

From the Thomas–Windle model to a phenomenological description of Case-II diffusion in polymers

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Abstract

The classic theory of Thomas and Windle has provided a powerful description of the processes involved in Case-II diffusion, in which a sharply defined front of solvent-swollen gel advances into a glassy polymer. We show how some aspects of the Thomas–Windle model can be introduced into a recent formulation by Rossi and coworkers to provide a phenomenological description of the slowing of the advancing front. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The study of anomalous diffusion phenomena in polymeric materials has been of interest for decades. One particular instance of non-Fickian transport is Case II diffusion [1], which is characterized by a sharp front moving into the polymer at a constant velocity. It has been intensively investigated experimentally and theoretically, and various microscopic and phenomenological models have been proposed to explain the observed features of Case II diffusion in glassy polymers. Of microscopic models, that of Thomas and Windle (TW) [2,3] appears to be the most successful. In this approach, the diffusion of solvent is accompanied by a swelling of the polymer that is driven by the osmotic pressure, and the front motion is controlled by the coupling between this osmotic-pressure-driven swelling and the nearly Fickian diffusion in the glassy region ahead of the front. Detailed reviews of the TW model can be found in Refs. [4–6]. The expression for the front velocity derived from this model has been quantitatively verified experimentally [7–9].

Of the many phenomenological models, that of Peterlin [10] first considered Fickian diffusion into a glassy core ahead of a sharp boundary that separates the swollen gel from the glassy core and which moves at constant velocity. Because it was assumed that the diffusion coefficient in the

swollen gel is infinite and that the front velocity is constant, this model was not able to describe the slowing-down of the front motion and the crossover from Case II to Case I behavior that is observed in a number of systems [11,12]. Astarita and Sarti (AS) [13] introduced a kinetic expression for the velocity of the glassy-swollen interface and treated the diffusion in the swollen gel as governed by Fick's law. The crossover from Case II to Case I behavior, as well as front propagation at constant velocity in the early stage of the diffusion, were predicted. However, this model did not take into account the diffusion of a small amount of solvent in the glassy core and thus treated the transition from the glassy to the swollen state as totally instantaneous. The neglect of the Fickian precursor ahead of the front does not affect the prediction of the early linear kinetics and the later crossover to Fickian behavior, but it does nevertheless leave the model at odds with the microscopic rate-control mechanism as revealed in the TW model and verified in a number of experimental observations. Astarita and Joshi (AJ) [14] extended the AS model to allow for some diffusion in the glassy core while keeping the kinetic expression for the front velocity unchanged. This was an improvement on the AS model, but still shed no light on the effect of glassy-core diffusion on the front velocity.

More recently, Rossi and coworkers [15,16] have provided some new insight with a phenomenological model that also incorporates diffusion into the glassy core. Two important time scales associated with the establishment of a diffusing front and the crossover from Case II to Case I behavior were predicted. In their approach, a

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plasticization-imposed constraint was used for the solvent flux across the glassy-swollen interface. As a result, the front velocity became independent of the solvent concentration immediately behind the advancing front. This approximation is not consistent with the rate-control mechanism in the TW model and is not entirely in accord with the experimental observations [11,12]. Theoretically, lack of dependence of the velocity on solvent concentration decouples the diffusion in the two distinct regions separated by a discontinuity of the solvent concentration. The Fickian precursor is determined only by the characteristic concentration ϕ_c that distinguishes the glassy from the plasticized state, by the diffusion coefficient D_g in the glassy core, and by the constant front velocity v_0 , but not by any property of the plasticized region.

The purpose of this paper is to present a phenomenological model that takes into account the diffusion in both the glassy core and the swollen gel and that includes the rate-controlled motion of the front separating these two regions. In particular, the rate-control mechanism of the TW model is used to construct an expression for the front velocity. This expression leads to a coupling between the diffusion in the two distinct regions. It is then shown that such a coupling can be treated in the adiabatic approximation, by which we mean the separation of the problem into two time scales and the treatment of the rapid motion in a quasistatic framework. The adiabatic criterion is found to be $D_s/D_g \gg 1$, which requires the diffusion coefficient D_s in the swollen state to be much larger than that in the glassy one. With the aid of our model we reach the following conclusions: (1) in the early stage, the boundary separating the glassy core from the swollen gel moves at a nearly constant velocity; (2) as the diffusion proceeds, the discontinuity in solvent concentration across the boundary decreases with time, as does the front velocity; (3) although the front velocity decreases, the shape of the Fickian tail ahead of the discontinuity can be determined, and the effect on the front velocity of a slowly varying Fickian precursor can be explicitly obtained; and (4) the expression for the front velocity in the adiabatic limit appears as a simple generalization of the TW expression for a constant front velocity.

2. Model

It has been experimentally observed that a critical solvent concentration must be reached before a Case II diffusion front is formed [17]. Here we first introduce ϕ_c , the characteristic solvent concentration distinguishing the glassy from the swollen state, as in Refs. [13–16]. This ϕ_c is the threshold concentration for swelling. So, in the swollen region, the solvent concentration ϕ is above ϕ_c , while in the glassy region, $\phi < \phi_c$. We then assume that the diffusion equations in the glassy core and the swollen gel are

respectively given by

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left[D_g(\phi) \frac{\partial \phi}{\partial x} \right], \quad (1a)$$

and

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left[D_s(\phi) \frac{\partial \phi}{\partial x} \right], \quad (1b)$$

where ϕ is the solvent concentration, x the distance from the polymer surface exposed to the solvent, t the time, and $D_g(\phi)$ and $D_s(\phi)$ are the diffusion coefficients in the glassy and the swollen states. For simplicity, we will use ϕ -independent D_g and D_s in this paper.

In common with other phenomenological models [10,13–16], we take as given the existence of a sharp, moving boundary that separates the glassy core from the swollen gel. We define $x = \lambda(t)$ to be the location of this boundary, across which the concentration discontinuously changes from ϕ_c (at $x = \lambda + 0^+$ on the glassy side) to ϕ_b (at $x = \lambda - 0^+$ on the swollen side). Eq. (1a) thus refers to concentrations $\phi \leq \phi_c$, while Eq. (1b) applies to concentrations $\phi \geq \phi_c$. The continuity equation across the boundary then reads

$$D_g \frac{\partial}{\partial x} \phi(\lambda(t) + 0^+, t) - D_s \frac{\partial}{\partial x} \phi(\lambda(t) - 0^+, t) = [\phi_b(t) - \phi_c] \frac{d\lambda(t)}{dt}. \quad (2)$$

To complete the specification of the problem, we require a constitutive equation for the front velocity, $v = d\lambda/dt$. This can be derived by consideration of various physical mechanisms, including the kinetics of swelling [13,14] and the plasticization-imposed constraint on the solvent flux across the boundary [15,16].

According to the TW model, the steady-state front velocity in the Case II regime is determined as follows [7,8]. Ahead of the boundary moving with a constant velocity v_0 , a steady Fickian precursor can be expressed as $\phi_{g0}(x, t) = \phi_c \exp\{-v_0[x - \lambda(t)]/D_g\}$, with $x \geq \lambda$ and $d\lambda/dt = v_0$. The rate of change with time of ϕ at $\phi(\lambda + 0^+, t) = \phi_c$ is thus given by $\partial \phi / \partial t|_{\phi_c} = \phi_c v_0^2 / D_g$. Meanwhile, this $\partial \phi / \partial t|_{\phi_c}$ is also the swelling rate determined by the osmotic pressure that results from the difference between the local concentration ϕ_c and the local equilibrium concentration ϕ_{eq} . This equilibrium concentration is the saturated surface concentration, and is approximately equal to ϕ_b if one assumes that the concentration gradient behind the front is negligible in the steady-state stage. TW then propose that $\partial \phi / \partial t|_{\phi_c} = P(\phi_c, \phi_b) / \eta(\phi_c)$, where $P \approx \Omega^{-1} k_B T \ln(\phi_b / \phi_c)$ is the osmotic pressure at $x = \lambda + 0^+$ (Ω is the partial molecular volume and T the temperature) and η is the viscosity associated with polymer swelling. As a result, the velocity expression is found to be $v_0 = \sqrt{D_g P / \phi_c \eta}$.

In our model, we generalize the TW velocity expression to the case of time-varying v and ϕ_b , and then use it as the

constitutive equation for $v \equiv d\lambda/dt$ in Eq. (2). While the swelling rate is again given by $\partial\phi/\partial t|_{\phi_c} = P(\phi_c, \phi_b)/\eta(\phi_c)$, the Fickian precursor, although still governed by Eq. (1a), is now subject to the boundary condition Eq. (2) with v and ϕ_b varying with time. No longer is either this precursor or $\partial\phi/\partial t|_{\phi_c}$ determined by the instantaneous $v(t)$. Nevertheless, $\partial\phi/\partial t|_{\phi_c}$ remains always related to $\partial\phi/\partial x|_{\phi_c}$ by the relation $\partial\phi/\partial t|_{\phi_c} = -v\partial\phi/\partial x|_{\phi_c}$. As a result, the front velocity can be expressed as

$$v = -\frac{P(\phi_c, \phi_b)/\eta(\phi_c)}{\partial\phi/\partial x|_{\phi_c}}. \quad (3)$$

Because v now depends on ϕ_b , ϕ_c , and $\partial\phi/\partial x|_{\phi_c}$ simultaneously, a coupling is induced between the diffusion processes in the glassy core and the swollen gel. By contrast, we note that a constant v results in a Fickian precursor of the constant shape given above as $\phi_{g0}(x, t)$ [15,16]. This leads to cancellation in Eq. (2), which reduces to $-D_s\partial\phi(\lambda(t) - 0^+, t)/\partial x = v_0\phi_b$, and which serves as the boundary condition for Eq. (1a) only. By avoiding this assumption, we can develop a more realistic model.

It is clear that the flux immediately behind the boundary, $-D_s\partial\phi(\lambda(t) - 0^+, t)/\partial x$, cannot be kept equal to $v_0\phi_{eq}(0)$, a value that is required to maintain $\phi_b = \phi_{eq}(0)$ and $v = v_0$, unless $D_s \rightarrow \infty$. In fact, with a finite D_s and an increasing penetration depth $\int_{t_1}^t v(\tau) d\tau$, the moving boundary has to undergo a continuous drop in ϕ_b to make $\partial\phi(\lambda(t) - 0^+, t)/\partial x$ large enough to sustain the propagation of the front. This has been predicted in the models of AS [13], AJ [14], and Rossi and coworkers [15,16]. Nevertheless, in these three models the Fickian tail is either ignored ($D_g = 0$) [13], or included but not coupled with the front velocity (v depends on ϕ_b and ϕ_c only) [14], or treated as a steady state ($v = \text{const.}$ and $\phi(x > \lambda, t) = \phi_{g0}$) [15,16]. Thus none of these models fully considers the effect of glassy-core diffusion on the front velocity.

3. Adiabatic limit

The initial stage of Case II diffusion involves some complex swelling dynamics at the surface [4,17]. This will not be discussed in the present paper. Instead, we focus on how the diffusion proceeds after the surface concentration $\phi(0, t)$ reaches the equilibrium value $\phi_{eq}(0)$ set by the external solvent activity. We assume that after an appropriate exposure time t_1 , the Case II front is formed and moves in accordance with Eqs. (1)–(3). We now seek some simplification that will allow a rapid solution of these equations.

This simplification is to be found by making use of the fact that the diffusivity in the swollen gel is generally much greater than in the glass, so that $D_s \gg D_g$. When this relation is taken to its extreme, so that $D_s \rightarrow \infty$, we retrieve the models in which the front velocity v is constant in time and the Fickian tail in the glass has the form of $\phi_{g0}(x, t)$. We do

not make this limiting assumption, but assume only that D_s is sufficiently larger than D_g that the rate of change, dv/dt , of the front velocity is small enough that the diffusion tail in the glass has time to conform to the changing velocity, just as if the front velocity were constant. We refer to this as the adiabatic approximation.

We explore the range of validity of this approximation by supposing that the solution is indeed in the form

$$\phi_{ad}(x, t) = \phi_c \exp\left\{-\frac{v(t)}{D_g}\left[x - \int_{t_1}^t v(\tau) d\tau\right]\right\}, \quad (4)$$

with $x \geq \lambda(t) = \int_{t_1}^t v(\tau) d\tau$. Substitution into Eq. (1a) shows that $\phi_{ad}(x, t)$ is a good solution, provided terms of the form

$$\frac{|dv/dt|}{D_g}[x - \lambda(t)] \exp\left\{-\frac{v(t)}{D_g}[x - \lambda(t)]\right\}$$

may be neglected in comparison with

$$\frac{v^2(t)}{D_g} \exp\left\{-\frac{v(t)}{D_g}[x - \lambda(t)]\right\}.$$

Since the exponential contribution in ϕ_{ad} is negligible for $x - \int_{t_1}^t v(\tau) d\tau > l_g \approx D_g/v(t)$ (l_g is the decay length of Fickian tail), the above equation need hold only for $0 \leq x - \int_{t_1}^t v(\tau) d\tau \leq l_g$. The adiabatic condition is thus found to be

$$|dv/dt|/v \ll v^2/D_g, \quad (5)$$

which means that the characteristic time associated with the variation of the front velocity, $v/|dv/dt|$, is much larger than that associated with the establishment of a steady shape. Now let us suppose that the advancing front experiences a reduction of ϕ_b from $\phi_{eq}(0)$ to $\phi_{eq}(0) - \Delta\phi_b$ together with a reduction of v from v_0 to $v_0/2$ in the time duration from $t = t_1$ to $t = t_1 + t_v$. Eq. (2) can be put in the approximate form of $D_s\Delta\phi_b/v_0t_v \approx v_0(\phi_{eq}(0) - \Delta\phi_b)$. Assuming $\phi_{eq}(0)$ and $\Delta\phi_b$ are of the same order of magnitude, we thus obtain the characteristic time $v/|dv/dt| \approx D_s/v_0^2$. Combining this with Eq. (5), we find the adiabatic criterion to be $D_s/D_g \gg 1$, a relation generally satisfied for polymeric materials [18].

With the help of Eq. (4), we can express the front velocity in Eq. (3) as

$$v = \left[\frac{D_g P(\phi_c, \phi_b)}{\phi_c \eta(\phi_c)}\right]^{1/2} \quad (6)$$

by using the relation $-\partial\phi_{ad}/\partial x|_{\phi_c} = v\phi_c/D_g$. The validity of the expression for the steady-state front velocity v_0 in the TW model is thus generalized to the case of retardation of the front motion in the adiabatic limit. As a consequence, the front velocity now depends only on ϕ_b (ϕ_c is treated as a material constant). Meanwhile, Eq. (2) is reduced to $-D_s\partial\phi(\lambda(t) - 0^+, t)/\partial x = v(t)\phi_b$. While the diffusion in the glassy core might seem to be decoupled from that in the swollen gel with the help of the adiabatic approximation, the effect of the Fickian precursor is in fact manifested in the

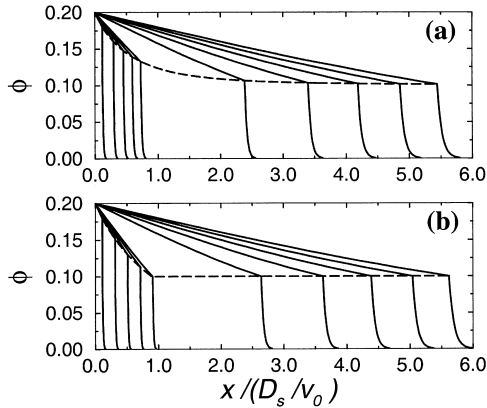


Fig. 1. Solvent concentration ϕ is shown as a function of position by the solid lines for various times. The dashed lines show the dependence on the front position of the concentration ϕ_b of solvent at the swollen side of the front. The concentration profiles are shown at times (given in units of D_s/v_0^2) equal to 0, 0.2, 0.6, 0.8, 4.8, 8.8, 12.8, 16.8, and 20.8. (a) Present model, showing continuous decrease of ϕ_b with time. (b) Model of Refs. [14,15], in which ϕ_b becomes constant after the front has passed the point $x = 0.90D_s/v_0$.

new velocity expression (6). We note that the above adiabatic approximation is also applicable to the AJ model, in which the front velocity is assumed to depend only on a time-varying ϕ_b and constant ϕ_c .

We are now left with a simpler phenomenological model, which consists of the diffusion equation (1a), the boundary condition $-D_s \partial \phi(\lambda(t) - 0^+, t) \partial x = v \phi_b$, and the velocity expression (6), together with the adiabatic Fickian precursor ϕ_{ad} in Eq. (4). It is worth noting that the adiabatic approximation reduces the mathematical complexity to that of AS [13], which simply puts $D_g = 0$ and needs the solution of Eq. (1a) only. Various conclusions obtained in Ref. [13] for the gel are thus applicable to our model. For example, it was shown there that for $t \rightarrow \infty$, $\phi_b - \phi_c$ becomes vanishingly small and the asymptotic behavior of the system is of Case I

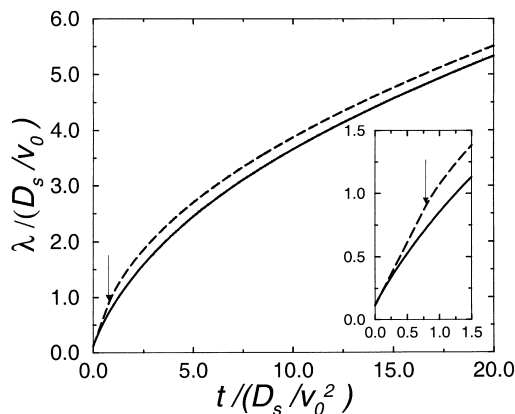


Fig. 2. Front location plotted as a function of time. The solid line is the result from the present model and the dashed line is that from the model of Refs. [14,15]. The inset shows the detail for $t = 0$ to $t \sim D_s/v_0^2$. An arrow marks the point where ϕ_b becomes equal to ϕ_c and after which $d\lambda/dt$ begins to decrease.

type, with the solution for ϕ in the swollen gel approaching [19]

$$\phi(x, t) = \phi_c + [\phi_{eq}(0) - \phi_c] \left[1 - \frac{\text{erf}(x/2\sqrt{D_s t})}{\text{erf}(m)} \right]. \quad (7)$$

Here the vanishing discontinuity is located at $\lambda(t) = 2m\sqrt{D_s t}$, where m is the solution of $\sqrt{\pi} m e^{m^2} \text{erf}(m) = [\phi_{eq}(0) - \phi_c]/\phi_c$. The validity of solution (7) is independent of the functional dependence of v in Eq. (6) on ϕ_b as long as $v \rightarrow 0$ for $\phi_b \rightarrow \phi_c$. It is readily seen that for the asymptotic front velocity $d\lambda/dt = m\sqrt{D_s t}$, the adiabatic condition (5) becomes $D_s/D_g \gg 1$ if $[\phi_{eq}(0) - \phi_c] \sim \phi_c$ and so $m \sim 1$. This is consistent with the adiabatic criterion derived for the early stage of diffusion. However, the validity of the model itself becomes suspect in this limit, as the distinction between gel and glass is lost if $\phi_b - \phi_c \ll \phi_b$.

4. Discussion and numerical results

A distinguishable Case II front motion requires that the induction time t_i for establishing the front be much smaller than the time scale t_v associated with the slowing-down of front propagation. Denoting the initial constant velocity by v_0 , we have $t_i \sim D_g/v_0^2$ since v_0^2 is given by $D_g \partial \phi / \partial t|_{\phi_c} / \phi_c$ with $\partial \phi / \partial t|_{\phi_c} = P(\phi_c, \phi_{eq}(0)) / \eta(\phi_c)$ being the characteristic polymer-swelling rate at the surface [3,4]. The relation $t_i \sim D_g/v_0^2$ can also be deduced from the constant-flux boundary condition at the solvent-polymer interface $x = 0$ [16]. It is now clear that $t_i \ll t_v \approx D_s/v_0^2$ requires the same condition $D_s \gg D_g$ as the adiabatic approximation.

The velocity expression in the present phenomenological description is based on the TW model but involves a few simplifications. No solvent concentration discontinuity is predicted in the TW model, although a sharp decrease in ϕ does exist if there is a strong concentration dependence of η . By treating the concentration gradient at the front as infinite, the local equilibrium concentration ϕ_{eq} at $x = \lambda + 0^+$ is then determined to be $\phi(\lambda - 0^+, t) = \phi_b$ for the osmotic pressure $P(\phi_c, \phi_{eq})$. By further assuming that the effect of osmotic pressure on the diffusion in the glassy core is insignificant compared to that of the concentration gradient [18], we found the Fickian precursor to be governed by Eq. (1a). The velocity expression here is thus a result of equating $\partial \phi / \partial t|_{\phi_c} = P(\phi_c, \phi_b) / \eta(\phi_c)$ from polymer swelling kinetics to $\phi_c v^2 / D_g$ from solvent diffusion. The velocity dependence on $\partial \phi / \partial t|_{\phi_c}$, D_g , and $\eta(\phi_c)$ so obtained is regarded as the most important prediction of the TW model and has been experimentally verified in the steady-state stage [7–9].

To illustrate the effects of including the concepts embodied in TW in the models of AS, AJ, and Rossi and coworkers, we have performed some numerical calculations. In one set we used our model, in which the front velocity varies with time, while in the other set the front velocity was held constant following the prescription of Rossi and coworkers. We choose v_0 , the initial velocity of

penetration, as the velocity unit and D_s/v_0 as the length unit. Accordingly, the time unit becomes D_s/v_0^2 . For the purpose of comparison, we use the same initial concentration profile $\phi(x, t = 0)$ and the same initial front velocity v_0 in the two model calculations. We require $\phi(x, t = 0)$ to have a very short penetration depth $\lambda_0 (\lambda_0 \ll D_s/v_0)$, to exhibit a Fickian tail of the form ϕ_{g0} , and to satisfy the boundary condition Eq. (2). The numerical values of the parameters used were $\phi_{eq}(0) = 0.2$, $\phi_c = 0.1$, and $D_g/D_s = 0.01$. Ideally, the starting point of the calculation should have λ_0 be vanishingly small. For practical reasons, it was necessary to start with a finite value of λ_0 , and this was chosen to be $\lambda_0 = 0.1D_s/v_0$. The results were found to be insensitive to this initial choice. We also verified that different choices of the initial shape of the Fickian tail result in nearly the same evolution of $\phi(x, t)$ from $t \sim t_1$ as long as the initial tail width is of the order of magnitude of D_g/v_0 . Figs. 1 and 2 show a comparison of the results of the present model with those of the model used by Rossi and coworkers. Fig. 1 depicts a set of $\phi(x, t)$ curves for several selected values of t . The dependence of front concentration ϕ_b on front location λ is shown as a dashed line. In Fig. 1(a) (our model) the front concentration ϕ_b approaches $\phi_c = 0.1$ in an asymptotic way while in Fig. 1(b) (Rossi's model) ϕ_b becomes equal to ϕ_c at $\lambda = 0.8983D_s/v_0$ and remains constant thereafter. It is seen that compared with the model of Rossi and coworkers, our model predicts a smoother decrease of the front concentration ϕ_b with increasing λ , and consequently a more gradual slowing of the advancing front. This is directly seen in Fig. 2 which depicts the front location as a function of time t . Although both models produce the typical Case I behavior for $t \gg D_s/v_0^2$, a difference is noted for the initial Case II stage and the later crossover to Case I behavior. While the model of Rossi and coworkers predicts a constant front velocity $d\lambda/dt = v_0$ for $0 \leq t \leq 0.7872D_s/v_0^2$ and then a decreasing $d\lambda/dt$ for $t > 0.7872D_s/v_0^2$, our model predicts a continuous slowing of the advancing front from $t = 0$, and thus a smoother crossover from Case II to Case I behavior.

To conclude, we note that the approach presented here may readily be generalized. Although we have made use of the TW model to determine the front velocity, our phenomenological description can just as well be applied in conjunction with any other microscopic model that takes into account the coupling between the diffusion processes in the swollen gel and the glassy core. The adiabatic treatment employed here should then also be applicable.

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