

# On Diffusion Through Soft Filter

K. Y. Volokh

Faculty of Civil and Environmental Engineering,  
Technion—Israel Institute of Technology,  
Hafia 32000, Israel  
e-mail: cvolokh@technion.ac.il

*Diffusion through soft polymer filters is a nonlinear process: the increase of the pressure on the filtrating liquid does not trigger the proportional increase of the flux through the filter. There are two sources of nonlinearity: the diffusivity properties of the filter and its high deformability. In the present work we use a theoretical formulation coupling large deformations and diffusion to describe a liquid flux through a polymeric filter. Two key factors making the present formulation simple are the molecular incompressibility condition and the nonlinear mobility tensor. The developed model is calibrated based on the experiments on toluene-rubber filtration. [DOI: 10.1115/1.4005578]*

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## 1 Introduction

Gibbs [1] started modeling the chemomechanical coupling and diffusion and the subsequent progress concerning diffusion in soft materials was essentially due to the work in Flory and Rehner [2,3], see also Ref. [4]. Modern developments are profoundly based on continuum mechanics and they are present, for example, in Refs. [5–10]. The quoted works differ in the complexity of the theoretical formulations. Combining the approaches of the quoted works, we set a coupled deformation-diffusion problem aiming at the *simplest possible formulation*, which includes a nonlinear diffusion. The formulation is used to solve the problem of the diffusion of toluene through a soft rubber filter.

## 2 Governing Equations

We assume that the inertia effects of the infiltrating liquid are negligible as well as the momentum transfer from the liquid to the solid. These assumptions allow us to describe the filtration process by the altering concentration of the liquid within a solid particle—an infinitesimal volume of soft filter.

Thus, the first governing equation sets the equilibrium for the infiltrated solid without inertia and body forces

$$\oint \boldsymbol{\sigma} \mathbf{n} dA = \mathbf{0} \quad (2.1)$$

where  $\boldsymbol{\sigma}$  is the Cauchy stress tensor and  $\mathbf{n}$  is the unit outward normal to the body surface  $A$ .

By using the divergence theorem it is possible to localize the equilibrium equation as follows

$$\text{div} \boldsymbol{\sigma} = \mathbf{0} \quad (2.2)$$

where  $(\text{div} \boldsymbol{\sigma})_i = \partial \sigma_{ij} / \partial y_j$  is calculated with respect to the spatial coordinates.

Boundary conditions on tractions or placements read accordingly

$$\boldsymbol{\sigma} \mathbf{n} = \bar{\mathbf{t}} \quad \text{or} \quad \mathbf{y}(\mathbf{x}) = \bar{\mathbf{y}} \quad (2.3)$$

where the barred quantities are prescribed and  $\mathbf{x}$  designates the referential position of the particle moved to position  $\mathbf{y}(\mathbf{x})$  after the deformation.

The equilibrium equation and boundary conditions should be coupled with the balance equation for the infiltrating liquid, which can be set in the form

$$\frac{d}{dt} \int c dV = \int \xi dV + \oint \boldsymbol{\varphi} \cdot \mathbf{n} dA \quad (2.4)$$

where  $c$  is the true concentration, i.e., the number of molecules/ moles of the liquid per unit current volume of the mixture;  $\xi$  is its volumetric supply and  $\boldsymbol{\varphi}$  is its flux through the body surface.

Localizing Eq. (2.4) we formulate the differential balance equation for the infiltrating liquid

$$\frac{\partial c}{\partial t} + \text{div}(c\mathbf{v}) = \text{div} \boldsymbol{\varphi} + \xi \quad (2.5)$$

Its boundary conditions read

$$\boldsymbol{\varphi} \cdot \mathbf{n} = \bar{\boldsymbol{\varphi}}_n \quad \text{or} \quad f(c) = 0 \quad (2.6)$$

where  $f$  is a boundary constraint imposed on the concentration.

The initial condition takes form

$$c(t=0) = \bar{c} \quad (2.7)$$

Since the deformed boundary is generally not known in advance, it can be advantageous to use the referential description where Eqs. (2.1)–(2.7) take the following forms accordingly:

$$\oint \mathbf{T} \mathbf{n}_0 dA_0 = \mathbf{0} \quad (2.8)$$

$$\text{Div} \mathbf{T} = \mathbf{0} \quad (2.9)$$

$$\mathbf{T} \mathbf{n}_0 = \bar{\mathbf{t}}_0 \quad \text{or} \quad \mathbf{y}(\mathbf{x}) = \bar{\mathbf{y}} \quad (2.10)$$

$$\frac{d}{dt} \int c_0 dV_0 = \int \xi_0 dV_0 + \oint \boldsymbol{\varphi}_0 \cdot \mathbf{n}_0 dA_0 \quad (2.11)$$

$$\frac{\partial c_0}{\partial t} = \text{Div} \boldsymbol{\varphi}_0 + \xi_0 \quad (2.12)$$

$$\boldsymbol{\varphi}_0 \cdot \mathbf{n}_0 = \bar{\boldsymbol{\varphi}}_{0n} \quad \text{or} \quad f_0(c_0) = 0 \quad (2.13)$$

$$c_0(t=0) = \bar{c}_0 \quad (2.14)$$

where  $\mathbf{T}$  is the 1st Piola-Kirchhoff stress tensor and  $(\text{Div} \mathbf{T})_i = \partial T_{ij} / \partial x_j$  is calculated with respect to the referential coordinates.

The spatial (Eulerian) and referential (Lagrangian) quantities are related as follows

$$dV = J dV_0 \quad (2.15)$$

$$\mathbf{n} dA = J \mathbf{F}^{-T} \mathbf{n}_0 dA_0 \quad (2.16)$$

$$\boldsymbol{\sigma} = J^{-1} \mathbf{T} \mathbf{F}^T \quad (2.17)$$

$$c = J^{-1} c_0 \quad (2.18)$$

$$\xi = J^{-1} \xi_0 \quad (2.19)$$

$$\boldsymbol{\varphi} = J^{-1} \mathbf{F} \boldsymbol{\varphi}_0 \quad (2.20)$$

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where

$$\mathbf{F} = \partial \mathbf{y} / \partial \mathbf{x} \quad (2.21)$$

is the deformation gradient and  $J = \det \mathbf{F}$ .

In addition to the balance laws, it is necessary to formulate the constitutive equations that can generally be written in the following form

$$\mathbf{T} = \mathbf{T}(\mathbf{C}, c_0, \nabla c_0) \quad (2.22)$$

$$\boldsymbol{\varphi}_0 = \boldsymbol{\varphi}_0(\mathbf{C}, c_0, \nabla c_0) \quad (2.23)$$

$$\xi_0 = \xi_0(\mathbf{C}, c_0, \nabla c_0), \quad (2.24)$$

where  $\mathbf{C} = \mathbf{F}^T \mathbf{F}$  is the right Cauchy-Green deformation tensor and  $(\nabla c_0)_i = \partial c_0 / \partial x_i$ .

It is important to emphasize that the flux should depend on the gradient of the concentration to provide the *second order* of the balance equations.

### 3 Diffusion Through Filter

Based on the described theoretical framework, we examine the problem of the diffusion of the *toluene* liquid through a rubber filter—Fig. 1—that was considered in the experiments of Paul and Ebra-Lima [11].

The rubber filter is placed on a permeable porous plate and the liquid diffuses through it under pressure  $p_2 > p_1$ . We assume that the volumetric source is zero:  $\xi_0 = 0$ ; and the process is steady state:  $\dot{c}_0 = 0$ . Under these assumptions the balance equations reduce to

$$\text{Div } \mathbf{T} = \mathbf{0} \quad (3.1)$$

$$\text{Div } \boldsymbol{\varphi}_0 = \mathbf{0} \quad (3.2)$$

The constitutive equations can be defined as follows; for example,

$$\mathbf{T} = 2\mathbf{F} \frac{\partial W(\mathbf{C}, c_0)}{\partial \mathbf{C}} \quad (3.3)$$

$$\boldsymbol{\varphi}_0 = \mathbf{M}(c_0, \mathbf{C}) \nabla \mu \quad (3.4)$$

$$\mu = \frac{\partial W(\mathbf{C}, c_0)}{\partial c_0} \quad (3.5)$$

where  $W$  is the Helmholtz free energy function,  $\mathbf{M}$  is the *mobility tensor*, and  $\mu$  is the *chemical potential*.

Following Ref. [9], we assume the *molecular incompressibility constraint*

$$\gamma(c_0, \mathbf{F}) = 1 + v c_0 - J = 0 \quad (3.6)$$

where  $v$  is the volume of one molecule of the liquid.

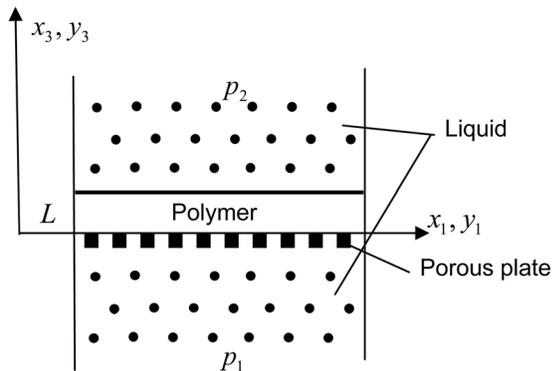


Fig. 1 Diffusion through a soft polymer filter

The increment of this constraint takes form

$$\dot{\gamma} = \frac{\partial \gamma}{\partial c_0} \dot{c}_0 + \frac{\partial \gamma}{\partial \mathbf{F}} : \dot{\mathbf{F}} = v \dot{c}_0 - J \mathbf{F}^{-T} : \dot{\mathbf{F}} = 0 \quad (3.7)$$

Multipliers  $v$  and  $-J \mathbf{F}^{-T}$  in Eq. (3.7) represent the workless chemical potential and stress accordingly, which can be scaled by arbitrary factor  $\Pi$ . With account of Eq. (3.7), we modify Eq. (3.3) and Eq. (3.5) as follows

$$\mathbf{T} = 2\mathbf{F} \underbrace{\frac{\partial W}{\partial \mathbf{C}}}_{\tilde{\mathbf{T}}} - J \Pi \mathbf{F}^{-T} = \tilde{\mathbf{T}} - J \Pi \mathbf{F}^{-T} \quad (3.8)$$

$$\mu = \frac{\partial W}{\partial c_0} + v \Pi \quad (3.9)$$

Since the thickness of the filter is small as compared to its width, we can consider the field variations in the lateral directions only. Specifically, we set the deformation and concentration gradients in the following forms accordingly

$$\mathbf{F} = \mathbf{e}_1 \otimes \mathbf{e}_1 + \mathbf{e}_2 \otimes \mathbf{e}_2 + \lambda(x_3) \mathbf{e}_3 \otimes \mathbf{e}_3 \quad (3.10)$$

$$\boldsymbol{\varphi}_0 = \varphi_{03} \mathbf{e}_3 \quad (3.11)$$

Substituting Eqs. (3.10)–(3.11) in Eq. (3.8) and Eq. (3.4), we get the following nontrivial stresses and fluxes

$$T_{11} = T_{22} = \tilde{T}_{11} - \lambda \Pi \quad (3.12)$$

$$T_{33} = \tilde{T}_{33} - \Pi \quad (3.13)$$

$$\varphi_{03} = M_{33} \frac{\partial \mu}{\partial x_3} \quad (3.14)$$

We notice that the traction/placement boundary conditions take the following forms on the upper and lower surfaces of the membrane accordingly

$$T_{33}(L) = -p_2 \quad (3.15)$$

$$y_3(0) = 0 \quad (3.16)$$

Since the stress tensor is divergence-free and  $T_{33} = \text{constant}$ , we can obtain the unknown multiplier  $\Pi$  from the boundary condition in Eq. (3.15)

$$\Pi = \tilde{T}_{33} + p_2 \quad (3.17)$$

Substituting Eq. (3.17) in Eq. (3.9), we obtain for the chemical potential

$$\mu = \frac{\partial W}{\partial c_0} + v \tilde{T}_{33} + v p_2 \quad (3.18)$$

We also notice that, due to the molecular incompressibility condition, the concentration is related to the stretch as follows

$$v c_0 = \lambda - 1 \quad (3.19)$$

Substituting Eqs. (3.18)–(3.19) and Eq. (3.14) in Eq. (3.2), we get a second order ordinary differential equation of the chemical balance in term of stretches. To solve it, we need to impose two boundary conditions

$$f(\lambda_1) = \mu(\lambda_1) - p_1 v = 0 \quad (3.20)$$

$$f(\lambda_2) = \mu(\lambda_2) - p_2 v = 0 \quad (3.21)$$

where  $\lambda_1 = \lambda(0)$  and  $\lambda_2 = \lambda(L)$ .

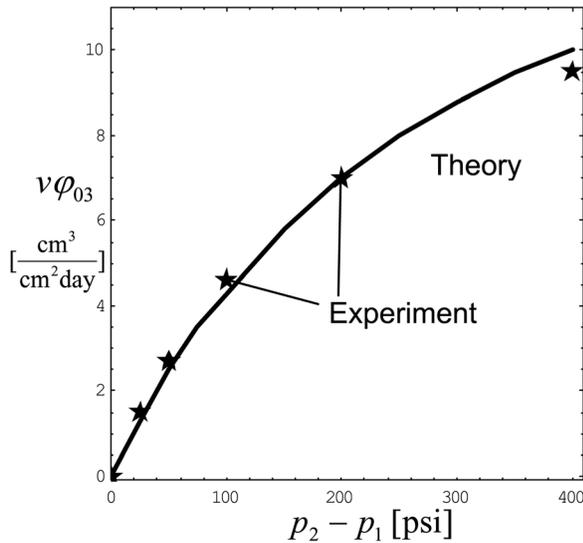


Fig. 2 Flux versus pressure

We define the mobility tensor and the Helmholtz free energy function as follows

$$\mathbf{M} = (\alpha c_0 v)^{\beta-1} \frac{c_0 D}{kT} \mathbf{C}^{-1} \quad (3.22)$$

$$W = \underbrace{\frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \log[\lambda_1 \lambda_2 \lambda_3])}_{\text{Elastic energy}} - \underbrace{\frac{kT}{v} \left( v c_0 \log \left[ 1 + \frac{1}{v c_0} \right] + \frac{\chi}{1 + v c_0} \right)}_{\text{Energy of mixing}} \quad (3.23)$$

where  $\alpha$  and  $\beta$  are dimensionless material constants to be fitted to experiments;  $D$  is the diffusion coefficient for the solvent molecules,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $N$  is the number of polymer chains in the gel divided by the reference volume,  $\chi$  is a dimensionless parameter, and  $\lambda_i$  are the principal stretches.

We notice that the neo-Hookean elastic energy and the Flory-Huggins energy of mixing in Eq. (3.23) follow the standard formulation based on the microscopic statistical considerations—see Ref. [4], for example. Contrary to the statistical considerations the choice of the mobility tensor in Eq. (3.22) is purely phenomenological. In the case of  $\beta = 1$  we have the linear diffusion, which, unfortunately, does not allow fitting the experimental data obtained in Ref. [11]. In the case of  $\beta > 1$ , more flexibility is introduced into the theory to account for the nonlinear diffusion—see also Ref. [7]. Of course, some statistical reasoning justifying the choice of the phenomenological parameters  $\alpha$  and  $\beta$  would be highly welcome. We will not pursue the statistical approach in the present work, however, regarding the simple phenomenology as a good approximation.

Substituting Eq. (3.22) in Eq. (3.4) and accounting for Eqs. (3.10)–(3.11) we obtain

$$\varphi_{03} = (\alpha c_0 v)^{\beta-1} \frac{c_0 D}{kT} \lambda^{-2} \frac{\partial \mu}{\partial x_3} \quad (3.24)$$

Differentiating Eq. (3.23) with respect to stretches and concentration and accounting for Eq. (3.19) we find

Table 1 Toluene-rubber data

$k$	$1.38 \cdot 10^{-23}$ Nm/K
$T$	303° K
$p_1$	$10^5$ N/m <sup>2</sup>
$v$	$17.7 \cdot 10^{-29}$ m <sup>3</sup>
$D$	$2.36 \cdot 10^{-10}$ m <sup>2</sup> /s
$N$	$6.36 \cdot 10^{25}$ 1/m <sup>3</sup>
$L$	$2.65 \cdot 10^{-4}$ m
$\chi$	0.425
$\alpha$	5.7
$\beta$	3

$$\tilde{T}_{33} = NkT(\lambda - \lambda^{-1}) \quad (3.25)$$

$$\frac{\partial W}{\partial c_0} = kT \left( \log \frac{\lambda - 1}{\lambda} + \frac{1}{\lambda} + \frac{\chi}{\lambda^2} \right) \quad (3.26)$$

Substituting Eqs. (3.25)–(3.26) in Eq. (3.18) we have finally

$$\mu = kT \left( \log \frac{\lambda - 1}{\lambda} + \frac{1}{\lambda} + \frac{\chi}{\lambda^2} \right) + Nv kT (\lambda - \lambda^{-1}) + v p_2 \quad (3.27)$$

Substituting Eq. (3.27) in Eq. (3.14) and Eq. (3.2), we have a second-order ordinary differential equation, which is completed by the boundary conditions noted in Eqs. (3.20)–(3.21).

Based on the numerical solution of the boundary-value problem it is possible to calculate the increase of the flux through the filter with the pressure increase—Fig. 2—for the *toluene-rubber* data shown in the Table 1.

We notice that all parameters in Table 1 are given except for  $\alpha = 5.7$  and  $\beta = 3$  that were fitted to the experimental data.

#### 4 Conclusion

A simple model of a liquid diffusion through the soft polymer filter was developed and calibrated for the toluene-rubber data. The simplicity was achieved by the use of the molecular incompressibility condition and the nonlinear mobility tensor. The proposed scheme can be easily applied to other filtration problems if necessary.

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