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Mass Transport in Polymers Through the Theory of Stochastic Processes Possessing Finite Propagation Velocity

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Non-Fickian behaviors in mass transport are very common in polymeric materials. The classical Fickian law, dictating the instantaneous response of the mass flux to changes in the driving force (namely the concentration gradient), seems to be too simplistic for mass transport in viscoelastic materials, generally linked through characteristic times to stress relaxation or structural changes. A constitutive equation in which the evolution of the mass flux is governed by a characteristic relaxation time thus appeared to be the most natural choice in order to catch *anomalous* behaviors. This has led since the '80s to the hyperbolic formulation of the transport equations, known as Cattaneo-Maxwell equations in the one-dimensional case. However, hyperbolic equations use for mass transport applications were limited by the well known but never understood the unpredictable appearance of inconsistencies (read unphysical concentration overshoots and negative concentration values). Recently, inconsistencies are explained by letting the hyperbolic formulation of transport equations in polymeric systems be derived from the theory of stochastic processes possessing finite propagation velocity, namely the Poisson-Kac processes. In this paper, the hyperbolic transport model based on partial probability waves is introduced and discussed. The model was applied to two relevant literature cases, showing to be suitable for the description of anomalous diffusional phenomena.

1. Introduction

In many cases of practical interest, the classical theory of mass transport, based on Fickian laws has often proved to be unsuitable for process description. This is the case, for instance, of low molecular weight penetrants (toluene) in polymer matrices (e.g. Rath et Al., 2018) or of local drug transport in mucoadhesive alginate pastes with embedded liposomes (Shtenberg et Al., 2018).
The limit of the classical (Fickian) theory emerges quite easily from the observation that related equations correspond, at the microscopic level, to Wiener stochastic dynamics (i.e. Brownian motion) in which particles velocities are unbounded, uncorrelated and Gaussian distributed. This is obviously a too simple microscopic framework when dealing with cases, as those cited here, in which, for example, the interaction between solute and polymer matrix both limits particles velocities and induces correlations among them.
One of the first attempts to provide a mass transport equation suitable for such cases was due to the mathematician Carlo Cattaneo (Cattaneo, 1958). The Cattaneo equation, actually proposed in order to solve a physical inconsistency affecting the classical (Fickian) theory (namely the infinite propagation velocity), is a one-dimensional hyperbolic formulation of a transport equation obtained through the introduction of a new constitutive law, relating flux and concentration gradient and depending on a relaxation time. Such equation, although fruitfully used for analysis of mass transport in polymers with relaxation (Doghieri et Al., 1993), has shown to be affected by inconsistencies (namely unphysical concentration overshoots and negative concentration values). Doghieri et Al. (1993) demonstrated, basing on simplified thermodynamic assumptions, that it is possible to avoid such troubles by suitably imposing a functional form for the relaxation time. Some

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authors (Brasiello et Al., 2016a; Giona et Al., 2016) basing on the partial waves formulation described in the following mathematical section, showed the reason for such inconsistencies without any simplified assumptions. Moreover, in the papers of Giona et Al. (2017a, 2017b, 2017c), the authors extended the hyperbolic transport formulation to higher dimensions.
In this work, we will show for the first time and discuss the results of applications of the hyperbolic transport model derived by Poisson-Kac process to some recent literature data characterized by anomalous diffusional transport. In particular, two relevant cases have been selected for the purpose: toluene transport in polyurethane-urea/clay nanocomposites (Rath et Al., 2018) and doxorubicin transport in muco-adhesive alginate pastes with embedded liposomes (Shtenberg et Al., 2018). The first case was chosen because of the importance of the mass transport of low molecular weight solutes in polymer matrices in the field of solvent recovery, packaging, etc. The second case is an interesting application in the field of drug release for oral cancers treatments.

2. Mathematical model

In 1974, M. Kac demonstrated, in his seminal paper (Kac, 1974), that it was possible to build a coherent microscopic framework, which is now called Poisson-Kac process, from which to derive a hyperbolic mass transport model. In one-dimensional form such model corresponds to the Cattaneo-Maxwell equations.
The one-dimensional formulation of the Poisson-Kac process reads

$$dx(t) = c(-1)^{\chi(t)}dt \tag{1}$$

in which c represents a velocity modulus and χ is a stochastic Poisson process. It describes the elementary movements dx along a straight line of microscopic particles, which invert velocity directions according to the stochastic process. This means that:

1. Particle velocities switch randomly between $-c$ and $+c$.
2. The probability of having n velocity inversions in a certain time period t is given by the following Poisson distribution: $e^{-at}(at)^n / n!$; a being the transition rate.
3. Particle trajectories are almost everywhere continuous.

This last represents a fundamental issue concerning the Poisson-Kac process, which makes it a suitable microscopic Lagrangian description overcoming the intrinsic physical limitation of the Wiener process, which is the microscopic framework historically adopted for the description of Brownian motion (whose Eulerian description is the classical diffusion equation). In a Wiener process, in fact, we have (stochastic) Gaussian independent elementary movements, which imply unbounded particles velocities; this reflects on the derived classical diffusion equation: $\partial_t p(x,t) = D\partial_x^2 p(x,t)$ which admits unbounded propagation velocities. The last issue makes such equation useless in transport phenomena description when dealing with very short timescales (Brasiello et Al, 2016b and references therein) as well as when wave-like behaviours or correlations emerge as in the case of transport behaviour in polymer matrices (Thomas and Windle, 1982).
From Eq. (1) the following definition of probability density functions (also known as partial probability waves) arises:

$$\begin{aligned} p^+(x,t)\,dx &= \text{Prob}\{X(t) \in (x, x+dx) : (-1)^{\chi(t)} = +1\} \\ p^-(x,t)\,dx &= \text{Prob}\{X(t) \in (x, x+dx) : (-1)^{\chi(t)} = -1\} \end{aligned} \tag{2}$$

$p^+(x,t)$ is the probability density function of the distribution of particles with $+c$ velocity, while $p^-(x,t)$ is the probability density function related to the distribution of particles having $-c$ velocity.

It is possible to demonstrate (Giona et Al., 2015) that $p^{\pm}(x,t)$ satisfy the following dissipative wave equations:

$$\begin{aligned} \frac{\partial p^+(x,t)}{\partial t} &= -c\frac{\partial p^+(x,t)}{\partial x} - a p^+(x,t) + a p^-(x,t) \\ \frac{\partial p^-(x,t)}{\partial t} &= c\frac{\partial p^-(x,t)}{\partial x} - a p^-(x,t) + a p^+(x,t) \end{aligned} \tag{3}$$

Eqs. (3) are hyperbolic with linear recombination terms $\pm\left(-ap^{+}+ap^{-}\right)$. From Eq. (3), by defining the overall probability density function $p(x,t)=p^{+}+p^{-}$ and the diffusion flux $J(x,t)=c(p^{+}-p^{-})$, we derive the following equations:

$$\begin{aligned}&\frac{\partial p(x,t)}{\partial t}=-\frac{\partial J(x,t)}{\partial x}\\&\tau\frac{\partial J(x,t)}{\partial t}+J(x,t)=-D\frac{\partial p(x,t)}{\partial x}\end{aligned} \tag{4}$$

in which $\tau=1/(2a)$ is the relaxation time and $D=c^{2}/(2a)$ is the diffusion coefficient. From Eqs. (4), the well-known Cattaneo equation, $\tau\partial_{t}^{2}p(x,t)+\partial_{t}p(x,t)=D\partial_{x}^{2}p(x,t)$, derives.

It is possible to recover the classical transport equations (Fickian transport) as a limit condition when both a and c parameters diverge but the following limit holds (Kac limit):

$$\lim_{a,c\to\infty}\frac{c^{2}}{2a}=D_{Fick} \tag{5}$$

In such a case, the relaxation time thus vanishes in Eqs. (4) and the Fick's constitutive law $J=-D\partial_{x}p$ is then obtained.

More complex cases can be described through suitable generalizations of Eq. (1) (and hence of Eqs. (4)): In order to include the action of a deterministic velocity field $v\left(x\right)$ imposed from outside (advection-diffusion transport) a suitable advection term can be added; moreover, if a non-constant velocity modulus c is also considered, the Poisson-Kac process (Eqs. (1)) modifies as follows:

$$dx(t)=v\left(x(t)\right)dt+c\left(x(t)\right)(-1)^{\chi(t)}dt \tag{2}$$

while the dissipative wave equations become:

$$\begin{aligned}&\frac{\partial p^{+}(x,t)}{\partial t}=-\frac{\partial v^{+}(x,t)p^{+}(x,t)}{\partial x}-ap^{+}(x,t)+ap^{-}(x,t)\\&\frac{\partial p^{-}(x,t)}{\partial t}=-\frac{\partial v^{-}(x,t)p^{-}(x,t)}{\partial x}-ap^{-}(x,t)+ap^{+}(x,t)\end{aligned} \tag{4}$$

where $v^{+}(x,t)=v(x,t)+c(x,t)$ and $v^{-}(x,t)=v(x,t)-c(x,t)$. It is worth noting that a further generalization can be possible by letting a to be non-constant. However, this means to change the law of occurrence of velocities switches in the recombination terms. An exhaustive discussion about the topic is provided by Giona et Al. (2017a, 2017b, 2017c).

3. Results and discussion

3.1 Anomalous toluene transport in model segmented polyurethane-urea/clay nanocomposites.

A wide literature showed that transport properties in polymer are often widely dependent on chemistry, polymer size and by the presence of incorporated nanosized particles, which could interact with penetrants, leading to deviation from Fickian behavior (Rath et Al., 2018 and references therein). This is the case of segmented polyurethane-urea/clay nanocomposites.

Several works showed that the introduction of clays nanoparticles into the polymer matrix influences phase morphology and transport properties (Rath et Al., 2018). Anomalous behaviors are observed but not understood. This causes the lack of good mathematical models for accurate process description.

Experimental sorption data of toluene into a 1 mm depth slice of polyurethane-urea/clay nanocomposites are taken from the paper of Rath et Al., 2018. Data for several sorption experiments, differing by clay nanoparticles content (wt%), are available. Details about nanocomposite preparation and experimental setups are reported in the original paper.

In Figure 1, the comparison between experimental and predicted data is reported. M_{t} is the weight uptake at time t; M_{inf} is its equilibrium value. The adopted model, based on dissipative wave equations, is able to capture with good accuracy the experimental trends. Since the objective is to test the prediction capabilities of

the model, no functional form for parameters is introduced (i.e. no additional parameters). In Table 1 parameters values obtained from a suitable regression procedure are also reported. It is worth noting that, from the observation of the parameters value it is possible to argue that all the analyzed cases are far from being representative of a Fickian transport. A common method to assess the statement is to evaluate the deviation from 0.5 of the slope of a straight line passing through the data (in log-log form). For the purpose, in Figure 1B, log-log plots, in which such deviation can be appreciated together with the slope values, are also reported. Slopes oscillate among 0.65 and 0.7. This means intermediate behaviors between Fickian and Case II.

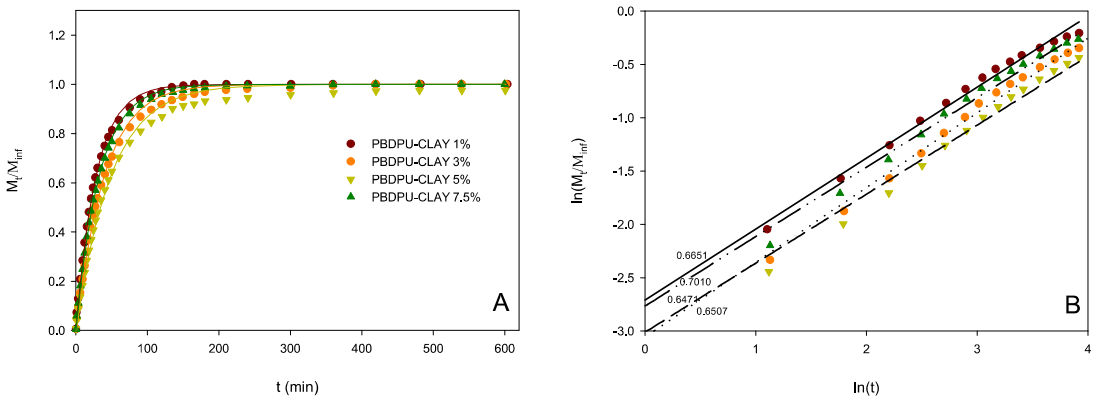

Figure 1: Toluene sorption in polyurethane–urea nanocomposite with 1, 3, 5 and 7.5 wt% clay content. Data are taken from Rath et Al., 2018 (A) Comparison between experimental and predicted data. Parameters values are reported in Table 1. (B) log - log plot of the experimental data. Straights lines of the linear fits and related slopes are also reported.

Table 1: Parameters values for the dissipative wave equations obtained from a suitable regression procedure from the data reported in Rath et Al., 2018.

Nanocomposite	c ($mm \cdot min^{-1}$)	a (min^{-1})	h ($mm \cdot min^{-1}$)	v ($mm \cdot min^{-1}$)
PBDPU-1	0.491	3.682	0.071	0.169
PBDPU-3	0.497	3.596	0.051	0.099
PBDPU-5	0.509	3.924	0.042	0.050
PBDPU-7.5	0.497	2.507	0.061	0.0

3.2 Doxorubicin transport in muco-adhesive alginate pastes with embedded liposomes

Mucoadhesive polymers with embedded liposomes seem to be promising in treatments of oral cancers as drug carriers. Polymer attaches on oral mucosa inducing local release of drugs, while liposomes avoids drug degradation also improving cells absorption. The aim is both tumor size reduction and tumor cells dissemination. The paper of Shtenberg et Al., 2018, from which data are taken, is an experimental study in which they analyze different alginate/liposomes innovative formulations from the point of view of mucoadhesive properties and drug release evolution. Here, we apply the dissipative wave equation to the description of the time evolution of liposomes release from alginate pastes with different alginate concentrations in simulated saliva buffers (Shtenberg et Al., 2018). Details of materials and experiments can be found therein.

From the comparison between predicted and experimental data, reported in Figure 2, the good prediction capability of the model is observed. Model's parameters are also reported in Table 2. It is worth noting that in this case, differently from the preceding, the advection term is not introduced (v=0). This means that, being no neat flux imposed from outside, the transport mechanism is purely leaded by molecular fluctuations which, differently from the classical diffusional transport, takes also into account molecular correlations.

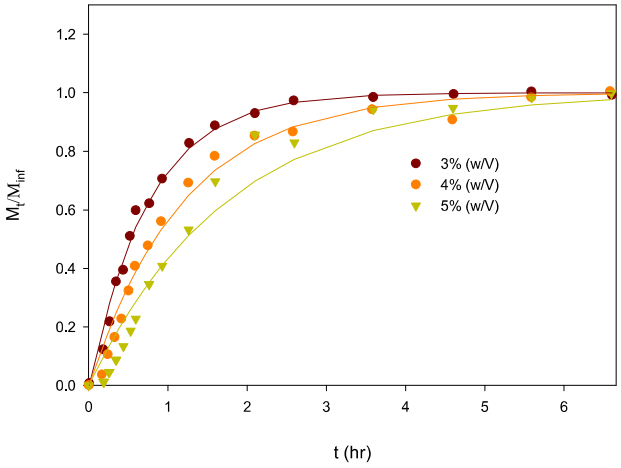

Figure 2: Doxorubicin release in simulated saliva buffers from muco-adhesive alginate pastes with embedded liposomes with 3%, 4%, 5%(w/V) alginate concentration. Data are taken from Shtenberg et Al., 2018: Comparison between experimental and predicted data.

Table 2: Parameters values for the dissipative wave equations obtained from a suitable regression procedure from the data reported in Shtenberg et Al., 2018.

Alginate concentration	c ($mm \cdot hr^{-1}$)	a (hr^{-1})	h ($mm \cdot hr^{-1}$)	v ($mm \cdot hr^{-1}$)
3%(w/V)	$6.85*10^{-5}$	6.740	0.131	0.000
4%(w/V)	0.0421	7.020	0.0838	0.000
5%(w/V)	0.244	7.087	0.0586	0.000

4. Conclusion

In this paper, we discussed the hyperbolic equations for mass transport based on the definition of partial waves and derived from Poisson-Kac process. Equations have been here applied to the description of two literature cases of mass transport in complex matrices, showing good prediction capabilities. The aim was to underline the advantages of the new approach, which, overcoming the concentration-flux paradigm, allows the treatment of several different transport conditions going from wave-like transport to classical Fickian behavior by using partial waves as fundamental variables. Such variables, although having a less immediate correspondence with the experimental responses, generally in terms of flow and concentration, have in our opinion a deeper meaning because they provide a more intimate and immediate link with the underlying stochastic reality.

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