# CONTRIBUTION TO THE THEORY OF NONFICKIAN DIFFUSION OF GAS IN A POLYMER

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Based on the previous work on rational thermodynamics of a fluid–solid mixture in linear approximation, an expression for the diffusion flux was derived. This (with tensor phenomenological coefficients) depends linearly on the temperature gradient and on the isothermal gradient of chemical potential, hence not only on the gas concentration gradient but also on the second deformation gradient of the polymer and on the gradient of the internal parameter (characterizing long-term memory effects in the polymer). Nonequilibrium values of the internal parameter may cause a diffusion flux also directly. However, this is not the case in an isotropic solid or fluid polymer, where the tensor phenomenological coefficients and thus also the diffusion coefficient are reduced to scalars. The results are discussed in relation to the classical diffusion in fluids.

Diffusion of gases in polymers is accompanied by phenomena known as the so-called nonfickian diffusion[1,2], which are difficult to describe in terms of classical theories, *e.g.* linear irreversible thermodynamics[3]. Rational thermodynamics developed during the last two decades[4,5] is, in principle, suitable to describe such phenomena, since it is not limited by linearity or closeness to equilibrium. Our preceding work[6] was concerned with the rational thermodynamic theory of mixtures of a fluid (g) and a substance with arbitrary symmetry (s), the linearized version of which leads to an equation for nonfickian diffusion of a gas (g) in a polymer (s), as shown in the text below.

We start from the equations for a linear model mixture of a fluid (g) and solid (s) in ref.[6] and use the same notation; the equations taken from ref.[6] will be numbered with the prefix *I*, *e.g.* Eq. (*I-22*) is equation (*22*) from ref.[6].

We define the chemical potential $g$ of the gas

$$g \equiv \frac{\partial \varrho \hat{f}}{\partial \varrho_g}, \qquad (1)$$

where $\varrho$ denotes density of the mixture, $\hat{f}$ its (specific) free energy and $\varrho_g$ density of the gas (compare Eqs (*I-21, 22, 42*)).

By using Eqs $(I\text{-}22, 59)$ we obtain

$$g = f_g + \frac{P_g}{\varrho_g}, \tag{2}$$

where $P_g$ is the partial pressure and $f_g$ (partial) free energy of component $g$. Hence, $g = \hat{g}(\varrho_g, \mathbf{F}, T, \beta)$, $\mathbf{F}$ denotes the deformation gradient of the polymer (s), $T$ temperature, $\beta$ internal parameter, characterizing the long-term memory of the polymer.

Now, we express the interaction volume force $\mathbf{k}$ from the momentum balance $(I\text{-}10)$ of the gas and use Eqs $(1)$, $(2)$, $(I\text{-}22, 58)$ to obtain

$$\mathbf{k} = \varrho_g \frac{D_g \mathbf{v}_g}{Dt} - \varrho_g \mathbf{b}_g + \varrho_g \operatorname{grad} g + \frac{\partial \varrho_g \hat{f}_g}{\partial \varrho_g} \mathbf{h} + \varrho_s \frac{\partial \hat{f}_s}{\partial \varrho_g} \mathbf{h} - \operatorname{grad} \varrho_g f_g, \tag{3}$$

where $\mathbf{v}_g$ denotes velocity of the gas, $D_g \mathbf{v}_g / Dt$ its acceleration $(cf.$ Eq. $(I\text{-}3))$, $\mathbf{b}_g$ external volume force, and $\mathbf{h} = \operatorname{grad} \varrho_g$. The term $\mathbf{k}$ can be expressed from the constitutive equation $(I\text{-}72)$ and the last gradient is calculated on the basis of Eq. $(I\text{-}56)$. After rearrangement and using Eq. $(2)$ we obtain an equation for the diffusion rate $\mathbf{u}$

$$-\mathbf{K}_1 \mathbf{u} = -\mathbf{k}_0 + \varrho_g \operatorname{grad}_T g + \varrho_g \frac{D_g \mathbf{v}_g}{Dt} - \varrho_g \mathbf{b}_g + \left(\frac{\partial \hat{P}_g}{\partial T} \mathbf{1} + \mathbf{K}_2\right) \mathbf{g}, \tag{4}$$

where $\mathbf{1}$ denotes unit tensor (the tensor coefficients $K_1^{ij}$ and $K_2^{ij}$ are in direct notation) and the isothermal gradient of chemical potential is defined as

$$\operatorname{grad}_T g \equiv \operatorname{grad} g - \frac{\partial \hat{g}}{\partial T} \mathbf{g} \tag{5}$$

with $\mathbf{g} = \operatorname{grad} T$. Hence,

$$(\operatorname{grad}_T g)^i = \frac{\partial \hat{g}}{\partial \varrho_g} h^i + \frac{\partial \hat{g}}{\partial F^{jJ}} G^{jJK} F^{-1Ki} + \frac{\partial \hat{g}}{\partial \beta} (\operatorname{grad} \beta)^i. \tag{6}$$

Eq. $(4)$ enables us to express the diffusion flux $\mathbf{j}$ of the gas in the solid

$$\mathbf{j} \equiv \varrho_g \mathbf{u} \tag{7}$$

in the form used in irreversible thermodynamics of liquid mixtures[3,4] (we assume the existence of the inversion $\mathbf{K}_1^{-1}$)

$$-\mathbf{j} = \mathbf{l}_0 + \mathbf{L}\mathbf{y} + \mathbf{L}_q \mathbf{g}. \tag{8}$$

Here, the driving force of diffusion is defined as (Eq. $(51.4)$ in ref.[4])

$$\boldsymbol{y} = \mathrm{grad}_T\, g - \boldsymbol{b}_g + \frac{\mathrm{D}_g \boldsymbol{v}_g}{\mathrm{D}t} \tag{9}$$

and the phenomenological coefficients are the vector $\boldsymbol{l}_0$ and the tensors $\boldsymbol{L}$ and $\boldsymbol{L}_q$

$$\boldsymbol{l}_0 \equiv -\varrho_g \boldsymbol{K}_1^{-1} \boldsymbol{k}_0\,, \quad \boldsymbol{L} \equiv \varrho_g^2 \boldsymbol{K}_1^{-1}\,,$$

$$\boldsymbol{L}_q \equiv \varrho_g \boldsymbol{K}_1^{-1} \left( \frac{\partial \hat{P}_g}{\partial T}\, \boldsymbol{1} + \boldsymbol{K}_2 \right). \tag{10}$$

It is obvious that these coefficients depend on $\beta_g$, $\boldsymbol{F}$, $T$, and $\beta$. (An equation similar to $(8)$ can be obtained from the constitutive equations for the heat flux $(I\text{-}73)$ by substituting Eq. $(4)$ for $\boldsymbol{u}$; it turns out that the Onsager reciprocal relations follow from rational thermodynamics only after introducing additional asumptions, as shown in ref.[4], Section 51.)

In practical cases, we usually have to deal with isothermal diffusion $(\boldsymbol{g} = \boldsymbol{o})$ without external fields and inertial forces $(\boldsymbol{b}_g = \boldsymbol{o}, \mathrm{D}_g\boldsymbol{v}_g/\mathrm{D}t = \boldsymbol{o})$ (ref.[4], Section 52). The nonfickian diffusion will then be described by the equation

$$-j^i = l_0^i + L^{ij} \left( \frac{\partial \hat{g}}{\partial \varrho_g}\, {}^i h^j + \frac{\partial \hat{g}}{\partial F^{kJ}}\, G^{kJK} F^{-1KJ} + \frac{\partial \hat{g}}{\partial \beta} (\mathrm{grad}\, \beta)^j \right), \tag{11}$$

where the vector $\boldsymbol{l}_0$ and tensor $\boldsymbol{L}$ of the second order are functions of $\varrho_g$, $\boldsymbol{F}$, $T$, and $\beta$.

We shall discuss first the terms connected with the coefficient $\boldsymbol{L}$. The first one belongs to the classical law of Fick (the deviations are discussed below with Eqs $(13)$ and $(14)$) with a tensor diffusion coefficient, $\boldsymbol{L}(\partial\hat{g}/\partial\varrho_g)$ (ref.[3], Eq. $IV\text{-}23$) and the remaining terms are the cause of "nonfickian" diffusion: the second one expresses the effect of deformation on the diffusion flux (due, *e.g.*, to swelling of the polymer during the experiment) and the third gives the effect of the gradient of the internal parameter $\beta$. This parameter is involved implicitly also in the term $\boldsymbol{l}_0$, however when $\beta$ attains its "equilibrium" value $\beta^+$ (for which Eq. $(I\text{-}75)$ is valid) the vector $\boldsymbol{l}_0$ is equal to zero (see the first one of Eqs $(10)$ and $(I\text{-}76)$). This occurs (except for the trivial case of equilibrium $(I\text{-}46)$ where no diffusion takes place) if the relaxation processes related to $\beta$ are sufficiently rapid or negligible (material without influence of the internal parameter). Besides that, the vector $\boldsymbol{l}_0$ is equal to zero in an isotropic and liquid membrane material. In isotropic material, this is clear from the first of equations $(I\text{-}84)$ and $(10)$; the second term in Eq. $(6)$ can be replaced in an analogous way as in deriving the last expressions in $(I\text{-}80)$ and $(I\text{-}72)$. Thus, nonfickian dif-

fusion in an isotropic material (isothermal without external and inertial forces) is described by the equation

$$-j^i = L^{ij}\left(\frac{\partial \tilde{g}}{\partial \varrho_g} h^j + \frac{\partial \tilde{g}}{\partial B^{lk}} (\text{grad } \boldsymbol{B})^{lkj} + \frac{\partial \tilde{g}}{\partial \beta} (\text{grad } \beta)^j\right), \qquad (12)$$

since in this case $g = \tilde{g}(\varrho_g, \boldsymbol{B}, T, \beta)$ and $\boldsymbol{L} = \tilde{\boldsymbol{L}}(\varrho_g, \boldsymbol{B}, T, \beta)$. Here, the terms have similar significance as in Eq. (11). The tensor $\boldsymbol{L}$ as well as the tensor diffusion coefficient $\boldsymbol{L}(\partial \tilde{g}/\partial \varrho_g)$ in an isotropic material is reduced to a scalar only in special cases[6], e.g. in undistorted reference, during volume expansion or compression, and in infinitesimal deformations.

Finally, if the polymer material is also liquid, the vector $\boldsymbol{l}_0$ is cancelled again (we have again the first of equations (10) and (I-84), compare (I-88)) and the second term in Eq. (6) is replaced as in the derivation of the last term in Eq. (I-88) from the last term in Eq. (I-72). The tensor coefficient $\boldsymbol{L}$ is reduced to a scalar $L$ as follows by introducing Eq. (I-88) into (3) with regard to the second of Eqs (10); similarly $\boldsymbol{L}_q$ is also reduced to a scalar. Thus, the diffusion of a fluid (g) in a fluid (s) (isothermal without external and inertial forces) will be described by the equation

$$-\boldsymbol{j} = L\left(\frac{\partial \bar{g}}{\partial \varrho_g} \boldsymbol{h} + \frac{\partial \bar{g}}{\partial \varrho_s} \boldsymbol{h}_s + \frac{\partial \bar{g}}{\partial \beta} \text{grad } \beta\right), \qquad (13)$$

where $\boldsymbol{g} = \bar{g}(\varrho_g, \varrho_s, T, \beta)$ and $\boldsymbol{h}_s = \text{grad } \varrho_s$; the scalar phenomenological coefficient $L$ depends also on $\varrho_g, \varrho_s, T,$ and $\beta$.

The meaning of the second term in Eq. (11) or (12) with respect to diffusion in a mixture of liquids now becomes apparent. If we neglect the last term (i.e. the effect of internal parameters), we should obtain the classical law of Fick, however this is the case only for $\boldsymbol{h}_s \approx \boldsymbol{o}$ (e.g. at low concentrations of the diffusing component), leading to the diffusion coefficient $L(\partial \tilde{g}/\partial \varrho_g)$. In the more general case, the difference is due to the fact that the derivation of Fick's law from irreversible thermodynamics[3] involves $T$, $P$, and $w_g$ ($w_g$ is mass fraction of component (g) and $P$ total pressure) rather than $T$, $\varrho_g$, and $\varrho_s$. This is due to replacement of the density in the equations $\varrho_g = w_g \varrho$ and $\varrho_s = (1 - w_g) \varrho$ by using the inverted relation $P = \bar{P}(\varrho_g, \varrho_s, T)$; $P$ is equal to the sum of partial pressures of the components, $P_g + P_s$ (compare Eqs (I-87, 59, 86); $\beta$ is disregarded). The isothermal gradient based on these variables is different from that in Eq. (5) (compare Eq. III-23 in ref.[3] or (51.3) in ref.[4]); if we use it instead of (5) (after substituting Eq. (I-88) into (3)), we obtain Eq. (51.5) in ref.[4] for a binary mixture (we disregard the friction tensor and use Eq. (43.41) in ref.[4]), whence the classical results can be obtained (Sections 51 and 52 in ref.[4], XI.2 in ref.[3]). For example, for isothermal diffusion without external and inertial

forces and with the use of the new variables, Eq. $(13)$ is replaced by

$$-\boldsymbol{j} = L\left(\frac{\partial g}{\partial w_g}\operatorname{grad} w_g + \frac{\partial g}{\partial P}\operatorname{grad} P + \frac{\partial g}{\partial \beta}\operatorname{grad}\beta\right), \qquad (14)$$

where $g = g(T, P, w_g, \beta)$ and $L = L(T, P, w_g, \beta)$. This equation is in the case of iso-thermal and isobaric diffusion (without external and inertial forces and internal parameter $\beta$) reduced to the classical Fick law

$$-\boldsymbol{j} = L\,\frac{\partial g}{\partial w_g}\operatorname{grad} w_g \qquad (15)$$

with the diffusion coefficient $L(\partial g/\partial w_g)$ (compare Sections 51 and 52 in ref.[4] or XI in ref.[3]). As mentioned in ref.[6], the phenomenological coefficients $L$ and $\boldsymbol{L}$ are nonnegative or positively semidefinite; the same applies to the diffusion coefficients, since the thermodynamic multiplier is positive owing to stability (see, *e.g.*, ref.[4], Section 48).

We thus arrive at the conclusion (disregarding internal parameters) that the second deformation gradient $\boldsymbol{G}$ in the driving force $(11)$ for fluids corresponds to baro-diffusion and has therefore a classical "Fickian" character.

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