INTERNATIONAL JOURNAL OF
NUMERICAL ANALYSIS AND MODELING
Volume 8, Number 2, Pages 226–251

FINITE ELEMENT APPROXIMATION OF A NON-LOCAL PROBLEM IN NON-FICKIAN POLYMER DIFFUSION

SIMON SHAW

(Communicated by Mark Ainsworth)

Abstract. The problem of non-local nonlinear non-Fickian polymer diffusion as modelled by a diffusion equation with a nonlinearly coupled boundary value problem for a viscoelastic 'pseudostress' is considered (see, for example, DA Edwards in Z. angew. Math. Phys., **52**, 2001, pp. 254—288). We present two numerical schemes using the implicit Euler method and also the Crank-Nicolson method. Each scheme uses a Galerkin finite element method for the spatial discretisation. Special attention is paid to linearising the discrete equations by extrapolating the value of the nonlinear terms from previous time steps. *A priori* error estimates are given, based on the usual assumptions that the exact solution possesses certain regularity properties, and numerical experiments are given to support these error estimates. We demonstrate by example that although both schemes converge at their optimal rates the Euler method may be more robust than the Crank-Nicolson method for problems of practical relevance.

Key words. *a priori* error estimates, nonlinear diffusion, non-Fickian diffusion, finite element method, linearisation, extrapolation, implicit Euler, Crank-Nicolson

1. Introduction and background

In [12, 11] Thomas & Windle demonstrated by experiment that diffusion of a solvent in a viscoelastic polymer matrix is highly non-Fickian with the solvent concentration developing a steep, and possibly travelling, wave front. This front demarcates a concentration-forced phase transition of the polymer from a 'glassy' state to a 'rubbery' state. The viscoelastic time constants in the viscoelastic stress-strain constitutive equation vary sharply across this transition, and this variation is believed to be basic driving mechanism behind the formation of the steep stationary or travelling fronts.

To date most modern attempts at modelling this phenomenon mathematically have been based on introducing a temporal nonlocality into the classical Fickian diffusion law using a hereditary integral for a concentration-induced 'stress'. The motivation is of course from the phenomenological theory of viscoelasticity, e.g. [8], where stress is usually written as a convolution of strain with a 'relaxation function'. The decaying exponential form of this relaxation function then allows the stress in the non-Fickian diffusion law to be represented in terms of an ordinary differential equation (in time). This equation is nonlinearly coupled to the partial differential equation for the concentration. See [4, 5] for more on this and [2, 10] for some related numerical analysis.

In an alternative approach Edwards in [6, 7] argued the need to also permit spatial nonlocality due to the 'long chain' polymer molecules being much larger than the penetrant's molecules. He then proposed a non-Fickian diffusion model based on the introduction of a spatially nonlocal 'viscoelastic *psuedostress*'. The

Received by the editors April 30, 2010 and, in revised form, July 22, 2010.
2000 *Mathematics Subject Classification.* 74S05 (FEM), 74S20 (FDM), 76R50 (diffusion), 74D10 (nonlinear constitutive equations), 82D60 (polymers).

result is still a non-Fickian diffusion law but with this time the 'stress' governed by an elliptic partial differential equation which, again, is nonlinearly coupled.

It is important to realise that at present, in the absence of a 'fundamental theory', these models have been proposed with the aim of developing a mathematical formalism that can capture the experimentally observed behaviour. This type of experimental mathematics requires numerical solution and so, with that motivation, our goal here is to give fully discrete formulations and derive *a priori* stability and error estimates. First we review Edwards' model and then we pose it in a form more suited for our purpose.

The model proposed by Edwards in [6] for the concentration, C, and pseudostress, Θ, takes the form,

$$C_\tau = DC_{yy} + M\Theta_{yy}, \tag{1}$$

$$-(\beta(C)^{-1}\Theta_y)_y + \beta(C)\Theta = \eta C - \varkappa C_y, \tag{2}$$

with D, M, η and $\varkappa$ constant with the first three positive and the last non-negative.

Edwards considers this problem on an unbounded domain, but if we restrict to $(a,b) \subset \mathbb{R}$, the pseudostress is given in [6] by,

$$\Theta(y,t) := -\frac{1}{2}\int_a^b f(C(y',t), C_{y'}(y',t)) \exp\left(-\left|\int_{y'}^{y} \beta(C(z,t))\, dz\right|\right) dy' \tag{3}$$

with $f(C, C_y) := -\eta C + \nu C_y$ for $\eta > 0$, $\nu > 0$ and $\beta(\mathbb{R}) > 0$. In this β^{-1}, the *dependence length*, represents the radius of the smallest sphere, centred at z, that contains a typical polymer chain passing through z. Since these chains will be entangled in a random spaghetti-like manner 'holes' or 'pockets' are formed at their intersections and these provide sites for the penetrant's molecules. The ability of such a molecule to diffuse then depends on the strength (density) of the entanglement, β^{-1}, which in turn is influenced by the degree of penetrant saturation. Indeed the key ingredient in this model is the observation that, due to swelling, β^{-1} in the saturated rubber phase is expected to be much larger than β^{-1} in the drier and more crystalline glassy phase. We will return to this below, but note that it is this effect that generates the nonlinear coupling. The spatial nonlocality arises because a 'path of holes' needs to be formed for the penetrant molecule to move, but we expect the entanglment density far from the molecule to have less influence than that nearby—hence the decay built in to (3).

Although it is not necessary to non-dimensionalise this problem it is convenient to simplify it by scaling out some unneccessary parameters. Setting, $\beta_0 := \sqrt{\eta/D}$, $x = \beta_0 y$, $t = \eta\tau$, $u = \eta C$ and $\sigma = \beta_0\Theta$, with the definitions, $\gamma(u) = \beta(C)/\beta_0$, $\nu = \beta_0\varkappa/\eta$ and $E = \beta_0 M$, and then generalising to many space dimensions (since there is no reason not to), we arrive at our model problem.

Let $\Omega \subset \mathbb{R}^d$ $(d = 1, 2, 3)$ be a bounded (polygonal or polyhedral for $d = 2$ or 3) domain and $I := (0, T]$ a finite time interval. We consider the degenerate problem: find u and σ such that,

$$u_t = \nabla^2 u + E\nabla^2\sigma \tag{4}$$

$$-\nabla\cdot\gamma(u)^{-1}\nabla\sigma + \gamma(u)\sigma = u - \boldsymbol{\nu}\cdot\nabla u, \tag{5}$$