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Dynamics of complex interfaces. II. Diffusion and morphology

A. El Afif[a)]
Mathematics Department, Center for Computational Science, Tulane University, New Orleans, Louisiana 70118

D. De Kee
Chemical Engineering Department, Center for Computational Science, Tulane University, New Orleans, Louisiana 70118

R. Cortez
Mathematics Department, Center for Computational Science, Tulane University, New Orleans, Louisiana 70118

D. P. Gaver III
Biomedical Engineering Department, Center for Computational Science, Tulane University, New Orleans, Louisiana 70118

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In this contribution, we theoretically investigate the isothermal mass transport of a simple fluid into a blend of two immiscible Newtonian polymers. Using internal state variables, we derive a nonlinear formulation that addresses the effects of the diffusion/interface coupling on both the mass transport as well as on the morphology of the interface. The approach uses a scalar and a second-order tensor to directly track the dynamic changes of the size and shape of the interface. The mass flux governing equation includes new terms that lead to non-Fickian behavior attributed to the viscoelatic contribution of the interface. In turn, the size and shape of the interface are modified by diffusion. In one-dimensional analysis, we examine the nature of propagation of both nonlinear hyperbolic and linear dispersive waves. Explicit formulas for the characteristic speed, phase velocity, and attenuation are provided. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1571053]

I. INTRODUCTION

Mass transport of small molecules into structured media does not generally obey Fick's laws.[1] The deformation of the internal structure couples to diffusion and brings about inertia and viscoelasticity into the molecular process. In this paper, we investigate, in the absence of an applied flow and external forces, the behavior of mass transport of small molecules into blends of immiscible Newtonian polymers. Since the polymers are Newtonian and do not interpenetrate, the internal structure of the mixture stems exclusively from the presence of the interface separating the different immiscible components and not from their conformation. The interface may be deformed and distorted by internal diffusion fluxes, and as such, interesting and unexpected non-Fickian behavior may be observed. As the conformational changes of the polymers do not play a significant role in the process of mass transport, the non-Fickian character arises mainly from the coupling between diffusion and interfacial changes. Our aim here is to study the effects of the diffusion-interface coupling on the behavior of both the mass transfer as well as on the interfacial morphology changes. Examples where results of this study are applicable involve immiscible polymeric blends with tailor made morphology.

Before studying the diffusion/interface coupling occurring in blends of immiscible polymers embedding an interface, we first provide an outline of previous investigations[2–30] devoted to the effects of the diffusion/conformation coupling carried out for polymeric media that do not involve an interface. Even though the blend consists of Newtonian components, it may behave as a viscoelastic medium due to the presence of the interface and its deformation. Therefore, in both couplings, the internal structure (i.e., the interface in the former and the conformation in the latter) exhibits viscoelasticity. Due to the large number of both experimental and theoretical investigations devoted to the diffusion-conformation/stress coupling,[2–30] a good understanding of the collected data has been reached. For these complex media, Fick's laws and their modified forms[10] fail to provide a reasonable explanation for the experimental observations. Indeed, these laws do not take into account the contribution of the internal structure; a property that is inherent to complex fluids. In these structured fluids, the microstructure may strongly interact with the diffusion process to cause inertial and viscoelastic effects. From a qualitative point of view, when the relaxation characteristic time scale is larger than or comparable to the diffusion characteristic time scale, deviations from Fickian diffusion are expected.[21–24] Thereby, the internal structure changes have to be associated with the mathematical formulation of diffusion. This has been achieved by requiring the compatibility of diffusion with thermodynamics. The driving force for diffusion is no longer the gradient of the concentration as stipulated by Fick's law but rather the gradient of the chemical potential. As a result, the expression for the mass flux contains addi-

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[a)] Author to whom correspondence should be addressed. Electronic mail: aelafif@tulane.edu and alielafif@hotmail.com

tional terms accounting for the viscoelastic contribution. Due to the anisotropy brought about by the internal structure, its state variable is generally chosen to be a second order tensor. Two choices can be adopted: an indirect macroscopic description embodied by the stress tensor, $\boldsymbol{\sigma}$, and a direct and more microscopic description given by the conformation tensor of the polymeric chains. The latter state variable is generally recommended. To close the set of the governing equations, the non-Fickian formulation necessitates a time evolution equation accounting for the deformation of the internal structure. Based on the experience collected in the field of rheology,[27,31] several viscoelastic models, if appropriately adapted to diffusion, can be used. In previous macroscopic descriptions, the Maxwell,[12] the Kelvin–Voig,[28] and the Jeffrey-type[29] models have been adopted where the stress tensor, $\boldsymbol{\sigma}$, was chosen as the state variable. In more microscopic descriptions, where the conformation tensor has been selected as a state variable, the polymeric chains have been described as Hookean or more generally as finitely extensible non linear elastic dumbbells (FENE-P).[20] In this case, the models were appropriately modified to take into account the volume changes of the polymeric fluid (swelling) attributed to diffusion.

Here, our objective is to propose a new approach suitable for discussing non-Fickian behavior that is caused by the interface/diffusion coupling occurring in immiscible (Newtonian) polymeric systems embedding an interface. We aim at deriving a comprehensive model that includes both the effects of inertia in the diffusion mass flux and of the viscoelasticity resulting from the presence of the interface. Reductions to special cases, such as inertia-free models, will be discussed based on the nature and the physical properties of the penetrant/blend overall mixture under investigation. In this part, we investigate predictions implied by the family of models introduced in Paper I. We restrict our investigation to diffusion (soaking, sorption, desorption, permeation, etc.) under mechanical equilibrium and in the absence of both overall flow and external forces. The model involves in addition to the mass fraction, the mass flux density $\mathbf{J}$ as an independent state variable to conform to the irreversible thermodynamics approaches.[35,36] Furthermore, the interface contribution must be included into the formulation. As discussed in Paper I, we characterize the interface by two state variables, a scalar Q and a second-order tensor $\mathbf{q}$, denoting, respectively, its size and shape.[32] Therefore, the set of the independent state variables used in this theoretical formulation for describing the evolution of such mixtures is $(c,\mathbf{J},Q,\mathbf{q})$. The corresponding governing equations appear in Sec. II. For the qualitative analysis of solutions of the governing equations, we use the method of characteristics for discussing the formation and propagation of discontinuities (hyperbolic) and linear (dispersive) waves in a one-dimensional setting (Sec. III). In the last section, we discuss some limiting cases of the model and provide new reduced theoretical descriptions, in which some of the state variables become dependent. This analysis leads to models describing diffusion into blends in which (i) the behavior is dominantly Fickian; (ii) the interface evolves isotropically; (iii) the size is conserved, but not the shape; and (iv) both the size and shape of the interface undergo significant changes to influence mass transport. In these four special cases, the inertia in the mass flux can be neglected when considering mass transport.

II. MODEL DERIVATION

We investigate the mass transport of a simple fluid, s such as a solvent into a blend of two immiscible Newtonian polymers, $b\equiv \mathrm{A/B}$. In our model, we regard the immiscible blend b as a pseudo-one-component fluid in which an interface is embedded (see Paper I). In the absence of interpenetration between the immiscible fluids A and B, the whole mixture, can be regarded as consisting of two fluids,[33] $\{b+s\}$: one is the pseudo-one-component immiscible blend b with an apparent mass density ρ_b and an apparent momentum density $\mathbf{u}_b=\rho_b\mathbf{v}_b$ (b refers to blend) and the other is the simple fluid, s with an apparent mass density ρ_s and an apparent momentum density $\mathbf{u}_s=\rho_s\mathbf{v}_s$. Since, the solvent, s and the blend, b are miscible they can be regarded as two interpenetrating media. As discussed earlier (Paper I, and references therein), we choose to describe the interface by its area density distribution function $f(\mathbf{r},\mathbf{n},t)$ or by its moments: the scalar $Q(\mathbf{r},t)$,

$$Q=\int d^2n f(\mathbf{r},\mathbf{n},t), \tag{1}$$

and the traceless second order tensor

$$\mathbf{q}=\int d^2n(\mathbf{nn}-\tfrac{1}{3}\mathbf{I})f(\mathbf{r},\mathbf{n},t), \tag{2}$$

denoting, respectively, the interfacial area and the anisotropic orientation tensor densities. $\mathbf{I}$ is the unit second order tensor, $\mathbf{nn}$ is a dyadic tensor, and d^2n is the differential solid angle. These two quantities are defined as moments of the distribution function f representing the area density of the interface. Therefore the state variables of the whole mixture become $(\rho_s,\rho_b,\mathbf{u}_s,\mathbf{u}_b,Q,\mathbf{q})$.

Using the one-to-one transformation (56) given in Paper I, the whole mixture is described by the global mass density, $\rho=\rho_s+\rho_b$, the overall momentum density $\mathbf{u}(\mathbf{r})=\mathbf{u}_s(\mathbf{r})+\mathbf{u}_b(\mathbf{r})$, the mass fraction $c(\mathbf{r})=\rho_s/(\rho_s+\rho_b)$ and the mass flux density $\mathbf{J}(\mathbf{r})=(\rho_b/(\rho_s+\rho_b))\mathbf{u}_s(\mathbf{r})-(\rho_s/(\rho_s+\rho_b))\mathbf{u}_b(\mathbf{r})$ of the simple fluid and the two interfacial variables defined above. We have derived in Paper I equations governing the time evolution of the state variables $(\rho,\mathbf{u},c,\mathbf{J},Q,\mathbf{q})$. In this paper, we limit our study to the following special situation; we consider the mixture, in the absence of an applied overall flow,

$$\mathbf{u}=\mathbf{0}, \tag{3}$$

and under mechanical equilibrium

$$\partial_\alpha p+\partial_\beta\sigma_{\beta\alpha}=0, \tag{4}$$

where p is the hydrodynamic pressure given by Eq. (43) and $\boldsymbol{\sigma}$ is the extra stress tensor whose expression is $\boldsymbol{\sigma}=\mathbf{JJ}/\rho c(1-c)+\boldsymbol{\sigma}^{(\mathrm{Interface})}$. The quantity, $\boldsymbol{\sigma}^{(\mathrm{Interface})}$ is provided by Eq. (44) (see Paper I) and denotes the contribution of the interface. The notation, $\partial_\alpha\equiv\partial/\partial r_\alpha$ $\alpha\in\{1,2,3\}$, is used throughout this paper, where $\mathbf{r}$ is the position vector. Under the constraints (3–4) and the overall incompressibility requirement ($\rho=\text{const}$), the model derived in Paper I [Eqs. (78)–(84)] leads to

$$\rho\frac{\partial c}{\partial t}=-\partial_\alpha J_\alpha, \tag{5}$$

$$\frac{\partial J_\alpha}{\partial t}=-\partial_\gamma\left(\frac{J_\alpha J_\gamma}{\rho c}\right)-c\,\partial_\alpha\varphi_c-\Lambda_J J_\alpha, \tag{6}$$

$$\begin{aligned}\frac{\partial Q}{\partial t}={}&\left(\frac{J_\alpha}{\rho(1-c)}\right)\partial_\alpha Q+q_{\alpha\gamma}\partial_\alpha\left(\frac{J_\gamma}{\rho(1-c)}\right)\\&+\frac{Q}{3}\partial_\alpha\left(\frac{J_\alpha}{\rho(1-c)}\right)-\Lambda^Q\varphi_Q-\Lambda^{qQ}_{\alpha\beta}\varphi_{q_{\alpha\beta}},\end{aligned} \tag{7}$$

$$\begin{aligned}\frac{\partial q_{\alpha\beta}}{\partial t}={}&\left(\frac{J_\gamma}{\rho(1-c)}\right)\partial_\gamma q_{\alpha\beta}+q_{\alpha\gamma}\partial_\beta\left(\frac{J_\gamma}{\rho(1-c)}\right)\\&+q_{\beta\gamma}\partial_\alpha\left(\frac{J_\gamma}{\rho(1-c)}\right)-\frac{q_{\alpha\beta}q_{\theta\gamma}}{Q}\partial_\gamma\left(\frac{J_\theta}{\rho(1-c)}\right)\\&+\frac{Q}{3}\left(\partial_\beta\left(\frac{J_\alpha}{\rho(1-c)}\right)+\partial_\alpha\left(\frac{J_\beta}{\rho(1-c)}\right)\right)\\&-\frac{1}{3}\left(q_{\alpha\beta}+\frac{2Q}{3}\delta_{\alpha\beta}\right)\partial_\gamma\left(\frac{J_\gamma}{\rho(1-c)}\right)\\&-\frac{2}{3}\delta_{\alpha\beta}q_{\theta\gamma}\partial_\gamma\left(\frac{J_\theta}{\rho(1-c)}\right)-\Lambda^{qQ}_{\alpha\beta}\varphi_Q-\Lambda^{q}_{\alpha\beta ij}\varphi_{q_{ij}}.\end{aligned} \tag{8}$$

These equations are supplemented by the expression,

$$\begin{aligned}\alpha^{(\text{Interface})}_{\alpha\beta}={}&2q_{\alpha\gamma}\varphi_{q_{\gamma\beta}}+q_{\alpha\beta}\varphi_Q+\frac{2Q}{3}\varphi_{q_{\alpha\beta}}\\&-\frac{q_{\alpha\beta}q_{\gamma\nu}}{Q}\varphi_{q_{\gamma\nu}}-\frac{2}{3}\delta_{\alpha\beta}(Q\varphi_Q+2q_{\nu\theta}\varphi_{q_{\nu0}})\\&-\frac{2}{3}\delta_{ij}\left(q_{\alpha\beta}+\frac{1}{3}Q\delta_{\alpha\beta}\right)\varphi_{q_{ij}}\end{aligned} \tag{9}$$

representing the internal stresses created by diffusion within the immiscible fluid. By solving the governing Eqs. (5)–(8) we arrive at an explicit expression for the distribution of the interfacial stresses in terms of the state variables *c*, *Q*, and **q**. In Eqs. (5)–(9), we have used, the following notation: $\varphi_c=\partial\varphi/\partial c$, $\varphi_Q=\partial\varphi/\partial Q$, $\varphi_{q_{\alpha\beta}}=\partial\varphi/\partial q_{\alpha\beta}$ to denote the partial derivative of φ with respect to *c*, *Q*, and **q**, respectively. We recall that the governing equations are parameterized by the free energy φ and by the kinetic coefficients Λ_J, Λ^Q, $\mathbf{\Lambda}^{Qq}$, and $\mathbf{\Lambda}^q$ entering the dissipation potential, Ψ. These kinetic parameters, which satisfy the positive and semidefinite requirements implied by the GENERIC formalism are written as (see Paper I)

$$\begin{aligned}\Lambda^{\mathbf{q}}_{\alpha\beta ij}={}&\int d^2n(f(\mathbf{n},\mathbf{r},t)-f^*)\Lambda_f[n_in_jn_\alpha n_\beta-\tfrac{1}{3}\delta_{\alpha\beta}n_in_j\\&-\tfrac{1}{3}\delta_{ij}n_\alpha n_\beta+\tfrac{1}{9}\delta_{ij}\delta_{\alpha\beta}],\end{aligned} \tag{10}$$

$$\Lambda^Q=\int d^2n(f(\mathbf{n},\mathbf{r},t)-f^*)\Lambda_f, \tag{11}$$

$$\Lambda^{qQ}_{ij}=\int d^2n(f(\mathbf{n},\mathbf{r},t)-f^*)\Lambda_f[n_in_j-\tfrac{1}{3}\delta_{ij}], \tag{12}$$

where Λ_f stands for the rate of relaxation of the distribution function *f*. f^* is a certain local equilibrium distribution function for the deformed interfacial area density. The internal free energy density, $\varphi=\varphi(c,Q,\mathbf{q})$, which still remains unspecified at this point, is an independent function of the mass flux density **J**. Its expression can approximately be written as a sum of two contributions: a Flory–Huggins[34] term for mixing and an additional term describing the interface contribution,

$$\varphi(c,Q,\mathbf{q})=\varphi^{\text{mixing}}(c)+\varphi^{\text{Interface}}(c,Q,\mathbf{q}). \tag{13}$$

The formulations (5)–(9) provide a three-dimensional and nonlinear description for (i) diffusion, (ii) interface dynamic changes, and (iii) distribution of stresses created within the polymeric immiscible blend. Four independent state variables, *c*, **J**, *Q*, and **q**, with their coupled governing equations, are necessary for describing the time evolution of the mixture under investigation in mechanical equilibrium and in the absence of external flow and forces.

Equation (5) is the mass conservation of the simple fluid (penetrants continuity equation). Equation (6), which introduces inertia, is the time evolution equation for the mass flux, **J**. The motivations for introducing inertia into diffusion stem from both physical insight and experimental points of view. It is well known that the diffusion parabolic equation, obtained via Fick's laws, predicts a propagation of diffusion signals with infinite speed.[35,36] Consequently, such a propagation will instantaneously influence the whole system; a phenomenon which is not physically admissible. Due to experimental measurements of mass transport carried out in polymeric solutions, gels, and particularly for glassy systems, it has become obvious that inertia may play a key role in the occurrence of non-Fickian behavior. An interesting case that has aroused the interest of many groups is the so-called case II diffusion,[3,6,7] also known as shock-wave-type mass transport due to its resemblance with shock waves observed in compressible gases.[37,38] Generally speaking, the limitations of the Fickian description are found to arise mainly from its inability to correctly include two important non-Fickian effects: one related to relaxation processes and a second one to nonlinear phenomena.

The attempt to describe nonlinear effects and relaxation processes based on the concept of inertia has been the subject of several works.[11,13,20,25–27,35,36,39–42] It came about as a natural extension to existing linear constitutive equations in order to consider nonlinear effects observed in complex media. The physical reason has been mainly attributed to the interactions occurring between the medium and applied generalized forces. Generally speaking, when the coupling between the applied forces and the response of the medium becomes significant, one expects the occurrence of nonstandard phenomena whose descriptions are beyond the scope and range of validity of linear laws, such as Fick's law or Fourier's law, for example. Since the medium actively participates in such physical processes, its response, dictated by its internal structural changes, has to be explicitly taken into account. One should then identify an appropriate (or a set of) internal state variable (s) that provides the best description of these structural changes. In the case of mass transport without chemical reactions, the changes of the internal structure are mechanical in their nature, and thereby provide an indication of the type of the internal state variables to be chosen.

Equation (6) has the advantage of providing an extension to Fick's theory when the interface couples to diffusion in the absence of external forces. To gain a better physical interpretation, we write Eq. (6) (using $c\partial_\alpha\varphi_c = c\varphi_{cc}\partial_\alpha c + c\varphi_{cQ}\partial_\alpha Q + c\varphi_{cq_{\beta\gamma}}\partial_\alpha q_{\beta\gamma}$) as follows:

$$\frac{\partial J_\alpha}{\partial t} = -\partial_\gamma\left(\frac{J_\alpha J_\gamma}{\rho c}\right) - \Lambda_J(J_\alpha + \rho D(\partial_\alpha c + A\partial_\alpha Q + E_{\beta\gamma}\partial_\alpha q_{\beta\gamma})), \tag{14}$$

where

$$D = \frac{c\varphi_{cc}}{\rho\Lambda_J} \tag{15}$$

is identified as the diffusion coefficient. Equation (14) also involves a scalar

$$A = \frac{\varphi_{cQ}}{\varphi_{cc}}, \tag{16}$$

and a second order tensor

$$E_{\alpha\beta} = \frac{\varphi_{cq_{\alpha\beta}}}{\varphi_{cc}}, \tag{17}$$

which depend on the state variables c, Q, and $\mathbf{q}$. We refer to the second derivative of φ with respect to c, (c, Q) and $(c,\mathbf{q})$ by $\varphi_{cc} = \partial^2\varphi/\partial c^2$, $\varphi_{cQ} = \partial^2\varphi/\partial c\partial Q$, $\varphi_{cq_{\alpha\beta}} = \partial^2\varphi/\partial c\partial q_{\alpha\beta}$, respectively. The quantities, A and $\mathbf{E}$ compare, respectively, the effects of the interfacial tension and of the anisotropy of the interface, with the contribution of the total internal free energy. Such a qualitative interpretation results from the physical insight expressed in the internal free energy density (13). If the contribution of the interfacial free energy density is written as

$$\varphi^{\text{Interface}} = \Gamma(c)Q + \tfrac{1}{2}\alpha(c)\mathbf{q}:\mathbf{q}, \tag{18}$$

where Γ is the interfacial tension and α is a parameter related to the degree of anisotropy, therefore $\varphi_{cQ} = \Gamma_c$ and $\varphi_{c\mathbf{q}} = \alpha_c\mathbf{q}$. On the other hand, in view of Eqs. (13) and (18), we see that the second derivative of φ with respect to c is $\varphi_{cc} = \varphi_{cc}^{\text{mixing}} + Q\Gamma_{cc} + (\mathbf{q}:\mathbf{q}/2)\alpha_{cc}$, where the first term on the right-hand side is given by $\varphi_{cc}^{\text{mixing}} \propto RT/\tilde{V}_s$, where R is the gas constant, T is temperature, and $\tilde{V}_s$ is the solvent molar volume. It is thus clear that the scalar A and the second order tensor $\mathbf{E}$ are strong functions of concentration provided the surface tension Γ and the anisotropy parameter α are not constant.

Finally, the last two Eqs. (7) and (8) are the governing equations for the interface state variables. By involving explicitly the mass fraction and the diffusion mass flux, the behavior of the interface is directly and nonlinearly influenced by the diffusion processes. These nonlinear terms are necessary if the fluid undergoes volume changes or in case of an abrupt propagation of the solvent front.[3,6,7] Moreover, as in Paper I, we consider that both direct and indirect processes contribute to the relaxation of the interface through cross coupling terms. This assumes that the relaxation processes of the size and shape are strongly related. However, a decoupling may occur if the interface evolves either isotropically ($\mathbf{q} = \mathbf{0}$) or by conserving its size ($Q = \text{const.}$) during diffusion.

III. TRAVELING WAVES

Here, we examine the propagation of both hyperbolic and dispersive waves produced by disturbances in the mass fraction. To discuss solutions of Eqs. (5)–(8), it is useful to rewrite them into the compact form

$$\frac{\partial U}{\partial t} + \mathbf{M}\nabla U = -\mathbf{N}U, \tag{19}$$

where $\mathbf{U} = (c,\mathbf{v},Q,\mathbf{q})^T$ is the set of the state variables, $\mathbf{M}$ and $\mathbf{N}$ are the matrices that arise by identifying Eq. (19) with Eqs. (5)–(8). We have used the velocity $\mathbf{v}$ of the solvent front propagation, as a state variable, instead of the diffusion mass flux $\mathbf{J} = \rho c\mathbf{v}$. The $\mathbf{v}$-description is well suited for discussing, mathematically, the nature of traveling waves, while the $\mathbf{J}$-description is generally used for a direct comparison with measured data obtained by the classical experiments of mass transport (sorption, permeation, pervaporation, etc.). As many experimental observations are unidirectional, we derive predictions of Eq. (19) for a one-dimensional setting. In this setting, $U = (c,v,Q,\mathbf{q})^T$, where v is the component of the velocity in the direction of diffusion. As diffusion in polymeric fluids is usually accompanied by swelling,[3,6,7] the changes occurring in the internal structure are assumed to be significant in the x-direction representing the direction of diffusion. Therefore, in this simplified picture, the symmetry of this problem reduces the number of the components of the tensor $\mathbf{q}$ to one independent variable q_{xx} to be denoted by q. While the off-diagonal components vanish, the remaining two diagonal components are expressed as: $q_{yy} = -q/2$ and $q_{zz} = -q/2$, satisfying the traceless property of the tensor $\mathbf{q}$. Consequently, the matrices $\mathbf{M}$ and $\mathbf{N}$ arising in Eq. (19) are given by

$$\mathbf{M} = \begin{pmatrix} v & c & 0 & 0 \\ a_{21} & v & a_{22} & a_{23} \\ a_{31}v & a_{32} & a_{33}v & 0 \\ a_{41}v & a_{42} & 0 & a_{33}v \end{pmatrix},$$

$$\mathbf{N} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Lambda_J & 0 & 0 \\ 0 & 0 & \nu_1 & \nu_{12} \\ 0 & 0 & \nu_{12} & \nu_2 \end{pmatrix}, \tag{20}$$

where, for the sake of brevity, we have used the following notation:

$$\rho a_{21} = \varphi_{cc}, \quad \rho a_{22} = \varphi_{cQ}, \quad \rho a_{23} = 3\varphi_{cq}$$

$$a_{33}=-\frac{c}{(1-c)},\quad a_{j1}=\frac{a_{j2}}{c(1-c)}=-\frac{r_{j-3}}{(1-c)^2},\quad j=3,4,$$
$$r_0=q+\frac{Q}{3},\quad r_1=q-\frac{q^2}{Q}+\frac{4}{9}Q,\tag{21}$$

for the parameters arising in matrix **M** and

$$\nu_1=\frac{\Lambda^Q\varphi_Q}{Q},\quad \nu_{12}=\frac{3\Lambda^{qQ}\varphi_q}{q},\quad \nu_{21}=\frac{\Lambda^{qQ}\varphi_Q}{Q},$$
$$\nu_2=\frac{3\Lambda^q\varphi_q}{q},\tag{22}$$

for the ones used in matrix **N**. The symmetry property of **N** requires that $q\varphi_Q=3Q\varphi_q$.

We use the theory of characteristics[36–38] to study the nature of the nonlinear wave propagation due to the concentration disturbances. The characteristics corresponding to Eq. (19) are the curves $\tau\rightarrow(t(\tau),x(\tau))$ in the $(x,\,t)$ plane, where τ is a parameter. These characteristics are generated, respectively, by

$$\frac{dt}{d\tau}=1,\quad \frac{dx}{d\tau}=-\frac{cv}{1-c},$$
$$\frac{dt}{d\tau}=1,$$
$$\frac{dx}{d\tau}=v+\left[\frac{1}{\rho}\left(c\varphi_{cc}-\frac{c}{1-c}(r_0\varphi_{cQ}+3r_1\varphi_{cq})\right)\right]^{1/2},$$
$$\frac{dt}{d\tau}=1,$$
$$\frac{dx}{d\tau}=v-\left[\frac{1}{\rho}\left(c\varphi_{cc}-\frac{c}{1-c}(r_0\varphi_{cQ}+3r_1\varphi_{cq})\right)\right]^{1/2}.\tag{23}$$

The set of the governing Eq. (19) with Eq. (20) is time-hyperbolic if the eigenvalues of **M** are real. This requirement leads to the following condition:

$$\kappa=\frac{1}{\rho}\left(c\varphi_{cc}-\frac{c}{1-c}(r_0\varphi_{cQ}+3r_1\varphi_{cq})\right)\geqslant 0,\tag{24}$$

where the characteristic speed of these nonlinear hyperbolic waves is given by $\sqrt{\kappa}$. Moreover, the solutions are stable if the real parts of the eigenvalues of **N** are non-negative. The requirement of stability leads to

$$\Lambda_J\geqslant 0,$$
$$\nu_1\geqslant 0,\quad \nu_2\geqslant 0,\quad \nu_{12}\leqslant\sqrt{\nu_1\nu_2}.\tag{25}$$

Expressions (24) and (25) constitute the stability conditions for diffusion described by Eq. (19) in the one-dimensional setting. The waves obtained as solutions of these equations are called osmotic waves.[20]

Now we turn our attention to linear dispersive waves. These waves are created by small-amplitude perturbations to an equilibrium state characterized by $U_{\mathrm{eq}}(C_{\mathrm{eq}}0,Q_{\mathrm{eq}},q_{\mathrm{eq}})$ assumed to be time and position independent. Here, we assume that the interface is locked into an anisotropic shape, so q_{eq} is different from zero. The special case where the interface is isotropic can be deduced by setting $q_{\mathrm{eq}}=0$. Such waves can be written as $U=U_{\mathrm{eq}}+\tilde{U}\exp(i(kx+\omega t))$, where ω is the real frequency and k refers to a complex wave number. By inserting the expression of U into Eq. (19) and keeping only the terms that are linear in $\tilde{U}$, we arrive at the dispersion relation $\mathbf{k}=\mathbf{k}(\omega)$,

$$\det\left[\mathbf{I}+\left(\frac{k}{\omega}\right)\tilde{\mathbf{M}}-\left(\frac{i}{\omega}\right)\tilde{\mathbf{N}}\right]=0,\tag{26}$$

where $\tilde{\mathbf{M}}=\mathbf{M}|_{\mathrm{eq}}$ and $\tilde{\mathbf{N}}=\mathbf{N}|_{\mathrm{eq}}$. By solving Eq. (26), we arrive at

$$\left(\frac{k}{\omega}\right)^2=X+iY,\tag{27}$$

where

$$X(\omega)=\frac{\omega^2A_1B_1+A_2B_2}{\omega^2A_1^2+A_2^2},\quad Y(\omega)=\frac{\omega(A_1B_2-A_2B_1)}{\omega^2A_1^2+A_2^2},\tag{28}$$

written as functions of the following parameters:

$$A=A_1+i\frac{A_2}{\omega},\quad B=B_1+i\frac{B_2}{\omega},$$

with

$$A_1=\left[\kappa+\frac{ca_{21}}{\omega^2}(\nu_{12}^2-\nu_1\nu_2)\right]_{\mathrm{eq}},$$
$$A_2=[a_{33}(\nu_{12}(r_1a_{23}+r_0a_{24})-r_0\nu_2a_{23}-r_1\nu_1a_{24})$$
$$-ca_{21}(\nu_1+\nu_2)]_{\mathrm{eq}},$$
$$B_1=\left[1+\frac{\nu_{12}^2-\nu_1\nu_2-\Lambda_J(\nu_1+\nu_2)}{\omega^2}\right]\Bigg|_{\mathrm{eq}},$$
$$B_2=-\left[\Lambda+\nu_1+\nu_2+\frac{\Lambda_J(\nu_{12}^2-\nu_1\nu_2)}{\omega^2}\right]\Bigg|_{\mathrm{eq}}.\tag{29}$$

Equation (26) predicts two wave solutions, but one is discarded by considering positive values of wave speed. Therefore, the phase velocity has the following form:

$$v_{\mathrm{ph}}=\frac{\omega}{\mathrm{Re}(k)}=\sqrt{\frac{2}{X+\sqrt{X^2+Y^2}}}\tag{30}$$

and the attenuation of the intensity is given by

$$\alpha(\omega)=-2\,\mathrm{Im}(k)=-\omega Yv_{\mathrm{ph}}=-\omega Y\sqrt{\frac{2}{X+\sqrt{X^2+Y^2}}}.\tag{31}$$

At the high frequency limit, $\omega\rightarrow\infty$, we arrive at

$$v_{\mathrm{ph}}^{\infty}\cong\sqrt{\kappa_{\mathrm{eq}}},\tag{32}$$

$$\alpha^{\infty}\cong\frac{(\Lambda_{J_{\mathrm{eq}}}+\nu_{1\mathrm{eq}}+\nu_{2\mathrm{eq}})\kappa_{\mathrm{eq}}+A_2}{\kappa_{\mathrm{eq}}\sqrt{\kappa_{\mathrm{eq}}}}.\tag{33}$$

The phase velocity reduces to the characteristic speed of the hyperbolic waves, and the attenuation has a positive value discarding any amplification of such waves. Note that these two quantities are frequency independent. We recover the results predicted by Fick's laws by setting in Eqs. (32)–(33) $Q=0$, $\mathbf{q}=0$ $\nu_i=0$, and $\nu_{ij}=0$ $(\forall i,j)$. We recall that Fickian diffusion presents some limitations,[35] such as a prediction of infinite values for the speed and intensity attenuation at small relaxation times $(\Lambda_J\to\infty)$. These limitations are removed by introducing inertia into the process of diffusion which is expressed both in the equation of the mass flux and also by taking the influence of the interface into account.

At the low frequency limit, $\omega\to 0$, Eqs. (30)–(31) become

$$v_{\mathrm{ph}}^{0}(\omega)\cong\sqrt{2D\omega}, \tag{34}$$

$$\alpha^{0}(\omega)\cong\sqrt{\frac{2\omega}{D}}, \tag{35}$$

where D is the diffusion coefficient defined in Eq. (15). Both the phase velocity and the attenuation are directly proportional to the square root of the frequency, and therefore tend to zero. These results agree with previous developments obtained in gases[35] and in polymeric fluids[20] where these quantities become functions of one parameter, the diffusion coefficient.

IV. LIMITING CASES

In this section, we look for some particular cases of the family of models (5)–(9), where some state variables become dependent variables. In this reduction, we show that the family encompasses the well-known Fickian diffusion and also new extended formulations where the changes of both the size and shape of the interface contribute to the mass flux. The reduction to simpler models requires us to elucidate, among others, the relevance of inertia in nonstandard diffusion processes. The latter depends on the system under consideration, and in particular, on the time scales involved. Vrentas *et al.*[21–24] have applied the concept of the Deborah number to mass transfer which provides a very useful tool for a determination of the range of validity of inertial as well as viscoelastic effects. The Deborah number compares the characteristic time scale of the relaxation of the internal structure described by (nonconserved) internal variables to the characteristic time scale of diffusion. Here we have two types of (nonconserved) structural state variables, one is the diffusion mass flux and the other variables are associated with the interface. Each nonconserved variable relaxes to its equilibrium state in a certain (or a set of) relaxation time(s). Following Vrentas *et al.*,[21–24] and Neogi[11] we define a *J*-Deborah number as a ratio of the relaxation characteristic time for the diffusion flux to the diffusion characteristic time scale. The treatment of interfacial variables requires particular consideration, since it depends on the nature of the morphology of the interface and the probable presence of a length scale. To identify dimensionless quantities that are of importance to this dynamic process, we introduce the following dimensionless quantities for the time, space, and the state variables:

$$\theta=t/\tau_d,\quad \partial_\alpha=\frac{1}{L_0}\nabla_\alpha,\quad C=\frac{c}{C_{\mathrm{eq}}}\tilde{\mathbf{J}}=\frac{\mathbf{J}\tau_d}{\rho C_{\mathrm{eq}}L_0},$$

$$\tilde{Q}=\frac{Q}{Q_0},\quad \tilde{\mathbf{q}}=\frac{\mathbf{q}}{Q_0}, \tag{36}$$

where

$$\tau_d=\frac{L_0^2}{D_0} \tag{37}$$

refers to the diffusion characteristic time scale. D_0, Q_0, and L_0 are the diffusivity coefficient, the interfacial size density, and the thickness of the medium, respectively, at the initial state. C_{eq} is the equilibrium mass fraction. The dimensionless form for the mass flux time evolution equation is

$$\frac{\partial\tilde{J}_\alpha}{\partial\theta}=-\nabla_\gamma\left(\frac{\tilde{J}_\alpha\tilde{J}_\gamma}{C}\right)$$
$$-\frac{1}{De_J}(\tilde{J}_\alpha+\tilde{D}(\nabla_\alpha C+\tilde{A}\nabla_\alpha\tilde{Q}+\tilde{E}_{\beta\gamma}\nabla_\alpha\tilde{q}_{\beta\gamma})), \tag{38}$$

where $\tilde{D}=D/D_0$, $\tilde{A}=A/g_0$, and $\tilde{\mathbf{E}}=\mathbf{E}/g_1$. The quantities g_0 and g_1 are dimensionless groups of physical parameters to be defined. This equation involves three dimensionless quantities, the most important of which is the *J*-Deborah number,

$$\mathrm{De}_J=\frac{\tau_J}{\tau_d}, \tag{39}$$

where $\tau_J=\Lambda_J^{-1}$ is the relaxation time for the diffusion mass flux density. Several special cases arise as dictated mainly by the magnitude of the dimensionless number De_J. Inertial terms become relevant for large a *J*-Deborah number. The analogy of this case with flows of high Reynolds number is straightforward. For small De_J, diffusion is mainly governed by the Fickian term and the extension provided by the changes occurring at the interface. Two other numbers, of importance in this case, are

$$g_0=\frac{\Gamma_o Q_o\tilde{V}_s}{RT}\quad\text{and}\quad g_1=\frac{\alpha_o Q_o^2\tilde{V}_s}{RT}. \tag{40}$$

The quantities Γ_o and α_o are the interfacial tension and the modulus of anisotropy, at the initial state, respectively. We will discuss, in the following sections, the implications of the magnitudes of these two groups on diffusion. Note that these two groups of numbers (g_0 and g_1) show that the behavior of mass transport intimately depends on the physical properties of both the blend and of the penetrants as well as on the experimental conditions. Finally, for intermediate values of De_J, mass transport is influenced by both inertia and the deformation of the interface.

Now let us turn our attention to the interface time evolution equations. Two possible cases arise from the presence or absence of a length scale in the blend. If the interface has a length scale, it becomes possible to define a time scale and therefore a Deborah number. The relaxation time becomes related to the size of the droplets constituting the minor phase. In the case of spherical droplets with an initial radius R_o, the relaxation time scale of the interface is given by $\tau_{Qq}=3\eta_o\phi/(Q_o\Gamma_o)$, where η_o is the matrix constant viscosity, $Q_o=3\phi/R_o$ refers to the interfacial size density, and ϕ is the volume fraction of the minor phase in the blend. If the system is composed of two co-continuous media, there is no natural length scale in the system.[32]

Let us focus on the case of blends possessing a length scale for which $\Lambda_f = \Lambda_f^0$ is constant. The dimensionless form of the governing Eqs. (7)–(8) reads as follows:

$$\frac{\partial \tilde{Q}}{\partial \theta} = \left.\frac{\partial \tilde{Q}}{\partial \theta}\right|_{\text{diffusion}} + \left.\frac{\partial \tilde{Q}}{\partial \theta}\right|_{\text{relaxation}}, \tag{41}$$

$$\frac{\partial \tilde{q}_{\alpha\beta}}{\partial \theta} = \left.\frac{\partial \tilde{q}_{\alpha\beta}}{\partial \theta}\right|_{\text{diffusion}} + \left.\frac{\partial \tilde{q}_{\alpha\beta}}{\partial \theta}\right|_{\text{relaxation}}. \tag{42}$$

The interface Deborah number defined as

$$\mathrm{De}_{Qq} = \frac{\tau_{Qq}}{\tau_d} \tag{43}$$

emerges naturally in the relaxation part of the interface governing equations as

$$\left.\frac{\partial \tilde{Q}}{\partial \theta}\right|_{\text{relaxation}} = -\frac{1}{\mathrm{De}_{Qq}}\left((\tilde{Q} - \tilde{Q}^*)\tilde{\varphi}_{\tilde{Q}} + (\tilde{q}_{\alpha\beta} - \tilde{q}^*_{\alpha\beta})\tilde{\varphi}_{\tilde{q}_{\alpha\beta}}\right), \tag{44}$$

$$\left.\frac{\partial \tilde{q}_{\alpha\beta}}{\partial \theta}\right|_{\text{relaxation}} = -\frac{1}{\mathrm{De}_{Qq}}\left((\tilde{q}_{\alpha\beta} - \tilde{q}^*_{\alpha\beta})\tilde{\varphi}_{\tilde{Q}} + \left(\frac{\tilde{q}_{ij}\tilde{q}_{\alpha\beta}}{\tilde{Q}} - \frac{\tilde{q}^*_{ij}\tilde{q}^*_{\alpha\beta}}{\tilde{Q}^*} \right)\tilde{\varphi}_{\tilde{q}_{ij}} \right), \tag{45}$$

where q^* and Q^* are certain local equilibrium values for the shape and size of the interface, and $\tilde{\varphi} = \varphi/(\Gamma_o Q_o)$ is a normalized expression of the internal free energy density.

The presence of these four dimensionless groups (De_J, De_{Qq}, g_o, and g_1) in the family of models provides us with several special cases. Our aim, in these papers, is to derive a comprehensive model under a general form and to discuss its special cases based on the importance of its dimensionless numbers. In the following, we shall discuss in more detail the relevance of inertia in the mass flux and discuss some particular situations encompassing the Fickian description and some of its extended forms. Such a reduction can be seen as analogous to the reduction of the Navier–Stokes equation to the Stokes equation for low Reynolds number in fluid dynamics.

This task necessitates an accurate evaluation of the different time scales involved during the dynamic process. We should point out that a precise determination of the magnitude of the relaxation time for the diffusion mass flux, **J**, is required from microscopic considerations that are still missing at this time. This issue has been already arisen in many previous theoretical investigations.[25,27] Therefore, the *J*-Deborah number becomes, here, a parameter of the model that has to be determined from experimental measurements in a similar way as that has been used by Neogi.[11] As in several media, the inertial terms in the governing equation for **J** are not relevant to mass transport. This occurs when the relaxation characteristic time scale $(\Lambda_J)^{-1}$ becomes smaller than the diffusion characteristic time scale. Therefore, **J** equilibrates faster than the interfacial variables Q and $\mathbf{q}$ and we can assume that $d\mathbf{J}/dt \sim \mathbf{0}$ in Eq. (14). The mass flux density, **J**, becomes a dependent state variable. In the following, we shall discuss four models derived as special cases of the inertia-free formulation where the *J*-Deborah number is considered very small compared to unity.

A. *c*-model

It is well known that diffusion in simple media is adequately described by Fick's laws. In such systems, the changes of the internal structure do not contribute to the diffusion process and only the mass fraction suffices to describe the behavior of mass transport. The Fickian behavior is also expected to occur in blends of immiscible components in which the coupling between the diffusion and the changes of the interfacial morphology are very weak. Consider, for instance, mass transport of methanol into a thin film of the immiscible blend [polydimethylsiloxane (PDMS)/polyisobutylene (PIB)] of thickness 10^{-3} m at room temperature. The methanol has a molar volume of 4.05×10^{-5} and a diffusivity of the order of 10^{-11} m^2/s. The blend has a viscosity of 100 Pas,[42] an interfacial tension of 2.4×10^{-3} N/m,[42] an anisotropy modulus estimated at 10^{-11} N,[43] a minor phase volume fraction of 0.5, and a size density of 3×10^4 m^{-1}. Therefore, the coupling constants arising in Eq. (38) are approximately equal to $g_0 \sim 10^{-6}$ and $g_1 \sim 10^{-10}$. Since $g_0 \ll 1$ and $g1 \ll 1$, we can assume that $\mathrm{Max}(|A|,|E_{\beta\gamma}|) \ll 1$ in Eq. (14). Therefore, we can ignore, in addition to inertial terms, the third and fourth terms on the right-hand side of Eq. (14) or (38) and arrive at the familiar expression for the Fickian mass flux,

$$J_\alpha = -\rho D \partial_\alpha c. \tag{46}$$

A combination of Eq. (46) with the mass balance Eq. (5) leads to the diffusion parabolic equation,

$$\frac{\partial c}{\partial t} = \partial_\alpha (D \partial_\alpha c) \tag{47}$$

describing the time evolution of the solvent concentration into the Fickian immiscible blend. We recall that Eq. (47) is obtained by assuming that the changes of the interface cause small effects in the diffusion mass flux (i.e., $|\varphi_{cQ}| \ll |\varphi_{cc}|$ and $|\varphi_{c\mathbf{q}}| \ll |\varphi_{cc}|$).

Even though mass transfer is Fickian, it still affects the size and shape of the interface via the diffusion mass flux appearing in the Q and $\mathbf{q}$ governing equations. These equations involve, as discussed earlier, the interface Deborah number $\mathrm{De}_{Qq} = 3\eta_0 \phi D_0/(Q_o \Gamma_o L_0^2)$ which is of the order of 10^{-5} for the MeOH–(PDMS/PIB) mixture. The relaxation part is dominant in the governing equations of the interface (43)–(44), and the size and shape relax rapidly to their final equilibrium values.

Note that the Fickian description can also be obtained for immiscible fluids with a frozen morphology in which there are no changes in both the size and shape of the interface during the whole process. In this case, no interfacial stresses are created.

B. (c,Q)-model: Isotropically evolving interfaces

Here, we discuss the case where diffusion does not affect the isotropy of the interface during the whole dynamic process. In this case $\mathbf{q}=\mathbf{0}$, and only Q is kept as the only state variable characterizing the interface. From Eq. (38), this occurs when

$$g_1 \ll \min(1,g_0) \tag{48}$$

which leads to a size density satisfying $Q_0 \ll \min(\sqrt{RT/\tilde{V}\alpha_o},\Gamma_o/\alpha_o)$. This provides an indication of the size of the droplets constituting the minor phase and also the range of applicability of this reduced model. If we consider, for instance, the MeOH–(PDMS/PIB) mixture, we see that the size of the droplets approaches the nanoscale. From Eqs. (40) and (48), we also deduce that an increase of the interfacial tension or a change in the experimental conditions such as a decrease in temperature may also lead to situations in which the shape changes do not contribute to mass transport. If we examine the effects of the interface Deborah number on mass transport, non-Fickian behavior is expected for values of De_{Qq} in the vicinity of unity. In the case of the immiscible blend (PDMS/PIB), the relaxation time for the interface, τ_{Qq} is of the order of seconds. Therefore, a nonstandard behavior may be observed for a diffusion characteristic time scale of order of 1 s, that is $L_0^2 \sim D_0$. Realistically, one should seek a compromise among the model parameter values. Here, these parameters are the morphology and physical properties of the blend, the physical properties of the penetrants and the geometry of the sample.

The shape state variable, $\mathbf{q}$, in addition to the mass flux density $\mathbf{J}$ becomes thus dependent state variable (we recall that we have already assumed that Λ_J is very large). Hence, the set of the independent variables is reduced to (c, Q). Therefore, the diffusion mass flux (14) simplifies to

$$J_\alpha = -\rho D(\partial_\alpha c + A\partial_\alpha Q). \tag{49}$$

By substituting this expression into Eqs. (5) and (7), we obtain

$$\frac{\partial c}{\partial t} = \partial_\alpha(D\partial_\alpha c) + \partial_\alpha(AD\partial_\alpha Q), \tag{50}$$

$$\frac{\partial Q}{\partial t} = -\left(\frac{D}{(1-c)}\right)\partial_\alpha c\,\partial_\alpha Q - \left(\frac{DA}{(1-c)}\right)\partial_\alpha Q\,\partial_\alpha Q - \frac{Q}{3}\partial_\alpha\left(\frac{D}{(1-c)}\partial_\alpha c\right) - \frac{Q}{3}\partial_\alpha\left(\frac{AD}{(1-c)}\partial_\alpha Q\right) - \Lambda^Q\varphi_Q, \tag{51}$$

which constitute the governing equations for diffusion in isotropically evolving immiscible media. Note that Eq. (51) involves nonlinear terms in the gradients of c and Q. Here, we assume that diffusion does not cause any changes in the anisotropy. Furthermore, setting $\mathbf{q}=\mathbf{0}$ in Eq. (8) leads to the following constraint for the diffusion mass flux:

$$\partial_\beta\left(\frac{J_\alpha}{\rho(1-c)}\right) + \partial_\alpha\left(\frac{J_\beta}{\rho(1-c)}\right) = \frac{2}{3}\delta_{\alpha\beta}\partial_\gamma\left(\frac{J_\gamma}{\rho(1-c)}\right). \tag{52}$$

Once the solutions of Eqs. (50) and (51) are determined, we can calculate the distribution of isotropic stresses created in the immiscible fluid using

$$\sigma_{\alpha\beta}^{(\mathrm{Interface})} = -\tfrac{2}{3}\delta_{\alpha\beta}Q\varphi_Q. \tag{53}$$

This expression, which in fact stands for the Laplace term, is obtained as a special case of Eq. (9) by setting $\mathbf{q}=\mathbf{0}$.

Note that here the non-Fickian diffusion is produced by the coupling between the mass flux and the changes of the interfacial size, while the shape has no effect on mass transport. Another interesting case may occur if there are no concentration gradients within the system $(g_0 \gg 1)$. We deduce from Eq. (49) that the diffusion mass flux reduces to $J_\alpha = -\rho DA\partial_\alpha Q$. Note that any local changes of the interfacial size density may also cause diffusion of the penetrant molecules.

C. (c,q)-model

Changes occurring in the shape but not in the size may also cause non-Fickian behavior. This phenomenon can also be predicted by the model (5)–(9). From Eq. (38), we deduce that the following condition has to be satisfied:

$$g_o \ll \min(1,g_1), \tag{54}$$

which gives an indication of the size density $\Gamma_o/\alpha_o \ll Q_0 \ll (RT/\tilde{V}\Gamma_o)$. Similarly, for the MeOH–(PDMS/PIB) mixture, the size of the droplets may also attain the nanoscale, provided the other physical properties remain unchanged. The change in the size of the interface may be overlooked and the size density variable can be assumed as a constant during the whole process of diffusion, i.e., $Q=Q_0$. Therefore, the mass flux density becomes

$$J_\alpha = -\rho D(\partial_\alpha c + E_{\beta\gamma}\partial_\alpha q_{\beta\gamma}). \tag{55}$$

Inserting Eq. (55) into Eq. (5) yields

$$\frac{\partial c}{\partial t} = \partial_\alpha(D\partial_\alpha c) + \partial_\alpha(DE_{\beta\gamma}\partial_\alpha q_{\beta\gamma}) \tag{56}$$

which depends on $\mathbf{q}$ (representing the shape variable) whose governing equation is given by Eq. (8) but with the diffusion mass flux density $\mathbf{J}$ replaced by Eq. (55). Similarly, the stress tensor is now given by

$$\sigma_{\alpha\beta}^{\mathrm{Interface}} = 2q_{\alpha\gamma}\varphi_{q_{\alpha\beta}} + \Gamma q_{\alpha\beta} + \frac{2Q_0}{3}\varphi_{q_{\alpha\beta}} - \frac{q_{\alpha\beta}q_{\gamma\nu}}{Q_0}\varphi_{q_{\gamma\nu}} - \frac{2}{3}\delta_{\alpha\beta}(Q_o\Gamma + 2q_{\nu\theta}\varphi_{q_{\nu\theta}}) - \frac{2}{3}\delta_{ij}\left(q_{\alpha\beta} + \frac{1}{3}Q_0\delta_{\alpha\beta}\right)\varphi_{q_{ij}}. \tag{57}$$

In this model, a non-Fickian behavior is predicted to occur only through the coupling between the interfacial shape changes and the diffusion mass flux, while the changes of the size are not assumed to significantly affect mass transport. The same discussion as for the (c, Q)-model holds here; that is, only shape changes may be a source of creation of mass fluxes within the blend $(g_1 \gg 1)$.

D. (c, Q, q)-models

Here, we address a more general case where both the size and shape undergo substantial changes and contribute to the diffusion mass flux. In this case, the magnitudes of dimensionless constants g_0 and g_1 become significant and strongly couple diffusion to interfacial changes. From Eq. (40) an increase in the size density, or in the interfacial and anisotropy coefficients, as well as a decrease in the temperature of the experiment may lead to such a physical situation. Nanodispersions may also fall into this category. Therefore, the governing equation (14), for the mass flux reduces to

$$J_\alpha = -\rho D(\partial_\alpha c + A\partial_\alpha Q + E_{\beta\gamma}\partial_\alpha q_{\beta\gamma}). \tag{58}$$

Fick's second law, initially expressed as a linear function of the gradient of the concentration is now extended by two additional terms involving the gradients of the area Q and anisotropy $\mathbf{q}$ densities of the interface. The solvent mass balance, obtained by substituting Eq. (58) into Eq. (5), transforms to the following parabolic equation:

$$\frac{\partial c}{\partial t} = \partial_\alpha(D(\partial_\alpha c + A\partial_\alpha Q + E_{\beta\gamma}\partial q_{\beta\gamma})) \tag{59}$$

which involves the interfacial variables Q and $\mathbf{q}$, whose governing equations are given by Eqs. (7) and (8), respectively, provided the mass flux expression is given by Eq. (58). Note that the independent state variables in the $(c, Q, \mathbf{q})$-model are the mass fraction, the surface area, and the anisotropy tensor. By solving the governing equations (59) and (7)–(8) in which $\mathbf{J}$ is replaced by Eq. (58), we obtain information concerning their profiles and also the distribution of stresses (9) created by the deformation of the interface.

V. CONCLUSION

The main result of this paper is the set of the governing Eqs. (5)–(9) of a new model of isothermal diffusion of a simple fluid into a blend of two immiscible polymers under mechanical equilibrium and in the absence of external flow and forces. The state variables describing such mixtures are the mass fraction and the diffusion mass flux density of the simple fluid and two interfacial structural variables, a scalar and a symmetric traceless second order tensor. The scalar and the tensor denote the size of the area density and the anisotropy of the shape of the interface, respectively. The main outcome is that diffusion–interface coupling may become significant and may influence the behavior of mass transport as well as that of the morphology of the interface. Consequently, mass transport becomes non-Fickian due to the interfacial dynamic changes and in turn the size and shape of the interface may undergo substantial deformations produced by the mass fluxes. As a result, diffusion may be accompanied by a development and propagation of internal stresses whose consequences are creation of interfacial cracks and crazes. An explicit formula for such stresses is provided. The model consists of four first order partial differential equations parameterized by the internal free energy density and the kinetic coefficients entering the dissipation potential. All the physical parameters and properties of the penetrants and of the blend as well as of the experimental conditions are explicitly included into the governing equations.

As many experiments are unidirectional, we have investigated the nature of hyperbolic and dispersive waves in a one-dimensional setting, and provided explicit formulas for the characteristic speed, phase velocity, and attenuation of the intensity. In the high frequency limit, the phase velocity coincides exactly with the characteristic speed of the osmotic waves (hyperbolic). The attenuation of the intensity reduces to a positive constant value discarding any amplification of the high frequency waves. In the low frequency limit, both the phase velocity and the attenuation become proportional to the square root of the frequency.

The dimensionless form of the model shows that the effects of the diffusion–interface coupling on mass transport as well as on the interface depend on the magnitude of four dimensionless groups of physical parameters. Two are Deborah numbers and two are coupling constants that relate diffusion to interfacial changes. We have discussed some limiting cases of Eqs. (5)–(9) in which the diffusion mass flux becomes the dependent state variable. By further reducing the number of independent variables, we have examined diffusion in both isotropically evolving interfaces $(\mathbf{q} = \mathbf{0})$ and in interfaces with a constant size but with a transient shapes. In both cases, an expression for the interfacial stress tensor is provided.

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