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Macroscopic description of the kinetics of swelling for a cross-linked elastomer or a gel

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We consider the diffusion of a solvent in a cross-linked polymer network and the corresponding swelling and deswelling. Recently, we obtained equations describing the time evolution of the concentration profile of a polymer (or solvent) in one dimension and three dimensions with radial symmetry. In this paper we discuss in detail the properties of these equations and the experimental predictions which can be inferred from them. In particular, we find that a number of features commonly regarded as a signature for anomalous or "non-Fickian" behavior, can in fact be found as a consequence of Fick's law once the presence of moving boundaries is properly taken into account. We briefly discuss the problems associated in extending our treatment to a general two- or three-dimensional geometry and its possible use in interpreting the surface morphologies and fracture behavior observed in the swelling process.

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I. INTRODUCTION

Swelling of a cross-linked elastomer or a gel immersed in a good solvent is a common phenomenon. Both the equilibrium properties of the swollen specimen and the kinetics of the swelling process have been studied since the early days of polymer science [1–5]. Flory and Rehner first obtained predictions for the equilibrium swelling concentration by minimizing an appropriate free-energy function. Their method amounts to balancing the (local) osmotic pressure with the elastic reaction exerted by the swollen network: the method has been generalized to deal with a number of situations involving constrained specimens [6–8]. The microscopic parameters controlling the equilibrium swelling concentration are the degree of cross linking and the quality of the solvent: the latter can be a function of temperature, pressure, and other physical parameters. Several experiments in the past decade have been aimed at determining the response of the equilibrium concentration to changes in these parameters [9–13].

Experiments dealing with the kinetics of the swelling process have uncovered a varied phenomenology, whose interpretation presents challenging theoretical problems. In a number of instances, during the swelling process, surface patterns have been observed to form on an initially smooth rubber or gel specimen [14–16]. Often these patterns disappear before the final equilibrium state is reached. This behavior is reminiscent of surface morphologies observed upon swelling in photographic emulsions [17,18]. While pattern formation seems to be widespread and has been seen both in loose gels and in dense rubbers, it is by no means a general phenomenon: often no visible patterns are observed and the surface of the swelling specimen appear to remain smooth throughout the swelling process. A further finding of obvious practical importance has been the observation that in some instances mechanical deformations induced in the network in the course of swelling (or deswelling) cause irreversible modifications, i.e., microscopic and large scale fracture, in the elastomeric material. At this stage there appears to be no simple empirical way to classify the conditions leading to these effects, so that the need arises for a theoretical framework able to describe the swelling (and deswelling) kinetics. A correct description of the kinetics is also needed in order to have consistent experimental procedures to measure the phenomenological parameters (diffusion coefficients) controlling swelling.

Our ultimate goal is a macroscopic theory of the kinetics of swelling able to account for both the formation of the observed surface patterns and the onset of fracture in terms of a few phenomenological parameters, e.g., diffusion coefficient, elastic constants of the network, and final equilibrium concentration of the polymer component. A stability analysis of the differential equations describing swelling within such a theory should provide information as to the range of values of these parameters for which surface patterns develop. Furthermore, a comparison of the calculated maximum stress arising in the swelling material with the conditions for chain scission within the network [8] may elucidate the circumstances leading to fracture. Recent macroscopic theories of dendritic growth [19] have been successful in carrying out a similar program to account for interface evolution and sidebranching for an advancing solidification front.

In a recent Rapid Communication [20] we presented a treatment which, under what we regard as a set of reasonable assumptions, accounts for diffusion of solvent in a swelling polymer network, e.g., for displacement of the network as solvent moves in (or out). We were able to write closed-form equations controlling the swelling process and we showed how to obtain numerical solutions for these equations. Our treatment is limited to situations where the swelling process can be described in terms of a single space coordinate: it should be regarded as a step towards the theoretical program outlined above. In this paper we present a number of further results relating to the description put forward in Ref. [20].

This paper is organized as follows. In the next section the closed-form equations of Ref. [20] are rederived and discussed. In Sec. III we discuss numerical solutions to these equations for both swelling and deswelling. We examine the role played by a concentration dependence of the diffusion coefficient. We also show that features of the solvent uptake curves which are usually described as "non-Fickian" (e.g., "sigmoidal" uptake) can in fact be found as a consequence of Fick's law when the movement of the network as solvent diffuses in is properly taken into account. In the last section we give a brief discussion of the problems encountered when one attempts to modify our procedure to deal with situations where two or more independent space coordinates are needed in order to describe the swelling process; we also address the issue of dealing with the kinetics of constrained swelling.

II. EQUATIONS DESCRIBING THE SWELLING PROCESS

The method given in Ref. [20] deals with the swelling of a cross-linked polymer network using the same physical assumptions on which the ordinary diffusion equation is based. These are (i) the validity of Fick's phenomenological law of diffusion throughout the region of space where polymer is present and (ii) the assumption that, at the boundary of the region occupied by polymer, equilibrium is reached as soon as the polymer network is put in contact with the solvent. Polymeric material is displaced as solvent diffuses in the network: once the above physical assumptions have been agreed upon, the problem is reduced to finding a way to describe consistently such displacement and to deal with boundary conditions which hold at the moving boundary of the region occupied by polymer. Since the overall change in volume upon mixing for the polymer plus solvent system is ordinarily very small [21] we neglect this effect altogether. Indeed, here we shall deal with a model situation where the density of the polymer ρ_R and the density of the solvent ρ_S are fixed and are both equal to one, so that concentrations and volume fractions coincide. Denoting with $\phi_S(x,t)$ and $\phi_R(x,t)$ the solvent and polymer concentration, respectively, the relation

$$\phi_S(x,t)+\phi_R(x,t)=1 \tag{1}$$

has to be satisfied everywhere throughout the swelling process.

Consider the one-dimensional (1D) problem. Let A and B be two markers attached to the network, located respectively at $x=x_0$ and $x=x_0+\Delta x_0$ at time $t=0$, i.e., before the network begins to swell. At a later time t after the swelling process has begun the markers A and B will have moved to new positions $x=x_R(x_0,t)$ and $x=x_R(x_0,t)+\Delta x_R(x_0,t)$, respectively. The increase in the amount of solvent between A and B in the time between t and $t+\Delta t$ is

$$\Delta\phi_S(x_R,t)\Delta x_R=\Delta t(\text{net flux through } A - \text{net flux through } B)\ . \tag{2}$$

In order to satisfy conservation of mass for the polymer and solvent component the change in distance between the markers and the solvent and polymer concentrations have to be related by

$$\phi_R\Delta x_R=\phi_R^{\text{new}}\Delta x_R'\ , \tag{3}$$

$$(\phi_S+\Delta\phi_S)\Delta x_R=\phi_S^{\text{new}}\Delta x_R'\ . \tag{4}$$

Here $\Delta x_R'$ is the distance between A and B at time $t+\Delta t$, while ϕ_R (ϕ_S) and ϕ_R^{new} (ϕ_S^{new}) are respectively the polymer (solvent) concentrations between A and B at times t and $t+\Delta t$.

Using (1) we obtain

$$\Delta x_R'=\Delta x_R(1+\Delta\phi_S) \tag{5}$$

and ignoring higher powers of $\Delta\phi_S$, we find

$$\phi_S^{\text{new}}=\phi_S+\phi_R\Delta\phi_S\ . \tag{6}$$

Then (2) can be rewritten in the form

$$\frac{\phi_S^{\text{net}}-\phi_S}{\Delta t}=-\frac{\phi_R}{\Delta x_R}(\text{net flux through } B - \text{net flux through } A)\ , \tag{7}$$

so that in the continuum limit

$$\frac{\partial\phi_S(x_R,t)}{\partial t}=-\phi_R(x_R,t)\frac{\partial\mathcal{J}}{\partial x_R}\ , \tag{8}$$

which is the continuity equation written in the frame of the moving network ($\mathcal{J}$ denotes the flux).

Next we use Fick's law and assume that the flux appearing in Eq. (8) is proportional to the local gradient of the concentration at time t. The proportionality constant (diffusion coefficient) is in general a function of concentration. Therefore

$$\frac{\partial\phi_S(x_R,t)}{\partial t}=\phi_R(x_R,t)\frac{\partial}{\partial x_R}\times\left[D(\phi_S(x_R,t))\frac{\partial\phi_S(x_R,t)}{\partial x_R}\right]\ . \tag{9}$$

It is easy to see that the usual mutual diffusion coefficient D_M [22] is related to the diffusion coefficient D appearing in Eq. (9) by [23]

$$D(\phi_S)=\frac{D_M(\phi_S)}{\phi_R}\ . \tag{10}$$

In order to deal with Eq. (9), we have found it convenient to employ a coordinate transformation from the "running" coordinate x_R to the Lagrangian coordinate x_0 [24]: suppose that initially ($t=0$) our one-dimensional network is located between $-a_0\le x\le a_0$. At a later time t a volume element Δx_0 initially located at $x=x_0$ will have moved to a new position $x=x_R(x_0,t)$ and will occupy a volume $\Delta x_R(x_0,t)$ such that

$$\phi_R(x_0,t)\Delta x_R(x_0,t)=\Delta x_0\ . \tag{11}$$

Therefore x_R and x_0 are related by

$$x_R(x_0,t)=\int_0^{x_0}\frac{dx_0}{\phi_R(x_0,t)}\ , \tag{12}$$

and using (1) we can rewrite (9) as

$$\frac{\partial \phi_R(x_0,t)}{\partial t} = \phi_R^3(x_0,t) D(\phi_R) \frac{\partial^2 \phi_R(x_0,t)}{\partial x_0^2} + \phi_R^2(x_0,t) \left[\frac{\partial \phi_R(x_0,t)}{\partial x_0} \right]^2 \times \left[\frac{\partial}{\partial \phi_R} (\phi_R D(\phi_R)) \right] . \tag{13}$$

This is the closed-form equation [25] controlling the swelling process in one dimension: it describes the time evolution of the polymer concentration $\phi_R(x_0,t)$ in the volume element which was initially located at $x=x_0$. Equation (13) is written in terms of the Lagrangian coordinate x_0, so that the spatial domain over which it has to be solved does not change with time.

The value of the network equilibrium swelling concentration $\Phi_R^{(\mathrm{eq})}$ enters our treatment through the boundary conditions. For an initially unswollen network located between $-a_0$ and a_0, the appropriate boundary conditions for Eq. (13) are $\phi_R(x_0,t)=1$ at $t=0$ for $|x_0|<a_0$ and $\phi_R(x_0,t)=\Phi_R^{(\mathrm{eq})}$ at $x_0=\pm a_0$ for all t. Equation (13) subject to these boundary conditions describes a process in which a fraction $(1-\Phi_R^{(\mathrm{eq})})$ of the polymeric material found initially between $-a_0$ and a_0 is depleted (changed into solvent) with time, until as $t \to \infty$, $\phi_R(x_0,t) \to \Phi_R^{(\mathrm{eq})}$ throughout the domain $|x_0|<a_0$.

An example of our procedure to obtain the time evolution of the concentration profiles is shown in Fig. 1. In this case a swollen network initially found in the domain $|x|<a$ is deswelling from an initial concentration $\Phi_R^{(i)}=0.4$ to a final concentration $\Phi_R^{(\mathrm{eq})}=0.8$. We solve Eq. (13) in the domain $|x_0|<a_0$, where $a_0=a\Phi_R^{(i)}$, subject to the boundary conditions $\phi_R(x_0,t)=\Phi_R^{(i)}$ at $t=0$ for $|x_0|<a_0$ and $\phi_R(x_0,t)=\Phi_R^{(\mathrm{eq})}$ at $x_0=\pm a_0$. The solution can be found numerically using an implicit finite differences algorithm [26]. Five snapshots of $\phi_R(x_0,t)$ at different times are shown in the left portion of Fig. 1. Once the solution $\phi_R(x_0,t)$ has been found, one can obtain the actual (laboratory-frame) polymer concentration profile by transforming back to the $x=x_R(x_0,t)$ coordinate appropriate for time t using Eq. (12). The right portion of Fig. 1 shows the result of this transformation for the solutions plotted on the left. Note that mass conservation for the polymer implies that the area under the curves on the right does not change with time.

From an experimental viewpoint the easiest quantity to measure is solvent uptake, namely the difference $M(t)$ [27] between the volume occupied by the network at time t and its initial volume. We will discuss our numerical results for the solvent uptake in the next section. Here we note that Eqs. (12) and (13) imply that $M(t)$ scales as $t^{1/2}$ at short times. Indeed consider the case of a semi-infinite network which is initially unswollen and located on the left of the origin. Equation (13) can be rewritten as an ordinary differential equation with respect to the variable $\eta = x_0/(2t^{1/2})$ (Boltzmann transformation) [22], so that the solutions $\phi_R(x_0,t)$ of the equation depend on x_0 and t only through η. Therefore using (12) we find for the solvent uptake

$$M(t)=x_R(x_0=0,t)=\int_{-\infty}^{0} dx_0 \frac{\phi_S(x_0,t)}{\phi_R(x_0,t)} = 2t^{1/2}\int_{-\infty}^{0} d\eta\, f(\eta) \propto t^{1/2} , \tag{14}$$

where $f(\eta)$ is a function of η only. At short times the concentration profile ϕ_R at either one of the two edges of a finite specimen is the same as the profile at the edge of a semi-infinite network; therefore $M(t) \propto t^{1/2}$. The same argument can be given for different boundary conditions.

Experiments have been devised [28] where swelling is constrained to one dimension. However, it is clear that in order to interpret these experiments correctly the effect of the constraint has to be accounted for; the equation given above does not necessarily provide a good model for such situations. Indeed the simplest experiments to perform and interpret involve unconstrained swelling of a three-dimensional specimen. The problems encountered when one tries to extend the treatment given above to an arbitrary 3D geometry are discussed in Sec. IV. However, in the special case of a three-dimensional

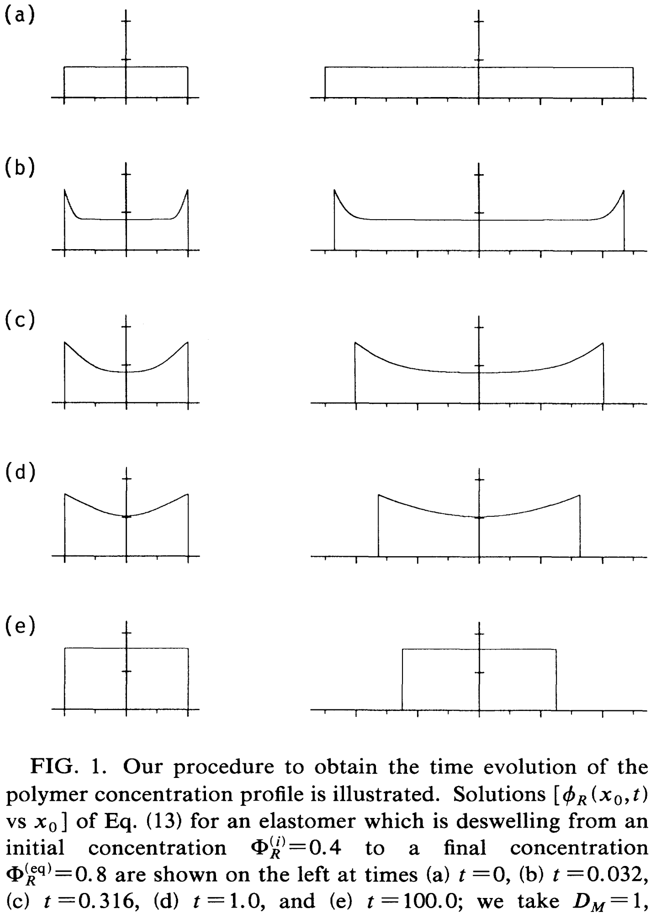

FIG. 1. Our procedure to obtain the time evolution of the polymer concentration profile is illustrated. Solutions $[\phi_R(x_0,t)$ vs $x_0]$ of Eq. (13) for an elastomer which is deswelling from an initial concentration $\Phi_R^{(i)}=0.4$ to a final concentration $\Phi_R^{(\mathrm{eq})}=0.8$ are shown on the left at times (a) $t=0$, (b) $t=0.032$, (c) $t=0.316$, (d) $t=1.0$, and (e) $t=100.0$; we take $D_M=1$, $a_0=1$. The corresponding polymer concentration profiles, i.e., $\phi_R(x,t)$ vs x, are shown on the right; they are found using Eq. (12) to transform back to $x=x_R(x_0,t)$.

spherically symmetric geometry the argument leading to Eq. (9) can be repeated step by step and it leads to the equation

$$\frac{\partial\phi_S(r_R,t)}{\partial t}=\frac{\phi_R(r_R,t)}{r_R^2}\frac{\partial}{\partial r_R}\left[D(\phi_S)r_R^2\frac{\partial\phi_S(r_R,t)}{\partial r_R}\right]. \tag{15}$$

Again it is convenient to perform a coordinate transformation from the "running" coordinate r_R to the Lagrangian coordinate r_0. It is easy to see that at a time $t>0$ the radial position $r_R(r_0,t)$ of an infinitesimal shell of polymeric material which initially was located at $r=r_0$ is

$$r_R^3(r_0,t)=3\int_0^{r_0}\frac{r_0^2dr_0}{\phi_R(r_0,t)}. \tag{16}$$

This equation is the analog of Eq. (12): the difference between the three-dimensional and the one-dimensional case is that the relation between dr_R and dr_0 involves r_R explicitly, i.e., it is a nonlocal function of $\phi_R(r_0,t)$. As a result the differential equation for $\phi_R(r_0,t)$ is also nonlocal [29]: using (15) and (16) we obtain

$$\begin{aligned}\frac{\partial\phi_R}{\partial t}=\frac{2r_R\phi_R^2D(\phi_R)}{r_0^2}\left[2-\frac{r_R^3\phi_R}{r_0^3}\right]\left[\frac{\partial\phi_R}{\partial r_0}\right]&\\+\frac{r_R^4\phi_R^2}{r_0^4}\left[\frac{\partial(\phi_RD(\phi_R))}{\partial\phi_R}\left[\frac{\partial\phi_R}{\partial r_0}\right]^2&\\+\phi_RD(\phi_R)\frac{\partial^2\phi_R}{\partial r_0^2}\right].&\end{aligned} \tag{17}$$

This equation can be dealt with using the same numerical methods employed to solve Eq. (13). The computational procedure is somewhat more involved, however, since powers of r_R appear explicitly in Eq. (17) so that an additional set of quadratures is required at each time step. Figures 2 and 3 show results obtained from this procedure for the concentration profiles of polymeric material in the case of a sphere which is swelling to eight times its original size (so that its radius is doubled): we have used $D_M=1$ in Fig. 2 and $D_M=D_0e^{\alpha\phi_S}$ with $D_0=1$ and $\alpha=6$ in Fig. 3 [30,31].

We conclude this section by commenting briefly on the two assumptions stated at the beginning, which are at the basis of our treatment. It has been shown above that, as long as the swelling process can be described in terms of a single space coordinate, these assumptions allow a simple consistent description of the swelling kinetics in terms of a minimum number of phenomenological parameters, namely the equilibrium polymer concentration $\Phi_R^{(eq)}$ and the constants entering the diffusion coefficient.

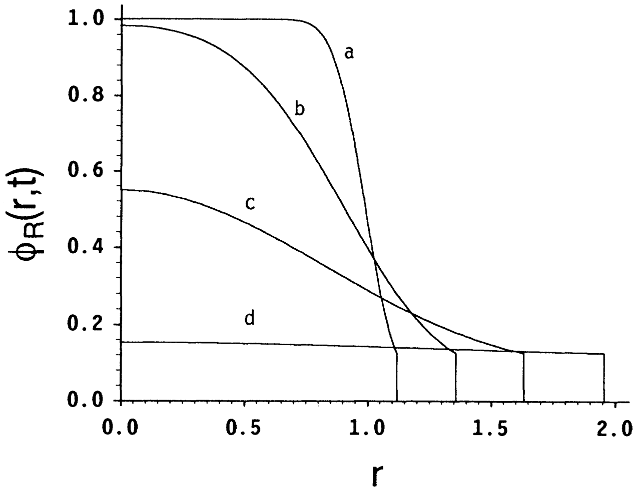

FIG. 2. Polymer concentration profiles $\phi_R(r,t)$ vs r for a sphere (of initial radius $r=1$) swelling to a final concentration $\Phi_R^{(eq)}=0.125$ (i.e., to a final radius $r=2$) are shown at times (a) $t=0.005$, (b) $t=0.05$, (c) $t=0.2$, and (d) $t=1.0$. We have taken $D_M=1$.

In kinetic models where mixing of two incompressible fluids of small molecular weight occurs as a result of local random motions, Fick's law can be seen to arise from very general probabilistic considerations. In polymeric systems deviations of experimental results from naive predictions based on Fick's law are usually found when mixing between the polymer and solvent component is accompanied by physical phenomena involving some change in the state of the polymer, the standard example being plasticization (i.e., lowering of the glass transition temperature) in the case of polymer glasses [32,33]. Deviations from ordinary Fick's behavior may also occur in the dissolution of a polymer melt or of a semidilute solution where the disappearance of the transient network is controlled by the reptation disengagement time [34]. For networks which are not very tightly cross linked and rubbers well above the glass transition temperature, there seems to be no obvious effect of this type; under these

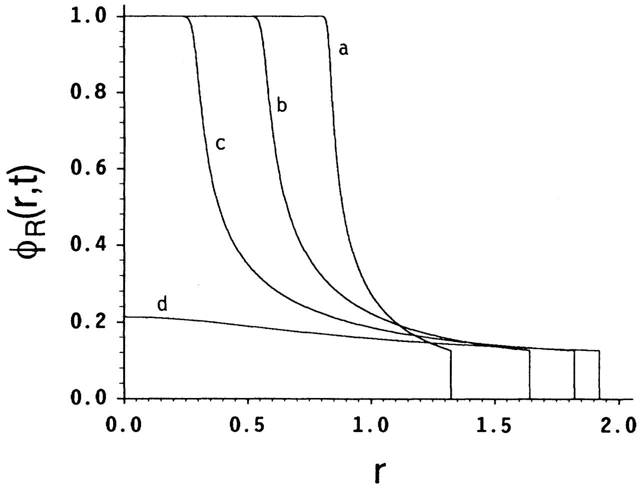

FIG. 3. Polymer concentration profiles $\phi_R(r,t)$ vs r for a sphere (of initial radius $r=1$) swelling to a final concentration $\Phi_R^{(eq)}=0.125$ (i.e., to a final radius $r=2$) are shown at times (a) $t=0.0005$, (b) $t=0.0025$, (c) $t=0.005$, and (d) $t=0.0075$; we have taken $D_M=D_0e^{\alpha\phi_S}$ with $D_0=1$ and $\alpha=6$.

conditions, corrections to Fick's expression for the flux may arise only due to elastic forces between portions of the network which are swollen to a different extent. In loose networks, it seems reasonable to expect these corrections to be small: our treatment corresponds to the limit where such corrections vanish altogether.

Our second assumption on the instantaneous onset of equilibrium at the boundary of the region where polymer is present is the simplest within a continuum description. In practice, a finite time is needed for a small volume element of network at the surface of the polymer specimen to respond to a change in the activity of the solvent. In fact, it can be argued that equilibrium is not reached at the surface until the elastic constraints exerted by the unswollen portions of network located under it become completely negligible. Since modeling these effects would introduce additional phenomenological parameters, it seems reasonable to adopt the second assumption as a working hypothesis. Indeed, the ultimate test for the validity of both our assumptions resides in how well the results of our treatment can match experimental data. We shall see in the next section that, since our treatment sets rather severe requirements on the form of the swelling and deswelling curves for the solvent uptake, a first experimental test of our assumptions may be obtained from simple sorption experiments [31].

III. RESULTS OF THE METHOD

In general, in a binary system made up of cross-linked polymer chains and solvent it seems reasonable to expect that the mutual diffusion coefficient will increase monotonically as a function of solvent concentration [35]. This is because as the concentration of solvent is increased it becomes possible for more and more local movements (of solvent molecules or of polymer chain segments) to take place without causing rearrangement of (heavily constrained) chain segments but rather by displacing small mobile solvent molecules.

In physical situations which can be accounted for by ordinary diffusion within fixed boundaries (for example, vapor diffusing into a rigid porous material), if the diffusion coefficient is independent of concentration, sorption and desorption take place at the same rate, i.e., the plots of weight uptake and weight loss versus time coincide. On the other hand, a diffusion coefficient increasing monotonically with penetrant concentration implies that sorption occurs faster than desorption [36]. This is because the boundary concentration is larger in the case of sorption and this in turn leads to a larger diffusion coefficient and a larger flux.

Similar considerations apply to our equations. However, in addition to any concentration dependence of D_M, there are now effects from the nonlinear terms [see Eqs. (13) and (17)] which account for movement of the boundaries. Moreover, in three dimensions, the fact that the area of the polymer occupied region is changing plays a role in determining the rate of sorption (or desorption). For example, the surface of a sphere which is swelling to a final equilibrium concentration $\Phi_R^{(\mathrm{eq})}$ will increase in the process by a factor $(\Phi_R^{(\mathrm{eq})})^{-2/3}$; therefore, even if the flux (referred to unit area) of solvent through the surface is largest at the initial stages of swelling, the surface of the final swollen sphere may have become large enough to offset any reduction in flux due to nonlinear effects when deswelling begins.

The net result of all these factors is that, when the mutual diffusion coefficient D_M is constant, our equations predict that deswelling will invariably occur at a rate faster than swelling, whereas for a concentration dependent D_M the result is determined by the competition between the effects described above. Figures 4 and 5 illustrate how, when the final solvent concentration is small ($\Phi_R^{(\mathrm{eq})} \approx 1$), the dependence of D_M on concentration can reverse the relative rate of swelling versus deswelling. On the other hand, if the final solvent concentration is large, our equations predict that initially deswelling will occur faster than swelling even if the diffusion coefficient increases substantially with solvent concentration [37]. This behavior is illustrated in Figs. 6 and 7 for the case of a spherical geometry; the same qualitative behavior is found for the solutions of the one-dimensional problem.

In the case of ordinary (fixed boundaries) diffusion, the plot of weight gain (or loss) versus $t^{1/2}$ starts as a straight line at $t \to 0$ and eventually flattens to the equilibrium value. The rate of increase in weight gain (or loss) (e.g., the first derivative with respect to $t^{1/2}$) is largest at $t = 0$. Since this result holds independently of the functional form of the diffusion coefficient, such a weight uptake curve has been generally regarded as a signature of Fickian diffusion. On the other hand weight uptake curves displaying an inflexion point with respect to $t^{1/2}$ (sigmoidal uptake) have been interpreted as evidence for anomalous diffusion and non-Fickian behavior [38].

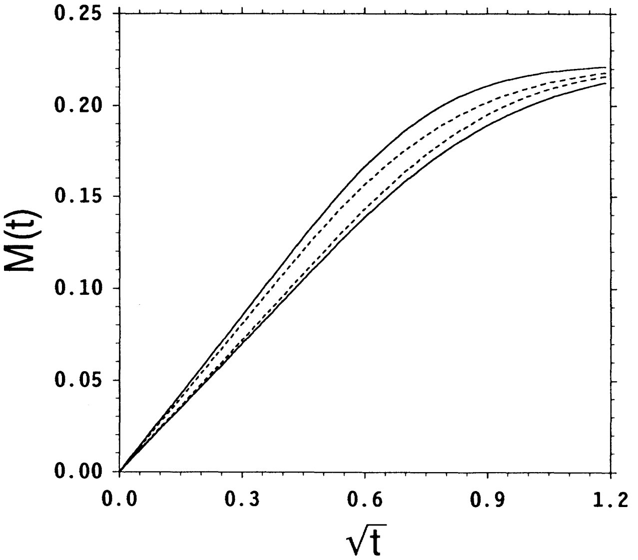

FIG. 4. Solvent uptake (solid curves) or loss (broken curves) vs $t^{1/2}$. The curves refer to the one-dimensional case for a final concentration $\Phi_R^{(\mathrm{eq})} = 0.9$. The two lower curves were obtained taking $D_M = 1$, while for the two upper curves we used $D_M = D_0 e^{\alpha\phi_S}$ with $D_0 = 1$ and $\alpha = 6$.

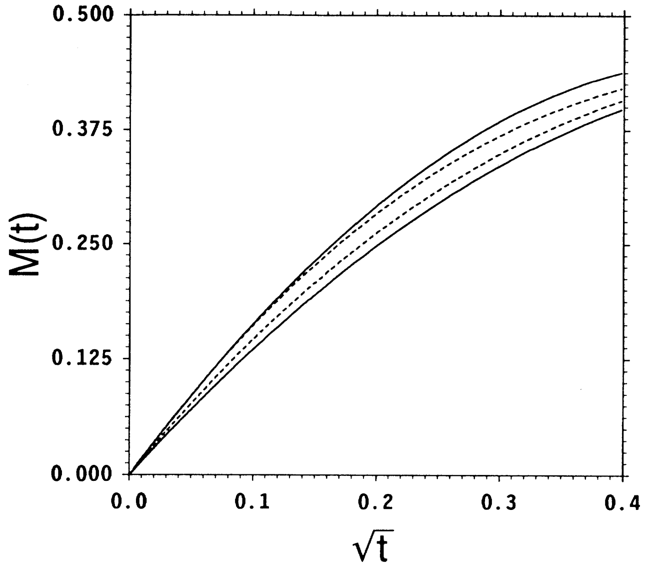

FIG. 5. Solvent uptake (solid curves) or loss (broken curves) vs $t^{1/2}$ for a sphere (of initial radius $r=1$) swelling to a final concentration $\Phi_R^{(\mathrm{eq})}=0.9$. The two lower curves refer to $D_M=1$, while the two upper curves refer to $D_M=D_0e^{\alpha\phi_S}$ with $D_0=1$ and $\alpha=6$.

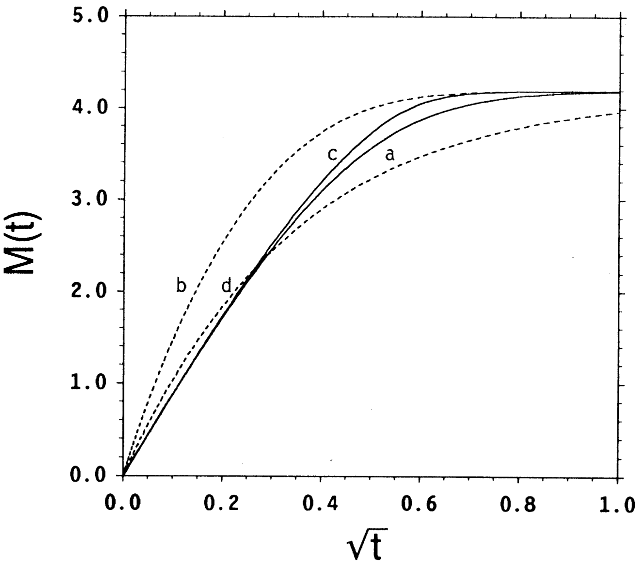

FIG. 7. Solvent uptake (solid curves) or loss (broken curves) vs $t^{1/2}$ for a sphere (of initial radius $r=1$) swelling to a final concentration $\Phi_R^{(\mathrm{eq})}=0.5$. Curves *a* and *b* are for $D_M=1$. Curves *c* and *d* are for $D_M=D_0e^{\alpha\phi_S}$ with $D_0=0.327$ and $\alpha=6$. For $\alpha=6$, D_0 was chosen so as to match the initial uptake in curve *a* (see text).

However, as the solid curves of Fig. 6 show, sigmoidal uptake is displayed by our results obtained from Eq. (17) in the case of high final solvent concentration [39], in spite of the fact that we have used Fick's law as one of the central ingredients of our treatment. While we are not suggesting that this is always the mechanism responsible for sigmoidal behavior, our results indicate that it is the nonlinearity associated to the presence of moving boundaries, rather than some violation of Fick's law, which is at the origin of sigmoidal uptake curves for swelling networks.

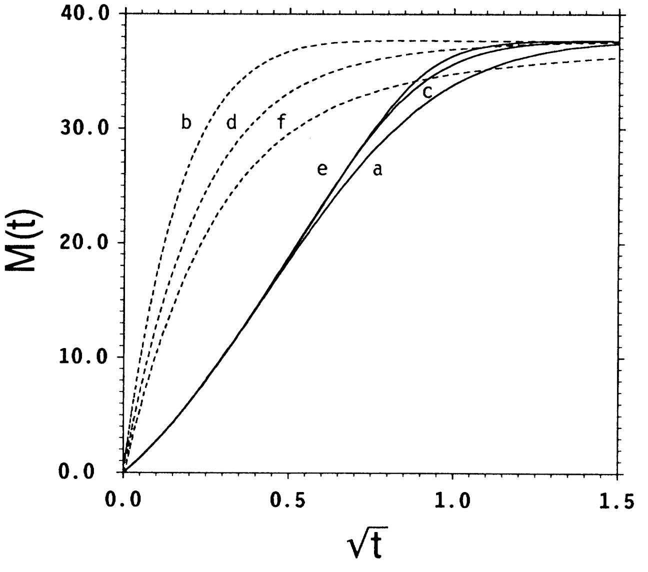

FIG. 6. Solvent uptake (solid curves) or loss (broken curves) vs $t^{1/2}$ for a sphere (of initial radius $r=1$) swelling to a final concentration $\Phi_R^{(\mathrm{eq})}=0.1$. Curves *a* and *b* are for $D_M=1$. Curves *c* and *d* are for $D_M=D_0e^{\alpha\phi_S}$ with $D_0=0.328$ and $\alpha=3$. Curves *e* and *f* are for $D_M=D_0e^{\alpha\phi_S}$ with $D_0=0.101$ and $\alpha=6$. For $\alpha=3$ and 6, D_0 was chosen so as to match the initial uptake in curve *a* (see text).

A second feature usually considered as an indication of non-Fickian behavior is the observation of a desorption curve intersecting the sorption curve at some finite time [38]. Again this feature is displayed by our results for certain ranges of the final equilibrium concentration $\Phi_R^{(\mathrm{eq})}$ and of the concentration dependence in the diffusion coefficient. Examples of this behavior are shown in curves *e* and *f* of Fig. 6 and in curves *c* and *d* of Fig. 7.

It might also be worth noting at this point that, in spite of our use of Fick's law, a sizeable concentration dependence in the diffusion coefficient leads to concentration profiles exhibiting rather sharp drops in concentration (see Fig. 3). Although clearly of a different origin, this behavior is somewhat reminiscent of the sharp diffusion fronts observed in polymeric glasses when so-called "case II" diffusion takes place [32,33].

As we have remarked at the end of the preceding section the ultimate test for the physical assumptions which are at the basis of our treatment consists in examining its agreement with experiments. Probably, the simplest experimental test consists in a comparison between sorption (or desorption) curves obtained for spherical specimens (in the absence of pattern formation) and our predictions for solvent uptake (or loss). It should be clear from the results shown in Fig. 6 that, once the final equilibrium concentration $\Phi_R^{(\mathrm{eq})}$ has been fixed, our predictions are quite insensitive to the form of the diffusion coefficient: for example, although in curve *a* of Fig. 6 the diffusion coefficient has been taken to be a constant and in curve *e* of Fig. 6 it changes by more than two orders of magnitude over the relevant concentration range, the two curves nearly coincide in a large portion of the $t^{1/2}$ domain (a similar behavior is displayed by curves *a* and *c* of Fig. 7). As a result, it is essentially impossible to fit an experimental sorption curve by fine tuning the form of the diffusion coefficient, unless it falls within the narrow range predicted by our solutions; therefore, the comparison of sorption data with our results should provide a quantitative test for our assumptions [31].

It should be noted in this respect that there has been some confusion in the literature [40] as to what constitutes a satisfactory test for a description of the kinetics of swelling. In particular, we note that neither the observation that swelling time is proportional to the square of the linear dimensions of the specimen nor the fact that the approach to equilibrium is exponential can be viewed as such a test. The first result is true for any governing equations which involve first derivatives with respect to time and second derivatives (or square gradients) with respect to position. The second is a very general result altogether independent of the details of the theory. Both these requirements are trivially satisfied by our treatment [41].

IV. DISCUSSION

Underlying the treatment put forward in the preceding sections is a picture of the swelling process where both the network and the solvent behave as incompressible fluids of small molecular weight except for the fact that convection is forbidden. Changes in the local amount of each component are controlled by Fick's law and in particular it is assumed that any elastic reaction which the network may offer to an increase in the local amount of solvent is adequately accounted for by the dependence of the diffusion coefficient on local concentration.

Using such a framework, we have been able to obtain a number of new results which may be of considerable value in interpreting experimental data, even though we have confined ourselves to problems which can be dealt with in terms of a single space coordinate. It is clear, however, that in order to carry forward the program described in the Introduction, and in particular to deal with the issues of surface pattern formation and of the onset of fracture, it is necessary to attack the full two- and three-dimensional problems. For example, performing a linear stability analysis requires a study of how perturbations from a radially symmetric geometry evolve in time.

Consider the case of a network of arbitrary shape which is swelling from the dry state: one can imagine the network as divided in a collection of domains; the boundaries between these domains play the role of the markers introduced in Sec. II for the one-dimensional problem (see also Ref. [20]). A procedure to extend the framework described above to this problem requires that at each time step the evolution should be consistent with the following prescriptions: (i) the amount of solvent in each domain should be allowed to change as prescribed by Fick's law: this operation fixes the new volume for each domain; and (ii) the shape of each domain should be changed in such a way to match the strain at the boundaries between neighboring domains and to make the outer surface of the specimen stress free.

Quite apart from the question of whether the above prescriptions are sufficient to determine the shape of the concentration profiles in a unique way, several problems are encountered when one attempts to implement such a program. In particular, one needs to solve at each time step a set of elasticity problems involving large deformations in situations where inhomogeneous strains are present. The theory of elasticity for large deformations (i.e., for non-Hookean materials) has been worked out in detail for the case of homogeneous strains [42], but there seems to be no general prescription allowing one to attack problems of this kind involving nonhomogeneous strains. In other words, for these materials there seems to be no procedure which allows one to solve for a general strain under general boundary conditions in the same way as is done [43] for a material obeying Hooke's law. Even assuming that one confines himself to situations involving small swelling ratios, so that Hooke's law can be applied, the problem of obtaining closed-form equations obeying the prescription given above remains a formidable one.

It is important to realize that the geometry of the specimen plays a special role in this problem and is essential in determining the shape of the sorption and desorption curves. Consider, for example, a thin rubber film: although one of the dimensions is much smaller than the other two, it is not permissible to treat this as a one-dimensional problem (with some end effect corrections). Indeed, one should expect that the final state will be a swollen film whose dimensions are all increased by the same amount (uniform affine deformation). On the other hand, it is clear that at the initial stages of swelling, when only the surface of the film is exposed to solvent, an affine deformation of the exposed part cannot occur without fracture of the sample. Therefore, in order to reach the final uniform affine deformation, elastic constraints from the unswollen portion must force the film to first swell mainly in the direction perpendicular to the plane of the film (surface instabilities may occur at this stage) and then gradually to rearrange to the final uniformly swollen state. It is natural to expect that the shape of the sorption curve is affected by the combination of these processes. These effects are by definition absent in the one-dimensional problem; however, they may play a role in the spherically symmetric case in the form of contributions to the flux coming from elastic forces between swollen and unswollen shells. These effects are neglected in the treatment given in Sec. II; nevertheless, the concentration dependence of the diffusion coefficient may account for such processes in some effective way.

In practice, one has often to deal with networks which are adhesively bonded to a rigid substrate or which are constrained in some other fashion [1,2,6–8]: indeed, the first example of surface instability [14] was observed in such a system. For a constrained network, the final equilibrium concentration is ordinarily nonuniform in the polymer occupied region, so that even for the spherically symmetric problem our equations and boundary conditions have to be modified in such a way to reproduce the final concentration profile. A similar situation (final nonuniform penetrant profile) is encountered in the case of ordinary (fixed boundary) diffusion taking place in the presence of an external potential [44]. Therefore, it seems that a reasonable way to account for such a situation is by introducing an *ad hoc* external potential which describes the effect of the constraint. This potential is chosen in such a way to reproduce the final concentration profile, which should be known *a priori* from equilibrium calculations [45].

In spite of the difficulties encountered in extending our treatment to a general three-dimensional geometry, we believe that further investigations towards this goal may well be worthwhile. The approach described here allows a direct description in terms of experimentally measurable material or system parameters and it should predict the conditions for surface instability and fracture in a given system in terms of such parameters. In this respect, we note that some recent studies [46,47] have examined the conditions for surface pattern formation in a swelling gel by introducing mechanical models (networks of springs) which mimic the microscopic structure of the polymer network. While these models are useful in pointing to physical situations which reproduce the qualitative features of pattern formation and growth, it is difficult to interpret the parameters appearing in these models in terms of measurable quantities in actual systems.

We conclude observing that, although the treatment discussed in this paper was developed to deal with the specific problem of swelling in elastomeric materials and polymeric gels, the macroscopic equations that we have obtained depend on the detailed molecular structure of these materials only insofar as this microscopic structure ensures that the physical requirements on which our treatment is based are satisfied. These requirements (absence of convection, diffusion described by Fick's law, volume unchanged upon mixing, and instantaneous onset of equilibrium at the boundaries) may be satisfied in systems whose molecular features are very different from those of a polymer network and we expect our macroscopic equations to be useful in describing transport processes in such systems.

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$$\partial\phi_S(x,t)/\partial t=\partial/\partial x[D_M(\phi_S(x,t))\partial\phi_S(x,t)/\partial x]\ ,$$

namely, the ordinary diffusion equation with diffusion coefficient D_M.

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[36] Both weight uptake and weight loss are proportional to $t^{1/2}$ for $t\to 0$ but the proportionality coefficient is larger in the first case.

[37] We have recently obtained unambiguous experimental confirmation for this result (i.e., desorption taking place at a rate faster than sorption in the case of high solvent concentrations) for polyisoprene spheres swollen by immersion in toluene (see Ref. [31]). We are unaware of any experimental data collected for low final solvent concentration in the case of spherical specimens. However, sorption and desorption data at low solvent vapor pressure (final solvent concentration of the order of a few percents) have been reported for a number of rubber films: see S. Prager and F. A. Long, J. Am. Chem. Soc. **73**, 4072 (1951) and M. J. Hayes and G. S. Park, Trans. Faraday Soc. **51**, 1134 (1955). Swelling is faster than deswelling in these cases. Although the two upper curves in Fig. **4** are very similar to the result found in these papers, one should not expect anything more than gross qualitative agreement between data obtained for films and predictions such as those of Figs. 4 and 5 found from Eq. (13) or (17). As we stress in Sec. IV, the geometry of the sample is important and we feel that neither a spherical geometry nor the one-dimensional problem constitute an adequate model for the swelling of a finite slab or a film.

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$$\partial c(x,t)/\partial t=\partial/\partial x[D(c)\partial c(x,t)/\partial x+c(x,t)V(x)]\ .$$

In order for the solution $c(x,t)$ of this equation to approach the equilibrium concentration profile $c^{(\mathrm{eq})}(x)$ as $t\to\infty$, the function $V(x)$ has to satisfy

$$V(x)=-[D(c^{(\mathrm{eq})})/c^{(\mathrm{eq})}(x)][\partial c^{(\mathrm{eq})}(x)/\partial x]\ .$$

Likewise it is easy to see that if in place of Eq. (13) one has

$$\partial\phi_S(x_0,t)/\partial t=\phi_R^2(x_0,t)\partial/\partial x_0[D_M(\phi_R)\partial\phi_S(x_0,t)/\partial x_0+\phi_R(x_0,t)\phi_S(x_0,t)V(x_0)]\ ,$$

then

$$V(x_0)=-(D_M(\phi_R^{(\mathrm{eq})})/\{\phi_R^{(\mathrm{eq})}(x_0)[1-\phi_R^{(\mathrm{eq})}(x_0)]\})\partial\phi_R^{(\mathrm{eq})}(x_0)/\partial x_0$$

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