

Gibbs fluctuation theory in the context of electrochemical equilibrium noise*

Boris M. Grafov

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninskii Prospekt, Moscow 119991, Russia

Abstract: The electrochemical noise verification of the Gibbs fluctuation theory shows that the Gibbs ergodic idea works perfectly with respect to the pair correlations of the electrode charge thermal fluctuations. At the same time, the Gibbs formulae for the triple- and higher-order correlations of the electrode charge thermal fluctuations are outside of the ergodic hypothesis. This failure of the Gibbs ergodic idea suggests that the noise version of the electrochemical charge-transfer theory should be developed. In the context of nano-electrochemistry, the second- and higher-order correlations of the electrochemical noise processes may be considered as the quantities suitable for the nano-electrochemical characterization of both the electrode processes and electrochemical devices.

Keywords: electrochemical charge-transfer theory; electrochemistry; electrode charge thermal fluctuations; ergodic hypothesis; Gibbs fluctuation theory.

INTRODUCTION

Thermal fluctuations play a decisive role in electrochemical kinetics [1]. The Gibbs fluctuation theory is the general foundation for the elementary act theory. The aim of this paper is to discuss the paradox of the Gibbs fluctuation theory. Using the Nyquist fluctuation dissipation theorem and the Langevin stochastic equation, I demonstrate that the thermal fluctuation correlations of high order do not satisfy the Gibbs ergodic idea. The nonergodicity of the Gibbs fluctuation theory suggests that the ergodic fluctuation version of the electrochemical charge-transfer theory should be developed. In the context of nano-electrochemistry, the high-order correlations of the thermal fluctuations may be considered as the quantities suitable for the nano-electrochemical characterization of both the electrode process and electrochemical device.

Besides electrochemistry, the possible implications of this work concern the numerous scientific fields, including the fluctuation chemical kinetic theory [2], the stochastic ergodic theory [3], the electronic noise and fluctuations [4,5], the anomalous transport theory [6,7], the nonlinear Brownian motion with a non-Gaussian bath [8], the Langevin equation technique [9], the nonlinear fluctuation–dissipation relations [10], the work fluctuation theorems [11–15], and the stochastic resonance theory [16].

The experimental approaches for the electrochemical verification and possible electrochemical applications of the implications of this work may be organized in line with the ASTM Standardization of Electrochemical Noise Measurement [17]. It is needed to use the impedance measurement technique [18] simultaneously.

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GIBBS FLUCTUATION THEORY

The Gibbs basic idea is striking [19]. It is assumed that any system of the Gibbs equilibrium ensemble transfers permanently from one state to another due to the random interaction with the environment. At the same time, it is assumed that the distribution function in the Gibbs equilibrium ensemble does not depend on the character and parameters of the random interaction. The only exclusion is a temperature that is the same for the thermostat and the Gibbs ensemble of the macroscopically identical systems.

Let us consider the simplest electrochemical situation. Let the faradaic current be controlled by the one-step, one-electron charge transfer. The electric circuit for such a situation is shown in Fig. 1.

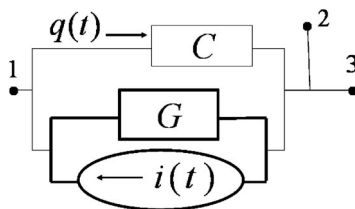


Fig. 1 The small-signal (linear) electric circuit for the electrode with the faradaic process: the G is the noiseless faradaic conductance, the $i(t)$ is the current white noise source corresponding to the one-step, one-electron faradaic process, the bold lines mark out the noisy faradaic conductor, the C is the double-layer capacity, and the $q(t)$ is the fluctuating electrode charge.

The electrode circuit includes the faradaic small-signal conductance G and the double-layer differential capacity C in parallel. Point 1 corresponds to the bulk of electrode under study. Point 2 corresponds to the reference electrode. Point 3 corresponds to the counterelectrode. In the frame of the macroscopic electrochemistry, the slow electron transfer is modeled by a noiseless active conductance G . However, in the context of nano-electrochemistry, we have to add the current white noise source $i(t)$ (t is time) to the conductance G in parallel. The faradaic current white noise source $i(t)$ excites the electrode charge random fluctuations $q(t)$. In general, one may expect that the charge covariance $\langle q^2(t) \rangle$ and other charge stochastic moments depend on the character and parameters of the current noise source $i(t)$. However, in line with the Gibbs fluctuation theory [9,20], one has

$$\langle q^2(t) \rangle = kTC \quad (1)$$

$$\langle q^3(t) \rangle = (kT)^2 \partial C / \partial E \quad (2)$$

$$\langle q^4(t) \rangle - 3\langle q^2(t) \rangle \cdot \langle q^2(t) \rangle = (kT)^3 \partial^2 C / \partial E^2 \quad (3)$$

where k is the Boltzmann constant, T is temperature, and E is the electrode potential. The left-hand side in eq. 3 equals the charge cumulant of 4th order. The cumulant sequence 1–3 may be continued. The equation for the 5th moment of the random charge fluctuations $\langle q^5(t) \rangle$ is as follows:

$$\langle q^5(t) \rangle - 4\langle q^2(t) \rangle \cdot \langle q^3(t) \rangle = (kT)^4 \partial^3 C / \partial E^3 \quad (4)$$

It is remarkable that in line with the Gibbs theory any parameter of the random Faradaic current source $i(t)$ is not involved in eqs. 1–4 for the stochastic moments of the electrode charge fluctuations. Such a situation is preserved with respect to higher stochastic moments.

LANGEVIN STOCHASTIC EQUATION

The Langevin stochastic equation [21] is a base for the noise approach to the theory of thermal fluctuations. Following [22], we may write the following Langevin equation for the thermal fluctuations of the electrode charge $q(t)$ as the Kirhgoff equation in its linear form

$$\partial q / \partial t + GC^{-1}q(t) = i(t) \quad (5)$$

The linear character of Langevin's stochastic equation for the thermal fluctuations is extremely important. The linearity of the Langevin equation reflects the essence of the Nyquist fluctuation dissipation theorem. It is well known [23,24] that the Nyquist fluctuation dissipation theorem involves just the linear response.

Langevin's stochastic equation (5) may be read as a mapping equation. In line with [25,26], Langevin's stochastic equation (5) maps the ensemble of the current noise realizations $\{i(t)\}$ to the ensemble of the voltage noise realizations $\{C^{-1}q(t)\}$, where $C^{-1}q(t)$ is the fluctuation component of the electrode potential.

The stochastic properties of the random current $i(t)$ are defined completely by the set of cumulant functions. According to properties of the white noise one may write the cumulant functions in such a form:

$$\langle i(0), i(t) \rangle = i_2 \delta(t) \quad (6)$$

$$\langle i(0), i(t_1), i(t_2) \rangle = i_3 \delta(t_1) \delta(t_2) \quad (7)$$

$$\langle i(0), i(t_1), i(t_2), i(t_3) \rangle = i_4 \delta(t_1) \delta(t_2) \delta(t_3) \quad (8)$$

where $\delta(t)$ is the Dirac δ -function. We use the Malakhov notations (with comma) for the cumulant functions [27].

In eqs. 6–7, the symbols i_2 , i_3 , and i_4 stand for the intensities of cumulant functions of the 2nd, 3rd, and 4th order correspondingly. The set of the cumulant functions 6–8 may be continued. For example, one has for the cumulant function of the 5th order

$$\langle i(0), i(t_1), i(t_2), i(t_3), i(t_4) \rangle = i_5 \delta(t_1) \delta(t_2) \delta(t_3) \delta(t_4) \quad (9)$$

Knowing the set of cumulant functions 6–9 allows one to calculate the charge cumulants of the 2nd, 3rd, 4th, and 5th order.

NOISE APPROACH TO THERMAL FLUCTUATIONS

The stochastic equation (5) has the same character as the Langevin stochastic equation in the theory for the Einstein diffusion. According to [28], we may write the solution of eq. 5 in the following form:

$$q(t) = \int_{-\infty}^t dt_1 i(t_1) H(t - t_1) \quad (10)$$

where

$$H(t) = \exp(-tGC^{-1}) \text{ for } t \geq 0 \text{ and } H(t) = 0 \text{ for } t < 0 \quad (11)$$

Combining eqs. 10–11 and eqs. 6–9 yields

$$\langle q^2(t) \rangle = i_2 C / (2G) \quad (12)$$

$$\langle q^3(t) \rangle = i_3 C / (3G) \quad (13)$$

$$\langle q^4(t) \rangle - 3\langle q^2(t) \rangle \cdot \langle q^2(t) \rangle = i_4 C / (4G) \quad (14)$$

$$\langle q^3(t) \rangle - 4\langle q^2(t) \rangle \cdot \langle q^3(t) \rangle = i_5 C / (5G) \quad (15)$$

Now we are in a position to compare the set of eqs. 12–15 with the set of eqs. 1–4.

DISCUSSION

In line with the Nyquist fluctuation dissipation theorem [23,24], the following universal relation exists:

$$i_2 = 2kTG \quad (16)$$

Therefore, we have instead of eq. 12

$$\langle q^2(t) \rangle = kTC \quad (17)$$

We arrived at the remarkable result. Equations 1 and 17 are identical. This means that the Gibbs paradoxical idea works perfectly in respect to the correlations of the second order. However, the situation with the Gibbs description of the high correlations is completely different.

Let us assume that the statistics of the faradaic exchange current is Poissonian. In this case, we have [29]

$$i_3 = 0 \quad (18)$$

Therefore

$$\langle q^3(t) \rangle = 0 \quad (19)$$

One may see that in general, eq. 2 is not in compliance with eq. 19.

The Gibbs formula (2) does not work. An analogous situation arises with the correlations of 4th and 5th order. In line with [29], we write

$$i_4 = 2e^3I_0 \quad (20)$$

$$i_5 = 0 \quad (21)$$

Consequently, we have instead of eqs. 14 and 15

$$\langle q^4(t) \rangle - 3\langle q^2(t) \rangle \cdot \langle q^2(t) \rangle = (e^2/2)kTC \quad (22)$$

$$\langle q^5(t) \rangle - 4\langle q^2(t) \rangle \cdot \langle q^3(t) \rangle = 0 \quad (23)$$

Comparing eqs. 22 and 23 with eqs. 3 and 4 shows that the Gibbs formulae for the high correlations are outside the ergodic hypothesis.

CONCLUSIONS

The Gibbs ergodic idea is paradoxical. In line with the Gibbs theory, the thermodynamic system turns out in the equilibrium state due to the random interaction between the thermodynamic system and the environment. At the same time, according to the Gibbs ergodic idea, the variance and other statistical moments for the extensive quantities of the thermodynamic system do not depend on the parameters of the random interaction with the environment. In this paper, the Gibbs ergodic idea was verified by means of the equilibrium noise theory in the form of the Langevin stochastic equation, which is in compliance with the Nyquist fluctuation dissipation theorem. It was demonstrated that the variance of the double-layer charge fluctuations found on the basis of the Gibbs ergodic idea is consistent with the noise theory. At the same time, it was demonstrated that the Gibbs ergodic idea does not work with respect to the high-order moments of the charge thermal fluctuations. This failure of the Gibbs ergodic idea suggests that the noise version of the electrochemical charge-transfer theory should be developed. In the context of nano-electrochemistry, the second- and higher-order correlations of the thermal fluctuations may be considered as the quantities suitable for the nano-electrochemical characterization of both the electrode processes and electrochemical devices.

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