About Non-Fickian Hyperbolic Diffusion

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Abstract :

Fick's law expresses the proportionality of solute flux with respect to concentration gradient. Similar relations are Darcy's law for the fluid flow in porous media, Ohm's law for the electric flux and Fourier's law for heat transfers. When introduced in the corresponding balance equations, these flux laws yield diffusion equations of parabolic character. Different attempts have been made to obtain hyperbolic equations so as to point out propagative phenomena. This was done by adding a time derivative flux term to the flow law. In the paper we focus on solute transport. Two possible non-Fickian diffusion cases are addressed. We firstly investigate diffusion in fluids by a mechanistic approach. Secondly, we study the macroscopic diffusion law in composite materials with large contrast of diffusion coefficient. We show that the obtained diffusion law yields hyperbolicity for drastically small characteristic times or non-propagative waves, respectively.

Résumé :

La loi de Fick exprime la proportionalité du flux de soluté au gradient de concentration. Les lois de Darcy pour les écoulement en milieu poreux, d'Ohm en électricité et de Fourier pour la chaleur sont de même nature. Introduites dans les équations de bilan correspondantes, elles conduisent à des équations de diffusion paraboliques. Afin d'obtenir des phénomènes propagatifs, un terme de dérivée temporelle du flux est souvent introduit dans les lois d'écoulement. Dans la présente étude, nous étudions deux cas possibles de lois non-fickiennes : la diffusion dynamique de soluté dans un liquide et la diffusion dans un composite. Nous montrons qu'un comportement propagatif est obtenu dans le premier cas, mais pour des temps caractéristiques extrèmement courts, et ne peut être mis en évidence dans le deuxième cas.

Key-words :

Non-Fickian diffusion; propagation; composite material

1 Introduction

Isotropic Fick's law for diffusion of solute in fluids is written

$$\overrightarrow{J} = -D\overrightarrow{\nabla}c, \tag{1}$$

where $\overrightarrow{J}$ is the solute flux, D is the molecular diffusion and c is the solute concentration. When introduced in the solute balance equation

$$\overrightarrow{\nabla} \cdot \overrightarrow{J} = -\frac{\partial c}{\partial t}, \tag{2}$$

equation (1) yields a diffusion equation of parabolic character

$$\overrightarrow{\nabla} \cdot D\overrightarrow{\nabla}c = \frac{\partial c}{\partial t}. \tag{3}$$

In such parabolic second order differential equations, information propagates at an infinite velocity, a property which is common to all diffusion processes, i.e., to Fick's, Fourier's, Ohm's or Darcy's processes. To overcome this "non-physical" behaviour, modifications are introduced in these laws so as to render equation (3) hyperbolic. First attempts concerned Fourier's law, see Maxwell (1867); Cattaneo (1958); Vernotte (1958a,b); Chester (1963); Volz *et al.* (1997); Moyne and Degiovanni (2003) and Duhamel (2001) for a more complete bibliography. Ohm's law is also addressed in a similar way, see, e.g., Cuevas *et al.* (1999). Darcy's law poses less difficulty since it is a momentum balance equation whose extension to dynamics is easily demonstrated, Levy (1979); Auriault (1980). That yields to Biot's law, Biot (1956), which shows added mass phenomenon. For solute transport, studies are not numerous. Scheidegger (1960) proposed a hyperbolic diffusion equation, which corresponds to a modified Fick's law, Hassanizadeh (1996). Let us consider the isotropic form of this hyperbolic diffusion law

$$\overrightarrow{J} + A\frac{\partial \overrightarrow{J}}{\partial t} = -D\overrightarrow{\nabla}c, \qquad (4)$$

where time $A > 0$ characterizes together with D the solute transport. Relation (4) is similar to Cattaneo-Vernotte law for heat flow, Cattaneo (1958); Vernotte (1958b). When introduced in the solute balance equation, such a non-Fickian law yields a hyperbolic equation which enables to point out finite velocity propagation phenomena: time A is responsible of inertial effects

$$\overrightarrow{\nabla} \cdot D\overrightarrow{\nabla}c = \frac{\partial c}{\partial t} + A\frac{\partial^2 c}{\partial t^2}. \qquad (5)$$

The form of transport equation (4) is often justified as being a consequence of material heterogeneity, Duhamel (2001). Anyhow, Moyne and Degiovanni (2003) have pointed out that a transport equation of propagative type could not be recovered in 1D composite materials.

In the paper, we present two attempts to recovering such a non-Fickian law (4). In part 2 we investigate transient solute diffusion in liquids by a mechanistic approach following Einstein's diffusion theory. We demonstrate that such a relation (4) is valid, but for very small characteristic transport characteristic times. Finally we discuss in part 3 the possible non-Fickian character of solute flow through a composite material with high contrast of diffusion coefficients. For this purpose, we revisit the paper by Auriault (1983) where the macroscopic equivalent heat flow law is obtained by upscaling the physics at the heterogeneity scale.

2 Non-Fickian hyperbolic diffusion in liquids

The molecular diffusion is related to the mobility b by the Einstein relation

$$D = kTb, \qquad (6)$$

where k is the Botzmann constant, $k \approx 1.38 \ 10^{-23}$ J K^{-1} and T is the absolute temperature.

2.1 Quasi-static diffusion coefficient

Consider a solute particle moving at a constant velocity v in a stagnant fluid. The fluid exercices on the particle a force F which is related to v by

$$F = \frac{v}{b}. \qquad (7)$$

In case of spherical particle, b is given by the Stokes formula

$$b = \frac{1}{6\pi\mu a}, \qquad (8)$$

where μ is the viscosity of the fluid and a is the particle radius. Therefore, we obtain the quasi-static diffusion coefficient in the form

$$D_0 = \frac{kT}{6\pi\mu a}. \tag{9}$$

2.2 Transient diffusion

When the particle velocity is not a constant and depends on time t, relation (7) becomes (see Landau and Lifchitz (1959), §24)

$$F = 2\pi\rho a^3 \left(\frac{1}{3}\frac{\mathrm{d}v}{\mathrm{d}t} + \frac{3\mu}{\rho a^2}v + \frac{3}{a}\sqrt{\frac{\mu}{\pi\rho}}\int_{-\infty}^{t}\frac{\mathrm{d}v}{\mathrm{d}\tau}\frac{\mathrm{d}\tau}{\sqrt{t-\tau}} \right). \tag{10}$$

Using (7) to obtain the value of b in the transient case and (6) for D yields the following non-Fickian law

$$-D_0\overrightarrow{\nabla c} = \frac{\rho a^2}{3\mu}\left(\frac{1}{3}\frac{\mathrm{d}\overrightarrow{J}}{\mathrm{d}t} + \frac{3\mu}{\rho a^2}\overrightarrow{J} + \frac{3}{a}\sqrt{\frac{\mu}{\pi\rho}}\int_{-\infty}^{t}\frac{\mathrm{d}\overrightarrow{J}}{\mathrm{d}\tau}\frac{\mathrm{d}\tau}{\sqrt{t-\tau}} \right). \tag{11}$$

Relation (11) represents the correct generalization of quasi-static Fick's law (1) to dynamics. It is different from (4), due to the presence of memory effects that are represented by the last term in the right hand member. The memory function is in the form

$$M(t) = \sqrt{\frac{\rho a^2}{\pi\mu t}}, \tag{12}$$

and its characteristic time is given by

$$T_m = \frac{\rho a^2}{\pi\mu}. \tag{13}$$

2.3 Estimation of the domain of validity of non-Fickian relation (11)

Assume that the fluid is water, $\mu = 10^{-3}$ kg m^{-1} s^{-1}, $\rho = 10^3$ kg m^{-3}. For $a = 10$ Å, we obtain $T_m \approx 3 \times 10^{-13}$ s. For $a = 10^{-6}$ m, we have $T_m \approx 3 \times 10^{-7}$ s.
On an other hand, the right hand member of relation (11) introduces two dimensionless numbers. Noting T_c the characteristic time of the process yields

$$\mathcal{P} = \frac{|\frac{1}{3}\frac{\mathrm{d}\overrightarrow{J}}{\mathrm{d}t}|}{|\frac{3}{a}\sqrt{\frac{\mu}{\pi\rho}}\int_{-\infty}^{t}\frac{\mathrm{d}\overrightarrow{J}}{\mathrm{d}\tau}\frac{\mathrm{d}\tau}{\sqrt{t-\tau}}|} = \frac{\pi}{9}\sqrt{\frac{T_m}{T_c}},$$

$$\mathcal{Q} = \frac{|\frac{1}{3}\frac{\mathrm{d}\overrightarrow{J}}{\mathrm{d}t}|}{|\frac{3\mu}{\rho a^2}\overrightarrow{J}|} = \frac{\pi}{9}\frac{T_m}{T_c}.$$

We can then point out three different behaviours :

- $T_c \gg T_m$. Relation (11) reduces to Fick's law (1).

- $T_c = \mathcal{O}(T_m)$. The flow law is given by (11) with its three terms in the right hand member. This is a non-Fickian law, but different from (4).

- $T_c \ll T_m$. The two last terms in (11) are negligible. This is a non-Fickian law which yields a hyperbolic behaviour as in (4), but without the first term in the right hand member.

However, as seen above, T_m is very small. Therefore, the two last behaviours are likely not to exist. Remark that the hyperbolic character in the two last behaviours comes from relation (10) where dynamics is considered.

3 Memory effects in composite materials

Consider a periodic composite material of period Ω, made of two constituents of diffusion coefficients D_1 and D_2 which occupy volumes Ω_1 and Ω_2, respectively. The interface is Γ. Medium 1 is connected whereas medium 2 is connected or not (see Figure 1 where medium 2 is not connected). Both constituents follow Fick's law (1) and equation (3). The characteristic size of the heterogeneities or of the period is noted l, whereas the characteristic size of the macroscopic sample or of the macroscopic solute flux is L and we assume a separation of scales: $l \ll L$. When $D_1 = \mathcal{O}(D_2)$, the macroscopic equivalent behaviour is Fickian (see Auriault (1983) where heat flow in composite materials is investigated): the macroscopic equivalent description is given by

$$\overrightarrow{\nabla} \cdot \mathbf{D}^{eff} \overrightarrow{\nabla} c = \frac{\partial c}{\partial t},$$

where $\mathbf{D}^{eff}$ is the effective diffusion tensor which depends on both constituents 1 and 2 and on the geometry at the fine scale. $D_2 = \mathcal{O}(D_1 \, l/L)$ or $D_2 = \mathcal{O}(D_1 \, (l/L)^3)$ are particular cases of the previous one.
We consider here the case where medium 2 is much less conductive than medium 1

$$\frac{D_2}{D_1} = \mathcal{O}(\frac{l}{L})^2 \ll 1.$$

The problem of a macroscopic equivalent behaviour was investigated in Auriault (1983) for
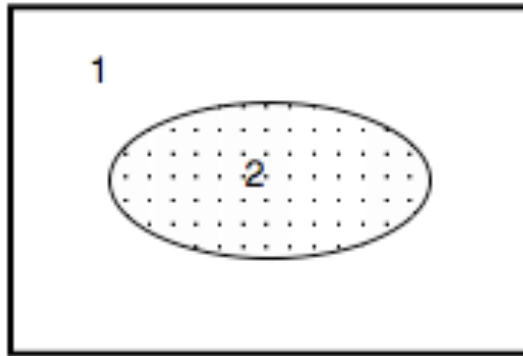

Figure 1: Schematic view of a period (2D case)

heat transfer by using the method of multiscale asymptotic expansions. The reader is referred to this paper for details of the upscaling process.
The upscaling process yields the following equivalent macroscopic behaviour, at the first order of approximation (the model is valid within a relative error $\mathcal{O}(l/L)$)

$$\overrightarrow{\nabla} \cdot \mathbf{D}_1^{eff} \overrightarrow{\nabla} c = \frac{\partial c}{\partial t} - \int_\infty^t K^{eff}(t-\tau) \frac{\partial^2 c(\tau)}{\partial \tau^2} \mathrm{d}\tau. \tag{14}$$

In the above relation, c represents the concentration in medium 1 and $\mathbf{D}_1^{eff}$ is the effective diffusion tensor of the composite material, when considering medium 2 as non diffusive. The macroscopic solute flux is shown to be

$$\overrightarrow{J} = -\mathbf{D}_1^{eff}\overrightarrow{\nabla} c. \tag{15}$$

The memory function $K^{eff}(t)$ is obtained as the inverse Fourier transform of $\bar{k}/i\,\omega$, where

$$\bar{k}(\omega) = \frac{1}{|\Omega|}\int_{\Omega_2} k(\omega)\mathrm{d}V, \tag{16}$$

and the complex periodic function $k(\omega)$ is the solution of the following boundary value problem in Ω_2

$$\overrightarrow{\nabla}\cdot D_2\overrightarrow{\nabla}k = i\omega(k-1), \tag{17}$$

$$k = 0 \qquad \text{on } \Gamma.$$

Illustrations for $\bar{k}$ are given in Auriault (1983) for layered media and for circular cylindrical or spherical inclusions. Important properties of the real and imaginary parts of $\bar{k}$ are that both are positive and verify, Auriault (1983), the following inequalities

$$\bar{k} = \bar{k}_1 + i\bar{k}_2,$$

$$0 < \bar{k}_1 \leq n, \qquad 0 < \bar{k}_2 \leq n, \qquad n = \frac{|\Omega_2|}{|\Omega|}, \tag{18}$$

and

$$\lim_{\omega\to 0}\frac{\bar{k}_2}{\omega} > 0.$$

Relation (14) can be seen as describing a Fickian process in presence of a source term represented by the second term in the right member: the macroscopic equivalent medium is described by solute concentration in medium 1 and Fick's law (15). Medium 2 plays the role of a solute reservoir connected to medium 1. Medium 1 is responsible of the macroscopic diffusion flux. However, the form of the source term in (14) incites us to look for an equivalent description in the form of non-Fickian relation (5). This can be done by considering solute flow at constant frequency ω. Relation (14) then becomes

$$\overrightarrow{\nabla}\cdot\mathbf{D}_1^{eff}\overrightarrow{\nabla}c = (1-\bar{k}_1)\frac{\partial c}{\partial t} - \frac{\bar{k}_2}{\omega}\frac{\partial^2 c}{\partial t^2}. \tag{19}$$

We recover (5), but with a different solute capacity $1 - \bar{k}_1 < 1$ and with $A = -\bar{k}_2/\omega < 0$. Therefore, differential equation (19) is elliptic, of different nature from (5) which is hyperbolic. There is no finite velocity propagation in the composite material. This result was also obtained by a different approach in Moyne and Degiovanni (2003) for 1-D heat flow. On the contrary to section 2, no dynamics is present at the heterogeneity scale nor is introduced later. That explain why we do not recover a propagative process at the macroscopic scale. It is likely that some dynamics should be introduced somewhere so as to obtain a propagative process. Remark that the upscaling method in use is rigorous in the sense that the macroscopic description is obtained from the fine scale description, without any prerequisite as it is usual with other methods.

4 Conclusion

Two attempts to justify non-Fickian Cattaneo-Vernotte law for solute diffusion have been conducted, in a view to enable finite velocity propagation of solute perturbations. By analyzing molecular diffusion through its mechanistic Einstein definition, it was shown that such a hyperbolic description is valid, but for transient solute flows with unrealistic very small characteristic times. In composite material with diffusion coefficients of similar or of very different order of magnitude, we did not recover Cattaneo-Vernotte law, but either a parabolic or an elliptic phenomenon.

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