DIFFUSION IN GLASSY POLYMERS

Thesis by

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> No, but I wish to go under; to visit the profound depths; once in a while to exercise my prerogative not always to act, but to explore; to hear vague, ancestral sounds of boughs creaking, of mammoths, to indulge impossible desires to embrace the whole world with the arms of understanding, impossible to those who act.
>
> Virginia Woolf, The Waves

ABSTRACT

Fluid diffusion in glassy polymers proceeds in ways that are not explained by the standard diffusion model. Although the reasons for the anomalous effects are not known, much of the observed behavior is attributed to the long times that polymers below their glass transition temperature take to adjust to changes in their condition. The slow internal relaxations of the polymer chains ensure that the material properties are history-dependent, and also allow both local inhomogeneities and differential swelling to occur. Two models are developed in this thesis with the intent of accounting for these effects in the diffusion process.

In Part I, a model is developed to account for both the history dependence of the glassy polymer, and the dual sorption which occurs when gas molecules are immobilized by the local heterogeneities. A preliminary study of a special case of this model is conducted, showing the existence of travelling wave solutions and using perturbation techniques to investigate the effect of generalized diffusion mechanisms on their form. An integral averaging method is used to estimate the penetrant front position.

In Part II, a model is developed for particle diffusion along with displacements in isotropic viscoelastic materials. The nonlinear dependence of the materials on the fluid concentration is taken into account, while pure displacements are assumed to remain in the range of linear viscoelasticity. A fairly general model is obtained for three-dimensional irrotational movements, with the development of the model being based on the assumptions of irreversible thermodynamics. With the help of some dimensional analysis, this model is simplified to a version which is proposed to be studied for Case II behavior.

TABLE OF CONTENTS

I. GASEOUS DIFFUSION IN GLASSY POLYMERS

II. DIFFUSION WITH SWELLING IN GLASSY POLYMERS; CASE II DIFFUSION

OVERVIEW

As new uses are continuously being found for polymers, both as replacements for traditional materials and in new technologies which rely on their special properties, it becomes important to understand and model their behavior. In the case of diffusion, it has been known for over thirty years [1] that the standard Fickian diffusion model

$$c_t = \nabla\cdot(D(c)\nabla c)$$

is incapable of describing the full range of behavior which is observed when a fluid diffuses through a polymer in the glassy state. Even so, the actual phenomena which are observed are not yet well understood. (Good summaries of the experimental evidence and proposed theories are given by Crank [2], Frisch [3], and Hopfenberg and Stannet [4].) In many of the applications, diffusion plays an important role. For example, moisture will eventually seep through polymer containers, causing degradation of any moisture sensitive contents. One of the lithographic techniques used in the fabrication of integrated circuits etches polymers with electron beams; the exposed material dissolves more readily than the unexposed material when the polymer surface is washed with solvents, creating an extremely fine pattern. Circuit manufacturers would like to make this pattern even finer.

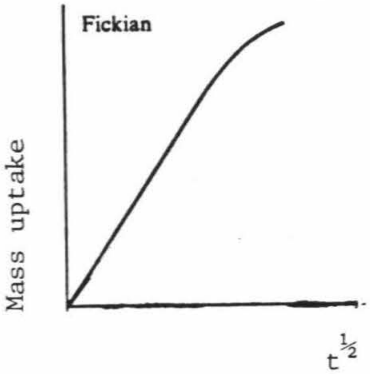
One of the most interesting and promising uses for polymers is in controlled-release drug delivery systems [5],[6] which dispense medication continuously for long periods of time, allowing for lower doses and less trauma to the patient's system. Some of these devices imbed the drug in the polymer, allowing it to diffuse slowly outward, The process by which the polymer is manufactured determines how fast the drug is released. Another concept takes advantage of Case II diffusion, described below; as the front moves inward, the swollen polymer behind the front releases the drug at a uniform rate. Still mainly experimental, a few controlled-release products are already on the market, including a patch for motion sickness which dispenses scaparlomine through the skin, and a small disk, used in glaucoma therapy, which sits under the eyelid.

At least four distinct responses are observed when a large membrane of dry glassy polymer is suddenly placed and held in a bath of fluid [2]: Fickian, or Case I; Case II (including Super Case II); two-stage diffusion; and sigmoid, or S-shaped sorption. The first two are considered limiting behaviors, while the latter two may possibly be intermediate between Case I and Case II diffusion responses.

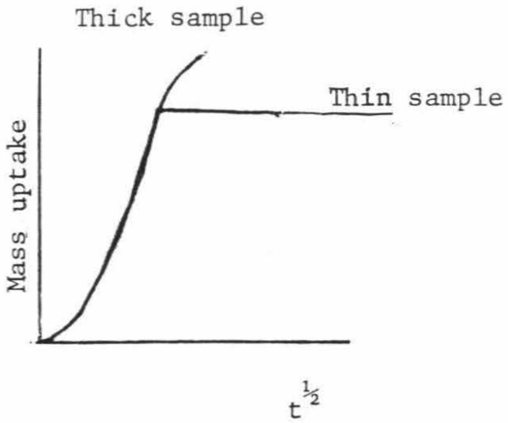
Fickian diffusion, also called Case I, follows closely the solution to the familiar diffusion equation

$$c_t = (D(c)c_x)_x,$$

with the concentration c held at the equilibrium value on the boundary. Mass uptake is initially proportional to the square-root of time, eventually slowing down, and no distinct boundary between wet and dry polymer is visible. No large stresses are observed.

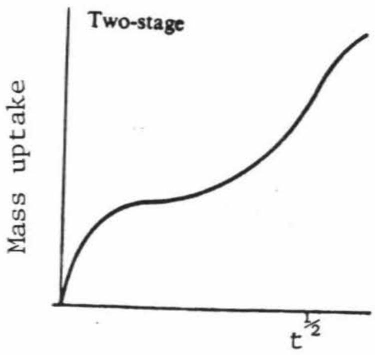


In Case II diffusion, on the other hand, mass uptake is proportional to time (faster for Super Case II)and is much faster than Fickian uptake, A distinct boundary is visible between an apparently dry inner core and a wet swollen region at or near the equilibrium concentration. This front moves at constant velocity (faster for Super Case II) and the stresses on the dry inner core can be large enough to cause crazing, and even fracturing of the core. Thomas and Windle [7] observed that in a wide enough sample (how wide decreases with the temperature), Case II fronts eventually slow down and weaken, with the regions behind and in front no longer at equilibrium and zero concentrations, respectively. The region behind the front may be soft and rubbery, or it may still be glassy.

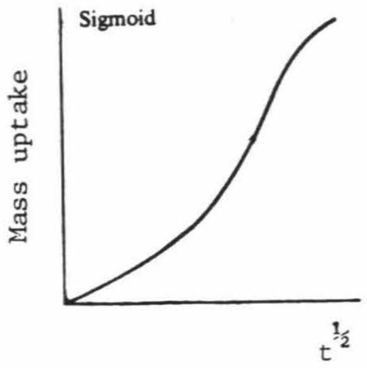


Case II

Two-stage sorption is characterized by an initially rapid mass uptake, apparently Fickian, followed by a lull and then another upsurge. This phenomenon is widely believed to be due to nonconstant boundary conditions.



Sigmoid, or S-shaped sorption mass uptake curves start off proportional to the square-root of time, increase and then taper off. These curves are also seen for diffusion in glassy metals.



By looking at the properties of glassy polymers, it is easy to see why Fickian diffusion does not always occur. One of the fundamental assumptions behind Fick's law is that the system reaches local equilibrium much more rapidly than diffusion proceeds, so that stresses and local inhomogeneities are instantaneously relieved. For glassy polymers in certain temperature and concentration ranges, this is simply an unrealistic assumption. The properties of glassy polymers are fairly thoroughly discussed in Haward [8]. Amorphous polymers in the glassy state are hard and can be brittle, with the polymer chains nearly frozen in place, causing them to be fairly sensitive to their past history, and to equilibrate slowly. They flow, albeit extremely slowly, under stress, having a very high viscosity. With increasing temperature or penetrant concentration, they soften and become more responsive, eventually going through a rapid transition region, generally considered to be a second order phase change, in the neighborhood of the glass transition temperature T_g. Above T_g they are rubbery or gelatinous. The slow relaxation may have a number of consequences. Not only are the properties of the polymer history-dependent, but the surface may take a significant amount of time to arrive at the equilibrium concentration. Local inhomogeneities and anisotropies may arise, opening up interstitial spaces and microvoids which immobilize diffusing particles, This process is known as dual sorption. Differential stresses between regions at different concentrations are not quickly relieved.

One of the important features of glassy polymers is the strong dependence of their current properties on their past history, or in other words, their slow relaxation. A number of models have been proposed to partially incorporate this history dependence. In Part I of this thesis, we generalize one of the earliest of these history-dependent models to include both dual sorption and different history dependent behavior. The model which we start with is a highly nonlinear one due to Crank [1]. Many of the other history-dependent models reduce to special cases of our model. We also show that Crank's model, with a simple dual sorption term added, allows travelling waves to propagate through the medium.

Ideally, one would like to have a single model incorporating all of the salient features of penetrant diffusion in glassy polymers. Although such a model was developed in the 1960's for the similar problem of nonlinear heat transfer in viscoelastic solids [9],[10], no model appears to exist for particle diffusion. In Part II of this thesis, a model is proposed that incorporates nonlinear particle diffusion, viscoelastic swelling and history dependence for an isotropic system. It is based on the assumption that, even though solid displacements may be large, most of the displacements are being made to accommodate the fluid, and the movements of the center of mass are small. This model, which is fairly general, is developed using the assumptions and techniques of irreversible thermodynamics. A collection of the relevant hypotheses of irreversible thermodynamics and their consequences is presented along with the derivation of the model, on the assumption that the reader should not need to be familiar with this subject, The model is therefore worked out in great detail. It is, of course, the final model that is of interest, and in the last section of this part a simplified version, which should be reasonable to analyze, is proposed for one-dimensional Case II diffusion.

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GASEOUS DIFFUSION IN GLASSY POLYMERS*

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Dedicated to Joseph Keller

Abstract. A model for gaseous diffusion in glassy polymers is developed with a view to accounting for the observations made in dual sorption and certain other phenomena in polymers below their glass transition temperature. In this paper a preliminary study of the effects of both the immobilizing mechanism and the generalized diffusion mechanism on travelling waves and the diffusive wavefronts is made.

1. Introduction. In the period 1953–1969 a partially successful chemical and mathematical theory was developed for the diffusion behavior of glassy polymers and the transition between rubbery and glassy states. Good summaries of this development are given in Crank [1] and Crank and Park [2]. While it was recognized at the time that many fundamental chemical mechanisms were still unknown, and also that the corresponding mathematical theory was inadequate due to its inherent and often ignored nonlinearity, nevertheless combinations of gross qualitative chemical theories and crude linearizations plus numerical studies gave acceptable answers for the problems of the time [2]. However, recent technological discoveries lead to a variety of new problems far exceeding the capabilities of the previously developed theories. Among these are problems in the disposal of chemical waste, the structural failure of plastics and polymers, the replacement of traditional materials by polymers, the development of barriers (e.g., plastic beverage bottles) to separate gas mixtures, the migration of impurity atoms in solids which should be ultra-pure for their use in solid-state electronic devices, and the role of diffusion in catalysis by porous solids.

Roughly speaking, the major effects depend upon whether the polymer is above (rubbery) or below (glassy) its glass transition temperature and whether the penetrant is a liquid or a gas, but this is only a crude over-simplification. A polymer in its rubbery state responds rapidly (almost instantaneously) to changes in its condition. This has many simplifying implications, and it is now universally agreed [1], [3] that diffusion in rubbery polymers is described by the standard Fickian diffusion equation $C_t = \operatorname{div}(D \operatorname{grad} C)$, in which the diffusivity D is at worst dependent upon the concentration C of the diffusing species; i.e., $D = D(C)$. Although problems involving this equation may be formidable nonlinear boundary value problems, the important qualitative features of diffusion in rubbery polymers can be obtained, and indeed, a rather complete theory [1] exists.

On the other hand, there is no unifying theoretical formulation for glassy polymers. There is not even a complete classification of the various anomalous effects. Glassy polymers respond slowly to changing conditions, and most of the anomalous effects are directly related to this. For example, the changing polymer structure influences the solubility and diffusional mobility. This leads to diffusion coefficients which can depend not only nonlinearly on the state of the system, but also on the previous history of the system, and sometimes even on previous rates of change of the system [1], [4]. Internal stresses can be induced due to differential swelling of different parts of the polymer [5]–[7]. Immobilization (and sometimes reaction) in the interstitial

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spaces and microvoids greatly affects the sorption of diffusing penetrants [8]–[10]. These and many other phenomena have given rise to a partial classification (Case II, Super-case II, dual-mode, anomalous non-Fickian, . . .) of glassy polymers according to various experimental observations. Indeed, the observations are sometimes so diverse that, rather than any kind of universal theory for glassy polymers it is probably the case that theories of glassy polymers by still to be defined type will be all that is obtainable. In any event, many more studies of special problems are necessary before some more or less global theory can be proposed.

In this paper we shall study the general problem of dual sorption in glassy polymers. We shall be more precise in § 2 where we present the equations of motion, but roughly speaking dual sorption involves two distinct mechanisms: (i) ordinary diffusion controlled sorption, and (ii) sorption resulting from the immobilization (or partial immobilization) of diffusing gas molecules by various sites in the polymer [9]. These sites are interstitial spaces and microvoids which are consequences of local heterogeneities, and which are intimately related to the slow relaxation processes associated with the glassy state of the polymer (probably close to the glass transition temperature).

We shall study systems of equations of the form

$$C_t = (DC_x)_x + R(C), \tag{1.1}$$

$$D_t = F'(C)C_t + \alpha(C)[G(C) - D], \tag{1.2}$$

and certain natural generalizations of this system for which the theories of Vieth and Sladek [8], Tshudy and von Frankenberg [9], Paul and Koros [10], and Petropoulos [11] are all special cases. Diffusion operators with diffusivity changing according to (1.2) were first proposed by Crank [1], [12] to account for totally different observations involving swelling when a liquid penetrant diffuses into a glassy polymer. Crank's arguments are cogent, and appropriate generalizations are broadly applicable to large classes of generalized diffusion problems. In § 2 we shall show how to obtain the standard dual mode sorption theories [8]–[11] from a generalization of Crank's model. In addition, we show that our model then unifies dual mode sorption with certain parts of the so-called Case II, Super-case II, and anomalous non-Fickian phenomena.

Because of the relative ease with which it can be obtained, both experimentally and theoretically, the single quantity most commonly used to define the kinetics of the sorption process [7] is

$$M_t = kt^n, \tag{1.3}$$

where M_t is the total amount of penetrant absorbed per unit area of polymer at time t, and k and n are system parameters. Standard Fickian diffusion (i.e., a polymer in its rubbery state above the glass transition temperature) corresponds to the usual $n = \frac{1}{2}$. Case II glassy polymers correspond to $\frac{1}{2} \leqq n \leqq 1$, and Super-case II corresponds to $n > 1$. However, this is not a hard and fast rule, and furthermore, in most glassy polymers M_t as a function of t does not look like t^n for one constant value of n. In dual mode sorption and in anomalous non-Fickian cases the most commonly observed function for M_t is what is now universally called "sigmoid" by polymer chemists [1], [3]. That is, M_t as a function of $t^{1/2}$ commonly exhibits a single point of inflection (most often at about 50% of equilibrium sorption). For example, in the penetration of cellulose acetate by acetone vapor [13], M_t versus $t^{1/2}$ is linear for both small and large time t joined for intermediate time by a curve with a single inflection point. The penetration of polystyrene by methane [14] exhibits an M_t versus $t^{1/2}$ with two linear regions connected by a nonlinear region.

This sigmoid absorption behavior can be controlled by either the diffusivity D or the kinetic-like term $R(C)$ in (1.1), (1.2). The following simple heuristic arguments give a feeling for the mechanisms involved: The function $\alpha(C)$ in (1.2) is a rate controlling function (empirically obtained) depending monotonically on C. From (1.2) it is clear that large α implies $D \sim G(C)$, the equilibrium diffusion coefficient, and small α implies $D \sim F(C)$, the instantaneous diffusion coefficient. (Note that in either state the concentration in an absorption process is increasing.) For intermediate values of α the diffusion coefficient D is history dependent (we shall show this in § 2), and it is this transition from small to large values of α which accounts for the so-called sigmoid absorption curve. We shall demonstrate this more explicitly in § 5 where we employ a Karman–Pohlhausen integral averaging method to obtain the time history of the penetration front.

The term $R(C)$ in (1.1) arises from a consideration of one or a combination of the following phenomena: (i) The immobilization of some diffusing molecules simply by filling voids, (ii) the immobilization (or partial immobilization) of some diffusing molecules by absorption at specific sites, or (iii) the intraconversion of two or more differently mobile penetration species. Equilibrium states exist in all these situations, and as we shall see, since the most commonly occurring form for $R(C)$ is a bimolecular rate function, then two equilibrium states usually exist. The sigmoid absorption behavior is manifested by a diffusion wave connecting these states. We prove the existence of these waves in § 3 and construct them via a perturbation scheme in a special case in § 4.

2. Dual sorption theory. Experimental results readily show that the sorption isotherms for gases such as CO_2, CH_4, and C_2H_6 in glassy polymers such as ethylene terephthalate and polystyrene are nonlinear [10], [14]–[16] and can best be described by a function of the form

$$C = \alpha p + \frac{\beta p}{1 + \gamma p}, \tag{2.1}$$

where C is the equilibrium concentration of gas in the polymer, p is the pressure, and α, β, and γ are various physical constants. It is standard [8]–[10], [14]–[16] to write (2.1) in the form

$$C = C_D + C_H, \tag{2.2}$$

where

$$C_D = \alpha p, \qquad C_H = \frac{\beta p}{1 + \gamma p}, \tag{2.3}$$

and to interpret (2.2) as implying that two separate sorption mechanisms are operating: (i) Standard linear sorption in which C_D denotes the gas dissolved according to Henry's law (i.e., $C_D = \alpha p$), and (ii) hole filling (or immobilization) in which C_H denotes gas adsorbed into holes according to a Langmuir-type isotherm (i.e., $C_H = \beta p/(1 + \gamma p)$). Note that C is linear in p for both small and large p; i.e.,

$$C \sim (\alpha + \beta)p \quad \text{for small } p, \tag{2.4}$$

$$C \sim \alpha p + \frac{\beta}{\gamma} \quad \text{for large } p. \tag{2.5}$$

This behavior, (2.4), (2.5), of two linear regions with a connecting nonlinear region is the typical experimental observation [8], [14] noted for gaseous diffusion in a glassy polymer.

In the theories assuming complete immobilization [8], [10] of the gas adsorbed in the holes one assumes that only the dissolved gas is free to diffuse so that (neglecting convection) the flux J of diffusing gas is given by

$$J = -D\frac{\partial C_D}{\partial x}, \tag{2.6}$$

where D is the diffusion coefficient of the dissolved penetrant. (For algebraic simplicity we shall stick to one dimension. The multi-dimensional derivation in which J is proportional to the gradient of C is easy to carry out.) The basic equation of continuity (i.e., conservation of mass) then becomes

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial t}(C_D + C_H) = -\frac{\partial J}{\partial x}. \tag{2.7}$$

Local equilibrium between C_D and C_H implies that at any position the pressure is the same for both species. Thus, since $p = C_D/\alpha$, we have

$$C_D + C_H = C_D + \frac{(\beta/\alpha)C_D}{1+(\gamma/\alpha)C_D}. \tag{2.8}$$

Hence,

$$\frac{\partial}{\partial t}\left(C_D + \frac{(\beta/\alpha)C_D}{1+(\gamma/\alpha)C_D}\right) = \frac{\partial}{\partial x}\left(D\frac{\partial C_D}{\partial x}\right), \tag{2.9}$$

or equivalently,

$$\left[1 + \frac{\beta/\alpha}{(1+(\gamma/\alpha)C_D)^2}\right]\frac{\partial C_D}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_D}{\partial x}\right). \tag{2.10}$$

The derivation of (2.10) can be carried out in a more sophisticated manner [10]–[11] by using various thermodynamic arguments and invoking a flux driven by gradients of a chemical potential rather than a concentration. This allows one to relax the assumption of complete immobilization and use instead the concept of partial immobilization of some gas molecules due to several possible mechanisms [1]. Nevertheless, the form of (2.10) remains the same with only slight modification in the specific constants and functional forms of the coefficients in (2.10).

A totally different formulation of the dual sorption implied by (2.2) is presented by Tshudy and von Frankenberg [9]. They assume that there are a fixed number of immobilizing sites distributed uniformly throughout the polymer and that each site can immobilize only one gas molecule according to some mechanism whose effect can be written as

$$\text{site} + \text{gas molecule} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{site molecule complex}. \tag{2.11}$$

By writing the specific function R describing the "reaction" (2.11) and by invoking ordinary diffusion they then write the basic continuity equation as

$$\frac{\partial C_D}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_D}{\partial t}\right) + R. \tag{2.12}$$

Partial immobilization can be accounted for through the use of a reversible reaction (2.11), and the effective rate constants k_1 and k_{-1} can be adjusted to yield the same equilibrium sorption isotherms as the other theories which start with (2.10).

In a different context, involving swelling of the polymer structure due to (mostly liquid) penetrants, Crank [1], [12] proposed a phenomenological approach which we now generalize to the present problem of dual sorption. This generalization embodies all of the above theories. Crank proposed the system

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right), \tag{2.13}$$

$$\frac{\partial D}{\partial t}=F'(C)\frac{\partial C}{\partial t}+\alpha(C)[G(C)-D]. \tag{2.14}$$

He presents simple convincing arguments, which we summarized in § 1, to interpret $F(C)$ as an instantaneous diffusion coefficient reflecting instantaneous changes in the polymer, $G(C)$ as an equilibrium diffusion coefficient reflecting the slow relaxation due to its glassy state, and $\alpha(C)$ as a rate function controlling the approach to equilibrium. Crank further points out that (2.14) implies that the diffusivity D depends not only on the concentration, but also on the time taken to reach that concentration, and thus, some previous history is also incorporated into (2.14).

Basic to all the theories mentioned above is the explicit assumption of a diffusion mechanism taking account of the relatively slow relaxation of a polymer in its glassy state. This mechanism is superposed on the usual classical diffusion in such a way that the total diffusion process models the experimental observations that at low concentration (and/or pressure) the process acts as a classical (i.e., Fickian) diffusion process with one (possibly concentration dependent) diffusion coefficient, and at high concentration (and/or pressure) the process acts the same way but with a different diffusion coefficient. These regimes are connected by a nonlinear region in which the dominant behavior is due to adjusting to the changing polymer structure (for example, the process of filling microvoids by the binding or immobilizing of some of the diffusion gas). With this observation it is clear that Crank's diffusion mechanism (2.13), (2.14) has the proper ingredients for describing the evolving diffusivity. In addition, lacking detailed knowledge of the complex physical and chemical processes taking place in the interstitial spaces, we can incorporate all possible processes in a general relation (2.11) of the Tshudy–von Frankenberg type. There is no need at this state to make specific assumptions on the distribution of sites or the process at each site, and we incorporate the observations that these complex processes depend on the rate of change and the local flux of the concentration. Thus, we propose

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)+R(x,t,C,C_t,C_x), \tag{2.15}$$

$$\frac{\partial D}{\partial t}=F'(C)\frac{\partial C}{\partial t}+\alpha(C)[G(C)-D], \tag{2.16}$$

where $R(x,t,C,C_t,C_x)$ represents the (at this stage unknown) kinetics implied by the process (2.11).

Note that (2.16) can be integrated to express D as

$$\begin{aligned} D &= D_0 \exp\left(-\int_0^t \alpha(C(x,\tau))\,d\tau\right) \\ &\quad + \int_0^t \exp\left(-\int_s^t \alpha(C(x,\tau))\,d\tau\right)[F'(C(x,s))C_t(x,s)+\alpha(C(x,s))G(C(x,s))]\,ds, \end{aligned} \tag{2.17}$$

where $D_0 = D$ at $t=0$. In this form we see explicitly the history dependence of D represented as an integral over time with a kernel

$$\exp\left(-\int_s^t \alpha(C(x,\tau))\,d\tau\right). \tag{2.18}$$

This kernel represents the delay (or heredity) inherent in the relaxation process. Progressing along these lines, we can replace (2.16) or (2.17) with the more general assumption that

$$D = \int_0^t K(t,s,C(x,s))f(C(x,s),C_t(x,s))\,ds \tag{2.19}$$

with an appropriate (hereditary or delay) kernel $K(t,s,C)$ and an appropriate concentration dependent f. The system consisting of (2.15) and (2.19) provides an appealing model for describing dual sorption and certain parts of the so-called Case II, Super-case II, and anomalous non-Fickian phenomena. Most of the current models are special cases of (2.15), (2.19). Thus, (2.15), (2.19) provides a unifying theory which so far appears to be justifiable without many of the restrictions of some of the special purpose models. Furthermore, with the diffusivity described by an integral law such as (2.19) we can explicitly incorporate the most important property of a glassy polymer, namely the finite relaxation time implied by the slow (rather than instantaneous) response to changing conditions.

The system (2.15), (2.19) in all its generality is very formidable. However, in the present paper we are studying the main features of the transition from a dry polymer to a fully saturated one in the dual sorption mode and its relationship to the sigmoid sorption process. Even with the assumptions invoked in all the common models [1]–[16] detailed knowledge of $R(x,t,C,C_t,C_x)$ from a molecular or statistical-dynamical theory would be difficult to obtain. However, for our continuum mechanics model we need only observe that $R(x,t,C,C_t,C_x)$ should provide the kinetics incorporating the change from a dry polymer to a fully saturated one. Qualitatively there should be little difference from the simple assumption of the most commonly occurring bimolecular stationary form

$$R(x,t,C,C_t,C_x) = \mu C(k-C), \tag{2.20}$$

where μ represents the "strength" of the reaction and k represents the equilibrium concentration (or carrying capacity) towards which the reaction is driven.

Further generalization of (2.19) incorporating spatial correlation and a more general functional dependence is also possible, but the system (2.15), (2.19) seems quite satisfactory at its present level.

3. Traveling waves. The structure of the transition between different regimes (e.g., sigmoid behavior or the change from a Henry isotherm to a Langmuir isotherm in gaseous diffusion) and the role of the various terms in the equations of motion is very often nicely revealed by a study of traveling wave solutions. Even in more general solutions transition zones in some appropriate scaled variables are often described by traveling waves. Thus, we shall first study traveling wave solutions.

We shall show the existence of traveling wave solutions of equations (2.15), (2.16), where we take

$$R(x, t, C, C_t, C_x) = \mu C(k - C), \qquad \mu, k > 0. \tag{3.1}$$

It will be convenient to treat this system in the nondimensional form

$$c_\tau = [(g(c) - w)c_\chi]_\chi + c(1 - c), \tag{3.2}$$

$$w_\tau = h(c)c_\tau - \beta(c)w, \tag{3.3}$$

where

$$\begin{gathered} c = \frac{C}{k}, \quad \tau = \mu k t, \quad \chi = \sqrt{\frac{\mu k}{G(0)}}x, \\ w = \frac{G(C) - D}{G(0)}, \quad g(c) = \frac{G(C)}{G(0)}, \quad f(c) = \frac{F(C)}{G(0)}, \\ \beta(c) = \frac{\alpha(C)}{\mu k}, \qquad h(c) = \frac{d}{dc}[g(c) - f(c)]. \end{gathered} \tag{3.4}$$

We seek *nonnegative* solutions of (3.2), (3.3) under the following hypotheses:

H-1. $\beta(0) > 0$.

H-2. $f(0) = g(0) = 1$.

H-3. $f(c)$, $g(c)$, and $\beta(c)$ are monotonically nondecreasing and $h(c) \geqq 0$ for $c \geqq 0$.

H-4. $f'(c)$, $g'(c)$, and $\beta(c)$ satisfy a Lipschitz condition for $c \geqq 0$.

The requirement of nonnegativity on c simply reflects the fact that physically the concentration C is always nonnegative. Conditions H-1 to H-3 are a consequence of the following observations: The diffusion coefficient should be positive so that the flow is from higher to lower concentrations. This coupled with the interpretation of $F(C)$ as an instantaneous diffusion coefficient and $G(C)$ as an equilibrium diffusion coefficient imply $G(C) \geqq F(C) > 0$. It is experimentally noted that relaxation gets faster as concentration increases, so that $\alpha(C)$ is monotonically nondecreasing. In a perfectly dry polymer, D should be constant which occurs if either $\alpha(0) = 0$ or if $F(0) = G(0)$; we use the latter. Finally, condition H-4 is a technical condition we need in our proofs; this is satisfied by all the functions used in practice.

Assume solutions of the form

$$c(\chi, \tau) = c(\xi), \qquad w(\chi, \tau) = w(\xi), \tag{3.5}$$

where

$$\xi = -(\chi + a\tau), \tag{3.6}$$

and where a is the constant nondimensional velocity. Define $u = -dc/d\xi$. Then, (3.2), (3.3) become

$$\begin{gathered} \frac{dc}{d\xi} = -u, \\ \frac{d}{d\xi}[(g(c) - w)u] = -au + c(1 - c), \\ \frac{dw}{d\xi} = \frac{\beta(c)}{a}w - h(c)u. \end{gathered} \tag{3.7}$$

We now study the system (3.7) in (c, u, w)-phase space.

The system (3.7) has two critical points given by

$$(c, u, w) = (0, 0, 0) \quad \text{and} \quad (c, u, w) = (1, 0, 0). \tag{3.8}$$

(If $\alpha(0) = 0$, then the w-axis is a singular line. Our results remain true in this case also, but the proof is more complicated.) The existence of a (nonnegative) traveling wave solution with $c \to 0$ as $t \to -\infty$ and $c \to 1$ as $t \to \infty$ is equivalent to the existence of a trajectory (in $c \geqq 0$) of (3.7) which starts at $(1, 0, 0)$ as $\xi \to -\infty$ and terminates at $(0, 0, 0)$ as $\xi \to \infty$. Condition H-4 guarantees the (local) existence of unique solutions of all initial value problems away from the surface $w = g(c)$. Trajectories can intersect only at the critical points (away from this surface), and these critical points can be reached only as $\xi \to \pm\infty$. Linearization about each critical point serves to determine the behavior near the critical points.

Some feel for the geometry of our phase space can be obtained from the numerical examples of Figs. 1–3 in which a connector or lack of one is illustrated. These figures show solution curves of (3.7) projected onto the (u, c) and (w, c) planes. The letters $A, B, C, \cdots$ identify the different projections of the same curve. Initial values are taken on **U**, the unstable manifold defined in (3.17). In Figs. 1 and 2 a connector exists. In Figure 3 a connector does not exist since u and w do not go to zero as c does.

Near $(0, 0, 0)$ the linearized equations are

$$\begin{aligned} \dot{c} &= -u, \\ \dot{u} &= c - au, \\ \dot{w} &= -h(0)u + \frac{\beta(0)}{a} w, \end{aligned} \tag{3.9}$$

where the superscript dot denotes $d/d\xi$. This system has eigenvalues ν and eigenvectors

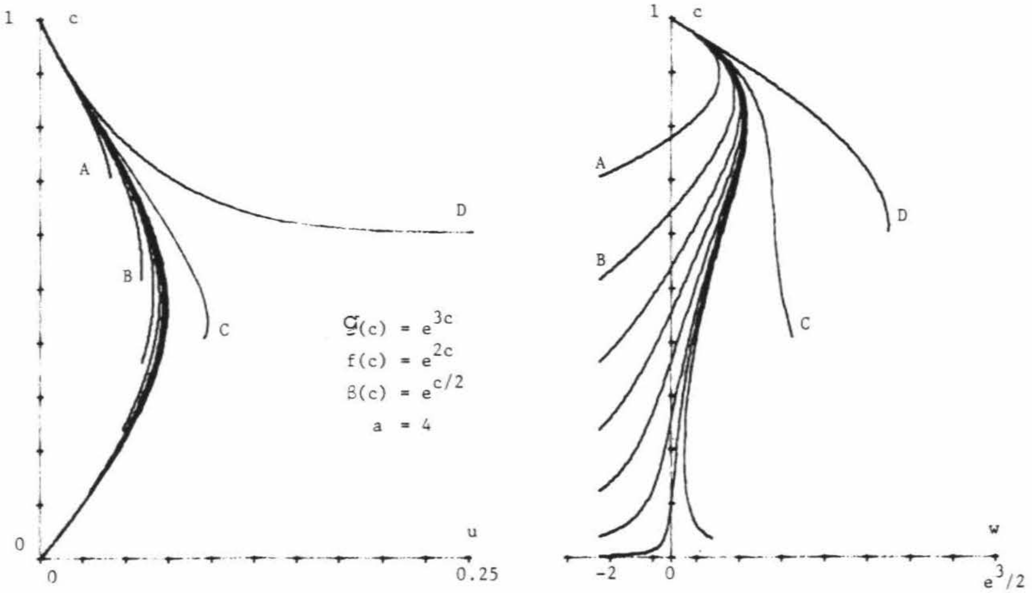

FIG. 1

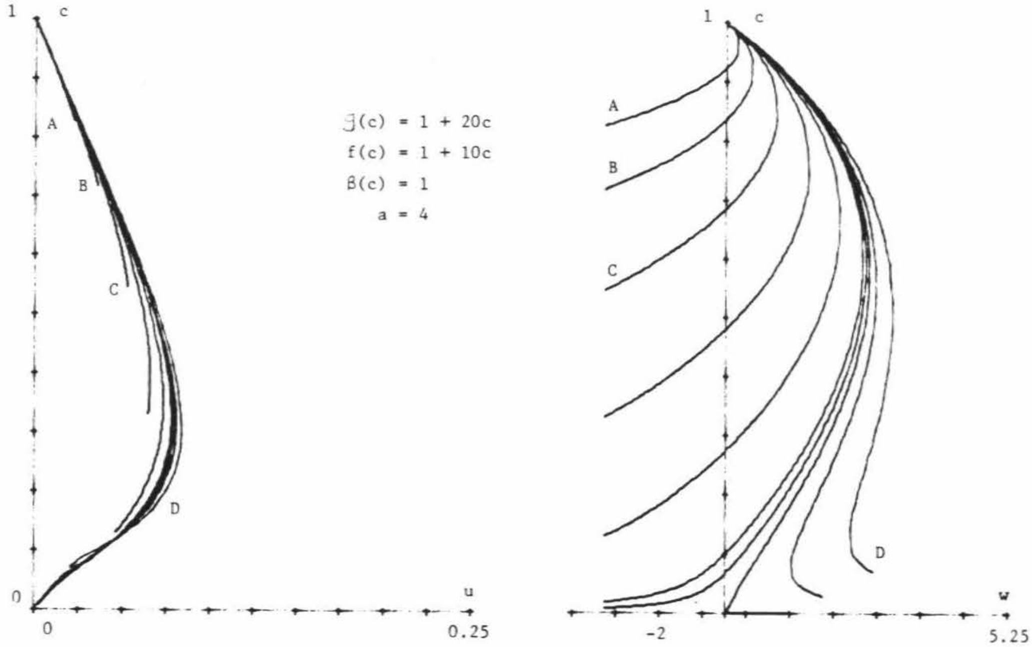

FIG. 2

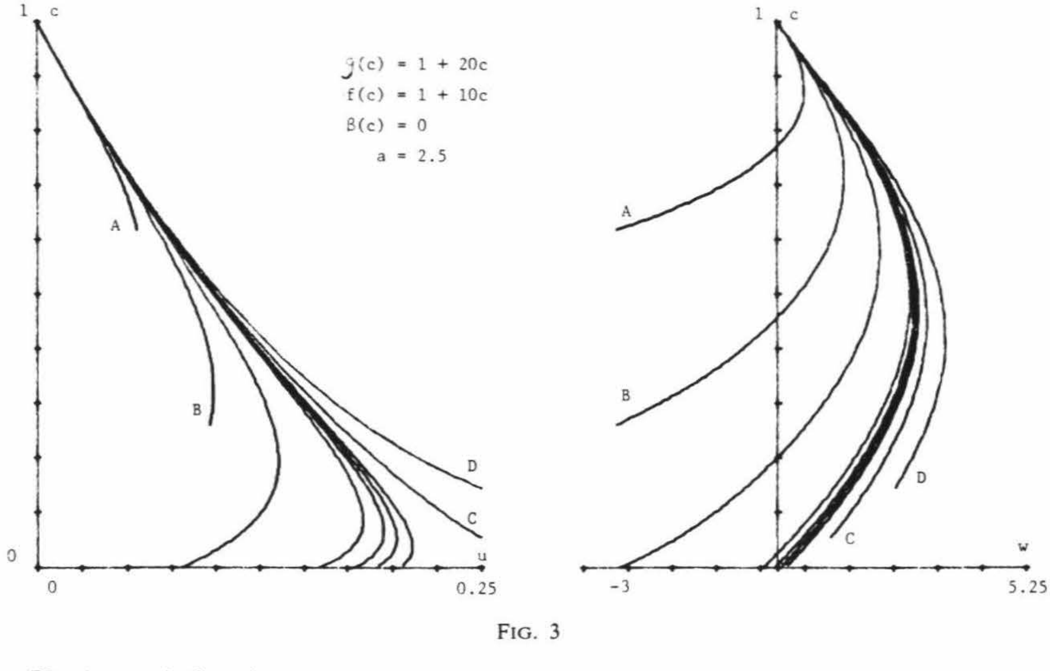

FIG. 3

$\mathbf{Y} \equiv (c, u, w)$ given by

$$\nu_0 = \frac{\beta(0)}{a}, \qquad \mathbf{Y}_0 = (0, 0, 1), \tag{3.10}$$

$$\nu_\pm = \frac{-a}{2} \pm \sqrt{\frac{a^2}{4} - 1}, \qquad \mathbf{Y}_\pm = \left(1, -\nu_\pm, \frac{\nu_\pm h(0)}{\nu_\pm - \nu_0}\right). \tag{3.11}$$

Near $(1, 0, 0)$ the linearized equations are (with $c_1 = 1 - c$)

$$\begin{aligned} \dot{c}_1 &= u, \\ \dot{u} &= \frac{c_1}{g(1)} - \frac{au}{g(1)}, \qquad (3.12) \\ \dot{w} &= -h(1)u + \frac{\beta(1)}{a} w, \end{aligned}$$

whose eigenvalues λ and eigenvectors $\mathbf{X} \equiv (c, u, w)$ are given by

$$\lambda_0 = \frac{\beta(1)}{a}, \qquad \mathbf{X}_0 = (0, 0, 1), \tag{3.13}$$

$$\lambda_\pm = \frac{-a \pm \sqrt{a^2 + 4g(1)}}{2g(1)}, \qquad \mathbf{X}_\pm = \left(1, \lambda_\pm, \frac{-h(1)\lambda_\pm}{\lambda_\pm - \lambda_0}\right). \tag{3.14}$$

Returning to the region near the origin, $(0, 0, 0)$, we see that the linearized system behaves in different ways according to the size of a.

(i) $a \geqq 2$. There are two negative eigenvalues, ν_+ and ν_-, and one positive one, ν_0. Thus, there is a two-dimensional surface of trajectories approaching $(0, 0, 0)$ and a pair of trajectories going away from $(0, 0, 0)$. This is essentially the three-dimensional analogue of a saddle point in the phase-plane.

(ii) $-2 > a > 2$. There are two complex eigenvalues, $\nu_\pm$, and one real one, ν_0. This implies that the trajectories approaching or leaving the origin spiral around it. Furthermore, since the eigenvectors $Y_\pm$ are not in the $c = 0$ plane, these trajectories must enter the (unphysical) region $c < 0$.

(iii) $a \leqq -2$. There are two positive eigenvalues, $\nu_\pm$, and one negative one, ν_0. Thus, there is a two-dimensional surface of trajectories leaving the origin and a pair of trajectories approaching it.

Note that

$$c = 0, \quad u = 0, \quad w = w_0 e^{\beta(0)\xi/a}, \tag{3.15}$$

and

$$c = 1, \quad u = 0, \quad w = w_0 e^{\beta(1)\xi/a} \tag{3.16}$$

are solutions of (3.7) for any constant w_0. Thus, the w-axis and the line $c = 1$, $u = 0$ are trajectories leaving the critical points if $a > 0$ and approaching the critical points if $a < 0$. Since we are looking for a trajectory in $c \geqq 0$ which starts at $(1, 0, 0)$ and terminates at $(0, 0, 0)$, we can rule out cases (ii) and (iii). That is, case (ii) with wave speeds $-2 < a < 2$ violates the requirement that $c \geqq 0$, and case (iii) with $a \leqq -2$ is ruled out since the only trajectories approaching the origin do so along the *w-axis* and must come from $w = \pm\infty$ with c and u zero for all ξ. Therefore, if there exist acceptable traveling wave solutions, they must have $a \geqq 2$. We shall now demonstrate their existence. Note that even if $a \geqq 2$ there may not exist such solutions as we see from Fig. 3.

Since λ_0 and λ_+ are positive and λ_- is negative, then near $(1, 0, 0)$ we have an unstable two-dimensional manifold of trajectories which has the form

$$\mathbf{U} \equiv \begin{pmatrix} 1 - c \\ u \\ w \end{pmatrix} = m\mathbf{X}_0 + n\mathbf{X}_+ + o(|m| + |n|). \tag{3.17}$$

The major part of our proof consists of showing that for an appropriately chosen region with the two critical points on its boundary there is a family of trajectories on **U** near (1, 0, 0) inside this region such that at least one member of this family meets the critical point at the origin. We use a continuity argument.

Let R be the closed region defined by

$$R=\{(c,u,w)\colon 0\leqq c\leqq 1,\ -\gamma\leqq w\leqq g(c)-f(c),\ 0\leqq u\},\tag{3.18}$$

where γ is any positive constant. A sketch of the region R is given in Fig. 4. We first show that for large enough wave speeds a, solutions of (3.7) which start inside R on **U** near (1, 0, 0) satisfy $u<\mu c(1-c)$ so long as they remain inside R. Here μ is a positive constant.

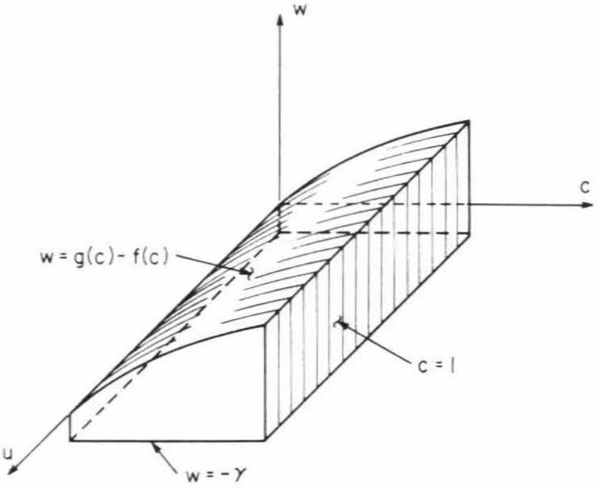

FIG. 4

Suppose that at $\xi=0$ we have a solution u such that

$$0<u<\mu c(1-c),\quad 0<c<1,\quad -\gamma<w<g(c)-f(c).\tag{3.19}$$

Then either (3.19) is satisfied for all $\xi\geqq 0$ which is what we want, or there exists a $\xi=s>0$ such that the trajectory touches or tries to cross the cylinder $u=\mu c(1-c)$ or leaves R through its boundary. If the trajectory stays in R, we must show that it cannot touch or cross $u=\mu c(1-c)$. If it does, at $\xi=s$ we have

$$u=\mu c(1-c),\quad 0<c<1,\quad -\gamma\leqq w\leqq g(c)-f(c).\tag{3.20}$$

We will show that $\mu>0$ can be chosen to contradict (3.20). Since $dc/d\xi=-u$, then c is monotonically decreasing for $\xi\in[0,s)$. Thus, in order for the trajectory to reach the cylinder $u=\mu c(1-c)$ at $\xi=s$, the slope du/dc of this trajectory must be less than the slope $(d/dc)[\mu c(1-c)]$ of the cylinder at $\xi=s$. This implies that at $\xi=s$

$$\frac{du}{d\xi}\geqq\frac{d}{d\xi}[\mu c(1-c)]=\mu(2c-1)u.\tag{3.21}$$

Upon combining (3.20), (3.21), and (3.7), we obtain

$$[(g(c)-w)(2c-1)-f'(c)c(1-c)]\mu^2+\left[a-\frac{w\beta(c)}{a}\right]\mu-1\leqq 0.\tag{3.22}$$

Clearly, for any $\mu > 0$ we can choose a value of a sufficiently large such that inequality (3.22) is violated. We now choose μ sufficiently large so that some part of the manifold $\mathbf{U}$ of (3.17) is contained in the new region W defined by

$$W \equiv \{(c, u, w): 0 \leqq c \leqq 1, 0 \leqq u \leqq \mu c(1-c), -\gamma \leqq w \leqq g(c) - f(c)\}. \tag{3.23}$$

A sketch of the region W is given in Fig. 5. A study of the derivatives of c, u, and w given by (3.7) shows that at some points on the boundary of W trajectories are leaving W. This leads us to define the immediate exit set W^- of W. W^- consists of the set of points in W where solutions of (3.7) immediately leave. More precisely, if $\mathbf{Y}_0 \equiv (c_0, u_0, w_0)$ is an initial value on the boundary ∂W of W for (3.7) and if $\mathbf{Y}(\xi, \mathbf{Y}_0)$ is the corresponding solution, then

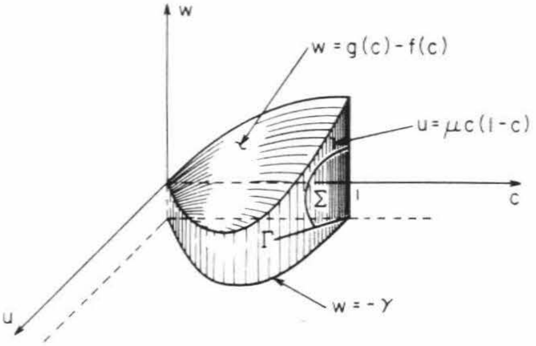

FIG. 5

$$W^- \equiv \{\mathbf{Y}_0 \in \partial W: \mathbf{Y}(\xi, \mathbf{Y}_0) \notin W \text{ for any } \xi \in (0, \xi_0), \text{ for some } \xi_0 > 0\} \tag{3.24}$$

The behavior of trajectories near the boundary of W is summarized in Table 1.

TABLE 1
Behavior of trajectories near the boundary of W.

Faces		
$u = 0$	$\dot{u} > 0$	enter W
$w = g(c) - f(c)$	$\frac{dw}{dc} < \frac{d}{dc}[g(c) - f(c)], \dot{c} < 0$	leave W
$u = \mu c(1-c)$	$\frac{du}{dc} > \mu \frac{d}{dc}[c(1-c)], \dot{c} < 0$	enter W
$w = -\gamma$	$\dot{w} < 0$	leave W
Edges		
$c = 1, u = 0$	$\dot{c} = 0, \dot{u} = 0$	stay on this line
$w = g(c) - f(c), u = 0$	$\dot{w} > 0, \dot{c} = 0$	leave W
$w = g(c) - f(c), u = \mu c(1-c)$	$\frac{dw}{dc} < \frac{d}{dc}(g(c) - f(c)), \dot{c} < 0$	leave W
$w = -\gamma, u = \mu c(1-c)$	$\dot{w} < 0$	leave W
$c = 0, u = 0$	$\dot{c} = 0, \dot{u} = 0$	stay on this line
$w = -\gamma, u = 0$	$\dot{w} < 0$	leave W
Corners		
$c = 1, u = 0, w = -\gamma$	$\dot{w} < 0$	leave W
$c = 1, u = 0, w = g(1) - f(1)$	$\dot{c} = 0, \dot{w} > 0, \dot{u} = 0$	leave W
$c = 0, u = 0, w = 0$		critical point
$c = 0, u = 0, w = -\gamma$	$\dot{w} < 0$	leave W

We can take γ small enough so that the two-dimensional manifold $\mathbf{U}$ of (3.17) intersects the plane $w = -\gamma$ near $(1, 0, 0)$ in a curve Γ. Since the trajectory $c = 1$, $u = 0$ is on $\mathbf{U}$ and is represented by taking $n = 0$ in (3.17), a circle of sufficiently small radius on $\mathbf{U}$ about $(1, 0, 0)$ will intersect both the curve Γ and the line $c = 1$, $u = 0$. Define Σ as the part of this circle which lies in W and has one endpoint on Γ and the other endpoint on a trajectory with $c < 1$ which exits W through the face $w = g(c) - f(c)$.

We shall show that there is a solution of (3.7) starting on Σ which stays inside W until $c = 0$ and thus terminates in the critical point at $(0, 0, 0)$ as $\xi \to \infty$. This is accomplished by showing that a condition in the following theorem of Wazewski is violated:

WAZEWSKI'S THEOREM. *Consider the differential equation*

$$\frac{dy}{dt} = F(y), \quad y \in \mathbb{R}^n, \tag{3.25}$$

where $F(y)\colon \mathbb{R}^n \to \mathbb{R}^n$ *is continuous and satisfies a Lipschitz condition. Let* $y(t; y_0)$ *be the unique solution of* (3.25) *satisfying* $y(0; y_0) = y_0$. *Given* $W \subseteq \mathbb{R}^n$, *let* W^- *denote the immediate exit set of* W. *For* $\Sigma \subseteq W$ *define* Σ^0 *to be those points* $y_0 \in \Sigma$ *where* $y(t; y_0)$ *is not in* W *for some finite* $t > 0$. *For* $y_0 \in \Sigma^0$, *define* $T(y_0) = \sup\{t\colon y(\tau; y_0) \subseteq W \text{ for all } \tau \in [0, t]\}$. $T(y_0)$ *is the exit time for a solution of* (3.25) *starting at* y_0. *Suppose that*

(i) *If* $y_0 \in \Sigma$ *and* $y(t; y_0) \subseteq$ *the closure of* W, *then* $y(t; y_0) \subseteq W$.

(ii) *If* $y_0 \in \Sigma$ *and* $y(t; y_0)$ *is in* W *but not in* W^-, *then there is an open set in* W *about* $y(t; y_0)$ *which is disjoint from* W^-.

(iii) $\Sigma = \Sigma^0$, Σ *is compact and intersects any trajectory of* (3.25) *at most once.*

Then, the mapping $y(T(y_0); y_0)$ *from* Σ *to its image on* W^- *is one-to-one, continuous, and has a continuous inverse.*

This version of Wazewski's theorem is due to Dunbar [18] who used it in a similar way.

Roughly speaking, the theorem says that, if hypotheses (i) and (ii) are satisfied, and if all trajectories through Σ exit W in finite time, then the image Σ^- of these trajectories on the exit set W^- is a continuous curve. From the definition of Σ we know that the trajectory through one endpoint exits W through the face $w = g(c) - f(c)$ while the trajectory through the other endpoint exits W through the face $w = -\gamma$. Since these two faces are disjoint in the exit set W^-, the curve Σ^- cannot be continuous. Thus, if we show that hypotheses (i) and (ii) are satisfied, we can conclude that there must exist a trajectory through Σ on which it takes infinite time to reach the boundary. Since c is monotonically decreasing, this curve must approach the other critical point at $(0, 0, 0)$ as $\xi \to \infty$.

Since W is closed, condition (i) is satisfied trivially. To show that condition (ii) is satisfied we must show that no trajectory crossing Σ can reach that part of the boundary of W which is not in W^- in finite time. Referring to Table 1, we see that the part of the boundary of W which is not in W^- contains

(i) both critical points, $(0, 0, 0)$ and $(1, 0, 0)$,

(ii) the trajectories along $c = 1$, $u = 0$ and along $c = 0$, $u = 0$,

(iii) the faces $u = 0$ and $u = \mu c(1 - c)$.

No trajectory can reach a critical point in finite time, nor do trajectories intersect away from critical points. This implies that, since Σ does not contain any point on the lines $c = 1$, $u = 0$ and $c = 0$, $u = 0$, no trajectory crossing Σ can reach these lines in finite time. Trajectories are entering W on the faces $u = 0$ and $u = \mu c(1 - c)$ so that no trajectory can approach them from inside. Thus, a solution of (3.7) with initial value on Σ is in the interior of W until it reaches W^-, and condition (ii) holds.

We have shown that the conclusion of Wazewski's theorem does not hold, yet conditions (i) and (ii) do hold. It must be, therefore, that condition (iii) does not hold. Since Σ is compact, and trajectories intersect it at most once, then $\Sigma \neq \Sigma^0$. Thus, there is at least one trajectory crossing Σ which never leaves W. From the previous paragraph, this trajectory remains in the interior of W for all finite time. So $u > 0$ and (3.7) imply that c is monotonically decreasing, and this trajectory must approach the origin.

We conclude that for large enough values of the wavespeed a, there is always at least one trajectory of (3.7) going from the critical point at $(1, 0, 0)$ to the critical point at the origin. This connecting trajectory is a traveling wave front solution of (3.2)–(3.3).

4. A constructive approximation. In the case where k is small we can construct and prove the convergence of an interative approximation which exhibits the analytic structure of the traveling wave solutions. Furthermore, we need not assume that the wave speed is large. We shall follow the method of Kopell and Howard [19] who also constructed a three-dimensional connector for a similar problem.

Thus, we again consider (2.15), (2.16) with $R(x, t, C, C_t, C_x)$ given by (3.1). Define

$$\varepsilon = \frac{\mu k}{\alpha(k)}, \quad X = \sqrt{\frac{\alpha(k)}{G(k)}}\,x, \quad T = \alpha(k)t,$$
$$V = \frac{\mu(C-k)}{\alpha(k)}, \qquad W = \frac{G(C)-D}{G(k)}, \tag{4.1}$$

so that (2.15), (2.16), (3.1) become

$$V_T = [(\Gamma(V) - W)V_X]_X - V(V+\varepsilon), \tag{4.2}$$

$$W_T = H(V)V_T - B(V)W, \tag{4.3}$$

where

$$\Gamma(V) = \frac{G(C)}{G(k)}, \quad H(V) = \frac{d}{dV}\left[\frac{G(C)-F(C)}{G(k)}\right], \quad B(V) = \frac{\alpha(C)}{\alpha(k)}. \tag{4.4}$$

We seek nonnegative traveling wave solutions of (4.2), (4.3) assuming only that $\alpha(0) > 0$ and $F(0) = G(0)$. Thus, assume that

$$V(X, T) = V(s), \qquad W(X, T) = W(s), \tag{4.5}$$

where

$$s = X + AT. \tag{4.6}$$

Note that $A = (\sqrt{G(0)\varepsilon/G(k)})a$, where a is the velocity of § 3. Define $U = dV/ds$, and then (4.2), (4.3) become

$$\frac{dV}{ds} = U,$$
$$\frac{d}{ds}[(\Gamma(V) - W)U] = AU + V(V+\varepsilon), \tag{4.7}$$
$$\frac{dW}{ds} = H(V)U - \frac{B(V)W}{A}.$$

This system has two critical points at

$$(V, U, W) = (0, 0, 0) \quad \text{and} \quad (V, U, W) = (-\varepsilon, 0, 0),$$

and as $\varepsilon \to 0$, the two critical points coalesce.

With the change of variables

$$\begin{aligned} &U = \varepsilon^2 Z_2, && W = \frac{\varepsilon^2 H(0) Z_2}{A + 1/A} + \varepsilon^2 Z_3, \\ &V = \varepsilon Z_1 + \frac{\varepsilon^2 Z_2}{A}, && t = \frac{\varepsilon s}{A}, \end{aligned} \tag{4.8}$$

the system (4.7) becomes

$$\begin{aligned} &\frac{dZ_1}{dt} = -Z_1(1+Z_1) - \frac{\varepsilon}{A}\left[\phi - \frac{d\psi}{dt}\right], \\ &\varepsilon \frac{dZ_2}{dt} = A^2 Z_2 + A Z_1(1+Z_1) + \varepsilon\left[\phi - \frac{d\psi}{dt}\right], \\ &\varepsilon \frac{dZ_3}{dt} = AH(V)Z_2 - B(V)Z_3 - \varepsilon \frac{AH(0)}{A^2+1}\frac{dZ_2}{dt} - \frac{AH(0)B(V)}{A^2+1} Z_2, \end{aligned} \tag{4.9}$$

where

$$\begin{aligned} &\phi = Z_2\left(1 + 2Z_1 + \frac{\varepsilon}{A} Z_2\right), \\ &\psi = Z_2\left[\Gamma(V) - \Gamma(0) - \varepsilon^2 \frac{AH(0)Z_2}{A^2+1} - \varepsilon^2 Z_3\right]. \end{aligned} \tag{4.10}$$

If $\varepsilon = 0$, the solution of (4.9) is given by

$$\begin{aligned} &Z_1 = \frac{1}{2}\left(\tanh\frac{t}{2} - 1\right), \\ &Z_2 = \frac{1}{4A}\operatorname{sech}^2\frac{t}{2}, \\ &Z_3 = \frac{A^2 H(0)}{\cancel{4}(A^2+1)}\operatorname{sech}^2\frac{t}{2}, \end{aligned} \tag{4.11}$$

where we have chosen the constant of integration so that $Z_1(0) = \frac{1}{2}$. The vector (Z_1, Z_2, Z_3) of (4.11) is the lowest order approximation to the trajectory we are seeking; it has the typical hyperbolic tangent structure describing the transition between two states.

Define $\eta(t)$ by

$$Z_1 = \frac{1}{2}\left(\tanh\frac{t}{2} - 1\right) + \varepsilon\eta(t). \tag{4.12}$$

System (4.9) is then equivalent to

$$\eta(t)=\frac{1}{A}\psi(t)+\left(\operatorname{sech}^2\frac{t}{2}\right)\left\{\frac{-1}{A}\psi(0)-\int_0^t\left[\left(\cosh^2\frac{s}{2}\right)\left(\varepsilon\ \eta^2(s)+\frac{\phi(s)}{A}\right)+\frac{1}{2A}\psi(s)\sinh s\right]ds\right\},$$

(4.13)

$$Z_2(t)=-\psi(t)+\frac{A}{\varepsilon}\int_t^\infty e^{A^2(t-s)/\varepsilon}\left[\frac{1}{4}\operatorname{sech}^2\frac{s}{2}+\rho(s)\right]ds,$$

$$Z_3(t)=\frac{AH(0)}{A^2+1}\psi(t)+\frac{1}{\varepsilon}\int_{-\infty}^t e^{(s-t)/\varepsilon}\left[\frac{A^2H(0)}{4(A^2+1)}\operatorname{sech}^2\frac{s}{2}+\Omega(s)\right]ds,$$

where

$$\rho(t)=A\psi(t)-\varepsilon\eta(t)\left[\tanh\frac{t}{2}+\varepsilon\eta(t)\right]-\frac{\epsilon\phi}{A}, \tag{4.14}$$

$$\Omega(t)=[(H(V)-H(0))(A^2+1)-H(0)(B(V)-1)]\frac{A}{A^2+1}Z_2$$

(4.15)

$$-[B(V)-B(0)]Z_3\qquad -\frac{AH(0)}{A^2+1}\left[\psi(t)+\varepsilon\phi+A\varepsilon\eta\left(\tanh\frac{t}{2}+\varepsilon\eta\right)\right]$$

Equations (4.13) form the basis for the following iteration scheme:

$$\eta^{(0)}(t)\equiv 0,$$

(4.16)

$$Z_2^{(0)}(t)=\frac{A}{4}\int_0^\infty e^{-A^2\theta}\operatorname{sech}^2\left(\frac{t+\varepsilon\theta}{2}\right)d\theta,$$

$$Z_3^{(0)}(t)=\frac{A^2H(0)}{4(A^2+1)}\int_{-\infty}^0 e^{\theta}\operatorname{sech}^2\left(\frac{t+\varepsilon\theta}{2}\right)d\theta,$$

$$\eta^{(n+1)}(t)=\frac{1}{A}\psi^{(n)}(t)-\left(\operatorname{sech}^2\frac{t}{s}\right)\left\{\frac{1}{A}\psi^{(n)}(0)+\int_0^t\left[\left(\cosh^2\frac{s}{2}\right)\left(\frac{\phi^{(n)}(s)}{A}+\varepsilon(\eta^{(n)}(s))^2\right)\right.\right.$$

(4.17)

$$\left.\left.+\frac{1}{2A}\psi^{(n)}(s)\sinh s\right]ds\right\},$$

$$Z_2^{(n+1)}(t)=Z_2^{(0)}(t)-\psi^{(n)}(t)+A\int_0^\infty e^{-A^2\theta}\rho^{(n)}(t+\varepsilon\theta)\,d\theta,$$

$$Z_3^{(n+1)}(t)=Z_3^{(0)}(t)+\frac{AH(0)}{A^2+1}\psi^{(n)}(t)+\int_{-\infty}^0 e^{\theta}\Omega^{(n)}(s+\varepsilon\theta)\,d\theta.$$

We will show that as $n\to\infty$, the iterates $(\eta^{(n)}(t), Z_2^{(n)}(t), Z_3^{(n)}(t))$ converge to a solution of (4.13) when ε is small and $|A|\gg\varepsilon^{1/3}$ and that this solution approaches the point $(\eta, Z_2, Z_3)=(0, 0, 0)$ as $t\to\pm\infty$.

First, we show that each iterate is bounded for ε sufficiently small and $|A|\gg\varepsilon^{1/3}$. Since $0<\operatorname{sech}^2(t/2)<1$,

$$|\eta^{(0)}(t)|=0,\quad |Z_2^{(0)}(t)|<\frac{1}{4A}<L,\quad |Z_3^{(0)}(t)|<\frac{A^2H(0)}{4(A^2+1)}<M, \tag{4.18}$$

where L and M simply denote upper bounds for $|Z_2^{(0)}(t)|$ and $|Z_3^{(0)}(t)|$, respectively. Now, (4.10) and (4.12) imply that

$$\phi(t) = Z_2 \tanh\frac{t}{2} + \varepsilon Z_2\left(\eta + \frac{1}{A}Z_2\right), \tag{4.19}$$

so that if $|Z_2(t)| < 2L$, then

$$\left|\operatorname{sech}^2\frac{t}{2}\int_0^t Z_2(s)\tanh\frac{s}{2}\cosh^2\frac{s}{2}\,ds\right| < 2L. \tag{4.20}$$

Furthermore, since $\Gamma(V)$, $H(V)$ and $B(V)$ are analytic near $V(0)$, then (4.8), (4.10) and (4.15) imply that

$$\psi(t) = \varepsilon\Gamma'(0)Z_1Z_2 + O(\varepsilon^2),$$

$$\Omega(t) = \varepsilon\left\{[H'(0)(A^2+1) - H(0)(B'(0) - \Gamma'(0))]\frac{AZ_2}{A^2+1} - B'(0)Z_3\right\}Z_1 + O(\varepsilon^2), \tag{4.21}$$

$$\rho(t) = \varepsilon A\Gamma'(0)Z_1Z_2 - \varepsilon\eta(t)\tanh\frac{t}{2} + O(\varepsilon^2).$$

$$\wedge\ -\varepsilon Z_2 \tanh t/2$$

Let ε be sufficiently small such that if $|\eta| < 4L/A$, $|Z_2| < 2L$ and $|Z_3| < 2M$ for all t, then

$$\begin{aligned}&\left|\frac{1}{A}\psi(t) - \left(\operatorname{sech}^2\frac{t}{2}\right)\right.\\ &\quad\cdot\left\{\frac{1}{A}\psi(0) + \int_0^t\left[\left(\cosh^2\frac{s}{2}\right)\left(\frac{\varepsilon}{A}Z_2(s)\left(\eta(s) + \frac{1}{A}Z_2(s)\right) + \varepsilon\ \eta^2(s)\right)\right.\right.\\ &\qquad\left.\left.\left. + \frac{1}{2A}\psi(s)\sinh s\right]ds\right\}\right| < \frac{2L}{A},\end{aligned} \tag{4.22}$$

$$\left|\psi(t) - A\int_0^\infty e^{-A^2\theta}\rho(t+\varepsilon\theta)\,d\theta\right| < L,$$

$$\left|\frac{AH(0)}{A^2+1}\psi(t) + \int_{-\infty}^0 e^\theta\Omega(s+\varepsilon\theta)\,d\theta\right| < M.$$

Then, $|\eta^{(0)}(t)| = 0 < 4L/A$, $|Z_2^{(0)}(t)| < 2L$, $|Z_3^{(0)}(t)| < 2M$, and (4.18), (4.20) and (4.22) imply that

$$|\eta^{(n)}(t)| < \frac{4L}{A}, \quad |Z_2^{(n)}(t)| < 2L, \quad |Z_3^{(n)}(t)| < 2M, \tag{4.23}$$

so that the iterates are uniformly bounded.

Using the uniform bounds, we next show that each iterate tends to zero as $t \to \pm\infty$. We present only the calculation for $t \to -\infty$; the case $t \to +\infty$ is similar. We need the preliminary result that if $\mathscr{F}(t)$ is bounded for all t, and if $\mathscr{F}(t) \sim bt^k e^t$ as $t \to -\infty$, where

b is a constant and $k>0$, then as $t \to -\infty$

$$\int_0^{\infty} e^{-A^2\theta}\mathcal{F}(t+\varepsilon\theta)\,d\theta \sim \frac{b}{A^2-\varepsilon} t^k e^k, \tag{4.24}$$

$$\int_t^0 \mathcal{F}(t)\sinh t\,dt \sim \frac{-b}{2(k+1)} t^{k+1}, \tag{4.25}$$

$$\int_t^0 \mathcal{F}(t)\cosh t\,dt \sim \frac{b}{2(k+1)} t^{k+1}, \tag{4.26}$$

$$\int_t^0 \mathcal{F}(t)\,dt \sim bt^k e^t, \tag{4.27}$$

$$\int_{-\infty}^0 e^{\theta}\mathcal{F}(t+\varepsilon\theta)\,d\theta \sim \frac{bt^k e^t}{1+\varepsilon}. \tag{4.28}$$

Note that (4.24) is valid only if $A^2>\varepsilon$; the integral is unbounded if $A^2 \leqq \varepsilon$. Using (4.24)–(4.28) and the fact that $\operatorname{sech}^2(t/2) \sim 4e^t$ as $t \to -\infty$, we find immediately that as $t \to -\infty$,

$$\eta^{(0)}(t) \sim 0, \quad Z_2^{(0)}(t) \sim \frac{A}{A^2-\varepsilon} e^t, \quad Z_3^{(0)}(t) \sim \frac{A^2H(0)}{(1+\varepsilon)(A^2+1)} e^t. \tag{4.29}$$

Then, using (4.29) in (4.17), we obtain that as $t \to -\infty$,

$$\begin{aligned} &\eta^{(1)}(t) \sim \frac{-\Gamma(-\varepsilon)}{A^2-\varepsilon} t e^t, \\ &Z_2^{(1)}(t) \sim \frac{A}{(A^2-\varepsilon)^2}[A^2-\varepsilon\Gamma(-\varepsilon)]e^t, \\ &Z_3^{(1)}(t) \sim A\left[\frac{AH(0)}{(A^2+1)H(0)} + O(\varepsilon)\right]e^t. \end{aligned} \tag{4.30}$$

By induction it can then be shown that as $t \to -\infty$

$$\begin{aligned} &\eta^{(n+1)}(t) \sim (\text{constant})\frac{\varepsilon^{2n}t^{n+1}e^t}{(n+1)!}, \\ &Z_2^{(n+1)}(t) \sim (\text{constant})\frac{\varepsilon^{2n+1}t^n e^t}{n!}, \\ &Z_3^{(n+1)}(t) \sim (\text{constant})\frac{\varepsilon^{2n-2}t^{n-1}e^t}{(n-1)!}. \end{aligned} \tag{4.31}$$

Therefore, $(Z_1^{(n)}(t), Z_2^{(n)}(t), Z_3^{(n)}(t))$ approaches the critical point $(-1, 0, 0)$ as $t \to -\infty$. In a similar manner we obtain that these iterates tend to the other critical point $(1, 0, 0)$ as $t \to +\infty$.

Finally, we show that the iterates converge to a solution of (4.13) for ε sufficiently small and $|A| \gg \varepsilon^{1/3}$. Define the norm

$$\|\chi(t)\| \equiv \sup_{-\infty<t<\infty} |\chi(t)|. \tag{4.32}$$

Then,

$$\begin{aligned}\|\eta^{(n+1)}-\eta^{(n)}\| &< \left(\frac{1}{A}+\frac{6\varepsilon L}{A^2}\right)\|Z_2^{(n)}-Z_2^{(n-1)}\| \\ &\quad +\frac{\varepsilon}{A}[6\varepsilon^2 L\|\eta^{(n)}-\eta^{(n-1)}\|+d_{12}\|Z_2^{(n)}-Z_2^{(n-1)}\|+6L\|Z_2^{(n)}-Z_3^{(n-1)}\|],\end{aligned} \tag{4.33}$$

$$\begin{aligned}\|Z_2^{(n+1)}-Z_2^{(n)}\| &< \frac{8\varepsilon L}{A}\|\eta^{(n)}-\eta^{(n-1)}\| \\ &\quad +\varepsilon[d_{21}\|\eta^{(n)}-\eta^{(n-1)}\|+d_{22}\|Z_2^{(n)}-Z_2^{(n-1)}\|+4L\|Z_3^{(n)}-Z_3^{(n-1)}\|],\end{aligned} \tag{4.34}$$

$$\|Z_3^{(n+1)}-Z_3^{(n)}\| < \varepsilon[d_{31}\|\eta^{(n)}-\eta^{(n-1)}\|+d_{32}\|Z_2^{(n)}-Z_2^{(n-1)}\|+d_{33}\|Z_3^{(n)}-Z_3^{(n-1)}\|]. \tag{4.35}$$

Here the d_{ij} are constants which are $O(1)$ in both A and ε. If we iterate once on the index, the resulting relations are

$$\begin{aligned}\|\eta^{(n+1)}-\eta^{(n)}\| &< \frac{8\varepsilon L}{A^2}\left(1+\frac{6\varepsilon L}{A}\right)\|\eta^{(n-1)}-\eta^{(n-2)}\|+\frac{6\varepsilon^3 L}{A^2}\|Z_2^{(n-1)}-Z_2^{(n-2)}\| \\ &\quad +\frac{\varepsilon}{A}(C_{11}\|\eta^{(n-1)}-\eta^{(n-2)}\|+C_{12}\|Z_2^{(n-1)}-Z_2^{(n-2)}\| \\ &\quad +C_{13}\|Z_3^{(n-1)}-Z_3^{(n-2)}\|),\end{aligned} \tag{4.36}$$

$$\begin{aligned}\|Z_2^{(n+1)}-Z_2^{(n)}\| &< \left\{\frac{8\varepsilon L}{A^2}\left(1+\frac{6\varepsilon L}{A}+\frac{\varepsilon}{A}d_{12}\right)+\frac{\varepsilon}{A}C_{22}\right\}\|Z_2^{(n-1)}-Z_2^{(n-2)}\| \\ &\quad +\frac{\varepsilon^2 L}{A}C_{21}\|\eta^{(n-1)}-\eta^{(n-2)}\|+\left(\frac{\varepsilon L}{A}\right)^2 C_{23}\|Z_3^{(n-1)}-Z_3^{(n-2)}\|,\end{aligned} \tag{4.37}$$

$$\begin{aligned}\|Z_3^{(n+1)}-Z_3^{(n)}\| &< \frac{\varepsilon}{A}d_{31}\|Z_2^{(n-1)}-Z_2^{(n-2)}\| \\ &\quad +\frac{\varepsilon^2}{A}\{C_{31}\|\eta^{(n-1)}-\eta^{(n-2)}\|+C_{32}\|Z_2^{(n-1)}-Z_2^{(n-2)}\| \\ &\quad +C_{33}\|Z_3^{(n-1)}-Z_3^{(n-2)}\|\},\end{aligned} \tag{4.38}$$

where c_{ij} are $O(1)$ constants.

Now, let

$$\mathbf{y}(t)=\begin{pmatrix}\eta(t)\\ Z_2(t)\\ Z_3(t)\end{pmatrix}, \tag{4.39}$$

and define

$$\|\mathbf{y}\|_0 \equiv \max\{\|\eta\|, \|Z_2\|, \|Z_3\|\}. \tag{4.40}$$

If $|A| \gg \varepsilon^{1/3}$, we can take $L \ll \varepsilon^{-1/3}$, so that $\varepsilon L/A^2$ is small if ε is small. Then, by inspection

$$\|\mathbf{y}^{(n+1)}-\mathbf{y}^{(n)}\|_0 < \left[\left(\frac{8\varepsilon L}{A^2}\right)\left(1+\frac{6\varepsilon L}{A}\right)+O\left(\frac{\varepsilon}{A}, \left(\frac{\varepsilon L}{A}\right)^2\right)\right]\|\mathbf{y}^{(n-1)}-\mathbf{y}^{(n-2)}\|_0. \tag{4.41}$$

Thus, for ε sufficiently small,

$$\|\mathbf{y}^{(2n+1)}-\mathbf{y}^{(2n)}\|<\alpha\|\mathbf{y}^{(2n-1)}-\mathbf{y}^{(2n-2)}\|, \tag{4.42}$$

and

$$\|\mathbf{y}^{(2n+2)}-\mathbf{y}^{(2n+1)}\|<\alpha\|\mathbf{y}^{(2n)}-\mathbf{y}^{(2n-1)}\|, \tag{4.43}$$

where $0<\alpha<1$. By the usual contraction mapping arguments, our sequence converges to a solution of (4.13).

5. The penetrant front. A crude but effective way to determine the behavior of the progressing penetrant front due to the type of diffusion given by (1.1), (1.2) is to employ an integral averaging method (commonly called the Karman–Pohlhausen method). A description of the method for problems in fluid mechanics together with a bibliography may be found in Schlichting [20]. An excellent more modern account of the method together with extensive references and applications to problems in heat transfer is given by Goodman [21].

We introduce the quantity $\delta(t)$ called the penetration distance (or propagating concentration front). For $x>\delta(t)$ the polymer is at its equilibrium (i.e., initial) concentration, and there is no flux transferred beyond $x=\delta(t)$. Thus,

$$C=0 \quad \text{at } x=\delta(t), \tag{5.1}$$

$$DC_x=0 \quad \text{at } x=\delta(t). \tag{5.2}$$

It is important to note that for our problem the "signal speed" is infinite. That is, solutions have a finite value for all x for all positive t for any initial or boundary data. This is a consequence of the fact that the characteristic surfaces for parabolic equations are parallel to the spatial axes. For practical purposes and often as a basis for sophisticated approximation techniques one defines a diffusion front as the locus of points moving with a given concentration. Clearly, on our problem we proceed in the standard way to take the concentration field $C(x, t)$ to be zero for $x>\delta(t)$ *to within the accuracy of the approximation* or equivalently we define the front to be the locus of a given (presumably small) concentration.

To assess the effect of our diffusive operator we consider

$$C_t=(DC_x)_x, \qquad x>0, \quad t>0, \tag{5.3}$$

$$D_t=F'(C)C_t+\alpha(C)[G(C)-D], \qquad x>0, \quad t>0, \tag{5.4}$$

$$C(0, t)=C_0, \qquad t\geqq 0, \tag{5.5}$$

$$C(x, 0)=0, \qquad x>0. \tag{5.6}$$

Here C_0 is a prescribed constant. The kinetic term R and variable boundary data can be incorporated, but this complicates the algebra without adding anything essential to our study. We will comment on this later.

Upon integrating (5.3) with respect to x from 0 to $\delta(t)$, and making use of (5.2), we obtain

$$\int_0^{\delta(t)} C_t\,dx=-[DC_x]|_{x=0}. \tag{5.7}$$

We now assume that $C(x, t)$ can be approximated by an Nth degree polynomial in x

with time-dependent coefficients. This approximation is required to satisfy the boundary condition (5.5) and the conditions (5.1) and (5.2) at the front $x=\delta(t)$. Thus,

$$C(x,t)=C_0\sum_{n=2}^{N}k_n\left[1-\frac{x}{\delta(t)}\right]^n \tag{5.8}$$

where

$$\sum_{n=2}^{N}k_n=1. \tag{5.9}$$

By differentiation in (5.3) it is possible (21) to derive $(N-2)$ conditions which the constants $k_n (n=2,\cdots,N)$ must satisfy in addition to (5.9). We thus obtain $(N-1)$ equations in $(N-1)$ unknowns for the k_n. We shall not need that information here.

We now find $\delta(t)$ by requiring (5.2) to be an approximation in the sense that (5.7) is satisfied. Upon substituting (5.8) into (5.7), we obtain

$$\lambda\frac{d\delta}{dt}-\frac{\nu D(0,t)}{\delta}=0 \tag{5.10}$$

where

$$\lambda=\sum_{n=2}^{N}\frac{k_n}{n+1},\qquad \nu=\sum_{n=2}^{N}nk_n. \tag{5.11}$$

The boundary condition (5.5) implies that $C_t(0,t)=0$. Thus, upon evaluating (5.4) at $x=0$, we obtain

$$D_t(0,t)+\alpha_0 D(0,t)=G_0, \tag{5.12}$$

where

$$\alpha_0=\alpha(C_0),\qquad G_0=G(C_0). \tag{5.13}$$

Thus,

$$D(0,t)=G_0+(F_0-G_0)\,e^{-\alpha_0 t}, \tag{5.14}$$

where $F_0=D(0,0)=F(C_0)$. Therefore, (5.10) and (5.14) yield the following equation for the motion of the penetrant front:

$$\lambda\frac{d\delta}{dt}-\frac{\nu[G_0+(F_0-G_0)\,e^{-\alpha_0 t}]}{\delta}=0, \tag{5.15}$$

the exact solution of which (satisfying $\delta(0)=0$) is

$$\delta^2(t)=\frac{\nu}{\lambda}G_0t-\frac{\nu}{\lambda\alpha_0}(F_0-G_0)\,e^{-\alpha_0 t}+\frac{\nu}{\lambda\alpha_0}(F_0-G_0). \tag{5.16}$$

Clearly,

$$\delta^2(t)\sim\frac{\nu}{\lambda}F_0t\quad\text{for small } t, \tag{5.17}$$

$$\delta^2(t)\sim\frac{\nu}{\lambda}G_0t+\frac{\nu}{\lambda\alpha_0}(F_0-G_0)\quad\text{for large } t. \tag{5.18}$$

Thus, (5.15) describes the motion of the penetrant front $x=\delta(t)$ and yields the transition (i.e., the sigmoid sorption curve) from the instantaneous diffusivity F_0 to the equilibrium diffusivity G_0. Retaining the kinetic term R in our problem (5.3)–(5.6) requires no changes in our procedure. We obtain instead of (5.15) a more complicated first order equation which possesses the asymptotic solution (5.17), (5.18).

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PART II

1. Introduction. In Part I of this thesis we dealt with one aspect of the diffusion of liquids and gases in glassy polymers, dual sorption. In this part we turn to another question, that of the swelling and stresses which are diffusion induced. In the following sections, we develop a model of the penetration process, using the concepts and postulates of continuum irreversible thermodynamics; presumably it could be obtained by other means. The reader unfamiliar with the subject of irreversible thermodynamics is referred to Callen [1], deGroot and Mazur [2], Prigogine and Defay [3] and Prigogine [4].

As in Part I, we consider that the slow internal relaxations, which cause the polymer properties to be history-dependent, are an important characteristic of glassy polymers which must be included in any model. The model that we obtain will be a rather general set of equations, in three dimensions, containing integrals over the past history of the material, with nonlinear kernels which will need to be determined from some knowledge of the materials themselves. In the final section of this part, we discuss a simplified version of the model in the context of one-dimensional Case II diffusion and propose that this model be studied further.

a. Review of existing models. Swelling and stresses are most dramatic in the fluid-polymer system when conditions are right for Case II diffusion to occur, differential stresses becoming so large that crazing and fracturing may occur [5],[6]. Most of the existing models are therefore aimed directly at either explaining or predicting this phenomenon, which is described in the overview of this thesis. All are one-dimensional, and most are attempts to patch an effect onto the Fickian diffusion equations. A fairly inclusive discussion of models proposed before 1979 is given by Thomas and Windle [7], and we shall not discuss in detail all of the models that they mention.

The most simplistic models, and the least satisfactory from an explanatory standpoint, are those which impose a discontinuity moving with constant velocity, with [5] or without [8] swelling behind the front. They do ensure that Case II behavior is roughly modelled, which some other models do not, but they are not capable of explaining or predicting the subtleties of real Case II fronts.

Another approach was inspired by the observation that the wet polymer behind the front is often rubbery; this was taken to imply that a process is occuring at the front, connected with the second order phase transition, which provides energy to drive it along [9],[10]. A later modification takes the process at the front to be due to small crazes. Recently, however, Case II diffusion has been observed when the wet polymer is glassy, and no crazing appears to occur at all [11]. Thus, although it may be that some fronts do follow crazing fronts, this does not seem to be a sufficient explanation.

Frisch, Wang and Kwei [12] proposed that the partial stress on the penetrant may add an extra term to the diffusion equation, and some further work has been done with this model [13]. Their postulate appears to be based on work done by Bearman [14] in order to obtain separate momentum equations, for each substance, in a mixture of Newtonian fluids. Besides the obvious objection that polymers are not Newtonian fluids, neither the concept of a partial stress, nor the formulation of it by Frisch, et. al., has been well received. Thomas and Windle [7], for example, dismiss this model as having no strong physical basis. However one views this, there does not seem to be a real need to introduce partial stresses into the formulation of the problem.

One of the first models which was intended as an explanation for Case II diffusion was proposed by Crank in 1953 [15] and later revived and revised by Petropoulos and Roussis [16]. When Case II diffusion proceeds through a membrane, the area of the membrane stays essentially uniform (and nearly constant) until the front reaches the middle of the sheet. This creates a tension on the central, dry region and a compression on the outer region, which Crank assumed was the driving force behind Case II diffusion. Both models are based on rapidly varying diffusion coefficients which depend on both concentration and stress, and an assumption about how big any given cross-section would be if free to swell. A force balance is obtained by taking the integral over the thickness of the membrane to be zero. Crank assumes a constant area for the surface of the membrane, while the later model allows the area to vary and adds a history-dependent stress-concentration relation (the only model proposed to date which incorporates any memory at all). There is a great deal of sense in these two models; unfortunately, numerical calculations by their authors indicate that they do not describe Case II diffusion, and there is a certain arbitrariness in their choice of assumptions.

More recently, Thomas and Windle have proposed their own model [17]. They assume that the front is being driven by an osmotic pressure difference, which can be expressed in terms of the activity and volume ratio using the relation for an ideal fluid. They also assume that the polymer is a viscous fluid. Their numerical results appear to closely resemble Case II diffusion. Although the assumption of an ideal solution is unrealistic, and they do not include the internal relaxations of the polymer (also the numerical method that they describe is open to question), we shall see that their one-dimensional model is a very reasonable one, and very similar to the one that we shall obtain under the special conditions of Case II diffusion.

A model for the diffusion of particles in elastic solids was proposed by Cahn in the context of pattern formation in metallic alloys [18]. His insights are useful, and a more elaborate model of Larche and Cahn [19] has been picked up by Neogi and Kim [20]. It may be that these models are valid for certain combinations of polymers and solvents in certain temperature and concentration ranges, but (so long as one assumes that the fourth order diffusion terms of Cahn's model are unimportant for the problem at hand,) the effect of adding the elasticity terms is merely to modify the diffusion coefficient and to obtain expressions for the stresses. So this model is not sufficient for our purposes.

Finally, it is worth mentioning attempts that have been made to modify the boundary conditions from the constant concentration condition of Fickian diffusion to a more realistic criterion. Bagley and Long [21] proposed that two-stage sorption is due to a time dependent surface concentration, and there is experimental evidence due to Long and Richman [22] that the surface relaxes exponentially to its final value. Larche and Cahn [19] propose that the proper boundary condition is a constant chemical potential. Due to internal relaxations, both hypotheses may be correct, but this by itself is not a sufficient explanation for Case II diffusion; we shall not attempt to tackle this question in this thesis.

In this thesis, the point of view taken is that a comprehensive model is needed to describe particle diffusion coupled to strain in viscoelastic solids. Such a model should be capable of describing all of the various observations made with respect to diffusion in glassy polymers, although it may be mathematically complex. We do make some simplifying assumptions.

b. Description of the process; assumptions. The process which we shall model is the diffusion of a fluid into an isotropic solid where the mixed fluid-solid region occupies more volume than the initial solid. Temperature variations and gravitational effects are assumed negligible and the solid does not react with or immobilize the fluid particles. Furthermore, deformation gradients are small, allowing us to treat local strains as infinitesimal. The bulk swelling which occurs will be locally isotropic; we assume that the geometry is sufficiently symmetric so that no local rotations are induced and the strain tensor is symmetric. The properties of the solid depend on its history, varying with fluid concentration, internal strains, temperature, etc. We assume that the properties of a uniform sample with fixed temperature, concentration and strains can be uniquely defined by its initial state and a set of internal parameters. These internal parameters, which play the same roles as Maxwell elements in a Wiechart model, describe the twisting, cross-linking, etc. of the polymer chains, and are analogous to the "extent of reaction" parameter (see deGroot and Mazur [2], Prigogine and Defay [4]).

The model will be developed in three steps. We begin by writing down the conservation equations for small deformations. In Section 2, we turn to the thermodynamics of irreversible processes to obtain the linear phenomenological relations which relate the fluxes and affinities. Next we look at the form of the material properties for small deformations and near equilibrium situations, still in the context of irreversible thermodynamics and put the equations together into a system. In the final section of this chapter, we discuss the model as it applies to the particular case of one-dimensional Case II diffusion, showing that the model simplifies when the parameters are in the ranges for which this special behavior is observed.

The derivation as given in Sections 2 and 3 is somewhat simplified in order to leave out unnecessary complications; the generalization is contained in the Appendix. Also, the model obtained in the main sections is more readily understood, and it is this model which is used in Section 4 to discuss the one-dimensional case. The ultimate justification of any model is its ability to describe the physical processes of interest, and we shall attempt to present the model in a transparent manner so that it is obvious what assumptions have been made. As the physical processes involved are understood better experimentally, this should allow the model to be easily refined to better account for such processes.

c. Basic equations: conservation of mass and momentum. The starting point is the equation for conservation of mass,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0 \tag{1.1}$$

plus conservation of the fluid and solid separately

$$\rho \left(\frac{\partial c_f}{\partial t} + \underline{v} \cdot \nabla c_f \right) + \nabla \cdot \underline{J}_f = 0, \tag{1.2}$$

$$c_s = 1 - c_f, \tag{1.3}$$

and the momentum equation in the absence of external forces

$$\rho \left(\frac{\partial \underline{v}}{\partial t} + (\underline{v} \cdot \nabla) \underline{v} \right) + \nabla \cdot (-\hat{\boldsymbol{\sigma}} + \hat{\mathbf{\Pi}}) = 0, \tag{1.4}$$

where

ρ, the total density, is the mass per unit volume of the mixture;

c_f and c_s, the fluid and solid concentrations, respectively, are the mass fractions $\left(c_i = \dfrac{\textit{mass of component } i \textit{ per unit volume}}{\textit{total mass per unit volume}} \right)$;

$\underline{v}_f$ and $\underline{v}_s$ are the fluid and solid velocities, respectively;

$\underline{v}$ is the center-of-mass velocity,

$$\underline{v} = c_f \underline{v}_f + c_s \underline{v}_s; \tag{1.5}$$

$\underline{J}_f$ is the flux of the fluid relative to the center of mass,

$$\underline{J}_f = \rho c_f (\underline{v}_f - \underline{v}); \tag{1.6}$$

$\hat{\boldsymbol{\sigma}}$ is the equilibrium stress tensor;

and $\hat{\boldsymbol{\Pi}}$ is the viscous pressure tensor.

Both $\hat{\boldsymbol{\sigma}}$ and $\hat{\boldsymbol{\Pi}}$ are symmetric:

$$\sigma_{ij} = \sigma_{ji}, \tag{1.7a}$$

and

$$\Pi_{ij} = \Pi_{ji}. \tag{1.7b}$$

d. Deformations: Let $\underline{u}$ be the displacement of the local center of mass, so that if $(\underline{\chi}, \tau)$ are coordinates fixed relative to the local center of mass, then

$$\underline{x} = \underline{\chi} + \underline{u}, \qquad t = \tau \tag{1.8}$$

gives the position in the reference frame of a particle travelling with the local center of mass, initially at $\underline{x} = \underline{\chi}$, with velocity

$$\underline{v} = \frac{\partial \underline{u}}{\partial \tau}. \tag{1.9}$$

Under the assumption of small deformation gradients and no local rotations, the components of the local strain tensor are given by

$$\varepsilon_{ij} := \frac{\partial u_i}{\partial \chi_j} = \frac{\partial u_j}{\partial \chi_i}, \tag{1.10}$$

and the ε_{ij} remain small.

In terms of the ε_{ij} and v_i, the coordinate transformations are given by

$$\begin{aligned} &\frac{\partial x_i}{\partial \chi_j} = \delta_{ij} + \varepsilon_{ij}\,, \frac{\partial t}{\partial \chi_i} = 0, \\ &\frac{\partial x_j}{\partial \tau} = v_j \quad \text{and} \ \frac{\partial t}{\partial \tau} = 1, \end{aligned} \tag{1.11}$$

where δ_{ij} is the Kroneker delta:

$$\delta_{ij} = \begin{bmatrix} 0 & i \neq j \\ 1 & i = j. \end{bmatrix}$$

Inverting (1.11) for small $\hat{\boldsymbol{\varepsilon}}$ and keeping the $O(\|\hat{\boldsymbol{\varepsilon}}\|)$ terms

$$\begin{aligned} &\frac{\partial \chi_i}{\partial x_j} = \delta_{ij} - \varepsilon_{ij}\,, \qquad \frac{\partial \tau}{\partial x_i} = 0 \\ &\frac{\partial \chi_j}{\partial x_j} = -v_j + \sum_i v_i \varepsilon_{ij}\,, \qquad \frac{\partial \tau}{\partial t} = 1. \end{aligned} \tag{1.12}$$

Under the assumption of small center-of-mass strains, the continuity equation (1.1) can be replaced with

$$\rho = \rho_o(1 - \varepsilon + O(\|\hat{\boldsymbol{\varepsilon}}\|^2)), \tag{1.13}$$

where ρ_o is the initial density, the initial strain is taken to be zero, $\|\hat{\boldsymbol{\varepsilon}}\|$ is a measure of the size of the ε_{ij} and

$$\varepsilon := \varepsilon_{\xi\xi} + \varepsilon_{yy} + \varepsilon_{zz} \tag{1.14}$$

is the volume dilation. (An infinitessimal volume which is initially given by ΔV_o becomes $\Delta V = \Delta V_o(1 + \varepsilon)$ after deformation.) Substituting (1.13) into the fluid conservation equation (1.2) and the momentum equation (1.4) and dropping all terms smaller than $\hat{\boldsymbol{\varepsilon}}$:

$$(1 - \varepsilon)\rho_o\left[\frac{\partial c_f}{\partial t} + \underline{v}\cdot\nabla c_f\right] + \nabla\cdot\underline{J_f} = 0, \tag{1.15}$$

and

$$(1-\varepsilon)\rho_o\left[\frac{\partial \underline{v}}{\partial t}+(\underline{v}\cdot\nabla)\underline{v}\right]=\nabla\cdot(\hat{\boldsymbol{\sigma}}-\hat{\boldsymbol{\Pi}}). \tag{1.16}$$

In center-of-mass coordinates these equations are, to first order in $\|\hat{\boldsymbol{\varepsilon}}\|$,

$$\rho_o\frac{\partial c}{\partial \tau}+\nabla\cdot\underline{J_f}=0 \tag{1.17}$$

and

$$\rho_o\frac{\partial \underline{v}}{\partial \tau}=\nabla\cdot(\hat{\boldsymbol{\sigma}}-\hat{\boldsymbol{\Pi}}). \tag{1.18}$$

2. Irreversible Thermodynamics, Entropy Production and the Linear Phenomenological Relations. In this section we obtain expressions for the fluid flux $\underline{J}$, the viscous pressure tensor $\hat{\Pi}$ and for $\frac{\partial \xi}{\partial \tau}$, the rate of change of an internal parameter ξ. These expressions, known as the "linear phenomenological laws", give $\underline{J}$, $\hat{\Pi}$ and $\frac{\partial \xi}{\partial \tau}$ as linear functions of the gradient of the chemical potential, the velocity gradients, and of the "affinities" of the internal parameters. The coefficients of the linear phenomenological relations are functions of the state of the system, which must in general be determined experimentally for the materials of interest, but are subject to some restrictions; the restrictions help to ensure that the process will proceed in a physically realistic manner.

For classical materials without memory (and thus with no internal parameters), the linear phenomenological laws reduce to very standard expressions: the viscous pressure tensor is given by

$$\hat{\Pi} = \eta \nabla \underline{v} + (\frac{1}{3}\eta + \eta_v)\nabla \cdot \underline{v}$$

(for a fluid this is used in obtaining the Navier Stokes equation from (1.22)). In addition, if there is no swelling, Fick's law results:

$$\underline{J} = D(c)\nabla c\,,$$

so that (1.17) becomes

$$c_t = \nabla(D(c)\nabla c).$$

When the internal parameters are introduced to describe the response of a material to its history, the resulting linear phenomenological laws are less standard, although still well-known (see deGroot and Mazur, [2] Chapter X.5-6, Prigogine [3] III.4-6). We give a general overview of the relevant theory in order to familiarize the reader with the concepts involved in obtaining these relations, and in order to highlight the assumptions made along the way.

a. Thermostatics. Inherent in the assumptions of irreversible thermodynamics are the assumptions of thermostatics (see any text on classical thermodynamics, e.g. Callen [1]), which we discuss briefly in this part. First, at equilibrium the state of a system is entirely defined by u, the internal energy per unit mass, and a fixed set of independent macroscopic parameters. In our case, we assume that the independent parameters are c, the fluid concentration, ε_{ij}, the independent components of the strain tensor, and the internal parameters. For simplicity of presentation, the model will be developed with a single scalar internal parameter ξ, and generalized in the appendix to incorporate more complex possibilities. The role of the internal parameters is discussed in more detail below; roughly, ξ describes the distribution of the solid between possible internal states.

The second assumption of thermostatics is the existence of the entropy, a unique (up to an additive constant) function of the internal energy and the other independent parameters, monotonically increasing in u, and maximized at equilibrium. If s is the entropy per unit mass, then

$$s = s(u, \hat{\boldsymbol{\varepsilon}}, c, \xi). \tag{2.1}$$

It follows from the monotonicity that the entropy function can be inverted to give the internal energy as a function of entropy and the other independent parameters:

$$u = u(s, \hat{\boldsymbol{\varepsilon}}, c, \xi). \tag{2.2}$$

Taking the differential of u,

$$du = \left(\frac{\partial u}{\partial s}\right) ds + \sum_{i \le j} \left(\frac{\partial u}{\partial \varepsilon_{ij}}\right) d\,\varepsilon_{ij} + \left(\frac{\partial u}{\partial c}\right) dc + \left(\frac{\partial u}{\partial \xi}\right) d\,\xi. \tag{2.3}$$

Here $\left(\frac{\partial u}{\partial \varepsilon_{ij}}\right) d\varepsilon_{ij}$ is the reversible mechanical work done by the strain, or $\left(\frac{\partial u}{\partial \varepsilon_{ij}}\right) d\varepsilon_{ij}$ = "force" times "distance". It follows that

$$\sigma_{ij} = \frac{1}{2}\rho\frac{\partial u}{\partial \varepsilon_{ij}}(1 + \delta_{ij}) = \sigma_{ij}(s,\hat{\boldsymbol{\varepsilon}},c,\xi). \tag{2.4a}$$

Likewise, $\left(\frac{\partial u}{\partial c}\right) dc$ is the reversible chemical work and $\frac{\partial u}{\partial c}$ is defined to be the chemical potential

$$\mu \equiv \frac{\partial u}{\partial c} = \mu(s,\hat{\boldsymbol{\varepsilon}},c,\xi). \tag{2.4b}$$

No real change of internal state is reversible, and thus at equilibrium $\frac{\partial u}{\partial \xi} = 0$; away from equilibrium, $\rho\frac{\partial u}{\partial \xi}$ acts as a force driving the changes in internal state, and is known as the affinity of the internal parameter,

$$A \equiv \rho\frac{\partial u}{\partial \xi} = A(s,\hat{\boldsymbol{\varepsilon}},c,\xi). \tag{2.4c}$$

In the absence of any other process $\left(\frac{\partial u}{\partial s}\right) ds$ is the heat transferred, and it is a matter of experience that $\frac{\partial u}{\partial s}$ is the temperature

$$T = \frac{\partial u}{\partial s}. \tag{2.4d}$$

Using these identities, (2.7) becomes the Gibbs equation

$$du = Tds + \sum_{ij} (\sigma_{ij}/\rho)d\varepsilon_{ij} + \mu dc + (A/\rho)d\xi. \tag{2.5}$$

For a process at constant temperature like ours, the entropy can be eliminated as an independent variable (one can think of solving

$T(s,\hat{\boldsymbol{\varepsilon}},c,\xi) = constant$ for $s(\hat{\boldsymbol{\varepsilon}},c,\xi)$) by transforming from u to f, the Helmholtz potential per unit mass,

$$f = u - Ts = f(\hat{\boldsymbol{\varepsilon}},c,\xi). \tag{2.6}$$

At constant T,

$$df = du - Tds$$

or

$$df = \sum_{ij} \frac{1}{\rho}\sigma_{ij}\, d\varepsilon_{ij} + \mu dc + \frac{1}{\rho}A d\xi, \tag{2.7}$$

and

$$\mu = \frac{\partial f}{\partial c} = \mu(\hat{\boldsymbol{\varepsilon}},c,\xi) \tag{2.8a}$$

$$\sigma_{ij} = \frac{1}{2}\rho\frac{\partial f}{\partial \varepsilon_{ij}}(1 + \delta_{ij}) = \sigma_{ij}(\hat{\boldsymbol{\varepsilon}},c,\xi) \tag{2.8b}$$

$$A = \rho\frac{\partial f}{\partial \xi} = A(\hat{\boldsymbol{\varepsilon}},c,\xi). \tag{2.8c}$$

b. Internal processes; irreversible changes in uniform systems. The next set of concepts concern the irreversible changes in uniform time-dependent systems, and thus the changes in the internal parameters. The system is assumed to stay near enough to equilibrium that its state at any time is described by the same set of independent parameters as at equilibrium, along with the initial conditions of the system. The entropy continues to be the same well-defined function of the independent parameters as at equilibrium. The assumption is added that entropy production is always positive for any real process.

The idea of using internal parameters to measure the extent of change of a system arises as a generalization of the "extent of reaction" parameter [3].

Example 2.1 Extent of reaction. A simple example is the reaction

$$2NH_3 \rightleftarrows N_2 + 3H_2.$$

Initially there are $n_{NH_3}{}^o$, $n_{N_2}{}^o$, and $n_{H_2}{}^o$ moles of each. For every ξ moles of N_2 created, 3ξ moles of H_2 are created and 2ξ of NH_3 are used up, or

$$n_{NH_3} = n_{NH_3}{}^o - 2\xi$$
$$n_{N_2} = n_{N_2}{}^o + \xi$$
$$n_{H_2} = n_{H_2}{}^o + 3\xi.$$

$\xi(t)$, $n_{NH_3}{}^o$,$n_{N_2}{}^o$ and $n_{H_2}{}^o$ determine the quantity of each substance in the system at time t. ξ measures the extent to which the reaction has proceeded.

Any reaction can be characterized by such an internal "extent of reaction" parameter, while simultaneous coupled reactions can be described by a set of internal parameters, with one for each reaction. Some other examples of simple internal processes which can be characterized by an internal parameter are ionizations, phase changes, or the increase in internal disorder in a metal alloy when the temperature is raised. The actual internal processes undergone by a polymer can be very complex, and it may take a complex set of internal parameters to characterize them. The theory is expanded to include more general internal processes in the appendix; until then we continue to develop the model with a single internal parameter. We do not pretend to know what the actual internal processes are, but for an idealized example of a simple process, one might imagine that the polymer molecules are straight in a dry polymer and bend in the middle as the fluid concentration increases.

Each of these processes is an internal irreversible process, which proceeds at a rate dependent on the state of the system. For our swelling problem,

$$\frac{d\xi}{dt} = r\left(\hat{\varepsilon}, c, \xi; n^{o}\right),$$

where n^{o} describes the initial state. The entropy production is $\frac{ds}{dt} = -\frac{A}{T}\frac{d\xi}{dt} = -\frac{A}{T}r$, assumed positive. The positivity of the entropy production can be thought of as assigning a direction to the internal process.

Note that the internal parameter cannot be directly controlled by the observer, unlike the fluid concentration and the strains; it is determined by the history of the system and can only be indirectly controlled through the variation of the external conditions.

c. Nonuniform processes; The linear phenomenological laws. The macroscopic theory of the thermodynamics of irreversible processes is based on the assumption that the system is near equilibrium inside each infinitessimal element of the system. Within each of these elements a local entropy is defined which has the same functional dependence on the local independent parameters as does the equilibrium entropy function. Local entropy production is always nonnegative, being strictly positive for an irreversible process. Furthermore, it is assumed that the local dependent parameters also depend only on the same set of independent parameters as at equilibrium. Thus relations (2.1-8) are valid and

$$T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_{ij}(\sigma_{ij}/\rho)\,d\varepsilon_{ij} - \mu\frac{\partial c}{\partial t} - (A/\rho)\frac{\partial \xi}{\partial t}, \qquad (2.9)$$

and similarly for ∇s.

Conservation of entropy requires that

$$\frac{\partial(\rho s)}{dt} + \nabla\cdot\underline{J}_{s,tot} = P \tag{2.10}$$

where $\underline{J}_{s,tot}$ is the total entropy flux and P is the rate of entropy production per unit volume. Substituting the local Gibbs relation (2.5) and the equations for conservation of mass, momentum and energy into (2.10), one obtains a new entropy conservation equation which gives P uniquely (deGroot and Mazur [2], chapter III). For our system,

$$TP = -\left[\underline{J}_f\cdot\nabla\mu + \sum_{ij}\Pi_{ij}\,\frac{\partial v_i}{\partial\chi_j} + A\,\frac{\partial\xi}{\partial\tau}\right] \geq 0, \tag{2.11}$$

and we see that TP is the sum of products of fluxes $\underline{J}_f$, $\widehat{\Pi}$, $\frac{\partial\xi}{\partial\tau}$, and generalized forces, called affinities $-\nabla\mu$, $-\nabla v$, and $-A$.

Letting F_i denote the affinities and J_i the fluxes, in general

$$T\,P = \sum_i J_i F_i \geq 0. \tag{2.12}$$

The affinities act as forces driving the fluxes; for example the gradient of the chemical potential causes fluid to diffuse until a uniform concentration is reached. We assume that the fluxes and affinities vanish together when equilibrium is reached. If the affinities could all vanish when fluxes were nonzero, then the material would have memory which was unaccounted for by the internal parameters, and would thus violate our assumption that the internal parameters entirely specify the state of our system. (Remark: Rather than specifying internal parameters, one could treat the fluxes as depending on the past history of the affinities and independent parameters X_i and write

$$J_i = \int_{-\infty}^{t} K(s\,;t\,,\underline{F},\underline{X})\,ds$$

where K is some function which could be expanded in the $\underline{F}$ (see Christensen [23], Chapter III) .) Assuming that the fluxes depend only on the affinities and the independent parameters, expanding the fluxes in the affinities near equilibrium gives (keeping only the linear terms) the linear phenomenological relations

$$J_i = \sum_j L_{ij} F_j \tag{2.13}$$

where the coefficients L_{ij} are functions of the local independent parameters to be determined phenomenologically. Onsager's relations (in the absence of a magnetic field)

$$L_{ij} = L_{ji} \tag{2.14}$$

are also assumed to hold. Substituting (2.13) into the expression (2.12) for the entropy production gives a quadratic function in the F_i

$$T\,P = \sum_{ij} L_{ij} F_i F_j \geq 0 \;, \tag{2.15}$$

with P strictly positive whenever any of the affinities is nonzero. Thus the matrix $\mathbf{L}$ with coefficients L_{ij} must be a positive definite symmetric matrix.

For an isotropic material, fluxes and affinities of different tensorial character cannot couple since they transform in different ways (the Curie symmetry principle) and the linear phenomenological laws become

$$\underline{J}_f = -\rho_o J_\mu \nabla\mu \tag{2.16a}$$

$$\frac{1}{3} tr\,\widehat{\Pi} = -\rho_o \nu^s \nabla\cdot\underline{v} - \nu_\xi A, \tag{2.16b}$$

$$\frac{\partial \xi}{\partial \tau} = -\nu_\xi \nabla \cdot \underline{v} - \frac{1}{\rho_o} LA, \tag{2.16c}$$

$$\widehat{\Pi}^o = -\rho_o \nu^o (\nabla \underline{v})^o, \tag{2.16d}$$

where the symmetric second order tensors $\widehat{\Pi}$ and $\nabla \underline{v}$ have been split up into their scalar trace $tr\,\widehat{\Pi}$, $\nabla \cdot \underline{v}$, and traceless symmetric tensors

$$\begin{aligned} \widehat{\Pi}^o &\equiv \widehat{\Pi} - \frac{1}{3}(tr\,\widehat{\Pi})\mathbf{I}, \\ (\nabla \underline{v})^o &\equiv \nabla \underline{v} - \frac{1}{3}(\nabla \cdot v)\mathbf{I}, \end{aligned} \tag{2.17}$$

(where $\mathbf{I}$ is the unit tensor). Each of the coefficients J_μ, ν^s, ν_ξ, L and ν^o in equations (2.16) is a ***scalar*** function of the independent parameters, $\widehat{\boldsymbol{\varepsilon}}$, c, and ξ (ν^o multiplies the entire tensor). Then P becomes

$$\begin{aligned} T\,P = \rho_o \nu^s (\nabla \cdot v)^2 + 2\nu_\xi (\nabla \cdot v) A + \frac{1}{\rho_o} LA^2 \\ + \rho_o J_\mu \nabla \mu \cdot \nabla \mu + \rho_o \nu^o \left[(\nabla \underline{v})^o \cdot (\nabla \underline{v})^o \right] \end{aligned} \tag{2.18}$$

The condition that this is positive definite gives the restrictions

$$J_\mu > 0, \ \nu^o > 0, \ \nu^s > 0, \ L > 0 \tag{2.19}$$

and

$$\nu^s L - \nu_\xi^2 > 0$$

on the coefficients of relations (2.16). These coefficients are functions of the independent parameters $\widehat{\boldsymbol{\varepsilon}}$, c, and ξ, which must be determined phenomenologically; any physically reasonable coefficients will satisfy (2.19).

Putting equation (2.16a) into the concentration equation (1.17) gives

$$\frac{\partial c}{\partial \tau} = \nabla \cdot \left[J_\mu \nabla \mu \right] \tag{2.20}$$

and putting (2.16b,d) into the momentum equation gives

$$\frac{\partial \underline{v}}{\partial \tau} = \nabla\cdot\hat{\boldsymbol{\sigma}}/\rho_o + \nabla\left[\nu^s \nabla\cdot\underline{v} + \nu_\xi A/\rho_o\right] + \nabla\cdot\left[\nu^o (\nabla\underline{v})^o\right]. \tag{2.21}$$

Recall that

$$\underline{v} = \frac{\partial \underline{u}}{\partial \tau}; \quad \underline{\varepsilon} = \nabla_\chi \underline{u}. \tag{2.22}$$

These, plus (2.16c)

$$\frac{\partial \xi}{\partial \tau} = -\nu_\xi \nabla\cdot\underline{v} - LA/\rho_o, \tag{2.23}$$

and the restrictions (2.19), form our system.

Example 2.2 As mentioned in the introduction to this section, if there is no swelling ($\underline{u} = 0$) and no memory (no ξ), then (2.16a) becomes Fick's Law

$$\underline{J} = \rho_o J_\mu(c)\nabla\mu(c) = \rho_o D(c)\nabla c,$$

with $J_\mu(c) > 0$ and $D(c) = J_\mu(c)\dfrac{d\mu}{dc}$ giving

$$\frac{\partial c}{\partial t} = \nabla(D(c)\nabla c),$$

the diffusion equation.

Example 2.3: If there is no memory and no diffusion, and if ν^s and ν^o are constants, (2.16) becomes

$$\frac{1}{3} tr\,\hat{\Pi} = \eta_v \nabla\cdot\underline{v}$$

$$\hat{\Pi}^o = 2\eta(\nabla\underline{v})^o = \eta(\nabla\underline{v} + (\nabla\underline{v})^T - \frac{2}{3}\nabla\cdot\underline{v}\ \mathrm{I})$$

For a fluid, $\hat{\boldsymbol{\sigma}} = -p\mathbf{I}$, where p is the hydrostatic pressure. Substituting these into the momentum equation yields

$$\rho \frac{\partial \underline{v}}{\partial \tau} = -\nabla p + (\eta_v + \frac{1}{3}\eta)\nabla(\nabla \cdot \underline{v}) + \eta \nabla^2 \underline{v}, \qquad (2.19)$$

the Navier-Stokes equation for a viscous compressible fluid in a Lagrangian coordinate system. Conditions (2.19) imply that η_v and η, the bulk and shear viscosities, respectively, are positive for any real fluid.

Our system (2.20-23) contains, besides the linear phenomenological coefficients, the functions μ, $\hat{\boldsymbol{\sigma}}$, and A. These last three functions are not independent of each other, since each is found by taking the partial derivative of the Helmholtz potential. In the next section, we study the general form of μ, $\hat{\boldsymbol{\sigma}}$ and A for small strains in a near equilibrium situation.

3. Material Properties. In this section we study the general form of the material properties of a homogeneous piece of our isotropic fluid-solid system under the assumption that the system remains near equilibrium. The material properties of interest are the relations between the stresses, chemical potential and affinities of the internal parameters and the strains, fluid concentration and internal parameters. Recall that the dependent parameters σ_{ij}/ρ, c and A/ρ are all partial derivatives of a single function of the independent variables, the Helmholtz potential. This puts restrictions on the functional form of the dependent parameters. That the Helmholtz potential must be minimized at equilibrium (equivalently, the entropy is maximized) gives a set of inequalities which must be satisfied for a physically stable system. We begin by writing out the general condition for stability, followed by an examination of the relaxation of the system to equilibrium when the concentration and strains are held fixed. We then expand the dependent parameters for small strains with the internal parameters near their equilibrium values, and apply the above restrictions. This gives $\hat{\boldsymbol{\sigma}}$, and A as linear functions and the chemical potential as a quadratic function of $\hat{\boldsymbol{\varepsilon}}$ and ξ, with coefficients which are nonlinear functions of the concentration, plus a set of stability inequalities which physically acceptable coefficients must satisfy. Substituting these expressions for $\hat{\boldsymbol{\sigma}}$, μ, and A back into (2.20 - 23) we obtain a system of equations in three dimensions for the concentration, the deformations and the internal parameter.

a. Stability. Recall the assumptions of the preceeding section that the local entropy and dependent parameters are the same well-defined functions of the independent parameters as at equilibrium, and can thus be manipulated in the same way. This allows us to take advantage of the isothermal nature of our process by transforming to the Helmholtz potential energy, which replaces the energy with the temperature as an independent parameter. Suppressing the temperature dependence, the Helmholtz potential energy per unit mass is given by

$$f = u - Ts = f(\widehat{\boldsymbol{\varepsilon}}, c, \xi) \tag{3.1}$$

and

$$df = \frac{1}{\rho}\sum \sigma_{ij} d\varepsilon_{ij} + \mu dc + (A/\rho) d\xi \tag{3.2}$$

with

$$\mu = \frac{\partial f}{\partial c} \tag{3.3a}$$

$$\sigma_{ij} = \frac{1}{2}\rho\frac{\partial f}{\partial \varepsilon_{ij}}(1 + \delta_{ij}) \tag{3.3b}$$

and

$$A = \rho\frac{\partial f}{\partial \xi}. \tag{3.3c}$$

For an isolated system, the total Helmholtz potential is minimized at equilibrium over all possible internal constraints. First, this implies that at equilibrium, $\widehat{\boldsymbol{\sigma}}$, μ, and A are uniform throughout ($A = 0$ by assumption). Secondly , d^2f is a nonnegative definite quadratic form at equilibrium (see Callen [1], chapter 8), where

$$\begin{aligned} d^2f &= \frac{1}{2}\sum_{i\le j}\sum_{kl}\frac{\partial(\sigma_{kl}/\rho)}{\partial\varepsilon_{ij}}d\varepsilon_{kl}d\varepsilon_{ij} + \sum_{ij}\frac{\partial(\sigma_{ij}/\rho)}{\partial c}d\varepsilon_{ij}dc + \frac{1}{2}\frac{\partial\mu}{\partial c}(dc)^2 \\ &+ \sum_{ij}\frac{\partial(\sigma_{ij}/\rho)}{\partial\xi}d\varepsilon_{ij}d\xi + \frac{\partial\mu}{\partial\xi}dc\,d\xi + \frac{1}{2}\frac{\partial(A/\rho)}{\partial\xi}(d\xi)^2. \end{aligned} \tag{3.4}$$

In obtaining this we have used the relations between the second derivatives of f :

$$\frac{\partial(\sigma_{ij}/\rho)}{\partial c} = \frac{1}{2}\frac{\partial\mu}{\partial\varepsilon_{ij}}(1 + \delta_{ij}) = \frac{\partial^2 f}{\partial\xi\partial\varepsilon_{ij}}, \tag{3.5a}$$

$$\frac{\partial(\sigma_{ij}/\rho)}{d\xi} = \frac{1}{2}\frac{\partial(A/\rho)}{\partial\varepsilon_{ij}}(1+\delta_{ij}) = \frac{\partial^2 f}{\partial\xi\,\partial\varepsilon_{ij}}, \tag{3.5b}$$

$$\frac{\partial(A/\rho)}{\partial c} = \frac{\partial\mu}{\partial\xi} = \frac{\partial^2 f}{\partial c\,\partial\xi}, \tag{3.5c}$$

and

$$\frac{\partial(\sigma_{ij}/\rho)}{\partial\varepsilon_{\mu\nu}}(1+\delta_{\mu\nu}) = \frac{\partial(\sigma_{\mu\nu}/\rho)}{\partial\varepsilon_{ij}}(1+\delta_{ij}). \tag{3.5d}$$

The condition that (3.4) be a nonnegative definite quadratic form is necessary for stability of the equilibrium state. We shall assume that it is, in fact, positive definite so that the system is stable. If it could vanish we would have to investigate higher order derivatives, requiring us to keep more than linear terms in ε_{ij} and ξ.

b. Relaxation. The *external independent parameters*, $\hat{\boldsymbol{\varepsilon}}$ and c, can take on any value at equilibrium, since they can be varied by the observer. This is not true of the internal parameter ξ, whose value ξ^{eq} at equilibrium must satisfy

$$A(\hat{\boldsymbol{\varepsilon}}, c, \xi^{eq}) = 0, \tag{3.6}$$

which we assume can be inverted to give $\xi^{eq}(\hat{\boldsymbol{\varepsilon}}, c)$ uniquely. Assume for the moment that we have a uniform system with $\hat{\boldsymbol{\varepsilon}}$ and c fixed in time. Then the properties of our system are determined by their initial values and $\xi(t)$, which varies according to (2.23). Supressing the dependence on the fixed parameters, (2.23) can be written

$$\frac{d\xi}{dt} = -L(\xi)A(\xi). \tag{3.7}$$

This governs the relaxation of the material toward equilibrium. $L(\xi)$ is positive from (2.19), and $\frac{d\xi}{dt}$ and $A(\xi)$ vanish together at the equilibrium value ξ^{eq}. ξ

cannot approach ξ^{eq} unless

$$L(\xi^{eq})\frac{dA}{d\xi}(\xi^{eq}) \geq 0,$$

in other words, unless $\frac{dA}{d\xi}(\xi^{eq}) \geq 0$, This restriction on A is equivalent, in this case, to the stability restriction that the Helmholtz potential be minimized at ξ^{eq}. The stronger restriction that $\frac{dA}{d\xi}(\xi^{eq}) \geq 0$ is sufficient to ensure that ξ^{eq} is a stable equilibrium value and also allows us to linearize (3.7) for ξ sufficiently near equilibrium:

$$\frac{d\xi}{dt} = -L(\xi^{eq})\frac{dA}{d\xi}(\xi^{eq})(\xi - \xi^{eq}).$$

c. Small strains; Near equilibrium. We are working in the domain of small deformation gradients, and we can thus expand our dependent functions in the strains, keeping only a few terms. We also assume that our system stays very near equilibrium, allowing us to expand in ξ about $\xi^{eq}(\widehat{\boldsymbol{\varepsilon}},c)$, where ξ^{eq} satisfies (3.6), and where ξ^{eq} can also be expanded in small strains

$$\xi^{eq}(\widehat{\boldsymbol{\varepsilon}},c) = \xi_o(c) + \sum_{ij}\xi_{ij}\varepsilon_{ij}, \tag{3.10}$$

keeping only the linear terms.

Once again, applying the Curie symmetry principle for our isotropic system, which tells us that tensors of different types cannot couple in the linear terms, and expanding in ε_{ij}, and $\Delta\xi = \xi - \xi^{eq}$, we obtain

$$\xi^{eq}(\widehat{\boldsymbol{\varepsilon}},c) = \xi_o(c) + \xi_\varepsilon(c)\varepsilon \tag{3.11}$$

and

$$\frac{1}{\rho}(\frac{1}{3}tr\,\sigma) = s(c) + \widetilde{s}_\varepsilon(c)\varepsilon + s_\xi(c)\Delta\xi, \tag{3.12a}$$

$$\mu = \mu_o(c) + \mu_\varepsilon(c)\varepsilon + \mu_\xi(c)\Delta\xi + \frac{1}{2}\mu_{\varepsilon\varepsilon}\varepsilon^2 + \mu_{\varepsilon\xi}(c)\varepsilon\Delta\xi$$
$$+ \frac{1}{2}\mu_{\xi\xi}(\Delta\xi)^2 + \frac{1}{2}\mu_{oo}\sum_{ij}(\varepsilon^o_{ij})^2, \tag{3.12b}$$

$$A/\rho = K(c)\Delta\xi, \tag{3.12c}$$

$$\frac{1}{\rho}\hat{\boldsymbol{\sigma}}^o = s_o(c)\hat{\boldsymbol{\varepsilon}}^o. \tag{3.12d}$$

Here $A(\hat{\boldsymbol{\varepsilon}}, c, \xi^{eq}) = 0$ has been enforced. We have kept the quadratic terms in the expression for μ because we need not only $\nabla\mu$ but also the second order spatial derivatives $\nabla^2\mu$ in the concentration equation. Applying relations (3.5) between the derivatives, and $\rho = \rho_o(1 - \varepsilon)$, (1.1 3), relations (3.12) become

$$\frac{1}{3}tr\,\sigma = \rho_o\left[s(c) + s_\varepsilon(c)\varepsilon - \xi_\varepsilon(c)K(c)\Delta\xi\right], \tag{3.13a}$$

$$\mu = \mu_o(c) + \frac{ds}{dc}\varepsilon - K(c)\frac{d\xi_o}{dc}\Delta\xi + \frac{1}{2}\frac{dK}{dc}(\Delta\xi)^2$$
$$+ \frac{d}{dc}(\xi_\varepsilon K)\varepsilon\Delta\xi + \frac{1}{2}\frac{d}{dc}(s_\varepsilon + s)\varepsilon^2 + \frac{1}{2}\frac{ds_o}{dc}\sum_{ij}\varepsilon^{o\,2}_{ij} \tag{3.13b}$$

$$A = \rho_o K(c)\Delta\xi, \tag{3.13c}$$

and

$$\hat{\boldsymbol{\sigma}}^o = \rho_o\left[s_o(c)\hat{\boldsymbol{\varepsilon}}^o\right], \tag{3.13d}$$

with $s_\varepsilon = \tilde{s}_\varepsilon - s(c)$. Here $\hat{\boldsymbol{\sigma}}^o$ is assumed to vanish with $\hat{\boldsymbol{\varepsilon}}^o$ as the system is initially only under isotropic stress. The components of the equilibrium stress tensor are given by

$$\sigma_{ij} = \rho_o s_o(c)\varepsilon_{ij} \quad \text{for } i \neq j, \tag{3.14a}$$

$$\sigma_{ii} = \rho_o\left[s(c) + s_o(c)\varepsilon_{ii} + \left[s_\varepsilon(c) - \frac{1}{3}s_o(c)\right]\varepsilon - K(c)\xi_\varepsilon(c)\Delta\xi\right]. \tag{3.14b}$$

Special Case: Linearity in concentration. Suppose that concentration changes are sufficiently small so that we can expand (3.13) in $\Delta c = c - c_o$. This gives the linear relations

$$\begin{aligned}
\frac{1}{3} tr\,\sigma &= \rho_o[s + \beta\Delta c + s_\varepsilon \varepsilon + \gamma\xi], \\
A &= \rho_o[\omega\Delta c + \gamma\varepsilon + \kappa\xi], \\
\mu &= \mu_o + \alpha\Delta c + \beta\varepsilon + \omega\xi, \\
\hat{\boldsymbol{\sigma}}^{o} &= \rho_o s_o \hat{\boldsymbol{\varepsilon}}^{o}
\end{aligned} \tag{3.15}$$

where all coefficients are constants. Here ξ^{eq} has been normalized to vanish with Δc and ε:

$$\xi^{eq} = -\frac{1}{\kappa}(\omega\Delta c + \gamma\varepsilon) \tag{3.16}$$

and we keep only linear terms in the equation for μ.

Example 3.1: Suppose that for the special case above, the internal process is not an important effect, so that we can drop ξ. Then

$$\begin{aligned}
\sigma_{ij} &= \rho_o s_o \varepsilon_{ij} \quad \text{for } i \neq j, \\
\sigma_{ii} &= \rho_o[s + s_o\varepsilon_{ij} + (s_\varepsilon - \frac{1}{3}s_o)\varepsilon + \beta\Delta c], \\
\Delta\mu &= \alpha\Delta c + \beta\varepsilon,
\end{aligned}$$

$\frac{1}{2}\rho_o s_o$ and $\rho_o s_\varepsilon$ correspond to the shear and bulk moduli for elastic materials. $b = -\beta/s_\varepsilon$ is the "bulk swelling coefficient" which determines the amount of the isotropic dilation or contraction which occurs for a stress-free change Δc. Thus if the fluid concentration changes by Δc, and $\hat{\boldsymbol{\sigma}}$ stays at its initial value, the dilation is $\varepsilon = b\,\Delta c$, with $\rho = \rho_o(1 - b\,\Delta c)$ the new density. The new solid density is given by

$$\rho_s = \rho c_s = \rho(1 - c),$$

or, in terms of the initial solid density $(\rho_s)_o$,

$$\rho_s = (\rho_s)_o\left[1 - \left[1 + b + \frac{c_o}{1 - c_o}\right]\Delta c\right].$$

We expect an initially dry solid to swell when fluid is added, or $1 + b > 0$, however b itself can have either sign depending on whether or not the fluid presence has a significant effect on the free volume of the solid.

In order to study the stability of equilibrium, we need to evaluate $d^2 f$. Taking the derivatives of the expansions for $\hat{\sigma}/\rho$, μ and A/ρ, and substituting into expression (3.4) gives

$$\begin{aligned} d^2 f &= \frac{1}{2} s_o(c) \sum (d\varepsilon_{ij}^{o})^2 + \frac{1}{2}(s(c) + s_\varepsilon(c))(d\varepsilon)^2 + \frac{ds}{dc} d\varepsilon dc \\ &+ \frac{1}{2}\alpha(c)(dc)^2 + \frac{1}{2} K(c)(d(\Delta\xi))^2 \end{aligned} \tag{3.17}$$

to first order in ε and $\Delta\xi$, where

$$\alpha(c) \equiv \frac{d\mu_o}{dc}. \tag{3.18}$$

$d^2 f$ will be a positive definite quadratic form only if

$$\begin{aligned} &s_o(c) > 0, \quad s(c) + s_\varepsilon(c) > 0, \alpha(c) > 0, \\ &K(c) > 0, \text{ and } (s + s_\varepsilon)\alpha - \left(\frac{ds}{dc}\right)^2 > 0. \end{aligned} \tag{3.19}$$

Note: More generally, $d^2 f$ can be positive definite only if at equilibrium ($\Delta\xi = 0$) relations such as

$$\frac{\partial\mu}{\partial c} > 0, \quad \frac{\partial\mu}{\partial c} \frac{\partial \frac{1}{3} tr\, \sigma/\rho}{\partial\varepsilon} > \left[\frac{\partial\mu}{\partial\varepsilon}\right]^2$$

hold for any values of c and ε. The first of these gives us the extra information that

$$\frac{\partial\mu}{\partial c} = \alpha(c) + \frac{d^2 s}{dc^2}\varepsilon > 0 \tag{3.19a}$$

must hold in order for the expansion to be valid to this order.

Linear case: Returning to the purely linear case,

$$\begin{aligned} d^2 f &= \frac{1}{2} s_o \sum (d\varepsilon_{ij}^o)^2 + \frac{1}{2}(s_\varepsilon + s)(d\varepsilon)^2 + \beta d\varepsilon dc \\ &\quad + \frac{1}{2}\alpha dc^2 + \gamma d\varepsilon d\xi + \omega dc d\xi + \frac{1}{2}\kappa (d\xi)^2, \end{aligned}$$

or

$$\begin{aligned} d^2 f &= \frac{1}{2} s_o \sum (d\varepsilon_{ij}^o)^2 + \frac{1}{2}(s_\varepsilon + s - \frac{\gamma^2}{\kappa})(d\varepsilon)^2 + (\beta - \frac{\omega\gamma}{\kappa}) d\varepsilon dc \\ &\quad + \frac{1}{2}(\alpha - \frac{\omega^2}{\kappa}) dc^2 + \kappa (d(\xi - \xi^{eq}))^2, \end{aligned} \tag{3.20}$$

which gives the inequalities

$$\begin{aligned} & s_o > 0,\ \kappa > 0, \\ & \alpha\kappa - \omega^2 > 0,\ (s_\varepsilon + s)\kappa - \gamma^2 > 0, \\ & \text{and} \quad \left[(s_\varepsilon + s) - \frac{\gamma^2}{\kappa}\right]\left[\alpha - \frac{\omega^2}{\kappa}\right] - \left[\beta - \frac{\omega\gamma}{\kappa}\right]^2 > 0, \end{aligned} \tag{3.21}$$

It follows that α and $(s_\varepsilon + s)$ are positive constants.

Example 3.2: In example 3.1, we considered the linear case with no memory. Returning to this example, conditions (3.21) tell us that the shear modulus, $\frac{1}{2}\rho_o s_o$, is positive, and that the initial stress plus the bulk modulus, $\rho_o(s + s_\varepsilon)$, is also positive.

Example 3.3: Suppose that we have diffusion with no swelling and no memory as in example A2.1, with

$$\mu = \mu^o(c)$$

and

$$\frac{\partial \mu}{\partial c} = \frac{d\mu^o}{dc} = \alpha(c).$$

The diffusion coefficient is defined as

$$D(c) = J_\mu(c)\alpha(c)$$

Since $J_\mu(c) > 0$ from (2.19), and $\alpha(c) > 0$ from the (3.19), we obtain the standard result that the diffusion coefficient is positive for any process for which the diffusion equation

$$c_t = \nabla(D(c)\nabla c)$$

is valid.

d. The equations. The final step in obtaining a set of equations which describe diffusion with swelling in a history-dependent material is to substitute the expansions (3.13) of $\hat{\boldsymbol{\sigma}}$, μ and A into system (2.20-23), at the same time expanding the linear phenomenological coefficients in ε and $\Delta\xi$. We now proceed to do this for the case of a single internal relaxation process, giving some simple examples and making a few comments on initial conditions and boundary values. At the end of this section we cite the results of the appendix, which take into account more general internal processes.

If we replace ξ with a new variable η, defined to vanish at equilibrium,

$$\eta = \Delta\xi = \xi - \xi^{eq}(\hat{\varepsilon}, c),$$

then system (2.20-23) is

$$\begin{aligned} \frac{\partial c}{\partial \tau} &= \nabla \cdot \left[D(\nabla c + \boldsymbol{d}_\varepsilon \nabla \varepsilon + \boldsymbol{d}_\eta \nabla \eta + \sum_{ij} \boldsymbol{d}_{ij} \nabla \varepsilon_{ij}^{o}) \right] \\ \frac{\partial \underline{v}}{\partial \tau} &= \nabla \cdot \hat{\boldsymbol{\sigma}} / \rho_o + \nabla \left[(\nu^s - \frac{1}{3} \nu^o) \nabla \cdot \underline{v} \right] + \nabla \cdot \left[\nu^o \nabla \underline{v} \right] + \nabla(\nu_\xi A / \rho_o) \\ \frac{\partial \eta}{\partial \tau} &= - \frac{\partial \xi^{eq}}{\partial \tau} - \nu_\xi \nabla \cdot \underline{v} - LA / \rho_o \end{aligned} \tag{3.22}$$

where

$$\underline{v} = \frac{\partial \underline{u}}{\partial \tau}, \quad \hat{\boldsymbol{\varepsilon}} = \nabla_X \underline{u} = (\nabla_X \underline{u})^T.$$

Here we have defined the coefficients

$$\begin{aligned} D &= D(\varepsilon, \hat{\boldsymbol{\varepsilon}}^o, c, \eta) \equiv J_\mu \frac{\partial \mu}{\partial c}, \\ \boldsymbol{d}_\varepsilon &= \boldsymbol{d}_\varepsilon(\varepsilon, \hat{\boldsymbol{\varepsilon}}^o, c, \eta) \equiv \frac{\partial \mu}{\partial \varepsilon} / \frac{\partial \mu}{\partial c}, \\ \boldsymbol{d}_\eta &= \boldsymbol{d}_\eta(\varepsilon, \hat{\boldsymbol{\varepsilon}}^o, c, \eta) \equiv \frac{\partial \mu}{\partial \eta} / \frac{\partial \mu}{\partial c}, \end{aligned} \tag{3.23}$$

and

$$\boldsymbol{d}_{ij} = \boldsymbol{d}_{ij}(\varepsilon, \hat{\boldsymbol{\varepsilon}}^o, c, \eta) \equiv \frac{\partial \mu}{\partial \varepsilon_{ij}^o} / \frac{\partial \mu}{\partial c}.$$

We want to replace each of the unknown functions in this system with its expansion in small $\hat{\boldsymbol{\varepsilon}}$ and η, but before we do so, let us consider the following remarks:

Note that although the ε_{ij} and η are assumed to be small, we have made no assumptions about the size of their derivatives. In fact, in the case of particular interest, Case II diffusion, where swollen and unswollen regions are separated only by a thin front, it is likely that their derivatives will be large in the region of the front. This tells us that we need to keep linear terms in $\hat{\boldsymbol{\varepsilon}}$ and η when we expand functions such as $D(\varepsilon, \hat{\boldsymbol{\varepsilon}}^o, c, \eta)$, which will be differentiated. It also means that we need to be careful about the coordinate system in which we are working. In the above system, the spatial derivatives denoted by the ∇ are taken in $(\underline{x}, t)$ coordinates, and those denoted by ∇_χ are taken in $(\underline{\chi}, \tau)$ coordinates, with the transformations between them given by (1.11) and (1.12). These transformations tell us that for any function g

$$\nabla g = (\nabla_\chi - \hat{\boldsymbol{\varepsilon}} \nabla_\chi) g$$

up to linear terms in $\hat{\varepsilon}$. If we transform the system entirely to $(\underline{\chi}, \tau)$ coordinates, then, to first order in $\hat{\boldsymbol{\varepsilon}}$, only the concentration and momentum equation are affected. These become

$$\frac{\partial c}{\partial \tau} = \nabla_\chi \cdot \left[J_\mu ((\hat{\mathbf{I}} - \hat{\boldsymbol{\varepsilon}}) \nabla_\chi) \mu \right] \tag{3.24a}$$

and

$$\begin{aligned} \frac{\partial v}{\partial \tau} &= \nabla_\chi \cdot \hat{\boldsymbol{\sigma}} / \rho_o + \nabla_\chi \left[(\nu^s - \frac{1}{3} \nu^o)(\nabla_\chi \underline{v} - \sum \varepsilon_{ij} \frac{\partial v_i}{\partial \chi_j}) \right] \\ &+ \nabla_\chi \left[\nu^o (\hat{\mathbf{I}} - \hat{\boldsymbol{\varepsilon}}) \nabla_\chi \underline{v} \right] + \nabla_\chi \left[\nu_\xi A \right]. \end{aligned} \tag{3.24b}$$

Let us now proceed to use the expansions in small $\hat{\boldsymbol{\varepsilon}}$ and η for the various functions in this system. Applying the Curie symmetry principle once more and expanding the linear phenomenological coefficients in $\hat{\boldsymbol{\varepsilon}}$ and η gives, together with conditions (2.19),

$$\begin{aligned}
J_\mu &= J_\mu(\varepsilon,\hat{\boldsymbol{\varepsilon}}^o,c,\eta) = J_\mu(c)\Big[1 + J_\varepsilon(c)\varepsilon + J_\eta(c)\eta\Big] > 0, \\
\nu^s &= \nu^s(\varepsilon,\hat{\boldsymbol{\varepsilon}}^o,c,\eta) = \nu^s(c) + \nu^s_\varepsilon(c)\varepsilon + \nu^s_\eta(c)\eta > 0, \\
\nu^o &= \nu^o(\varepsilon,\hat{\boldsymbol{\varepsilon}}^o,c,\eta) = \nu^o(c) + \nu^o_\varepsilon(c)\varepsilon + \nu^o_\eta(c)\eta > 0, \\
L &= L(\varepsilon,\hat{\boldsymbol{\varepsilon}}^o,c,\eta) = L(c) + L_\varepsilon(c)\varepsilon + L_\eta(c)\eta > 0, \\
\nu_\xi &= \nu_\xi(\varepsilon,\hat{\boldsymbol{\varepsilon}}^o,c,\eta) = \nu_\xi(c) + \nu_{\xi\xi}(c)\varepsilon + \nu_{\xi\eta}(c)\eta,
\end{aligned} \tag{3.25}$$

with

$$\nu^o L > \nu_\xi^2$$

for all c and for all $\hat{\boldsymbol{\varepsilon}}$ and η sufficiently small.

From (3.13) and the energy stability condition (3.19),

$$\frac{\partial\mu}{\partial c} = \alpha(c) + \frac{d\beta}{dc}\varepsilon + \frac{d\omega}{dc}\eta > 0.$$

Multiplying by J_μ and expanding gives the diffusion coefficient:

$$D(\varepsilon,\hat{\boldsymbol{\varepsilon}}^o,c,\eta) = J_\mu\left[\alpha + (\frac{d\beta}{dc} + \alpha J_\varepsilon)\varepsilon + (\frac{d\omega}{dc} + \alpha J_\eta)\eta\right] > 0 \tag{3.26}$$

for all c and all ε_{ij}, η sufficiently small. Here we have defined

$$\alpha(c) = \frac{d\mu_o}{dc}, \quad \beta(c) = \frac{ds}{dc} \quad \text{and} \quad \omega = -K(c)\frac{d\xi_o}{dc} \tag{3.27}$$

for simplicity. Also from (3.13),

$$\begin{aligned}
\frac{\partial\mu}{\partial\varepsilon} &= \beta(c) + \frac{d\gamma}{dc}\eta + \left|\beta(c) + \frac{ds_\varepsilon}{dc}\right|\varepsilon \\
\frac{\partial\mu}{\partial\eta} &= \omega(c) + \frac{dK}{dc}\eta - K(c)\frac{d\xi_\varepsilon}{dc}\varepsilon
\end{aligned}$$

and

$$\frac{\partial \mu}{\partial \varepsilon_{ij}^{o}} = \frac{ds_o}{dc}\, \varepsilon_{ij}^{o},$$

where

$$\gamma(c) = -K(c)\xi_\varepsilon(c). \tag{3.28}$$

Dividing by $\frac{\partial \mu}{\partial t}$, and expanding in ε and η, we obtain the expressions

$$\begin{aligned}
d_\varepsilon &= \frac{1}{\alpha(c)}\left[\beta(c) + \left(\beta(c) - \frac{1}{2\alpha(c)}\,\frac{d\beta^2}{dc} + \frac{ds_\varepsilon}{dc}\right)\varepsilon + \left(\frac{d\gamma}{dc} - \frac{\beta(c)}{\alpha(c)}\omega(c)\right)\eta\right], \\
d_\eta &= \frac{1}{\alpha(c)}\left[\omega(c) + \left(\frac{d\gamma}{dc} - \frac{\omega(c)}{\alpha(c)}\,\frac{d\beta}{dc}\right)\varepsilon + \left(\frac{dK}{dc} - \frac{1}{2\alpha(c)}\,\frac{d\omega^2}{dc}\right)\eta\right], \\
d_{ij} &= \frac{1}{\alpha(c)}\,\frac{ds_o}{dc}\,\varepsilon_{ij}^{o} = d_o\varepsilon_{ij}^{o}.
\end{aligned} \tag{3.29}$$

Next we turn to the terms in the momentum equation. Note that

$$\nabla\cdot\left(\frac{1}{\rho_o}\hat{\boldsymbol{\sigma}}\right) = \nabla\left(\frac{1}{\rho_o}\,\frac{1}{3}tr\,\sigma\right) + \nabla\cdot\left(\frac{1}{\rho_o}\hat{\boldsymbol{\sigma}}^{o}\right).$$

Expansions (3.13) for $\frac{1}{3}tr\,\sigma$, $\frac{1}{\rho_o}\hat{\boldsymbol{\sigma}}^{o}$ and A give

$$\begin{aligned}
\nabla\left(\frac{1}{\rho_o}\,\frac{1}{3}tr\,\sigma\right) &= \nabla\left(s_\varepsilon(c)\varepsilon\right) + \beta(c)\nabla c + \nabla(\gamma(c)\eta) \\
\nabla\cdot\left(\frac{1}{\rho_o}\hat{\boldsymbol{\sigma}}^{o}\right) &= \nabla\cdot\left(s_o(c)\hat{\boldsymbol{\varepsilon}}^{o}\right) = \nabla\cdot(s_o(c)\hat{\boldsymbol{\varepsilon}}) - \frac{1}{3}\nabla(s_o(c)\varepsilon)
\end{aligned} \tag{3.30}$$

and

$$\nabla(\nu_\xi \frac{1}{\rho_o}A) = \nabla(\nu_\xi K\eta) \tag{3.31}$$

to first order in ε_{ij} and η.

Substituting relations (3.25), and (2.29-31) into system (3.22) we obtain

$$\frac{\partial c}{\partial \tau} = \nabla \cdot [D(\nabla c + (d_\varepsilon - \frac{1}{3} d_o \varepsilon)\nabla \varepsilon + d_\eta \nabla \eta + \frac{1}{2} d_o \nabla (\sum_{ij} \varepsilon_{ij}^2))] \tag{3.32a}$$

where D, d_ε, d_η and d_o are given by (3.26) and (3.29),

$$\begin{aligned} \frac{\partial \underline{v}}{\partial \tau} = {} & \nabla \left[(s - \frac{1}{3} s_o)\varepsilon \right] + \nabla \cdot (s_o \varepsilon_{ij}) + \beta(c)\nabla c + \nabla \left[(\nu_\xi K + \gamma)\eta \right] \\ & + \nabla \left[(\nu^s - \frac{1}{3}\nu^o)\nabla \cdot \underline{v} \right] + \nabla \cdot (\nu^o \nabla \underline{v}) \end{aligned} \tag{3.32b}$$

and

$$\frac{\partial \eta}{\partial \tau} = \frac{\omega}{K} \frac{\partial c}{\partial \tau} + \left[\frac{\gamma}{K} - \nu_\xi \right] \frac{\partial \varepsilon}{\partial \tau} - KL\eta \tag{3.32c}$$

with

$$\underline{v} = \frac{\partial \underline{u}}{d\tau}, \quad \hat{\boldsymbol{\varepsilon}} = \nabla_\chi \underline{u} = (\nabla_\chi \underline{u})^T. \tag{3.32d}$$

The restrictions (3.19) on our coefficients tell us that, in our new notation,

$$\begin{aligned} & s_\varepsilon(c) + s(c) > d_\varepsilon \beta(c), \\ & K(c) > d_\eta \omega(c), \end{aligned}$$

and

$$s_o(c) > 0,$$

for all c and for ε and η sufficiently small, where

$$s(c) = -p_o/\rho_o + \int_{c_o}^{c} \beta(c)dc.$$

These restrictions along with those in (3.25) can be summarized as

$$D,\ L,\ s_\varepsilon,\ s_0,\ \nu^s,\ \nu^o, \text{ and } K \textit{ positive},$$
$$\nu^o L > \nu_\xi^2, \quad s_\varepsilon + s > d_\varepsilon \beta$$

and (3.33)

$$K > d_\eta \omega.$$

The equation for η can be integrated in $(\underline{\chi},\tau)$ coordinates holding $\underline{\chi}$ fixed, η can be replaced by

$$\begin{aligned}\eta = \eta(\underline{\chi},0)\exp[-\int_0^\tau LKd\tau'] \\ + \int_0^\tau \exp[-\int_s^\tau LKd\tau']\left[\frac{\omega}{K}\frac{\partial c}{\partial \tau}(\underline{\chi},s) + (\frac{\gamma}{K} + \nu_\xi)\frac{\partial \varepsilon(\underline{\chi},s)}{d\tau}\right]ds\end{aligned} \tag{3.32c'}$$

to give a set of integro-partial differential equations in $(\underline{\chi},\tau)$ coordinates for c and $\underline{u}$.

System (3.32), along with appropriate initial values and boundary conditions, is a three-dimensional set of equations describing the movements of an isotropic two-component system. The system is assumed to be initially undeformed and stress-free, except for a possible isotropic pressure p^o. The equations are valid, so long as deformations are irrotational and local strains are sufficiently small, for any material which undergoes a simple internal relaxation process. The strains, although small, can vary rapidly both with position and with time. In general, systems will undergo more complex internal processes and these are discussed in the Appendix.

The coefficients in system (3.32) must be determined experimentally for the materials of interest, as a function *not only* of the concentration, strain and time, but also of the temperature and past history of the material. As long as the process remains reasonably stable, the coefficients will satisfy the inequalities in (3.33).

Example 3.4: No memory; no inertia. If the solid is elastic, so that both memory and viscous effects are negligible, then system (3.32) simplifies to

$$\frac{\partial c}{\partial \tau} = \nabla\cdot\left[D\left(\nabla c + (d_\varepsilon - \frac{1}{3}\varepsilon d_o)\nabla\varepsilon + \frac{1}{2}d_o\sum_{ij}\nabla(\varepsilon_{ij})^2\right)\right]$$

$$\frac{\partial \underline{v}}{\partial \tau} = s_o\nabla\cdot\hat{\boldsymbol{\varepsilon}} + \left[s_\varepsilon - \frac{1}{3}s_o\right]\nabla\varepsilon + \left[\beta + \frac{ds_\varepsilon}{dc}\varepsilon\right]\nabla c + \frac{ds_o}{dc}\hat{\boldsymbol{\varepsilon}}^o\cdot\nabla c.$$

If the sorption process occurs sufficiently smoothly (or, equivalently, the dependence of D and d_ε on ε is sufficiently weak and d_o is sufficiently small) so that the nonlinear terms in $\nabla\varepsilon_{ij}\cdot\nabla\varepsilon_{ij}$, $\nabla\varepsilon_{ij}\cdot\nabla c$ and $\varepsilon_{ij}\nabla c$ can be neglected, then the concentration equation becomes ($\nabla = \nabla_\chi$)

$$\frac{\partial c}{\partial \tau} = \nabla_\chi\cdot\left[D(c)(\nabla_\chi c + d_\varepsilon(c)\nabla_\chi\varepsilon)\right].$$

If, furthermore, s_ε and s_o are independent of concentration and the system remains locally in mechanical equilibrium, so that the inertial terms $(\frac{\partial \underline{v}}{\partial \tau} = \frac{\partial \underline{v}}{\partial t} + \underline{v}\cdot\nabla\underline{v})$ in the momentum equation are negligible, then to first order in ε,

$$0 = s_o\left[\nabla_\chi\cdot\hat{\boldsymbol{\varepsilon}} - \frac{1}{3}\nabla_\chi\varepsilon\right] + s_\varepsilon\nabla_\chi\varepsilon + \beta\nabla_\chi c.$$

Noting that the irrotationality implies

$$(\nabla_\chi\cdot\hat{\boldsymbol{\varepsilon}})_i = \left[\nabla_\chi\cdot(\nabla_\chi\underline{u})^T\right]_i = \sum_j \frac{\partial}{\partial\chi_j}\frac{\partial u_j}{\partial\chi_i} = \frac{\partial}{\partial\chi_i}\nabla_\chi\cdot\underline{u} = \frac{\partial\varepsilon}{\partial\chi_i},$$

we can thus write the momentum equation as

$$0 = (s_\varepsilon + \frac{2}{3}s_o)\nabla_\chi\varepsilon + \beta(c)\nabla_\chi c$$

and replace $\nabla_\chi\varepsilon$ in the concentration equation to obtain a single equation

$$\begin{aligned}\frac{\partial c}{\partial \tau} &= \nabla_\chi\cdot\left[D(c)\left[1 - \frac{d_\varepsilon\beta}{s_\varepsilon + \frac{2}{3}s_o}\right]\nabla_\chi c\right]\\ &= \nabla_\chi\cdot\left[\tilde{D}(c)\nabla_\chi c\right].\end{aligned}$$

Therefore, under all of the above assumptions, the concentration satisfies the diffusion equation with a modified diffusion coefficient. This is the standard result, and agrees with the one-dimensional model derived by Cahn [18] when fourth-order diffusion is unimportant, and when $Dd_\varepsilon\beta/(s_\varepsilon + \frac{2}{3}s_o)$ is a constant. Note that the restrictions we have obtained for our coefficients do not actually prevent $\widetilde{D}$ from becoming negative in the case where

$$s(c) = -\frac{p_o}{\rho_o} + \int^{c} \beta(c)dc$$

is positive; however if $D(c)$ approaches zero or becomes negative, neglected terms become important.

It is useful to keep in mind the expressions for both the equilibrium stress tensor and the viscous pressure tensor. The force on the solid surface provides us with a natural boundary condition: a measurable stress may be applied, or the surface may be advancing freely against the fluid, whose resistance will presumably be negligible compared with stresses which cause crazing(or, if neither negligible or measurable, can be calculated). Also, one is often interested in calculating the internal stresses on the system in order to predict mechanical failures. From (3.14), the components of $\hat{\boldsymbol{\sigma}}$ are

$$\sigma_{ij} = \rho_o\left[s_o\varepsilon_{ij} + \delta_{ij}\left[-\frac{p_o}{\rho_o} + \int_{c_o}^{c} \beta(c)dc + (s_\varepsilon - \frac{1}{3}s_o)\varepsilon + \gamma\eta\right]\right. \tag{3.34a}$$

and from (2.16)

$$\Pi_{ij} = -\rho_o\left[\nu^o\frac{\partial\varepsilon_{ij}}{\partial\tau} + \delta_{ij}\left[(\nu^s - \frac{1}{3}\nu^o)\frac{\partial\varepsilon}{\partial\tau} + \nu_\xi K\,\eta\right]\right]. \tag{3.34b}$$

Applying the boundary conditions on the surface is not a trivial matter, because the solid surface will be moving. Thus, we will either have a problem with a moving boundary, or we must switch to solid-based coordinates. The following example serves to illustrate this problem.

Example 3.5: No volume change or memory; one dimension. For the case where the displacement u of the local center of mass is zero everywhere, the solid swells to accommodate the fluid. The total density remains constant in this case, and the solid density ρ_s is given in terms of the initial density ρ_o and the fluid concentration c by

$$\rho_s = \rho_o(1-c),$$

while coordinates $(\underline{\chi}_s, t_s)$ fixed to the solid are displaced from their original position by the vector $\underline{u}_s$, i.e.

$$x = x_s + \underline{u}_s(x_s, t_s), \quad t = t_s$$

so that the solid strain and velocity are

$$(\widehat{\boldsymbol{\varepsilon}}_s)_{ij} = \frac{\partial(u_s)_i}{\partial(x_s)_j}, \quad \underline{v}_s = \frac{\partial \underline{u}_s}{\partial t_s}.$$

The concentration, in the case of no memory, will satisfy

$$\frac{\partial c}{\partial t} = \nabla\cdot(D(c)\nabla c)$$

while the solid swelling is given by conservation of the solid

$$\frac{\partial \rho_s}{\partial t} + \nabla\cdot(\underline{v}_s \rho_s) = 0.$$

The boundaries of the solid are moving in $(\underline{x}, t)$ coordinates, whereas they remain fixed in $(\underline{x}_s, t_s)$ coordinates. For simplicity, let us examine the case of one-dimensional diffusion:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}(D(c)\frac{\partial c}{\partial x})$$
$$\frac{\partial}{\partial t}(\rho_s) + \frac{\partial}{\partial x}(v_s \rho_s) = 0.$$

If the solid is initially between $x = -d$ and $x = d$, then it is between $x^*_\pm(t)$ at a later time, where

$$\begin{aligned} x^*_\pm &= \pm d + u_s(\pm d, t_s) = \pm d + u_s(x^*_\pm, t) \\ &= \pm d + \int_0^{\pm d} \varepsilon_s(x_s, t)\,dx_s = \pm d + \int_0^{x^*_\pm} \frac{\partial u_s}{\partial x}dx. \end{aligned}$$

Switching to solid coordinates in the second equation

$$\frac{\partial}{\partial t_s} = \frac{\partial}{\partial t} + v_s \frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial x_s} = (1 + \varepsilon_s) \frac{\partial}{\partial x}$$

so that

$$\frac{\partial \rho_s}{\partial t_s} + \frac{\rho_s}{1 + \varepsilon_s} \frac{\partial v_s}{\partial x_s} = 0,$$

where

$$\frac{\partial v_s}{\partial x_s} = \frac{\partial \varepsilon_s}{\partial t_s}$$

and, dividing by ρ_s,

$$\frac{\partial}{\partial t_s}\Big[\ln \rho_s + \ln(1 + \varepsilon_s)\Big] = 0$$

or

$$\rho_s = \rho_{s_o} / (1 + \varepsilon_s),$$

ρ_{s_o} the initial density of the solid. From above,

$$\rho_s = \rho_o(1 - c)$$

so that we gain an expression for ε_s in terms of the concentration

$$1 + \varepsilon_s = \frac{\rho_{s_o}}{\rho_o(1 - c)} = \frac{1 - c_o}{1 - c},$$

c_o the initial concentration. In order to find an expression for x^* in (x, t) coordinates, we need

$$\frac{\partial u}{\partial x_s} = \frac{\varepsilon_s}{1 + \varepsilon_s} = \frac{c - c_o}{1 - c_o}.$$

Then

$$x_{\pm}^*(t) = \pm d + \int_0^{x_{\pm}^*} \frac{c - c_o}{1 - c_o} dx = \pm(1 - c_o)d + \int_0^{x_{\pm}^*(t)} c\,dx$$

and we would have to solve

$$c_t = (D(c)c_x)_x$$

with boundary conditions at $x^{*}_{\pm}$. In this case, however, we can simplify the problem by switching to (x_s, t_s) coordinates.

The velocity v_s can be obtained from equation (1.5) for $\underline{v}$, with $\underline{v} = 0$:

$$v_s = -\frac{1}{1-c} c v_f = -\frac{1}{\rho_o(1-c)} J_f = \frac{1}{(1-c)} D(c) \frac{\partial c}{\partial x}.$$

Transforming coordinates, the concentration equation is

$$\frac{\partial c}{\partial t_s} = \frac{v_s}{1+\varepsilon_s} \frac{\partial c}{\partial x_s} + \frac{1}{1+\varepsilon_s} \frac{\partial}{\partial x_s}\left[D(c) \frac{1}{1+\varepsilon_s} \frac{\partial c}{\partial x_s}\right].$$

Replacing c with ε_s,

$$dc = (1-c_o) \frac{1}{(1+\varepsilon_s)^2} d\varepsilon$$
$$v_s = \frac{1+\varepsilon_s}{1-c_o} D(c) \frac{(1-c_o)}{(1+\varepsilon_s)^2} \frac{\partial \varepsilon_s}{\partial x_s}$$

and thus the concentration equation becomes

$$\frac{1}{(1+\varepsilon_s)^2} \frac{\partial \varepsilon_s}{\partial t_s} = \frac{D(c)}{(1+\varepsilon_s)^4}\left[\frac{\partial \varepsilon_s}{\partial x_s}\right]^2 + \frac{1}{1+\varepsilon_s} \frac{\partial}{\partial x_s}\left[\frac{D(c)}{(1+\varepsilon_s)^3} \frac{\partial \varepsilon_s}{\partial x_s}\right]$$

or

$$\frac{\partial \varepsilon_s}{\partial t_s} = \frac{\partial}{\partial x_s}\left[\frac{D(c)}{(1+\varepsilon_s)^2} \frac{\partial \varepsilon_s}{\partial x_s}\right] = \frac{\partial}{\partial x_s}\left[D_s(\varepsilon_s) \frac{\partial \varepsilon_s}{\partial x_s}\right].$$

Thus, the solid strain satisfies a diffusion equation, and the total displacement can be found by integrating ε_s from a fixed point, much as one integrates the concentration in order to find mass uptake. In fact, this should come as no surprise since we have merely replaced the mass fraction concentration with the volume fraction concentration, where ε_s is the change in volume fraction of the solid.

Remark: This result also holds for the case discussed in example 3.4, where D is replaced by $\widetilde{D}$, As long as the solid is sufficiently thin so that the inertia term can be totally neglected.

In Section 4 we will set up and discuss the general problem for one-dimension, which is an approximation to the common experimental situation of a very large sheet which is dipped in a bath.

We have derived system (3.32) from the point of view that we would incorporate all terms which might be important, in fairly general form. The result is a rather formidable set of coupled, highly nonlinear equations containing a large number of parameters which are functions of the concentration. When at the end of this section we add the contributions from more general internal processes, the resulting system is even more complex. It does not make sense to begin studying the behavior of this system by attacking it in its most general form. This is not only because the functional form of most of the parameters is unknown and because of the difficulty in dealing with the full equations, but also because one would expect that the Case II behavior is driven by only a few of the terms, with the rest causing secondary effects. One would like to isolate the effects of various members of the equations and determine which ones are necessary for Case II behavior to occur.

One obvious simplification of the system is to ignore any nonlinear dependence of the material properties, while retaining the history dependence and momentum effects, which gives us the following special case:

Linear case: For the special case where the dependence of the material properties on the independent parameters is sufficiently weak, and the changes in these parameters are sufficiently small so that the chemical potential, stress and affinity A can be treated as linear functions and the linear phenomenological coefficients can be treated as constants, system (3.34) reduces to

$$\begin{aligned}
\frac{\partial c}{\partial \tau} &= D\left(\nabla^2 c + \frac{\beta}{\alpha}\nabla^2 \varepsilon + \frac{\omega}{\alpha}\nabla^2 \xi\right) \\
\frac{\partial \underline{v}}{\partial \tau} &= \left[s_\varepsilon + \frac{2}{3}s_o + \gamma \nu_\xi\right]\nabla\varepsilon + (\beta + \omega\nu_\xi)\nabla c \\
&\quad +(\gamma + K\nu_\xi)\nabla\xi + \left(\nu^s + \frac{2}{3}\nu^\rho\right)\nabla^2 \underline{v} \\
\frac{\partial \xi}{\partial \tau} &= -\nu_\xi \nabla\cdot\underline{v} - L(\omega\Delta c + \gamma\varepsilon + \kappa\xi)
\end{aligned} \tag{3.35}$$

where

$$\varepsilon = \nabla_\chi \cdot \underline{u}, \underline{v} = \frac{\partial \underline{u}}{\partial \tau}, \nabla \underline{u} = \nabla \underline{u}^T.$$

The coefficients

$$D,\ \alpha,\ s_\varepsilon,\ s_o,\ \kappa,\ \nu^s,\ \nu^o, \text{ and } L$$

are all positive constants, and

$$\begin{aligned} &\nu^s L > \nu_\xi^2, \quad \kappa > \omega^2/\alpha, (s + s_\varepsilon)\kappa > \gamma^2, \\ &\text{and } (\kappa(s + s_\varepsilon) - \gamma^2)(\alpha\kappa - \omega^2) > (\beta\kappa - \omega\gamma)^2 , \end{aligned} \tag{3.36}$$

where $\rho_o s$ is the initial stress. The equilibrium stress tensor and viscous pressure tensors have the components

$$\begin{aligned} \sigma_{ij} &= \rho_o \left[s_o \varepsilon_{ij} + \delta_{ij}(s + \beta\Delta c + (s_\varepsilon - \frac{1}{3}s_o)\varepsilon + \gamma\xi) \right], \\ \pi_{ij} &= -\rho_o \left[\nu^o \frac{\partial v_i}{\partial x_j} + \delta_{ij}((\nu^s - \frac{1}{3}\nu^o)\nabla \cdot \underline{v} + \nu_\xi(\omega\Delta c + \gamma\varepsilon + \kappa\xi)) \right] . \end{aligned} \tag{3.37}$$

The only nonlinearities in this system are hidden in the coordinates. As before, if $\nabla \cdot \hat{\boldsymbol{\varepsilon}}$ is not small, then the transformation to center-of-mass coordinates (which allows us to easily replace $\hat{\boldsymbol{\varepsilon}}$ and $\underline{v}$ with derivatives of $\underline{u}$) gives $\nabla^2 = \nabla_\chi{}^2 - (\nabla_\chi \cdot \hat{\boldsymbol{\varepsilon}}) \cdot \nabla_\chi$ to first order in ε_{ij}. For fixed χ, the equation for ξ can be integrated to give

$$\xi = \xi_o e^{-L\kappa\tau} - \int_0^\tau \left[\nu_\xi \frac{\partial \varepsilon}{\partial \tau} + L(\omega\Delta c + \gamma\varepsilon) \right] e^{-L\kappa(\tau - s)} ds , \tag{3.35c'}$$

where

$$\nabla \cdot \underline{v} = \frac{\partial \varepsilon}{\partial \tau} \left(1 + O(\| \hat{\boldsymbol{\varepsilon}} \|) \right)$$

have been employed.

If we wish to write the system entirely in the fixed coordinates $(\underline{x}, t)$, then the nonlinearity becomes more complex. Not only does the transformation $\frac{\partial}{\partial \tau} = \frac{\partial}{\partial t} + \underline{v} \cdot \nabla$ contribute a convection term $\underline{v} \cdot \nabla$ to each equation, but also the definitions of $\hat{\boldsymbol{\varepsilon}}$ and $\underline{v}$ in terms of $\nabla \underline{u}$ and $\frac{\partial \underline{u}}{\partial t}$ are nonlinear: $\hat{\varepsilon} = \nabla \underline{u} + (\nabla \underline{u})^2 + O(\nabla \underline{u})^3$ and $\underline{v} = \frac{\partial \underline{u}}{\partial t} + \nabla \underline{u} \frac{\partial \underline{u}}{\partial t}$ (where $\nabla \underline{u}$ is manipulated like a matrix). Of course, if $\underline{v}$ is small and spatial derivatives of the strain are small, then the system can be linearized, and the choice of coordinates is unimportant.

Example 3.6: For the linear case with negligible swelling, the equation for the concentration is

$$\begin{aligned} \frac{\partial c}{\partial t} &= D\left[\nabla^2 c(\underline{x}, t) - L\frac{\omega^2}{\alpha}\int_0^t e^{-LK(t-s)} \nabla^2 c(\underline{x}, s)\, ds\right] \\ &= D\left[\delta(t) - L\frac{\omega^2}{\alpha} e^{-L\kappa t}\right] * \nabla^2 c(x, t), \end{aligned} \tag{3.38}$$

where $(*)$ indicates the convolution product with respect to time and $\delta(t)$ is the Dirac delta function. This equation was derived by P. Neogi [24]. Thus, for the linear case, the diffusion coefficient is replaced by a time dependent operator analogous to the replacement of the elastic cofficients for linear viscoelastic materials. One could therefore propose by analogy the more general model, found in the Appendix, of

$$\frac{\partial c}{\partial t} = D(t) * \nabla^2 c(x, t)$$

where $D(t)$ is a kernel which decays with time.

Differentiating (3.38) with respect to time, and adding $L\kappa\cdot$(3.38) to the result yields the partial differential equation

$$c_{tt} + L\kappa c_t = D\left[\nabla^2 c_t + L(\kappa - \omega^2/\alpha)\nabla^2 c\right].$$

Conditions 3.36 tell us that D, α, $L\kappa$, and $L(\kappa-\omega^2/\alpha)$ are all positive. If we nondimensionalize by taking $\tilde{t} = t/L\kappa$ and $\tilde{\underline{\boldsymbol{x}}} = \left(\frac{L\kappa}{D}\right)^{\frac{1}{2}}\underline{\boldsymbol{x}}$, then this equation is

$$c_{\tilde{t}\tilde{t}} + c_{\tilde{t}} = \tilde{\nabla}^2 c_{\tilde{t}} + \left(1 - \frac{\omega^2}{\alpha\kappa}\right)\tilde{\nabla}^2 c$$

with $0 < 1 - \frac{\omega^2}{\alpha\kappa} \le 1$ and $\tilde{\nabla}^2 = \sum \frac{\partial}{\partial \tilde{x}_i^2}$, or, in one dimension,

$$c_{\tilde{t}\tilde{t}} + c_{\tilde{t}} = c_{\tilde{x}\tilde{x}\tilde{t}} + \left(1 - \frac{\omega^2}{\alpha\kappa}\right)c_{\tilde{x}\tilde{x}}.$$

Example 3.7: Suppose that we have a uniform piece of solid, initially stress-free, and subject it to isotropic compression. The stress-strain relation is given by (3.37)

$$(\hat{\boldsymbol{\sigma}} - \hat{\boldsymbol{\Pi}})/\rho_o = f\,\hat{\mathbf{I}} = \left[(s_\varepsilon + \gamma\nu_\xi)\varepsilon + (\gamma + \nu_\xi\kappa)\xi + \nu^s\frac{d\varepsilon}{dt}\right]\hat{\mathbf{I}}$$

where

$$\xi = \xi_o e^{-L\kappa t} - \int_0^t e^{-L\kappa(t-s)}\left(L\gamma\varepsilon + \nu_\xi\frac{d\varepsilon}{dt}\right)ds.$$

Substituting ξ into the expression for f,

$$\begin{aligned} f &= (s_\varepsilon + \gamma\nu_\xi)\varepsilon + \nu^s\frac{d\varepsilon}{dt} \\ &\quad + (\gamma + \nu_\xi\kappa)\left[\xi_o e^{-L\kappa t} - \int_0^t e^{-L\kappa(t-s)}\left(L\gamma\varepsilon + \nu_\xi\frac{d\varepsilon}{dx}\right)ds\right] \end{aligned}$$

where, since $f = 0$ initially and stays zero if $\varepsilon \equiv 0$, $\xi_o = 0$. Integrating by parts,

$$
\begin{aligned}
f &= (s_\varepsilon - \gamma^2/\kappa)\varepsilon + \nu^s \frac{d\varepsilon}{dt} + (\gamma^2/\kappa - \kappa\nu_\xi^2)\int_0^t e^{-L\kappa(t-s)} \frac{d\varepsilon}{ds} ds \\
&= \frac{1}{\rho_o} B(t) * \frac{d\varepsilon}{dt}.
\end{aligned}
$$

Here the $B(t)$ is the bulk relaxation modulus

$$
B(t) = \rho_o\left[\left[\left(s_\varepsilon - \frac{\gamma^2}{\kappa}\right) + \left(\frac{\gamma^2}{\kappa} - \kappa\nu_\xi^2\right) e^{-L\kappa t}\right] H(t) + \nu^s \delta(t)\right],
$$

where $H(t)$ is the unit step function. The constraints on our coefficients tell us that $s_\varepsilon - \gamma^2/\kappa$, ν^s, L, $\nu^s L - \nu_\xi^2$ and κ are all positive. (The analog model for this stress-strain response is three elements in parallel: a spring with spring constant $\rho_o(s_\varepsilon - \gamma^2/\kappa) > 0$, a dashpot with viscosity $\rho_o\nu^s > 0$, and a Maxwell element with decay rate $L\kappa$ and strength $\gamma^2 - \kappa\nu_\xi{}^2$). ($\rho_o(s_\varepsilon - \gamma^2/\kappa)$ tells the final volume change which occurs under a constant compression, $\rho_o\nu^s$ the resistance to rapid compression.)

In general, the relaxation modulus will be more complex, with B(t) some function which decays over time.

If we were to apply either a shear or uniaxial tension to our solid, rather than isotropic compression as in example 3.7, we would find that the model does not incorporate any history-dependence. This occurs because the internal parameter was taken to behave like a scalar. By adding internal parameters that behave under coordinate transformations as tensors, a more general model can be obtained. These calculations appear in the Appendix for the case when the quadratic dependence of the chemical potential and the dependence of the linear phenomenological coefficients on the strains and internal changes can be neglected. The resulting model is

$$
\frac{\partial c}{\partial \tau} = \nabla\cdot\left[J_\mu(c)\nabla\mu - \int_0^\tau K(\underline{\chi},\tau,\theta)\nabla\mu(\underline{\chi},\theta)\,d\theta\right] \tag{3.39a}
$$

$$
\begin{aligned}
\mu(\underline{\chi},\tau) &= m_o(\tau,c) + \beta(c)\varepsilon - \int_0^\tau d\theta\big(M_c(\underline{\chi},\tau,\theta) \\
&\quad + M_\varepsilon(\underline{\chi},\tau,\theta)\varepsilon(\underline{\chi},\theta) + M_\nu(\underline{\chi},\tau,\theta)\nabla\cdot\underline{v}(\underline{\chi},\theta)\big),
\end{aligned} \tag{3.39b}
$$

$$
\frac{\partial \underline{v}}{\partial \tau} = \nabla\cdot(\hat{\sigma} - \hat{\Pi})/\rho_o, \tag{3.39c}
$$

and

$$
\begin{aligned}
(\hat{\boldsymbol{\sigma}} - \hat{\boldsymbol{\Pi}})/\rho_o = &\int_0^\tau [B(\underline{\chi},\tau,\theta) + B_\varepsilon(\underline{\chi},\tau,\theta) - \frac{1}{3}S_\varepsilon(\underline{\chi},\tau,\theta))\varepsilon(\underline{\chi},\theta) \\
&+ (B_\nu(\underline{\chi},\tau,\theta) - \frac{1}{3}S_\nu(\underline{\chi},\tau,\theta))\nabla\cdot\underline{v}(\underline{\chi},\theta)]d\theta\, \hat{\mathbf{I}} \\
&+ \int_0^\tau [S_\nu(\underline{\chi},\tau,\theta)\nabla\underline{v}(\underline{\chi},\theta) + S_\varepsilon(\underline{\chi},\tau,\theta)\hat{\boldsymbol{\varepsilon}}(\underline{\chi},\theta)]d\theta.
\end{aligned}
\tag{3.39d}
$$

Each of the time-dependent kernels K^ν, M_c, M_ε, M_ν, B, B_ε, B_ν, S_ε and S_ν depend on the values of the concentration for times in $[0,\tau]$, while m_o depends on c for times in $[0,\tau]$. The $\underline{\chi}$-dependence arises solely from this concentration dependence. We could write this in explicitly by using the notation

$$K(\underline{\chi},c,\eta) = K(\tau,\theta,c(\underline{\chi},[\theta,\tau]))$$

for each of the kernels.

When chemical potential and stresses depend linearly on the concentration, and the linear phenomenological coefficients are constants, this model simplifies to (A2.18):

$$\frac{\partial c}{\partial \tau} = \nabla\cdot[(\delta(\tau) + \kappa(\tau)) * \nabla\mu(\underline{\chi},\tau)\,], \tag{3.40a}$$

$$\mu(\underline{\chi},\tau) = D(\tau) * \frac{\partial c}{\partial \tau}(\underline{\chi},\tau) + D_\varepsilon(\tau) * \frac{\partial \varepsilon}{\partial \tau}(\underline{\chi},\tau) + D_\nu(\tau) * \nabla\cdot\underline{v}(\underline{\chi},\tau), \tag{3.40b}$$

$$
\begin{aligned}
\frac{\partial \underline{v}}{\partial \tau} = &\nabla\left[B(\tau) * \frac{\partial c}{\partial \tau}(\underline{\chi},\tau) + \frac{1}{\rho_o}\lambda(\tau) * \frac{\partial \varepsilon}{\partial \tau}(\underline{\chi},\tau)\right] \\
&+ \nabla\cdot\left[\frac{2}{\rho_o}G(\tau) * \frac{\partial \hat{\boldsymbol{\varepsilon}}}{\partial \tau}(\underline{\chi},\tau)\right] - \frac{1}{2}(\eta_o \sum_{ij} \nabla\varepsilon_{ij}\,\frac{\partial \varepsilon_{ij}}{\partial \tau} \\
&+ \nu^o \nabla\varepsilon\cdot\frac{\partial \hat{\boldsymbol{\varepsilon}}}{\partial \tau})
\end{aligned}
\tag{3.40c}
$$

where $g * f$ denotes the convolution product

$$g * f = \int_0^\tau g(\tau-\tau')f(\tau')d\tau$$

and where $\delta(\tau-\tau')$ is the Dirac delta function. The stress components are given by (A2.19)

$$
\begin{aligned}
\sigma_{ij} - \Pi_{ij} = &\, G(\tau) * \frac{\partial \varepsilon_{ij}}{\partial \tau}(\underline{\chi},\tau) + \delta_{ij}[\lambda(\tau) * \frac{\partial \varepsilon}{\partial \tau}(\underline{\chi},\tau) \\
&+ \rho_o(B_o(\tau) + B(\tau) * \frac{\partial c}{\partial \tau}(\underline{\chi},\tau))].
\end{aligned}
$$

Example: If the initial stress on a uniform isotropic solid is zero and a uniform strain history $\hat{\boldsymbol{\varepsilon}}(t)$ is applied, then the stress components are

$$f_{ij} = \sigma_{ij} - \Pi_{ij} = 2G(t) * \frac{d\,\varepsilon_{ij}}{dt} + \lambda(t) * \frac{d\,\varepsilon}{dt}.$$

This is the standard stress-strain relation for a linear isotropic viscoelastic material, and our derivation of this relation is equivalent to the Wiechert formulation of the stress-strain relations [25]. This is easily seen, because the separated equations satisfied by the internal parameters are in the same form as those satisfied by Maxwell elements. The relaxation modulus

$$G(t) = G_\infty + \int_0^\infty \tilde{g}(k) e^{-\lambda^s(k)t}\,dk$$

can be written as

$$G(t) = G_{ij} + \int_0^\infty g(T) e^{-t/T}\,dT$$

if we let

$$g(T) = \frac{\tilde{g}(k)}{\dfrac{d\lambda^s(k)}{dk}} \left(-\frac{1}{T^2}\right)$$

and

$$T = \frac{1}{\lambda^s(k)}\,.$$

Similarly, $\lambda(t)$ can be written in standard form.

4. One-dimension and Case II diffusion: a simplified model. In this section, we discuss the model as it applies to a common experimental situation: diffusion through a membrane of glassy, amorphous polymer, which is initially in equilibrium at a fluid concentration c_0 and negligible pressure ($\hat{\sigma} = 0$), and which at time zero is placed in a reservoir of the fluid. If the surface area of the polymer sheet is large enough, and if we are interested only in the behavior in the regions far from the edges, it can be idealized as infinite. By examining the available data on a particular polymer which is known to exhibit Case II diffusion, we are able to obtain a simplified model for Case II diffusion and demonstrate that Case II behavior is indeed a possible consequence of the model. This model predicts that the sharp fronts between wet and dry regions are carried along by the coupled nonlinear convection, viscosity and relaxation, with diffusion occurring only in the front region. Inertial effects are found to be negligible.

a. Model for an infinite sheet. For an infinite sheet subject to uniform surface conditions, movement can occur only in the direction orthogonal to the sheet, and the problem reduces to one dimension. Letting x denote that direction, the nonlinear model (A3.32) with a single scalar internal process reduces to

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x}\left[D\left(\frac{\partial c}{\partial x} + d\,\frac{\partial \varepsilon}{\partial x} + d_\eta\,\frac{\partial \eta}{\partial x}\right)\right], \tag{4.1a}$$

$$\frac{\partial v}{\partial \tau} = \frac{\partial}{\partial x}\Big[b(c)\varepsilon + (\nu_\xi K + \gamma)\eta\Big] + \beta(c)\,\frac{\partial c}{\partial x} + \frac{\partial}{\partial x}\left[\nu(c)\,\frac{\partial v}{\partial x}\right], \tag{4.1b}$$

and

$$\frac{\partial \eta}{\partial \tau} = \frac{\omega}{K}\,\frac{\partial c}{\partial \tau} + \left[\frac{\gamma}{K} - \nu_\xi\right]\frac{\partial \varepsilon}{\partial \tau} - KL\eta, \tag{4.1c}$$

where

$$\varepsilon = \frac{\partial u}{\partial \chi}, \qquad v = \frac{\partial u}{\partial \tau}, \tag{4.1d}$$

and u is the displacement of the center-of-mass in the x-direction. Here D, $d = d_\varepsilon + \frac{2}{3} d_o \varepsilon$ and d_η may be linear functions of ε and η and nonlinear functions of c, while $b = s_\varepsilon + \frac{2}{3} s_o$, $\nu = \nu^s + \frac{2}{3} \nu^o$, β, ν_ξ, K, L, ω and γ are all nonlinear functions of the concentration. Rather than writing down the more general model (3.39) in one dimension, we shall assume, for the purpose of discussion, that these equations are valid.

Initially the sheet is between $x = \pm l$, and $c = c_o$, $\varepsilon = \eta = 0$. If the diffusion process were Fickian, then the surface of the solid would come instantly to equilibrium at the final concentration c_1. The question of whether or not this remains a valid boundary condition for the process of diffusion with swelling will be left alone for the present. For example, there is some evidence that, in the case when two-stage diffusion is observed, the surface relaxes slowly to its final equilibrium value [22]. For Case II sorption, the assumption of an instantaneous jump to the final concentration c does seem consistent with the travelling front evidence, but this is, of course, something which must be evaluated.

A second boundary condition comes from assuming that the fluid exerts a negligible surface stress on the solid surface. If we let $\hat{\boldsymbol{\sigma}}$ denote the total stress, rather than the equilibrium stress, then $\sigma_{ij} = 0$ for $i \neq j$ and

$$\sigma_{xx} = \rho_o \left[\int_{c_o}^{c} \beta(c)dc + b(c)\varepsilon + (\nu_\xi K + \gamma)\eta + \nu(c)\frac{\partial \varepsilon}{\partial \tau} \right] \tag{4.2a}$$

$$\sigma_{yy} = \sigma_{zz} = \rho_o \left[\int_{c_o}^{c} \beta(c)dc + s_\varepsilon(c)\varepsilon + (\nu_\xi K + \gamma)\eta + \nu^s(c)\frac{\partial \varepsilon}{\partial \tau} \right]. \tag{4.2b}$$

Thus $\sigma_{xx} = 0$ on the solid surface gives an equation relating ε, $\frac{\partial \varepsilon}{\partial \tau}$ and η on the boundary, and this condition will prove useful later.

b. Solid-fixed coordinates. As mentioned in example (3.5), the main difficulty in applying the boundary conditions is to determine the position of the fluid-solid interface. The transformation from (x,t) to (x_s,t_s) coordinates is easily obtained in one dimension. The solid density ρ_s and solid velocity $v_s = \dfrac{\partial x}{\partial t_s}$ are given by the definitions of the total density and center-of-mass velocity (1.5), (1.6)

$$\rho = \rho_s + \rho_f = \rho_s + \rho c,$$

and

$$\rho v = \rho_s v_s + \rho_f v_f = \rho(1-c)v_s + J_f + \rho c v,$$

since $J_f = \rho_f(v_f - v)$ is the fluid flux. In one dimension, the densities satisfy (exactly)

$$\rho = \rho_o/(1+\varepsilon), \quad \rho_s = \rho_{s_o}/(1+\varepsilon_s),$$

where ρ_{s_o} is the initial solid density, and where ε_s is the solid strain: $\varepsilon_s = \dfrac{\partial x}{\partial x_s} - 1$. From this, we obtain the transformation from (x,t) to (x_s,t_s) coordinates:

$$\begin{aligned} \frac{\partial x}{\partial x_s} &= \frac{1+\varepsilon}{1-c}(1-c_o), & \frac{\partial x}{\partial t_s} &= v - \frac{J_f(1+\varepsilon)}{\rho_o(1-c)} \\ \frac{\partial t}{\partial t_s} &= 1 \qquad , & \frac{\partial t}{\partial x_s} &= 0. \end{aligned} \tag{4.3}$$

For the single relaxation process of (4.1),

$$\frac{1}{\rho_o} J_f = D\left[\frac{\partial c}{\partial x} + d\,\frac{\partial \varepsilon}{\partial x} + d_\eta \frac{\partial \eta}{\partial x}\right]. \tag{4.4}$$

In solid coordinates the boundaries are fixed at $x_s = \pm l$, while in fixed coordinates they are at $x = \pm x_d$, moving at a velocity

$$v_s = v - \frac{J_f}{\rho_o}\left[\frac{1+\varepsilon}{1-c}\right]. \tag{4.5}$$

c. Case II behavior: an example and a proposed model. In system (4.1), there are a large number of parameters, whose values and functional form depend on the choice of material. By looking at a characteristic glassy polymer which exhibits classical Case II diffusion, we can get a good idea of the relative sizes of the parameters, and the scales which are involved when Case II diffusion occurs. Experimental evidence does not yet exist for the newly defined parameters; however, by making use of the available information, the inequalities (3.33) and a few assumptions, we can obtain a reasonable picture of what is happening.

Such a polymer is the linear polymer *polymethyl methacrylate* (PMMA), for which a fair amount of information is available in the open literature, and which displays clear-cut Case II behavior over a fairly wide range of temperatures.

Example. Thomas and Windle performed a series of experiments, at different temperatures, on polymethyl methacrylate [7,26]. The samples were membranes 1-3 mm thick, initially dry, which were suspended freely in a bath of methanol at time zero. Their observations indicated that, except near the edges, the behavior was one-dimensional. They found that at temperatures well below the glass transition temperature ($105°C$ for dry PMMA), the diffusion process exhibited classical Case II diffusion, with a sharp front moving inward at near constant velocity, separating a wet, swollen yet glassy region from the dry region in front of the front. At higher temperatures, the fronts break down as they move into the material; the region just behind the front is no longer at its final concentration and the fronts slow down as they move inward. By $62°C$, no initial Case II behavior is observed at all. Front velocities increase with increasing temperature.

The front appears to speed up slightly at $0°C$, and thus diffusion of PMMA varies from Case II, or even so-called Super Case II, at temperatures low enough that even the wet polymer is glassy, through Case II diffusion with a wet region in the glass transition region, up to Fickian diffusion with a wet rubbery region.

Let us concentrate on the measurements where the polymer stays glassy. At $0°C$ the front velocity is 3.9×10^{-9} cm/sec, increasing to 3.9×10^{-8} cm/sec at $15°C$. In both cases the mass uptake is 21%. The front thickness appears to be on the order of 10^{-3} cm. At $15°C$, where the swollen polymer is just below the glass transition region, the samples swelled from 1 mm to 1.23 mm, so that $\varepsilon_s = .23$ and $c = .17$. Using these in the formula (4.3) $1 + \varepsilon = \frac{1 - c}{1 + \varepsilon_s}$ gives $\varepsilon = -.04$, which is only a rough estimate, but indicates that ε is indeed fairly small.

In order to model the diffusion process in PMMA (or any other substance) with (4.1), we need a rough estimate of the parameters appearing in the equations. The effects of temperature increases and of fluid concentration increases on the properties of a glassy polymer are very similar because the free volume and internal mobility of the polymer increases with both. This allows us to estimate the concentration dependence of a property, even when only the temperature dependence is known.

The density of PMMA is about $1 gm/cm^3$. The diffusion coefficient increases rapidly with concentration from 10^{-14} or 10^{-13} to $10^{-10} cm^2/sec$ within the glassy region [17]. Under a small applied constant strain, the stress in dry PMMA is initially about $10^{10} dynes/cm^2$ throughout the glassy region, decaying to zero as time goes to infinity. The rate of decay is very temperature sensitive. The time to decay to one-third the initial value decreases from roughly $10^9 sec$ at $20°C$ to

$10^7 sec$ at $40°C$ up to $10^4 sec$ just below the glass transition temperature [25]. Under a small applied stress, the initial rate of strain per unit stress is about $10^{-18} cm\cdot sec/gm$ at $20°C$, increasing with time by a factor of 10 or 100 and also increasing with temperature [27].

If a uniform strain is applied to a dry solid which is initially stress-free and in equilibrium, and which is modelled by (4.1) and (4.2), the stress σ_{xx} is given by (4.2a) and (4.1c) combined as

$$\sigma_{xx} = \rho_o \left[b\,\varepsilon + \frac{1}{K}\left(\gamma^2 - (\nu_\xi K)^2\right) \int_0^t e^{-KL(t-s)} \frac{d\varepsilon(s)}{dt} ds + \nu \frac{d\varepsilon}{dt} \right].$$

The stress due to a step in strain $\varepsilon = \varepsilon_o H(t)$ is

$$\sigma_{xx} = \rho_o \left[b + \frac{1}{K}\left(\gamma^2 - (\nu_\xi K)^2\right) e^{-KLt} \right] \varepsilon_o .$$

Since the stress decays to zero for all temperatures within the glassy region, we can assume that $b(c) \equiv 0$. The inequalities (3.33) and definitions (3.29) of d_ε and d_o then imply that $\beta(c)$ is also zero, and d is order $(|\varepsilon| + |\eta|)$. Setting b to zero, and using Laplace transforms to invert the stress-strain relation gives

$$\varepsilon = \frac{1}{\rho_o \nu} \int_0^\tau \left[\left(1 - \frac{KL}{\Omega} \right) e^{-\Omega(t-s)} + \frac{KL}{\Omega} \right] \sigma(s) ds ,$$

where

$$\Omega = KL + \frac{1}{K\nu}\left(\gamma^2 - K^2 \nu_\xi^2\right) > 0.$$

The response to an applied stress step $\sigma_{xx} = \sigma_o H(t)$ is thus

$$\varepsilon = \frac{1}{\rho_o \nu} \left[\frac{KL}{\Omega} t + \frac{1}{\Omega}\left(1 - \frac{KL}{\Omega}\right)\left(1 - e^{-\Omega t}\right) \right] \sigma_o$$

and

$$\frac{d\varepsilon}{dt} = \frac{1}{\rho_o \nu}\left[\frac{KL}{\Omega}(1 - e^{-\Omega t}) + e^{-\Omega t}\right]\sigma_o .$$

Then for PMMA in the glassy region at about 15°C

D increases with c from about 10^{-13} to $10^{-10} cm^2/sec$,

KL increases with c from roughly $10^{-8} sec^{-1}$ to $10^{-3} sec^{-1}$,

$\frac{1}{K}(\gamma^2 - (\nu_\xi K)^2)$ is fairly constant, about $10^{10} cm^2/sec^2$, and

ν is roughly $10^{18} cm^2/sec$, decreasing with increasing c, although how rapidly it decreases is difficult to ascertain.

If we nondimensionalize system (4.1) by letting

$$\bar{x} = x/X_o, \quad \bar{\tau} = \tau/T_o, \quad \bar{u} = u/X_o, \quad \bar{v} = T_o v/X_o,$$

for characteristic lengths X_o and T_o, we obtain

$$c_{\bar\tau} = \frac{T_o}{X_o^2}\left[D(c_{\bar x} + d\,\varepsilon_{\bar x} + d_\eta \eta_{\bar x})\right]_{\bar x}, \tag{4.6a}$$

$$\bar{v}_{\bar\tau} = \left(\frac{T_o}{X_o}\right)^2\left[(b\,\varepsilon + (\gamma + \nu_\xi K)\eta)_{\bar x} + \beta(c)c_{\bar x}\right] + \frac{T_o}{X_o^2}\left[\nu(c)\bar{v}_{\bar x}\right]_{\bar x}, \tag{4.6b}$$

$$\eta_{\bar\tau} = \frac{\omega}{K}c_{\bar\tau} + \left[\frac{\gamma}{K} - \nu_\xi\right]\varepsilon_{\bar\tau} - KLT_o\eta, \tag{4.6c}$$

$$\bar{u}_{\bar x} = \varepsilon, \quad \bar{u}_{\bar\tau} = \bar{v}, \tag{4.6d}$$

with

$$\bar{x} \in (-l/X_o, l/X_o)$$

initially.

In a glassy PMMA, and for any other glassy polymer without cross-links, b and β both vanish, so that the middle equation becomes

$$\bar{v}_{\bar{\tau}} = \frac{T_o}{X_o^2}\Big[T_o(\gamma + \nu_\xi K)\eta + \nu(c)\bar{v}_{\bar{x}}\Big]_{\bar{x}}. \tag{4.6b'}$$

This system contains the nondimensional parameters

$$\frac{DKL}{\gamma},\ \frac{\nu KL}{\gamma},\ \frac{D}{(2l)^2KL},\ d,\ d_\eta,\ \nu_\xi,\ \frac{\gamma}{K} \text{ and } \frac{\omega}{K}.$$

If we assume that γ/K is an order 1 quantity and that d, d_η, ν_ξ and ω/K are order 1 or smaller, then the possible length and time scales are given by

$$X_o/2l,\ T_oKL,\ \frac{DT_o}{X_o^2},\ \gamma\left(\frac{T_o}{X_o}\right)^2 \text{ and } \frac{\nu T_o}{X_o^2}.$$

In order for the inertia terms in the momentum equation to balance the stress gradients on the right-hand side, T_o/X_o must be about $10^{-5}sec/cm$, or else T_o/X_o^2 must be less than $10^{-13}sec/cm^3$. Since the maximum distance of interest is the sample thickness of $10^{-1}cm$, T_o is no more that $10^{-6}sec$ when this balance occurs, and the inertia terms can participate only in the initial transients. Neglecting them allows us to integrate the momentum equation, and obtain

$$0 = \sigma_{\bar{x}\bar{x}}/\rho_o = \left[(\gamma + K\nu_\xi)\eta + \frac{1}{T_o}\nu(c)\bar{v}_{\bar{x}}\right]$$

or

$$\eta = -\frac{\nu}{T_o(\gamma + K\nu_\xi)}\bar{v}_{\bar{x}}. \tag{4.6b''}$$

Choosing $X_o = 2l$, $T_o = 1/KL$ gives that

$$\frac{DT_o}{X_o^2} = \frac{D}{(2l)^2 KL}$$

is somewhere in the range of 10^{-5} to 10^{-3} in the glassy region; and

$$\frac{\nu}{T_o\gamma} = \frac{\nu KL}{\gamma},$$

which is on the order of 1 in the dry polymer at $20°C$, and may not vary much with c and T (ν decreases while KL increases and γ stays nearly constant).

Of course, KL, D and ν all vary rapidly with concentration changes, but we can choose a representative value for the scaling (For example the values in the dry polymer can be used). Let Ω_o and ν_o be these values for KL and D, respectively, and let

$$\delta \equiv \frac{D_o}{(2l)^2\Omega_o},\ \overline{D} = \frac{D}{D_o},\ \overline{KL} = \Omega_o KL,$$
$$X_o = 2l \text{ and } T_o = \frac{1}{\Omega_o}.$$

Using (4.6b'') to eliminate η from (4.6a,c), and dropping the bars on the variables gives

$$\begin{aligned} c_\tau &= \delta\left[\overline{D}\left(c_x + d\,\varepsilon_x - d_\eta\left(\frac{\nu\Omega_o}{(\gamma + K\nu_\xi)}v_x\right)_x\right)\right]_x, \\ -\left(\frac{\nu\Omega_o}{(\gamma + K\nu_\xi)}v_x\right)_\tau &= \frac{\omega}{K}c_\tau + \left(\frac{\gamma}{K} - \nu_\xi\right)\varepsilon_\tau + \frac{\overline{KL}\,\nu\Omega_o}{(\gamma + K\nu_\xi)}v_x, \\ v = u_\tau,\quad \varepsilon &= u_\chi \end{aligned} \tag{4.7}$$

with $\delta \ll 1$. Setting $\delta = 0$, we obtain the outer equations

$$c_\tau = 0,$$

and

$$v_{x\tau} + \overline{KL}v_x + \frac{\gamma^2 - (\nu_\xi\kappa)^2}{K\Omega_o\nu}\varepsilon_\tau = 0$$

or, since $\frac{\partial}{\partial x} = (1 + \varepsilon)^{-1}\frac{\partial}{\partial \chi}$, in center-of-mass coordinates,

$$\begin{aligned} c_\tau &= 0 \\ \varepsilon_{\tau\tau} + R(c)\varepsilon_\tau &= 0 \end{aligned}$$

with

$$R(c) = \overline{KL} + \frac{\gamma^2 - (\nu_\xi \kappa)^2}{K\Omega_o \nu}.$$

The transformation to solid-fixed coordinates gives

$$\frac{\partial}{\partial \tau} = \frac{\partial}{\partial t_s} + \delta \overline{D}(c_x + d\,\varepsilon_x + d_\eta \eta_x)\frac{\partial}{\partial x_s}$$

so that, to first order, $\frac{\partial}{\partial \tau} = \frac{\partial}{\partial t_s}$ and integrating gives

$$\begin{aligned} c &= c(x_s), \\ \varepsilon_{t_s} &+ R(c)\varepsilon = g(x_s). \end{aligned}$$

In (x,t) coordinates, $c = constant$ and

$$\frac{d\varepsilon}{dt} + R(c)\varepsilon = constant$$

along lines given by $\frac{dx}{dt} = v_s = v$, with

$$v_x = \varepsilon_t + v\,\varepsilon_x$$

defining the slope of the lines at any given point (or

$$\frac{\partial v}{\partial x_s} = \frac{\partial \varepsilon_s}{\partial t_s} = \frac{\partial}{\partial t_s}\left[\frac{1 + \varepsilon}{1 - c}\right](1 - c_o) = \frac{\partial \varepsilon}{\partial t_s}\left[\frac{1 - c_o}{1 - c}\right]).$$

From the observer's point of view, this is an hyperbolic system, and if the velocities v are not constant, shocks are possible. Whether or not a discontinuity occurs depends on the initial values and boundary conditions. It is easy to see that a travelling wave is a solution to this system: let

$$c = C(x - vt), \quad \varepsilon = E(x - vt).$$

Then

$$c_\tau = c_t + vc_x = -C'v_\tau = 0$$

if $v_\tau = 0$. Similarly, $\varepsilon_\tau = 0$ if $v_\tau = 0$, implying that $v_{x_s} = 0$ and

$$\varepsilon_\tau + R(c)\varepsilon = R(c)E.$$

Since $v_\tau = 0$, the velocity of each characteristic is constant and its position is given by $x = vt + x_o$. If any of these straight characteristics cross, a shock may form with a jump in velocity across the shock. If $C(x)$, $E(x)$ are not constants, c and ε will also jump across the shock. Since $v_{x_s} = 0$, there will be regions of constant velocity (expansion fans will not occur) which intersect and form a shock. Clearly, it is possible that such travelling waves could form under the experimental conditions; if swelling occurs, a shock must form between a still region and a region moving at constant velocity.

When any discontinuities in the outer solutions or boundary data occur, such as initially near $x = \pm\frac{1}{2}$ and later along the shock, we can stretch the coordinates in system (4.7) to obtain an equation which describes the system behavior in the discontinuous region. Let $\tilde{x} = x/X_1$, $\tilde{\tau} = \tau$ and take $X_1 = \delta^{\frac{1}{2}}$. Then

$$c_{\tilde{\tau}} = \left[\bar{D}\left[c_{\tilde{x}} + d\,\varepsilon_{\tilde{x}} - d_\eta\left(\frac{\nu\Omega_o}{\gamma + K\nu_\xi}\tilde{v}_{\tilde{x}}\right)_{\tilde{x}}\right]\right]_{\tilde{x}},$$

$$\left(\frac{\nu\Omega_o}{\gamma + K\nu_\xi}\tilde{v}_{\tilde{x}}\right)_{\tilde{\tau}} + \frac{\overline{KL}\,\nu\Omega_o}{(\gamma + K\nu_\xi)}\tilde{v}_{\tilde{x}} + \frac{\omega}{K}c_{\tilde{\tau}} + \left(\frac{\gamma}{K} - \nu_\xi\right)\varepsilon_{\tilde{\tau}} = 0,$$

with $\tilde{v} = \frac{\partial \tilde{u}}{\partial \tilde{\tau}}$ and $\tilde{u} = u/\delta^{\frac{1}{2}}$. Thus the inner equations are the full system.

Linearization of this system shows that it is locally parabolic everywhere. The linearized equations can be written as a single equation for c

$$c_{\theta\theta} + c_{\theta} = c_{yy} + \left(1 + \frac{\omega^2}{\alpha K}\right) c_{yy\theta},$$

where $\theta = R\tilde{t}$ and $y = \overline{D}^{\frac{1}{2}}\tilde{x}$, and where

$$R = \overline{KL} + \frac{1}{K\nu\Omega_o}\left(\gamma^2 - (K\nu_{\xi})^2\right) > 0.$$

Due to the parabolic nature of the full equations, the solution will be smooth in the stretched variables, and it is obvious that it is the nonlinearities in the system, in particular the convection coupled to relaxation which drive the front.

Although further analysis of this model needs to be done (in particular the effect of appropriate boundary conditions needs to be ascertained), it appears to contain the basic qualitative features of Case II diffusion. The scaling is also roughly correct. $X_o / T_o = KL \cdot 2l$ increases with temperature, about $10^{-8} cm/sec$ at $40°C$ in the dry polymer, or about the same as the front velocity at $15°C$, while $2l\delta^{\frac{1}{2}}$ is about $10^{-2.5}$ or $10^{-3} cm$, which corresponds to the barely visible front thickness in the microdensometer traces given by Thomas and Windle.

Special Case: Under certain circumstances, system (4.7) will reduce to the equations proposed by Thomas and Windle [17]. Changing their notation, they have two equations, one which balances osmotic pressure and viscous flow

$$c_{\tau} = -f(c)(\ln c - \Delta\mu / RT)$$

and the concentration equation

$$c_\tau = \left[\frac{D(c)c}{RT} (\Delta\mu)_z \right]_z .$$

Eliminating $\Delta\mu$ gives

$$\begin{aligned} c_\tau &= \left[D(c)c \left[(\ln c)_z + \left[\frac{1}{f(c)} c_\tau \right]_z \right] \right]_z \\ &= \left[D(c) \left[c_z + \frac{c c_{\tau z}}{f(c)} - \frac{c f'(c) c_z c_\tau}{f^2} \right] \right]_z . \end{aligned} \tag{4.8}$$

If, in our system, we assume that $\eta_\tau = 0$ then the second equation in (4.7) becomes

$$\left[\frac{\overline{KL} \nu \Omega_0}{(\gamma + K\nu_\xi)} + \frac{\gamma}{K} - \nu_\xi \right] v_z = \frac{\omega}{K} c_\tau$$

to first order in ε. Using this expression, v_z can be eliminated from the first equation in (4.7). Setting $\mathbf{d}_\eta = c$, $\mathbf{d} = 0$ ($\mathbf{d}$ is $O(|\varepsilon| + |\eta|)$ anyway), in the result gives an equation of the same form as (4.8).

The properties of PMMA are similar to those of many other glassy polymers. Therefore, it seems reasonable to propose system (4.7), along with proper boundary conditions, as a model which contains the basic features of the Case II diffusion processs, although it may not contain all of the subtleties observed in the experiments.

Appendix:
Generalization to complex internal processes.

In the development of the model in the main sections, it was assumed that only a single, scalar internal process could occur. In general, more complex internal relaxations and reorderings can, and will, take place inside the solid. The internal parameters characterizing the process may transform like tensors of any order, and many processes may occur simultaneously. Besides coupled processes characterized by discrete sets of internal parameters, it may also be necessary to have a continuum of internal parameters (see deGroot and Mazur [2], Ch. X). In this Appendix, we generalize the derivation of Sections 2 and 3 in order to include all of these possibilities in our model, although we shall discover that internal processes whose tensor character is greater than two do not have any effect on the diffusion-swelling process in an isotropic system.

We begin with a short discussion on tensorial internal parameters which serves to introduce the notation that is employed in the derivation. In Section 2, the equations are derived for the case where the material properties can be regarded as constants, independent of the fluctuations in the system properties. These constants are replaced in Section 3 with concentration-dependent material properties. The derivation follows the same procedure as that of the previous sections, and therefore the presentation is much less detailed, containing only the changes in that model. However, we do depart in one significant way from that derivation; in the nonlinear model, no attempt is made to incorporate either the quadratic dependence of the chemical potential on the strains and internal parameters, or the dependence of the linear phenomenological coefficients on these quantities.

a. Preliminaries: Tensorial internal parameters and notation. The concept of an internal parameter was discussed in Section 2, but only a single scalar internal process was taken into account in the model. In general, many complex internal rearrangements may occur at the same time. The internal parameters that describe the internal changes of state may conceivably be tensors of any order. It may be possible to describe the system changes with a discrete set of variables $\hat{\boldsymbol{\xi}}_k$, but in the most general case it will be necessary to represent at least some of the changes with a continuum of variables $\hat{\boldsymbol{\xi}}(k)$ for k in some index set I, where I may contain discrete points as well as intervals. For convenience, we introduce some simplifying notation: Let $\hat{\boldsymbol{\xi}}$ and $\hat{\boldsymbol{\eta}}$ be tensors of order p, with q covariant and r contravariant indices. $\hat{\boldsymbol{\xi}}$ and $\hat{\boldsymbol{\eta}}$ have components $\xi_{\underline{i}}^{\underline{j}}$ and $\eta_{\underline{i}}^{\underline{j}}$ where $\underline{i} = i_1, i_2, \cdots, i_q$, $i_k \in \{1,2,\ldots,q\}$ and $\underline{j} = j_1, j_2, \cdots, j_r$, $j_k \in \{1,2,\cdots,r\}$. The scalar, or dot, product between $\hat{\boldsymbol{\xi}}$ and $\hat{\boldsymbol{\eta}}$ is defined as the sum over all products $\xi_{\underline{i}}^{\underline{j}}\eta_{\underline{i}}^{\underline{j}}$ and denoted

$$\hat{\boldsymbol{\xi}} \cdot \underline{\eta} \equiv \sum_{i_k=1}^{q} \sum_{j_k=1}^{r} \xi_{\underline{i}}^{\underline{j}}\eta_{\underline{i}}^{\underline{j}}. \tag{A1.1}$$

Tensors of order two or more can, in general, be broken down into components that transform under coordinate changes like lower order tensors, and into tensors that are inherently higher order. For example, a second order tensor $\hat{\boldsymbol{\xi}}$, such as the stress tensor, is the sum of its scalar trace times the identity $\hat{\mathbf{I}}$, an antisymmetric tensor $\hat{\boldsymbol{\xi}}^a$ and a symmetric traceless second order tensor $\hat{\boldsymbol{\xi}}^o$, or

$$\hat{\boldsymbol{\xi}} = (tr\hat{\boldsymbol{\xi}})\hat{\mathbf{I}} + \hat{\boldsymbol{\xi}}^a + \hat{\boldsymbol{\xi}}^o.$$

$\hat{\boldsymbol{\xi}}^o$ has five independent components, $\hat{\boldsymbol{\xi}}^a$ has three ($\hat{\boldsymbol{\xi}}^a$ transforms like a contravariant vector) and $(tr\hat{\boldsymbol{\xi}})\hat{\mathbf{I}}$ has one. Tensors of higher orders can be broken down in a similar manner. Since the choice of internal parameters is arbitrary, we can choose them so that each is of a distinct tensorial character, independent of lower rank tensors. Let $\xi^s(k)$, $\underline{\xi}^v(k)$, $\hat{\boldsymbol{\xi}}^o(k)$ and $\hat{\xi}^r(k)$ denote internal parameters which behave under coordinate transformations as scalars, covariant vectors, symmetric traceless second-order tensors and the remainder, respectively, and let I^s, I^v, I^o and I^r denote their respective index sets.

A symmetric traceless second order tensor has nine components, only five of which are independent. If $\tilde{\eta}_j$ denotes the independent components of the traceless symmetric second-order tensor $\hat{\boldsymbol{\eta}}$, we can take the $\tilde{\eta}_j$ to be

$$\tilde{\eta}_1 = \eta_{\xi\xi}, \quad \tilde{\eta}_2 = \eta_{yy}, \quad \tilde{\eta}_3 = \eta_{xy},$$
$$\tilde{\eta}_4 = \eta_{yz} \quad \text{and} \quad \tilde{\eta}_5 = \eta_{zx}.$$

Similarly, the $\xi^r(k)$ will have independent components $\tilde{\xi}_j^r(k)$.

b. Generalization: Linear case. In this section, we will derive the model for the case when the linear phenomenological coefficients can be treated as constants and the dependent parameters of the system can be treated as linear functions of the independent parameters. The procedure for deriving the equations with more general internal processes is nearly identical to that which was used in Chapter 1, Sections 2 and 3. All the assumptions of those sections remain valid, except for the addition of independent internal variables. The following presentation is therefore terse, containing only the relevant changes in details, and the reader is referred to Chapter 1 for an explanation of the reasoning and assumptions involved in the derivation.

The independent parameters of our isothermal process are assumed to be c, ε, $\tilde{\varepsilon}_j^o$, $\xi^s(k)$, $\xi_j^v(k)$, $\tilde{\xi}_j^o(k)$ and $\tilde{\xi}_j^r(k)$ for all possible indices j of the independent components of the $\hat{\xi}(k)$ and all k in the index sets I^s, I^v, I^o and I^r, where s, v, o, and r are used to refer to scalar, vector, traceless symmetric second-order tensors and all remaining tensors, respectively. The Helmholtz potential energy function per unit mass is a function of these parameters

$$f = f\,(c, \varepsilon, \widetilde{\varepsilon}_j^o, \xi^s(k), \underset{\sim}{\xi}^v(k), \widetilde{\xi}_j^o(k), \widetilde{\xi}_j^r(k))$$

with

$$\begin{aligned} df &= \mu dc + \frac{1}{\rho}\Big[\frac{1}{3} tr\,\widehat{\sigma}\, d\varepsilon + \sum_{j=1}^{5} \widetilde{\sigma}_j^o d\widetilde{\varepsilon}_j^o + \int_{\Gamma^s} A^s(k)\, d\xi^s(k) \\ &+ \int_{\Gamma^v} \underset{\sim}{A}^v(k) \cdot d\underset{\sim}{\xi}^v(k) + \int_{\Gamma^o, \Gamma^r} \sum \widetilde{A}_j(k)\, d\widetilde{\xi}_j(k)\Big] \end{aligned}$$

where the dependent parameters are defined by

$$\begin{aligned} &\mu = \frac{\partial f}{\partial \xi^s}, \quad \frac{1}{3} tr\,\widehat{\boldsymbol{\sigma}} = \rho \frac{\partial f}{\partial \varepsilon}, \quad \frac{1}{\rho}\widetilde{\sigma}_j^o = \frac{\partial f}{\partial \widetilde{\varepsilon}_j^o}, \\ &A^s(k) = \rho \frac{\partial f}{\partial \xi^s}, \quad A_j^v(k) = \rho \frac{\partial f}{\partial \xi_j^v}, \\ &\widetilde{A}_j^o(k) = \rho \frac{\partial f}{\partial \widetilde{\xi}_j^o} \text{ and } \widetilde{A}_j^r(k) = \rho \frac{\partial f}{\partial \widetilde{\xi}_j^r}. \end{aligned} \tag{A2.1}$$

Here we have used the notation $\int_{\Gamma^i}$ to indicate both the sum over all discrete indices and the integral over all continuous indices in the set Γ^i.

Defining the tensors $\mathbf{A}^o(k)$ and $\mathbf{A}^r(k)$ by the equalities

$$\mathbf{A}^o(k) \cdot d\widehat{\boldsymbol{\xi}}^o(k) = \sum_{j=1}^{5} \widetilde{A}_j^o(k)\, d\widetilde{\xi}_j^o(k) \tag{A2.2a}$$

and

$$\mathbf{A}^r(k) \cdot d\xi^r(k) = \sum_j \widetilde{A}_j^r(k)\, d\widetilde{\xi}_j^r(k), \tag{A2.2b}$$

allows us to write more concisely

$$df = \mu dc + \frac{1}{\rho}\widehat{\boldsymbol{\sigma}} \cdot d\widehat{\boldsymbol{\varepsilon}} + \frac{1}{\rho}\int_I \mathbf{A}(k) \cdot d\xi(k),$$

where I includes all possible indices for all internal parameters.

Note that $\mathbf{A}^o(k)$ and $\mathbf{A}^r(k)$ are the same type of tensors as $\hat{\boldsymbol{\xi}}^o(k)$ and $\hat{\boldsymbol{\xi}}^r(k)$, respectively, and the traceless stress tensor $\hat{\boldsymbol{\sigma}}^o$ satisfies

$$\hat{\boldsymbol{\sigma}}^o \cdot d\hat{\boldsymbol{\varepsilon}}^o = \sum_i \tilde{\sigma}_j^o d\tilde{\varepsilon}_j^o. \tag{A2.2c}$$

For the second-order symmetric tensors $\hat{\boldsymbol{\eta}}$ and $\mathbf{A}$, setting $\sum_{i=1}^{4} \tilde{A}_i d\tilde{\eta}_i = \sum_{ij} A_{ij} d\eta_{ij}$ gives

$$\begin{aligned} &A_{\xi\xi} = \frac{2}{3}\tilde{A}_1 - \frac{1}{3}\tilde{A}_2, \quad A_{yy} = \frac{2}{3}\tilde{A}_2 - \frac{1}{3}\tilde{A}_1, \quad A_{zz} = -\frac{1}{3}(\tilde{A}_1 + \tilde{A}_2), \\ &A_{yx} = A_{xy} = \frac{1}{2}\tilde{A}_3, \quad A_{xz} = A_{zx} = \frac{1}{2}\tilde{A}_4 \quad \text{and} \quad A_{yz} = A_{zy} = \frac{1}{2}\tilde{A}_5. \end{aligned} \tag{A2.3}$$

We can use these identities to relate $\tilde{\sigma}_j^o$ and $\tilde{A}_j^o(k)$ to σ_{ij}^o and $A_{ij}^o(k)$.

For an initially uniform system which remains near its initial concentration c_o, with small strains and small internal parameters, we can expand the dependent parameters in the independent parameters. If we assume that the linear terms are sufficient, then, for an isotropic system,

$$\mu - \mu_o = \mu_c(c - c_o) + b_c\varepsilon + \int_{I^s} \mu_\xi(k)\xi^s(k)dk, \tag{A2.4a}$$

$$\frac{1}{3}tr\,\hat{\boldsymbol{\sigma}}/\rho_o = b_o + b_c(c - c_o) + b_\varepsilon\varepsilon + \int_{I^s} b_\xi(k)\xi^s(k)dk, \tag{A2.4b}$$

$$A^s(k)/\rho_o = a_o^s(k) + \mu_\xi(k)(c - c_o) + b_\xi(k)\varepsilon + \int_{I^s} a^s(j,k)\xi^s(j)dj, \tag{A2.4c}$$

$$\hat{\boldsymbol{\sigma}}^o/\rho_o = s_\varepsilon\hat{\boldsymbol{\varepsilon}}^o + \int_{I^o} s_\xi(k)\hat{\boldsymbol{\xi}}^o(k)dk, \tag{A2.4d}$$

$$\mathbf{A}^o(k)/\rho_o = s_\xi(k)\hat{\boldsymbol{\varepsilon}}^o + \int_{I^o} a^o(j,k)\hat{\xi}^o(j)dj, \tag{A2.4e}$$

$$\utilde{A}^{v}(k)/\rho_o = \int_{I^v} a^{v}(j,k)\utilde{\xi}^{v}(j)\,dj \tag{A2.4f}$$

and

$$\mathbf{A}^{r}(k)/\rho_o = \int_{I^r} a^{r}(j,k)\hat{\boldsymbol{\xi}}^{r}(j)\,dj \tag{A2.4g}$$

where $a^i(j,k) = a^i(k,j)$. In obtaining these equations, we have enforced the relations among the derivatives of the chemical potential, the equilibrium stresses and the affinities which must hold due to their definition in terms of derivatives of the energy.

We have also made use of $\rho = \rho_o(1-\varepsilon)$ and the symmetry relations for an initially isotropic system. The isotropy also implies that all nonscalar forces vanish initially. All coefficients in (A2.4) are scalars.

Then

$$d^2f = d^2f^{s} + d^2f^{v} + d^2f^{o} + d^2f^{v}$$

with

$$\begin{aligned} d^2f^{s} = {}& \frac{1}{2}\mu_c(dc)^2 + b_c\,d\varepsilon\,dc + \int_{I^s}\mu_\xi(k)\,d\xi^{s}(k)\,dc \\ &+\frac{1}{2}(b_o + b_\varepsilon)(d\varepsilon)^2 + \frac{1}{2}\int_{I^s} a^{s}(j,k)\,d\xi^{s}(j)\,d\xi^{s}(k) \end{aligned} \tag{A2.5a}$$

$$d^2f^{v} = \frac{1}{2}\int_{I^v} a^{v}(j,k)\,d\utilde{\xi}^{v}(j)\cdot d\utilde{\xi}^{v}(k) \tag{A2.5b}$$

$$d^2f^{o} = \frac{1}{2}s_\varepsilon\,d\hat{\boldsymbol{\varepsilon}}^{o}\cdot d\hat{\boldsymbol{\varepsilon}}^{o} + \int_{I^o} s_\xi(k)\,d\hat{\boldsymbol{\xi}}^{o}(k)\cdot d\hat{\boldsymbol{\varepsilon}}^{o} + \frac{1}{2}\int_{I^o} a^{o}(j,k)\,d\hat{\boldsymbol{\xi}}^{o}(j)\cdot d\hat{\boldsymbol{\xi}}^{o}(k) \tag{A2.5c}$$

$$d^2f^{r} = \frac{1}{2}\int_{I^r} a^{r}(j,k)\,d\hat{\boldsymbol{\xi}}^{r}(j)\cdot d\hat{\boldsymbol{\xi}}^{r}(k). \tag{A2.5d}$$

Each of the d^2f^i depends only on the variations of the i-type tensors. In order for d^2f to be positive for all nonzero variations of the independent parameters, $d^2 f^i$ must be positive when any of the variations of tensors of type i are nonzero.

Assuming that Onsager's relations hold, the linear phenomenological laws for this case are

$$J_f = -\rho_o J_\mu \nabla\mu - \int_{\Gamma^v} J_\xi(k)\underline{A}^v(k)dk, \tag{A2.6a}$$

$$\frac{\partial\underline{\xi}^v(k)}{\partial\tau} = -J_\xi(k)\underline{A}^v(k) - \frac{1}{\rho_o}\int_{\Gamma^v} L^v(j,k)\underline{A}^v(j)dj; \tag{A2.6b}$$

$$tr\,\widehat{\mathbf{\Pi}} = -\nu^s(k)\nabla\cdot\underline{v} - \int_{\Gamma^s} \nu_\xi^s(j)A^s(j)dj, \tag{A2.6c}$$

$$\frac{\partial\xi^s(k)}{\partial\tau} = -\nu_\xi^s(k)\nabla\cdot\underline{v} - \frac{1}{\rho_o}\int_{\Gamma^s} L^s(j,k)A^s(j)dj; \tag{A2.6d}$$

$$\widehat{\mathbf{\Pi}}^o = -\rho_o\nu^o(\nabla\underline{v})^o - \int_{\Gamma^o} \nu_\xi^o(k)\mathbf{A}^o(k)dk, \tag{A2.6e}$$

$$\frac{\partial\underline{\xi}^o(k)}{\partial\tau} = -\nu_\xi^o(k)\nabla\underline{v}^o - \frac{1}{\rho_o}\int_{\Gamma^o} L^o(j,k)\mathbf{A}^o(j)dj, \tag{A2.6f}$$

and

$$\frac{\partial\underline{\xi}^r(k)}{\partial\tau} = -\frac{1}{\rho_o}\int_{\Gamma^r} L^r(j,k)\mathbf{A}^r(j)dj, \tag{A2.6g}$$

where $L^i(j,k) = L^i(\mathrm{k},\mathrm{j})$. The linear phenomenological coefficients $\rho_o J_\mu$, $J_\xi(k)$, $\rho_o\nu^s$, $\nu_\xi^s(k)$, $\rho_o\nu^o$, $\nu_\xi^o(k)$ and $\frac{1}{\rho_o}L^i(j,k)$ are all scalars, and in general are functions of the independent parameters. In this section we assume, however, that they can be regarded as constants.

It is then obvious from the expressions (A2.4g) for $\mathbf{A}^r$ that the variations of $\hat{\xi}^r(k)$ have no effect at all on the rest of the system. In particular, they have no effect on the externally observable quantities, the concentration and displacements. They are left out of consideration from now on.

The remaining linear phenomenological relations are decoupled into three pairs of equations, with each pair containing affinities and fluxes of a single tensor type. Substituting these into the expression

$$TP = -\left[\underline{J}_f \cdot \nabla\mu + \frac{1}{2} tr\,\hat{\Pi}\,\nabla\cdot\underline{v} + \hat{\Pi}^o \cdot (\nabla\underline{v})^o + \int_I \mathbf{A}(k)\cdot \frac{\partial\hat{\xi}(k)}{\partial\tau} dk\right],$$

for the entropy production, TP decouples into $TP = P^s + P^v + P^o$, with

$$\begin{aligned} P^s &= \rho_o \nu^s (\nabla\cdot\underline{v})^2 + 2\int_{I^s} \nu_\xi^s(k) A^s(k) \nabla\cdot\underline{v}\, dk \\ &\quad + \frac{1}{\rho_o}\int_{I^s} L^s(j,k) A^s(j) A^s(k)\, dj dk, \end{aligned} \tag{A2.7a}$$

$$\begin{aligned} P^v &= \rho_o J_\mu \nabla\mu\cdot\nabla\mu + 2\int_{I^v} J_\xi(k) \underline{A}^v(k)\cdot\nabla\mu\, dk \\ &\quad + \frac{1}{\rho_o}\int_{I^v} L^v(j,k) \underline{A}^v(j)\cdot \underline{A}^v(k)\, dj dk, \end{aligned} \tag{A2.7b}$$

and

$$\begin{aligned} P^o &= \rho_o \nu^o (\nabla\underline{v})^o \cdot (\nabla\underline{v})^o + 2\int_{I^o} \nu_\xi^o(k) \mathbf{A}^o(k)\cdot\hat{\boldsymbol{\varepsilon}}^o\, dk \\ &\quad + \frac{1}{\rho_o}\int_{I^o} L^o(j,k) \mathbf{A}^o(k)\cdot \mathbf{A}^o(j)\, dj dk. \end{aligned} \tag{A2.7c}$$

TP is assumed to be positive when any of the affinities is nonzero; in order for this to hold, each of these must be positive definite functions of the affinities of the given tensor type.

Substituting expressions (A2.4c,e,f) for $A^s(k)$, $\underline{A}^v(k)$ and $\mathbf{A}^o(k)$ into the equations for the variations of the internal parameters (A2.6b,d,g) gives a set of equations which for fixed values of $\underline{\chi}$ can be regarded as ordinary differential equations for the internal parameters

$$\frac{\partial \xi^s(k)}{\partial \tau} = -\nu_\xi^s(k)\nabla\cdot\underline{v}$$
$$-\int_{\Gamma^s} L^s(j,k)\left[a_o^s(j) + \mu_\xi(j)(c - c_o) + b_\xi(j)\varepsilon + \int_{\Gamma^s} a^s(j,l)\xi^s(l)dl\right]dj,$$
$$\frac{\partial \underline{\xi}^v(k)}{\partial \tau} = -J_\xi(k)\nabla\mu - \int_{\Gamma^v} L^v(j,k)a^v(j,l)\underline{\xi}^v(l)dl\,dj,$$
$$\frac{\partial \hat{\boldsymbol{\xi}}^o(k)}{\partial \tau} = -\nu_\xi^o(k)(\nabla\underline{v})^o - \int_{\Gamma^o} L^o(j,k)\left[s_\xi(j)\hat{\varepsilon}^o + \int_{\Gamma^o} a^o(j,l)\hat{\boldsymbol{\xi}}^o(l)dl\right].$$

These equations are each of the form

$$\frac{dy(k)}{dt} = -\int K(k,j)y(j)dj + f(t,k).$$

We make one final simplifying assumption, that the $\xi^i(k)$ can be chosen so that the equations decouple, with

$$\int_{\Gamma^i} L^i(j,l)a^i(l,k)dl = \lambda^i(j)\delta(j-k).$$

This assumption is equivalent to the assumption that $L^i(j,k)$ and $a^i(j,k)$ commute, since

$$\int_{\Gamma^i} L^i(j,l)a^i(l,k)dl = \lambda^i(j,k) = \lambda^i(k)\delta(j-k),$$
$$\int_{\Gamma^i} L^i(k,l)a^i(l,j)dl = \lambda^i(k,j) = \lambda^i(k)\delta(j-k)$$

and
$$L^i(k,l) = L^i(l,k), \quad a^i(k,l) = a^i(l,k)$$

are both positive definite linear operators. ($L^i(j,k)$ is positive definite because the entropy production must be positive, and $a^i(j,k)$ is positive definite because the energy is minimized.) This also implies that L^i and a^i can be simultaneously diagonalized through the proper choice of $\xi^i(k)$,

$$L^i(j,k) = \frac{\lambda^i(j)}{a^i(j)}\delta(j-k), \quad \frac{\lambda^i(j)}{a^i(j)} > 0, \quad a^i(j,k) = a^i(j)\delta(j-k), \quad a^i(j) > 0 \quad \text{(A2.8)}$$

and $\lambda^i(j)$ is positive.

Solving the separated equations gives

$$\begin{aligned}\xi^s(k) = {} & \xi^s_o(k)e^{-\lambda^s(k)\tau} - \frac{a^s_o(k)}{a^s(k)}\left[1 - e^{-\lambda^s(k)\tau}\right] \\ & - \frac{1}{a^s(k)}\left[\mu_\xi(k)(c - c_o) + b_\xi(k)\varepsilon\right] \\ & - \int_0^\tau d\tau'\left[\nu^s_\xi(k)\nabla\cdot\underline{v} - \frac{1}{a^s(k)}\left[\mu_\xi(k)\frac{\partial c}{\partial\tau} + b_\xi(k)\frac{\partial\varepsilon}{\partial\tau}\right]\right]e^{-\lambda^s(k)(\tau - \tau')},\end{aligned} \tag{A2.9a}$$

$$\underline{\xi}^v(k) = -\int_0^\tau d\tau'\, J_\xi(k)\nabla\mu e^{-\lambda^s(k)(\tau-\tau')}, \tag{A2.9b}$$

and

$$\begin{aligned}\widehat{\boldsymbol{\xi}}^o(k) = {} & -\frac{s_\xi(k)}{a^v(k)}\widehat{\boldsymbol{\varepsilon}}^o \\ & - \int_0^\tau d\tau'\left[\nu^o_\xi(k)(\nabla\underline{v})^o - \frac{s_\xi(k)}{a^v(k)}\frac{\partial\widehat{\boldsymbol{\varepsilon}}^o}{\partial\tau}\right]e^{-\lambda^o(k)(\tau-\tau')}\end{aligned} \tag{A2.9c}$$

Here $\underline{\xi}^v(k)$ and $\widehat{\boldsymbol{\xi}}^o(k)$ vanish initially due to the isotropy and $\xi^s_o(k)$ is the initial value of $\xi^s(k)$. These expressions can then be used to eliminate the internal parameters from the expansions (A2.4) of the dependent parameters. The expressions for the affinities $A^i(k)$ become

$$\begin{aligned}A^s(k)/\rho_o &= a^s_o(k) + \mu_\xi(k)(c - c_o) + b_\xi(k)\varepsilon + a^s(k)\xi^s(k) \\ \widehat{\mathbf{A}}^o(k)/\rho_o &= s_\xi(k)\widehat{\boldsymbol{\varepsilon}}^o + a^o(k)\widehat{\xi}^o(k)\end{aligned}$$

and

$$\underline{A}^v(k)/\rho_o = -a^v(k)\int_0^\tau d\tau' J_\xi(k)\nabla\mu e^{-\lambda^s(k)(\tau-\tau')}.$$

Substituting $A^s(k)$ into the linear phenomenological relation (A2.6a) gives the fluid flux as

$$\underline{J}_f/\rho_o = -J_\mu\left[\nabla\mu - \int_0^\tau d\tau' K^v(\tau - \tau')\nabla\mu(\underline{\chi},\tau')\right] \tag{A2.10}$$

where

$$K^v(\tau) = \frac{1}{J_\mu}\int_{I^v} a^v(k)J^2_\xi(k)e^{-\lambda^v(k)\tau}dk. \tag{A2.11}$$

Substituting $\widehat{\mathbf{A}}^o$ and A^s into the remaining linear phenomenological equations

(A2.6) and subtracting the resulting expressions for the viscous pressure tensor from expansions (A2.4) of the equilibrium stress gives the total stress:

$$\frac{1}{3}tr(\hat{\sigma} - \hat{\Pi})/\rho_o = b_o + \int_{\Gamma^s} \nu_\xi^s(k) a_o^s(k)\,dk + (b_c + \int_{\Gamma^s} \nu_\xi^s(k)\mu_\xi(k)\,dk)(c - c_o) + \left[b_\varepsilon + \int_{\Gamma^s} \nu_\xi^s(k) b_\xi(k)\,dk\right]\varepsilon + \int_{\Gamma^s} (b_\xi(k) + \nu_\xi^s(k) a^s(k))\xi^s(k)\,dk + \nu^s \nabla\cdot\underline{v}$$

and

$$(\hat{\sigma}^o - \hat{\Pi}^o)/\rho_o = [s_\varepsilon + \int_{\Gamma^o} \nu_\xi^o(k) s_\xi(k)\,dk]\hat{\varepsilon}^o + \int_{\Gamma^o} (s_\xi(k) + \nu_\xi^o(k) a^o(k))\,\hat{\xi}^o(k)\,dk + \nu^o(\nabla\underline{v})^o.$$

Using (A2.9a,c) to eliminate the internal parameters from these equations for the stress, we obtain a relation between the stress and the history of the concentration and displacements:

$$\frac{1}{3}tr(\hat{\sigma} - \hat{\Pi})/\rho_o = B_o(\tau) + \int_0^\tau d\tau'[B_c(\tau - \tau')\frac{\partial c}{\partial \tau}(\chi,\tau') + B_\varepsilon(\tau - \tau')\frac{\partial \varepsilon}{\partial \tau}(\chi,\tau') + B_\nu(\tau - \tau')\nabla\cdot\underline{v}(\chi,\tau')] + \nu^s \nabla\cdot\underline{v} \tag{A2.12a}$$

and

$$(\hat{\sigma}^o - \hat{\Pi}^o)/\rho_o = \int_0^\tau d\tau'\left[S_\varepsilon(\tau - \tau')\frac{\partial \hat{\varepsilon}^o}{\partial \tau}(\chi,\tau') + S_\nu(\tau - \tau')(\nabla\underline{v}\ (\chi,\tau'))^o\right] + \nu^o(\nabla\underline{v})^o, \tag{A2.12b}$$

where

$$B_o(\tau) = b_o + \int_{\Gamma^s} [\nu_\xi^s(k) a_o^s(k) + (b_\xi(k) + \nu_\xi^s(k) a^s(k)) \times (\xi_o^s(k) e^{-\lambda^s(k)\tau} - \frac{a_o^s(k)}{a^s(k)}(1 - e^{-\lambda^s(k)\tau})]\,dk, \tag{A2.13a}$$

$$B_c(\tau) = b_c + \int_{\Gamma^s} \left[-b_\xi(k)(1 - e^{-\lambda^s(k)\tau}) + \nu_\xi(k) a^s(k) e^{-\lambda^s(k)\tau}\right]\frac{\mu_\xi(k)}{a^s(k)}\,dk, \tag{A2.13b}$$

$$B_\varepsilon(\tau) = b_\varepsilon + \int_{\Gamma^s} \left[-b_\xi(k)(1 - e^{-\lambda^s(k)\tau}) + \nu_\xi^s(k) a^s(k) e^{-\lambda^s(k)\tau}\right]\frac{b_\xi(k)}{a^s(k)}\,dk, \tag{A2.13c}$$

$$B_\nu(\tau) = -\int_{\Gamma^s} (b_\xi(k) + \nu_\xi^s(k) a^s(k)) \nu_\xi^s(k) e^{-\lambda^s(k)\tau} dk, \tag{A2.13d}$$

$$\begin{aligned} S_\varepsilon(\tau) &= s_\varepsilon \\ &- \int_{\Gamma^o} \left[s_\xi(k)(1 - e^{-\lambda^o(k)\tau}) - \nu_\xi^o(k) a^o(k) e^{-\lambda^o(k)\tau} \right] \frac{s_\xi(k)}{a^o(k)} dk \end{aligned} \tag{A2.13e}$$

and

$$S_\nu(\tau) = -\int_{\Gamma^s} (s_\xi(k) - \nu_\xi^o(k) a^o(k)) \nu_\xi^o(k) e^{-\lambda^o(k)\tau} dk. \tag{A2.13f}$$

Substituting the expression for ξ^s into the expansion of μ in (A2.4a) gives

$$\mu = \frac{1}{J_\mu}\left[D_o(\tau) + D(\tau) * \frac{\partial c}{\partial \tau} + D_\varepsilon(\tau) * \frac{\partial \varepsilon}{\partial \tau} + D_\nu(\tau) * \nabla \cdot \underline{v} \right] \tag{A2.14}$$

where $(*)$ denotes the convolution product,

$$f * g = \int_0^\tau f(\tau - \tau') g(\tau') d\tau'$$

and

$$\begin{aligned} &\frac{1}{J_\mu} D_o(\tau) = \\ &\mu_o + \int_{\Gamma^s} \left[\xi_o^s(k) e^{-\lambda^s(k)\tau} - \frac{a_o^s(k)}{a^s(k)} (1 - e^{-\lambda^s(k)\tau}) \mu_\xi(k) \right] dk \end{aligned} \tag{A2.15a}$$

$$\frac{1}{J_\mu} D(\tau) = \mu_c - \int_{\Gamma^s} \frac{\mu_\xi^2(k)}{a^s(k)} \left[1 - e^{-\lambda^s(k)\tau} \right] dk \tag{A2.15b}$$

$$\frac{1}{J_\mu} D_\varepsilon(\tau) = b_o + b_c - \int_{\Gamma^s} \frac{\mu_\xi(k) b_\xi(k)}{a^s(k)} (1 - e^{-\lambda^s(k)\tau}) dk \tag{A2.15c}$$

$$\frac{1}{J_\mu} D_\nu(\tau) = \frac{1}{J_\mu} D_\varepsilon(\tau) - b_o - B_c(\tau), \tag{A2.15d}$$

and the fluid flux is

$$\begin{aligned} \underline{J}_f / \rho_o = &-\nabla \left[D(\tau) * \frac{\partial c}{\partial \tau} + D_\varepsilon(\tau) * \frac{\partial \varepsilon}{\partial \tau} + D_\nu(\tau) * \nabla \cdot \underline{v} \right] \\ &+ \int_0^\tau K^v(\tau - \tau') \nabla \left[D(\tau') * \frac{\partial c}{\partial \tau} + D_\varepsilon(\tau') * \frac{\partial \varepsilon}{\partial \tau} + D_\nu(\tau') * \nabla \cdot \underline{v} \right] d\tau', \end{aligned} \tag{A2.16}$$

Equations (A2.12) and (A2.16) give the desired relations that allow us to replace the fluid flux and stresses in the concentration equation and obtain a system in the unknowns c, $\underline{u}$, $\widehat{\boldsymbol{\varepsilon}}$ and $\underline{v}$. Before writing out this system, however, it is useful to do some manipulations on the stress relations which will simplify the results.

The gradients in $(\boldsymbol{x},t)$ and $(\underline{\chi},\tau)$ coordinates are related (up to linear terms in ε_{ij}) by (A1.12) as $\nabla = \nabla_\chi - \widehat{\boldsymbol{\varepsilon}}\nabla_\chi$ (where $\widehat{\varepsilon}$ operates on the gradient like a matrix on a vector) . We have the identity $\nabla_{\underline{\chi}}\underline{v} = \dfrac{\partial\widehat{\boldsymbol{\varepsilon}}}{\partial\tau}$ so that

$$\nabla\cdot\underline{v} = \nabla_{\underline{\chi}}\underline{v} - \sum_{ij}\varepsilon_{ij}\frac{\partial v_i}{\partial\chi_j} = \frac{\partial}{\partial\tau}(\varepsilon - \tfrac{1}{2}\widehat{\varepsilon}\cdot\widehat{\boldsymbol{\varepsilon}})$$

and

$$\nabla\underline{v} = \frac{\partial\widehat{\boldsymbol{\varepsilon}}}{\partial\tau} - \widehat{\boldsymbol{\varepsilon}}\,\frac{\partial\widehat{\varepsilon}}{\partial\tau}.$$

Using these relations in the expressions (A2.12) for the components of the total stress gives the components of the stress tensor as

$$\begin{aligned}
&(\sigma_{ij} - \Pi_{ij})/\rho_o \\
&\quad = \delta_{ij}\left[B_o(\tau) + B_c(\tau) * \frac{\partial c}{\partial\tau} + \frac{1}{\rho_o}\lambda(\tau) * \frac{\partial\varepsilon}{\partial\tau} - \frac{1}{2}(\eta_o\delta(\tau) + \eta(\tau))\right] * \frac{\partial}{\partial\tau}(\widehat{\varepsilon}\cdot\widehat{\varepsilon}) \qquad \text{(A2.17)} \\
&\quad + \frac{2}{\rho_o}G(\tau) * \frac{\partial\varepsilon_{ij}}{\partial\tau} - \frac{1}{2}(S_\nu(\tau) + \nu^o\delta(\tau)) * \sum_k \varepsilon_{ik}\frac{\partial\varepsilon_{kj}}{\partial\tau}
\end{aligned}$$

where

$$\begin{aligned}
&\frac{1}{\rho_o}\lambda(\tau) = B_\varepsilon(\tau) + B_\nu(\tau) + \nu^s\delta(\tau) - \frac{2}{3\rho_o}G(\tau), \\
&\frac{2}{\rho_o}G(\tau) = S_\varepsilon(\tau) + S_\nu(\tau) + \nu^o\delta(\tau), \qquad \text{(A2.18)} \\
&\eta(\tau) = B_\nu(\tau) - \frac{1}{3}S_\nu(\tau), \quad \eta_o = \nu^s - \frac{1}{3}\nu^o.
\end{aligned}$$

The second-order terms $\eta(\tau) * \dfrac{\partial}{\partial\tau}(\widehat{\boldsymbol{\varepsilon}}\cdot\widehat{\boldsymbol{\varepsilon}})$ and $S_\nu(\tau) * \widehat{\boldsymbol{\varepsilon}}\,\dfrac{\partial\widehat{\boldsymbol{\varepsilon}}}{\partial\tau}$ contribute only terms of order $\|\widehat{\boldsymbol{\varepsilon}}\|$ to the system, assuming that $\eta(\tau)$ and $S_\nu(\tau)$ are bounded functions. The momentum equation contains the gradient of the stress, and taking spatial derivatives of these terms

$$\begin{aligned}
&\left|\frac{\partial}{\partial\chi_i}\left(\eta * \frac{\partial}{\partial\tau}(\widehat{\boldsymbol{\varepsilon}}\cdot\widehat{\boldsymbol{\varepsilon}})\right)\right| = \left|\frac{\partial}{\partial\chi_i}\int_0^\tau \eta(\tau - \tau')\frac{\partial}{\partial\tau}(\widehat{\boldsymbol{\varepsilon}}\cdot\widehat{\boldsymbol{\varepsilon}})\,d\tau'\right| \\
&\leq \max_{\tau'\in(0,\tau)}\Big[|\eta(\tau')|\Big]\left|\frac{\partial}{\partial\chi_i}(\widehat{\varepsilon}\cdot\widehat{\varepsilon})\right|
\end{aligned}$$

and

$$\left| \frac{\partial}{\partial \chi_i} \left(S_\nu \,\hat{*}\, \frac{\partial \hat{\boldsymbol{\varepsilon}}}{\partial \tau} \right)_{ij} \right| = \left| \frac{\partial}{\partial \chi_i} \int_0^\tau S_\nu(\tau - \tau') \sum_k \varepsilon_{ik} \frac{\partial \varepsilon_{kj}}{\partial \tau} d\tau' \right|$$
$$\leq \max\{S_\nu(\tau)\} \left[\sum_k \left| \frac{\partial \varepsilon_{ik}}{\partial \chi_i} \varepsilon_{kj} \right| + \sum_k \left| \varepsilon_{ik} \frac{\partial \varepsilon_{kj}}{\partial \chi_i} \right| \right].$$

Leaving out these terms, equations (A2.16) and (A2.17) for the flux and stress components imply that c, $\hat{\varepsilon}$, $\underline{v}$ and $\underline{u}$ satisfy

$$\begin{aligned} \frac{\partial c}{\partial \tau} &= \nabla^2 \int_0^\tau d\tau' \left[D(\tau - \tau') \frac{\partial c}{\partial \tau}(\chi, \tau') + D_\varepsilon(\tau - \tau') \frac{\partial \varepsilon}{\partial \tau}(\chi, \tau') \right. \\ &\quad \left. + D_\nu(\tau - \tau') \nabla \cdot \underline{v}(\chi, \tau') \right] \\ &\quad + \nabla \int_0^\tau d\tau' K^v(\tau - \tau') \nabla \int_0^{\tau'} d\tau'' \left[D(\tau' - \tau'') \frac{\partial c}{\partial \tau}(\chi, \tau'') \right. \\ &\quad \left. + D_\varepsilon(\tau' - \tau'') \frac{\partial \varepsilon}{\partial \tau}(\chi, \tau'') + D_\nu(\tau' - \tau'') \nabla \cdot v(\chi, \tau'') \right] \end{aligned} \tag{A2.18a}$$

and

$$\begin{aligned} \frac{\partial \underline{v}}{\partial \tau} &= \nabla \int_0^\tau \left[B_i(\tau - \tau') \frac{\partial c}{\partial \tau}(\chi, \tau') + \frac{1}{\rho_o} \lambda(\tau - \tau') \frac{\partial \varepsilon}{\partial \tau}(\chi, \tau') \right] d\tau' \\ &\quad + \nabla \cdot \int_0^\tau \frac{2}{\rho_o} G(\tau - \tau') \frac{\partial \hat{\boldsymbol{\varepsilon}}}{\partial \tau}(\chi, \tau') d\tau' \\ &\quad - \frac{1}{2} \eta_o \sum_{ij} \nabla \varepsilon_{ij} \frac{\partial \varepsilon_{ij}}{\partial \tau} - \frac{1}{2} \nu^o (\nabla \varepsilon) \cdot \frac{\partial \hat{\boldsymbol{\varepsilon}}}{\partial \tau} . \end{aligned} \tag{A2.18b}$$

The stress on the system is given, to first order in the ε_{ij} by

$$\sigma_{ij} - \Pi_{ij} = G(\tau) * \frac{\partial \varepsilon_{ij}}{\partial \tau} + \lambda(\tau) * \frac{\partial \varepsilon}{\partial \tau} \delta_{ij} + \rho_o \left(B_o(\tau) + B_c(\tau) * \frac{\partial c}{\partial \tau} \right) \delta_{ij} . \tag{A2.19}$$

The kernels D, D_ε, D_ν, K^v, B_c, λ, G and viscosities η^o and ν^o must be determined or approximated from knowledge of the behavior of the materials.

Note that no mention of the internal variables remains in the final model; their behavior has been consolidated into what is observed macroscopically, the memory of the material. Therefore, this model could have been proposed from a purely phenomenological point of view, without any mention of the concept of internal parameters.

c. Model with nonlinear concentration dependence. In the previous section, we developed a model with only linear dependence on the concentration. We want to extend this model to incorporate more general dependence of the material properties on the concentration, while still retaining the assumptions of small strain and internal variations. For simplicity, we will not take into consideration the quadratic dependence of the chemical potential on the strains and internal parameters, and we shall not discuss questions of stability.

When the chemical potential depends linearly, and the phenomenological coefficients do not depend at all, on the $\underline{\xi}(k)$, then it is obvious that the result of the previous section (that the $\underline{\xi}^r(k)$ can be ignored) remains valid. The linear phenomenological relations (A2.6) are assumed to hold; however, the linear phenomenological coefficients are no longer constant, but instead are functions of concentration.

For a system with small strains and internal parameters which remain near their equilibrium values, we can expand the dependent parameters in the strains and the $\hat{\boldsymbol{\xi}}(k)$. If we assume that the linear terms in the expansion are sufficient, then for an isotropic system

$$\mu = \mu_o(c) + \frac{db_o}{dc}\varepsilon + \int_{\Gamma^s} \frac{da^o}{dc}(k)\xi^s(k)dk, \tag{A3.1a}$$

$$\frac{1}{3}tr\,\hat{\boldsymbol{\sigma}}/\rho_o = b_o(c) + b_\varepsilon(c)\varepsilon + \int_{\Gamma^s} b_\xi(k;c)\xi^s(k)dk, \tag{A3.1b}$$

$$A^s(k)/\rho_o = a^o(k;c) + b_\xi(k;c)\varepsilon + \int_{\Gamma^s} a^s(j,k;c)\xi^s(j)dj, \tag{A3.1c}$$

$$\hat{\boldsymbol{\sigma}}^o/\rho_o = s_\varepsilon(c)\hat{\boldsymbol{\varepsilon}}^o + \int_{\Gamma^o} s_\xi(k;c)\hat{\boldsymbol{\xi}}^o(k)dk, \tag{A3.1d}$$

$$\hat{\mathbf{A}}^o(k)/\rho_o = s_\xi(k;c)\hat{\boldsymbol{\varepsilon}}^o + \int_{\Gamma^o} a^o(j,k;c)\hat{\boldsymbol{\xi}}^o(j)dj, \tag{A3.1e}$$

and

$$\underline{A}^{v}(k)/\rho_o = \int_{I^b} a^{v}(j,k;c)\underline{\xi}^{v}(j)dj . \tag{A3.1f}$$

Substituting these expressions for the affinities into (A2.6 b,d,g) gives, once again, a continuum of ordinary differential equations for each fixed value of $\underline{\chi}$ which this time are of the form

$$\frac{d\xi(k)}{d\tau} = -\int_I \Lambda(k,j;c(\tau))\xi(j)dj + f(k,\tau) , \tag{A3.2}$$

where

$$\Lambda(k,j;c) = \int_I L(k,l;c)a(l,j;c)dl , \tag{A3.3}$$

and where we have suppressed the $\underline{\chi}$ dependence.

We assume that there exists a unique fundamental solution kernel $\Phi(j,k;\tau)$ which solves the homogeneous equation with the initial condition that

$$\Phi(j,k;0) = \delta(j-k) \tag{A3.4a}$$

and that Φ has an inverse $\Phi^{-1}(j,k;\tau)$ for all time

$$\int_I dk\, \Phi(j,k;\tau)\Phi^{-1}(k,l;\tau) = \delta(j-l). \tag{A3.4b}$$

Then

$$\frac{d\Phi}{dt}(j,k;\tau) = \int_{dl} \lambda(j,l;c(\tau))\Phi(l,k;c(\tau)) \tag{A3.4c}$$

and solutions of the inhomogeneous equation can be written as

$$\xi(k;\tau) = \int_I \Phi(k,j;\tau)\xi_o(j)dj + \int_0^t d\theta \int_I Q(k,j;\tau,\theta)f(j,\theta)dj \tag{A3.5}$$

where

$$Q(k,j;\tau,\theta) = \int_I dl\ \Phi(k,l;\tau)\Phi^{-1}(l,j;\theta) \tag{A3.6}$$

and $\xi_o(k) = \xi(k;0)$.

The values assumed by the kernels $\Phi(k,j;\tau)$ and $Q(k,j;\tau,\theta)$ depend on the history of the concentration; $\Phi(k,j,\tau)$ depends on the concentration for times in the interval $(0,\tau)$, while Q depends on the concentrations between θ and τ. (This latter relation is seen by multiplying the differential equation for Φ by $\Phi^{-1}(l,j,\theta)$ and integrating over l,

$$\frac{d}{dt}\int_I \Phi(k,l;\tau)\Phi^{-1}(l,j;\theta)dl = \int_I \Lambda(k,l,c(\tau))\Phi(l,m;\tau)\Phi^{-1}(m,j;\theta)dldm$$

or

$$\frac{\partial Q}{\partial t}(j,k;\tau,\theta) = \int_I \Lambda(k,l;c(t))Q(l,j;\tau,\theta)dl$$

and

$$Q(j,k;\theta,\theta) = I.$$

Thus Q depends only on the values of c for times in (θ,τ).) It is important to keep this dependence in mind; for simplicity, we will not write it explicitly. Substituting the expressions for the forcing functions into the formula for $\xi(k)$ gives

$$\begin{aligned}\xi^s(k) &= \int_{I^s} \Phi^s(k,j;\tau)\xi_o^s(j)dj \\ &- \int_0^\tau d\theta \int_{I^s} Q^s(k,j;\tau,\theta)\Big[\nu_\xi^s(j;c(\theta))\nabla\cdot\underline{v}(\theta) \\ &+ \int_{I^s} dl\ L^s(j,l;c)[a^o(l;c(\theta)) + b_\xi(l;c(\theta))\varepsilon(\theta)]dl\Big]dj\end{aligned} \tag{A3.7a}$$

$$\underline{\xi}^v(k;\underline{x},\tau) = -\int_0^\tau d\theta \int_{I^b} Q^v(k,j;\tau,\theta)J_\xi(j;c(\theta))dj\ \nabla\mu(\theta) \tag{A3.7b}$$

and

$$\hat{\xi}^o(k;\underset{\sim}{\chi},\tau) = -\int_0^\tau d\theta \int_{I^o} Q^o(k,j;\tau,\theta)[\nu_\xi^o(j,c)(\nabla\underline{v}(\theta))^o + \int_{I^o} L^o(j,l;c(\theta))s_\xi(l;c(\theta))dl\,\hat{\boldsymbol{\varepsilon}}^o(\theta)]\mathrm{d}j \tag{A3.7c}$$

where we have assumed that $\underset{\sim}{\xi}^v$ and $\hat{\boldsymbol{\xi}}^o$ are zero initially, and have left out the $\underset{\sim}{\chi}$ dependence.

Using these expressions to eliminate the internal parameters from (A3.1a) for μ,

$$\mu = m_o(\tau,c(\tau)) + \frac{db}{dc}\varepsilon - \int_0^\tau d\theta\{M_c(\tau,\theta) + M_\varepsilon(\tau,\theta)\varepsilon(\tau) + M_\nu(\tau,\theta)\nabla\cdot\underline{v}(\theta)\} \tag{A3.8}$$

for each fixed value of $\underset{\sim}{\chi}$, where

$$m_o(\tau,c(\tau)) = \mu_o(c) + \int_{I^s} \frac{da^o}{dc}(k;c(\tau))\Phi^s(k,j,\tau)\xi_o(j)djdk, \tag{A3.9a}$$

$$M_c(\tau,\theta) = \int_{I^s} \frac{da^o}{dc}(k;c(\tau))Q^s(k,j;\tau,\theta)L^s(j,l;c(\theta))a^o(l;c(\theta))dl\ dj\ dk, \tag{A3.9b}$$

$$M_\varepsilon(\tau,\theta) = \int_{I^s} \frac{da^o}{dc}(k;c(\tau))Q^s(k,j;\tau,\theta)L^s(j,l,c(\theta))b_\xi(l;c(\theta))dl\ dj\ dk \tag{A3.9c}$$

and

$$M_\nu(\tau,\theta) = \int_{I^s} \frac{da^o}{dc}(k;c(\tau))Q^s(k,j;\tau,\theta)\nu_\xi^s(j;c(\theta))djdk. \tag{A3.9d}$$

Eliminating the internal parameters from the expansion of $\underset{\sim}{A}^v$, and substituting the resulting expression into the linear phenomenological equation (A2.6a), gives the fluid flux as

$$\underline{J}_f/\rho_o = -J_\mu(c)\nabla\mu + \int_0^\tau K^v(\tau,\theta)\nabla\mu(\theta)d\theta \tag{A3.10a}$$

for each fixed value of $\underline{\chi}$, where

$$K^v(\tau,\theta) = \int_{I^s} J_\xi(k;c(\tau))Q^v(k,j;\tau,\theta)J_\xi(j;c(\theta))dj\ dk. \tag{A3.10b}$$

Substituting expansions (A3.1c,e) for A^s and $\hat{\mathbf{A}}^o$ into the remaining two linear phenomenological equations for the components of the viscous pressure tensor, and subtracting the result from equations (A3.1b,d) for the components of the equilibrium stress, gives the total stress tensor in terms of the independent parameters as

$$\begin{aligned}\frac{1}{3}tr(\hat{\boldsymbol{\sigma}} - \hat{\Pi})/\rho_o &= \boldsymbol{f}_o(c) + \boldsymbol{f}_\varepsilon(c)\varepsilon \\ &+ \int_{I^s} \boldsymbol{f}_\xi(k;c)\xi^s(k)dk + \nu^s(c)\nabla\cdot\underline{v}\end{aligned} \tag{A3.11a}$$

and

$$(\hat{\boldsymbol{\sigma}}^o - \hat{\Pi}^o)/\rho_o = F_\varepsilon(c)\hat{\boldsymbol{\varepsilon}}^o + \int_{I^s} F_\xi(k;c)\hat{\boldsymbol{\xi}}^o(k)dk + \nu^o(c)(\nabla\underline{v})^o, \tag{A3.11b}$$

where

$$\boldsymbol{f}_o(c) = \boldsymbol{b}_o(c) + \int_{I^s} \nu^s_\xi(j;c)\boldsymbol{a}^s_o(j;c)dj, \tag{A3.12a}$$

$$\boldsymbol{f}_\varepsilon(c) = \boldsymbol{b}_\varepsilon(c) + \int_{I^s} \nu^s_\xi(j;c)\boldsymbol{b}_\xi(j;c)dj, \tag{A3.12b}$$

$$\boldsymbol{f}_\xi(k;c) = \boldsymbol{b}_\xi(k;c) + \int_{I^s} \nu^s_\xi(j;c)\boldsymbol{a}^s(j,k;c)dj, \tag{A3.12c}$$

$$F_\varepsilon(c) = s_\varepsilon(c) + \int_{I^o} \nu^o_\xi(j;c)s_\xi(j;c)dj, \tag{A3.12d}$$

and

$$F_{\xi}(k;c) = s_{\xi}(k;c) + \int_{\Gamma^o} \nu_{\xi}^{o}(j;c)a^{o}(j,k;c)dj. \tag{A3.12e}$$

Using (A3.7a,c) to eliminate ξ^s and $\hat{\boldsymbol{\xi}}^o$, we end up with

$$\begin{aligned}\frac{1}{3}tr(\hat{\boldsymbol{\sigma}} - \hat{\boldsymbol{\Pi}})/\rho_o = \int_0^{\tau} [B(\tau,\theta) + B_{\varepsilon}(\tau,\theta)\varepsilon(\theta) \\ + B_{\nu}(\tau,\theta)\nabla\cdot v(\theta)]d\theta\end{aligned} \tag{A3.13a}$$

and

$$(\hat{\boldsymbol{\sigma}}^o - \hat{\boldsymbol{\Pi}}^o)/\rho_o = \int_0^{\tau} [S_{\varepsilon}(\tau,\theta)\hat{\boldsymbol{\varepsilon}}^o(\theta) + S_{\nu}(\tau,\theta)(\nabla \underline{v}\ (\theta))^o]d\theta, \tag{A3.13b}$$

where

$$\begin{aligned}B(\tau,\theta) = \delta(\tau-\theta)\left[f_o(c) + \int_{\Gamma^s} f_{\xi}(k;c(\tau))\Phi^s(k,j;c)\xi_o^s(j)djdk\right] \\ - \int_{\Gamma^s} Q^s(j,k;\tau,\theta)f_{\xi}(k;c(\tau))L^s(j,l;c(\theta))a^o(l,c(\theta))\ dk\ kl\ ,\end{aligned} \tag{A3.14a}$$

$$\begin{aligned}B_{\varepsilon}(\tau,\theta) = \delta(\tau-\theta)f_{\varepsilon}(c) \\ - \int_{\Gamma^s} Q^s(j,k;\tau,\theta)f_{\xi}(k;c(\tau))L^s(j,l;c(\theta))b_{\xi}(l;c(\theta))dj\ dk\ dl\ ,\end{aligned} \tag{A3.14b}$$

$$\begin{aligned}B_{\nu}(\tau,\theta) = \delta(\tau-\theta)\nu^o(c) \\ - \int_{\Gamma^s} Q^s(j,k;\tau,\theta)f_{\xi}(k;c(\tau))\nu_{\xi}^{s}(j;c(\theta))dj\ dk\ ,\end{aligned} \tag{A3.14c}$$

$$\begin{aligned}S_{\varepsilon}(\tau,\theta) = \delta(\tau-\theta)F_{\varepsilon}(c) \\ - \int_{\Gamma^o} Q^o(j,k;\tau,\theta)F_{\xi}(k;c(\tau))L^o(j,l;c(\theta))s_{\xi}(l;c(\theta)))dj\ dk\ dl\end{aligned} \tag{A3.14d}$$

and

$$S_{\nu}(\tau,\theta) = \delta(\tau-\theta)\nu^o(c) - \int_{\Gamma^o} Q^o(j,k;\tau,\theta)F_{\xi}(k;c(\tau))\nu_{\xi}^{o}(j;c(\theta))dj\ dk\,. \tag{A3.14e}$$

Substituting the expression for the fluid flux into the concentration equation, the system of equations which describe the moments of the diffusion driven swelling process are

$$
\begin{aligned}
\frac{\partial c}{\partial \tau} &= \nabla \cdot \left[J_\mu(c) \nabla \mu \right] - \nabla \cdot \int_0^\tau K^v(\underline{\chi}, \tau, \theta) \nabla \mu(\underline{\chi}, \theta) d\,\theta \\
\frac{\partial \underline{v}}{\partial \tau} &= \nabla \left(\frac{1}{3} tr \left(\widehat{\boldsymbol{\sigma}} - \widehat{\Pi} \right) / \rho_o \right) + \nabla \cdot \left(\widehat{\boldsymbol{\sigma}}^o - \widehat{\mathbf{\Pi}}^o \right) / \rho_o
\end{aligned}
$$

with the chemical potential and stress given for each fixed value of $\underline{\chi}$ by (A3.8) and (A3.11). Each of the kernels appearing in these relations, which have a specific time dependence, depends on the past history of the concentration.

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