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Analogy between electrochemical oscillations and quantum physical processes

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Abstract. In (photo) electrochemical oscillations, the discretization of phase oscillators leads to a sequence of time dependent oscillator density functions which describe the passing of the oscillators through their minimum at each cycle. Two consecutive oscillator density functions are connected by a Markov process represented by a linear integral equation of second order which is homogeneous in the case of sustained oscillations. The kernel of the integral equation is a normalized Greens Function and represents the probability density for the periods of the oscillators. Both together, the oscillator density function and the two-dimensional probability density for the periods of the oscillators define a random walk. The relation of the model to the holographic principle is discussed briefly. Further, a detailed analysis of a kernel of the integral equation leads to a frequency distribution g for the period length. Additionally, it is possible to determine the energy E in dependence on the period length from the electrochemical process. The product $g\ E$ shows qualitatively the same behaviour as the radiation of a black body, indicating that the discretization of phase oscillators, when represented by phase space analysis, show an analogy to quantum processes.

1. Introduction

The oscillatory behaviour of silicon electrodes has been reported about two decades ago [1]. Particularly, electrochemical oscillations on Si photo-electrodes have been extensively studied [2]. Several models were developed based on self-oscillating domains [3], the so-called current bursts [4], and oxide-induced interfacial stress [5-9] relating to the observation of nano-dimensioned pores, fluctuating with the phase of the oscillating (photo)current of Si electrodes immersed in dilute ammonium fluoride solutions. The latter model was presented by a special phase space analysis based on a discretization of phase oscillators indicating that two types of oxides (with different nanopore densities) can explain sustained current oscillations. In section 2 the relation of the model to a random walk and to the holographic principle is discussed. In section 3 the frequency distribution g and the energy E in dependence on the period length is determined in the case of sustained and damped oscillations. The product $g\ E$ is compared with the radiation of a black body.

2. Oscillatory process and mathematical model

The basic process at the electrode surface domain $\Omega \subseteq R^2$ is characterised by a cyclic oxidation of a small silicon layer (with a thickness of ca. 10 nm) and the following removal of the oxide by etching. The oxide thickness evolves not uniformly at the electrode due to cracks and nanopores at the oxide


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which result from stress due to the lattice mismatch between silicon and its oxide. The oxide thickness is given at the time *t* at each point *(x,y)* of the electrode surface by

$$d(t,x,y)=\frac{\cos(\varphi(t,x,y)+\pi)+1}{2}(d^{\max}-d^{\min})+d^{\min} \quad \text{for} \quad i\,2\pi\le\varphi(t,x,y)\le(i+1)2\pi\,,\ i=0,1,2,... \tag{1}$$

at which the phase φ propagates nonlinear monotonically increasing. In [9], the so called phase oscillator φ is discretized in the phase space $\Phi=\{(x,y,\varphi)\,|\,(x,y)\in\Omega,\varphi\in R_+\}$ by registering its value only at the so-called snap-shot screens $S_i=\{(x,y,i\,2\pi)\,|\,(x,y)\in\Omega\}$ that are planes with a constant phase difference of 2π. The result is the time dependent oscillator density function $p_i(t)$ which defines for the time *t* the differential number of oscillators passing their minimum $d^{\min}$ at the *i*-th time. In the following, we assume that all phase oscillators pass $i\,2\pi$ during the time interval $[t_i^{\min},t_i^{\max}]$ at the *i*-th cycle. Then two consecutive oscillator density functions are connected by a Markov process represented by a linear integral equation of second order (figure 1 top left)

$$p_i(t)=\int_{t_{i-1}^{\min}}^{t_{i-1}^{\max}} p_{i-1}(s)\,q_{i,s}(t-s)\,ds \qquad \text{for } i=1,2,3,... \text{ and } t\in[t_i^{\min},t_i^{\max}] \tag{2}$$

Eq. (2) is homogeneous in the case of sustained oscillations i.e. $f(t)$ is zero in the eq. $p_i(t)=p_{i-1}(t-\overline{T})+f(t)$ ($\overline{T}$ - macroscopic oscillation period). The kernel $q_{i,s}(t-s)$ of the integral equation is a normalized Greens Function [8] and represents the probability density for the periods $t-s$ of the oscillators in dependence on the starting times *s* of the oscillators during the *i*-th cycle.

Both together, the oscillator density function $p_{i-1}(s)$ and the two-dimensional probability density $q_{i,s}(t-s)$ for the periods of the oscillators define a random walk

$$P_i=P_{i-1}+Q_{i,s} \qquad \text{for } i=1,2,3,... \text{ and } s\in[t_{i-1}^{\min},t_{i-1}^{\max}] \tag{3}$$

for which P_i and P_{i-1} denote random variables and $Q_{i,s}$ the random process. $p_i(t)$ defines the probability density for P_i and $q_{i,s}(t-s)$ for $Q_{i,s}$. The random variable P_i assigns to each event (oscillation process starting with a bare silicon electrode) the time *t* at which the phase oscillator $\varphi(t,x,y)$ equals $i\,2\pi$. The *s* dependent random variable $Q_{i,s}$ assigns to each event the period $t-s$ at which the phase oscillator equals $(i-1)\,2\pi$ at the time *s* and $i\,2\pi$ at the time *t*.

The given description of the oscillatory process reveals a relation to the holographic principle as presented in [10]. We describe in [5-9] via phase oscillators a process in the space volume (evolution of a finite set of pores in the grown oxide) by a process at the two-dimensional snap shoot screen S_i (unique fingerprint of the pore evolution at the minimum oxide thickness in terms of strings of intersection between the phase and S_i). S_i is a holographic screen located at an equipotential surface corresponding to a constant potential at the minimum oxide thickness. Hence all important information of the process can be displayed at the holographic screen and the space volume has one holographic direction perpendicular to the electrode surface directed into the bulk.

3. Mathematical model and the black body radiation

We determine the frequency distribution *g* for the period length *T* from the probability density $q_i(t,s)\,(=q_{i,s}(t-s))$ for the periods $t-s$ of the oscillators. In the case of sustained oscillations we choose for *q* a normalized Greens Function [8] and introduce additionally a damping parameter *v* which defines the transition from sustained $(v=0)$ to damped $(v>0)$ oscillations (figure 1 top left) i.e.

$$q_i(t,s)=\begin{cases}\dfrac{2(t-\overline{T})}{(L+v)s}, & for \quad \overline{T}\le t\le \overline{T}+\dfrac{L+v}{L}s \\ \dfrac{2(\overline{T}+L+v-t)}{(L+v)(L+v-\dfrac{L+v}{L}s)}, & for \quad \overline{T}+\dfrac{L+v}{L}s\le t\le \overline{T}+L+v\end{cases} \tag{4}$$

for $s\in[t_{i-1}^{\min},t_{i-1}^{\max}]$, $L=t_{i-1}^{\max}-t_{i-1}^{\min}$ and $\overline{T}$ denotes the macroscopic oscillation period. The coordinate transformation $T=t-s$ transforms q_i to g which means $g_{\overline{T},L}^{v}(T,s)=q_i(T+s,s)$ defines the frequency distribution for all period lengths T which create one macroscopic oscillation in dependence on v, $\overline{T}$, L and s. To eliminate the dependence on s, we integrate and get $g_{\overline{T},L}^{v}(T)=L^{-1}\int_0^L g_{\overline{T},L}^{v}(T,s)\,ds$ (figure 1 top right). In the next step, the dependence on L is eliminated by integration (figure 1 bottom left) with the result $g_{\overline{T}}^{v}(T)=\overline{T}^{-1}\int_0^{\overline{T}} g_{\overline{T},L}^{v}(T)\,dL$. Let the time $\overline{T}_{\max}$ denote the temporal analogue to the maximum wavelength which corresponds to the size of a black body. For an arbitrarily positive integer k we consider the mode $\overline{T}_{\max}k^{-1}$. Then the equations (2) and (4) define oscillations with a sequence of macroscopic periods $\overline{T}_i=(\overline{T}_{\max}k^{-1}+iv_k2^{-1})$ which have (arranged one after another) to match $\overline{T}_{\max}$ i.e. $\sum_{i=1}^{\mu_k}\overline{T}_i=\overline{T}_{\max}$. Hence, the integer μ_k equals k in the case of sustained oscillations $(v_k=0)$ and $v_k=4({\mu_k}^2+\mu_k)^{-1}(1-\mu_k k^{-1})\overline{T}_{\max}$ for $0<\mu_k<k$ in the case of damped oscillations. Finally, the frequency distribution g for the periods T is defined by

$$g(T)=\sum_{k=1}^{m}\sum_{i=1}^{\mu_k}g_{\overline{T}_i}^{v_k}(T) \tag{5}$$

Oscillations with macroscopic periods shorter than $\overline{T}_{\max}m^{-1}$ are excluded to avoid an unrealistic unlimited velocity of the oscillation process. In the model, the current resulting from one macroscopic oscillation with period $\overline{T}$ is defined by $I_i^{\overline{T}}(t)=\int_{t_i^{\min}}^{t_i^{\max}}p_i(s)I_{elem}^{\overline{T}}(t-s)\,ds$ where $I_{elem}^{\overline{T}}$ denotes the elementary current peak [7] resulting from the oxide growth. The related (per oscillation cycle i) quantized energy is given by $E_{\overline{T}}=U\int_{t_i^{\min}}^{t_i^{\max}+\Delta t}I_i^{\overline{T}}(t)\,dt$ where U denotes the potential at the boundary between the silicon and its oxide and Δt the oxide growth time. Measurements [11] indicate that during each of the μ_k oscillations the same energy quant $E_{\overline{T}_{\max}k^{-1}}$ is emitted. Hence, the energy density is defined by

$$\rho(T)=\sum_{k=1}^{m}E_{\overline{T}_{\max}k^{-1}}\sum_{i=1}^{\mu_k}g_{\overline{T}_i}^{v_k}(T) \tag{6}$$

Defining $E(T)=\rho(T)(g(T))^{-1}$, equation (6) leads to the relation $\rho(T)=E(T)g(T)$. Measurements [11] show, that for larger modes $\overline{T}_{\max}k^{-1}$ sustained oscillation appear i.e. $v_k=0$ for $k=1,2,...,n$. For shorter modes the oscillations are more and more damped i.e. $0<v_{n+1}<v_{n+2}<...<v_m$. The energy $\mu_k E_{\overline{T}_{\max}k^{-1}}$ (resulting from μ_k oscillations during the time $\overline{T}_{\max}$) depends on the mode $\overline{T}_{\max}k^{-1}$ i.e. on k. In the case of sustained oscillations, the resulting energy increases progressively for shorter modes reflected by the graph $(\overline{T}_{\max}k^{-1},k\,E_{\overline{T}_{\max}k^{-1}})$ for $k=1,2,...,n$. Moreover, during sustained oscillations measurements [11] of $E_{\overline{T}}$ indicate additionally a progressive increase of $E_{\overline{T}}$ for decreasing $\overline{T}$. In the

case of damped oscillations, the resulting energy $\mu_k E_{\bar{T}_{\max} k^{-1}}$ decreases because the number μ_k of periods decreases for $k = n+1,...,m$. Also, $E_{\bar{T}_{\max} k^{-1}}$ decreases because the oxide growth time falls more and more below a time limit for a sufficiently large oxide growth. This behaviour of the energy is reflected by $E(T) = c(T^2(e^{d T^{-1}} - 1))^{-1}$ quantitatively. Finally, a suitable and with measurements [11] consistent choice of the model parameters n, m, $n > \mu_{n+1} > \mu_{n+2} > ... > \mu_m > 0$, and $E_{\bar{T}_{\max} k^{-1}}$ for $k = 1,2,...,m$ leads to a fit of $g(T)E(T)$ to the radiation of a black body (figure 1 bottom right).

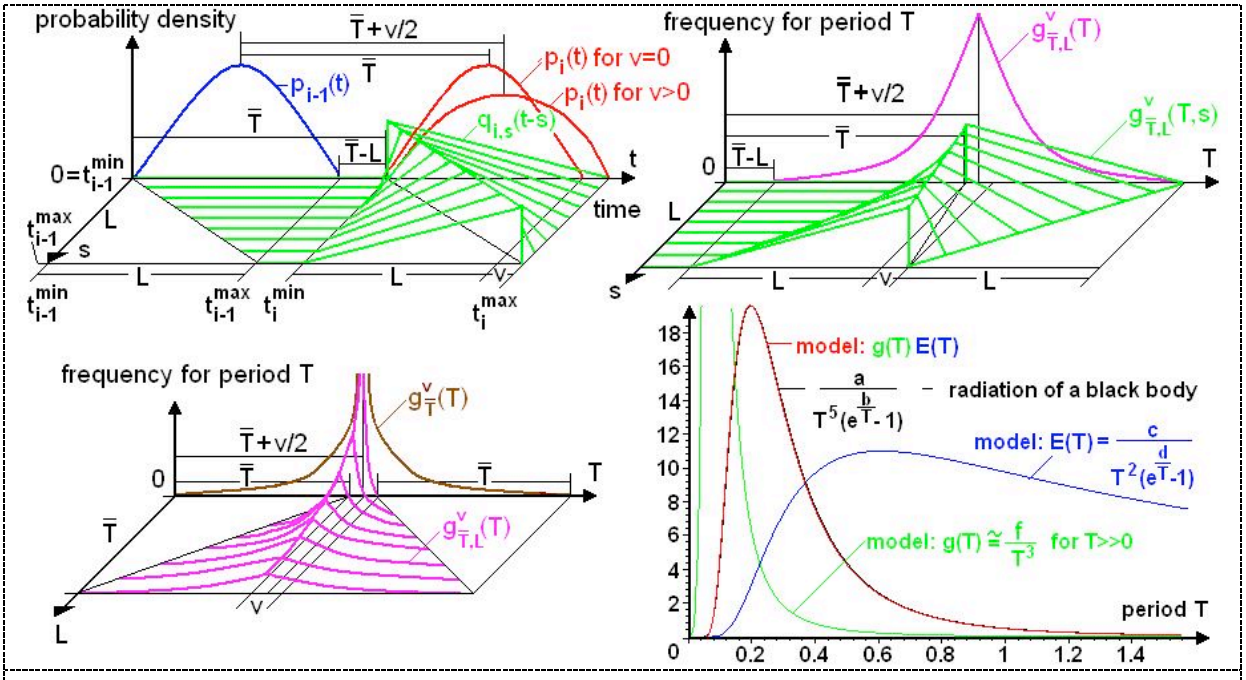


Figure 1. Relation between the probability density $q_{i,s}(t\text{-}s)$ for the periods t-s of the oscillators, the various frequency distributions g for the period lengths T and the radiation of a black body compared with the model. The magnitude of the coordinate axes is chosen arbitrarily and $a,b,\ldots, f$ are constants.

4. Conclusions

The mathematical concept of the discretization of phase oscillators leads to a linear integral equation of second order representing a Markov process and a random walk. The relation of the model to the holographic principle is shown. Moreover an analysis of the frequency distribution for the periods of the phase oscillators and of the energy of the (photo) electrochemical system leads to the graph of the radiation of a black body. Particularly the energy is quantized in the model.

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