Homogenization of a Nonlinear Elliptic Boundary Value Problem Modelling Galvanic Interactions on a Heterogeneous Surface

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Summary. We study a nonlinear elliptic boundary value problem arising from electrochemistry. The boundary value problems occurs in the study of heterogeneous electrode surfaces. The boundary condition is of an exponential type and is normally associated with the names of Butler and Volmer and the notions of galvanic corrosion. We examine the questions of existence and uniqueness of solutions to this boundary value problem. We then treat the problem from the point of view of homogenization theory. The boundary condition has a periodic structure. We find a limiting or effective problem as the period approaches zero, along with a correction term and convergence estimates. We also do numerical experiments to investigate the behaviour of galvanic currents near the boundary as the period approaches zero.

Key words: galvanic corrosion, homogenization, nonlinear boundary condition

1 Introduction

Galvanic corrosion is a phenomenon caused by electrochemical interaction between different parts of the same surface. We study this phenomenon. A galvanic interaction occurs when galvanic current flows either between an electrode surface and a counterelectrode or between different parts of the same heterogeneous surface. In Figure 1(a) the silver strip is cathodic, and reduction takes place (Ag gains electrons.) Simultaneously oxidation takes place at the zinc strip, zinc loses electrons, and is said to be anodic. Zinc dissolves into the solution, the zinc electrode is being corroded and the electron flow is known as galvanic current.

In Figure 1(b), a similar oxidation-reduction reaction is taking place between different parts of the same surface. Here, in this paper, we consider a cylindrically shaped domain, and model the oxidation-reduction reaction occurring between different parts of our heterogeneous surface, *i.e.* the two dimensional

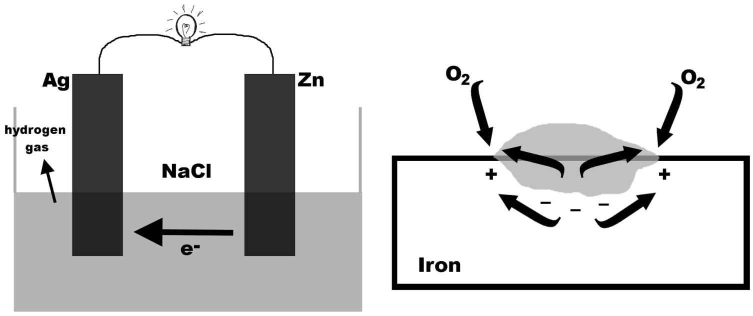

Fig. 1. (a) Zinc loses electrons to Silver, (b) A similar reaction occurs between different parts of the same surface

base of our cylindrically shaped domain Ω. The base, which we will refer to as Γ, contains a periodically regular arrangement of anodic islands in a cathodic plane. All the anodes are the same uniform material. The cathodic plane is also uniform in material (see Figure 2.)

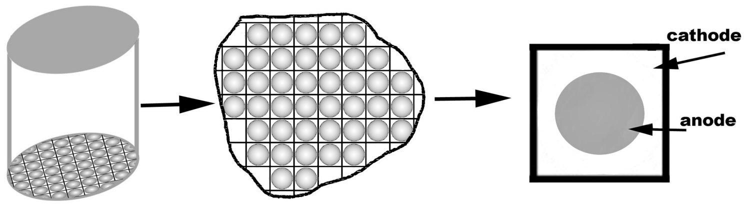

Fig. 2. The base of the cylinder is a heterogeneous surface.

The electrolytic voltage potential, ϕ satisfies the following nonlinear elliptic boundary value problem,

$$
\begin{aligned}
\Delta\phi &= 0 \text{ in } \Omega \\
-\frac{\partial\phi}{\partial n} &= J_A[e^{\alpha_{aa}(\phi - V_A)} - e^{-\alpha_{ac}(\phi - V_A)}] \text{ on } \partial\Omega_A \\
-\frac{\partial\phi}{\partial n} &= J_C[e^{\alpha_{ca}(\phi - V_C)} - e^{-\alpha_{cc}(\phi - V_C)}] \text{ on } \partial\Omega_C \\
-\frac{\partial\phi}{\partial n} &= 0 \text{ on } \partial\Omega \setminus \{\partial\Omega_A \cup \partial\Omega_C\}
\end{aligned}
$$

The boundary condition is called the Butler-Volmer exponential boundary condition, where:

$$\alpha_{aa}, \alpha_{ac} = \text{anodic transfer coefficients}, \alpha_{aa} + \alpha_{ac} = 1$$

$$\alpha_{ca}, \alpha_{cc} = \text{cathodic transfer coeff.}, \alpha_{ca} + \alpha_{cc} = 1$$
$$J_A, J_C = \text{anodic/cathodic polarization parameters}$$
$$V_A, V_C = \text{anodic/cathodic rest potential}$$
$$\nabla\phi = \text{galvanic current}$$

In the electrochemistry community, Morris and Smyrl [MS88] have tried numerically to simulate the behaviour of corrosion current for fixed ratios of anodic to cathodic areas(3-D model). Morris and Smyrl concluded that corrosion current is determined by the ratio of anodic area to active perimeter. They claim current increases with active perimeter.

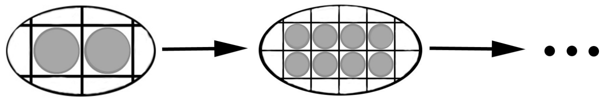

Fig. 3. Area remains constant as perimeter increases.

As a special case of increasing perimeter with fixed anodic area, we consider a periodic structure with period going to zero. Mathematically we study,

$$\begin{aligned} \Delta u_\epsilon &= 0 \text{ in } \Omega \\ -\frac{\partial u_\epsilon}{\partial n} &= f(x/\epsilon, u_\epsilon) \text{ on } \Gamma \\ -\frac{\partial u_\epsilon}{\partial n} &= 0 \text{ on } \partial\Omega \setminus \Gamma \end{aligned}$$

where $f(y,v) = \lambda(y)[e^{\alpha(y)(v-V(y))} - e^{-(1-\alpha(y))(v-V(y))}]$ for any $v \in \Re$ and $y \in Y = [0,1] \times [0,1]$. Here λ, α, and V are smooth real Y-periodic functions, we also assume there exist constants $\lambda_0, \Lambda_0, \alpha_0, A_0$ and V_0 such that $0 < \lambda_0 \leq \lambda(y) \leq \Lambda_0$ and $0 < \alpha_0 \leq \alpha(y) \leq A_0 < 1$ and $|V(y)| \leq V_0$. Recall Ω is a bounded cylindrical domain in $\Re^3$. Here letting $\epsilon \to 0$ represents increasing perimeter with fixed anodic area.

2 The Method of Homogenization

Engineering and scientific problems often deal with materials formed from multiple constituents(e.g. composite materials, fluid filled porous solids.) We try to find simpler equations that smooth out whatever substructure variations that arise with the spatially heterogeneous material. Beginning with a problem that includes the structural variations we derive a simpler problem that serves as a first term approximation. Here we begin by first assuming the solution ϕ_ϵ has an asymptotic expansion of the form,

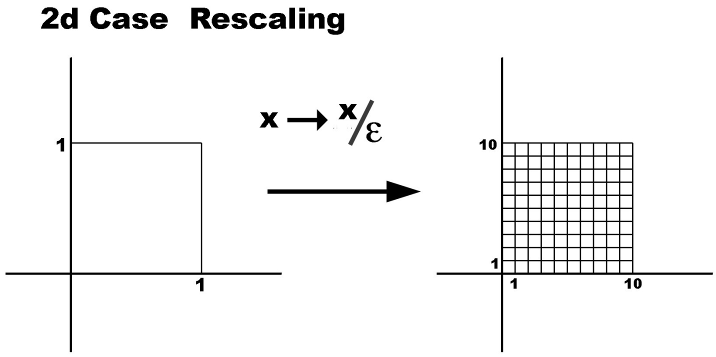

Fig. 4. Example of 2D rescaling when $\epsilon = 1/10$.

$$\phi_\epsilon \sim \phi_0 + \epsilon\phi_\epsilon^{(1)} + \epsilon^2\phi_\epsilon^{(2)} + \cdots$$

The general procedure is to substitute the above expansion back into the original boundary value problem to determine associated boundary value problems for $\phi_0,\ \phi_\epsilon^{(1)},\ \phi_\epsilon^{(2)},\ \ldots$. In this case we claim ϕ_0 satisfies,

$$\begin{aligned} \Delta\phi_0 &= 0 \text{ in } \Omega \\ -\frac{\partial\phi_0}{\partial n} &= f_0(\phi_0) \text{ on } \Gamma \\ -\frac{\partial\phi_0}{\partial n} &= 0 \text{ on } \partial\Omega \setminus \Gamma \end{aligned}$$

where $f_0(v) = \int_Y f(y,v)dy,$ for any $v \in \Re$ and $\phi_\epsilon^{(1)}$ satisfies,

$$\begin{aligned} \Delta\phi_\epsilon^{(1)} &= 0 \text{ in } \Omega \\ -\frac{\partial\phi_\epsilon^{(1)}}{\partial n} &= (f(x/\epsilon,\phi_0) - f_0(\phi_0))/\epsilon + e_\epsilon \text{ on } \Gamma \\ -\frac{\partial\phi_\epsilon^{(1)}}{\partial n} &= 0 \text{ on } \partial\Omega \setminus \Gamma \\ \int_\Omega \phi_\epsilon^{(1)} &= 0 \end{aligned}$$

where, $e_\epsilon = \frac{1}{\epsilon}\int_\Gamma (f_0(\phi_0) - f(x/\epsilon,\phi_0))$. Note that it is not *a priori* obvious that these are the appropriate boundary conditions. Subsequent convergence estimates will show that these are the right choices for boundary functions. To whit we can show(proof omitted) that there exist constants C_1, C_2, C_3, C_4 independent of ϵ such that:

$$\begin{aligned} \|\phi_\epsilon - \phi_0 - \epsilon\phi_\epsilon^{(1)}\|_{H^1(\Omega)} &\le \mathrm{C}_1\epsilon \\ \|\phi_\epsilon - \phi_0\|_{H^1(\Omega)} &\le \mathrm{C}_2\sqrt{\epsilon} \\ \|\phi_\epsilon - \phi_0\|_{L^2(\Omega)} &\le \mathrm{C}_3\epsilon \\ \|\phi_\epsilon^{(1)}\|_{L^2(\Gamma)} &\le \mathrm{C}_4 \end{aligned}$$

3 Existence and Uniqueness

Consider the problem,

$$\begin{aligned} \Delta u_\epsilon &= 0 \text{ in } \Omega \\ -\frac{\partial u_\epsilon}{\partial v} &= f(x/\epsilon, u_\epsilon) \text{ on } \Gamma \\ -\frac{\partial u_\epsilon}{\partial v} &= 0 \text{ on } \partial\Omega \setminus \Gamma \end{aligned} \tag{1}$$

where $f(y,v) = \lambda(y)[e^{\alpha(y)(v-V(y))} - e^{-(1-\alpha(y))(v-V(y))}]$. We consider the 3-D problem, *i.e.* let $\Omega \subset \Re^3, \Gamma \subset \Re^2$. Here $Y = [0,1]^2$ and λ, α, and V are piecewise smooth real valued Y-periodic functions, we also assume there exist constants $\lambda_0, \Lambda_0, \alpha_0, A_0$ and V_0 such that $0 < \lambda_0 \le \lambda(y) \le \Lambda_0$ and $0 < \alpha_0 \le \alpha(y) \le A_0 < 1$ and $|V(y)| \le V_0$. We show that the energy minimization forms of the problem (1) have unique solutions in $H^1(\Omega)$. For a given ϵ, define the following energy functional,

$$E_\epsilon(v) = \frac{1}{2}\int_\Omega |\nabla v|^2 d\tilde{x} + \int_\Gamma F(x/\epsilon, v)dx$$

where,

$$F(y,v) = \frac{\lambda(y)}{\alpha(y)} e^{\alpha(y)(v-V(y))} + \frac{\lambda(y)}{1-\alpha(y)} e^{-(1-\alpha(y))(v-V(y))}.$$

Theorem 1 (Existence and Uniqueness of the Minimizer). *There exists one function $u_\epsilon \in H^1(\Omega)$ solving $E_\epsilon(u_\epsilon) = \min_{u \in H^1(\Omega)} E_\epsilon(u)$.*

Proof: Note that

$$\frac{\partial^2}{\partial v^2}F(y,v) = \lambda(y)\alpha(y)e^{\alpha(y)(v-V(y))} + \lambda(y)(1-\alpha(y))e^{-(1-\alpha(y))(v-V(y))},$$

since $\lambda > 0, \alpha > 0$, and $1 - \alpha > 0$ we have that $\frac{\partial^2}{\partial v^2}F > 0$. It is easy to see that the partial derivative is bounded below. That is, there exists a constant c_0, independent of y and v such that,

$$\frac{\partial^2}{\partial v^2}F(y,v) \ge c_0 > 0.$$

Since F is smooth in the second variable, for any $v, w \in H^1(\Omega)$ and for any y, there exists some ξ between $v + w$ and $v - w$ such that

$$F(y, v+w) + F(y, v-w) - 2F(y,v) = \frac{\partial^2}{\partial v^2}F(y,\xi)w^2$$

which from the lower bound yields

$$F(x/\epsilon, v+w) + F(x/\epsilon, v-w) - 2F(x/\epsilon, v) \geq c_0 w^2$$

whence

$$E_\epsilon(v+w) + E_\epsilon(v-w) - 2E_\epsilon(v) \geq \int_\Omega |\nabla w|^2 d\tilde{x} + c_0 \int_\Gamma w^2 dx$$
$$\geq \tilde{c}_0 \|w\|^2_{H^1(\Omega)} \tag{2}$$

where the last inequality follows by a variant of Poincare. Now let $\{u_\epsilon^n\}_{n=1}^\infty$ be a minimizing sequence, that is

$$E_\epsilon(u_\epsilon^n) \to \inf_{u \in H^1(\Omega)} E_\epsilon(u) \qquad \text{as} \qquad n \to \infty.$$

note that clearly $\inf_{u\in H^1(\Omega)} E_\epsilon(u) > -\infty$. Let

$$v = \frac{u_\epsilon^n + u_\epsilon^m}{2}$$

and

$$w = \frac{u_\epsilon^n - u_\epsilon^m}{2}$$

then note that $v + w = u_\epsilon^n$ and $v - w = u_\epsilon^m$ and so

$$E_\epsilon(v+w) + E_\epsilon(v-w) - 2E_\epsilon(v) \geq \frac{\tilde{c}_0}{4} \|u_\epsilon^n - u_\epsilon^m\|^2_{H^1(\Omega)}$$

which implies,

$$E_\epsilon(u_\epsilon^n) + E_\epsilon(u_\epsilon^m) - 2 \inf_{v\in H^1(\Omega)} E_\epsilon(v) \geq \frac{\tilde{c}_0}{4} \|u_\epsilon^n - u_\epsilon^m\|^2_{H^1(\Omega)}.$$

Now if we let $m, n \to \infty$, we see that $\{u_\epsilon^n\}_n$ is a Cauchy sequence in the Hilbert Space $H^1(\Omega)$. Define u_ϵ to be its limit in $H^1(\Omega)$. Then we have

$$u_\epsilon^n \to u_\epsilon \ \text{ in } \ H^1(\Omega)$$

which by the Trace Theorem implies,

$$u_\epsilon^n \to u_\epsilon \ \text{ in } \ L^2(\Gamma)$$

which implies (Rudin [Rud66],p.68) there exists a subsequence $\{u_\epsilon^{n_k}\}_k$, such that

$$u_\epsilon^k \to u_\epsilon \ \text{ a.e. in } \ \Gamma.$$

So now we claim

$$F(x/\epsilon, u_\epsilon) = \liminf_{k\to\infty} F(x/\epsilon, u_\epsilon^k) \ \text{ a.e..} \tag{3}$$

Since F is smooth in the second variable, and $u_\epsilon^k \to u_\epsilon$ a.e. in Γ we have that $F(\frac{x}{\epsilon}, u_\epsilon) = \lim_{k\to\infty} F(\frac{x}{\epsilon}, u_\epsilon^k)$ a.e which clearly implies (3). Now note that clearly $F(\frac{x}{\epsilon}, u_\epsilon^k) > 0 \;\forall k, k = 1, 2, \ldots$. So that by Fatou's Lemma(Rudin [Rud66], p.23) we can claim,

$$\int_\Gamma F(x/\epsilon, u_\epsilon)dx \leq \liminf_{k\to\infty} \int_\Gamma F(x/\epsilon, u_\epsilon^k)dx$$

Thus we can conclude from this and the fact the the first term of E_ϵ is weakly lower semicontinuous that,

$$E_\epsilon(u_\epsilon) \leq \liminf_{k\to\infty} E_\epsilon(u_\epsilon^k) \quad \left(= \lim_{k\to\infty} E_\epsilon(u_\epsilon^k) = \inf_{u\in H^1(\Omega)} E_\epsilon(u) \right)$$

that is $E_\epsilon(u_\epsilon) = \inf_{u\in H^1(\Omega)} E_\epsilon(u)$. So we have shown the existence of a minimizer. The uniqueness of the minimizer follows trivially from (2).

Suppose u_ϵ and u_δ are both minimizers of the energy functional, i.e. $E_\epsilon(u_\epsilon) = \inf_{u\in H^1(\Omega)} E_\epsilon(u) = E_\epsilon(u_\delta)$. Now if we let $v = \frac{u_\epsilon + u_\delta}{2}$ and $w = \frac{u_\epsilon - u_\delta}{2}$ then $v + w = u_\epsilon$ and $v - w = u_\delta$. Then substituting v and w into (2) yields,

$$E_\epsilon(u_\epsilon) + E_\epsilon(u_\delta) - 2E_\epsilon(\frac{u_\epsilon + u_\delta}{2}) \geq \frac{\tilde{c}_0}{4}\|u_\epsilon - u_\delta\|^2_{H^1(\Omega)}$$

but since $\frac{u_\epsilon + u_\delta}{2} \in H^1(\Omega)$ we have $\inf_{u\in H^1(\Omega)} E_\epsilon(u) \leq E_\epsilon(\frac{u_\epsilon + u_\delta}{2})$ whence,

$$\frac{\tilde{c}_0}{4}\|u_\epsilon - u_\delta\|^2_{H^1(\Omega)} \leq E_\epsilon(u_\epsilon) + E_\epsilon(u_\delta) - 2 \inf_{u\in H^1(\Omega)} E_\epsilon(u) = 0.$$

So $u_\epsilon = u_\delta$ a.e. in $H^1(\Omega)$. Thus we have shown the uniqueness of the minimizer. □

Note that this argument can be generalized to address the n-dimensional problem, *i.e.* the case in which we have $\Omega \subset \Re^n, \Gamma \subset \Re^{n-1}$ with boundary period cell $Y = [0, 1]^{n-1}$.

4 Numerical Experiments

Finally we wish to numerically observe the behaviour of the homogenized boundary value problems as a way to describe the behaviour of the current near the boundary. We plan to use a finite element method approach to the 2-D problem. For the 2-D problem the domain Ω is a unit square and the boundary Γ is the left side of the unit square, that is $\Gamma = \{(x_1, x_2) : x_1 = 1\}$. In this case we impose a grid of points(called nodes) on the unit square and triangulate the domain, then introduce a finite set of piecewise continuous basis functions. Now we wish to minimize the energy functional with respect to these basis functions. In particular we assume that the minimizer can be written as a linear combination of basis functions, we write

$$\phi = \sum_{i=1}^{m} \eta_i b_i$$

where m is the number of nodes, and $\{b_i\}_{i=1}^m$ is the set of basis functions. We attempt to minimize the energy over the set of coefficients $\{\eta_i\}_{i=1}^m$ using a conjugate descent algorithm developed by Hager * and Zhang. We are currently implementing this minimization and refer the reader to future publications for numerical results.

Acknowledgments: All figures appear courtesy of Valerie Bhat.

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* www.math.ufl.edu/~hager