Rate Type Equations for the Diffusion in Polymers: Thermodynamic Constraints

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Conditions imposed by the second law of thermodynamics on viscoelastic rate type constitutive equations for the diffusive mass flux are considered. The analysis of three different rate type models proposed in the literature points out that presently physically unrealistic predictions are possible in desorption processes. The thermodynamic analysis of such models, based on the entropy inequality and on the stability requirement of the equilibrium states, leads to precise relationships among relaxation times, diffusion coefficients, and entropy equations of state. In particular, the analysis shows that relaxation times and diffusion coefficients cannot be simply constant numbers. When the thermodynamic constraints imposed on the constitutive equations are introduced, the models do not show physically unrealistic behaviors any more; Fickian diffusion close to the pure penetrant or pure polymer regions is also recovered. Finally, it is shown that the stability requirement for the equilibrium states may introduce very rigid requirements for the model feasibility, well beyond what appears explicitly from the kinetic equations alone.

Introduction

A large number of experimental data are now available for the process of mass transport in solid polymers, and they provide evidence that a large variety of behaviors is attainable by varying the polymer-penetrant pair or the experimental conditions. A model for diffusion in polymers which provides a comprehensive description of all the observed phenomena is not yet available although different efforts have been made in the past decade and more recently by Carbonell and Sarti (1990) and by Lustig et al. (1992). A detailed modeling of the process is indeed a very tough challenge due to the need for accounting for the deformation and stress fields that are developed in the solid and possibly for the simultaneous heat transfer. This enforces the coupling of mass, momentum and energy balance equations, in which constitutive expressions for the diffusive mass flux, the heat flux and the stress tensor must be inserted.

We are interested here in a restricted class of simplified models which, away from such a detailed and comprehensive representation of the process, simply introduce a viscoelastic constitutive equation for the diffusive mass flux in order to predict some of the non-Fickian effects which are observed for the case of diffusion in polymers close to, or below, the glass transition temperature.

Indeed, use of Fick's constitutive equation for the diffusive mass flux in modeling a sorption problem leads to a predicted initial weight uptake proportional to the square root of time, whatever the concentration dependence of the diffusion coefficient may be (Crank, 1956). This is in contrast to the kinetics of absorption of low molecular weight species in glassy polymer films, which often shows a weight gain directly proportional to the elapsed time: this is the so called "Case II diffusion" (Nicolais et al., 1977; Thomas and Windle, 1978). The latter is also characterized by concentration profiles, which exhibit a sharp discontinuity, separating a swollen outer region from an internal dry core and traveling in the solid with a velocity which is often constant in time. In fact, Fick's law invariably fails in predicting the above features insofar as the corresponding mass balance equation turns out to be parabolic, and an instantaneous change in the concentration over the entire field is predicted as a disturbance is applied at the boundaries (Riemann jump boundary conditions). Discontinuities in the concentration profiles may possibly be described by Fick's law if a discontinuous concentration dependence of the diffusion coefficient is used; however, the predicted discontinuity ve-

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locity may not be a constant but rather decreases as $t^{1/2}$ and is infinite at time equal to zero.

To allow for a simplified and effective description of the above effects as well as of other unusual behaviors like overshoots and oscillations sometimes observed for the sorbed mass in a solid polymer (Baird et al., 1971; Titow et al., 1974; Kim et al., 1992), several viscoelastic equations for the diffusive mass flux have been proposed (Aifantis, 1980; Taylor and Aifantis, 1982; Neogi, 1983; Durning, 1985; Camera-Roda and Sarti, 1986, 1990; Kalospiros et al., 1991).

Here we first take a close view at some specific equations for the diffusive flux which attained good results in predicting qualitative behaviors of sorption kinetics in glassy polymers. It will be pointed out, however, that as they have appeared in the literature, the above models may lead to unrealistic predictions for desorption processes. This is not a general feature of such viscoelastic equations, but is simply a consequence of the use of expressions for the transport coefficients which violate the second law of thermodynamics. In many respects, the problem considered here is very similar to well-known problems in fluid mechanics in which, for instance, it is well established that the Reiner-Rivlin constitutive equation may violate the second law inequality unless the coefficients are suitable functions of the deformation rate.

Based on a thermodynamic analysis of the model constitutive equations, the corresponding conditions for the transport properties are then derived which are imposed by the second law of thermodynamics. Lastly, it is shown that the implementation of these conditions indeed allows the viscoelastic models to prevent the previously observed shortcomings.

Viscoelastic Models

The viscoelastic models considered for the mass flux constitutive equation are very similar to the linear viscoelastic constitutive equation for the mechanical stress. As usual, they can be represented either through integral or through differential equations. The mechanical viscoelastic equation dates back to the pioneering work by Maxwell, and an analogous equation was introduced for the heat flux by Cattaneo (Cattaneo, 1948).

Analogous constitutive equations for the diffusive mass flux have been formally derived by Aifantis (1980) based on species mass and momentum balances and on general representation theorems for vector and tensor objective functions. In that analysis, different rate type constitutive equations have been obtained in which the time rate of change of the diffusive flux is important on the very short time scale in which the species inertia terms are dominant with respect to the viscous terms in the species momentum equation. On the other side, the usual relaxation times encountered in solid polymers are much higher and are associated to viscous and elastic effects.

Similar constitutive equations for the diffusive mass flux have been considered recently, after the work by Neogi (1983), in the works by Durning (1985), Camera Roda and Sarti (1986, 1990) and Kalospiros et al. (1991), in which the relaxation times are not restricted to very short values.

Within the broader family of rate type constitutive equations for the diffusive flux, we will hereafter focus our attention on three specific viscoelastic models which appeared in Camera-Roda and Sarti (1986, 1990) and Kalospiros et al. (1991).

For the sake of clarity, we will first consider the pure hyperbolic Cattaneo-Maxwell (CM) model, for the diffusive mass flux, analyzed in the work by Camera-Roda and Sarti (1986).

In order to obtain algebraically simpler forms which avoid the heavier formalism implied by the material objectivity requirements, we confine our analysis to the case of diffusion in a solid sample in which the velocity of the center of mass can be neglected; in that case, the Cattaneo-Maxwell equation takes the form:

$$\underline{J} + \tau \frac{\partial \underline{J}}{\partial t} = -\mathfrak{D}\underline{\nabla}\phi \tag{1}$$

where $\underline{J}$ and ϕ are the diffusive volume flux and the volume fraction of penetrant species, while $\mathfrak{D}$ and τ are diffusivity and relaxation time respectively, which possibly are functions of concentration, but not of $\underline{J}$ and $\underline{\nabla}\phi$.

In modeling sorption processes into glassy polymers, when a step variation in time of solute chemical potential in the outer phase is considered, the previous constitutive equation can be coupled with boundary conditions which ask for a time-dependent interface concentration, as originally proposed in the work by Long and Richman (1960). The same characteristic time τ appearing in Eq. 1 is then used to describe the relaxation at the interface:

$$\tau \frac{d\phi}{dt} + (\phi - \phi_{\text{fin}}) = 0 \quad \text{at the boundary}$$

$$\phi = \phi_w \quad \text{at the boundary at } t = 0 \tag{2}$$

where ϕ_{fin} is the equilibrium value of volume fraction pertinent to the actual solute fugacity, while ϕ_w is its initial value, which of course could be other than the equilibrium volume fraction pertinent to the initial solute fugacity.

Coupled with the species balance equation, Eq. 1 leads to a hyperbolic set of equations the properties of which have been analyzed in Camera-Roda and Sarti (1986). When the case of sorption in thin polymeric films is considered, it appears most natural to use a diffusivity and a relaxation time that are exponentially dependent on concentration, as established by simplified versions of the free volume theory (Vrentas and Duda, 1977, 1979; Zielinski and Duda, 1992):

$$\mathfrak{D} = \mathfrak{D}_0 \exp[k_D\phi] \quad k_D > 0 \tag{3}$$

$$\tau = \tau_0 \exp[-k_T\phi] \quad k_T > 0 \tag{4}$$

In so doing we use an expression for $\mathfrak{D}$ which is obtained analyzing experimental data through Fick's law; we point out, however, that in steady-state processes, Eq. 1 actually reduces to Fick's law with $\mathfrak{D}$ as the diffusion coefficient. On the other hand, use of Eq. 4 is simply based on an expected, although not necessarily required, analogy between the τ entering Eq. 1 and the relaxation time entering the constitutive equation for the mechanical stress.

In that case (Camera-Roda and Sarti, 1986) the most relevant dimensionless parameter is the diffusive Deborah number

$$De = \frac{\tau_{\text{eq}}\mathfrak{D}_{\text{eq}}}{\delta^2} \tag{5}$$

where τ_{eq} and $\mathfrak{D}_{\text{eq}}$ respectively stand for the values of relaxation time and diffusivity evaluated at the concentration ϕ_{eq}, while δ is the half-thickness of the film.

Fickian behavior is predicted by the model in the limit of low Deborah numbers while Case II is approached when the relaxation time has the same order of magnitude of the diffusion time. Finally, overshoot and damped oscillations in the weight uptake are predicted for larger values of De.

This model however does not accommodate any Fickian behavior for the very high Deborah numbers which are obtained for very low penetrant concentrations.

For what follows, it seems useful to show the results of the application of this particular model to a specific case of absorption into a polymeric sample: in Table 1 the set of equations and boundary conditions are reported which refer to the application of the CM model to the case of diffusion into a thin film. The problem has been solved through a numerical procedure which was introduced in the work by Lax and Wendroff (1960) and modified as suggested by Louriero and Rodrigues (1991) on the basis of the work of Book et al. (1975). The case of exponential dependence of τ and $\mathfrak{D}$ on composition was considered, as expressed by Eqs. 3 and 4, when

$$k_D=k_T=10 \quad \phi_{\mathrm{fin}}=\phi_{\mathrm{eq}}=0.3 \quad \phi_{\mathrm{in}}=0 \quad \phi_w=0.24 \quad De=1 \qquad (6)$$

A Case II sorption kinetics is predicted (Figure 1) followed by damped oscillations of the absorbed mass.

In Figure 2, solute concentration is reported as function of the position, from the center of the film ($x=0$) to the external surface ($x/\delta=1$) at different times. A sharp discontinuity initially travels towards the center of the film, then it is reflected back to the external surface, resulting in an inner concentration which oscillates around the equilibrium value. Further discussion of the CM model properties and the related expression for the shock wave velocity, although interesting, are not our main concern presently, and may be found in the works by Cattaneo (1948), Camera-Roda and Sarti (1986, 1990) and Camera-Roda et al. (1991).

Table 1. Equations of Sorption Processes for the Cattaneo-Maxwell Model

	$J+\tau\dfrac{\partial J}{\partial t}=-\mathfrak{D}\dfrac{\partial \phi}{\partial x}$	
	$\dfrac{\partial \phi}{\partial t}+\dfrac{\partial J}{\partial x}=0$	
BC	$J=0$	as $x=0,\ t\geq 0$
	$\tau\dfrac{d\phi}{dt}+(\phi-\phi_{\mathrm{fin}})=0$	as $x=\delta,\ t\geq 0$
IC	$\phi=\phi_w$	as $x=\delta$ and $t=0$
	$J=0$	as $t=0,\ 0\leq x\leq \delta$
	$\phi=\phi_{\mathrm{in}}$	as $t=0,\ 0<x\leq \delta$

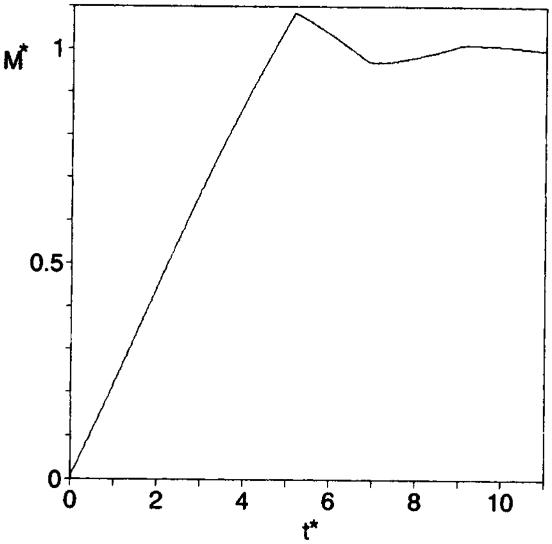

Figure 1. Sorption kinetics into a thin polymer film.

Data computed for the CM model with relaxation time exponentially dependent on concentration: $k_D=k_T=10$; $\phi_{\mathrm{fin}}=0.3$; $\phi_{\mathrm{in}}=0$; $\phi_w=0.24$; $De=1$.

With the aim to avoid some shortcomings of the CM model and in order to accommodate a broader spectrum of features, a different rate type model was then proposed by the same authors (Camera-Roda and Sarti, 1990), which will be henceforth indicated as the CMRT model. According to that scheme the diffusive mass flux can be expressed as the sum of two contributions: the first is a purely Fickian term while the second embodies a relaxation effect. Assuming that the diffusivities and the relaxation time depend only on the concentration, the model may be expressed by the following set of equations:

$$\begin{aligned} \underline{J}&=\underline{J}_R+\underline{J}_F \\ \underline{J}_F&=-\mathfrak{D}_F\underline{\nabla}\phi \\ \underline{J}_R&=-\mathfrak{D}_R\underline{\nabla}\phi-\tau\frac{\partial \underline{J}_R}{\partial t} \end{aligned} \qquad (7)$$

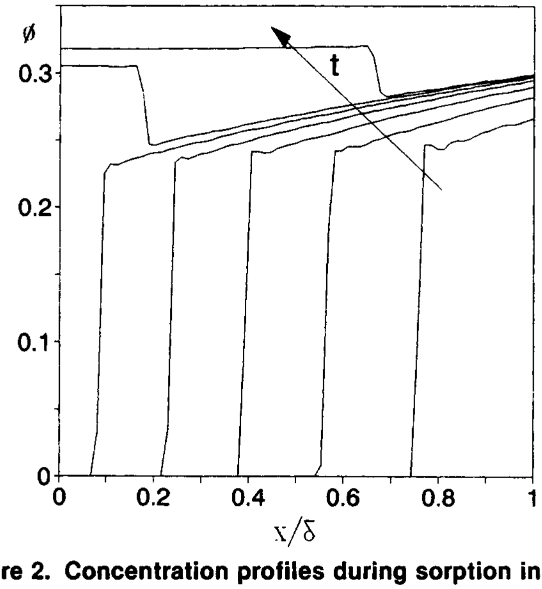

Figure 2. Concentration profiles during sorption into a thin polymer film.

Data computed for the CM model with relaxation time exponentially dependent on concentration: $k_D=k_T=10$; $\phi_{\mathrm{fin}}=0.3$; $\phi_{\mathrm{in}}=0$; $\phi_w=0.24$; $De=1$.

which ultimately leads to the following rate type constitutive equation including retardation terms (CMRT):

$$\tau \frac{\partial \underline{J}}{\partial t} + \underline{J} = -(\mathfrak{D}_F + \mathfrak{D}_R)\underline{\nabla}\phi - \tau \mathfrak{D}_F \frac{\partial}{\partial t}(\underline{\nabla}\phi) - \tau \frac{d\mathfrak{D}_F}{d\phi}\frac{\partial \phi}{\partial t}\underline{\nabla}\phi \quad (8)$$

By considering that $\mathfrak{D}_F$ has the physical meaning of initial diffusivity for a system with erased memory, Camera-Roda and Sarti simplified the above expression through the adoption of a constant value of $\mathfrak{D}_F$, which may eventually depend on the value of the initial concentration.

When, on the contrary, relaxation time τ and diffusivities $\mathfrak{D}_F$ and $\mathfrak{D}_R$ are taken as constant parameters the model originally proposed in the work by Neogi (1983) is recovered.

After proper concentration dependencies have been assumed for τ, $\mathfrak{D}_F$, $\mathfrak{D}_R$, coupling Eq. 8 with the species balance equation leads to a parabolic set in which, together with the Deborah number, a dimensionless parameter is present representing the ratio between the two limit diffusivities $\mathfrak{D}_F$ and $\mathfrak{D}_\infty = \mathfrak{D}_F + \mathfrak{D}_R$.

Fickian like behavior is approached by the model for very low and very high Deborah numbers with two different diffusivities, provided that $\mathfrak{D}_F \neq \mathfrak{D}_\infty$. Anomalous diffusion and overshoot or damped oscillations in the weight gain are predicted for intermediate *De*, while larger differences between $\mathfrak{D}_F$ and $\mathfrak{D}_\infty$ enlarge the deviations from Fickian behavior. A more detailed discussion of the CMRT model features is beyond our present aim and can be found in the work by Camera-Roda and Sarti (1990). The model was also found recently useful to describe the time-dependent behavior of the species fluxes in the pervaporation through PTMSP poly[1-(trimethylsilyl)-1-propine] membranes (Camera-Roda et al., 1992).

The spectrum of behaviors which can be accommodated by the Cattaneo-Maxwell model has been broadened to include also two stage sorption, in a recent model proposed in the work by Kalospiros et al. (1991), (KOAM model), the basic features of which are briefly recalled hereafter. The diffusive mass flux is given by:

$$\underline{J} + \tau \frac{\partial \underline{J}}{\partial t} = -L\underline{\nabla}p \quad (9)$$

where p is the fugacity of the penetrant species.

The fugacity is then related to the concentration through an internal state variable, H, defined as

$$H = \frac{\phi}{p} \quad (10)$$

H stands for a structural state parameter for the polymer and its kinetics is described by

$$\frac{\partial H}{\partial t} = F(p,H) = \frac{H^*(p) - H}{\theta} \quad (11)$$

where the superscript $*$ labels the equilibrium value of H for a given value of the fugacity p.

In that frame, a sudden jump of the fugacity at the interface imposed as boundary condition results in an interface concentration which relaxes toward the equilibrium value, according to the relaxation time θ, without need of additional assumptions.

Once a constant value for τ, $\mathfrak{D} = L/H$ and θ are assumed, the hyperbolic set of equations resulting by applying the KOAM model to sorption into thin films contains two dimensionless parameters:

$$De = \frac{\tau\mathfrak{D}}{\delta^2} \quad \epsilon = \frac{\theta}{\tau} \quad (12)$$

which represent the ratios between the three characteristic times: of the process diffusion time $\delta^2/\mathfrak{D}$, relaxation time τ and swelling time θ.

By varying those two parameters many of the anomalous diffusion phenomena in solid polymers are described from a qualitative point of view, including a two-stage sorption.

Unrealistic Predictions

All the three models we considered in the previous section are able to predict anomalous or Case II sorption kinetics as well as overshoot and damped oscillations for the sorbed mass and the Fickian limiting behavior for low Deborah numbers. Only CMRT can recover the Fickian limiting behavior observed during sorption in the limiting region of rather dry polymer, which is characterized by high Deborah number values.

As briefly recalled above, the CM, CMRT, KOAM, as well as Neogi's models, appear to give simple and reasonably adequate descriptions of the transport behavior during sorption processes, of course with the different features already mentioned and discussed in detail in the original works.

It is rather remarkable to point out, however, that all of them in their present formulation suffer from a severe drawback when desorption processes are considered. Indeed, there are parameter choices which appear reasonable for the description of sorption processes which, during desorption, may lead to an unrealistic persistency of a diffusive flux even after the entire mass of the diffusant has been desorbed.

For simplicity, we hereafter analyze this aspect only for the Cattaneo-Maxwell model, and refer to the same equations and initial and boundary conditions (IC and BC) reported in Table 1, where we set now:

$$\phi_{\text{in}} = \phi_{\text{eq}} = 0.3 \quad \phi_{\text{fin}} = \phi_w = 0 \quad (13)$$

The model equations have been numerically solved by considering diffusivity and relaxation time as exponentially dependent on concentration, according to Eqs. 3 and 4. For any finite value of the Deborah number, a finite mass flux leaving the film is calculated even for very long times, when all the solute initially present into the solid sample is already desorbed; that ultimately results in negative values of solute mass within the polymer. In Figure 3, the results are reported for the desorption kinetics as computed for $k_D = k_T = 10$ and $De = 1$. The corresponding concentration profiles are shown in Figure 4. They clearly demonstrate that even at short times negative volume fractions for the solute species are predicted by the model. We may now anticipate that the above unphysical results are not associated to a particular concentration depend-

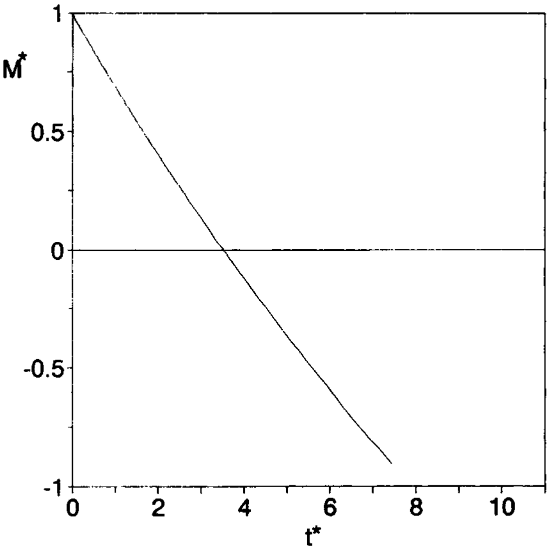

Figure 3. Absurd behavior computed for the desorption kinetics from a thin polymer film.

Data computed for the CM model with relaxation time exponentially dependent on concentration: $k_D = k_T = 10$; $\phi_{\text{fin}} = 0$; $\phi_{\text{in}} = 0.3$; $\phi_w = 0$; $De = 1$.

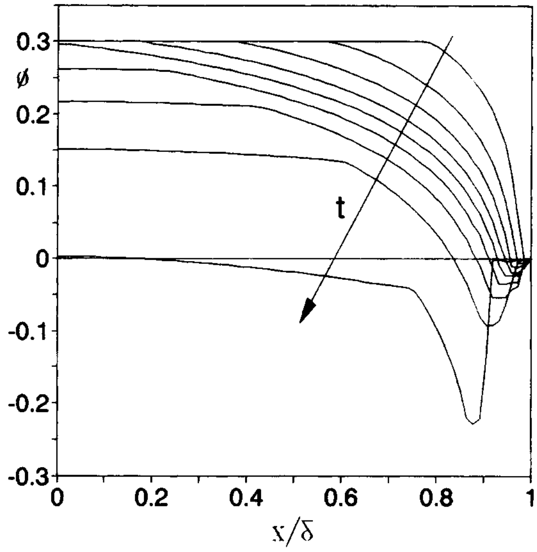

Figure 4. Absurd concentration profiles during desorption from a thin polymer film.

Data computed for the CM model with relaxation time exponentially dependent on concentration: $k_D = k_T = 10$; $\phi_{\text{fin}} = 0$; $\phi_{\text{in}} = 0.3$; $\phi_w = 0$; $De = 1$.

ence for relaxation time and diffusivity, but is rather a consequence of considering τ and $\mathfrak{D}$ independent of each other.

With very similar features in terms of diffusion flux and concentration profiles, the same unacceptable behavior is easily obtained if one uses the KOAM model for desorption, which is represented by a hyperbolic set of equations, with constant coefficients.

Use of CMRT or Neogi's models, on the other hand, which are not given by a hyperbolic set of equations, leads to diffusive fluxes and concentration profiles which show qualitative differences with respect to CM; however, the possibility to obtain the already mentioned physically unacceptable response still remains, albeit the effect is numerically very small to be as evident as in the previous cases.

A closer analysis of the constitutive Eqs. 1, 9-11 and 8 respectively can qualitatively explain those results. Indeed, in all cases a finite outward flux may be predicted, for vanishing or even for positive concentration gradients, whenever the relaxation time is large enough not to allow the memory effects which sustain the flux itself, to fade away before all the penetrant mass has diffused out of the sample. That is what frequently happens for all models if the relaxation time is either a constant or a monotonously decreasing function of the penetrant volume fraction.

On the other hand, it is rather obvious that a diffusion model can be accepted with some confidence only if it holds both during sorption and desorption and is not restricted to one case only.

The crucial problem that we are faced with after the above considerations is represented by the physical admissibility of the rate type diffusion models considered; in particular, one has to find out the conditions which must be satisfied by the relevant coefficients entering the models, relaxation time and diffusivities, in order to avoid any physically unacceptable behavior.

In its nature, this problem is the same as those encountered in many other branches of physics; in non-Newtonian fluid mechanics, for instance, it is well known that the Reiner-Rivlin constitutive equation gives rise to unacceptable behaviors when the two coefficients are both nonzero and constant and when they do not satisfy some restrictions (Astarita and Marrucci, 1974).

Clearly, the solution of the above admissibility problem involves a thermodynamic analysis through which one finds the restrictions imposed by the second law on the constitutive equations for the diffusive mass flux.

Thermodynamic Consistency

We will now develop a thermodynamic consistency analysis of the rate type constitutive equations for the diffusive mass flux by imposing that the entropy production rate associated with each model be nonnegative for every possible process, that is, for arbitrary field variables.

The latter condition may be reformulated in terms of the entropy volumetric density s and entropy flux $\underline{\psi}$ in the following form:

$$\frac{\partial s}{\partial t} + \underline{\nabla} \cdot \underline{\psi} \geq 0 \tag{14}$$

s and $\underline{\psi}$ being functions of the field variables.

The analysis is developed according to the Lagrange multipliers method, introduced in the work by Liu (1972). It is worth recalling that, consistently with the basic hypothesis of the rate type models examined, for the sake of simplicity we consider only cases in which the entropy production is generated by the diffusion process alone, and we neglect the simultaneous presence of heat and momentum transfer; thus, no use will be made in the following of the momentum and energy balance equations.

We first consider the case of the CMRT model from which CM can be recovered by assuming $\mathfrak{D}_F = 0$.

Within that model, the entropy inequality must hold under the following conditions:

species mass balance $$\frac{\partial \phi}{\partial t}+\underline{\nabla}\cdot\underline{J}=0$$

constitutive equation for $\underline{J}$ $$\tau\left(\frac{\partial \underline{J}}{\partial t}+\mathfrak{D}_F\frac{\partial \underline{g}}{\partial t}\right)+(\underline{J}+\mathfrak{D}_\infty \underline{g})+\tau\frac{d\mathfrak{D}_F}{d\phi}\frac{\partial \phi}{\partial t}\underline{g}=0$$

definition of $\underline{g}$ $$\underline{\nabla}\phi-\underline{g}=0 \tag{15}$$

The independent field variables of the problem are (ϕ, $\underline{J}$, $\underline{g}$), while τ, $\mathfrak{D}_F$, and $\mathfrak{D}_\infty$ are assumed to depend only on the penetrant volume fraction ϕ, according to underlying assumption of linearity with respect to the vector variables.

The second law imposes that the following inequality holds for every time or spatial derivatives of the field variables:

$$\frac{\partial s}{\partial t}+\underline{\nabla}\cdot\underline{\psi}-\xi\left(\frac{\partial \phi}{\partial t}+\underline{\nabla}\cdot\underline{J}\right)-\underline{\lambda}\cdot\left\{\tau\frac{\partial \underline{J}}{\partial t}+\mathfrak{D}_F\tau\frac{\partial \underline{g}}{\partial t}+\underline{J}+\mathfrak{D}_\infty\underline{g}+\tau\frac{d\mathfrak{D}_F}{d\phi}\frac{\partial \phi}{\partial t}\underline{g}\right\}-\underline{\zeta}\cdot(\underline{\nabla}\phi-\underline{g})\geq 0 \tag{16}$$

The quantities ξ, $\underline{\zeta}$, and $\underline{\lambda}$ are the Lagrange multipliers introduced by Liu and are themselves functions of the field variables, just as are the entropy density s and the entropy flux $\underline{\psi}$. By applying the chain rule in the first two terms, the previous inequality Eq. 16 can be rewritten in the form:

$$\left(\frac{\partial s}{\partial \phi}-\xi-\tau\frac{d\mathfrak{D}_F}{d\phi}\underline{\lambda}\cdot\underline{g}\right)\frac{\partial \phi}{\partial t}+\left(\frac{\partial s}{\partial \underline{J}}-\tau\underline{\lambda}\right)\frac{\partial \underline{J}}{\partial t}+\left(\frac{\partial s}{\partial \underline{g}}-\tau\mathfrak{D}_F\underline{\lambda}\right)\frac{\partial \underline{g}}{\partial t}+\left(\frac{\partial \underline{\psi}}{\partial \phi}-\underline{\zeta}\right)\cdot\underline{\nabla}\phi+\left(\frac{\partial \underline{\psi}}{\partial \underline{J}}-\xi\underline{\underline{1}}\right):\underline{\nabla}\,\underline{J}+\frac{\partial \underline{\psi}}{\partial \underline{g}}:\underline{\nabla}\,\underline{g}+\underline{\zeta}\cdot\underline{g}-\underline{\lambda}\cdot(\underline{J}+\mathfrak{D}_\infty\underline{g})\geq 0 \tag{17}$$

This is the basic inequality from which all the restrictions imposed by the second law are derived by demanding that it holds for all arbitrary processes.

By requiring that Eq. 17 holds for all time and spatial dependencies of the field quantities, it is easy to recognize that the following relationships are imposed among the constitutive equations for s and $\underline{\psi}$ and the Lagrange multipliers:

$$\frac{\partial s}{\partial \phi}-\xi-\tau\frac{d\mathfrak{D}_F}{d\phi}\underline{\lambda}\cdot\underline{g}=0;\quad \frac{\partial s}{\partial \underline{J}}-\tau\underline{\lambda}=0;\quad \frac{\partial s}{\partial \underline{g}}-\tau\mathfrak{D}_F\underline{\lambda}=0; \tag{18}$$

$$\frac{\partial \underline{\psi}}{\partial \phi}-\underline{\zeta}=0;\qquad \frac{\partial \underline{\psi}}{\partial \underline{J}}-\xi\underline{\underline{1}}=0;\quad \frac{\partial \underline{\psi}}{\partial \underline{g}}=\underline{\underline{0}} \tag{19}$$

The entropy inequality in Eq. 17 thus reduces to:

$$-\underline{\lambda}\cdot(\underline{J}+\mathfrak{D}_\infty\underline{g})+\underline{\zeta}\cdot\underline{g}\geq 0 \tag{20}$$

The above dissipation inequality will impose further explicit restrictions on the material parameters once the Lagrange multipliers $\underline{\lambda}$ and $\underline{\zeta}$ have been expressed in terms of the independent field variables. By using the representation theorem for the objective vector function $\underline{\psi}=\underline{\psi}(\phi,\ \underline{J},\ \underline{g})$ from Eqs. 19.2 and 19.3, it is easy to recognize that ξ does not depend on both $\underline{J}$ and $\underline{g}$, so we obtain:

$$\xi=\xi(\phi);\quad \underline{\zeta}=\frac{\partial \underline{\psi}}{\partial \phi}=\frac{d\xi}{d\phi}\underline{J}; \tag{21}$$

In view of Eqs. 19.2 and 21.1 the entropy flux constitutive equation thus becomes:

$$\underline{\psi}=\xi(\phi)\underline{J} \tag{22}$$

From Eqs. 18.2 and 18.3, the following relation between entropy derivatives results:

$$\mathfrak{D}_F\frac{\partial s}{\partial \underline{J}}=\frac{\partial s}{\partial \underline{g}} \tag{23}$$

which allows to conclude that the entropy density dependence on the field variables may be rewritten as follows:

$$s=s(\phi,\underline{q});\quad \underline{q}=\underline{J}+\mathfrak{D}_F\underline{g}; \tag{24}$$

and consequently, provided τ is not zero:

$$\underline{\lambda}=\frac{1}{\tau}\frac{\partial s}{\partial \underline{J}}=\underline{\lambda}(\phi,\underline{q}) \tag{25}$$

Then deriving the lefthand side of Eq. 18.1 with respect to $\underline{J}$ and $\underline{g}$ we obtain:

$$\frac{\partial^2 s}{\partial \phi\partial \underline{q}}-\tau\frac{d\mathfrak{D}_F}{d\phi}\frac{\partial \underline{\lambda}}{\partial \underline{q}}\cdot\underline{g}=\underline{0} \tag{26}$$

$$\mathfrak{D}_F\left(\frac{\partial^2 s}{\partial \phi\partial \underline{q}}-\tau\frac{d\mathfrak{D}_F}{d\phi}\frac{\partial \underline{\lambda}}{\partial \underline{q}}\cdot\underline{g}\right)-\tau\frac{d\mathfrak{D}_F}{d\phi}\underline{\lambda}=-\tau\frac{d\mathfrak{D}_F}{d\phi}\underline{\lambda}=\underline{0} \tag{27}$$

We may then conclude that, in view of the thermodynamic consistency of the Eqs. 15, diffusivity $\mathfrak{D}_F$ must be taken as a constant value and Eq. 18.1 simplifies to:

$$\frac{\partial s}{\partial \phi}=\xi(\phi) \tag{28}$$

which allows to rewrite the entropy density function in the form:

$$s=s_o(\phi)+k(\underline{q}) \tag{29}$$

where s_o represents the equilibrium entropy function of the mixture and k is the out of equilibrium entropy function.

Since any equilibrium state, which is characterized by the field variables (ϕ, $\underline{0}$, $\underline{0}$), has to be stable, one concludes that the equilibrium entropy equation $s_o=s_o(\phi)$ is given by a convex function, while the out of equilibrium contribution k, which may be expressed as $k(q^2)$ in view of the objectivity requirement, is endowed with the following properties:

$$k(0)=0; \quad k(q^2)\leq 0 \tag{30}$$

In addition, we introduce for k the otherwise weak hypothesis that its first-order derivative $k'=dk/d(q^2)$ exists and is nonzero for vanishing q^2. From the extremum conditions we obtain:

$$\lim_{q^2\to 0} k' = -\eta < 0 \tag{31}$$

Then, from either Eqs. 18.2 or 18.3 we can write:

$$\underline{\lambda} = \frac{2k'}{\tau}\,(\underline{J}+\mathfrak{D}_F\underline{g}) \tag{32}$$

From Eqs. 21, 18.1 and 25 we have:

$$\underline{\zeta} = \frac{d^2s_o}{d\phi^2}\,\underline{J} \tag{33}$$

Finally, by using Eqs. 31 and 33 the residual inequality in Eq. 20 becomes:

$$\frac{-2k'}{\tau}J^2 + \left[\frac{d^2s_o}{d\phi^2} - \frac{2k'}{\tau}(\mathfrak{D}_F+\mathfrak{D}_\infty)\right]\underline{J}\cdot\underline{g} - \frac{2k'}{\tau}\mathfrak{D}_F\mathfrak{D}_\infty g^2 \geq 0 \tag{34}$$

The inequality in Eq. 34 must hold for every arbitrary process, and in particular also for the case in which, for any arbitrarily fixed vectors $\underline{a}$ and $\underline{b}$, and for any scalar ϵ we have:

$$\underline{J}=\epsilon\underline{a}; \quad \underline{g}=\epsilon\underline{b} \tag{35}$$

Recalling that based on Eq. 31

$$k' = k'(0) + \mathcal{O}(\epsilon^2) = -\eta + \mathcal{O}(\epsilon^2) \tag{36}$$

where $\mathcal{O}(\epsilon^2)$ indicates terms which are infinitesimal of order ϵ^2 at least, substitution of Eqs. 35 into the inequality in Eq. 34 gives:

$$\epsilon^2\left\{\frac{2\eta}{\tau}a^2 + \left[\frac{d^2s_o}{d\phi^2} + \frac{2\eta}{\tau}(\mathfrak{D}_F+\mathfrak{D}_\infty)\right]\underline{a}\cdot\underline{b} + \frac{2\eta}{\tau}\mathfrak{D}_F\mathfrak{D}_\infty b^2\right\} \geq 0 + \mathcal{O}(\epsilon^4) \tag{37}$$

Based on the arbitrariness of ϵ and of the vectors $\underline{a}$ and $\underline{b}$, the inequality in Eq. 35 implies that the coefficient of ϵ^2 in the inequality in Eq. 37 be a quadratic form positive semidefinite; since η is positive we thus have:

$$\tau > 0 \tag{38}$$

$$4\mathfrak{D}_F\mathfrak{D}_\infty \geq \left\{\frac{\tau}{2\eta}\frac{d^2s_o}{d\phi^2} + (\mathfrak{D}_F+\mathfrak{D}_\infty)\right\}^2 \tag{39}$$

Besides, the latter inequality may be also rewritten in the form:

$$-\frac{\tau}{\eta}\frac{d^2s_o}{d\phi^2}(\mathfrak{D}_F+\mathfrak{D}_\infty) \geq \left(\frac{\tau}{2\eta}\frac{d^2s_o}{d\phi^2}\right)^2 + (\mathfrak{D}_F-\mathfrak{D}_\infty)^2 \tag{40}$$

Remembering that $d^2s_o/d\phi^2$ is always negative, we easily recognize that in view of Eqs. 39 and 40 both the diffusivities $\mathfrak{D}_F$ and $\mathfrak{D}_\infty$ must have nonnegative value.

The inequality in Eq. 39 represents a condition restricting the concentration dependence of τ and $\mathfrak{D}_\infty$, whose specific form depends on the equilibrium entropy function of the mixture $s_o=s_o(\phi)$. An interesting conclusion may, however, be drawn in general for the limiting case of very dilute solutions; we recall, indeed, that the following limiting values for the entropy second derivative hold for any binary mixture:

$$\lim_{\phi\to 0}\frac{d^2s_o}{d\phi^2} = \lim_{\phi\to 1}\frac{d^2s_o}{d\phi^2} = -\infty \tag{41}$$

and considering that all terms in the inequality in Eq. 39 are finite, we may conclude that:

$$\lim_{\phi\to 0}\tau = \lim_{\phi\to 1}\tau = 0 \tag{42}$$

It is worth pointing out in passing that the relationships in Eqs. 38 and 39 above have been obtained under rather general conditions and are not limited to a linear dependence of k on q^2 as was done in an early presentation of the results within an otherwise more restricted framework (Camera-Roda et al., 1991).

Equation 42 represents a simple and remarkable result insofar as, for the relaxation time τ, it rules out the acceptability not only of constant values, but also of monotonous concentration functions in order to satisfy the inequality in Eq. 39. Recalling the constitutive equation, Eq. 8, in addition, Eq. 42 immediately allows one to recover Fickian behaviors in either upper and lower concentration limits.

The relaxation time entering the above diffusion model is obviously different from the relaxation time used in mechanical viscoelasticity, since no stress analysis was incorporated in the models here considered; it is worth pointing out additionally that the two quantities show a rather different concentration dependence since the mechanical relaxation time is monotonously decreasing as ϕ increases.

Turning now to the CM model, the conditions imposed by the second law of thermodynamics may be obtained by setting $\mathfrak{D}_F=0$ in the previous results. The following relationships are then obtained:

$$s = s_o(\phi) + k(J^2); \tag{43}$$

with

$$k(J^2)\leq 0; \quad k(0)=0; \quad k'(0) = -\eta < 0 \tag{44}$$

while the entropy flux is:

$$\underline{\psi} = \xi(\phi)\underline{J} = \frac{ds_o}{d\phi}\underline{J} \tag{45}$$

The transport properties are bound to be:

$$\tau > 0; \quad \mathfrak{D} > 0 \tag{46}$$

$$\tau = -2\eta \mathfrak{D}(\phi)\left(\frac{d^2 s_o}{d\phi^2}\right)^{-1} \tag{47}$$

The latter equation provides for an expression for the relaxation time function once the diffusion coefficient and the equilibrium entropy of mixing are known; that is actually the only expression for the relaxation time which allows the mathematical model to be thermodynamically consistent. We also remark here that in the present CM case, τ, of course, obeys the limits of Eq. 42, which demand a vanishing relaxation time when the mixture approaches either the pure polymer or the pure penetrant phases; in both limits, the Fickian behavior is now recovered also for the CM model, contrary to what occurred in its previous formulation, and observations analogous to those illustrated in the previous CMRT case hold true.

Moving finally to the KOAM model, several different conclusions may be drawn by applying the same thermodynamic analysis illustrated above. In view of some appreciable differences associated with the introduction of the internal state variable H, we need to briefly follow the derivation procedure. We simply anticipate now that while some results are rather similar to those derived for the previous cases, there will also be some other different intriguing conclusions, which seriously question the physical validity of the model structure.

In this case, we must require that for every process the entropy inequality in Eq. 14 holds under the following conditions:

species mass balance $\quad \dfrac{\partial(pH)}{\partial t} + \underline{\nabla} \cdot \underline{J} = 0$

internal state variable kinetics $\quad \dfrac{\partial H}{\partial t} - F = 0$

constitutive equation for $\underline{J}$ $\quad \tau \dfrac{\partial \underline{J}}{\partial t} + \underline{J} + L\underline{\nabla} p = 0 \quad (48)$

The entropy density s and entropy flux $\underline{\psi}$ are considered functions of the independent field variables $(p, H, \underline{J})$, while τ, L and F are considered functions of p and H only, in view of the requirement of linearity with respect to the vector variables.

Introducing the Lagrange multipliers ξ, β, $\underline{\lambda}$, the problem can be reformulated by asking that the following inequality holds for any value of the time or spatial derivatives of the field:

$$\frac{\partial s}{\partial t} + \underline{\nabla} \cdot \underline{\psi} - \xi\left(\frac{\partial(pH)}{\partial t} + \underline{\nabla} \cdot \underline{J}\right) - \beta\left(\frac{\partial H}{\partial t} - F\right) - \underline{\lambda} \cdot \left(\tau \frac{\partial \underline{J}}{\partial t} + \underline{J} + L\underline{\nabla} p\right) \geq 0 \tag{49}$$

Following the same procedure used for the case of the CMRT model, the following conditions for the entropy density and the entropy flux functions are derived:

$$\frac{\partial s}{\partial p} - \xi H = 0; \quad \frac{\partial s}{\partial H} - \beta - \xi p = 0; \quad \frac{\partial s}{\partial \underline{J}} - \tau \underline{\lambda} = 0; \tag{50}$$

$$\frac{\partial \underline{\psi}}{\partial p} - L\underline{\lambda} = \underline{0}; \quad \frac{\partial \underline{\psi}}{\partial H} = \underline{0}; \quad \frac{\partial \underline{\psi}}{\partial \underline{J}} - \xi \underline{\underline{1}} = \underline{\underline{0}} \tag{51}$$

Based on the representation theorem for the objective vector functions $\underline{\psi}$ and $\underline{\lambda}$, use of Eqs. 51 leads to the following results:

$$\xi = \xi(p) \tag{52}$$

$$\underline{\psi} = \xi(p)\underline{J} \tag{53}$$

$$\underline{\lambda} = \frac{\xi'(p)}{L(p,H)}\underline{J}; \quad \xi' \equiv \frac{d\xi}{dp} \tag{54}$$

In view of Eq. 50, the entropy density function becomes:

$$s = \Xi(p)H + Y(H, \underline{J}); \quad \text{with} \quad \frac{d\Xi}{dp} = \xi \tag{55}$$

The equilibrium is achieved for $\underline{J} = 0$ and $H = H^*$ where $H^*(p)$ is defined from the implicit equation:

$$F(H^*, p) = 0 \tag{56}$$

We can thus split the entropy function into an equilibrium contribution $s_o(p)$ and an out of equilibrium term k (p, H, J^2):

$$s = s_o(p) + k(p, H, J^2) \tag{57}$$

where s_o is defined as:

$$s_o = s(p, H^*, 0) = s_o(p) \tag{58}$$

The out of equilibrium term k is endowed with the following properties:

$$k(p, H^*, 0) = 0; \quad k(p, H, J^2) \leq 0 \tag{59}$$

the latter condition being demanded by the stability requirement of an equilibrium state.

In view of Eq. 55 the out of equilibrium entropy density function may be alternatively rewritten as:

$$k = \Xi(p)H + Y(H, J^2) - s_o(p) \tag{60}$$

The Lagrange multipliers β and $\underline{\lambda}$ can now be obtained from Eqs. 50.2 and 50.3 by taking advantage either of Eq. 55 or 57; if τ is nonzero we have:

$$\beta = -p\xi(p) + \frac{\partial k}{\partial H} = -p\xi(p) + \Xi(p) + \frac{\partial Y}{\partial H} \tag{61}$$

$$\underline{\lambda} = \frac{2}{\tau}\frac{\partial k}{\partial(J^2)}\underline{J} = \frac{2}{\tau}\frac{\partial Y}{\partial(J^2)}\underline{J} \tag{62}$$

The comparison between Eqs. 54 and 62 allows to obtain the following result:

$$\frac{\partial Y}{\partial (J^2)}=\frac{\xi'(p)\tau(p,H)}{L(p,H)} \tag{63}$$

Since Eq. 63 must hold for all field variables and its lefthand side does not depend on $\underline{J}$ one concludes that:

$$\frac{\partial Y}{\partial (J^2)}\equiv N(H) \tag{64}$$

and

$$\tau=\frac{2L(p,H)N(H)}{\xi'(p)} \tag{65}$$

Equation 64 says that the entropy density function is linearly dependent on J^2 so that we can then specify the expression of function $Y(H, J^2)$ in the form:

$$Y=M(H)+N(H)J^2 \tag{66}$$

Equation 65 imposes a precise dependence on the state variables p and H for the relaxation time τ in the case under consideration, just as it was also derived for the other two rate type CM and CMRT models examined in the previous sections; in particular, the strict similarity of Eq. 65 with Eq. 47 is self-evident.

In close analogy with the previous CMRT case, we here suppose that the derivative $\partial k/\partial (J^2)$ exists and is always nonzero, particularly also when J^2 becomes vanishingly small.

By using Eqs. 50, 51, 61 and 62, the dissipation inequality in Eq. 49 finally reduces to the following:

$$\frac{2}{\tau}\frac{\partial k}{\partial (J^2)}J^2+\left(\frac{\partial k}{\partial H}-p\xi\right)F\geq 0 \tag{67}$$

which, after Eqs. 60 and 66, may be rewritten as:

$$\frac{2N}{\tau}J^2+\left(\Xi(p)+\frac{dM}{dH}+\frac{dN}{dH}J^2-p\xi\right)F$$
$$=\left(F\frac{dN}{dH}-\frac{2N}{\tau}\right)J^2+\left(\Xi(p)-p\xi+\frac{dM}{dH}\right)F\geq 0 \tag{68}$$

In view of the linearity in J^2 of the l.h.s. of Eq. 68, the following conclusions are imposed:

$$F(p,H)\left(\Xi(p)-p\xi+\frac{dM}{dH}\right)\geq 0 \tag{69}$$

$$\tau\geq\frac{2N}{F\,dN/dH} \tag{70}$$

Thus far, we have obtained the restrictions imposed by the second law on the constitutive equations entering the KOAM model in close analogy with what has been obtained for the other rate type models; in particular, the conclusion is drawn that the relaxation time cannot be a simple constant value since Eq. 65 must be obeyed.

The thermodynamic analysis of the model must be completed by deriving further conditions imposed by the dissipation inequality on the constitutive equations for the out of equilibrium entropy. Even if the latter equation does not enter the set (Eq. 48) which represents the model formulation, the thermodynamic analysis must be concluded, not only for the sake of formal completeness, but rather to find out further conditions for the material properties of the model.

Let us consider a state of stable equilibrium characterized by $(p, H^*, 0)$ spatially uniform over the material element. In view of the stability requirement, F is negative for $H>H^*$ and positive for $H<H^*$; as a consequence of Eq. 69, the quantity $\Xi-p\xi+dM/dH$ is nonpositive for $H>H^*$ and nonnegative for $H<H^*$. Thus, if the material properties are represented by continuous functions we have:

$$\Xi-p\xi+\frac{dM}{dH}=0 \quad \text{for} \quad H=H^* \tag{71}$$

On the other hand, in a stable spatially uniform equilibrium state at the fixed value p, the entropy function reaches its maximum value consistent with the fugacity p so that

$$s(p,H^*,0)\geq s(p,H,J^2) \tag{72}$$

In view of Eqs. 55 and 66 that implies:

$$0=\left.\frac{\partial s}{\partial H}\right|_{\substack{H=H^*\\ \underline{J}=\underline{0}}}=\Xi(p)+\left.\frac{dM}{dH}\right|_{H=H^*} \tag{73}$$

$$0\geq\left.\frac{\partial s}{\partial (J^2)}\right|_{\substack{H=H^*\\ \underline{J}=\underline{0}}}=N(H^*) \tag{74}$$

By comparing Eqs. 71 and 73 we have:

$$\xi(p)=0 \tag{75}$$

Although Eq. 75 refers to a quantity which does not appear in the model formulation, undoubtedly it throws a rather negative shadow on its admissibility since the model presents some serious inconsistencies which are not simply solved by the introduction of suitable concentration dependent coefficients.

Indeed, in view of Eqs. 50.1 and 53, Eq. 75 implies:

$$\frac{\partial s}{\partial p}=0;\quad \underline{\psi}=\underline{0} \tag{76}$$

From Eqs. 54 and 50.3, we also have

$$\underline{\lambda}=\underline{0} \tag{77}$$

$$\frac{\partial s}{\partial \underline{J}}=\underline{0} \tag{78}$$

$$s=s(H) \tag{79}$$

Equations 75-79 can hardly be accepted on a physical basis since entropy is usually a function of concentration or of fugacity, and the entropy flux is always nonzero during the diffusion processes. To our surprise, we are then led to the conclusion that when the model is made consistent with the second law, the requirement of the stable equilibrium state with spatially uniform variables gives rise to physically unacceptable results. Indeed, the above features could be avoided by introducing some modifications in the mathematical structure of the model, either in Eq. 48.2 or in Eq. 48.3; this analysis, however, goes well beyond the aim of the present work and will not be discussed any further here.

Use of Thermodynamically Consistent Material Properties

In order to support the conclusion that the physically unrealistic predictions mentioned in the previous sections are not associated to some intrinsic properties of the rate type model but rather to inadmissible choices for the expressions of the relaxation time and diffusivity, we now consider again the case of desorption from a polymeric film using the CM model as a constitutive equation for the diffusive mass flux, with parameter values which satisfy the constraints dictated by the second law.

Equations and boundary conditions are the same used before (see Table 1 and conditions in Eq. 13) and an exponential dependence of diffusivity on concentration was assumed again. However, now the relaxation time was computed according to Eq. 47. As the simplest possible expression for the entropy of mixing the Flory-Huggins equation, (Flory, 1953) was assumed to hold true:

$$\Delta S_{\text{mix}} = -R\{n_s \ln \phi + n_p \ln(1-\phi)\} \tag{80}$$

where n_s is the number of solute molecules in the mixture and n_p is that of the polymer. Based on the usual assumption of volume additivity, it is possible to show that:

$$\frac{d^2 s_0}{d\phi^2} = -\frac{\rho_s}{M_s}\frac{1}{\phi} - \frac{\rho_P}{M_p}\frac{1}{1-\phi} \tag{81}$$

ρ_i being the pure component density of the *i*th species and M_i the corresponding molecular weight. The relaxation time, as calculated by Eq. 47, is given by the following expression:

$$\tau = \tau_0 \frac{\exp(k_D\phi)}{\dfrac{1}{\phi} + \dfrac{\rho_P}{\rho_s}\dfrac{M_s}{M_p}\dfrac{1}{1-\phi}} \tag{82}$$

which can be numerically simplified when, as usual, M_p is much larger than M_s and the solute volume fraction is not close to unity:

$$\tau = \tau_0 \phi \exp(k_D \phi) \tag{83}$$

One may argue that, when considered valid in the entire concentration range, Eq. 80, together with the hypothesis of vanishing mixing enthalpy which was made in our thermodynamic analysis, is not consistent with the solubility gap for the solute-polymer mixture which is on the other hand considered when use is made of ϕ_{fin} in the boundary condition, Eq. 2.1. However, the use of a more accurate, as well as complicated, expression of ΔS_{mix}, which could account for a more appropriate behavior, would affect the expression of the relaxation time function, in a qualitative sense, possibly only in the concentration range close to the spinodal composition. On the other hand, we are interested here in inspecting the behavior in the concentration range $0 \le \phi \le \phi_{\text{fin}}$ in which the main features of the out of equilibrium entropy function which are relevant to our purposes are represented by:

$$\frac{d^2 s}{d\phi^2} < 0 \quad \text{and} \quad \lim_{\phi \to 0} \frac{d^2 s}{d\phi^2} = -\infty \tag{84}$$

In this respect use of Eq. 80 is fully justified.

Indeed, due to the decreasing of the relaxation time as the concentration decreases down to $\tau = 0$ for zero concentration, we expect that the polymer memory for the diffusive flux vanishes in the limit of dry solid, avoiding the possibility of predicting a finite outer flux when the solvent concentration has become vanishingly small.

That is exactly what we also obtained from the numerical solution of the corresponding set of equations; data for the desorption kinetics are reported in Figure 5 for $k_D = 10$ and $De = 1$. Concentration profiles, which are shown in Figure 6 for the same case, bring to evidence that the predicted volume fraction for the solute species is nonnegative over all the entire sample at any time.

Thus, were it necessary, we found that taking into account the thermodynamic constraints imposed by the second law, as given by Eq. 47, rules out the physically absurd behavior which was otherwise calculated.

Conclusions

Some of the viscoelastic models used to describe non-Fickian features observed in the diffusion through solid polymers have

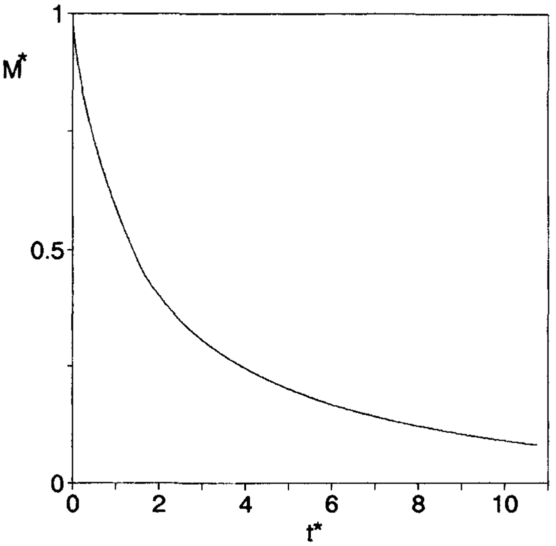

Figure 5. Desorption kinetics from a thin polymer film.

Data computed for the CM model with thermodynamically consistent material properties: $k_D = 10$; $\phi_{\text{fin}} = 0$; $\phi_{\text{in}} = 0.3$; $\phi_w = 0$; $De = 1$.

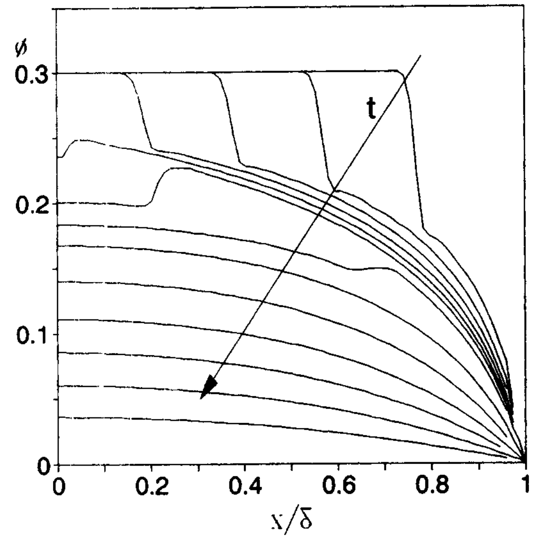

Figure 6. Concentration profiles during desorption from a thin polymer film.

Data computed for the CM model with thermodynamically consistent material properties: $k_D=10$; $\phi_{\text{fin}}=0$; $\phi_{\text{in}}=0.3$; $\phi_w=0$; $De=1$.

been considered which are based either on a Cattaneo-Maxwell constitutive equation or on an equation of Jeffrey's type, possibly completed with additional equations accounting for the time rate of change of the material structure. In the existing formulations, the relevant material properties, for example, the steady-state diffusivity, the relaxation time and the retardation time were all chosen as independent quantities both when they are considered as constants, as well as when they are allowed to change with the composition. As a consequence, some unexpected and definitely unrealistic behaviors have been obtained from the models such as desorption fluxes out of an already dried polymer matrix.

We analyzed the thermodynamic constraints imposed by the second law of thermodynamics on the above mentioned rate type constitutive equations. As a result, it is concluded in particular that steady-state diffusivity and relaxation time cannot be chosen independently of one another, but there are precise relationships among them and the equilibrium entropy or Gibbs free energy of the mixture.

When this requirement is taken into account, the relaxation time results to be zero for vanishing solute content. Fickian behavior is then spontaneously recovered in very low concentration limit and the physically unrealistic behaviors mentioned above are no longer present.

Those features are shown in detail for the case of the Cattaneo-Maxwell model when the Flory-Huggins expression for the free energy of mixing is used.

It is important to complete the thermodynamic analysis by deriving the conditions imposed by the residual inequality and by the stability requirement for equilibrium states, even if they are mainly focused on material properties, which do not appear explicitly in the kinetic models. In some cases, like CM and CMRT, simple and otherwise obvious conclusions are drawn (that is, relaxation times and diffusion coefficients are positive quantities); in the KOAM case, however, rather drastic conditions are imposed which seriously question the physical admissibility of the model structure.

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Notation

De = Deborah number
$\mathfrak{D}$ = diffusion coefficient
$\underline{J}$ = diffusive volume flux density for the solute species
$\underline{L}$ = diffusion coefficient
m = penetrant mass into the polymer film
M_i = molecular weight of the ith species
n = number of molecules
p = solute fugacity
R = gas constant
s = entropy density
s_o = equilibrium entropy density

Greek letters

δ = film semithickness
ρ_i = density of the pure component i
τ = relaxation time
ϕ = volume fraction of the solute species
$\underline{\psi}$ = entropy flux density

Subscripts

eq = refers to the equilibrium condition with external penetrant activity
p = refers to the polymer species
s = refers to the solute species

Dimensionless quantities

t^* = $t/\delta^2\mathfrak{D}(\phi_{\text{eq}})$
M^* = m/m_{eq}

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