Characterizing diffusive growth by uncertainty quantification

Abstract: Environmental models by their nature contain a great deal of uncertainty. Since the underlying behavior of the model is rarely controlled by an ordered process, any model characteristics will carry along with it a level of aleatory uncertainty governed by the natural disorder. This paper applies novel uncertainty quantification approaches to classes of diffusion problems which illustrate the benefit of assuming natural variability.

Introduction

Modeling with uncertainty quantification has application to such phenomena as oxidation, corrosion, thermal response, and particulate growth. These fall into the classes of phenomena governed substantially by diffusional processes. At its most fundamental, diffusion is a model of random walk. Without a strong convection or advection term to guide the process (e.g. provided by an electric or gravitational field), the kinetic mechanism of a particle generates a random trajectory that is well understood based on statistical physics principles. The standard physics approach is to solve a master diffusion equation under transient conditions. This turns into a kernel solution that we can apply to an arbitrary forcing function, such as provided by an input material flux or thermal impulse.

Yet, the environment that the particle resides in may not be as homogeneous as the ideal diffusion model would imply. Enough uncertainty in the essential diffusion parameters may exist that we need to ask some fundamental questions:

- Why do we assume the diffusion coefficient is a constant?
- How can we know the diffusional interface so precisely?

Within a heterogeneous media, the characteristic diffusion coefficient does not have to remain a fixed value. Varying amounts of defects and material composition can modulate the natural hopping rate and thus smear the diffusion coefficient well beyond the narrow tolerance that is typically assumed. In general, the assumption of a single diffusion coefficient works well for many behaviors ─ as the observed results are already smeared due to diffusion, while a greater level of uncertainty will not change the mean value of the diffused measures. This mean value approximation works well as a result of applying the central limit theorem of statistics.

Yet, under certain circumstances, the uncertainty in the coefficient or the uncertainty in the experimental geometry will have a subtle yet measurable impact on the diffusional transient behavior. This departure from ideality usually occurs over the short initial growth time, but will also manifest itself via the application of a modified impulse response function.

As an example, if we consider the heat equation, which models the thermal evolution of a transient heat impulse, we immediately note that the standard solution admits an infinite speed of propagation of the initial thermal transient, due to a singularity in the kernel solution expression. That first random walk step is instantaneous according to the math, yet we need to either integrate this transient out or invoke a model such as relativistic diffusion to account for the real system behavior. Furthermore, *and just as plausibly*, the initial transient is likely modified by unaccounted natural uncertainty and disorder in the thermal characteristics and environment, i.e. within the *thermal context*.

This uncertainty also manifests itself in other diffusion models. Deviations from the expected Fickian diffusional growth model lead to the Deal-Grove model[1] for Si oxide growth as a practical yet non-ideal heuristic.

In this paper, we apply straight-forward uncertainty quantification. The essential idea is to admit some uncertainty in the diffusion coefficient and in the interface location. By propagating the uncertainty into the diffusion response, certain issues disappear. For example, the infinite speed becomes finite and the kernel solution comes out very clean. This becomes part of the initial condition uncertainty that we know must exist in practice.

In the following work we apply two levels of uncertainty

- Vary the diffusion coefficient to maximum uncertainty with known mean
- Vary the diffusional interface to maximum uncertainty with known mean

As a result we generate a simple diffusion kernel that is much easier to reason with, and can explain several subtle anomalous diffusion behaviors

Example: SiO$_2$ growth

We first consider the well-known characterization of silicon dioxide, SiO2 as an example of dispersive growth. Originally characterized by Bruce Deal and Andrew Grove in the 1960's,[1] a careful application of a diffusion-based oxide growth model partially enabled the semiconductor revolution. The Deal-Grove model works as a heuristic model in so far as a rigorous first-principles derivation does not exist.
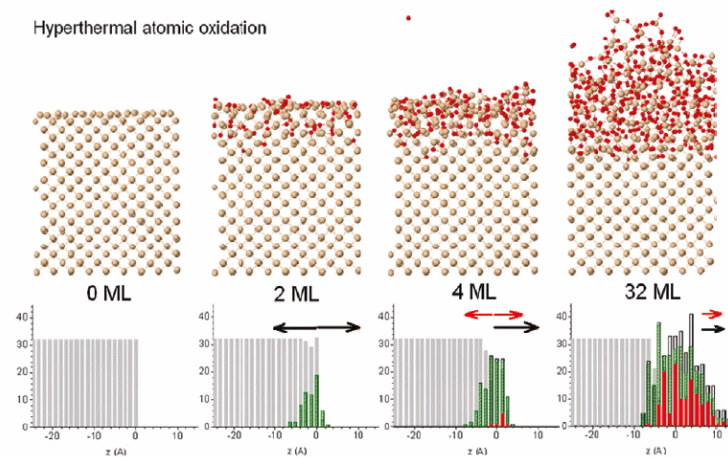

Figure 1: Chemical simulation of oxidation of silicon. A large degree of disorder is evidenced by the mixture of pure Si, SiO$_2$, and SiO and as indicated in the histograms by light gray bars, green bars, and red bars, respectively. Black and red arrows indicate the growth direction of the oxidized and silica (SiO) layers, respectively (from [Khalilov 2011] [2])

The following derivation improves on the Deal-Grove model by assuming that the diffusion coefficient and location of the growing oxide layer is smeared by a maximum entropy amount; i.e. we can estimate the mean but we leave higher-order moments to vary to maximize the entropy.

Diffusion Solution.

The standard approach for solving diffusion problems starts from master diffusion equation

$$\frac{\partial}{\partial t}C(t, x) = D \cdot \frac{\partial^2}{\partial x^2}C(t, x) \qquad (1)$$

also known as Fokker-Planck, this is a one-dimensional representation and only lacks the convective or drift term from the general formulation of Fokker-Planck. We also assume that D does not change with respect to spatial coordinates.

We can easily derive the solution of the response function if we think of the diffusion from a planar source outward. The kernel solution gives:

$$n(t, x|D) = \frac{1}{\sqrt{4\pi Dt}} \cdot e^{-x^2/4Dt} \qquad (2)$$

We place an impulse of reactants at x=0 and want to watch the evolution of the concentration, n, with time. As the concentration drops, we assume that the diffused material from that amount contributes to the growth of the oxide layer.
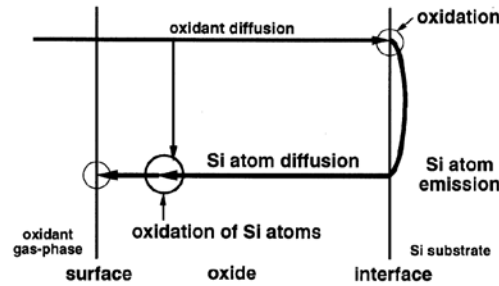

Figure 2: *Mechanism for diffusion (from [Uematsu 2002][3])*

Consider first that the kernel function represents a one-dimensional concentration profile, in units of number of atomic elements per thickness. The expression $n(t,x)$ describes how quickly the atomic concentration decreases from its initial value. So the accumulated concentration, representing the growth outward from the interface, is the spatial integral of the concentration density. Early on we assume that the region of the interface is spread over a width X.

$$N(t|X, D) = \int_0^X n(t, x|D)dx \qquad (3)$$

The average flux of atoms outward from the interface, $J(t|X, D)$, is proportional to the gradient of n, and we apply the diffusion coefficient as the standard proportionality term at position X:

$$J(t|X, D) = D \cdot \frac{\partial}{\partial X} N(t|X, D) = \frac{\sqrt{D}}{\sqrt{4\pi t}} \cdot e^{-X^2/4Dt} \tag{4}$$

Next, we have an idea of a mean value for the diffusion coefficient, D, but don't know how much it varies. Lacking that information, we apply a maximum entropy estimate for the variance assuming a mean value D_0.

$$p_d(D) = \frac{1}{D_0} \cdot e^{-D/D_0} \tag{5}$$

We can then integrate the concentration across the diffusion probability density function, and after applying a few integration tricks, the solution reduces to:

$$J(t|X) = \int_0^\infty J(t|X, D) p_d(D) dD = \frac{1}{4\sqrt{t}} \cdot e^{-X/\sqrt{D_0 t}} \cdot \left(\sqrt{D_0} + \frac{X}{\sqrt{t}}\right) \tag{6}$$

We also need to consider that for a highly disordered layer, we should place a maximum uncertainty around the value of X.

$$p_x(X) = \frac{1}{x_0} \cdot e^{-X/x_0} \tag{7}$$

Once again we can apply a probability density function, this time to the flux, which marginalizes X according to the following integration:

$$J(t) = \int_0^\infty J(t|X) p_x(X) dX = \frac{D_0}{4} \cdot \left(\frac{1}{x_0 + \sqrt{D_0 t}} + \frac{x_0}{(x_0 + \sqrt{D_0 t})^2}\right) \tag{8}$$

As a last step, we need to integrate the average flux over time to arrive at the growing width, W, of the oxide layer:

$$W(t) = \int_0^t J(\tau)d\tau = \frac{1}{2}\sqrt{D_0 t} \cdot \frac{\sqrt{D_0 t}}{x_0 + \sqrt{D_0 t}} \tag{9}$$

The time integral of this flux is the accumulated concentration of material with a constant inflow of material (i.e. molecular or elemental oxygen) from the surroundings. By integrating the diffusional response, we can demonstrate how the step input transiently supplies reactants to the growing interface. The second factor is the newly realized suppressive effect due to disorder. For small t, this compensates the lead term to provide a linear growth factor, which is the original heuristic in the Deal-Grove growth law.

In summary, we applied a two step maximum entropy estimation process to model the disorder in the growing oxide layer. Without any knowledge about the distribution of D and X, apart from asserting that they must exist, we applied the following series of transforms:

$$n(t, x|D) \rightarrow N(t|X, D) \rightarrow J(t|X, D) \rightarrow J(t) \rightarrow W(t) \tag{10}$$

This provides a diffusional response due to a continuously applied step concentration to model a growing thickness. For oxide growth, a step input of oxygen is supplied from one side of the interface, and the substrate supplies silicon atoms, see Figure 2. The figure below provides a model fit to recent data from a set of SiO_2 growth experiments.
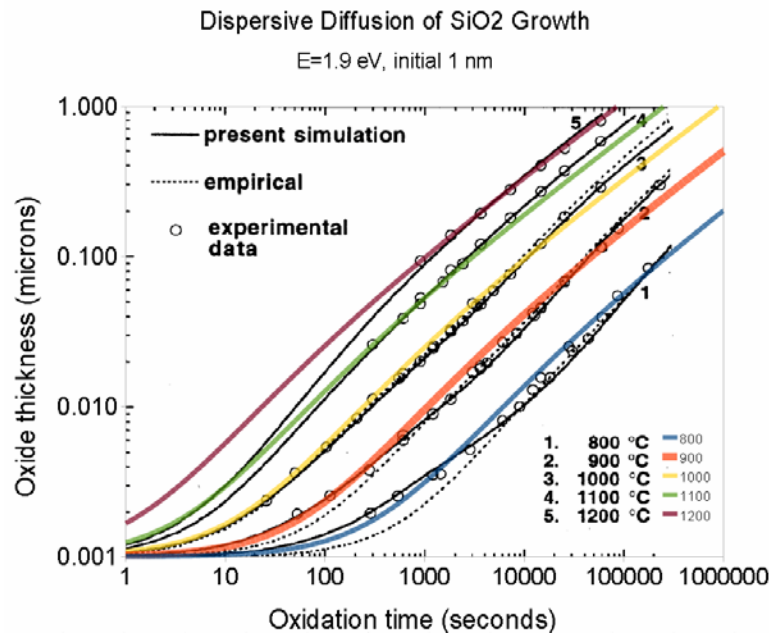

Figure 3: *Comparison of dispersive diffusion model against the convention Deal- Grove model (empirical dotted) and a detailed simulation based on reaction kinetics. For silicon, an immediate*

oxide layer is formed which generates a baseline thickness of about 1 nanometer (data and simulation from [Uematsu 2002][3])

Over time, the response will attain a square root growth law, indicative of the Fick's law regime of what is often referred to as parabolic growth[4]. The larger the mean diffusion coefficient or the smaller the uncertainty level x_0, the more quickly that the response will diverge from the short-term linear growth regime.
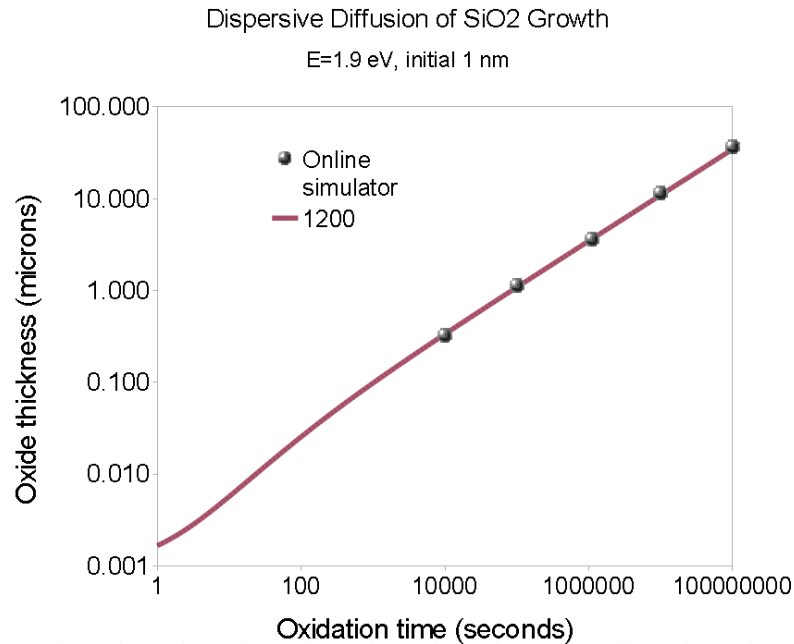

Figure 4: *In the Fickian growth regime, the dispersive diffusion formulation follows a square root time dependence, and can be confirmed with an online SiO_2 growth calculator http://www.cleanroom.byu.edu/ OxideThickCalc.phtml*

General Applicability.

The uncertainty quantification proposed here has more general applicability than just to oxide growth on silicon. Any diffusional process that contains a degree of uncertainty in its parameters is a candidate for this simplification.

The general dispersed response to an impulse at the smeared origin is generated by the marginalization of Eq. 2 with Eq.5 and Eq.7 with the result:

$$n(t) = \frac{2}{x_0 + \sqrt{Dt}} \tag{11}$$

This describes the damping of the peak concentration profile with time, cast in terms of a one-dimensional density. Alternatively, by scaling with a time constant, the impulse response can be normalized:

$$n(t) = \frac{1}{1 + \sqrt{\frac{t}{\tau}}} \tag{12}$$

Here, τ is a diffusional time constant, indicating how slowly the concentration disperses from the origin. This is also a measure of the persistence of a material to remain localized (see [Pukite 2011][5]). The scaling implications are important to allow us to generalize the behavior over a range of conditions [de Almeida 1999][6].

In fact, the dispersive formulation can extend to mathematically related behaviors such as corrosion and particulate growth. Corrosion acts very similar to oxidation in that the rate of the of the corrosive materials has to depend on diffusion of the reacting species with the replenishment of fresh substrate. Further, we can evaluate how well this applies to thermal diffusion, which uses the heat equation in a mathematical formulation very similar to particle diffusion.

Example: Thermal Dispesive Diffusion

The master model for thermal diffusion is referred to as the *heat equation*. This has the same formulation as Eq(1) with the role of material concentration played by temperature (which represents the local thermal excitation). In many practical applications, we may want to know the dissipation of heat from a source. In the case of a planar source of heat such as the surface of a CPU, we can use a one-dimensional model to illustrate the principle. Or we can demonstrate the flow of heat through a rod for different thermal conductivities (see Figure 5).

The ideal non-disordered impulse response should follow

$$\Delta T(t) = \frac{C}{\sqrt{Dt}} e^{\frac{-x^2}{Dt}} \tag{13}$$

The disordered variation of this is

$$\Delta T(t) = \frac{C}{\sqrt{Dt}} e^{\frac{-x}{\sqrt{Dt}}} \left(1 + \frac{x}{\sqrt{Dt}}\right) \tag{14}$$

Since each of the rods consists of a uniform homogeneous metal, one would expect that the response should be near to what theory predicts, and that is the case. [Sullivan 2008][7]

For each of the materials of Figure 5, the idealized impulse response works well (Eq. 13), while the disordered variant (Eq. 14) reveals a larger dispersive spread.
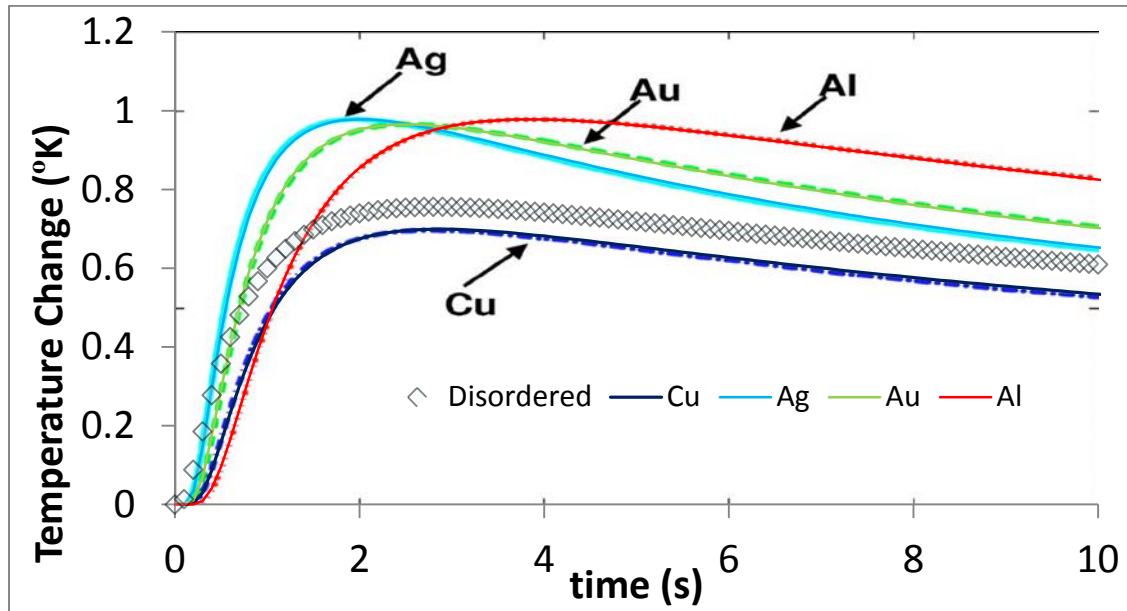
Figure 5: Experimentally measure thermal diffusion profiles for various metals showing excellent agreement with ordered diffusion. The dispersed diffusion profile is shown alongside.

Where we would like to apply the disordered response is to an interface that has a thermal stimulus on one side and an outlet on the other, which turns out to be a realization of a compartmental or box model for thermal dynamics.
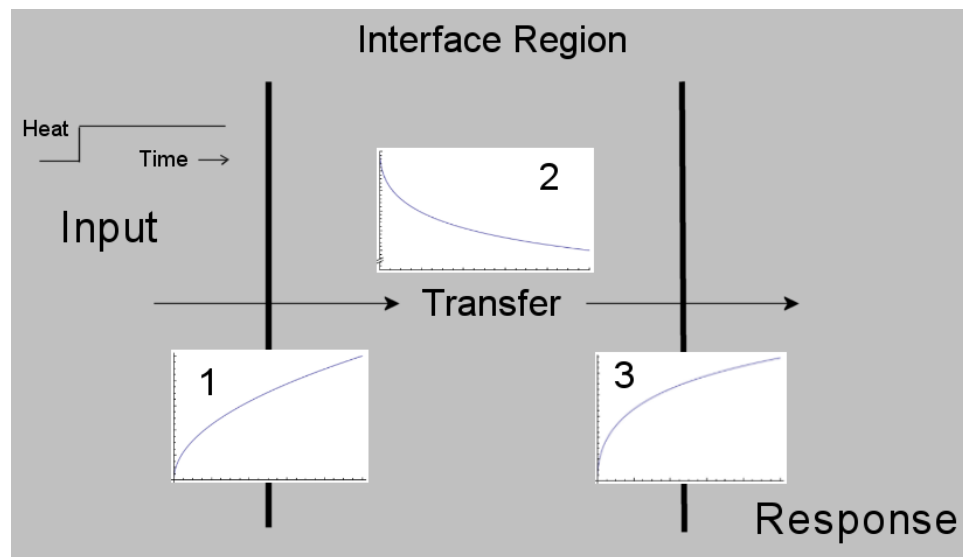

Figure 6: A box model for thermal dynamics assumes a stimulus representing an initial transient (1) convolved against a dissipative transfer function (2) to produce a modulated response (3).

The role of the box model is to model a thermal input along with a response which will allow an alternate path for dissipation of heat. In Figure 6, the input stimulus is a unit step which immediately creates a Fickian square root buildup near the interface (subgraph 1). This gets dissipated by a smeared impulse response function (subgraph 2) and the result is shown as a modulated response (subgraph 3) showing a

slower buildup than the square root rise. The modulated reduction results from heat that is dissipated from non-specific paths as described in [Sullivan 2008][7], described by Figure 7.
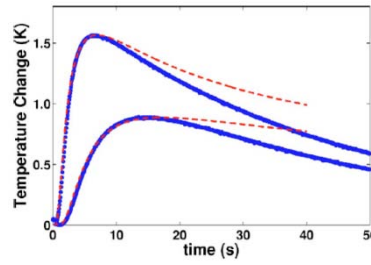

Figure 7: *Red lines indicate the theoretical profile under a non-lossy thermal environment.*

To analyze the thermal response we use the concept of a convolution to drive the response from a combination of input delta temperature change and the transfer function representing heat dissiation following secondary paths.

$$Response(t) = Input(t) \otimes Transfer(t) \tag{15}$$

At the origin of the thermal impulse, the smeared diffusive response is:

$$\Delta T(t) = \frac{1}{1 + \sqrt{t/\tau}} \tag{16}$$
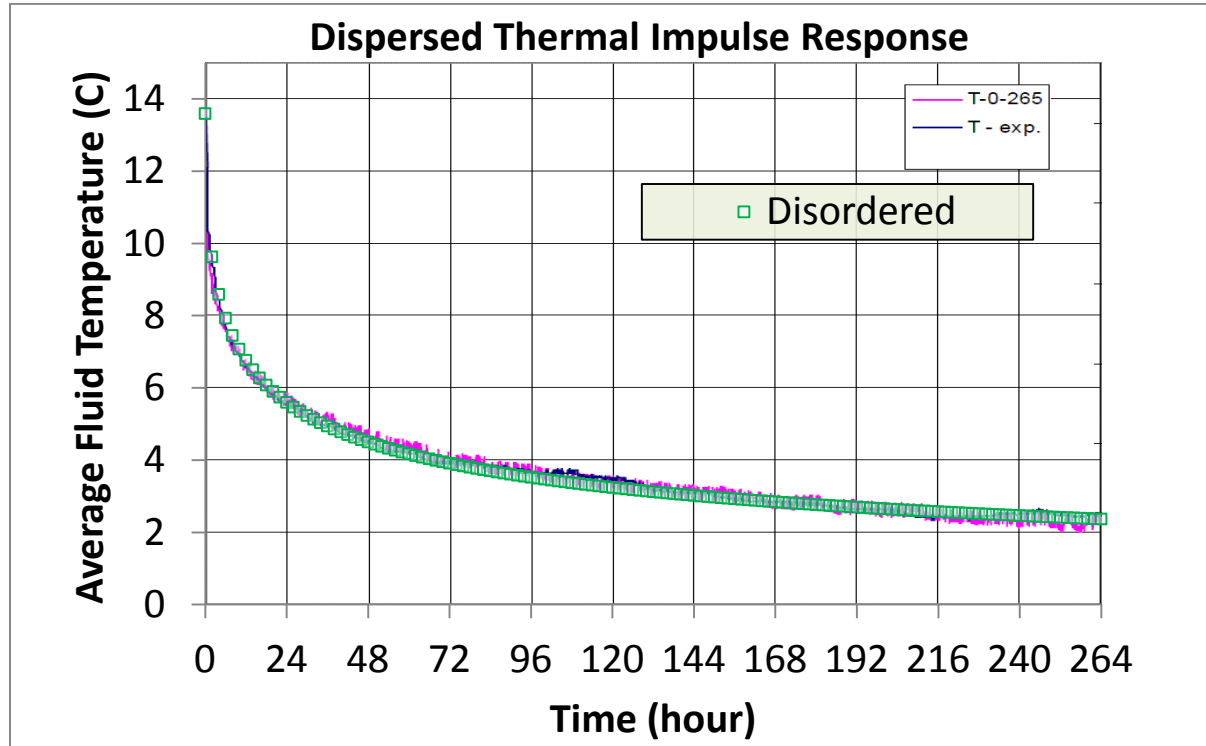
This agrees with measurements from experiments:

Figure 8: *Impulse response from a unit step thermal stimulus applied to an earthen mass (data from [Witte 2002][8]).*

If we take a strong dispersive diffusive decline and convolve with a Fickian growth curve to model the loss:

$$Response(t) = \sqrt{t} - \sqrt{t} \otimes \frac{d}{dt}\left(\frac{1}{1 + \sqrt{t/\tau}}\right) \tag{17}$$

The result is a modulated response:

$t > \tau$

$$Response(t) = \pi - \frac{2\cosh^{-1}\left(\sqrt{t/\tau}\right)}{\sqrt{\frac{t}{\tau} - 1}} \tag{18}$$

$t < \tau$

$$Response(t) = \pi - \frac{2\cos^{-1}\left(\sqrt{t/\tau}\right)}{\sqrt{1 - \frac{t}{\tau}}}$$

A contour of the response surface is shown below.

$$\text{plot} \qquad \pi - \frac{2\cosh^{-1}\left(\sqrt{\frac{t}{\tau}}\right)}{\sqrt{\frac{t}{\tau} - 1}}$$
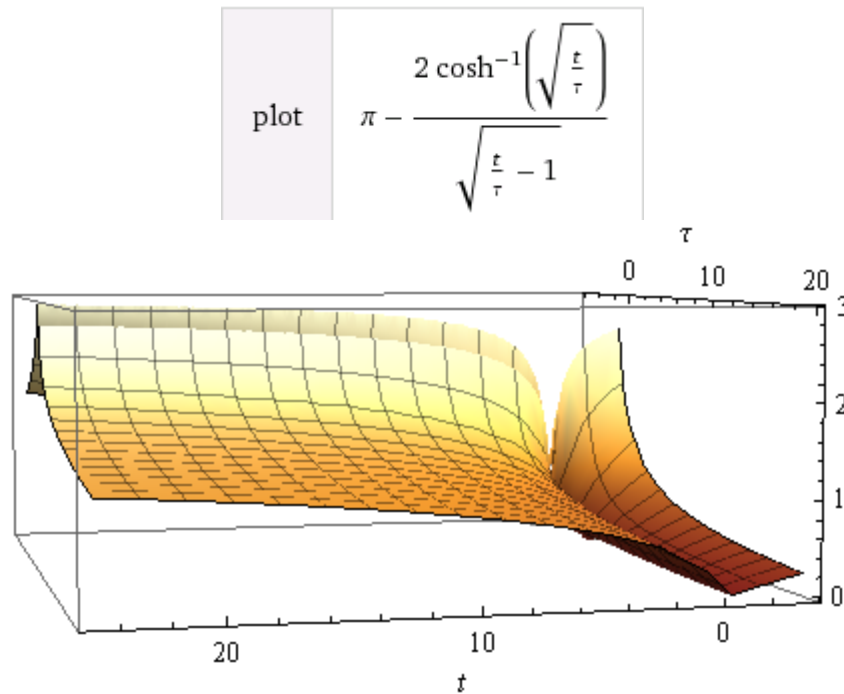

Figure 9: Response surface of the dissipative dispersion function

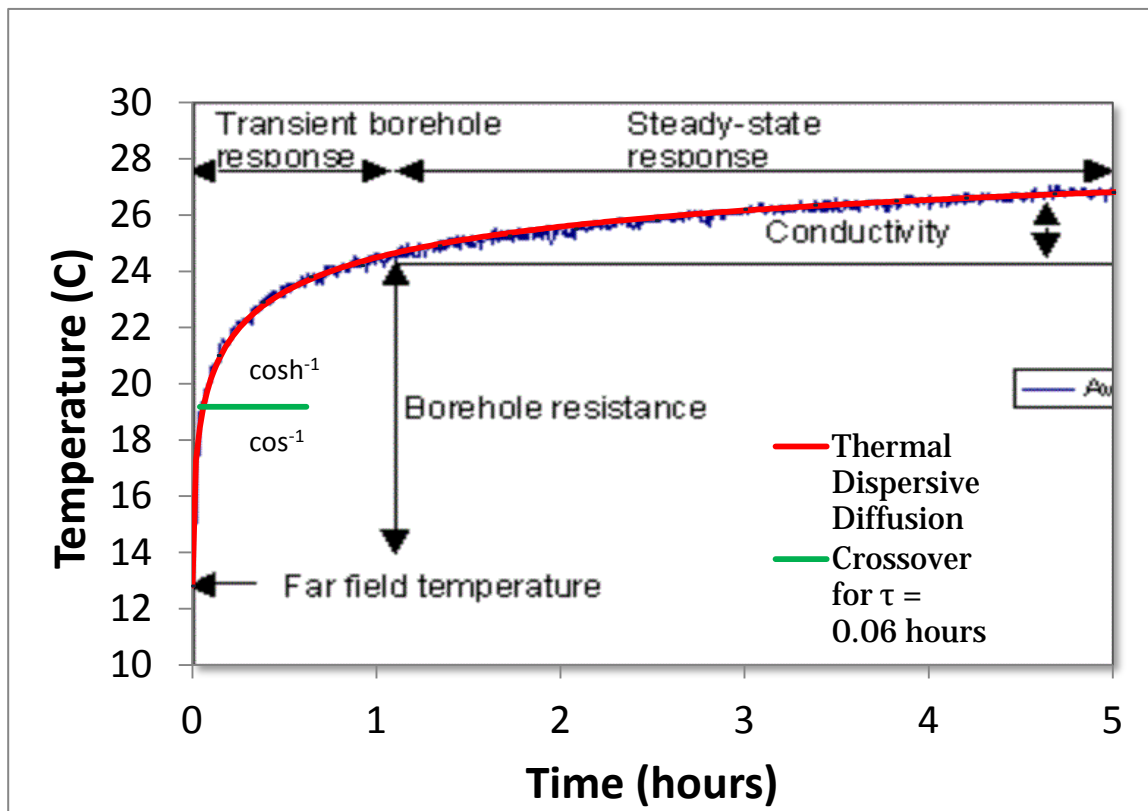This formulation accounts for the dispersed heat losses arising from diffusion through dispersed paths.

Figure 10: *Dispersed impulse response measured away from the stimulus. Note the crossover point separating the acosh and acos behavior (from* http://www.groenholland.com/nl/consultancy/site_testing_and_characterisation/trial_borehole_and_trt.php *).*

By applying a sequence of thermal impulse steps we can demonstrate how to model piecewise transients (see **Figure 11** below).
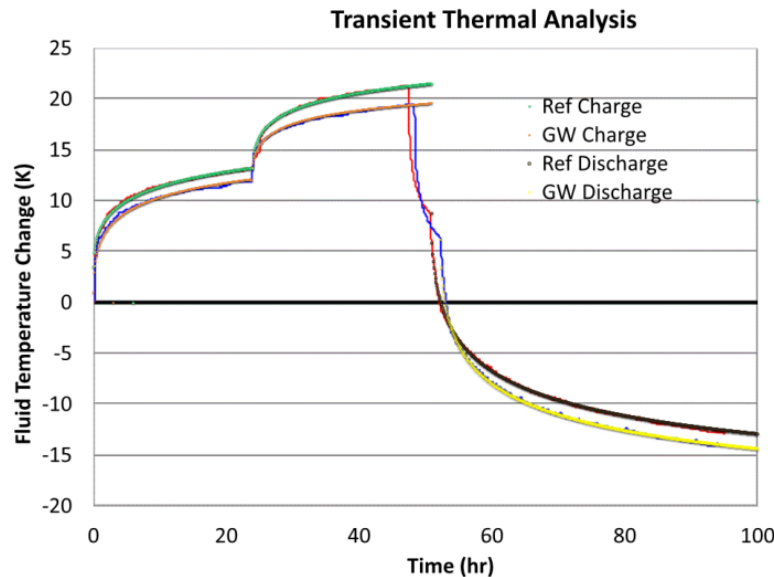

Figure 11: *Series of hot and cold unit step impulses applied to an earthen mass measured as a transient response (data from [Witte 2005]*[9] *to a groundwater (GW) or reference sink.*

In addition to the utility for large scale geothermal transients as just described, we can also apply this dispersive thermal approach to smaller scale contexts, such as a component or subsystem heat sink. Figure 12 shows typical thermal transients observed under various dissipation paths for a powered-up CPU card. Depending on whether the environment contains a well defined heat sink and cased enclosure, the transient will display markedly different apparent time constants. This by itself is not too surprising, but the dispersive diffusion response allows us a simple model to match up with the empirical results. In particular, where we have uncertainty in the environment, this approach excels, as it only requires a mean value estimate for the composite thermal diffusion coefficient or conductivity.
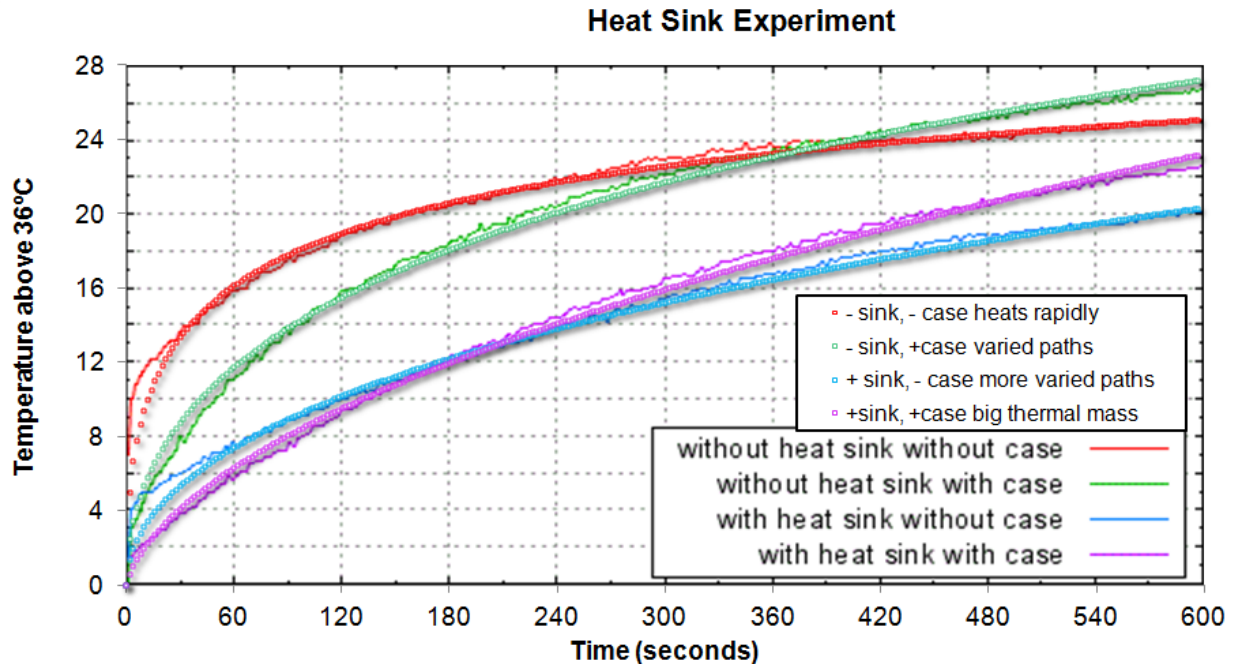
Heat Sink Experiment

Figure 12: Thermal transients observed within a CPU housing.

Example: Corrosive Growth

The salient principle behind the corrosion of metals is that rust growth mirrors that of the oxide growth of silicon. The number of random environmental factors involved in corrosion suggests that it would make an ideal candidate to apply the dispersive diffusion model. In the oxidation of steel, several different varieties of oxide are involved with varied atmospheric levels of corrosive reagents.

Figure 13 and Figure 14 show an oxide growth model and the results of experimental measurements for a steel composed structure left to weather under different climatic conditions. The behavior specified in Eq(7) was applied directly to the data with assumed mean values for an effective diffusion coefficient.

Uncontrolled rusting also has the propensity for peeling off, thus exposing fresh layers which will start the oxidation process over again. That tendency makes allows the possibility for a growth power law of ½ combining with a linear growth law leading to the 0.7 power law. This is the same rate observed for the dispersive diffusion model within the transition zone during the early oxidation process.
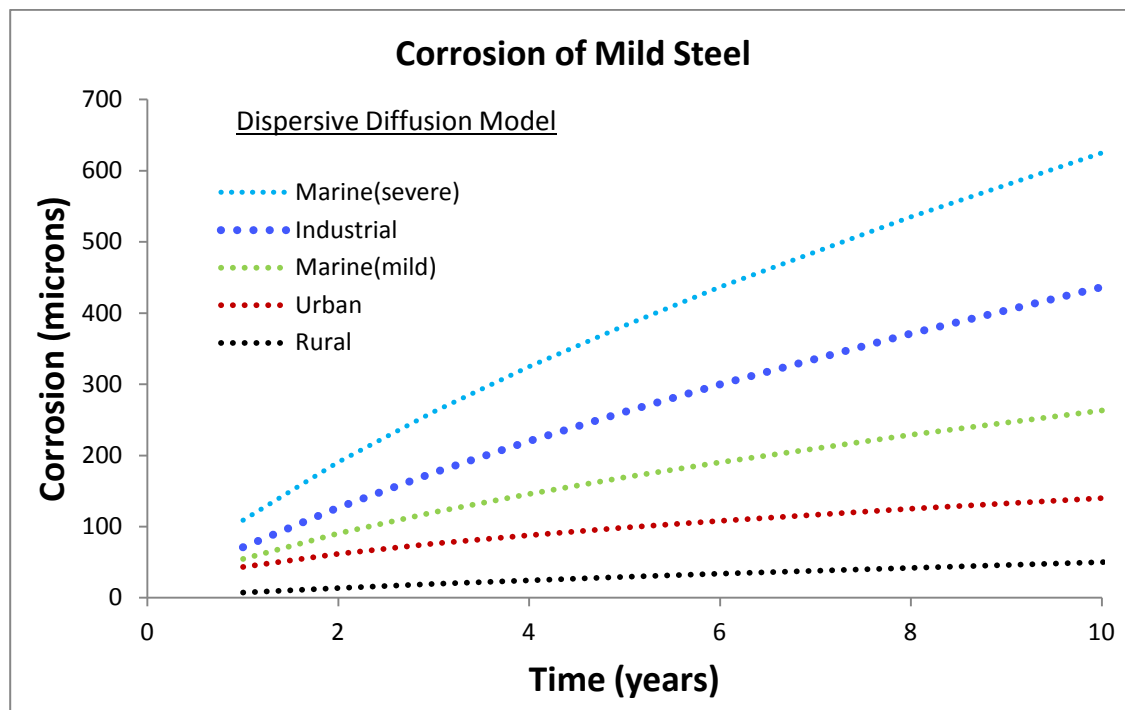
Figure 13: Corrosion growth rates on a linear scale

The dynamic range is limited but the rate of growth suggests and initial linear regime, which bends into a power law growth.
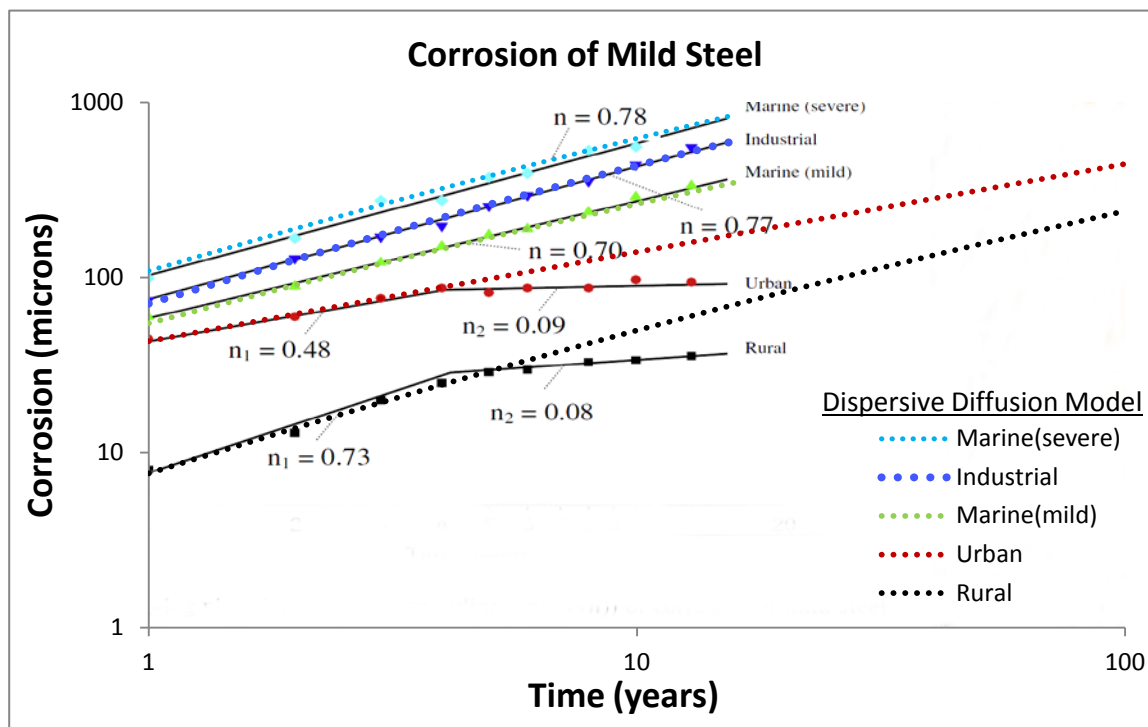

Figure 14: Corrosion growth rates on log scale compared against data from [de la Fuente 2011][10].

Conclusions.

The statistician George E.P. Box wrote a famous quote concerning the validity of models. Box's oft-quoted statement of *"All models are wrong, but some are useful"* not surprisingly misses some important context. We can find the original context in the book "Empirical Model-Building and Response Surfaces" by Box and Draper:[11]

> "The fact that the polynomial is an approximation does not necessarily detract from its usefulness because all models are approximations. Essentially, all models are wrong but some are useful. However, the approximate nature of the model must always be borne in mind."

In this case the context is to be careful in numerical computations so that the model numbers match the observations.

On the rest of that page, Box and Draper present a concise description of the differences between *epistemic* and *aleatoric* uncertainty, which is really the scope of the oxide growth and thermal modeling described in this paper, and of environmental modeling in general. Epistemic uncertainties are the systematic errors that one can introduce in a statistical model, while aleatoric errors are those that are fundamental in the natural behavior itself, be it noise or some other random effect.

So in this case, we can understand the basic mechanisms of oxide growth over many orders of magnitude via the parabolic Fickian diffusion law, but we may miss important details by how we numerically model the fundamental equations. To remedy this situation, we treated the diffusion coefficient and the Si/SiO_2 interface location with the correct amount of aleatory uncertainty. Our epistemic uncertainty remains in the validity of the model we applied, and how accurately we can measure against the empirical observations.

So Box essentially described why we should be careful in numerical errors in statistical modeling, while many people have interpreted Box's quote to question the validity of using models in the first place. That is clearly an incorrect argument — all one has to consider is that all of mathematical engineering is based on models, and look at how far that has gotten us! The Deal-Grove model essentially allowed oxidation processes to become well characterized and predictable, which essentially revolutionized the integrated circuit manufacturing process. The dispersive diffusion model derived in this paper should be taken in that spirit, a pragmatic model that could become useful in characterizing a fundamental physical process.

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