PHYSICS AND MATHEMATICS OF HEAT AND MASS TRANSFER IN POLYMERS

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Abstract – Heat and mass transfer phenomena may induce structural changes in polymeric materials; the kinetics of such changes are then coupled with those of the transport processes. Two categories of phenomena are considered: bulk structural changes taking place gradually throughout the polymers, and abrupt changes taking place at a surface of morphological discontinuity. For both categories both the physics and the mathematics are discussed in some detail. The content of this paper is largely a review of recent results, though some of the points presented are original ones.

INTRODUCTION

The transfer of heat or mass in a solid polymeric material may induce structural changes such as swelling, microcavity formation, primary and secondary phase transitions, etc. Such structural changes require rearrangement of polymeric segments, and therefore their kinetics are dominated by relaxation phenomena. The macroscopically observable kinetic behavior can therefore be dominated either by the transport phenomenon itself, or by relaxation, or by a coupling of the two. Furthermore, another cause of coupling is related to the fact that the transport properties (such as diffusivity and thermal conductivity) may change in response to the structural changes induced by the transfer of heat or mass.

This paper summarizes and critically reviews several recent results in the analysis of the phenomena described above; in addition, a few original results are reported. The material is organized by first introducing the physical aspects of the phenomena to be considered, and then discussing the resulting mathematical complexities. The emphasis is on the phenomenological modeling: we believe that only after such modeling has been completed successfully can one meaningfully attack the problem of understanding the microscopic physical phenomena responsible for the observable macroscopic behavior, though of course some intuitive idea about the underlying molecular physics forms the basis on which the phenomenological model is tentatively assumed.

The phenomena to be discussed fall into two broad categories, both of which are analyzed. The first category includes those processes where the structural change takes place gradually over the whole volume of the polymer sample, so that one may refer to "bulk structural changes", BSC. The second category includes those processes where an abrupt transition from one structure to another may take place; in these processes often a sharp front divides two regions of the polymeric material which have different structures. The front moves in time until the whole sample has the same structure, and therefore these processes fall into the broad category of "moving boundary phenomena", MBP.

PHYSICS OF BSC

Possibly the earliest explicit experimental evidence of gradual structural changes induced in a polymeric material by mass transfer is due to Bagley and Long in their work (1), published in 1955, on the absorption of acetone in cellulose acetate films. They reported that, as the film was exposed to a constant external partial pressure of acetone, its weight increased gradually until an "apparent equilibrium" was reached, with the weight apparently constant in time. However, if the experiment was carried out for a sufficient length of time,

eventually the weight of the sample would start increasing again, until a final equilibrium was reached. As the external partial pressure was increased in a stepwise fashion, this two-stage sorption behavior was observed again and again at each successive step.

The observed behavior clearly suggests a gradual structural change, taking place on a much longer time scale than diffusion. In the first of the two stages of sorption, diffusion takes place in the material still endowed with the original structure, until it gets saturated and exhibits an apparent equilibrium. At some later time, however, the structural change takes place showly, and a new final equilibrium is reached when the material has whatever structure is in equilibrium with the imposed conditions at the boundary, and is saturated as well. Thus in this case one would expect the first stage to be dominated by diffusion kinetics, and the second one by the relaxation kinetics.

If this interpretation is correct, one would expect this behavior to be more likely to occur in thin samples. In fact, the two-stage nature of the process requires the characteristic time of the relaxation process, Θ_R, to be much larger than that of the diffusion phenomenon, Θ_D. Since the former is presumably only a function of temperature, while the latter is inversely proportional to the square of the sample dimension, the condition $\Theta_R \gg \Theta_D$ is most likely to be fulfilled in very thin samples. Indeed, Bagley and Long's experiments were carried out on cellulose acetate membranes. Furthermore, as will be discussed below, this dependency of the observed qualitative bahavior on the size of the sample has been reported repeatedly in the literature.

In 1960, Long and Richman (2) measured the interface concentration of the solvent in the polymer for the same acetone-cellulose acetate system studied by Bagley and Long. They reported that the concentration changed exponentially in time, approaching asymptotically a final constant value, although the partial pressure at the interface was kept constant. This suggests that the relaxation kinetics are simple first-order, and indeed the relaxation time Θ_R extracted from long and Richman's data is well in excess of the estimated diffusion times for Bagley and Long's experimental conditions. Of course, it is conceivable that the two time scales Θ_R and Θ_D could not be widely separated in some cases, and if so a much more complex coupled behavior would be expected, rather than the simple additivity needed to explain the Bagley and Long data. This point will be further discussed in the next section.

The Bagley and Long data refer to a system where the structural change causes an increase in the solubility of the solvent: swelling appears an obvious candidate for the required structural change. In 1960, Jenckel and Nogay published a series of data (3) where the sample's weight increased to a maximum, and then slowly decreased to approach asymptotically a final value less than the maximum. Although at first sight this may appear a completely different phenomenon, in fact it is again suggestive of a diffusion phenomenon followed by a much slower structural change; only that in this case the structural change should result in a decreased solubility. Solvent-induced crystallization is a plausible structural change resulting in decreased solubility.

In 1978, Berens and Hopfenberg (4 & 5) reported a series of data on sorption of low molecular weight species in finely powdered polymers. Some of these data exhibit the typical two-stage sorption behavior; others exhibit a maximum, followed by a low apparent equilibrium and then by a final increase in weight; still others exhibit a monotonously increasing weight vs. time behavior which is not, however, of the type one would expect for ordinary diffusion phenomena. The second type of data suggests that two different structural changes may take place, in addition to diffusion, over different time scales; the third one suggests that the time scales of relaxation and diffusion may not be sufficiently different to result in a well-defined intermediate apparent equilibrium.

The BSC processes discussed so far are essentially reversible ones, in the sense that the structural change will take place in the opposite direction if the imposed external conditions are reversed. However, irreversible BSC phenomena have been reported in the literature (Refs. 6-8). In particular, Apicella et al. (8) have presented data which clearly show that the apparent solubility of water in epoxy resins depends on the past history of temperature and humidity to which the resin has been exposed. The irreversibility is demonstrated by the fact that, once a sample has been exposed to a temperature-humidity condition of a given severity, it acquires a (damaged) structure which does not change any more as long as the sample is not exposed to an even more severe condition. It has been proposed (Ref.8) that the physical nature of the structural change is the formation of microcavities; this implies that the damaged structure is, on a microscopic level, a two-phase one.

MATHEMATICS OF BSC

The reversible BSC phenomena of the type described by Bagley and Long (1) can be described mathematically by equations which are simple enough to allow for a closed solution. The exponential increase of the interface concentration suggests that the relaxation phenomenon is governed by simple linear kinetics. If the additional assumption is made that the diffusivity is constant, the relevant equations are, in dimensionless form,

$$u_{xx} - u_t = 0 \tag{1}$$

$$x = 0, \quad u = 1 - m \exp(-\phi^2 t) \tag{2}$$

$$x = 1, \quad u_x = 0 \tag{3}$$

$$t = 0, \quad u = 0 \tag{4}$$

where m is the ratio of the driving force corresponding to the initial structure to that corresponding to the final structure, and

$$\phi = \sqrt{(\theta_D/\theta_R)} = X/\sqrt{(D\,\theta_R)} \tag{5}$$

where X is the sample half-thickness and D is the diffusivity. Several observations about the system 1-5 are of interest.

First of all, the parameter ϕ, which provides the coupling between the relaxation and the diffusion phenomena, is reminiscent of the Thiele modulus arising in the theory of diffusion and reaction in porous catalysts. It is a dimensionless measure of the sample thickness, and (as will be seen below) indeed when ϕ is very small the overall behavior is governed by the kinetics of relaxation, while conversely when ϕ is very large it is governed by diffusion.

The second consideration is that, although the phenomenon considered is a BSC, the mathematical coupling takes place only through the boundary condition, eq.2, while the differential equation is simply the ordinary diffusion equation. This is a consequence of the assumption that the diffusivity does not change in response to structural changes.

Finally, it may be noticed that the difference between the behaviors observed by Bagley and Long (1) and by Jenckel and Nogay (3) is simply related to the value of m, with $m > 0$ in the former case and $m < 0$ in the latter one.

The quantity to be calculated is the weight of solvent sorbed, as a function of time. In dimensionless form :

$$w = \int_0^1 u \, dx \tag{6}$$

The closed form solution originally given by Long and Richman (2) can be cast in the following instructive form (Ref. 9) :

$$w = f_D(t) - m\left[f_{DR}(t) - \frac{\tan \phi}{\phi}(1 - e^{-\phi^2 t})\right] \tag{7}$$

where :

$$f_D(t) = 2 \sum \frac{1 - \exp(-a_N^2 t)}{a_N^2} \tag{8}; \quad f_{DR}(t) = 2 \sum \frac{1 - \exp(-a_N^2 t)}{a_N^2 - \theta^2} \tag{9}; \quad a_N = (N - \tfrac{1}{2})\pi \tag{10}$$

Eq.7 has the following two asymptotic expansions in terms of the value of ϕ :

$$\phi \gg \pi/2, \quad w = f_D(t) \tag{11}$$

$$\phi \ll \pi/2, \quad w = (1 - m) f_D(t) + m(1 - e^{-\phi^2 t}) \tag{12}$$

The first expansion, eq.11, simply reflects the fact that if relaxation is very fast one would observe ordinary diffusion behavior: the final equilibrium structure is reached on a time scale negligible as compared to that of the diffusion phenomenon. Conversely, the second expansion, eq.12, reflects the fact that, if relaxation is very much slower that diffusion, the effect of the two phenomena is simply additive: one would observe a first stage governed by diffusion in the original structure (giving rise to the intermediate plateau), followed by a second stage governed by relaxation where at all times the sample is saturated at the instantaneous structure's equilibrium value. Should the value of ϕ be the order of $\pi/2$, the coupling
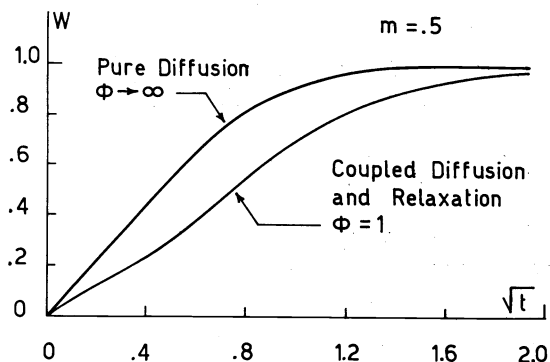
Fig. 1.

Amount sorbed vs. square root of time curves for pure diffusion and for coupled diffusion and relaxation.

provided by the term in square brackets in eq.7 should be taken into account, and no intermediate plateau would be observed. Figure 1 is a plot of w vs. $\sqrt{t}$ for pure diffusion ($\phi \to \infty$) and for coupled diffusion-relaxation ($\phi = 1$) for m = 0.5. Clearly no intermediate plateau at w = 1 - m = 0.5 is observed, but the curve for $\phi = 1$ is significantly different from that of pure diffusion.

Equations 1-5 are a mathematical description of a process where a single relaxation phenomenon, characterized by the two parameters m and θ_R, may take place in the polymer. It is of course conceivable that more than one such phenomenon may take place; if all the phenomena are governed by linear kinetics, the mathematical description would still be the same, with eq.2 taking the following form :

$$x = 0, \quad u = 1 - \sum m_i \exp(-\phi_i^2 t) \tag{13}$$

or, with non-linear kinetics of relaxation, one would have :

$$x = 0, \quad u = g(t) \tag{14}$$

The problem is still one where a closed form solution can be found, provided the function g(t) in eq.14 can be Laplace-transformed. In fact, let u°(x, t) be the (well-known) solution for the case where g(t) = 1 at t > 0

$$u°(x, t) = 1 - 2 \sum \frac{(-1)^N}{a_N} \exp\left[-a_N^2 t\right] \cos\left[a_N x\right] \tag{15}$$

A strightforward application of Laplace-transform techniques yields the solution u(x, t) for the general case :

$$u(x, t) = \int_0^t u°(x, t - \tau) \left[g'(\tau) + g(0)\right] d\tau \tag{16}$$

In particular, if eq.13 holds, and all the ϕ_i's are sufficiently small, simple additivity holds again and, instead of eq.12 one obtains :

$$w = (1 - \sum_i m_i) f_D(t) + \sum_i m_i (1 - e^{-\phi_i^2 t}) \tag{17}$$

Eq.17 has been proposed on the basis of heuristic arguments by Berens and Hopfenberg (5).

The irreversible BSC phenomena discussed by Apicella et al. (8) do not lead to any significant mathematical structure. In fact, the kinetics of sorption in an irreversibly damaged sample are still described by the ordinary diffusion equations, and the damaged structure reveals itself only in the values of the apparent diffusivity and solubility. It is interesting that, if the dual-sorption mechanism is postulated (Refs. 10-12), the values of the apparent diffusivity and solubility are related to each other; this prediction is well confirmed by the experimental data (13). The comparison is based on a linear equilibrium sorption isotherm, such as has in fact been observed experimentally (14).

PHYSICS OF MBP

BSC phenomena may manifest themselves by anomalous kinetics of diffusion, see e.g. the curve for $\phi = 1$. Anomalies in the kinetics of diffusion in polymeric materials have often been reported in the literature, but a large fraction of these cannot be explained on the basis of a BSC. Indeed, in many cases a sharp morphological discontinuity has been observed within

the polymer sample, indicating that the phenomenon to be considered is more likely to be one where the structure changes discontinuously from one to another of two possible states. In some sense a phase transition is taking place, though the analogy with phase transitions taking place in ordinary materials is a tenuous one, for a number of reasons to be discussed below.

Analysis of the anomalous diffusion behavior in polymers has for a long time been carried out by trying to formulate in an appropriate way the diffusion equation. The physical effects which have been considered are: the gradients of internal stresses caused by diffusion (Ref. 15, 16); the dependency of the diffusion coefficient on concentration (Refs. 17, 19); convective flux resulting from diffusion-induced density variations (Ref.18). Although all of these effects are real and may on occasion be significant, they are bulk effects; the physics of the phase transition taking place at the moving boundary are not taken into consideration. The first one to explicitly consider the two-phase nature of the phenomena under consideration was Peterlin (20) in 1969; shortly afterwards a lucid review of the whole area was published (Ref.21).

MBP of course take place also in ordinary low molecular weight materials whenever a phase transition occurs as a result of either heat or mass transfer:ice may melt either by heating or by addition of salt. These phenomena have been successfully modeled, and in fact a sophisticated mathematical literature on the subject is available, see e.g. Refs.22-25. However, one can easily convince oneself that these analyses do not apply to mass-transfer induced MBP in polymeric materials. In fact, the following experimental results have been observed, none of which can be explained by the classical theory.

i. Under a variety of conditions, both the distance of the moving boundary from the external surface and the total weight of solvent sorbed increase linearly with time, while the classical analysis predicts, under the same conditions, that both should be proportional to the square root of time (Ref. 21).

ii. When the conditions described above apply, the concentration of the solvent in the region between the external surface and the moving boundary is essentially constant (Ref.26).

iii. The initial velocity of the moving boundary depends non-linearly on the value of the activity of the solvent at the external surface, and its activation energy is significantly larger than what one would expect in a diffusion-controlled phenomenon (Ref.27).

These observations suggest that MBP in polymeric materials may be governed by the kinetics of the phase transition taking place at the moving boundary, rather than by diffusion. In the classical analysis, the kinetics of the phase transition are not taken into account, since the following two assumptions are made :

a). The two sides of an interface separating two phases are at physical equilibrium with each other. This corresponds, for heat transfer, to the requirement that temperature is the same on both sides of the interface, and for mass transfer that fugacity is the same. The analogous condition for momentum transfer is the no-slip condition, which is known to be occasionally violated (Ref. 28) in polymeric systems; a recent thorough discussion of this point is available (Ref. 29).

b). The interface separating two phases is at equilibrium conditions. For heat transfer, this implies that the temperature of the interface is the equilibrium phase-transition temperature. For mass transfer, the equivalent implication is that the fugacity at the interface has the value corresponding to the equilibrium phase transition.

Implicit in the two assumptions above is a third one, namely:

c). The rate at which the phase transition takes place is governed by the rate at which heat or mass is supplied at the moving boundary (to compensate for the discontinuity of enthalpy or concentration at the phase transition boundary).

Assumption c) of course neatly disposes of the need to model the kinetics of the phase transition; however, since for polymeric materials these kinetics may govern the macroscopic behavior, one needs to relax assumption c), and therefore, by implication, either assumption a), or b), or both. In addition to this, one needs to postulate a model for the kinetics of phase transition.

It is of interest to note that, in the classical theory of heterogeneous chemical kinetics, the affinity of chemical reactions is not assumed to be zero at an interface (Refs.30, 31),

i.e., assumption b) is relaxed. The rationale is that, while structural rearrangements in ordinary materials are essentially instantaneous, chemical reactions are not. This suggests that, in the case of polymeric materials for which structural rearrangements are <u>not</u> instantaneous, assumption b) may fail to be applicable.

Consider the two possible structures of the polymer at equilibrium with each other, i.e., under conditions where the rate of phase transition is zero. The concentrations of the solvent in the two structures will in general be different (since the solubility is different in the two structures); let c_1^* and c_2^* be the two equilibrium values, with $c_1^* > c_2^*$. In the classical analysis, assumption b) implies that, even under non-equilibrium conditions, the concentrations in the two structures at the moving boundary are still c_1^* and c_2^*; if that is the case, assumption a) is also satisfied. For polymeric materials, the arguments discussed above suggest that, if the $1 \to 2$ transition is to take place at any finite rate, the concentration at the moving boundary in phase 1, c_{1i}, may be different from c_1^* (in fact larger if the transition is to take place in the $1 \to 2$ direction) and in fact that the rate of phase transition r is governed by the local "driving force" $c_{1i} - c_1^*$:

$$r = F(c_{1i} - c_1^*) \qquad\qquad (18)$$

with the function F( ) being a monotonously increasing one. At equilibrium, $c_{1i} = c_1^*$ and r = 0, hence the function F( ) must have the following property :

$$F(o) = 0 \qquad\qquad (19)$$

Astarita and Sarti (32) presented the first analysis of MBP in polymers based on this approach; it is interesting to observe that, under the mild assumption that the function F( ) is differentiable almost everywhere (in particular at the value of c_1 imposed at the external boundary), the "anomalies" discussed above under i), ii) and iii) are predicted. Astarita and Sarti did not take position with respect to assumption a), since they considered only the special case where $c_2^* = 0$; however, it is physically intuitive that the concentration in the "2" structure is unlikely to exceed the solubility, and that therefore $c_{2i} \leq c_2^*$. This in turn implies that assumption a) is also violated; in particular, subsequent work on the mathematical modeling of mass-transfer induced MBP, to be discussed in the next section, has shown that the assumption $c_{2i} = c_2^*$ in the one which gives the best fit of experimental data.

While mass-transfer induced MBP in polymers have been frequently reported and discussed in the literature, much less information is available on heat-transfer induced ones. It is well known that, in the experimental determination of the glass transition temperature, the apparent value observed depends on the rate of heating, with the "true" value being the one which would be observed at zero rate of heating. This again suggests that the glass $\to$ rubber phase transition, when it takes place at a finite rate, does not take place at the <u>equilibrium</u> value of temperature, i.e., that assumption b) of the classical analysis is not applicable to polymers.

It is also of interest to consider the implications of assumption c) of the classical analysis in the case of a <u>secondary</u> phase transition, i.e., one characterized by a zero latent heat. Quite obviously a paradox is likely to emerge (as will be shown to be the case in the next section), a consideration which by itself suggests that the classical analysis cannot be applied to secondary phase transitions. It should also be borne in mind that a secondary phase transition cannot be a true equilibrium phase transition, since the equilibrium requirement of equal Gibbs free energy in the two phases would imply that the entropy difference between the two phases equals the latent heat divided by the equilibrium transition temperature. If the latent heat is zero, so should be also the entropy difference - but then in what sense would the two phases be different ?

Apart from the difficulties connected with secondary phase transitions, Migliaresi et al.(33) have reported MBP data in a polymeric material undergoing a primary phase transition. The material was a composite one, consisting of a polymeric matrix with imbedded a solid salt capable of undergoing a solid-solid primary phase transition. Their data clearly indicate that the classical analysis cannot be applied, for the following reasons:

i) Assumption c) of the classical analysis implies that, other things being equal, the rate of advance of the moving boundary is inversely proportional to the latent heat per unit volume. Since the latter is, for the experiments described in Ref.33, proportional to the volumetric fraction of the filler, an experimental check is easy. In fact, contrary to the

implications of assumption c), the rate of advance goes through a minimum as the filler's volumetric fraction is increased.

ii)The measured rate of advance of the front was about one order of magnitude larger than an estimate based on the classical analysis.

Point ii) above strongly suggests that the macroscopically observed rate is governed by a phenomenon other, and slower, that heat diffusion. Again, the kinetics of phase transition are presumably of importance, and indeed an analysis based on an equation analogous to eq.18 provided a perfect fit of the data (Ref. 34). It is interesting that the analysis is based again on relaxing both assumptions a) and b); in other words, a temperature discontinuity is assumed to exist across the moving boundary (just as a fugacity discontinuity was assumed in the analysis of mass-transfer induced MBP). This assumption not only provided a good fit of experimental data, but also removed a nucleation paradox which would have resulted from retaining assumption a) while relaxing assumption b).

MATHEMATICS OF MBP

The mathematical theory of MBP in ordinary materials is well developed, and theorems of existence and uniqueness of solutions as well as analytical and numerical solution techniques are available for a variety of initial and boundary conditions, see e.g. Ref.35. For one-dimensional problems (plane symmetry), the equations describing both heat- and mass-transfer induced MBP can be reduced to the form given below :

$$u_{xx} - u_t = 0 \qquad\qquad 0 < x < s(t) \qquad\qquad (20)$$

$$\gamma U_{xx} - U_t = 0 \qquad\qquad s(t) < x < 1 \qquad\qquad (21)$$

$$u(x,0) = h(x) > 0 \qquad\qquad 0 < x < s(0) \qquad\qquad (22)$$

$$U(x,0) = H(x) \leq 0 \qquad\qquad s(0) < x < 1 \qquad\qquad (23)$$

$$u(0,t) = f(t) > 0 \qquad\qquad f(0+) = 1 \qquad\qquad (24)$$

$$U_x(1,t) = 0 \qquad\qquad\qquad\qquad (25)$$

where γ is the ratio of the diffusivities in the two phases, the equilibrium values of either temperature or concentration have been set equal zero, concentrations or temperatures have been normalized with respect to the initial driving force (hence $f(0+) = 1$), and distance from the external surface have been normalized to the sample's half-thickness.

Equations 20-25 are not sufficient to determine the three functions $s(t)$, $u(x,t)$ and $U(x,t)$, and therefore a balance (of either heat or mass) across the boundary needs to be written. The general form of this balance is (Ref. 36) :

$$-u_x(s(t), t) + \beta U_x(s(t), t) = \left[\alpha + u(s(t), t) - \frac{\beta}{\gamma} U(s(t), t)\right] s'(t) \qquad (26)$$

where β is the ratio of conductivities (so that, for mass transfer MBP, $\beta = \gamma$), and α is a dimensionless latent heat (for heat transfer MBP) or a dimensionless equilibrium concentration difference (for mass transfer MBP).

Again, the system 20-26 is not sufficient, and the classical analysis is based on the assumption a) and b) discussed in the preceding sections, which are formulated mathematically as follows :

$$u(s(t), t) = U(s(t), t) = 0 \qquad\qquad (27)$$

It is evident that, when eq.27 is substituted into eq.26, the result is a formulation of assumption c), which is therefore seen to be a consequence of assumptions a) and b).

The paradox arising with the classical formulation in the case of secondary phase transitions is immediately evident. In fact, consider the case where $H(x) = 0$, so that the solution of eq.21 is, trivially, $U(x,t) = 0$. If eq.s 27 are assumed to hold, and the phase transition is a secondary one ($\alpha = 0$), eq.26 implies that either $u_x(s(t),t) = 0$ or $s'(t) \to \infty$. Since no significant solution of eq.20 can have both $u_x(s(t), t)$ and $u(s(t), t)$ equal to zero, one is left with $s'(t) \to \infty$: i.e., the secondary phase transition is predicted to take place instan

taneously throughout the sample.

The approach to the analysis of MBP in polymeric materials discussed in the preceding section is formulated mathematically by relaxing the first one of eq.27, and writing instead a constitutive equation for s'(t); Astarita and Sarti (32) have chosen the following power-law form:

$$s'(t) = \frac{|u(s(t), t)|^n}{\phi} \tag{28}$$

where $n > 0$ and ϕ is (proportional to) a relaxation time characteristic of the phase transition. Notice that, as $\phi \to 0$, eq.28 reduces back to the first one of eq.s 27 whenever s'(t) is finite, i.e., the classical analysis is seen to be an asymptotic expansion applying to the case where relaxation is essentially instantaneous.

A typical experiment is carried out by subjecting a sample, which is initially at uniform conditions, to an external condition which is kept constant in time, and such that at final equilibrium the sample will have undergone the phase transition. Mathematically, this corresponds to :

$$s(0) = 0 \tag{29}$$

$$f(t) = 1 \tag{30}$$

$$H(x) = - \delta \tag{31}$$

The constant δ is non-negative, and, in view of eq.29, the function h(x) has zero domain.

The quantities which may be measured are the position of the moving boundary ‾s(t), and the total amount w(t) of solvent sorbed (in mass transfer MBP) or of heat sorbed (in heat transfer MBP):

$$w(t) = \int_0^{s(t)} (u + \alpha)dx + \int_{s(t)}^1 Udx + \delta \tag{32}$$

We begin by considering the special case where $\delta = 0$, i.e., the initial condition of the sample is just at the threshold of the phase transition. In the classical approach where eq.s 27 are assumed to hold, an exact solution can be obtained :

$$s = 2K \sqrt{t} \tag{33}$$

$$w = 2\sqrt{t} \left[K(1 + \alpha) - \frac{\text{ierf } K}{\text{erf } K} \right] \tag{34}$$

where K is the solution of the following equation :

$$\sqrt{\pi} \, K \exp(-K^2) \, \text{erf } K = 1/\alpha \tag{35}$$

The solution holds only up to $t = 1/4K^2$.

Eq.35 immediately reveals the secondary phase transition ($\alpha = 0$) paradox. Apart from this, eq.s 33-34 show that both s and w are proportional to $\sqrt{t}$, contrary to the experimental observation that both s and w are linear functions of time over a wide range of conditions. Notice also that both s'(0) and w'(0) are predicted to approach infinity.

In contrast with this, consider the alternate approach where eq.28 is assumed to hold, with U(s(t), t) = 0 (i.e., with a discontinuity of either fugacity or temperature at the moving boundary). Eq.28 shows immediately that s'(0) = 1/ϕ, so that, in neighborhood of t = 0 one obtains the following expansion which is valid to within $O(t^2)$:

$$s = t/\phi \tag{36}$$

$$u = 1 - (\alpha + 1)x/\phi \tag{37}$$

$$w = (1 + \alpha)t/\phi \tag{38}$$

Eq.s 36 and 38 show that the linear dependency on time of both the boundary position and the total amount (of solvent of heat) sorbed is predicted by the approach considered. Indeed, the same result would be obtained for any form of the right-hand side of eq.28, provided it has a finite value of t = 0.

We now turn attention to the more general case where $\delta > 0$. One of the most striking features of the behavior of MBP in polymers is that the macroscopically observable behavior is qualitatively different for different sample sizes; this is predicted exactly by the approach

based on eq.28, as has been shown in Ref.37. A brief discussion on this point is given in the following.

Also when $\delta > 0$, in a neighborhood of t = 0 eq.s 36 and 37 hold, and the right-hand side of eq.38 gives the value of the first integral on the right-hand side of eq.32; however now the contribution to the value of w given by the next two terms on the right hand side of eq.28 has to be taken into account. The value of these two terms can be calculated explicitly as long as eq.36 holds true (20, 37); in particular the following two expansions hold true :

$$ t << \frac{1}{\gamma} \, , \quad \int_{s(t)}^{1} U dx + \delta = 2\delta \; \sqrt{(\gamma t/\pi)} \tag{39} $$

$$ t >> \frac{1}{\gamma} \, , \quad \int_{s(t)}^{1} U dx + \delta = \delta \tag{40} $$

It is now possible to establish different size ranges where different behaviors will be observed; these ranges are determined by the value of the parameter ϕ, which is directly proportional to the relaxation time and inversely proportional to the sample dimension. First consider the case where the following inequality is fulfilled :

$$ \phi >> 1 + \alpha \tag{41} $$

Eq.41 implies that u as given by eq. 37 is almost equal to unity even at the largest possible value of x, i.e., at x = 1. Hence eq.36 holds up to t = ϕ, when the whole sample has undergone the phase transition and is in equilibrium with the external condition.

At very short times, eq.39 shows that w is predicted to be proportional to the square root of time, since the right-hand-side of eq.39 will necessarily be much larger than that of eq.38; this will be true if t, in addition to being much less than $1/\gamma$ (so that eq.39 holds true), also fulfills the following condition:

$$ t << \frac{\delta^2 \phi^2 \gamma^2}{(1 + \alpha)^2} \tag{42} $$

which can easily be obtained by comparing the expression in eq.s 38 and 39. Although a square root of time initially predominant contribution to w is predicted whenever $\delta > 0$, its value (which is always less than δ) may be so small as compared to the final equilibrium value $1 + \alpha + \delta$ as to be unobservable in practice.

As time increases, the term in eq.39 will cease to be the dominant one for one of two different reasons: either because t exceeds $1/\gamma$, or because it exceeds the value in eq.42, whichever comes first. It follows that two distinct behaviors can be observed. First suppose that:

$$ \phi >> \frac{1 + \alpha}{\gamma\delta} \tag{43} $$

In this cases, the condition t << $1/\gamma$ will be violated before condition 42, and a range of t values will exist where w is dominated by the term in eq.40: in this region, w is constant, i.e., an intermediate apparent equilibrium will be observed which is reminiscent of the small sample behavior observable in BSC processes. This will be followed by a range of times where w is dominated by the term in eq.38, until final equilibrium is reached at t = ϕ.

Conversely, suppose that :

$$ \phi << \frac{1 + \alpha}{\gamma\delta} \tag{44} $$

but eq.41 is still satisfied (this is possible in mass-transfer MBP, since both γ and δ are very small numbers; in heat transfer phenomena, γ is of order unity, and unless δ is very small it is impossible to fulfill both equations 42 and 44).In this case, the initial square-root-of-time range will be followed directly by a linear region.

Finally, if :

$$ \phi << 1 + \alpha \tag{45} $$

the function s(t) will cease to be linear before s reaches its final value of unity. In the limit where $\phi \rightarrow 0$, one obtains again the classical result where s is proportional to $\sqrt{t}$ in a neighborhood of time zero.

In spite of the fact that, in the mathematical description of MSC and MBP as discussed above, coupling between relaxation and diffusion only takes place through a boundary condition, there is much more mathematical structure in MBP, because the coupling takes place through a condition imposed on a moving, rather than a fixed boundary. Some mathematical work on the differential equations describing MBP with boundary conditions analogous to the ones discussed in

this section is available (38, 39). A recent work in the area has been presented by Fasano (40), who has considered the specific problem of Eq.s 20-25, 29-31, with $\delta = 0$. Fasano has considered the general case where eq.18 holds, say in the nomenclature of this section :

$$s'(t) = F(u(s(t), t)) \tag{46}$$

and has demonstrated that, if F( ) is $C[0, 1]$ and $C^1(0, 1]$, f'>0, and f(0) = 0, than there is a unique global solution with s being $C^2[0, +\infty)$ and s"(t) being Hölder—continuous and negative.

CONCLUSIONS

Transport of heat or mass in polymeric materials may induce structural changes. The macroscopically observed behavior is different from the one typical of ordinary materials, the reason being that the relaxation times involved in the structural change are much larger in polymeric materials. The physics of such phenomena is by now reasonably well understood, and satisfactory mathematical models describing them can be constructed. Some of these models have a non-trivial mathematical structure, and analytical work in the area has just barely been started. A common framework of thought encompasses all the seemingly disparate phenomena which have been reported in the literature.

REFERENCES

1. E.Bagley, F.A.Long, J.Am.Chem.Soc. 23, 2172 (1955)
2. F.A.Long, D.Richman, J.Am.Chem.Soc. 82, 513 (1960)
3. E.Jenckel, A.Nogay, Forschungers-Landes Nordkhein-Westfalen n.392, Westdeutscher Verlag, Koln (1960)
4. A.R.Berens, J.Memb.Sci. 3, 247 (1978)
5. A.R.Berens, H.B.Hopfenberg, Polymer 5, 489 (1978)
6. E.L.McKague jr., J.D.Reynolds, J.Compos.Matl. 9, 2 (1975)
7. C.H.Shen, G.S.Springer, J.Compos.Matl. 10, 2 (1976)
8. A.Apicella, L.Nicolais, G.Astarita, E.Drioli, Polymer 20, 1143 (1979)
9. S.Joshi, G.Astarita, Polymer 20, 455 (1979)
10. W.R.Vieth, K.J.Sladek, Colloid Sci. 20, 1014 (1965)
11. D.R.Paul, W.J.Koros, J.Polym.Sci.Phys.Ed. 14, 675 (1976)
12. J.H.Petropoulos, J.Polym.Sci. A2, 1797 (1970)
13. A.Apicella, L.Nicolais, G.Astarita, E.Drioli, Polym.Engng.Sci. 21, 18 (1981)
14. A.Apicella, L.Nicolais, G.Astarita, E.Drioli, Polymer 22, 1064 (1981)
15. H.L.Frisch, T.T.Wang, T.K.Kwei, J.Polym.Sci.A2 7, 879 (1969)
16. T.T.Wang, T.K.Kwei, H.L.Frisch, J.Polym.Sci.A2 7, 2019 (1969)
17. J.Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, (1975)
18. J.L.Duda, S.Vrentas, J.Polym.Sci.A2 6, 675 (1968)
19. J.Crank, G.S.Park, Diffusion in Polymers, Academic Press, New York, (1968)
20. A.Peterlin, Makrom.Chem. 124, 136 (1969)
21. H.B.Hopfenberg, in "Membrane Science and Technology", Plenum Press, New York, (1970)
22. J.R.Cannon, D.C.Mill, J.Math.Mech. 17, 1 (1967)
23. J.R.Cannon, J.Douglas, C.D.Hill, J.Math.Mech. 17, 21 (1967)
24. J.R.Cannon, M.Primicerio, Ann.Mat.Pura Appl. 88, 177 (1971)
25. J.R.Cannon, M.Primicerio, Ann.Mat.Pura Appl. 88, 193 (1971)
26. N.Thomas, A.H.Windle, Polymer 19, 255 (1978)
27. L.Nicolais, E.Drioli, H.B.Hopfenberg, G.Caricati, J.Memb.Sci. 3, 231 (1978)
28. G.Astarita, G.Marrucci, G.Palumbo, Ind.Eng.Chem.Fund. 3, 333 (1964)
29. R.A.Mashelkar, A.Dutta, Natl.Chem.Lab.Pune, n°2886 (1981)
30. G.Astarita, Mass Transfer with Chemical Reaction, Elsevier, Amsterdam 1967
31. G.Astarita, D.W.Savage, A.L.Bisio, Gas Treating with Chemical Solvents, J.Wiley, New York expected for 1982
32. G.Astarita, G.C.Sarti, Polym.Engng.Sci. 18, 388 (1978)
33. C.Migliaresi, G.Astarita, L.Nicolais, S.Joshi, Polym.Comp. 2, 58 (1981)
34. S.Joshi, G.Astarita, Polym.Engng.Sci. 21, 457 (1981)
35. A.Fasano, M.Primicerio (Eds.), Free Boundary Problems: Theory and Applications, Research Notes in Mathematics, Pitman, New York, expected for 1982
36. G.Astarita, A Class of Free Boundary Problems Arising in the Analysis of Transport Phenomena in Polymers, in (35) (1982)
37. G.Astarita, S.Joshi, J.Memb.Sci. 4, 165 (1978)
38. C.D.Hill, D.B.Katlow, Arch.Ratl.Mech.Anal. 45, 63 (1972)
39. G.I.Siskin, Dokl.Akad.Nauk USSR 197, 1276 (1971)
40. A.Fasano, Paper presented at Workshop on Applied Nonlinear Functional Analysis, Berlin, September 1981.