NON - FICK DIFFUSIONS IN POLYMERS

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Résumé

Les déviations de la loi de Fick sont importantes quand on étude la diffusion des petites molécules pénétrantes dans les polymères vitreuses sous la température de transition dans l'état vitreux.

Ce problème est important parce que la diffusion joue un rôle de control dans plusieurs procès industriels et biologiques.

Particulièrement, il est important dans la centrifugation sèche des fibres, dans la couverture des substrats par la déposition et le sèchement séquentielle des solutions de polymères et dans la projection des systèmes d'approvisionnement avec médicaments.

Les longs temps de relaxation ont aussi une grande influence dans les procès de diffusion en verre et justifie par ailleurs, l'accent qui est mis sur l'étude des effets de relaxation en diffusion.

Riassunto

La equazione di Fick descrive diffusione in termodinamica dei processi irreversibilli. Ci sono situazioni quando comparono deviazioni de la legge di Fick. Questo articolo sta trattando su non-Fick diffusione, di piccole molecule penetrante in polimeri vetrati verso temperatura di transizione in stare vetrata.

Rezumat

Abaterile de la legea lui Fick sunt importante atunci când se studiază difuzia micilor molecule penetrante în polimerii vitroşi (sticloşi) sub temperatura de tranziţie în stare vitroasă.

Această problemă este importantă deoarece difuzia are un rol de control în multe procese industriale şi biologice.

În particular este de interes în centrifugarea uscată a fibrelor, în acoperirea substraturilor prin depunerea şi uscarea secvenţială a soluţiilor de polimeri şi în proiectarea sistemelor de alimentare cu medicamente.

Timpii lungi de relaxare au de asemenea o mare influenţă în procesele de difuziune din sticle şi astfel se justifică accentul care se pune pe studiul efectelor de relaxare în difuziune.

The Fick equation describes diffusion in non-equilibrium thermodynamics.

Diffusion plays a rate-controlling role in many industrial and biological processes.

$$J_x = -D\frac{\partial c}{\partial x}, (1)$$

Departures from the Fick law are important when studying the diffusion of small penetrant molecules into glassy polymers bellow the glass transition temperature.

Long relaxation times also have a great influence on diffusive processes in glasses and justify that special emphasis be put on the study of relaxational effects in diffusion.

The most common experiments where appears non-Fickian effects are sorption, desorption and permeation of a small solvent in a film or membrane of glassy polymer. The initial concentration (or the activity, in more rigorous terms) of the permeant is suddenly increased (sorption) or decreased (desorption) around the sample, or at one side of it (permeation).

The experimental quantities of interest are the mass uptake per unit surface as a function of time m(t), in sorption and desorption, experiments, or the volume throughput Q(t) per unit area of membrane, in permeation.

The mass uptake m(t) is defined as the mass of solvent absorbed by the film per unit area, i.e.

$$m(t) = M \int_0^t dx [c \ x,t \ -c_0], \ (2)$$

Where M is the molar mass of the solvent and c(x, t) its concentration in moles per unit volume, across the film, of thickness I. In permeation, the volume throughput per unit area is

$$Q(t) = \int_0^t dt' J(t'), \ (3)$$

With J the volume flux of the solvent.

We are interested about the short-time limit behaviour of m(t) and the long-time behaviour of Q(t), which in the classical Fickian theory are respectively given by

$$\frac{m(t)}{m(\alpha)} = \left(\frac{16 D t^{1/2}}{\pi l^2} \right)^{1/2},$$

$$\varphi(t) = \frac{Q(t)}{C_1 - C_0} \frac{D}{l} \left(t - \frac{l^2}{6D} \right), \ (4)$$

With c_1 and c_0 the concentrations of the solvent on each side of the membrane. It follows that m(t) /m(∞) behaves as $t^{1/2}$ at short timesand the time lag in permeation, the time at which φ(t) vanishes (given by $t^x = l^2/(6D)$), behaves as l^2.

Expressions (4) are usually satisfied far from the glass transition temperature.

Close to the transition, and below it, non-Fickian features appear and manifest themselves through several phenomena: case II and super-case II diffusion, two-stage sorption, sigmoidal sorption and pseudo-Fickian behaviour.
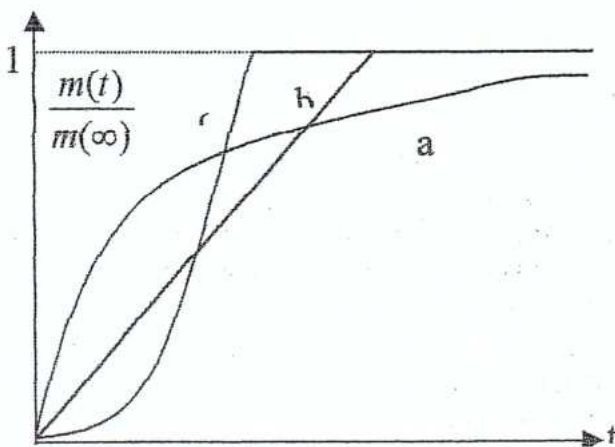

Fig. 1 Fractional mass uptake m)t) /m(∞) as a function of time t for normal diffusion (1), case II diffusion (2) and super-case II diffusion (3).

Alfrey, Gurnee and Lloyd observed for the first time in 1965 that when solvent molecules penetrate into the polymer, a sharp advancing boundary is produced between the inner glassy region and the outer swollen gel.

The boundary moves with a constant velocity in case II diffusion or it accelerates in super-case II diffusion. The short-time expression for the mass uptake may be expressed generally as a m(t)/m(∞) and t^n, with n=1 for case II, m>1 for super-case II and n=1/2 for usual Fickian diffusion.

Though a well-defined boundary could also appear in classical Fick diffusion with a sufficiently steep variation of the diffusion, coefficient with the concentration, such a boundary would advance as $t^{1/2}$ and not as t.

Case II diffusion has been observed in solutions of methanol in polymethyl metacrylate (PMMA) in the range $0° - 150 °C$, in solutions of alkanes in polystirene in the range $25 °C - 50 °C$, in solutions of benzene in epoxy resins.

Super-case II diffusion has been observed for ethanol, propanol and butanol in thin films of PMMA.

The fractional mass uptake in this model for times longer than l^2/D is given by

$$\frac{m(t)}{m(\infty)} = \frac{2}{l\sqrt{\frac{D}{\tau}}} t, \quad t \langle \frac{l}{2\sqrt{\frac{\tau}{D}}} ,$$

$$\frac{m(t)}{m(\infty)} = 1, \quad t \rangle \frac{l}{2}\sqrt{\frac{\tau}{D}} , \quad (5)$$

This corresponds to two fronts of solvent advancing from the left and from the right towards the center of the membrane with speed $(D/\tau)^{1/2}$, which is speed predicted by the Maxwell-Cattaneo equation. Each front must travel a distance l/2 before arriving at the center. When the fronts collide, they may occasionally clash and give rise to oscillations, which die away rapidly.

Some characteristics speeds of the fronts in case II diffusion are given in Table 1.

Table 1

Characteristics speeds of the fronts in case II diffusion

Speeds of fronts in case II diffusion		
System	Speed (cm/s)	T(°C)
n-pentane in biaxially oriented polystyrene	$1,4x10^{-4}$ $1,3x10^{-4}$	30 35
n-pentane in cast annealed polystyrene	$0,8x10^{-4}$ $0,7x10^{-4}$	30 35
Benzene in epoxy resins	$5,9x10^{-6}$	70
Methanol in PMMA	$1,0x10^{-7}$ $1,0x10^{-5}$	24 62

In super-case II, the front accelerates. This is observed in very thin membranes of the order of 1mm thickness. The acceleration of the front has been explained by the fact that the differential swelling stress increases when the residual thickness of the core is reduced.

Bibliography

1. De Groot, S.R., Mazur, P. Non-equilibrium thermodynamics, Dover Publications inc., New York 1962

2. Jou, D., Casas-Vazquez, J., Lebon, G., Extended Ireversible Thermodynamics, Springer Verlag, Berlin,Heidelberg, New York, 1996

3. Rumer, Y.B., Ryvkin, M.S., Thermodynamics, Statistical Physics, and Kinetics, Mir Publishers, Moscow 1980

4. Vîlcu R, Dobrescu, A., Termodinamica proceselor ireversibile, Editura Tehnică, București, 1982