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MATHEMATICAL MODELLING AND NUMERICAL ANALYSIS
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# NONEQUILIBRIUM REACTION-DIFFUSION STRUCTURES IN RIGID AND VISCO-ELASTIC MEDIA : KNOTS AND UNSTABLE NONINERTIAL FLOWS (*)

by Peter J. ORTOLEVA ([1])

Abstract — *A simple reaction-diffusion model is used to demonstrate the existence of asymptotic (i e long time) knotted solutions of reaction-transport problems. The knots are attained with respect to the surface of constant concentration. These solutions cannot be mapped continuously onto the plane and as such have no two dimensional analogue — they are strictly three dimensional structures*

*The existence of knotted solutions is first argued for intuitively using the properties of a simple reaction-diffusion system. A variational theorem for this system is then derived Extrema of the associated « energy » functional with knotted topology are obtained numerically The existence of a rich class of knotted and other strictly three dimensional solutions is also discussed*

*When the reaction-diffusion medium is subject to mechanical stresses, flows may result These flows may interact with emerging dissipative structure when the time scales for flow and reaction are comparable Imposed shears may orient compositional patterns If the rheologic properties of the medium depend on composition, vortices may emerge under conditions far below the critical Taylor shear rate*

## I. A FREE BOUNDARY REACTION-DIFFUSION MODEL

Consider the knotted structures of figures 1, 2. Our purpose here is to demonstrate that a surface of equal concentration for the long time solution of a reaction-transport system can take on such topologies. For concreteness consider the reaction-diffusion problem

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i + F_i(\underline{c}) \tag{I.1}$$

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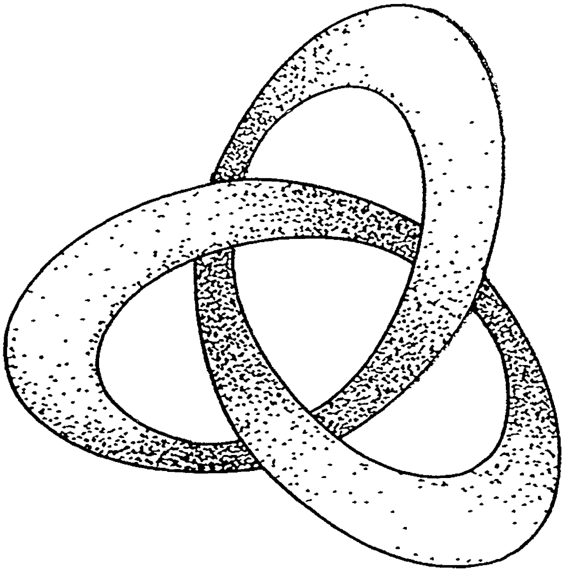

Figure 1.

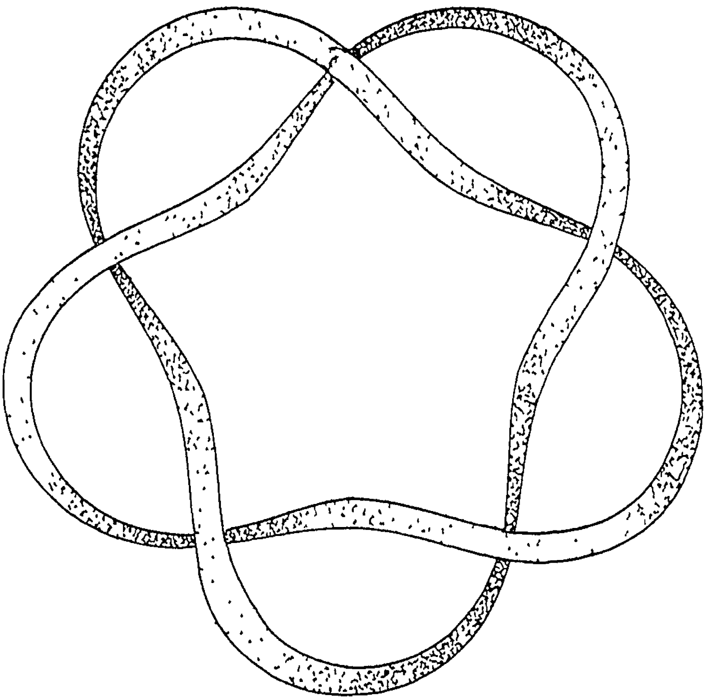

Figure 2.

with appropriate boundary conditions on the $N$ concentrations $i = 1, 2, \ldots, N$. Here $D_i$ is the diffusion coefficient for species $i$ and $F_i(\underline{c})$ is its net rate (a function of $\underline{c} = \{c_1, c_2, \ldots, c_N\}$). We seek to show that even if $\underline{F}$ does not explicitly depend on position $\vec{r}$ and if the domain has no holes or knotted shape, there exist asymptotic solutions of (I.1) such that there is a range of constants $\gamma_1, \gamma_2, \ldots, \gamma_N$ wherein the isoconcentration surfaces $c_i(\vec{r}, t) = \gamma_i$, have knotted structure as $t \to \infty$ [1].

To demonstrate the above conjecture consider the two species problem

$$\frac{\partial X}{\partial t} = D_x \nabla^2 X + \varepsilon^{1/2} F(X, Y) \tag{I.2}$$

$$\frac{\partial Y}{\partial t} = \varepsilon^{1/2} D_y \nabla^2 Y + \frac{1}{\varepsilon} G(X, Y) . \tag{I.3}$$

If the « slow manifold » $G(X, Y) = 0$ has the form as in figure 3 then it has been shown that as $\varepsilon \to 0$ the above problem maps onto a simple free boundary problem as follows [2] (see *fig.* 3 for definitions). There exists a surface denoted $S(\vec{r}, t) = 0$ such that $Y = Y^{\mathrm{I}}$ or $Y^{\mathrm{II}}$ for $S < (>) \, 0$ respectively. The value of $X$, denoted $X_0$ in figure 3, is such that as $\varepsilon \to 0$ the jump in $Y$ is stationary ; for $X \neq X_0$ a $Y$ jump from the lower to the upper branch moves with a velocity that approaches zero as $X \to X_0$. The concentration

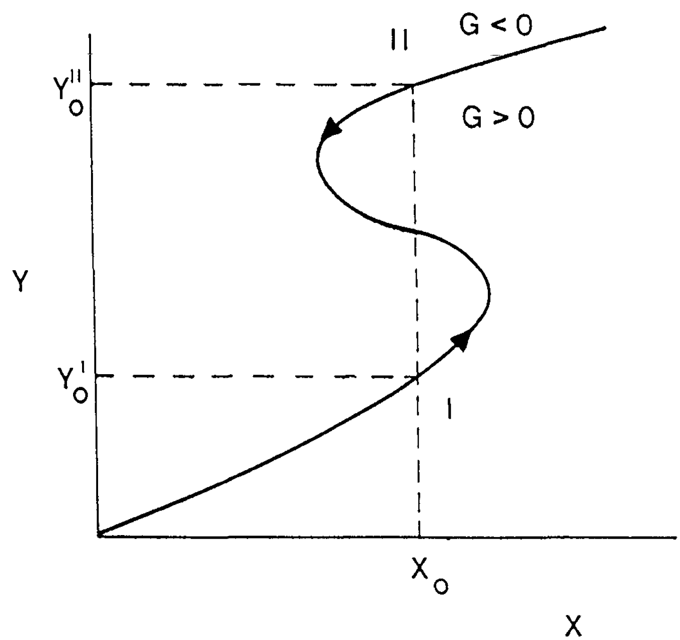


**Figure 3.**

$X$ always lies close to a well defined value $X_0$ such that $X = X_0 + \varepsilon^{1/2} X^*$ defining the scaled concentration deviation $X^*$. The latter satisfies

$$\frac{\partial X^*}{\partial t} = D_x \nabla^2 X^* + f(S) \tag{I.4}$$

$$f(S) = \begin{cases} F^{\mathrm{I}}, & S < 0 \\ F^{\mathrm{II}}, & S > 0 . \end{cases} \tag{I.5}$$

The constant $F^{\mathrm{I}}$ is given by $F^{\mathrm{I}} = F(X_0, Y^{\mathrm{I}})$ and similarly for $F^{\mathrm{II}}$. If $X$ satisfies no-flux boundary conditions then so does $X^*$ ; then we have

$$\frac{\partial X^*}{\partial n} = o \, , \quad \vec{r} \text{ on } \Sigma \tag{I.6}$$

for a system in a domain bounded by the surface $\Sigma$ (where $\partial/\partial n$ is a normal derivative). The above free boundary problem is complete upon specifying the dynamics of the surface $S(\vec{r}, t) = 0$ and imposing continuity of $X^*$ and its gradient across $S(\vec{r}, t) = 0$. The free boundary dynamics is given by

$$\frac{\partial S}{\partial t} = QX^* \left| \vec{\nabla} S \right| \, , \quad S(\vec{r}, t) = 0 \, , \tag{I.7}$$

for well defined constant $Q$.

The above free-boundary problem provides a relatively simple framework for arguing the possibility of knots [1]. In particulier we investigate the existence of steady state solutions ($\partial X^*/\partial t = \partial S/\partial t = 0$) wherein the free boundary $S = 0$ may take on the form of a knot as in figures 1, 2 or even more complex knotted and tangled structures.

## II. BASIC PROPERTIES OF THE FREE BOUNDARY PROBLEM

To motivate an intuitive argument for knotted structures, let us review known properties of simple solutions of the free boundary problem (I.4-7). Static one-dimensional structure along the $x$-spatial axis as in figure 4 may easily be calculated exactly. For $F^{\mathrm{I}} \approx - F^{\mathrm{II}}$ it has been demonstrated that such a structure is linearly stable [3]. When continued into a two-dimensional domain, in a strip for $-\infty < y < \infty$, deviations from planarity in the interface are smoothed out in time (at least when $Q$ is small) [1]. Double interface structures as in figure 5 are repelled from the walls and their width does not collapse [1]. Cylindrical or spherically symmetric solutions may be obtained [1].

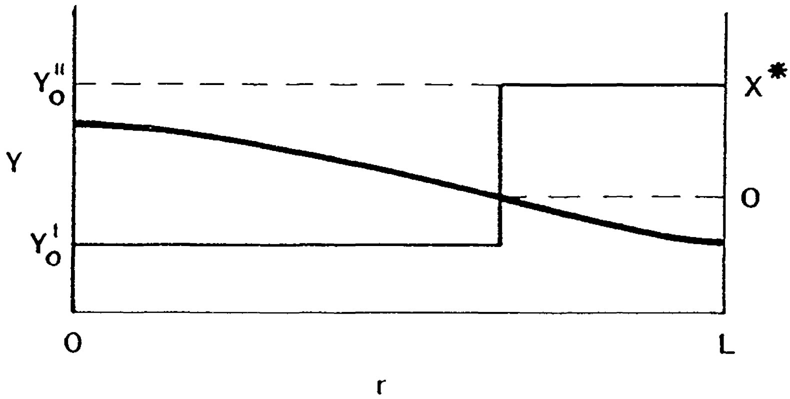


**Figure 4.**

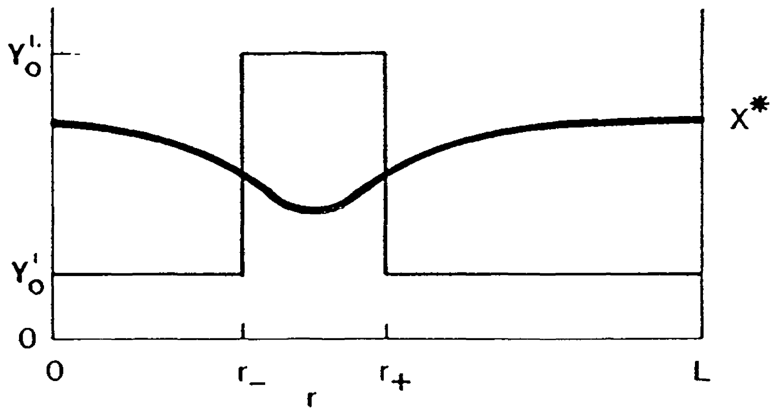


**Figure 5.**

The above mentioned structures and their properties suggest the following :

* the free boundary has a measure of morphological stability (they do not collapse when extended in two or three dimensions) ;

* the free boundaries are repelled by no-flux walls and by other free boundaries ; and

* the free boundaries may take on tubular structures.

This suggests that there may indeed be knotted, tubular free boundaries as in figures 1, 2.

## III. A VARIATIONAL THEOREM FOR STATIC STRUCTURES

Static solutions of the free boundary problem (I 4-7) are such that $X^* \lesseqgtr 0$ for $S \gtrless 0$ With this we may calculate static structures as the solution of

$$D_x \nabla^2 X^* + f(-X^*) = 0 \qquad \text{(III 1)}$$

$$\partial X^*/\partial n = 0 , \quad \vec{r} \text{ on } \Sigma \qquad \text{(III 2)}$$

The solutions of (III 1, 2) are the extrema of the functional $E[X^*]$

$$E[X^*] = \int d^3r \left\{ -\frac{1}{2} D_x |\vec{\nabla} X^*|^2 + X^* f(-X^*) \right\} \qquad \text{(III 3)}$$

This suggests a method for calculating knotted structures One may guess « trial functions » with knotted topology and then use the $E$ functional to optimize the form of the trial function

One approach is to construct a trial function by introducing a line source and then use the variational theorem to determine the equation of the line Let $\tau$ be a parameter generating a trajectory $\vec{r}_0(\tau)$ Introduce a « weight » $W(\tau)$ and range $\sigma(\tau)$ Then we have

$$X^* \sim \int d\tau\, W(\tau) \exp \left\{ - |\vec{r} - \vec{r}_0(\tau)|^2 / 4\,\sigma^2(\tau) \right\} + B(\vec{r}) \qquad \text{(III 4)}$$

where $B(\vec{r})$ is a term fixing the boundary condition on $X^*$ For example in a spherical vessel of radius $R$ take

$$B = B_0 + (R - r)\, e^{-\lambda (r-R)^2} \times$$
$$\times \int d\tau\, W(\tau) \frac{\partial}{\partial r} \exp \left\{ - |\vec{r} - \vec{r}_0(\tau)|^2 / 4\,\sigma^2(\tau) \right\} \qquad \text{(III 5)}$$

where $B_0$ and $\lambda$ are variational parameters and $r = |\vec{r}|$ for the sphere centered at $\vec{r} = \vec{0}$ With this one may use the functional $E[X^*]$ to obtain variational equations for $\vec{r}_0(\tau)$, $W(\tau)$, $\sigma(\tau)$, $B_0$ and $\lambda$ Knotted structures would then be periodic orbits which do not deform continuously onto the plane

To date a more modest approach was adopted, $W$ and $\sigma$ were taken to be independent of $\tau$ , $\vec{r}_0(\tau)$ $(= \{x_0, y_0, z_0\})$ was taken in the form

$$\left.\begin{aligned} x_0^2 + y_0^2 &= \mu^2 \\ x_0 &= \mu \cos \phi_0 \\ y_0 &= \mu \sin \phi_0 \\ \mu &= a + b \cos \tau \\ \phi_0 &= 2\,\tau/(2\,k + 1) \\ z_0 &= -c \sin \tau \end{aligned}\right. \qquad \text{(III 6)}$$

for variational parameters $a$, $b$, $c$. The parameter $k = 1, 2, 3, \ldots$ determines the multiplicity of the knot (see *figs.* 1, 2 for $k = 1, 2$ knots). With this we used a numerical integration algorithm to calculate $E(a, b, c, \sigma, W, \lambda)$ and then used the program STEPIT to determine the best values of the variational parameters for a given $k$ [4].

## IV. REMARKS

Having established the possibility of simple knotted asymptotic states of reaction-transport systems, it is clear that the structures obtained are just a few examples of a very rich class of tangled structures. These can be connected (arising as the weaving of a simple tube with connected ends) or they may involve the intertwining of a number of independent closed tubes. The possibilities are even seen to be greater when we recognize that such structures can themselves exist within larger tubes. Thus, for example, a simple knot may exist within one loop of a larger knot.

It is likely that under some conditions the knot structures may have a temporaly oscillatory nature. For example, it was found that patterns in a disc arising from the free boundary problem of Section I can rotate in specified ranges of parameters [2]. These dynamical states arise as a system parameter passes through a critical value beyond which a rotational frequency rises from zero.

## V. PATTERNING AND REACTING VISCO-ELASTIC MEDIA

The potential for instability and patterning in a reaction-diffusion problem is enhanced when chemical and mechanical variables are coupled. An interesting case in point is metamorphic differentiation. Metamorphic rocks have been subjected to conditions from 6 to 30 km in depth. The mineral content of such rocks is often observed to be distributed in banded, spotted, or concentric shells, or even as spiral (vortex patterns). A typical differentiation is on the cm scale and involves alternating concentrations of quartz and mica.

While rocks do flow, the vortex structures cannot be of the Taylor type. Rock flow is very slow so that their mechanics is non-inertial. Inertial effects are central to the development of a Taylor vortex driven by a shear flow. Hence vortex structures observed in metamorphic rocks cannot be of the Taylor type but rather must involve some type of mechano-chemical coupling.

To illustrate mechano-chemical coupling that can lead to the creation of the above-mentioned patterns, consider our rheologic model of a reacting, noninertial visco-elastic medium [5]. As suggested by the geological application, the medium is described by the distribution in space and time of the following variables :

$R_i$ = average radius of mineral $i$ grains
$n_i$ = number of mineral $i$ grains per volume
$c_\alpha$ = concentration of mobile molecular species $\alpha$ in the intergranular space
$\phi$ = volume fraction of medium occupied by intergranular space (assumed small and constant)
$\vec{u}$ = velocity of rock flow ; and
$\underline{\underline{\sigma}}^m$ = stress tensor (a macroscopic quantity defined as an average over a macrovolume element containing many grains).

In this way we describe the $M$ mineral ($i = 1, 2, \ldots, M$) and $N$ intergranular species ($\alpha = 1, 2, \ldots, N$). It is convenient to introduce the set of quantities $\Theta$ (the « texture ») defined via

$$\Theta = \{R_1, R_2, \ldots, R_M ; n_1, n_2, \ldots, n_M\} . \tag{V.1}$$

The phenomonological relation between $\underline{\underline{\sigma}}^m$ and $\vec{u}$ in rocks can be rather complex. The simplest such relation adopted in the rock mechanics literature is

$$\sigma_{ij}^m = - P^m \delta_{ij} + \eta \left[ \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{1}{3} \vec{\nabla} \cdot \vec{u} \delta_{ij} \right] \tag{V.2}$$

where $P_m = \frac{1}{3} \operatorname{tr} (\underline{\underline{\sigma}}^m)$ and $\partial u_i / \partial x_j$ is the derivative of the $i$-component of $\vec{u}$ with respect to the $j$-th cartesian coordinate ; and $\delta_{ij}$ is the identity matrix. An important source of coupling in the present model is via the texture dependence of the viscousity $\eta$. From $\underline{\underline{\sigma}}^m$ and $\vec{u}$ we are thus reduced to four independent variables that we take to be $u_1$, $u_2$, $u_3$, and $P^m$ (the mean stress). Equations to determine three of them come from momentum conservation ; for these non-inertial fluids we get

$$\sum_{j=1}^{3} \frac{\partial \sigma_{ij}^m}{\partial x_j} = 0 , \quad i = 1, 2, 3 . \tag{V.3}$$

A fourth equation will be derived below from consideration of grain growth kinetics.

The reaction-diffusion equations take the form

$$\vec{\nabla} \cdot (\phi \underline{\underline{D}} \vec{\nabla} \underline{c}) + \underline{\underline{\xi}} \underline{\omega} G = \underline{0} . \tag{V.4}$$

Here $\underline{\underline{D}}$ is a matrix of diffusion coefficients, $\underline{\underline{\xi}}$ is a matrix of stoichiometric coefficients multiplied by solid molar densities ($\xi$ is constant), $\omega$ is a

$M \times M$ diagonal matrix with entries $\omega_\iota = 4\,\pi n_\iota\, R_\iota^2$ and $G_\iota$ is the grain growth rate. Here we use the fact that the $\vec{u}$ is small (so that transport is mainly diffusional) and that the concentrations change adiabatically in response to the slow grain growth rates (i.e. there is no $\partial\phi \underline{c}/\partial t$ term).

Grain growth and number conservation imply

$$\frac{\partial R_\iota}{\partial t} = -\,\vec{u}\,.\,\vec{\nabla} R_\iota + G_\iota \tag{V.5}$$

$$\frac{\partial n_\iota}{\partial t} = -\,\vec{\nabla}\,.\,(\vec{u} n_\iota)\,. \tag{V.6}$$

Because the space between grains is small,the medium is completely filled with solid and hence

$$\sum_{\iota=1}^{M} 4\,\pi n_\iota\, R_\iota^3 = 3\,. \tag{V.7}$$

This may be combined with the grain growth and number conservation equations to obtain

$$\vec{\nabla}\,.\,\vec{u} = \sum_{\iota=1}^{M} 4\,\pi n_\iota\, R_\iota^2\, G_\iota\,. \tag{V.8}$$

These equations point out a second source of mechano-chemical coupling. The grain growth rates depend algebraically on $\underline{\underline{\sigma}}^m$ and $\Theta$ as well as on $\underline{c}$. This is because grain growth is sensitive to the stress on a grain ; the stress on a grain depends on the $\underline{\underline{\sigma}}^m$ acting on the macro-volume element containing it and on the mechanical properties of the grains contained within that element. Thus in an average sense, the rate of growth depends on $\Theta$. (See Refs. [5], [6] for detailed formulae for $G$.)

## VI. MECHANO-CHEMICAL FEEDBACK AND PATTERN FORMATION

The above model allows for a number of feedback mechanisms leading to pattern formation. Consider an initially uniformally textured medium. If the rate of growth of, say, mineral 1 increases with the local volume fraction occupied by mineral 1, then segregation of mineral 1 is indicated. For example, the reaction quartz $\rightleftarrows X$ (where $X$ is mobile $SiO_2$ in the intergranular space) has been taken to have rate in the form

$$G_{\text{quartz}} = k\,[c_X - K(\underline{\underline{\sigma}}^m, \phi_{\text{quartz}})] \tag{VI.1}$$

$$\phi_{\text{quartz}} = \frac{4}{3}\,\pi n_{\text{quartz}}\, R_{\text{quartz}}^3 \tag{VI.2}$$

where $\phi_{quartz}$ is the volume fraction of quartz in, say, the quartz-mica rock The tendency for segregation of quartz from mica is indicated by the fact that under some conditions $K$ decreases with $\phi_{quartz}$ Furthermore, the dependence of $\eta$ on $\phi_{quartz}$ may cause a decrease in $P^m$ with increasing $\phi_{quartz}$ This will again promote quartz segregation because $K$ tends to decrease with $P^m$ Note that the textural coupling through viscousity can only destabilize the uniform medium to infinitesimal perturbations when the uniform state is subject to a shear or other flow In the state of rest of the uniform medium, viscousity coupling is second order [7]

Linear stability analysis of the flow free uniform state shows that metamorphic differentiation can take place In particular the rate of growth of harmonic perturbations can have a well defined maximum as a function of wavelength [7], [8]

The full nonlinear problem has been simulated in one [6] and two [9] spatial dimensions In these simulations spots of mica were found to spontaneously develop in a quartz-mica rock perturbed slightly from uniformity for a model describing deep (20-30 km) rocks Concentric rings of quartz and mica were also observed [9] When a shear is imposed the spots become elongate, tending to align with the imposed flow In these simulations the texture dependence of the viscousity was neglected Even so, the imposed flow can have interesting effects As a spot elongates the associated secondary ring may be brought so close to the inner spot that the minimum wavelength for which patterns grow is passed and the ring may disappear With this an imposed shear may select band formation parallel to shear and with a well defined wavelength

Noninertial vorticies may emerge from a coupling of the spot forming process and texture dependent viscousity In future work it will be of interest to investigate the onset of vorticity as a function of the dependence of $\eta$ on texture, the rate of grain growth, and the mineral content of the initially uniform rock as well as on the imposed rate of shear

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