  $\gamma$  represents an average overlap factor for the mixture.  $E^*$  is an

additional activation term corresponding, according to Vrentas and Duda (1977), to the effective energy that a molecule needs to overcome attractive forces.

The last version of the theory (Vrentas and Vrentas, 1998; Vrentas *et al.*, 1996) provides a set of rules to calculate practically all parameters in Eq. (22). The useful relationships for polymer and diffusant parameters in Eq. (22) are gathered in Table 4 with key references providing additional details and sophistications.

The whole calculation procedures have been exemplified and tabulated for typical linear and aromatic solutes and different polymers (Vrentas and Vrentas, 1994, 1995; Vrentas *et al.*, 1996). Typical values are listed in Table 5.

Early versions of free-volume theories (Vrentas and Duda, 1977; Vrentas and Vrentas, 1994) required to fit parameters  $E^*$  and  $\xi$  from at least two experimental diffusion coefficients and might look empirical or semi-empirical as alternative ones (see section 7). The presented version of the free-volume theory (Vrentas and Vrentas, 1998) has to be considered, by contrast, as predictive, since all important parameters can be inferred from calculations or properties independent of diffusion ones. For diffusants including repeated patterns or sub-units, it has been shown independently by Fang *et al.* (2013) that properties could be extrapolated from one diffusant (with a molecular mass  $M_0$  and a geometric parameter  $\xi_0$ ) to a next one in the series from simple rules enabled by the scaling relationship in Eq. (19). Indeed,  $\xi - \xi_0$  was found well approximated by  $0.24 \ln\left(\frac{M}{M_0}\right)$  for all polymers and solute series considered by Vrentas *et al.* (1996). The main analogies and equivalences are listed in Table 6. They show in particular that

activation energy of linear solutes (*i.e.* aliphatic or aromatic) increases with the logarithm of the molecular mass.

At high temperature, free-volume theory predicts  $\alpha(T)\rightarrow 0$ . However, scaling exponents close to unity in agreement with Rouse theory have been reported for *n*-alkanes including from 8 to 60 carbons in many polymer systems (Chen and Ferry, 1968; Rhee *et al.*, 1977; Von Meerwall and Ferguson, 1979; von Meerwall *et al.*, 2007).

### 5.3 *Extension to flexible solutes*

The last version of the free-volume theory (Vrentas and Vrentas, 1998) does not have adjustable constants if the critical molar volume of polymer jumping units has been determined for the polymer of interest. This quantity is available for common polymers (Table 5). This theory assumes however that most of diffusants jump as single units. It is valid for rigid diffusants but questionable for large and flexible diffusants. Also, the average hole free volume associated with polymer and diffusant units are different.

For many diffusants of technological interest which tend to diffuse in a segment-wise manner, several physically driven modifications have been suggested: hybrid model for alkyl phenyl substances (Doong and Ho, 1992), modified free-volume model specifically for plasticizers in PVC (Coughlin *et al.*, 1990, 1991a, b; Mauritz and Storey, 1990; Mauritz *et al.*, 1990), or models for flexible and semi-flexible diffusants that are expected to move in a segmentwise manner (Deppe *et al.*, 1996; Ehlich and Sillescu, 1990). Zielinski (1996) was the first to relate  $\xi$  to the Kirkwood and Riseman (1948) theory (see Eq. (17)) for flexible diffusants.  $\xi$  was therefore related to the root-mean-squared end to end distance of the diffusants so that  $\xi$

can be estimated without diffusion data. Fang *et al.* (2013) followed similar ideas while including trapping effects due to the necessity of concerted displacements of blobs to get a significant translation of the center-of-mass. By following the same approach as used to derive Eq. (18) for simplest cases, the diffusion coefficients of many connected blobs was related to the equivalent diffusion coefficients of one single blob  $D_{blob}(T, T_g)$ :

$$D(\text{diffusant}, T, T_g) = \frac{D_{blob}(T, T_g)}{C(\text{diffusant}, T)} \quad (23)$$

where  $D_{blob}(T, T_g) = \exp\left(-\frac{K_a^{blob}}{K_b + T - T_g}\right)$  with  $K_a^{blob}$  and  $K_b$  constants are related to free-volume theory.  $C(\text{diffusant}, T)$  is a correlation term due to cumulated “trapping” effects with the polymer host. For convenience Eq. (23) can be recast for any diffusant chosen as reference and replacing  $D_{blob}(T, T_g)$ :

$$\frac{D(\text{diffusant}, T, T_g)}{D_0(\text{reference diffusant}, T_{ref})} = D_{\text{diffusant}_{\text{excess}}}(\text{diffusant}, T) D_{\text{polymer}}(T, T_g) \quad (24)$$

where  $D_0(\text{reference diffusant}, T_{ref})$  is a scaling parameter when diffusant=reference diffusant and  $T=T_{ref}$ .  $D_{\text{polymer}}(T, T_g) = \exp\left(-\frac{K_a}{K_b + T - T_g}\right)$  is the free volume contribution and coding for polymer effects via  $T_g$ .  $D_{\text{diffusant}_{\text{excess}}}(\text{diffusant}, T)$  is an excess diffusion coefficient when  $D$  values are extrapolated from the reference diffusant to any diffusant in the considered series regardless the considered polymer. In particular, it incorporates the effects of temperature on  $C(\text{diffusant}, T)$  which cannot be predicted by free-volume theories. The generalized free-

volume theory has been extensively tested on two homologous series of aromatic diffusants: diphenyl alkanes and oligophenyls in four different polymers at different temperatures covering from  $T_g+10$  K to  $T_g+110$  K. The main determinations are reported in Table 7.

## 6 Activation models and data

### 6.1 Apparent effects of temperature and pressure

The current review introduced several formal temperature dependences via Einstein relationship (Eq. (8)), scaling relationship (Eq. (19)), thermal expansion effects ( $\hat{V}_{FH}$  expression in Table 4), solute specific energy barrier ( $E^*$  expression in Table 4). None of these effects are captured via the familiar Arrhenius relationship. It is emphasized that the apparent discrepancy occurs because mechanistic theory descriptions cover a range of temperature much larger than the one covered usually experimentally: few tens of Celsius degrees. As a result, the Arrhenius relationship has to be seen as a local approximation of the real behavior around an absolute temperature  $T_0$  and a reference solute with a molecular mass  $M_0$  (or equivalently with a free volume parameter  $\xi_0$ ):

$$Ea(M_0, T_0) = -R \frac{\partial \ln D(M, T)}{\partial (1/T)} \Bigg|_{M=M_0, T=T_0} = T_0^2 R \frac{\partial \ln D}{\partial T} \Bigg|_{M=M_0, T=T_0} \quad (25)$$

Activation volumes are defined similarly and related to the effect of temperature:

$$Va(M_0, T_0) = -RT_0 \frac{\partial \ln D(M, T)}{\partial P} \Bigg|_{M=M_0, T=T_0} \quad (26)$$

Activation energies are very important quantities as soon as diffusion coefficients must be extrapolated to a different temperature: *e.g.* from room temperature to oven-heating or sterilization conditions or even to freezing conditions. Contrastingly, the polymers are not significantly compressible so that the values of activation volumes have mainly an interest except for predicting migration under very high pressure (beyond 200 MPa) such as those met in Pascalisation treatments (Dobiáš *et al.*, 2004; Juliano *et al.*, 2010; Lambert *et al.*, 2000; Le-Bail *et al.*, 2006) or to identify the molecular mechanisms of translation.

The activation energies and volumes for translation of paramagnetic probes in high density polyethylene (HDPE) are compared in Table 8 with the same quantities at molten state. They confirm the higher energies and activation volumes to induce a diffusant translation rather than to induce a local reorientation. The activation energies in HDPE are of the same order of magnitude as those associated with the relaxations  $\alpha$  and  $\alpha\beta$  of the polymer (Schmidt-Rohr and Spiess, 1991). For large polycyclic molecules, Ito *et al.* (1987) and Seta *et al.* (1984) showed that activation volume represents only a small fraction of the van-der-Waals volume of the diffusant ranged between 0.05 and 0.2. The fraction is smaller when the diffusant is more flexible. The experimental values of activation volumes validate independently the concept of jumping units smaller than the whole diffusant as found in the last free-volume theories (see section 5.3).

According to free-volume theory, the activation energy is expected to increase progressively from rubber to glassy state. The amount of reliable activation energy values tabulated in the literature is however insufficient to derive a general law. The difficulty to get reliable diffusion coefficients at glassy state arises from non-Fickian kinetics (Chernikov *et al.*, 1990; Geisel *et al.*, 1988) and ageing effects (Ehlich and Sillescu, 1990; Veniaminov and

Sillescu, 1999; Zhang and Wang, 1987). By comparing experimental determinations and theories, Tonge and Gilbert (2001b) argued that standard free-volume theories would tend to overestimate  $D$  values by neglecting the effect of waiting times before a jump can occur. Hall *et al.* (1999) showed that this effect could be included by assigning a proper value to parameter  $E^*$  in Eq. (22). In particular, the authors showed that an excess activation energy up to  $9 \text{ kJ}\cdot\text{mol}^{-1}$  was required for polar diffusants in a polar matrix.

The mechanisms of translation of additive-type molecules at different temperatures are summarized in Fig. 14 and compared with the available degree of freedoms in the polymer host. In the molten state ( $T > T_m$ ), the translation of diffusants is enhanced by the translation of the whole polymer chains. In the rubber state ( $T_g < T < T_m$ ), the translation of diffusants depends on local fluctuations of chain contours. In both cases, the activation energy must be envisioned as the consequence of local reorder of chain contours so that the activation energies are expected to increase slowly with the size and rigidity of the diffusant. In the glassy state, no degree of freedom is by contrast available for the polymer to open on a regular basis of free volumes and the translation can only occur occasionally when large reordering of polymer segments occurs. An example of such correlated displacement are the string-like motions of monomers in glassy polymers (Aichele *et al.*, 2003). The energetic barrier of translation must be seen as the consequence of the Poissonian distribution of such collective events as discussed within the framework of the transient state theory in Karayiannis *et al.*, (2001); Vitrac and Hayert, (2007b).

## 6.2 Activation energies

### 6.2.1 Effect of the molecular mass

The scaling law of diffusion coefficients for diffusants including linearly repeated sub-units (see Table 6) predicts a logarithm dependence of activation energy with molecular mass ( $M$ ). Fig. 15 plots on a log-log scale the evolution of  $Ea$  with  $M$  for linear and branched alkanes. The results were calculated from the work of European group SMT-CT98-7513 (EC, 2002b), partly reproduced by Begley *et al.*, (2005); Vitrac *et al.*, (2006) and available in the European database of diffusion coefficients hosted by the Safe-Food-Packaging Portal (INRA, 2011). As the data mixed diffusion coefficients published in peer-reviewed journals, data from migration tests and different kind of polyethylenes, the residual uncertainty is significant. The comparison with  $M$  shows however a systematic low dependence of  $D$  with  $M$ , which tend to confirm the proposed expression of  $Ea$  in Table 6. In details, volatile molecules ( $M < 100 \text{ g}\cdot\text{mol}^{-1}$ ) have  $Ea$  values close to  $50 \text{ kJ}\cdot\text{mol}^{-1}$  while the additive molecules have an activation energy comprising between  $85$  and  $100 \text{ kJ}\cdot\text{mol}^{-1}$ .

### 6.2.2 Polymer effects

The effects of the polymer host are analyzed in Fig. 16 by plotting the Van't Hoff diagrams of a model diffusant ( $2',5'$ -dimethoxy-acetophenone) in broad range of polymers: aliphatic, aromatic, with or without electrostatic interactions... It is emphasized that the data were obtained at or close to molten state with an intent of evaluating the properties of functional barriers of these polymers in co-extrusion conditions (Dole *et al.*, 2006a; Dole *et al.*, 2006b; Feigenbaum *et al.*, 2005). Comparisons between Figs. 15 and 16 show that polymer effects on  $D$

are one magnitude lower than solute ones at rubber state. Consistently with Fig. 12 and Eq. (23),  $D$  values are lower when  $T-T_g$  differences are smaller and apparent activation energies are higher in high  $T_g$  polymers. Indeed, high  $T_g$  polymers exhibit higher cohesive energies due to specific  $\pi-\pi$  interactions, polar,  $H$ -bonding, which turn to be also very sensitive to temperature. As reported in chapter 7 of Mark (2007) and in chapter 4.4 of van Krevelen and te Nijenhuis (2009), such interactions increase of the thermal expansion coefficient with temperature  $a(T) = -\gamma_p \left(\frac{\partial \rho}{\partial T}\right)_p$  and consequently activates dramatically the renewal rate of free volumes. Several models describing these effects were proposed by Simha and Boyer (1962) and have been incorporated in the Vrentas and Duda free-volume theory (see the expressions of  $\hat{V}_{FH}(T)$  beyond and below  $T_g$ ).

### 6.2.3 Combined solute and polymer effects

The activation energies collected around 40°C by Dole *et al.* (2006a) are plotted on a semi-log plot for a broad range of diffusants and polymers. They confirm the previously described trends: activation energies of additive-type substances are higher for larger substances and the activation energies are higher in high  $T_g$  polymers. In agreement with the extended free-volume theory proposed by Fang *et al.* (2013), the semi-log plot shows that  $E_a$  values tend to be linear with  $\ln M$  (see Table 6).

## 7 Alternative models to predict $D$ or to overestimate $D$

### 7.1 The justification of alternative models

Despite necessary adaptations, the polymer science community considers free-volume theories as the most reliable approach to estimate self- and trace diffusion coefficients in polymers as discussed in details in Meerwall *et al.*, (1998); Tonge and Gilbert, (2001a); Harmandaris *et al.*, (2002); Fang *et al.*, (2013). Its range of applicability has been broadly extended during the last four decades from polymer-solvent systems (Narasimhan, 2001) to arbitrary diffusants such as plasticizers (Coughlin *et al.*, 1990, 1991a, b; Mauritz and Storey, 1990; Mauritz *et al.*, 1990) or antioxidants (Boersma, 2003; Boersma *et al.*, 2003a, b), while including glassy polymers (Arnold, 2010; Romdhane *et al.*, 1995). In his literature review of “Models for Diffusion in Polymers”, Mercea (2008) quoted the free-volume theory as “classical approach” but concluded that they do not meet completely the following practical goals to provide enough incentives for the process engineer or the law enforcer: “(i) as simple as possible, (ii) rely on parameters which are well known and easily available, and (iii) at last but not least, the use of the method to predict diffusion processes should not consume more time and resources than the direct migration/diffusion experiments.” As a result, models so-called “alternative” by opposition with conventional ones (as listed in the review of Masaro and Zhu (1999)) have been sought for the food packaging applications.

The genesis and classification of such alternative models are difficult to reconstruct as they are used almost exclusively by a single scientific community (*i.e.* food packaging) and for a single purpose (*i.e.* compliance testing). The Piringer model, called Piringer “Interaction Model”,

is by far the most widely used by this community, which includes also us as authors. It has been firstly proposed by Baner *et al.* (1996) and is recommended by the EU commission for the implementation of diffusion modeling for the estimation of specific migration in support of EU regulation 10/2011/EC (EC, 2012c). The proponents argue that it has theoretical grounds whereas the Food and Drug Administration quotes it as “an empirical correlation based on the molecular weight of the migrant” (FDA, 1999, 2006). Piringer justified firstly his derivations in pages 158-169 of his book “Plastic Packaging Material for Food” (Piringer and Baner, 2000) and extended it in pages 163-193 of its second edition (Piringer and Baner, 2008). The general equation is said to be multipurpose: “a uniform model for predicting diffusion coefficients in gases and condensed phases, including plastic materials” (page 165 of the second edition). The demonstration is difficult to follow and apparently not available in peer-reviewed journals. The general form of equation Piringer (Eq. 6.17 of the second edition) is reshaped in this work to highlight its possible legacy with classical equations (Eq. (22)):

$$\begin{aligned} \frac{D}{D_0} &= \exp(w_n - A/A_0 - Ea/RT) \\ &= \underbrace{\exp\left(\frac{Rw_n}{R}\right)}_{\text{entropic contribution}} \underbrace{\exp(-A/A_0) \exp(-Ea/RT)}_{\text{enthalpic contribution}} \end{aligned} \quad (27)$$

In its general form, the model can be compared with classical theories to highlight possible similitudes. The exact meaning of the factor  $w_n$ , which is entropic by nature (*i.e.* not temperature dependent), is unclear. Based on the calculations of the contribution thermal vibration spectra to the long term translation of the center-of-mass (Fang *et al.*, 2013), the product  $Rw_n$  could be associated to the entropy of translation of a reference solute. The authors

showed indeed that the translational entropy increases with the number of atoms. The ratio  $A/A_0$  is the ratio of cross section respectively to a reference solute. It could be compared to  $\zeta-\zeta_0$  in classical free-volume theories (*i.e.* Table 6). However,  $w_n$ ,  $A$ ,  $A_0$  and  $Ea$  have only been inferred for the self-diffusion (see Eqs. 6.25-6.27, Fig. 6.3 and Table 6.7 in Piringer and Baner (2008)) and trace-diffusion of *n*-alkanes in polyethylene (see Eq. 6.28 and Fig. 6.4 in Piringer and Baner (2008)). In particular, the Eq. (27) fails to reproduce the correct scaling of  $D$  with  $M$  at different temperatures as reported in reference experiments on *n*-alkanes (Meerwall *et al.*, 1998; von Meerwall *et al.*, 2007). In practice, a simplified version of Eq. (27) is preferred instead (see Table 9) by using  $M$  as the unique descriptor of diffusant effects. Its goal is not to predict  $D$  values but to provide overestimates of  $D$ . Contrary to free-volume theories (see section 5 and discussions in Vrentas and Vrentas, (1995, 1998); Vrentas *et al.*, (1996)), the parameters cannot be determined without fitting existing  $D$  values. The overestimation concepts have been reviewed by Arvanitoyannis and Bosnea (2004) and have been subjected to several updates in the course of the European project SMT-CT98-7513 (EC, 2002b).

It is worth to notice that concurrent approaches have been proposed during the meanwhile. A very similar empirical equation has been proposed during the EU AIR Research Programme CT94-1025 (Feigenbaum *et al.*, 2002). Based on the same raw data collected during the project SMT-CT98-7513, Helmroth *et al.* (2005) and Vitrac *et al.* (2006) developed different approaches offering the possibility to retrieve either realistic estimates (*i.e.* with half chance to be either an underestimate or an overestimate) or overestimates with an arbitrary “safety margin”. The concepts of  $D$  overestimation and “safety margin” on migration (or equivalently  $C_F$ ) must not be confused. Effects of uncertainties and overestimations on  $D$  and other parameters such as

partitioning on  $C_F$  are particularly discussed in Vitrac and Hayert (2007a).  $C_F$  is a monotonously increasing function of  $D$  but usually not a linear function of  $D$ , so that an overestimation of  $D$  is not followed by a similar overestimation of  $C_F$ . For diffusion controlled monolayer materials (*e.g.*  $Bi > 100$ ,  $Fo < 0.6$ ), one has  $C_F \propto \sqrt{D}$ . By following similar considerations, the Helmroth model relies on a stretched exponential (see Table 9) and stochastic concepts to overestimate migration rather than simply diffusion coefficients. The probabilistic concept was formally stated and proven simultaneously by Vitrac and Hayert (2005) based on a stochastic resolution of Eq. (1). It is however important to note that the introduced law of probability represents the additional safety factor on  $D$  we need to consider due the lack of prediction of the considered model. For any model using only  $M$  as molecular descriptor, the uncertainty on  $D$  is assessed by the distribution of  $D$  values of solutes with similar  $M$  values in a prescribed polymer at a given  $T$ . The model of Vitrac *et al.* (2006) offers an alternative as it includes by contrast enough mechanistic descriptors (see section 7.3) and proper cross-validation procedures to predict  $D$  values to reach prediction errors in the same range as experimental errors.

## 7.2 Models overestimating $D$

Poças *et al.* (2008) and Helmroth *et al.* (2002a) have already reviewed the models, denoted  $\bar{D}_{(M,T)}$ , to overestimate  $D$  values. They are reported in Table 9 along with their apparent

scaling exponent with  $M$ :  $\bar{\alpha} = -\left. \frac{\partial \ln \bar{D}_{(M,T)}}{\partial \ln M} \right|_T$  with corresponding free parameters reported in

Table 10. Although all presented models claim to be a generalization of existing mechanistic models, they use simply molecular mass as the unique descriptor of all diffusant effects. In the

light of scaling theories (see section 4), their overestimation features at constant temperature are associated to the consequence of the underestimation of the true dependence of  $D$  to  $M$  for diffusants larger than a reference diffusant with molecular mass, denoted  $M_0$ :

$$\check{\alpha}(M,T) = -\frac{\partial \ln \check{D}_{(M,T)}}{\partial \ln M} \Bigg|_T \leq -\frac{\partial \ln D_{(M,T)}}{\partial \ln M} \Bigg|_T = \alpha(T, T_g, \text{diffusant series}) \quad \text{for } M \geq M_0 \quad (28)$$

In the Piringer model,  $A'P$  and  $\tau$  are polymer dependent parameters. A zero value for  $\tau$  leads to an apparent activation energy of  $87 \text{ kJ}\cdot\text{mol}^{-1}$ , which corresponds to a median activation energy in polyolefin matrices (see Figs. 15, 16 and 17).  $\tau$  is corrective activation parameter which depends only on polymer.

Contrary to mechanistic models (see Fig. 12 where  $\alpha$  is shown to be a function of the considered chemical series instead), all overestimating models invoke an equivalent scaling exponent  $\check{\alpha}$  which increases with  $M$ . Both Piringer and Helmroth models neglect the strong dependence of the true  $\alpha$  with  $M$ . Only the model of Limm and Hollifield (1996) takes into account some decrease of  $\check{\alpha}$  with  $T$  but not with  $T-T_g$ , as predicted by free-volume theory (see Eq. (22)). The values of  $\check{D}$ , calculated according to the three models (see equations and parameters listed in Tables 9 and 10) are compared with the 628  $D$  values and collected by the group SMT-CT98-7513 in Fig. 18. It is important to note that the reported  $D$  values cannot be considered as real  $D$  values, because there is no standard methods for measuring  $D$ , they were derived from different kinds of experiments published or not and arbitrary normalized at  $23^\circ\text{C}$ , by assuming an average action energy of  $85 \text{ kJ}\cdot\text{mol}^{-1}$  (EC, 2002b). In addition, since all the presented data were used to fit/set the free parameters involved in the Piringer and Helmroth models, the comparison with reported  $D$  values and calculated  $\check{D}$  ones does not constitute an

independent validation of these models. With the previous restrictions in mind, the best trade-off between too large overestimations and too large underestimations are obtained from the Piringer model. It underestimates the real  $D$  values in 5.2 %, 26.8% and 16.3% of cases, with maximum underestimation factors of 18, 17 and 365 (10 if 365 is considered to be an outlier), for LDPE, HDPE and PP, respectively. When it overestimates results, the overestimation ratio  $\bar{D}/D$  is ranged between a factor 1.3 and 193 (5<sup>th</sup> and 95<sup>th</sup> percentiles respectively) with an average value of 33 and a maximum value of  $1.5 \times 10^3$ . If migration is mainly diffusion controlled (*i.e.*  $C_F \propto \sqrt{D}$ ), it would lead to overestimations of  $C_F$  by factors 5.7 and 39, respectively.

The method to derive  $Ap'$  and  $\tau$  values is discussed in a recent European guidance document (EC, 2013). It is proposed to derive  $Ap'$  and  $\tau$  values for unknown polymers based on a small set of data and to use them extrapolate overestimates for a broader range of substances. From Fig. 18 and 19, it is obvious that the intangible dependence of  $\bar{D}$  with  $M$  cannot fit all polymers and the risk of underestimating  $D$  values is large if the reference experimental  $D$  values were based on molecules than those targeted by the use of the model. The experimentally determined values of  $\alpha$  from Fig. 12 and theoretical values of  $\bar{\alpha}$  calculated from Table 9 and 10 are compared in Fig. 19 for all three models. All models tend to underestimate true  $\alpha$  values far above  $T_g$ , in particular in oven-heating and sterilization conditions. As a result, the extrapolation of  $\bar{D}$  values to high temperatures might be unsafe in particular if the activation energies for low molecular weight compounds are overestimated.

The variations of the overestimation ratio offered by the Piringer model in two typical polymers at the rubbery state are reported in Fig. 20. The reference values ( $D$ ) were derived from the behaviors of aliphatic solutes and free-volume theory of flexible solutes (Fang *et al.*, 2013). It

is noticeable that iso- $D$  values and iso- $\bar{D}$  values are not parallel when there are plotted versus molecular length/weight and temperature. By itself, the concept of iso- $D$  value or of superposition principles of effects of ( $M, T, T_g$ ) is a consequence of the proximity of the core free-volume equation (22) and the Williams-Landel-Ferry one. Figs 20a) and b) show however that large and small substances with a similar diffusion coefficient at different temperatures according to the free-volume theory (see arrow) are seen with different  $\bar{D}$  overestimates presenting overestimation ratios varying over several decades. According to ratios  $\bar{D}/D$  reported in Figs 20c) and d), the overestimation is higher for larger substances and at lower temperatures. For volatile compounds or in high-temperature processes (e.g. oven-heating, pasteurization, sterilization,...), the ratio of overestimation vanishes exponentially with a significant risk of underestimation. As a result, it is recommended not to use the Piringer model for any purpose independently on the conditions used to set the model parameters. When the parameters need to be assigned for a new polymer or upgraded to include a broader range of conditions, European guidance documents recommend therefore usages of Piringer type diffusion models where extrapolation is likely to be robust (EC, 2012c, 2013). The recommendable directions and extents of extrapolation of  $\bar{D}$  values from a small set of experimental  $D$  values are summarized in Fig. 20e). As a rule of thumb and because the underestimation region (in red) is mainly located on the left hand-side, extrapolation from small to large molecules would be acceptable for substances belonging to the same category and within a small range of molecular masses (e.g. 50 g·mol<sup>-1</sup>). When a broader range of substances and conditions are required, reference  $D$  values should have to be collected at different temperatures higher than the targeted one and for molecules

representatives of the size and shape expected in future applications. Further sophistication would need a better consistency with free-volume theory.

Finally, one may notice that the Piringer model has been also proposed for non-thermoplastic materials such as paper and cardboard (Poças *et al.*, 2011; Störmer, 2010). As these materials are porous with a mass transfer occurring significantly in the gas phase, the general transfer mechanism does not obey to the previous diffusion-dissolution model presented in this review (see section 6.4 from Cussler (2009) for details). Since the detailed mechanisms depend on microscopic details (*e.g.* Knudsen diffusion, capillary condensation, surface diffusion...), they cannot fall within the category of “General recognized diffusion models” (see section 2). The relative higher importance of the transport through the gas phase will decrease the scaling exponents of effective diffusion coefficients  $\alpha$  down to 1/2 or 1/3. Due to a strong risk of underestimation of real  $D$  values when it is applied to substances different from tested ones, the usage of the Piringer model or of any free-volume theory should be avoided in these situations.

### 7.3 *Prediction of D based on decision trees and molecular descriptors*

Fig. 18 showed that diffusion coefficients cannot be explained by a sole molecular descriptor such as molecular mass,  $M$ , in particular for large diffusants. For a same  $M$  value, the uncertainty can reach three decades (Reynier *et al.*, 2001a). This variability for a same  $M$  is associated to coupled displacements of several host segments to reach a translation of large solutes. They cause a significant increase of delays between successive hoppings of diffusant elemental jumping-units. In the framework of generalized free-volume theory, these effects are

captured through the prefactor  $C(\text{diffusant}, T)$  (see in Eq. (23)). Using a different approach, Helmroth *et al.* (2005) proposed to solve the lack of prediction of simple models such as Piringer one by combining a master curve depending only on  $M$  with an upper envelope collecting all other effects not related to  $M$ . The values of  $D$  were assumed log-normal distributed with a standard deviation of  $\log \bar{D}$ ,  $s$ , as listed in Table 9. The integration of an upper confidence interval in the approach offers interesting overestimation capabilities but as in the Piringer model the overestimation ratio remains in essence variable for a same molecular mass and variable with temperature due to a global definition of  $s$  and the significant variation of  $\frac{\partial \ln D}{\partial \ln M}$  with temperature (see Fig. 19).

An alternative model was developed by Reynier *et al.* (2001b) and extended significantly by Vitrac *et al.* (2006) based on CART (classification and regression tree) methods. The main advantage of CART is that there are human readable while being able to describe any non-linear behavior (continuous or not). Starting from mechanistic considerations of diffusion close those used in Vrentas and Vrentas (1998), three descriptors (see Table 11) have been proposed to describe *a priori* the diffusion behavior of migrants regardless the considered polymer and temperature: van-der-Waals volume, gyration radius, shape factor. Their values are illustrated in Table 12 for typical diffusants. Without fitting, it has been shown that such a classification was able to gather homologous molecules with similar diffusion coefficients. This concept is illustrated on a commercial UV-stabilizer in Fig. 21. It demonstrates that the diffusant shape and rigidity are the main characteristics controlling the diffusion coefficients rather than the detailed chemistry.

Regression trees generalize classification trees with an aim of predicting  $D$  values while keeping similar simplicity (Breiman, 1984). It is a non-linear procedure, belonging to a broad range of machine learning methods, where the mathematical model is coded as a flow chart. Each internal node denotes a test on one of the three considered geometry factors. The last node (leaf) contains an estimate of  $D$  values: either the median of diffusion coefficients or an upper percentile. The model to predict diffusion coefficients in LDPE is depicted in Fig. 22. The predictions from pruned and cross-validated trees are plotted in Fig. 18. Contrary to previous models, the approach was able to keep the variability of original data (tested on 657  $D$  values including 267 substances, see Vitrac *et al.* (2006) for details).

## 8 Conclusions

The general discussion initiated by Gillet *et al.* (2009b) on the applicability of mathematical modeling for compliance testing showed that the interest in predictive methods drop dramatically when more than two parameters are unknown: identity of substances, concentration in the materials, diffusion and partition coefficients, external mass transfer resistance. Beyond two unknowns, uncertainty is increasing dramatically so that overestimated values of the migration tend to be systematically over all prescribed thresholds. Substituting point estimates of parameters (without limitations of their number) by their statistical distributions lessens the previous limitations, as demonstrated by Vitrac and Hayert (2005, 2007a) for monolayer and multilayer packaging materials respectively. Without providing additional knowledge, the probabilistic approach combines in various sources of uncertainty and variability, which is more acceptable in particular for risk assessment. Building a mechanistic

approach is however more satisfactory as it authorizes modeling as an extrapolation tool to new substances, polymers and conditions (plasticization, temperature). In silico methods are already available for partition coefficients (see introduction) but they start also to be available for diffusion coefficients. As a result, the paradigm of migration modeling may evolve from a prediction in worst-case conditions to real ones with controlled margin of safety. Recently the molecular concepts presented in this review have been integrated in a research collaborative project SafeFoodPack Design with an aim of developing an engineering approach of “safe” packaging materials (Nguyen *et al.*, 2013). Beyond the concepts optimizing packaging assemblies (*e.g.* with proper functional barriers) and their formulations (*e.g.* substances with lower diffusivities, solubilities and concentrations), intentionally added substances could be also redesigned to minimize the risk of migration for certain usages (*e.g.* sterilization, oven-heating). As a possible illustration, it has been shown that adding a flexible group close to the center of mass of the substances could decrease  $D$  by one decade for each 1.3 carbon added (Fang *et al.*, 2013). A list of strategies to reduce the leaching of additives has been itemized by Bart (2006) (see Table 2.19):

- 1) Maximizing solubility or minimize vapor pressure (by adding solubilizing groups, preferring compounds with a low melting point).
- 2) Minimizing volatility and solvent extractability (by adding large substances, preferring oligomeric additives).
- 3) Reducing diffusion (by adding oligomeric additives, polymeric additives).
- 4) Preferring polymer-bound additives (by copolymerization, reactive processing).

Several free and open databases tools and software implement the concepts presented here including: the Safe Food Packaging Portal (databases, real time probabilistic modeling, lectures...) (INRA, 2011), SFPP3 (multilayer modeling) (INRA, 2010), FMECAengine (Vitrac, 2012) (open source implementation of Failure Mode Effects and Criticality Analysis method for packaging and combining chained modeling, sensitivity analysis, migration modeling, expert systems). The end-user should find an incentive by noticing that the present concepts are not limited to thermoplastics but cover any dense polymer matrix cross-linked or not. Technical laboratories are encouraged to integrate the last progress in migration modeling to help the industry to comply with its legal requirements and to implement new integrated food management systems such as ISO 22000.

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Table 1. List of typical potential substances existing in different materials for food contact purpose.

	<i>Migrants</i>			<i>Source materials (state at ambient temperature 25°C)</i>	<i>In contact with</i>	<i>Refs</i>
	<i>Technical class</i>	<i>Chemical class</i>	<i>M (g·mol<sup>-1</sup>) &amp; chemical structure</i>			
<i>Additives</i>	Antioxidants	Hindered phenols, Phosphites,	200- 1200/BA	Glassy thermoplastics : PS, PA, PVC, PLA Rubbery thermoplastics : PE, PP	Food and other plastic layer	(Dopico-Garcia <i>et al.</i> , 2003), (Jamshidian <i>et al.</i> , 2012),
	UV stabilizers/UV absorbers	-Benzophenones, Oxanilides, Benzotriazoles -Activated charcoal	200- 2300/LA	- Glassy thermoplastics : PA, PVC, PC -Glassy thermoplastics : PET		(Nerin <i>et al.</i> , 2003b)
	Heat stabilizers	Calcium/zinc stearate or laurate Organotin compounds Tris(nonylphenyl) phosphite Polycarbodiimide	N/A	Glassy thermoplastics : PVC Glassy thermoplastics : PLA	Food and other plastic layer	(Adams <i>et al.</i> , 2011) (Al-Malack, 2001) (Yang <i>et al.</i> , 2008a)
	Plasticizers	Phthalic acid esters Epoxidised soybean oil Acetyl tri-n-butyl citrate Di(2-ethylhexyl)adipate Polyester of 1,2-propanediol and/or 1,3- or 1,4-butanediol 12-(Acetoxy)stearic acid 2,3-	200- 1000/LA/ B	Plasticized thermoplastics : PVC Glassy thermoplastics : PLA		(Fierens <i>et al.</i> , 2012) (Courgneau <i>et al.</i> , 2011)

	bis(acetoxy)propyl ester Poly(ethylene glycol)				
Antistatic	N,N-bis(2-hydroxyethyl)alkyl(C 8-C18) amine, Amino and quaternary ammonium compounds	<500/L	Glassy thermoplastics : PS Rubbery thermoplastics : PE Glassy thermoplastics : PVC	(Deshpande, 2002), (Metois <i>et al.</i> , 1998), (Barnes <i>et al.</i> , 2007)	Food
	Erucamide, oleamide, stearamide	<600/L	Glassy thermoplastics : PS Rubbery thermoplastics : PE Glassy thermoplastics : PVC		
Residues	-Ethylene -BPA -Styrene -Terephthalic acid, ethylene glycol, Bis(2-Hydroxyethyl) terephthalate -Vinyl chloride -Caprolactam -Acrylic acid, 2-ethylhexyl ester -1,4-butanediol - Alpha-methylstyrene - Perfluoromethyl perfluorovinyl ether	60-230/L/LA	-Rubbery thermoplastics :PE - Glassy thermoplastics : PC - Glassy thermoplastics : PS - Glassy thermoplastics : PET - Glassy thermoplastics : PVC - Glassy thermoplastics : PA - PAA or copolymers - PBT, PU - copolymers -	Food and other plastic layer	(Hoekstra and Simoneau, 2011)

				fluoropolymers		
	Catalysts	Antimony trioxide, calcium acetate	N/A	Glassy thermoplastics : PET	(Fordham <i>et al.</i> , 1995) (Pandey and Kim, 2011)	
	Cross-linking agents	-Isophorone diisocyanate (IPDI) trimer, -Acrylic polymer -Dicumyl peroxide, triallyl isocyanurate	<800/B	-Rubbery thermoplastics : PEPU -Glassy thermoplastics : PVC, PLA	(Jiang <i>et al.</i> , 2009) (Yang <i>et al.</i> , 2008b)	
	Processing aids (solvent/surface agents)	- <i>n</i> -alkylbenzenes ( <i>n</i> =10..13) -Acrylic polymer	210~340/LA	-Printing inks, lacquers, adhesives -PVC	(Aurela <i>et al.</i> , 2001), (Forrest, 2007)	
	Photoinitiators	2-isopropyl thioxanthone 2-ethylhexyl-4-dimethylaminobenzoate 1,3,5-Tris(4-benzoylphenyl)benzene	200~300/BA	Printing inks and lacquers Oxygen scavenging polymer	(Sanches-Silva <i>et al.</i> , 2009), (Forrest, 2007)	
	From can coatings	Bisphenol A diglycidyl ether	340/A	Thermoset polymer: epoxy resin, vinylic organosols	(Vera <i>et al.</i> , 2011), (Forrest, 2007)	
	From paper and cardboard	Perfluorinated surfactants Mineral oil	<1000	Paper, cardboard	(Trier <i>et al.</i> , 2011)	
NIAS	Reaction products	Polymer degradation products	2,2'-Azobis(2-methylpropionitrile), bis(p-methylbenzylidene)sorbitol, tetramethyl butanedinitrile and its hydrolyze acid, 4-	100-400/BA/L	Rubbery thermoplastics : PP Thermoset polymer: epoxy resin, vinylic	(Hakkarainen, 2008)

		methylbenzaldehyde, BADGE		organosols	
	Additive degradation products	2,2,6,6-Tetramethylpiperidine, , 2,2'-(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(2,1-diazenediyil)]bis[N-(2,5-dimethoxyphenyl)-3-oxo- butanamide	100-200/B	Rubbery thermoplastics	(Alin and Hakkaranen, 2011), (Marqué <i>et al.</i> , 1996), (Gryn'ova <i>et al.</i> , 2012), (Noguerol-Cal <i>et al.</i> , 2010), (Az <i>et al.</i> , 1991)
Contaminations from recycled materials		Mineral oils (saturated and aromatic hydrocarbons (< <i>n</i> -C28)) BPA, BPF, BADGE, BFDGE	<800/LA	Paper and cardboard	(Vollmer <i>et al.</i> , 2011), (Biedermann <i>et al.</i> , 2013), (Perez-Palacios <i>et al.</i> , 2012)
		- Volatile, aroma and flavor compounds (limonene, isopropylester of myristic and palmitic acids) -Degradation and secondary reaction products(acetaldehydes, oligomers and diethyleneglycol)	<500/L	Recycled PET, HDPE, PP, PC	(Camacho and Karlsson, 2000), (Nerin <i>et al.</i> , 2003a), (Pennarun <i>et al.</i> , 2004b), (Romao <i>et al.</i> , 2009), (Dutra <i>et al.</i> , 2011)
Contaminations from adhesives		1,6-dioxacyclododecane-7,12-dione and 1,4,7-trioxacyclotridecane-8,13-dione, Aromatic amines	90-200/BA	Thermoset polymer: PU, CA, Hotmelts	Plastic layer (Felix <i>et al.</i> , 2012), (Pezo <i>et al.</i> , 2012), (Vera <i>et al.</i> , 2011)

<i>Active substances</i>	antimicrobials, ethylene oxidation or oxygen scavenging materials	Antimicrobials (caffeine, thymol and carvacrol, citral), Peptides, enzymes, antioxidants (butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert-butylhydroquinone (TBHQ)),	N/A	Glassy thermoplastics : PET, EVOH Rubbery thermoplastics : PP, PE	Food	(Aznar <i>et al.</i> , 2012), (Grandá-Restrepo <i>et al.</i> , 2009), (Guillard <i>et al.</i> , 2010), (Peltzer <i>et al.</i> , 2009), (Nichols, 2004), (Buonocore <i>et al.</i> , 2003), (Han, 2003)
<i>Nanocomposites</i>	Nanoreinforcements, antimicrobial nanocomposites, oxygen scavenging nanocomposites, nanoscale enzyme immobilization systems	Clay and silicates, cellulose-based nanoreinforcements, carbon nanotubes, silica, starch nanocrystals, chitin/chitosan nanoparticles, silver, titanium dioxide	N/A	Glassy thermoplastics : PET, PLA, Polyolefin Rubbery thermoplastics : PCL	Food and other plastic layer	(Azeredo, 2009), (Busolo and Lagaron, 2012), (Llorens <i>et al.</i> , 2012), (Solovyov and Goldman, 2007), (Neethirajan and Jayas, 2011), (Smirnova <i>et al.</i> , 2012), (von Goetz <i>et al.</i> , 2013)

Note: BPA: Bisphenol A, BPF: bisphenol F. BADGE: bisphenol A diglycidyl ether, BFDGE: bisphenol F diglycidyl ether. PE: polyethylene, PP: polypropylene, PS: polystyrene, PVC: polyvinyl chloride, PET: polyethylene terephthalate, PC: polycarbonate, PA: polyamide. PEPU:

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polyester-polyurethane, PBT: polybutylene terephthalate, PU: polyurethane. PCL: polycaprolactone. PLA: polylactic acid, EVOH: ethylene-vinyl alcohol copolymer, CA: cyanoacrylate.

L: linear migrants, B: branched migrants, A: aromatic migrants. LA: linear aromatic migrants, BA: branched aromatic migrants.

Table 2. Main contamination routes of food by materials in direct or indirect contact

<i>Contamination modes</i>	<i>Description</i>	<i>Examples</i>	<i>Refs</i>
With direct contact with food	Direct contact with the food during packaging, filling, storage, use (i.e. vacuum heating, microwave heating)	Monolayer materials	Goulas <i>et al.</i> (2002), Caner <i>et al.</i> (2004), Berlinet <i>et al.</i> (2008)
Through of layer in contact with food	The substance must pass through one or more materials before coming into contact with the food	Multilayer materials, label, varnishes, decors	Trier <i>et al.</i> (2010), Simal-Gandara <i>et al.</i> (2000), Roduit <i>et al.</i> (2005), Miltz <i>et al.</i> (1997), Marque <i>et al.</i> (1998), Dole <i>et al.</i> (2006a), Feigenbaum <i>et al.</i> (2005)
Contamination of layer in contact with food before conditioning	Putting in contact the inner and outer faces of the packaging (set off phenomenon)	Films rolled, packaging or packaging components stored in stack...	Page and Lacroix (1992), Jung <i>et al.</i> (2010)
Without contact	Contamination via headspace or gas permeation	Ink solvents, flavors, off-flavors, contaminants coming from secondary packaging...	Freire <i>et al.</i> (1998), Sadler <i>et al.</i> (1996), Alin and Hakkarainen (2012), Cao and Corriveau (2008), Tehrany and Desobry (2004), Lorenzini <i>et al.</i> (2010), Nerin <i>et al.</i> (2009), Battelli <i>et al.</i> (2011), Anderson and Castle (2003), Pastorelli <i>et al.</i> (2008), (Linssen <i>et al.</i> , 1998)

Table 3. Scaling law and diffusion mechanisms associated with ideal mixtures ( $\Gamma = 1$ ).

No. of blobs $N$	Diffusion mechanisms (diffusion regime)	$\zeta$	$D \propto M^{-\alpha}$	$\alpha$	Ref
1	Molecule consisting of a bead with radius $R_H$ ( <b>Stokes-Einstein</b> ) in solution 	$6\pi\eta R_H$	$D = \frac{RT}{\zeta_0} \propto \frac{1}{M^{1/2}}$	1/2	(Einstein, 1905b)
$1 < N < 30$	Molecule consisting of $N$ beads ( <b>Rouse</b> ) in solution 	$N\zeta_0$	$D = \frac{RT}{N\zeta_0} \propto \frac{1}{M}$	1	(Prince E. Rouse, 1953)
$N \gg 30$	Molecule consisting of entangled $N$ beads, which only can translate along its contour ( <b>reptation</b> ) 	$N\zeta_0$	$D_{tube} = \frac{RT}{N\zeta_0} = \frac{l_{tube}^2}{\tau_{tube}} \propto \frac{N^2}{\tau_{tube}}$ $\tau_{tube} \propto N^3$ $D \propto \frac{R^2}{\tau_{tube}} \propto \frac{N}{N^3} = \frac{1}{N^2}$	2	(De Gennes, 1971) (Doi and Edwards, 1978)
	Reptation with constrained relaxation	N/A	N/A	> 2	(Lodge, 1999) (Bueche, 1968)

$R$ : gyration radius,  $N$ : the number of beads in the chain,  $\zeta_0$ : the friction coefficient associated to a single bead/blob, and  $l_{tube}$ : the length of the reptation tube.  $\tau_{tube}$ : the retention time in the tube.

Table 4. Calculation method of free volume parameters in Eq. (22)

<i>Approximation method</i>	<i>Calculation method</i>	<i>ref</i>
$\hat{V}_P^*$ Molecular simulation (Monte Carlo-type statistics)	$\hat{V}_P^* = \hat{V}_P^0(0)$ where $\hat{V}_P^0(0)$ is the specific volume of equilibrium liquid polymer at 0 K	(Howard, 1970)
$E^*$ Cohesive energy via solubility coefficients	$E^* = f \left[ (\delta - \delta_p)^2 \tilde{V}^0 \right]$ where $\delta$ and $\delta_p$ are solubility parameter for diffusant and polymer. $\tilde{V}^0$ are mole volume of diffusant at T	(Hansen, 2007) (van Krevelen and te Nijenhuis, 2009)
$\gamma$ William-Landel-Ferry approximation	$\gamma = \hat{V}_P^0(T_g) a \frac{2.303 C_1 C_2}{\hat{V}_P^0(0)}$ where $\hat{V}_P^0(T_g)$ is specific volume of polymer at $T_g$ , $a$ is thermal expansion coefficient for equilibrium liquid polymer, $C_1$ and $C_2$ are WLF constants.	(Kontogeorgis and Folas, 2009)
$\xi$ Geometrical description of diffusant along the main directions of translation	$\xi = \frac{\xi_L}{1 + \xi_L (1 - A/B)}$ with $\xi_L = \frac{\tilde{V}^0(0)}{\hat{V}_P^*(0)}$ where $B/A$ is an aspect ratio for the diffusant molecule which is a geometry-based descriptor of molecular shape. $\tilde{V}^0(0)$ is mole volume of equilibrium liquid diffusant at 0 K. $\hat{V}_P^*$ is critical hole free volume per mole of polymer jumping units required for a jump.	(Vrentas et al., 1996)
$\hat{V}_{FH}$ Polymer thermal expansion properties	$\hat{V}_{FH} = \hat{V}_P^0(T_g) [f_H^G + a(T - T_g)] \quad T \geq T_g$ $\hat{V}_{FH} = \hat{V}_P^0(T_g) [f_H^G + (a_g - a_{cg})(T - T_g)] \quad T < T_g$ where $\hat{V}_P^0(T_g)$ is specific volume of polymer at $T_g$ . $f_H^G$ is fractional hole free volume of polymer at $T_g$ . $a_g$ and $a_{cg}$ are thermal expansion coefficient for glassy polymer and the sum of the specific occupied volume and the specific interstitial free volume for the glassy polymer respectively.	(Vrentas and Vrentas, 1998)

Table 5.  $\xi$  and  $E^*$  values for 8 diffusant-polymer systems.

<i>diffusant</i>	<i>polymer</i>	<i>B/A</i>	$\xi$	$E^* \text{ (kcal/g}\cdot\text{mol}^{-1}$	$\tilde{V}_p^* \text{ (cm}^3/\text{mol)}$
Methanol	PS	1.251	0.23	-	135
	PMMA		0.19	5.3	135
	PVAC		0.31	3.4	88.8
	PPMS		-	3.1	345
acetone	PS	1.160	-	-	135
	PMMA		0.39	2.8	135
	PVAC		0.60	1.0	88.8
	PPMS		0.15	3.1	345
toluene	PS	1.242	0.56	0	135
	PMMA		0.54	0.21	135
	PVAC		0.75	-0.24	88.8
	PPMS		0.23	4.4	345
ethylbenzene	PS	1.409	0.59	0.61	135
	PMMA		0.54	1.7	135
	PVAC		0.78	-0.11	88.8
	PPMS		0.26	4.4	345

Table 6. Formal equivalences between scaling law of diffusion coefficients and free-volume theory for diffusants based on linearly repeated sub-units (see Fig. 5) in rubber polymers (Fang *et al.*, 2013)

	<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 <sub>12</sub> , K <sub>22</sub> are polymer free-volume parameters.
Relative activation energy $Ea(M, T) - Ea(M_0, T) =$ $Ea(\xi, T) - Ea(\xi_0, T) =$ $\frac{\partial \ln \frac{D(M, T)}{D(M_0, T)}}{\partial 1/T} =$	$K_\alpha \frac{RT^2}{(T - T_g + K_\beta)^2} \ln \frac{M}{M_0}$	$\underbrace{E^*(\xi) - E^*(\xi_0)}_{\rightarrow 0} + (\xi - \xi_0) \frac{\gamma \bar{V}_P^*}{K_{12}} \frac{RT^2}{(K_{22} + T - T_g)^2}$

Table 7. Equivalent terms in Eq. (24) for two homologous series of aromatic diffusants.

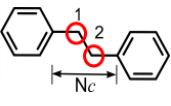
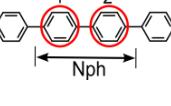
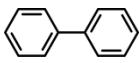
	$D_0(\text{reference diffusant}, T_{\text{ref}})$	$D_{\text{polymer}}(T, T_g)$ $= \exp\left(-\frac{K_a}{K_b + T - T_g}\right)$	$D_{\text{diffusant excess}}(\text{diffusant}, T)$
Diphenyl alkanes   $N_C$ : number of carbons between two phenyls	$D_0(\text{biphenyl}, T_{\text{ref}})$ : D values of biphenyl at $T$ .	$K_a = 600 \text{ K}$ $K_b = 58 \text{ K}$	$\exp\left(-\ln 10 \frac{N_C}{N_{C10}}\right)$  $N_{C10}$ : number of carbons required to decrease $D$ by 10.
Oligophenyls   $N_P$ : number of phenyl rings between two phenyls	 $N_C=0, N_{Ph}=2$		$\exp\left(-\frac{\Delta A_{\text{diffusant excess}}(N_{Ph}-2)}{RT}\right)$  $\Delta A_{\text{diffusant excess}}(N_{Ph}-2)$ : solute free energy barrier varying with $N_{Ph}$ .

Table 8. The activation energy and volume responsible for rotation and translation of the additive-type molecule in high density polyethylene at macroscopic and molecular scale. (after Kovarski (1997)).

		<i>macroscopic quantities</i>		<i>molecular magnitudes</i>	
		<i>rotation</i>	<i>translation</i>	<i>rotation</i>	<i>translation</i>
		kJ·mol <sup>-1</sup>	μs	cm <sup>3</sup> ·mol <sup>-1</sup>	Å <sup>3</sup>
Activation energy	solid state ( $T > T_g$ )	20-50	50-150	$10^{-5} - 1$	> 1
	molten state ( $T > T_m$ )	10-20	15-40	$10^{-7} - 10^{-5}$	$10^{-6} - 1$
Activation volume	solid state ( $T > T_g$ )	20-70	50-150	30-115	80-250
	Molten state ( $T > T_m$ )	8-15	13-30	10-25	20-50

Table 9. Main models to overestimate  $D$  values for compliance testing

$\ln D_{(M,T)} \leq \ln \check{D}_{(M,T)}$	$\check{\alpha} = -\left. \frac{\partial \ln \check{D}_{(M,T)}}{\partial \ln M} \right _T$	Theoretical justifications
Limm model (Limm and Hollifield, 1996):		
$\ln \check{D}_{(M,T)} = \ln D_0 + aM^{\frac{1}{2}} - \frac{bM^{\frac{1}{3}}}{T}$	$- \frac{aM^{1/2}}{2} + \frac{bM^{1/3}}{3T}$	Apparent cross section of diffusant
$a$ and $b$ are adjustable parameters which are specific for each polymer type.		
See Table 10		
Helmroth model (Helmroth <i>et al.</i> , 2005):		
$\ln \check{D}_{(M,T)} = \ln D_0 - \left( \frac{M}{M_0} \right)^c + F^{-1}(P 0,S)$	$c \left( \frac{M}{M_0} \right)^c$	Close to free-volume theories
$c$ is polymer dependent parameter.		
$F^{-1}(P 0,S)$ is the normal inverse distribution with zero mean and standard deviation $s$ . For $P=50\%$ ( $F^{-1}(0.5 0,S)=0$ ), it gives an estimate and an overestimate for $P>50\%$ .		
See Table 10		
Piringer model (Begley <i>et al.</i> , 2005; Piringer and Baner, 2000, 2008):		
$\ln \check{D}_{(M,T)} = A' - 0.1351M^{2/3} + 0.003M - \frac{\tau + 10454}{RT}$	$0.09007M^{2/3}$ $-0.003M$	Gas kinetic theory
See Table 10		

Table 10. Available parameter values of main models for different polymers as reported in (Limm and Hollifield, 1996; Begley *et al.*, 2005; Helmroth *et al.*, 2005; EC, 2012a)

<i>Polymer</i>	<i>Limm model</i>			<i>Helmroth model</i>			<i>Piringer model</i>	
	<i>Ln D<sub>0</sub></i>	<i>a</i>	<i>b</i>	<i>Ln D<sub>0</sub></i>	<i>c</i>	<i>s</i>	<i>A'P</i>	<i>τ(K)</i>
LDPE,LLDPE	4.16	0.555	1140.5	-13.633	0.37	1.3	11	0
	0.90	0.819	1760.7	-14.144	0.39	N/A	14	1565
	- 2.10	0.597	1335.7	-17.779	0.36	2.0	13	1565
	N/A	N/A	N/A	N/A	N/A	N/A	11	0
	N/A	N/A	N/A	N/A	N/A	N/A	0	0
	N/A	N/A	N/A	N/A	N/A	N/A	1	0
	N/A	N/A	N/A	N/A	N/A	N/A	6	1565
	N/A	N/A	N/A	N/A	N/A	N/A	6	1565
	N/A	N/A	N/A	N/A	N/A	N/A	5	1565
	N/A	N/A	N/A	N/A	N/A	N/A	2	0
PVC	N/A	N/A	N/A	N/A	N/A	N/A	0	0

LDPE, LLDPE: low density and Linear low-density polyethylene, PP: polypropylene, PS: polystyrene, HIPS: high impact polystyrene, PET: polyethylene terephthalate, PBT: polybutylene terephthalate, PEN: polyethylene naphthalate, PA: polyamide, PVC: polyvinyl chloride.

Table 11. Main geometric parameters used in CART approaches (Vitrac *et al.*, 2006) and their physical justifications. Conformers are usually obtained from molecular dynamics simulation to reach representative configurations at the considered temperature.

<i>Property</i>	<i>Ensemble average</i>	<i>Associated mechanism</i>
van-der-Waals volume	$\langle V_{VdW} \rangle_{\text{configurations}}$	Scaling law $D \propto M^{-\alpha}$ Activation volume represents a fraction of VdW volum
gyration radius	$\langle \rho \rangle_{\text{configurations}}$	Translation by rotation around a position different than the center of gravity
Shape parameter	$\langle I_z / I_x \rangle_{\text{configurations}}$	Translation in a favour direction (or corollary: a direction of translation is severely disadvantaged)

Table 12. Values of topological descriptors for six typical molecules as associated to their state of minimum internal energy. The values are ordered as  $V_{vdW}$ ,  $\rho$ ,  $I_z / I_x$  (see Table 11). All molecules were oriented along their main axes (x, y and z); the three main projected surfaces are also depict.

$\beta$ -pinene			Limonene			BHT			Chimasorb 90			Irganox 1076			Irgafos 168		
15	2.	1.6	15	2.	4.	24	3.5	2.6	20	3.	5.9	59	9.7	22	67	5.7	1.9
4	5	8	8	91	75	3	6	5	7	9	7	3	3		5	2	4

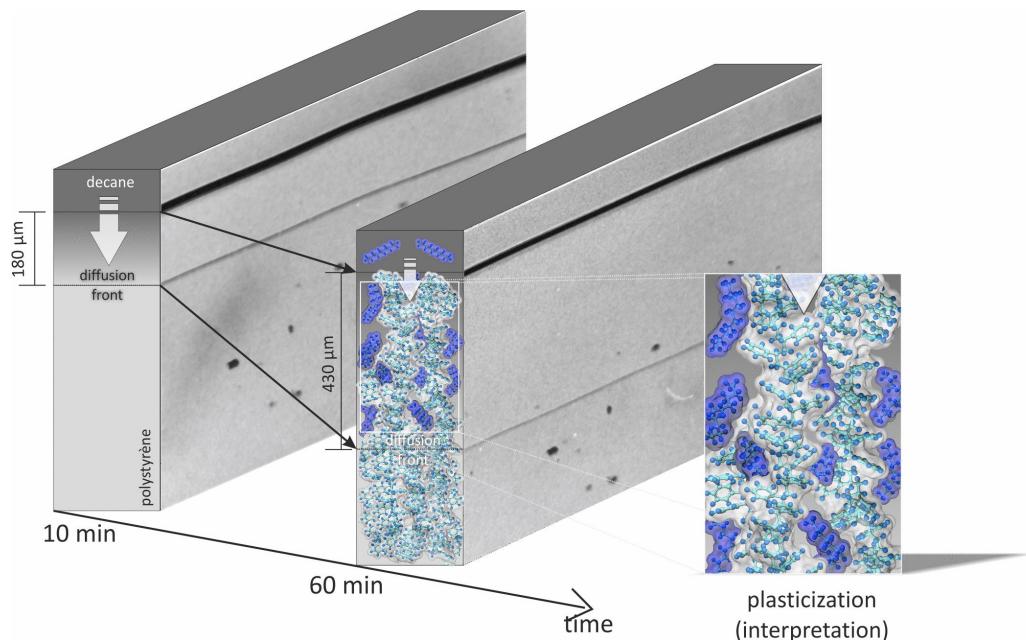


Figure 1. Microscopic observations in visible light and its molecular interpretation of the sorption of decane in atactic polystyrene at 70 °C (after Morrissey and Vesely (2000)).

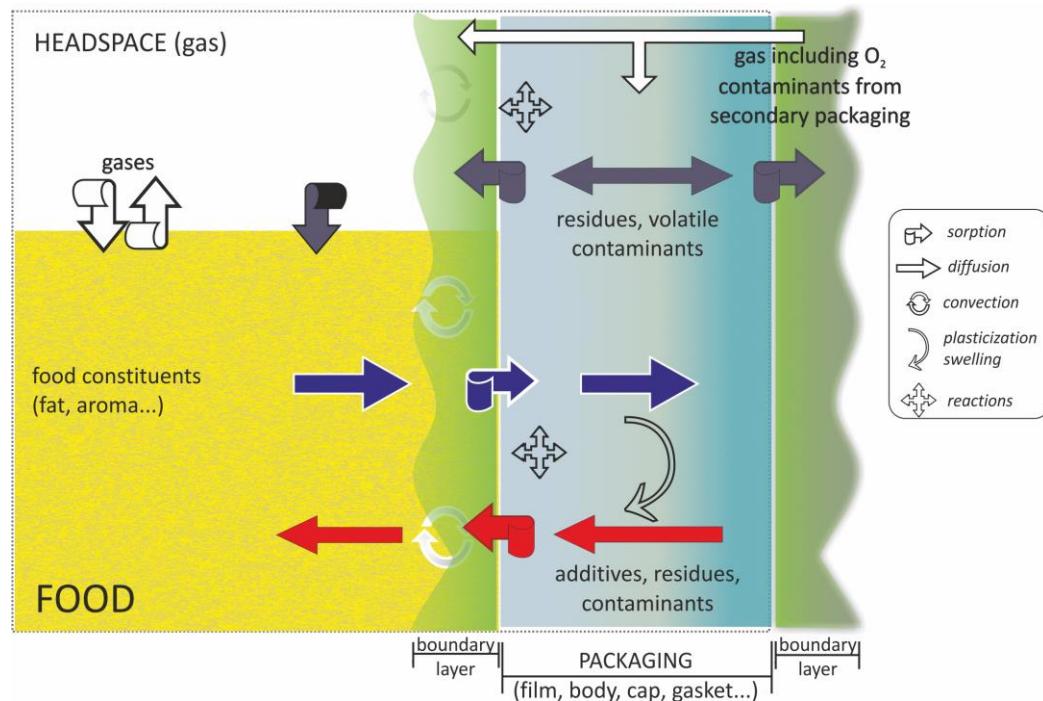


Figure 2. Main mass transfer from, to and cross packaging materials (after Rahman (2007), Vitrac and Hayert (2007a)).

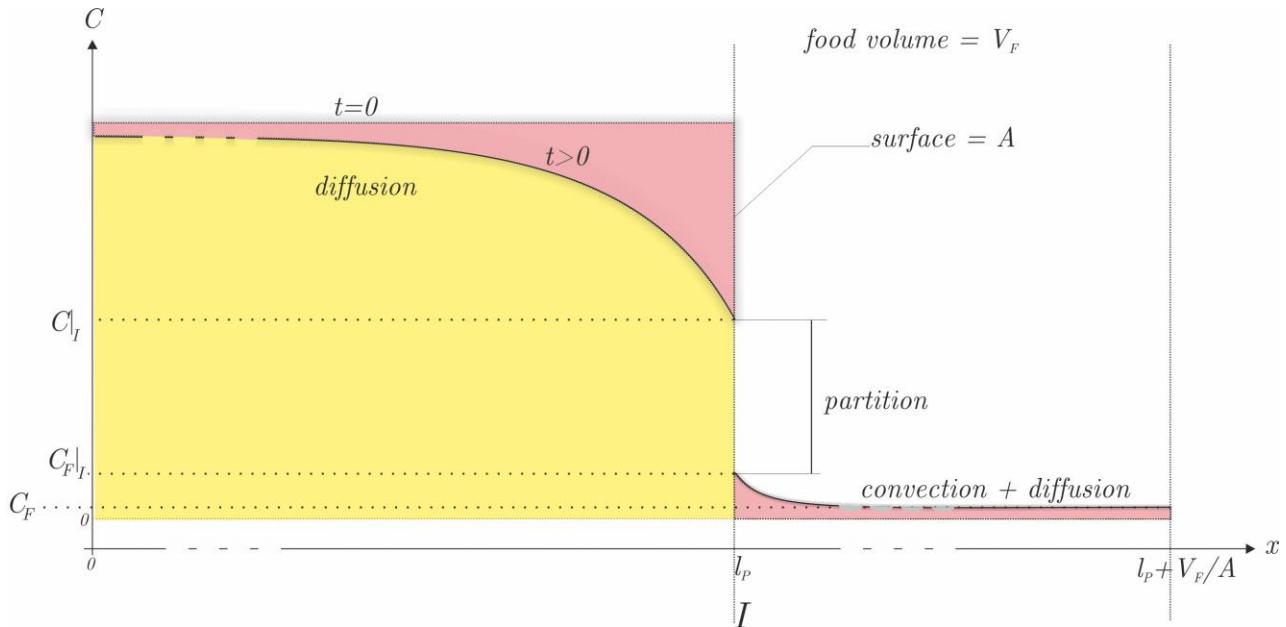


Figure 3. Concentration profile of migrants (e.g. additive) along the thickness of the food-packaging system as detailed in Vitrac and Hayert (2006). When  $t=0$ , migrants are assumed to be distributed homogeneously in the packaging material so that a uniform concentration profile can be assumed. For  $t>0$ , mass balance enforces that the surface area below the concentration profile on the food side is equal to complementary surface area between the profiles at  $t=0$  and  $t>0$  on packaging side.

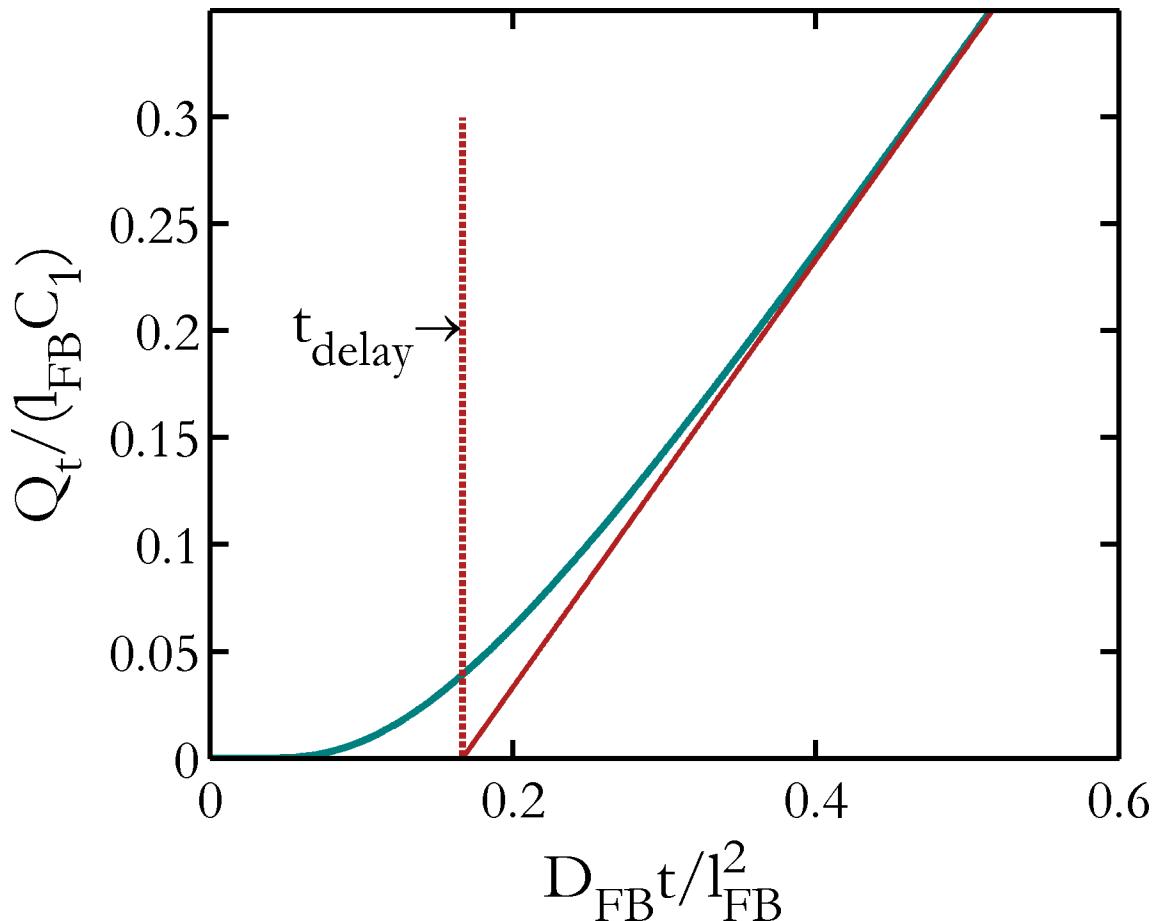


Figure 4. Cumulated amount of diffusant ( $Q_t$ ) crossing a plane sheet of thickness,  $l_{FB}$ , with upstream concentration  $C_1$  versus dimensionless time  $D_{FB}t/l_{FB}^2$ . The intercept of tangent line with  $Q_t=0$  at  $t_{delay}=l_{FB}^2/6D_{FB}$  gives the typical time lag to get a significant permeation across the film.  
(after Fig. 4.2 in book of Crank (1979))

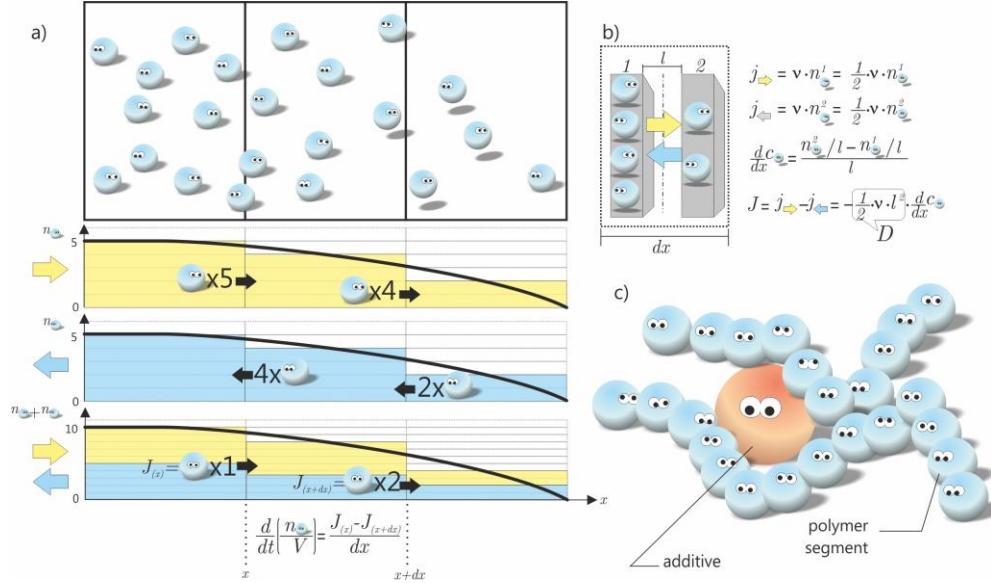


Figure 5. One-dimensional interpretation of molecular diffusion with “eyed” particles a) as populations in contiguous elemental volumes exchanging particles, b) as a local hopping process and c) as mutual diffusion of a bulky additive among connected polymer beads. In the real life (at macroscopic scale), the particles and the direction of jumps are indiscernible. To enable particles counting, the direction of the sight gives here the direction of the next jump. In details, situations in (a) and (b) illustrate the concepts of macroscopic and microscopic mass balance applied implicitly in second and first Fick equations, respectively.

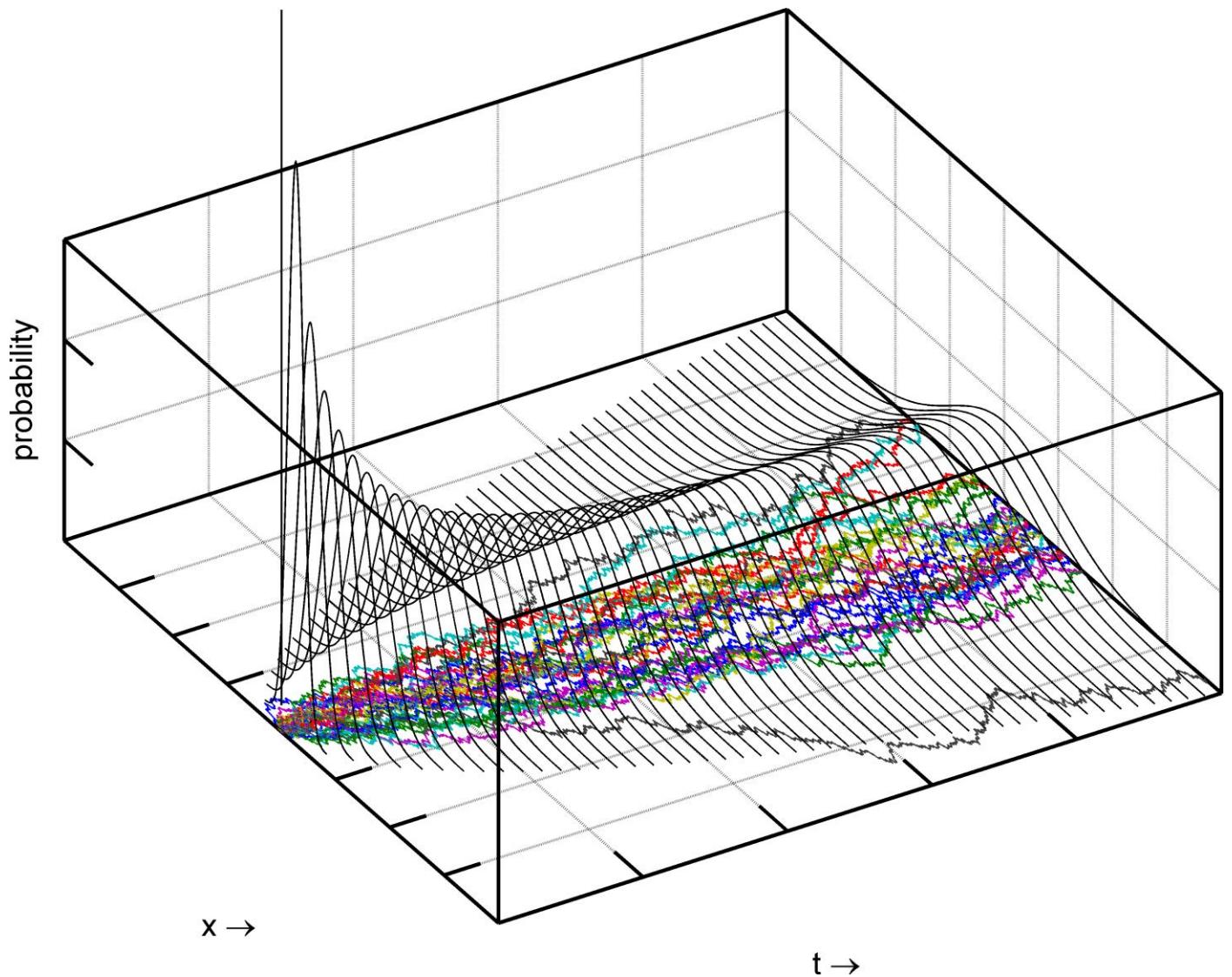


Figure 6. Simulation of 10 one-dimension random walks starting from a same initial position.

The continuous probability Gaussian distributions associated to an infinite number of trajectories are also represented for different times. (see Eqs. (6) and (7)).

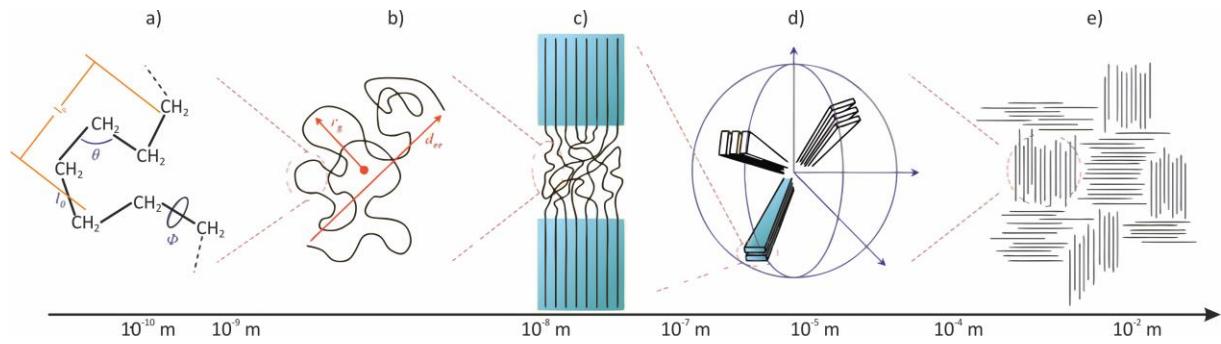


Figure 7. Schematic representation of multi-scales of the organization of polymer materials (e.g. polyethylene). a) chemical structure (Baschnagel *et al.*, 2004), b) intermingled chains (Baschnagel *et al.*, 2004), c) semi-crystalline structure (Queyroy and Monasse, 2012), d) polycrystalline structure (Callister and Rethwisch, 2011), e) heterogeneous materials (Muller-Plathe, 1991).  $l_0$ : length of a C-C bond,  $l_p$ : persistence length,  $\theta$ : bond angle,  $\phi$ : torsion angle,  $r_g$ : gyration radius,  $d_{ee}$ : end-to-end distance.

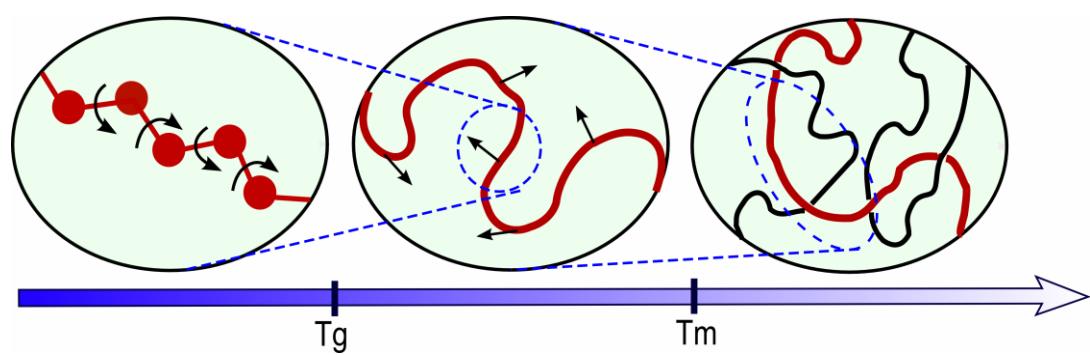


Figure 8. Largest polymer displacements versus temperature.  $T_g$  is the glass transition temperature,  $T_m$  is the melting temperature, (after Paul and Smith (2004)).

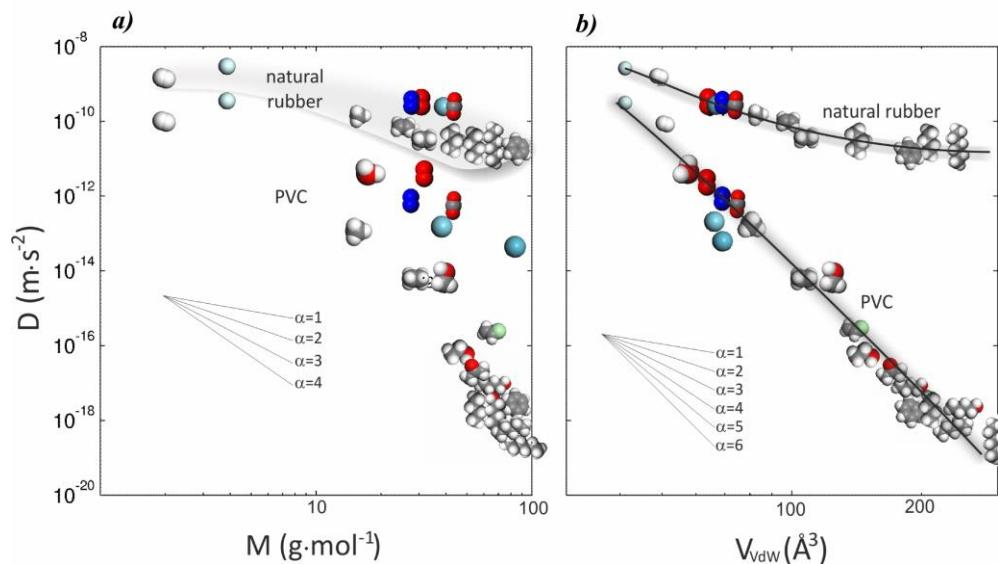


Figure 9. Scaling of diffusion coefficients in natural rubber and polyvinyl chloride (PVC) with a) molecular mass ( $M$ ) and b) van-der-Waals volume ( $V_{\text{VdW}}$ ) of diffusant (Berens, 1981).

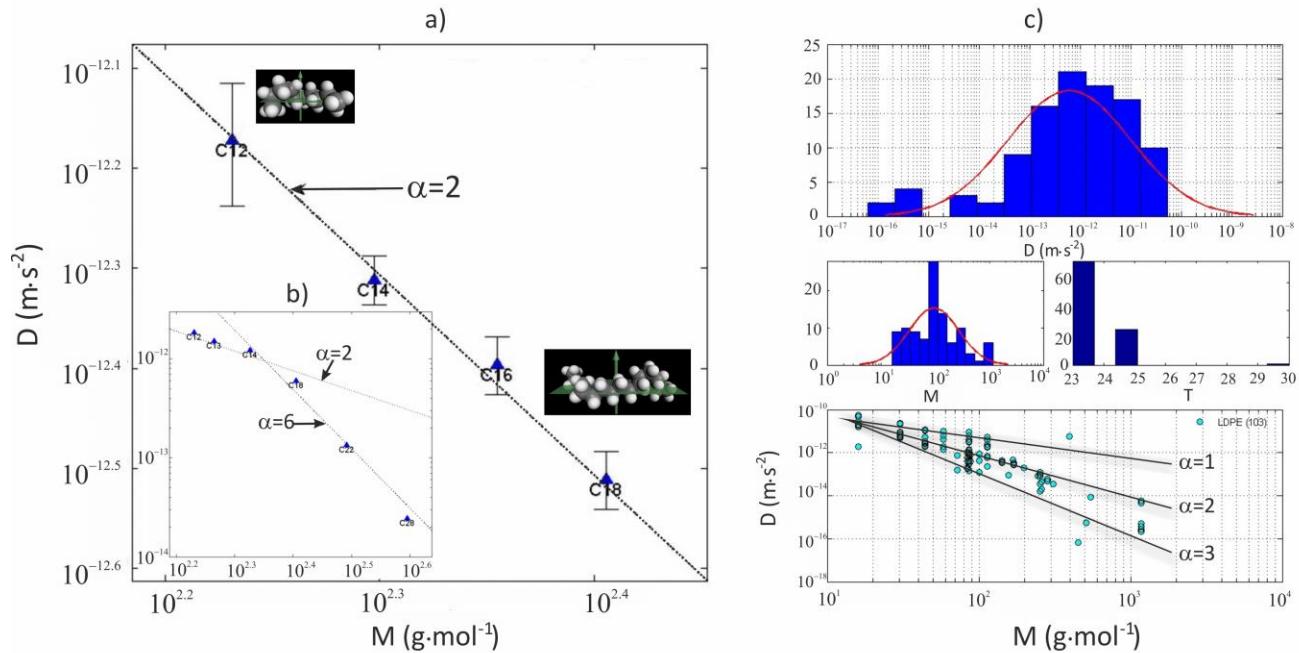


Figure 10. Scaling laws associated to the diffusion a-b) of linear  $n$ -alkanes (at 40 °C, according to Reynier *et al.* (2001b), Vitrac *et al.* (2007)) and c) linear or branched alkanes (between 23 °C and 30 °C, data collected by EU working group SMT-CT98-7513 and published by Begley *et al.*, (2005), Vitrac *et al.*, (2006) and available within the EU database hosted on the Safe food packaging portal (INRA, 2011) for low density polyethylene.

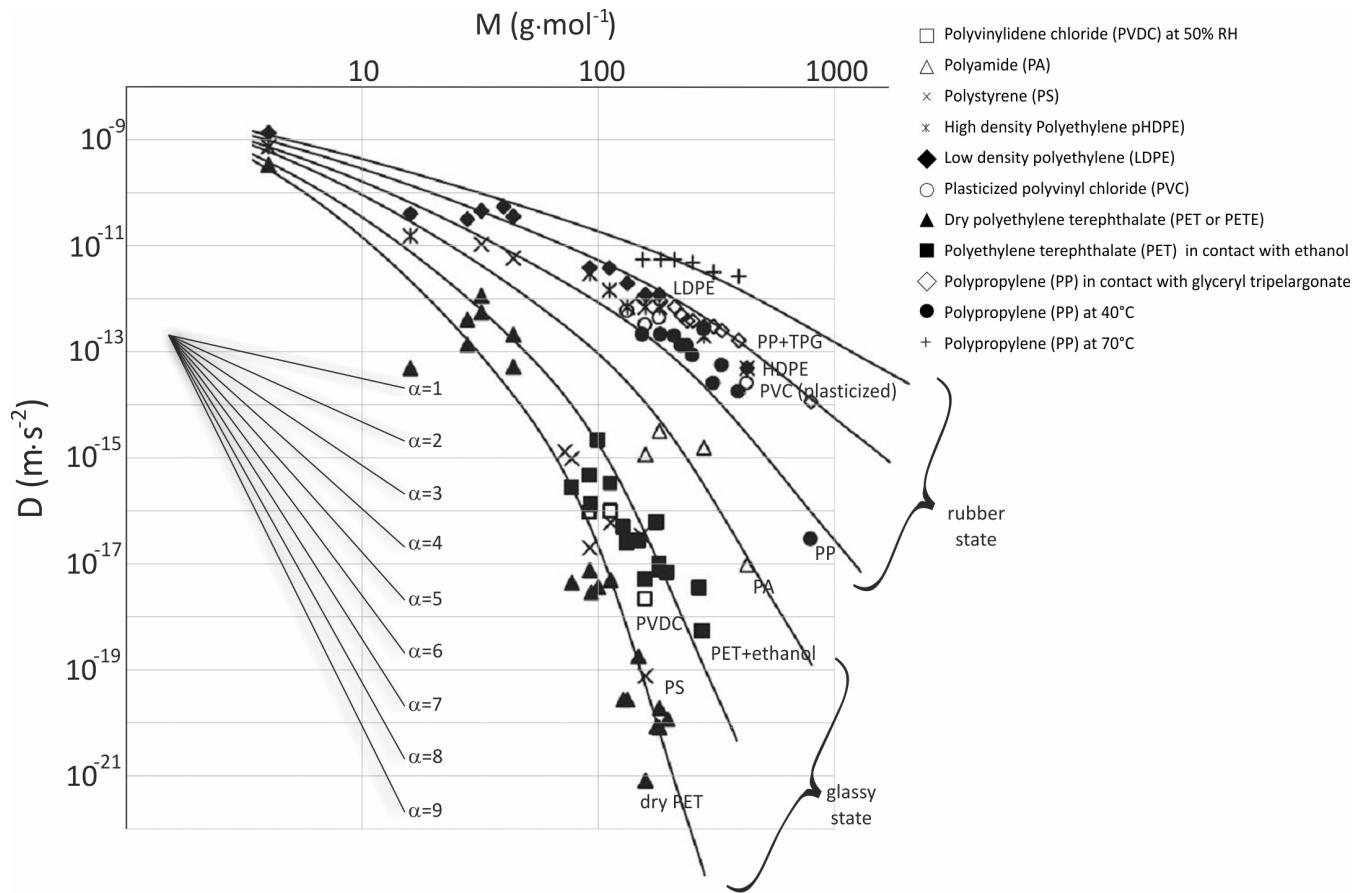


Figure 11. Scaling laws identified for additive-type molecules in different thermoplastic materials at 298K (Dole *et al.*, 2006a).

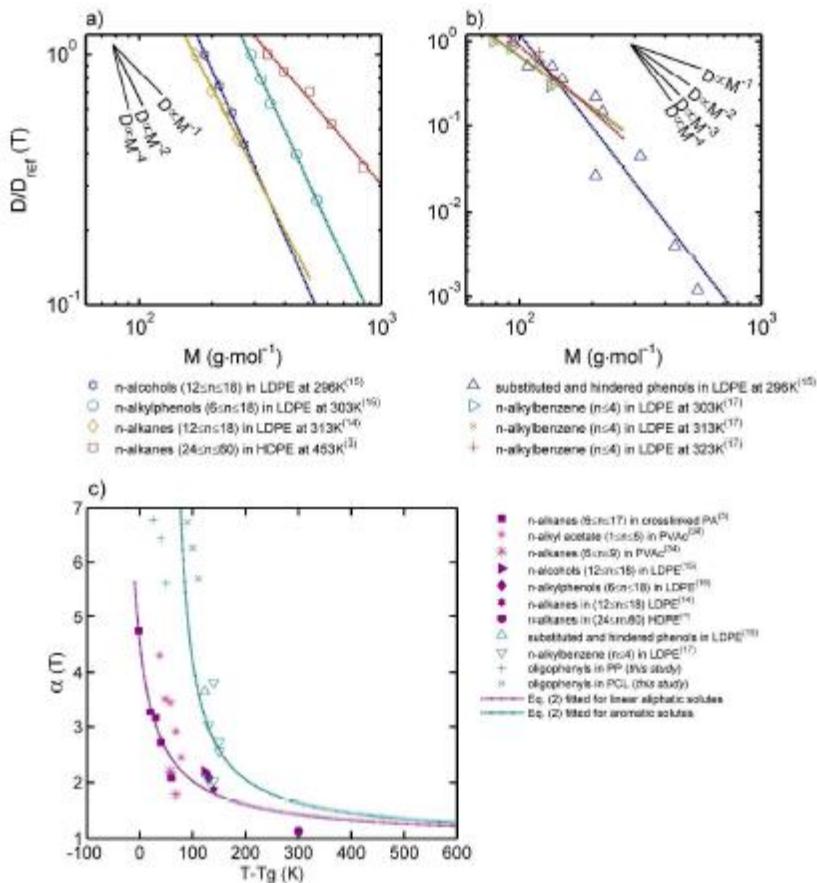


Figure 12. a, b) Log-log plots of trace diffusion coefficients in polyethylene of linear aliphatic and aromatic solutes. c) The corresponding scaling exponents  $\alpha$  versus  $T-T_g$  for both linear aliphatic solutes (Koszinowski, 1986; Arnould and Laurence, 1992; Möller and Gevert, 1994; Kwan *et al.*, 2003; Vitrac *et al.*, 2007; von Meerwall *et al.*, 2007) and aromatic solutes (Koszinowski, 1986; Doong and Ho, 1992; Fang *et al.*, 2013).

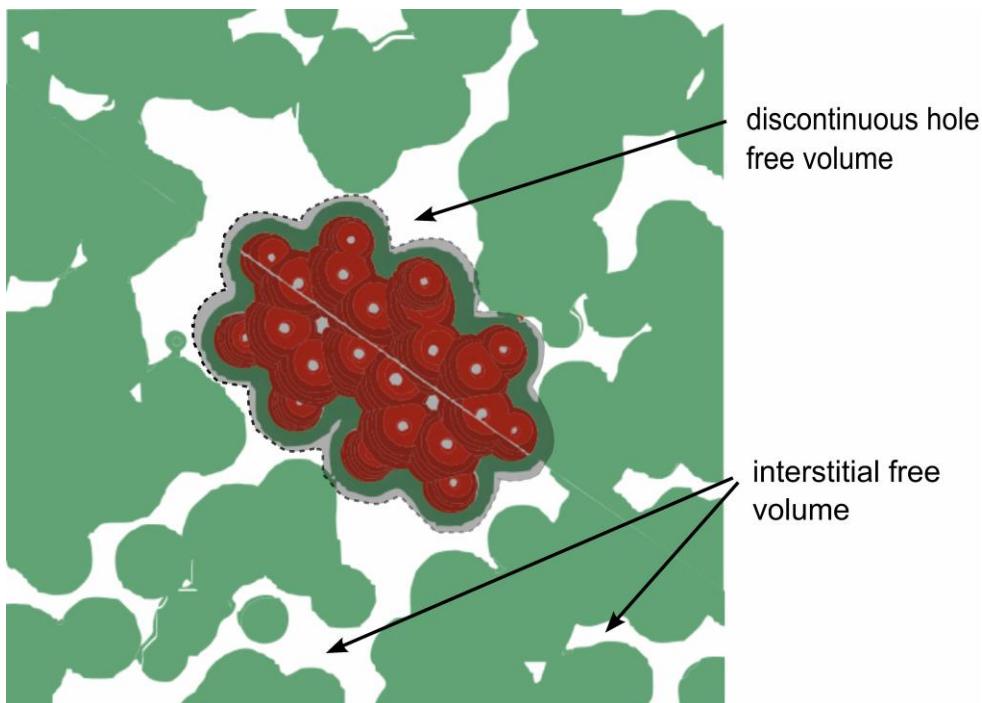


Figure 13. Distribution of free volumes around a planar and rigid diffusant (fluorene) in high density polyethylene at room temperature pressure as extracted by isobaric and isothermal molecular dynamics simulation. The image is obtained by plotting the projected Connolly surfaces onto the plane defined by the main axes of the diffusant. Only the atoms included in the thickness of the diffusant are considered.

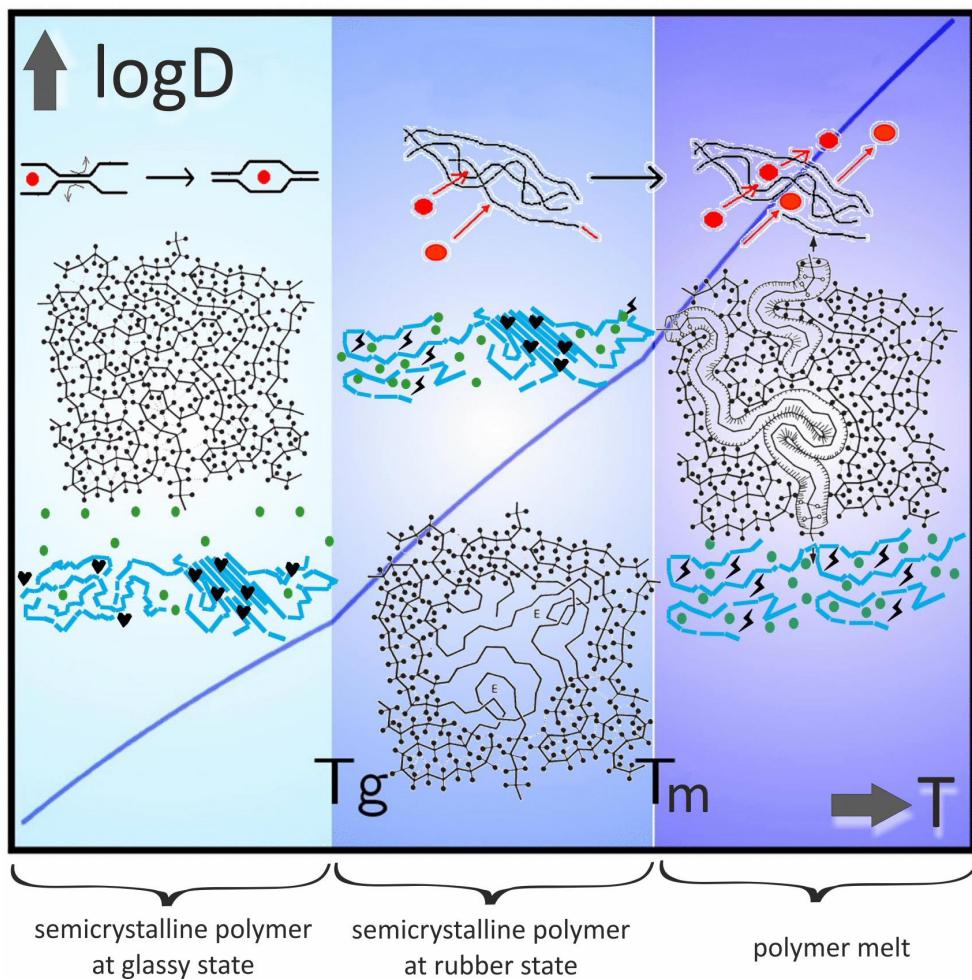


Figure 14. Interpretation of the translation of additive-type molecules according to the state of the polymer.

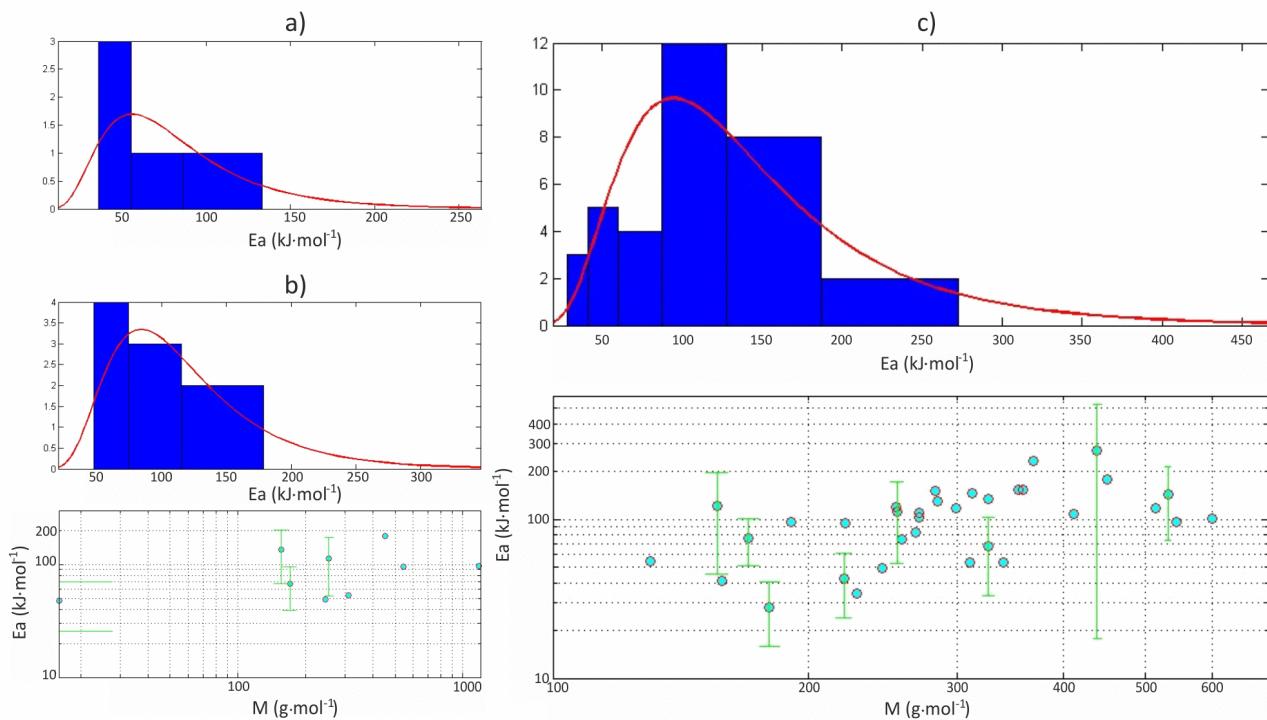


Figure 15. Estimated activation energies between 20 and 40°C in low density polyethylene: a) smalls molecules  $M < 100 \text{ g}\cdot\text{mol}^{-1}$ , b) linear alkanes, c) additive molecules with  $100 < M < 600 \text{ g}\cdot\text{mol}^{-1}$ . Data extracted from the European database of diffusion coefficients (INRA, 2011).

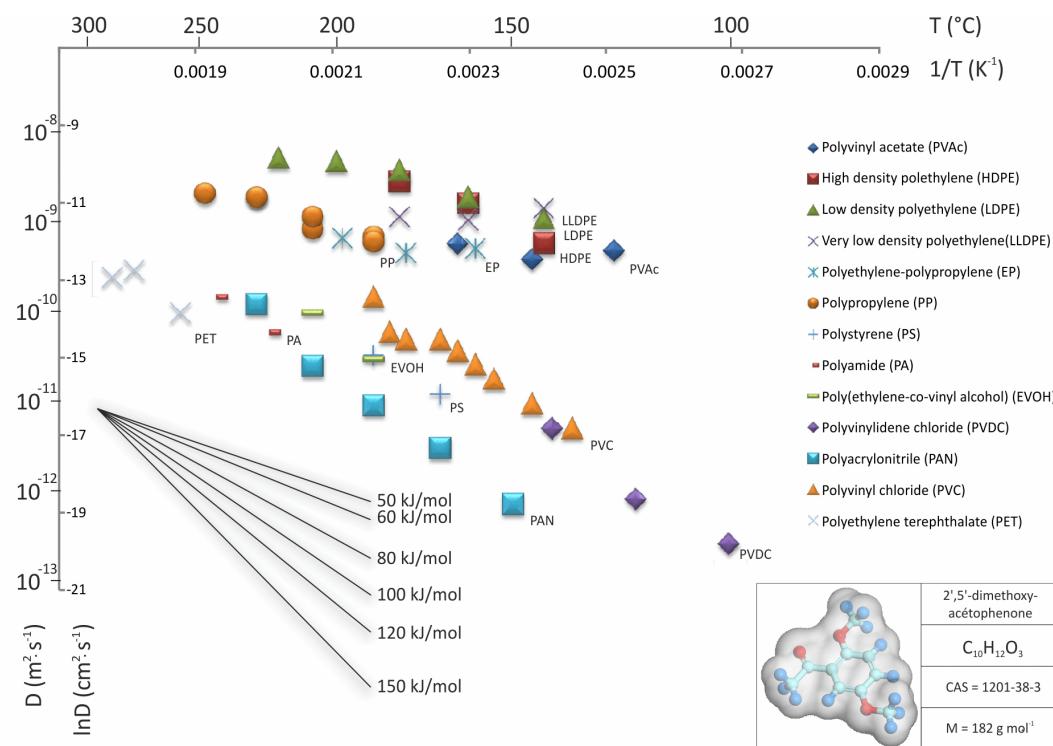


Figure 16. Van't Hoff diagram of diffusion coefficient of 2',5'-dimethoxy-acetophenone in different polymers at high temperature (near to processing temperature). (after Feigenbaum *et al.* (2005), Dole *et al.* (2006a), Dole *et al.* (2006b)).

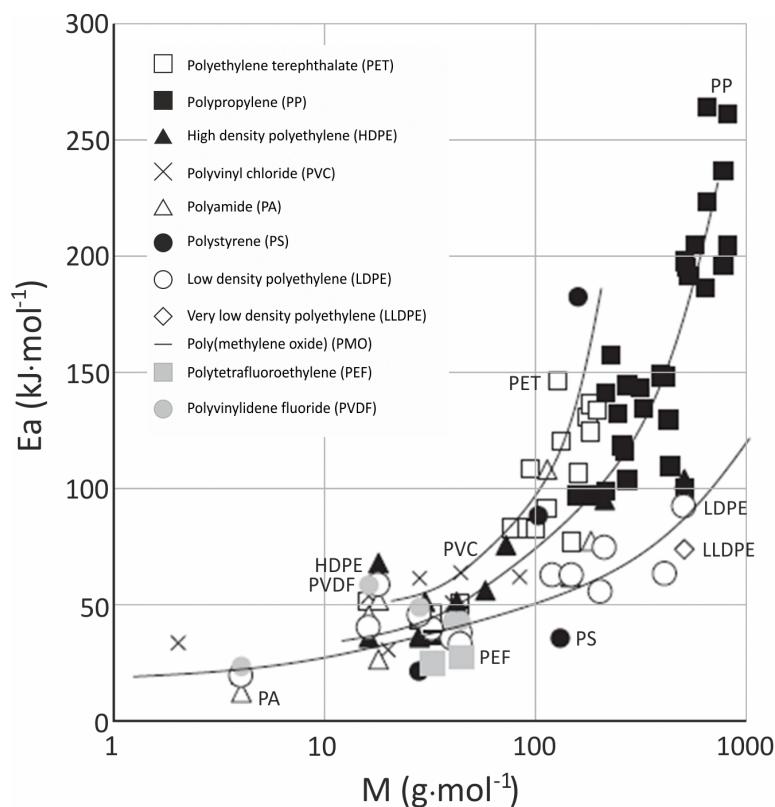


Figure 17. Variation of activation energy for different polymers between 20 and 40°C according to Dole *et al.* (2006a).

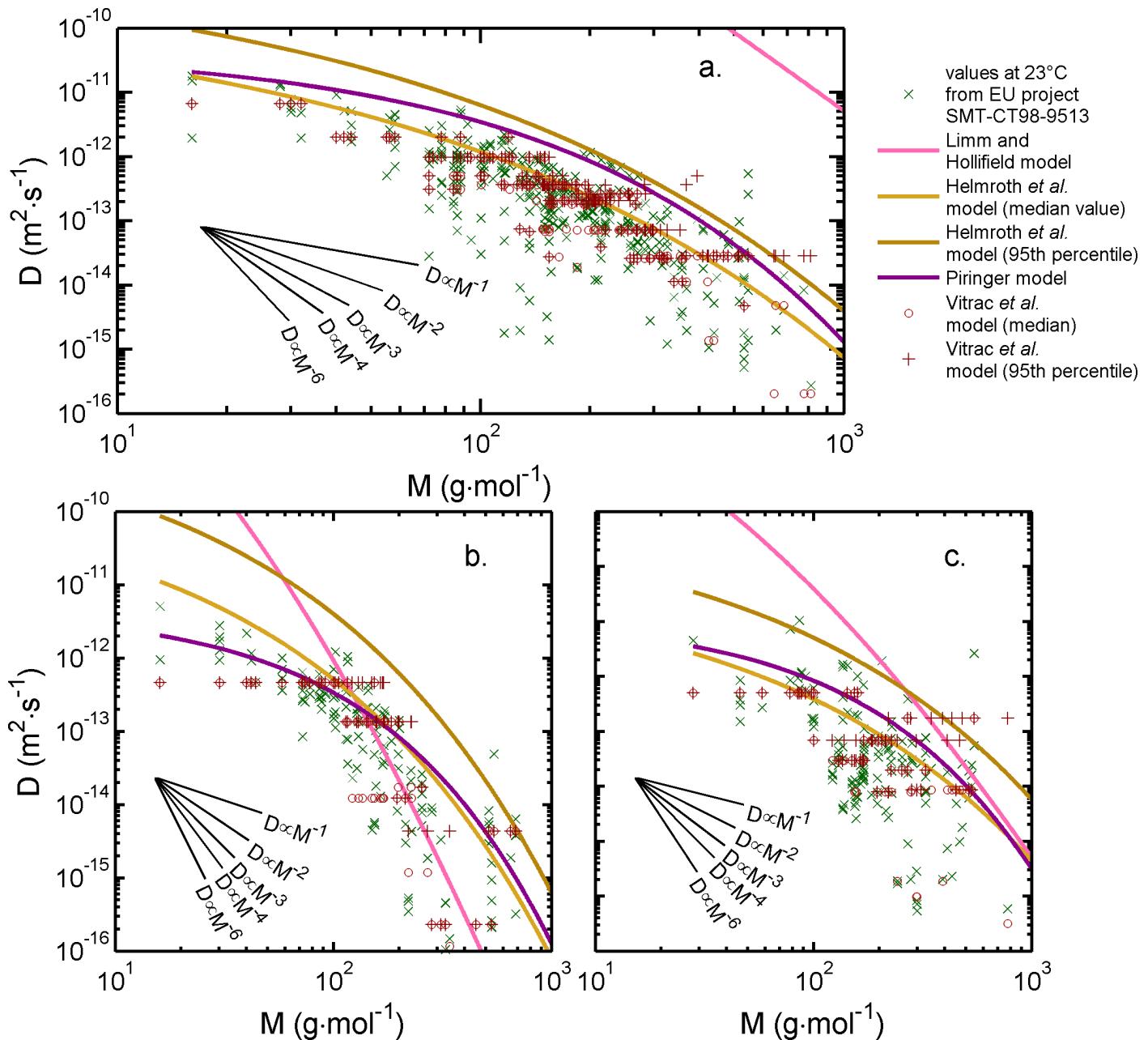


Figure 18. Estimation of  $D$  with molecular weight by both models listed in Table 9 and Vitrac model (see section 7.3) and validation of these models by comparison with data collected by the EU project SMT-CT98-7513 (EC, 2002b) and renormalized at 23°C in a) LDPE (345 values), b) HDPE (142 values) and c) PP at 23°C (141 values).

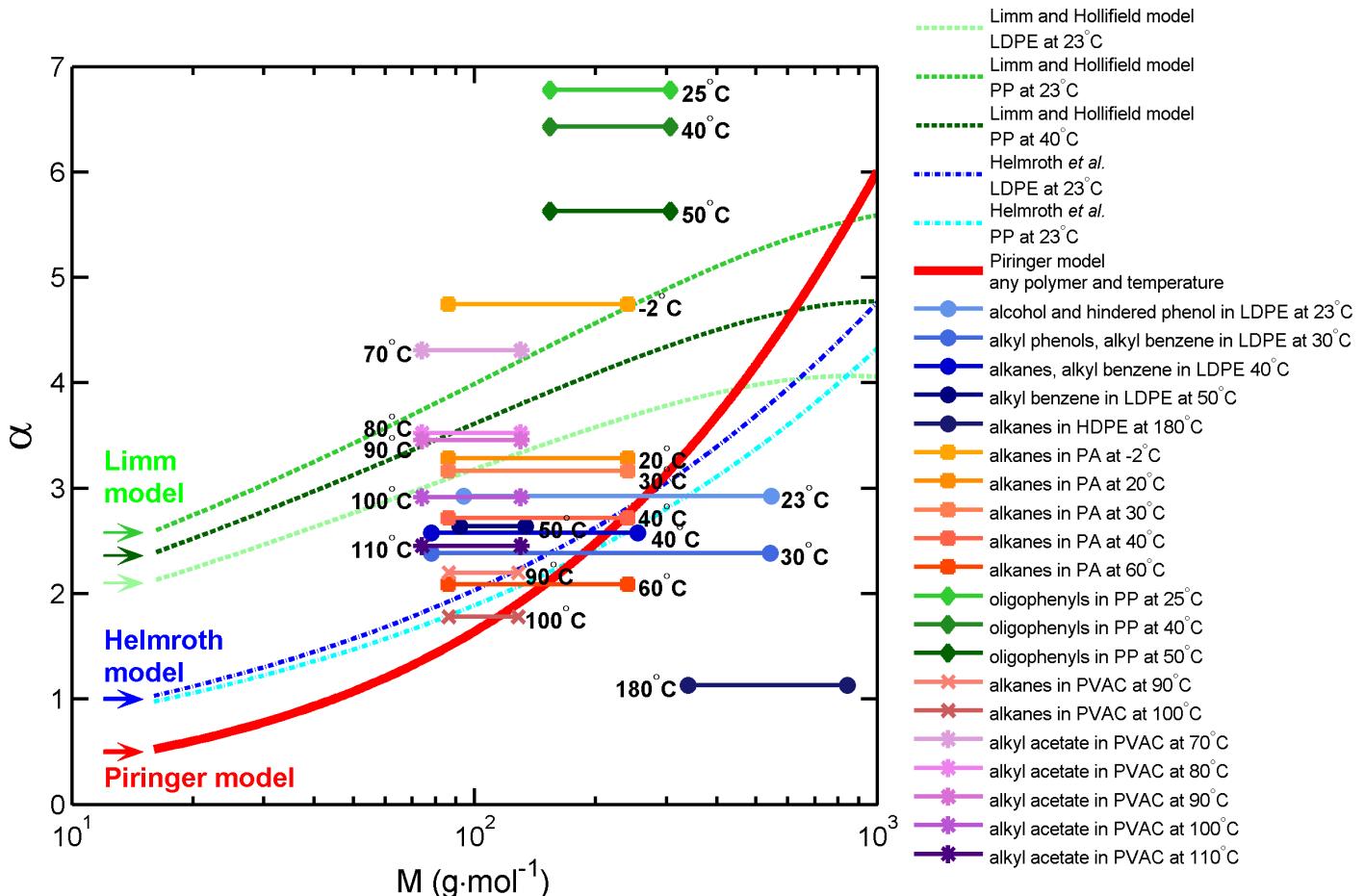


Figure 19. Plot of scaling exponents  $\alpha$  with molecular weight for different models in Table 9 and reported averaged experimental  $\alpha$  values in corresponding range of tested molecular weight (after Fang *et al.* (2013)). Each horizontal segment represents the range of molecular masses used to determine  $\alpha$ .

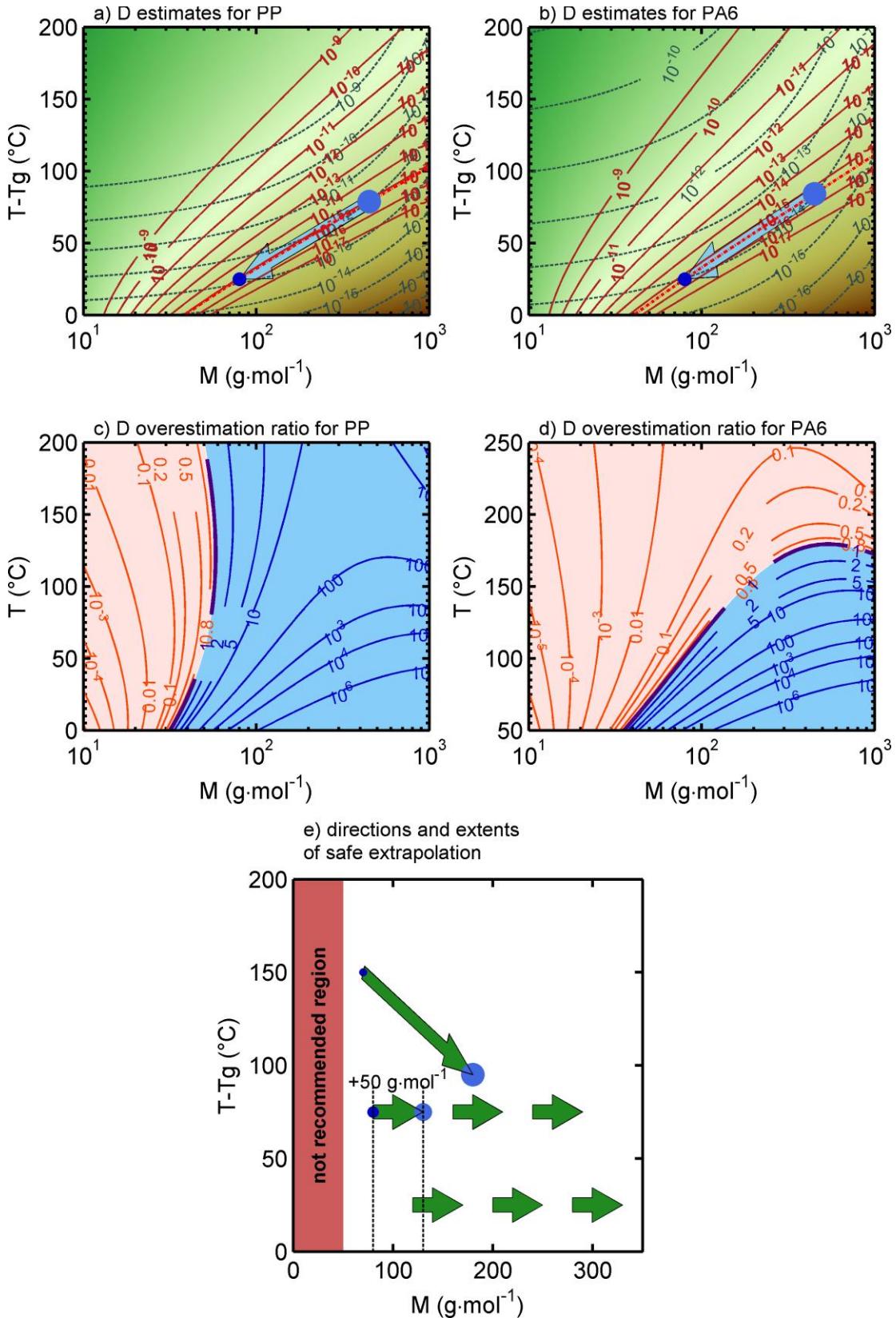


Figure 20: Evaluation of the robustness of the Piringer model for two typical polymers above their  $T_g$ : a), c) polypropylene ( $T_g=0^\circ\text{C}$ ) and b), d) polyamide ( $T_g=50^\circ\text{C}$ ). The considered diffusants are aliphatic solutes (e.g. alkanes and alkyl acetates) below the entanglement length. a-b) Comparison between iso- $D$  values (from Fang *et al.* (2013), see Table 6, solid lines) and iso- $\check{D}$  values obtained from Piringer model (see Table 9, dashed lines). c,d) Corresponding iso-ratios  $\check{D}/D$  where “safe regions” (with overestimations) are depicted in light blue. e) Safe strategies to extend the Piringer model to new polymers in presence of scarce data.

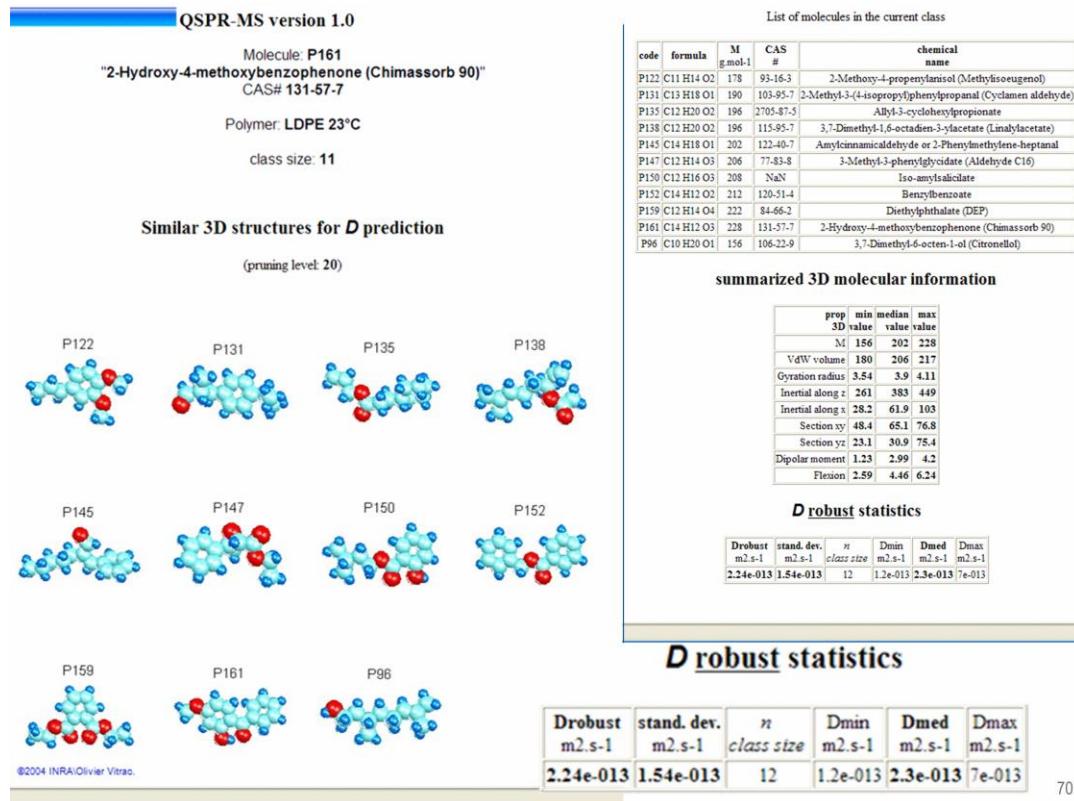


Figure 21. Example of automatic classification of Chimassorb 90 (Vitrac *et al.*, 2006). The request has been typed online on the Safe Food Packaging Portal (INRA, 2011), which gives in return all substances in the EU database with similar  $D$  values.

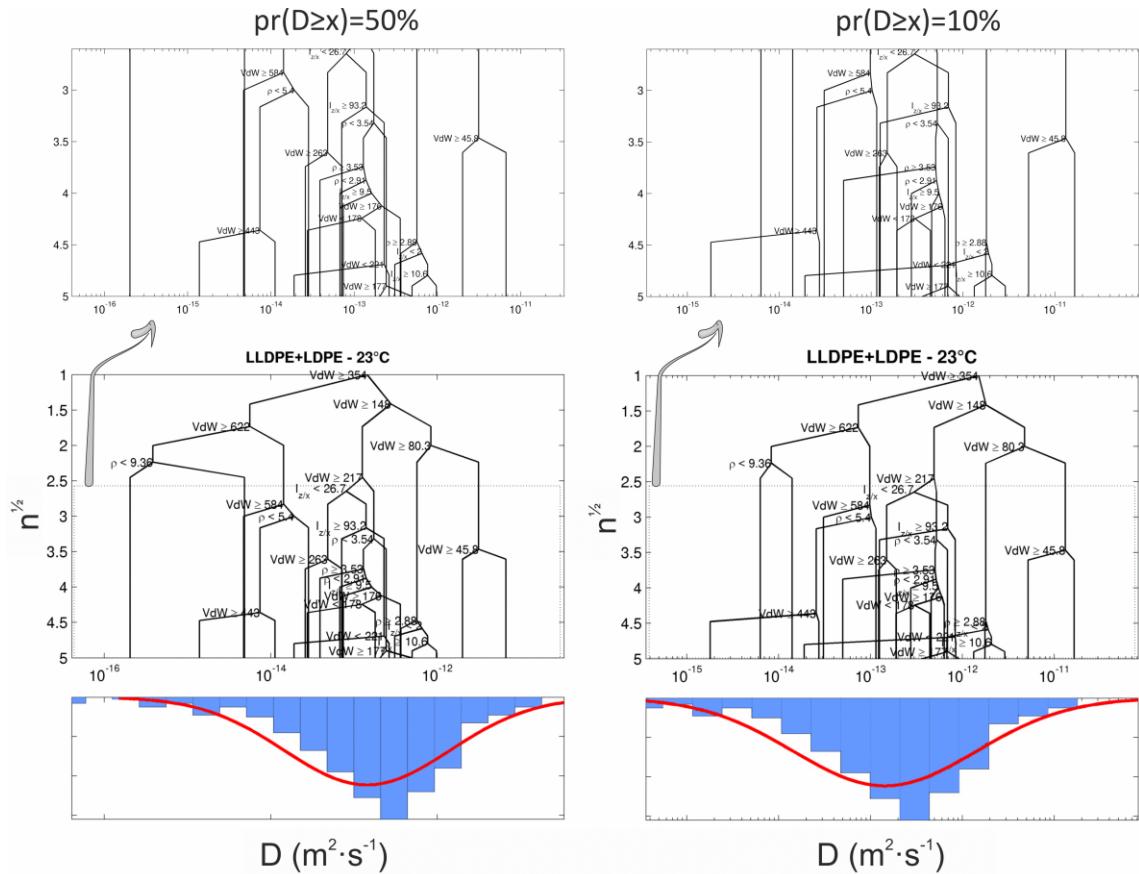


Figure 22: Decision tree for the prediction of diffusion coefficients in LDPE at 23° with different risks of overestimations: 50% or 10% (after Vitrac *et al.* (2006)).