On the Nonequilibrium Thermodynamics of Non-Fickian Diffusion

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ABSTRACT: Following the methods of extended irreversible thermodynamics, a set of coupled evolution equations are found for the diffusion flux and the viscous pressure tensor in a binary fluid mixture. The resulting equation for the diffusion flux reduces in some limiting cases to a relaxational Maxwell–Cattaneo equation or to a set of equations analogous to the ones used in the Thomas–Windle and the Durning–Tabor descriptions of case II diffusion.

1. Introduction

In usual circumstances, Fick's equations give a good description of diffusion processes. However, in glassy polymers near the glass transition temperature, diffusion exhibits some non-Fickian features, which have attracted the interest of many researchers.[1-12] Such features are usually studied in experiments of sorption and of permeation of low molecular weight species in thin polymeric membranes. The phenomenology is very rich, exhibiting case II and supercase II diffusion, two-stage sorption, sigmoidal sorption, pseudo-Fickian behavior, crazing, and other anomalies.[2,3]

The importance of diffusion as a rate-controlling phenomenon in many industrial and biological processes, such as fiber spinning, film casting and coating, development of photoresists, design of drug-delivery systems, neurotransmitters' transport, etc., and the theoretical challenge of a complete understanding of such anomalies justify that these phenomena are studied from a variety of perspectives and techniques.

Here, we present a theoretical description of diffusion from the point of view of extended irreversible thermodynamics (EIT), a nonequilibrium thermodynamic theory that has been much developed in the last decade.[13-16] In fact, non-Fickian diffusion, and especially case II diffusion, has been the subject of several works from the point of view of nonequilibrium thermodynamics.[17-19] In these works, the classical formalism of nonequilibrium thermodynamics with internal variables is used and leads to relaxational equations for the diffusion flux.

The point of view adopted here presents some differences with the previous ones. Here, we follow the formalism of extended irreversible thermodynamics, which includes the dissipative fluxes in the set of basic independent variables of the thermodynamic theory and aims to formulate evolution equations for them, compatible with the second law of thermodynamics. As will be shown in this paper, the evolution equations thus obtained reduce in some limit to several equations that have been proposed to describe non-Fickian aspects of diffusion in glassy polymers for small driving forces.

After presenting the general formulation in section 2, we comment in sections 3 and 4 on its relation with previous thermodynamic developments. Section 5 is devoted to some concluding remarks concerning the nonequilibrium chemical potentials.

2. Extended Thermodynamics of Diffusion

Extended irreversible thermodynamics[13] includes the dissipative fluxes (such as the heat flux, the diffusion flux, the electric current density, the bulk viscous pressure, and the viscous pressure tensor, for instance), in the space of independent thermodynamic variables. Instead of relating them directly to the gradients of the usual variables (temperature, pressure, velocity, concentrations), it treats them as independent variables for which evolution equations are needed. This point of view is motivated by the situations where the experimental time is of the order of the relaxational times of the fluxes, characterizing their decay toward their local-equilibrium values. Such situations arise either when the relaxation times are long or when experiments are performed at a frequency on the order of the inverse of the relaxation times, as in light scattering in gases or neutron scattering in liquids.

The point of view of extended irreversible thermodynamics is more systematic than that of the theories with internal variables. The additional nonequilibrium variables are identified from the beginning, either if the system has actually internal variables (as in the case of the macromolecular configuration in polymer solutions, for instance) or if the system has no internal variable at all (as in monatomic ideal gases). The disadvantage of this generality could be, in principle, to provide a description too independent of the microscopic details of the system and, thus, not much clarifying about them. This limitation can be avoided when the general results obtained in EIT are compared with the more microscopic and particular approaches of other theories. It is precisely the distinctive feature of thermodynamics of the search of the common aspects underlying a wide diversity of systems.

Here, we study a two-component fluid system and take as independent variables the specific internal energy per unit mass u, the specific volume v, the mass fraction c_k of the constituents, defined as $c_k = \rho_k/\rho$, with ρ_k and ρ the densities of species k and the total density, the diffusion flux $\mathbf{J}_1$ of the solvent with respect to the baricentric velocity, the traceless viscous pressure tensor $\overset{\circ}{\mathbf{P}}{}^{\mathrm{v}}$, and the bulk viscous pressure p^{v}. One could also have included as independent variables the heat flux $\mathbf{q}$, but this will not be done here for the sake of simplicity and because isothermal conditions are quite usual in the mentioned experiments. We will follow closely the approach in ref 13.

As the starting point, we write the generalized Gibbs equation for the generalized specific nonequilibrium entropy s as

$$ds = T^{-1}\,du + T^{-1}p\,dv - T^{-1}\tilde{\mu}\,dc_1 - v\alpha_1\mathbf{J}_1\cdot d\mathbf{J}_1 - v\alpha_0 p^{v}\,dp^{v} - v\alpha_2\mathring{\mathbf{P}}^{v}{:}d\mathring{\mathbf{P}}^{v} \quad (2.1)$$

with c_1 as the concentration (mass fraction) of the low molecular weight penetrant, $\tilde{\mu} = \mu_1 - \mu_2$ as the difference between the specific chemical potentials of the penetrant and of the polymer matrix, T and p as the absolute temperature and the pressure, and α_0, α_1, and α_2 as parameters whose physical meaning will become apparent below. We have taken into account that $c_1 + c_2 = 1$ and that $\mathbf{J}_1 + \mathbf{J}_2 = 0$, because of the definitions of c_k and $\mathbf{J}_k$.[21]

As it is usual in EIT, we assume that the entropy flux depends on all the dissipative fluxes and that it has the form

$$\mathbf{J}^{s} = T^{-1}\mathbf{q} - T^{-1}\tilde{\mu}\mathbf{J}_1 + \beta_2\mathring{\mathbf{P}}^{v}\cdot\mathbf{J}_1 + \beta_0 p^{v}\mathbf{J}_1 \quad (2.2)$$

where we have neglected the nonclassical contribution due to the heat flux. The first two terms are the usual ones in local-equilibrium theories,[21] and the two latter ones are the most general vectors that may be constructed from p^{v}, $\mathring{\mathbf{P}}^{v}$, and $\mathbf{J}_1$ (the scalar coefficients β_0 and β_2 may, in principle, depend on p, T, c_i, and the classical invariants of $\mathring{\mathbf{P}}^{v}$).

The energy and the mass balance equations are[21]

$$\rho\dot{u} = -\nabla\cdot\mathbf{q} + \mathbf{P}{:}(\nabla\mathbf{v}) \quad (2.3)$$

$$\rho\dot{c}_i = -\nabla\cdot\mathbf{J}_i \quad (2.4)$$

with $\mathbf{P}$ the total pressure tensor and $\mathbf{v}$ the baricentric velocity, and we have assumed that no external body forces are acting on the constituents. Combination of (2.1), (2.3), and (2.4) yields for the time derivative of the entropy

$$\rho\dot{s} = -T^{-1}\nabla\cdot\mathbf{q} + T^{-1}\tilde{\mu}\nabla\cdot\mathbf{J}_1 + T^{-1}\mathring{\mathbf{P}}^{v}{:}\mathring{V} + T^{-1}p^{v}\nabla\cdot\mathbf{v} - \alpha_1\mathbf{J}_1\cdot\dot{\mathbf{J}}_1 - \alpha_0 p^{v}\dot{p}^{v} - \alpha_2\mathring{\mathbf{P}}^{v}{:}(\mathring{\mathbf{P}}^{v})^{\bullet} \quad (2.5)$$

with the upper dot representing the material time derivative and $\mathring{V}$ the traceless symmetric part of the velocity gradient.

When the two first terms are integrated by parts and the subsequent expression for $\rho\dot{s}$ is combined with the divergence of (2.2), one obtains for the entropy production σ per unit time and volume, defined by

$$\rho\dot{s} + \nabla\cdot\mathbf{J}^{s} = \sigma \quad (2.6)$$

the expression

$$\sigma = \mathbf{J}_1\cdot[-\nabla(T^{-1}\tilde{\mu}) - \alpha_1\dot{\mathbf{J}}_1 + \nabla\cdot(\beta_2\mathring{\mathbf{P}}^{v}) + \nabla(\beta_0 p^{v})] + \mathbf{q}\cdot\nabla T^{-1} + p^{v}[-T^{-1}\nabla\cdot\mathbf{v} - \alpha_0\dot{p}^{v} + \beta_0\nabla\cdot\mathbf{J}_1] + \mathring{\mathbf{P}}^{v}{:}[-T^{-1}\mathring{V} - \alpha_2(\mathring{\mathbf{P}}^{v})^{\bullet} + \beta_2\langle\nabla\mathbf{J}_1\rangle] \quad (2.7)$$

where $\langle\nabla\mathbf{J}_1\rangle$ stands for the symmetric and traceless part of $\nabla\mathbf{J}_1$.

From now on we consider an isothermal situation ($\nabla T = 0$) and neglect the heat flux $\mathbf{q}$. Then, the simplest evolution equations for $\mathbf{J}_1$, p^{v}, and $\mathring{\mathbf{P}}^{v}$ compatible with the positive definite character of the entropy production σ as given by (2.7) are

$$-T^{-1}\nabla\tilde{\mu} - \alpha_1\dot{\mathbf{J}}_1 + \nabla\cdot(\beta_2\mathring{\mathbf{P}}^{v}) + \nabla(\beta_0 p^{v}) = \vartheta_1\mathbf{J}_1 \quad (2.8)$$

$$-T^{-1}\nabla\cdot\mathbf{v} - \alpha_0\dot{p}^{v} + \beta_0\nabla\cdot\mathbf{J}_1 = \vartheta_0 p^{v} \quad (2.9)$$

$$-T^{-1}\mathring{V} - \alpha_2(\mathring{\mathbf{P}}^{v})^{\circ} + \beta_2\langle\nabla\mathbf{J}_1\rangle = \vartheta_2\mathring{\mathbf{P}}^{v} \quad (2.10)$$

with $\vartheta_1 \geqslant 0$, $\vartheta_0 \geqslant 0$, and $\vartheta_2 \geqslant 0$. On comparison of these equations with the classical Fick's law for diffusion and Newton–Stokes laws for viscous pressure

$$\mathbf{J}_1 = -\tilde{D}\nabla\tilde{\mu}, \quad p^{v} = -\zeta\nabla\cdot\mathbf{v}, \quad \mathring{\mathbf{P}}^{v} = -2\eta\mathring{V} \quad (2.11)$$

with ζ and η bulk and shear viscosities, respectively, and $\tilde{D}$ a coefficient related to the usual diffusivity coefficient, one may identify

$$\vartheta_1 = (\tilde{D}T)^{-1}, \quad \vartheta_0 = (\zeta T)^{-1}, \quad \vartheta_2 = (2\eta T)^{-1} \quad (2.12)$$

Furthermore, one may identify the respective relaxation times of $\mathbf{J}_1$, p^{v}, and $\mathring{\mathbf{P}}^{v}$ as

$$\tau_1 = \alpha_1/\vartheta_1; \quad \tau_0 = \alpha_0/\vartheta_0; \quad \tau_2 = \alpha_2/\vartheta_2 \quad (2.13)$$

One may use, instead of $\nabla\tilde{\mu}$, the concentration (mass fraction) gradient ∇c_1 and the diffusivity $D = \tilde{D}(\partial\tilde{\mu}/\partial c_1)_{T,p}$ and rewrite (2.8) and (2.10) as

$$\tau_1\dot{\mathbf{J}}_1 + \mathbf{J}_1 = -D\nabla c_1 + \tilde{D}T\nabla\cdot(\beta_2\mathring{\mathbf{P}}^{v}) + \tilde{D}T\nabla(\beta_0 p^{v}) \quad (2.14)$$

$$\tau_0\dot{p}^{v} + p^{v} = -\zeta\nabla\cdot\mathbf{v} + \zeta T\beta_0\nabla\cdot\mathbf{J}_1 \quad (2.15)$$

$$\tau_2(\mathring{\mathbf{P}}^{v})^{\bullet} + \mathring{\mathbf{P}}^{v} = -2\eta\mathring{V} + 2\eta T\beta_2\langle\nabla\mathbf{J}_1\rangle \quad (2.16)$$

Equations of this form, with $\mathbf{J}_1$ replaced by $\mathbf{q}$ and the Fickian term $-D\nabla c_1$ replaced by the Fourier term $-\lambda\nabla T$, may be found in ref 13.

Assume now that the velocity $\mathbf{v}$ is zero. In such a situation, (2.15) and (2.16) reduce to

$$\tau_0\dot{p}^{v} + p^{v} = \zeta T\beta_0\nabla\cdot\mathbf{J}_1 \quad (2.17)$$

$$\tau_2(\mathring{\mathbf{P}}^{v})^{\bullet} + \mathring{\mathbf{P}}^{v} = 2\eta T\beta_2\langle\nabla\mathbf{J}_1\rangle \quad (2.18)$$

To simplify the calculations, we linearize (2.14), (2.17), and (2.18) and assume that all coefficients appearing in them are constant. This linearization is valid for the study of differential variations in the concentration, as differential sorption or differential permeation. In general, it will not be valid, because the actual coefficients do in fact depend strongly on the concentration. In the linear approximation one obtains from (2.17) and (2.18)

$$p^{v}(t) = (\zeta T\beta_0/\tau_0)\int_{-\infty}^{t}\exp[-(t-t')/\tau_0]\nabla\cdot\mathbf{J}_1(t')\,dt' \quad (2.19)$$

$$\mathring{\mathbf{P}}^{v}(t) = (2\eta T\beta_2/\tau_2)\int_{-\infty}^{t}\exp[-(t-t')/\tau_2]\langle\nabla\mathbf{J}_1(t')\rangle\,dt' \quad (2.20)$$

These equations may be inserted into (2.14), leading to

$$\tau_1\dot{\mathbf{J}}_1 + \mathbf{J}_1 = -D\nabla c_1 + D_2\nabla\cdot\int_{-\infty}^{t}\exp[-(t-t')/\tau_2] \times \langle\nabla\mathbf{J}_1(t')\rangle\,dt' + D_0\nabla\int_{-\infty}^{t}\exp[-(t-t')/\tau_0]\nabla\cdot\mathbf{J}_1(t')\,dt' \quad (2.21)$$

with

$$D_2 = 2\eta T^2\beta_2^{\,2}\tilde{D}/\tau_2; \quad D_0 = \zeta T^2\beta_0^{\,2}\tilde{D}/\tau_0 \quad (2.22)$$

Let us note that (2.17) and (2.18) indicate a coupling between the diffusion flux and the viscous pressure tensor. This may be easily understood in terms of a swelling of the polymer produced by the diffusion of penetrant into it. This idea is at the basis of almost all models of non-Fickian diffusion. Indeed, near the glass transition temperature the polymer has a long relaxation time and remains for a long time in a nonequilibrium state. Far from the glass transition, the relaxation time becomes very small (in the liquid state above T_g) or extremely long (in the glassy state far below T_g). In such cases, the effects of the relaxation become negligible: in the first case, the system relaxes very fast to equilibrium and the usual local-equilibrium description is accurate enough. It is usual to speak in this case of "viscous diffusion". In the second case, the relaxation time is so long that the polymer stays in a single nonequilibrium state, so that the relaxation does not interact with the diffusion process. One speaks in this case of "elastic diffusion".

Vrentas and Duda[5b] have given a quantitative form to this basic idea, by defining a Deborah number as the ratio of the relaxation time of the polymer ($\tau_0 = \tau_2$ in (2.17–2.18)) and the characteristic time of the diffusion process, of the order of $t^* = l^2/D^*$, with l the thickness of the sample and D^* an effective diffusivity. These authors consider that for Deborah numbers between, say, 10^{-1} and 10 one would have "viscoelastic" non-Fickian diffusion, and for Deborah numbers less than 10^{-1} or higher than 10 one would have, respectively, "viscous" or "elastic" Fickian diffusion, respectively, with different diffusion constants in each case.

3. Maxwell–Cattaneo Law for Diffusion

The simplest generalization of Fick's law arising from (2.21) is provided by the assumption $D_2 = D_0 = 0$. In this case, it reduces to a simple relaxational equation of the form

$$\tau_1 \dot{\mathbf{J}}_1 + J_1 = -D\nabla c_1 \tag{3.1}$$

An equation of this form is known as the Maxwell–Cattaneo equation in the context of heat transport,[13-22] with the heat flux $\mathbf{q}$ instead of $\mathbf{J}_1$ and the Fourier term $-\lambda\nabla T$ with thermal conductivity instead of the Fick term $-D\nabla c_1$. The Maxwell–Cattaneo equation arose in 1949, after a long period of neglect since its first proposal by Maxwell in the 1860s, in order to avoid infinite speed of propagation of thermal pulses or high-frequency heat waves.

When (3.1) is combined with the mass balance law (2.4), one obtains the following speed of propagation for diffusion signals

$$c = (D/\rho\tau_1)^{1/2} \tag{3.2}$$

In fact, τ_1 cannot be strictly constant, because this would yield in some cases negative concentrations. However, we will assume a small perturbation in the concentration c_1 in such a way that this does not happen and (3.1) may be considered as linear.

An equation like (3.1) has been derived by Neogi[17] in the context of classical nonequilibrium thermodynamics with internal variables.[21] The internal variable was not specified explicitly: it could be related to changes in orientation, or in molecular conformation, or in internal stresses or fluidity. Neogi writes his constitutive equation for the diffusion flux as

$$\mathbf{J}_1(t) = \int_{-\infty}^{t} \psi(t-t')\, \nabla c_1(t')\, \mathrm{d}t' \tag{3.3}$$

with

$$\psi(t-t') = D_{\mathrm{i}}\, \delta(t-t') + (D_0 - D_{\mathrm{i}})\tau_1^{-1} e^{-(t-t')/\tau_1} \tag{3.4}$$

with D_{i} the initial and D_0 the final values of the diffusivity. The simple Maxwell–Cattaneo equation corresponds to $D_{\mathrm{i}} = 0$ in (3.4).

Neogi has applied the Maxwell–Cattaneo equation to the description of case II diffusion.[1-11] In this phenomenon, the penetration of the solute into the polymer is characterized by a sharp front advancing at constant speed. Though a sharp boundary could arise in Fick's equation with a sufficiently steep variation of the diffusivity as a function of the concentration, its position would change as $t^{1/2}$ instead of at a constant speed. Thus, case II diffusion is a typical manifestation of non-Fickian behavior. Behind the front there is a swollen zone, at constant penetrant concentration.

Neogi[17] has solved the diffusion equation with the Maxwell–Cattaneo form of the flux to analyze the time dependence of the mass uptake in differential sorption experiments. In these, the concentration (activity) of the solvent around a membrane is suddenly increased in a small amount at $t = 0$, and the mass uptake is measured as a function of time. In permeation experiments, the concentration is increased only at one side of the membrane and the mass throughout is measured as a function of time.

According to Fick's law, the fractional mass uptake $M(t)/M(\infty)$ is a function of $t^{1/2}/l$, with l the thickness of the membrane, and at short times it behaves as

$$M(t)/M(\infty) \approx (16Dt/\pi l^2)^{1/2} \tag{3.5}$$

To derive this result, one assumes not only Fick's laws but also an instantaneous equilibration at the boundaries, in which the equilibrium concentration is immediately reached. In contrast to this hypothesis, Neogi has used the Maxwell–Cattaneo equation and a boundary condition of the form

$$c_{\mathrm{b}} = c_{\mathrm{i}} + (c_{\mathrm{f}} - c_{\mathrm{i}})[1 - e^{-t/\tau_1}] \tag{3.6}$$

with c_{b} as the boundary concentration and c_{i} and c_{f} as its respective initial and final values. Indeed, it was observed[24] that the rearrangement of the polymer on the boundary to accommodate the equilibrium permeant concentration is not instantaneous but takes some time τ_1 (since both the delay and the Maxwell–Cattaneo equation as in the boundary conditions are attributed to the polymer rearrangement, one takes the same time for both relaxation phenomena).

When τ_1 is long as compared with l^2/D, the mass uptake $M(t)$ as a function of time is given by

$$M(t)/M(\infty) = (2/l)(D/\rho\tau_1)^{1/2}t, \quad \text{for } t < (l/2)(D/\rho\tau_1)^{-1/2}$$

$$M(t)/M(\infty) = 1, \quad \text{for } t \geqslant (l/2)(D/\rho\tau_1)^{-1/2} \tag{3.7}$$

This behavior is easily understood as the penetration of two fronts, from the left and from the right toward the center, at the constant speed in (3.2). Every front must move a distance $l/2$. The velocities of these fronts, sometimes called Alfrey's fronts, are on the order of 1.4×10^{-4} cm/s for n-pentane in biaxially oriented polystyrene at 30 °C and of 0.8×10^{-4} cm/s in cast annealed polystyrene,[17,25] and for benzene in epoxy resins it is on the order of 5.9×10^{-6} cm/s at 70 °C.

The supercase II diffusion[23,26] corresponds to situations in which the fractional mass uptake $M(t)/M(\infty)$ changes as t^n, with $n > 1$, so that the front accelerates with time. Gostoli and Sarti[26b] have attributed the acceleration of the front to the differential swelling stress, which increases as the residual thickness of the glassy core is reduced. Supercase II diffusion is found in thin membranes with solvents with an initially low velocity of penetration. It has been observed in ethanol, propanol, and butanol in PMMA.

Let us finally note that an equation such as (3.1), of the Maxwell–Cattaneo form, for the diffusion of photons in the stellar chromosphere has been used to describe the double-peak structure in the temporal luminosity profiles observed in X-ray bursters in astrophysics.[27]

4. Higher Order Transport Equations

The Maxwell–Cattaneo equation of the preceding section does not exhibit explicitly the interconnection between diffusion and stress. Models more explicit in this point would be more illustrative and close to the real experimental situations. Furthermore, they are able to describe complexities of non-Fickian sorption curves that fall beyond the scope of the simple Maxwell–Cattaneo equation. These models assume that the intrinsic relaxation time for diffusion, τ_1, is negligibly short and that the non-Fickian features come from the viscoelastic time $\tau_0 = \tau_2$ characterizing the relaxation of the viscous stress in the polymeric matrix.

The usual models and experiments are essentially one-dimensional. Thus, for the sake of comparison we write (2.14), (2.17), and (2.18) in the case when the only stress is longitudinal and described by $P_{xx}{}^{\mathrm{v}}$, the only nonvanishing component of the viscous pressure tensor. We furthermore assume that $\tau_0 = \tau_2 = \tau_l$ and $\beta_0 = \beta_2 = \beta_l$. Taking into account the traceless part $\overset{\circ}{\mathbf{P}}{}^{\mathrm{v}}$ and adding (2.17) and (2.18), we obtain

$$\tau_l(P_{xx}{}^{\mathrm{v}})^{\cdot} + P_{xx}{}^{\mathrm{v}} = +T\beta_l\eta_l(\partial J_1/\partial x) \tag{4.1}$$

with $\eta_l = (4/3)\eta + \zeta$ is the longitudinal viscosity. On the other hand, (2.14) may be written as

$$J_1 = -\tilde{D}\frac{\partial}{\partial x}[\tilde{\mu} - T\beta_l P_{xx}{}^{\mathrm{v}}] \tag{4.2}$$

These two equations are the basis of the Thomas–Windle model for case II diffusion[4,7] in the modified form proposed by Durning[12b] and Durning and Tabor.[19b] Indeed, the basic idea of the Thomas–Windle model is to take into account the effects of the nonequilibrium viscous pressure on the chemical potential of the solvent by considering that the nonequilibrium pressure plays a role similar to an "osmotic" pressure. Thus, they write

$$\mu_1(T,p+P_{xx}{}^{\mathrm{v}},c_i) - \mu_{1\,\mathrm{eq}}(T,p,c_i) = \int_p^{p+P_{xx}{}^{\mathrm{v}}}(\partial\mu_1/\partial p)\,\mathrm{d}p \tag{4.3}$$

Here $\mu_1(T,p+P_{xx}{}^{\mathrm{v}},c_i)$ is the actual nonequilibrium chemical potential of the solvent submitted to a total pressure $p + P_{xx}{}^{\mathrm{v}}$, with p the equilibrium pressure, and $\mu_{1\,\mathrm{eq}}(T,p,c_i)$ the chemical potential of the solvent under local-equilibrium conditions. Thus, (4.3) may be written, in the linearized approximation, as

$$\mu_1(T,p+P_{xx}{}^{\mathrm{v}},c_i) = \mu_{1\,\mathrm{eq}}(T,p,c_i) + \bar{V}_1P_{xx}{}^{\mathrm{v}} \tag{4.4}$$

with $\bar{V}_1$ the mean value of the partial molar volume of the solvent. In the spirit of the Thomas–Windle theory, the quantity in brackets in (4.2) may be considered as a generalized chemical potential μ_{noneq}

$$\tilde{\mu}^*{}_{\mathrm{noneq}} = \tilde{\mu}_{\mathrm{eq}} + \bar{V}_1P_{xx}{}^{\mathrm{v}} \tag{4.5}$$

provided one identifies

$$-T\beta_l = \bar{V}_1 \tag{4.6}$$

Note that this identification allows one to write the generalized entropy flux (2.2) as

$$\mathbf{J}^{\mathrm{s}} = T^{-1}\mathbf{q} - T^{-1}\tilde{\mu}\mathbf{J}_1 + \beta P_{xx}{}^{\mathrm{v}}\mathbf{J}_1 = T^{-1}\mathbf{q} - T^{-1}\tilde{\mu}^*\mathbf{J}_1 \tag{4.7}$$

This effect corresponds to a reversible process, which is linked to the flow of entropy across the boundaries rather than to a production of entropy.

Equation 4.4 by itself is not sufficient to settle a model for non-Fickian diffusion, but it has to be complemented by another hypothesis concerning $P_{xx}{}^{\mathrm{v}}$ to obtain a closed set of equations for c_1. The hypothesis of Thomas and Windle is essentially to assume

$$P_{xx}{}^{\mathrm{v}} = \bar{V}_1\eta_l\rho(\partial c_1/\partial t) \tag{4.8}$$

which comes from (4.1) when (4.6) and (2.4) are considered. In other words, they assume that the rate-controlling step is the mechanical viscous resistance of the polymer to increase in volume and change in shape; in other words, the rate at which the solvent is absorbed, given by $V_1\rho\partial c_1/\partial t$, must be compatible with the swelling rate controlled by the creep deformation in the polymer. This equation must be supplemented with further hypotheses concerning the explicit dependence of $\eta_l(c_1)$ and $D(c_1)$ of the viscosity and the diffusivity on the solvent concentration. The explicit form of these expressions lies, of course, beyond the reach of nonequilibrium thermodynamics and must be obtained either from a phenomenological basis or from a statistical mechanical method based on structural considerations about the material.

Equation 2.4 for mass conservation, eq 4.2 for the diffusion flux, and eq 4.8 for the viscous pressure, together with the relations for $D(c_1)$ and $\eta_l(c_1)$, yield a closed set of equations for c_1, which may be solved explicitly to obtain a description of the evolution of $c_1(x,t)$. Note that Thomas and Windle work with ϕ, the volume fraction of the solvent, rather than with c_1, its mass fraction. This difference does not affect in an essential way the formalism exposed here.

The consequences of the Thomas–Windle model have been examined by several authors,[4,7,12] and they provide an essentially correct description of case II diffusion, in many aspects. The theory, however, has some limitations: it predicts vanishing diffusion when η_l is very high, in contrast with what is experimentally observed,[12] or underestimates the swelling rate at low c_1 (or ϕ) and overestimates it when c_1 (or ϕ) is high.[7] To overcome the first limitation, Durning and Tabor[12b,19] have proposed to take into account the relaxational viscoelastic effects on $P_{xx}{}^{\mathrm{v}}$, and they take as a connection between $P_{xx}{}^{\mathrm{v}}$ and the rate of solvent sorption the full equation (4.1), so that instead of (4.8) they have essentially

$$\tau_l(\partial P_{xx}{}^{\mathrm{v}}/\partial t) + P_{xx}{}^{\mathrm{v}} = \bar{V}_1\eta_l\rho(\partial c_1/\partial t) \tag{4.9}$$

The consequences of this model on classical and oscillatory sorption have been examined in detail in ref 19. Note that now three characteristic times appear: τ_l the relaxational time of $P_{xx}{}^{\mathrm{v}}$; l^2/D the characteristic diffusion time, and $c_\infty a^+\bar{V}_1{}^2\eta_l/RT$ (with $a^\mp$ the initial activity and c_∞ the equilibrium concentration at long times), a rheological time depending on η_l. Only the two latter times appear in the Thomas–Windle theory (the Deborah number in their theory would be based on the latter two times). In the more general situation, two Deborah numbers may be defined as the ratios of such characteristic times[12b]

$$\theta = \tau_l D/l^2, \quad \Lambda = c_\infty a^{\mathrm{t}} \bar{V}_1{}^2 \eta_l D/RTl^2 \qquad (4.10)$$

The Thomas–Windle theory based on (4.4) and (4.8) corresponds to $\tau_l = 0$ ($\theta = 0$). Durning et al.[12a] have analyzed the theory with $\theta = 0$ and have found that it cannot predict a two-stage sorption and that it predicts a vanishing transport for high values of Λ, in contrast with observations. Introduction of $\theta \neq 0$ allows us to overcome these limitations. Durning[12b] has evaluated the parameters appearing in the theory for methyl acetate/PMMA near 30 °C. He has studied several situations according to the initial solvent concentration X (grams of solvent/grams of polymer). For small X ($0 < X < 0.04$) he finds that both θ and Λ are much higher than 1, with θ/Λ small, and he finds a sigmoidal sorption curve for the fractional mass uptake as a function of $t^{1/2}$. For $0.04 < X < 0.16$, θ and Λ are of order unit. Durning takes $\theta/\Lambda = {}^1/_3$ to fit the experimental data. For θ between 3 and 10 (X near 0.05) he obtains a two-stage sorption, whereas for θ between 1 and 3 ($0.09 < X < 0.12$) one is led to pseudo-Fickian behavior. At higher X, θ and Λ are small (of the order of 0.01) and one recovers the classical behavior.

Note that one of the first attempts to include the influence of the stress tensor on the diffusion flux equations as a basis for the description of the case II diffusion was carried out by Frisch et al.[20] who proposed an equation of the form

$$\mathbf{J}_1 = -\Omega[\nabla\mu_1 + (1/c)\nabla\cdot\boldsymbol{P}^{v}] \qquad (4.11)$$

with Ω a transport coefficient and c the concentration per unit volume. The motivation for this term was sought in the kinetic theory of gases,[13,28,29] where a coupling between $\boldsymbol{P}^{v}$ and $\mathbf{J}$ appears in the so-called second-order approximations. Note that this equation is analogous to (4.2). When $\partial\mu/\partial x \ll \partial P_{xx}{}^{\mathrm{v}}/\partial x$ and when $P_{xx}{}^{\mathrm{v}}$ is proportional to the mass uptake, Frisch et al.[20] derived from (4.11) a constant speed of propagation for the solvent front.

A diffusion equation of the form (2.21) or, in the one-dimensional case, but neglecting τ_1 and taking into account the balance equation (2.4)

$$\mathbf{J}_1 = -D(\partial c_1/\partial x) - D'\frac{\partial}{\partial x}\int_{-\infty}^{t} \exp[-(t-t')/\tau_l](\partial c_1/\partial t')\,\mathrm{d}t' \qquad (4.12)$$

has been proposed by several authors[19,30] on the basis of a modification of the chemical potential by including in it the effects related to relaxing internal variables. One assumes that, under isothermal and isobaric conditions, retardation effects come from the interaction part μ_{int}, in the chemical potential, but not from the ideal part. Following a sudden change of concentration Δc at $t = 0$, the interaction part $\Delta\mu_{\mathrm{int}}$ relaxes from the initial increase $(\partial\mu_{\mathrm{int}}/\partial c)_\infty\Delta c$ to a smaller increase $(\partial\mu_{\mathrm{int}}/\partial c)_{\mathrm{o}}\Delta c$, with o and infinity denoting the low- and high-frequency responses. Thus, one writes for μ[30a]

$$\mu(t) = kT\ln c(t) + (\partial\mu_{\mathrm{int}}/\partial c)_{\mathrm{o}}c(t) + [(\partial\mu_{\mathrm{int}}/\partial c)_\infty - (\partial\mu_{\mathrm{int}}/\partial c)_{\mathrm{o}}]\int_{-\infty}^{t}\phi(t-t')\,(\partial c(t')/\partial t')\,\mathrm{d}t' \qquad (4.13)$$

with $\phi(t-t')$ the memory function describing this relaxation. If, furthermore, one defines

$$\mathbf{J}(t) = -Bc(t)\,\nabla\mu(t) \qquad (4.14)$$

with B the constant mobility of the solvent molecules, and one neglects the nonlinear terms arising from $c\nabla c$, one obtains (4.12) with $\phi(t-t')$ instead of the exponential, with $D = Bk_{\mathrm{B}}T$ the ideal part of the diffusion coefficient (k_{B} is the Boltzmann constant) and $D' = Bc_0[(\partial\mu_{\mathrm{int}}/\partial c)_\infty - (\partial\mu_{\mathrm{int}}/\partial c)_{\mathrm{o}}]$. Though in our case we have used the viscous pressure as a single internal variable, much more general kinds of memories could have been achieved had we considered it as a sum of contributions decaying with different relaxation times.[31]

5. Concluding Remarks

The evolution equations of the diffusion flux and the viscous pressure in a two-component fluid mixture have been written by following the standard procedure of EIT.[13] The resulting equations show an interplay between the nonequilibrium viscous pressure and the diffusion flux. The ensuing evolution equations for the diffusion flux contain as particular cases several equations that had been previously proposed for the analysis of the non-Fickian features arising in differential sorption and permeation of vapors in glassy polymers.

A development similar to that of the present paper was performed in the context of heat transport in solids at low temperatures,[13] where the generalized equations of EIT allow for the description of several non-Fourier features, as thermal waves or phonon hydrodynamics. A similar analysis could probably be of interest for heat transport in glassy polymers.

Equations 2.14–2.16 proposed here have, in principle, a quite general character. They are also found in the kinetic theory of gases in Burnett (second-order) developments.[13,28] The differences between ideal gases and the glassy polymers are, notwithstanding, obvious: in the former one the relaxation times τ_l are on the order of 10^{-9} s, whereas in the polymer τ_l may be on the order of 10^{-2}–10^{2} s. It is this fact that makes the non-Fickian effects in glassy polymers much more compelling and interesting than in gases, where they are scarcely perceptible in a few extreme situations.

Some final comments concerning the nonequilibrium chemical potential are in order. The Thomas–Windle model assumes that

$$\mu_{\mathrm{noneq}} = \mu_{\mathrm{eq}}(T,p,c_{\mathrm{i}}) + \bar{V}_1 P_{xx}{}^{\mathrm{v}} \qquad (5.1)$$

On the other hand, we could write the generalized entropy (2.1) explicitly as

$$\mathrm{d}s = T^{-1}\,\mathrm{d}u + T^{-1}p\,\mathrm{d}v - T^{-1}\tilde{\mu}\,\mathrm{d}c_1 - (v\tau_1/\tilde{D}T)\mathbf{J}_1\cdot\mathrm{d}\mathbf{J}_1 - (v\tau_0/\zeta T)p^{\mathrm{v}}\,\mathrm{d}p^{\mathrm{v}} - (v\tau_2/2\eta T)\boldsymbol{P}^{v}:\mathrm{d}\boldsymbol{P}^{v} \qquad (5.2)$$

where we have used the identifications (2.12) and (2.13). Here, all the coefficients have an explicit meaning and define, therefore, an explicit generalized entropy. In the case when only longitudinal viscous pressure is important, we could write instead of (5.2)

$$\mathrm{d}s = T^{-1}\,\mathrm{d}u + T^{-1}p\,\mathrm{d}v - T^{-1}\tilde{\mu}\,\mathrm{d}c_1 - (v\tau_l/\eta_l T)P_{xx}{}^{\mathrm{v}}\,\mathrm{d}P_{xx}{}^{\mathrm{v}} \qquad (5.3)$$

This could also be written as

$$s(u,v,c_{\mathrm{i}},P_{xx}{}^{\mathrm{v}}) = s_{\mathrm{eq}}(u,v,c_{\mathrm{i}}) - (v\tau_l/2\eta_l T)P_{xx}{}^{\mathrm{v}2} \qquad (5.4)$$

From (5.4) a nonequilibrium chemical potential could be obtained in the form

$$\mu_{\mathrm{noneq}}(u,v,c_{\mathrm{i}},P^{\mathrm{v}}) = -T(\partial s/\partial c_{\mathrm{i}}) = \mu_{\mathrm{eq}}(u,v,c_{\mathrm{i}}) + T[\partial[v\tau_l/2\eta_l T]/\partial c_{\mathrm{i}}]P_{xx}{}^{\mathrm{v}2} \qquad (5.5)$$

One could then ask for the relation between the two nonequilibrium chemical potentials (5.1) and (5.5). The key to understanding this is to realize that at constant temperature the internal energy u under a nonvanishing $P_{xx}{}^{\mathrm{v}}$ is different from the internal energy in equilibrium, u_{eq}, corresponding to $P_{xx}{}^{\mathrm{v}} = 0$. One should identify the equilibrium chemical potential as $\mu_{\mathrm{eq}}(u_{\mathrm{eq}})$ rather than as $\mu_{\mathrm{eq}}(u)$, which is the first term on the right-hand side of (5.5). Thomas and Windle keep the classical local-equilibrium form for the chemical potential, but they take into account the fact that the pressure is no longer the equilibrium pressure but that it has nonequilibrium contributions. From this point of view, (5.5) could be written in the more convenient and illustrative way

$$\mu_{\mathrm{noneq}}(T,p+P_{xx}{}^{\mathrm{v}},c_{\mathrm{i}}) = \mu_{\mathrm{eq}}(T,p) + \bar{V}_1 P_{xx}{}^{\mathrm{v}} + (\partial[\upsilon\tau_l/2\eta_l]/\partial c_{\mathrm{i}})P_{xx}{}^{\mathrm{v}2} \quad (5.6)$$

The first two terms would correspond to the Thomas–Windle approximation, the third one being the contribution characteristic of EIT. Since in the Thomas–Windle theory τ_l is taken to be zero, the third term vanishes in the context of their hypotheses.

The physical meaning and origin of both nonequilibrium terms in (5.6) is very different. The first one may be related to the work of expansion of the polymer under the penetration of the solvent. The second one, on the other side, is related to the purely dissipative effects produced during the decay of the nonequilibrium configuration to the local-equilibrium one.[13] The latter contribution only appears in the generalized Gibbs equation, but it does not influence the transport equations in the linear approximation. However, they could have an influence in the nonlinear approximation. The influence of similar second-order nonequilibrium terms in a heat conduction problem in solids at low temperature has been examined by Coleman et al.[32] and Jou and Casas-Vazquez.[33] These terms are seen to influence the speed of heat pulses in the presence of a temperature gradient: pulses along the mean heat flux are slower than the pulses going against the mean heat flux. This suggests the possible interest to measure the speed of the penetration fronts in case II diffusion in a sample submitted initially to a concentration gradient of solvent. The differences in speed along and against the initial concentration gradients would contain information on the nonlinearities of the system. The problem, of course, would be more involved than the one treated in refs 32 and 33, where the only nonlinear effect was the one coming from the second-order terms arising from the generalized entropy.

As a consequence of the analysis in this paper, it turns out that EIT is a suitable thermodynamic framework for the thermodynamic description of non-Fickian aspects of diffusion. Comparison with the Thomas and Windle theory allows us to identify some coefficients appearing in the equations of EIT. The dynamic scheme of the evolution equations for the fluxes gives further formal support to the model of Durning and Tabor,[12,19], taking into account the relaxation effects in the "osmotic" nonequilibrium pressure. As a difference with this model, EIT contributes some nonequilibrium second-order terms to the chemical potential.

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