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# Turbulent pulsations of the microelectrode limiting diffusion current*

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Flat mounted microelectrodes, for which the longitudinal length, $L$, is small in comparison with the diffusion entrance region are used to measure wall shear stress fluctuations. However, microelectrode turbulent noise depends both on wall shear stress fluctuations (i.e. longitudinal velocity pulsations) and on normal pressure gradient fluctuations (i.e. normal velocity pulsations). The relative value of these two factors depends on the microelectrode length. The influence of normal and longitudinal velocity pulsations on the microelectrode turbulent noise are the same order of magnitude if the length $L$ is approximately 10 or 20 times the thickness of the viscous sublayer. Consequently it is possible to determine statistical characteristics of normal and longitudinal velocity fluctuations by using a number of microelectrodes of different lengths in the flow direction.

## 1. Introduction

One of the promising directions of electrodiffusion diagnostics is the investigation of the turbulent pulsations of velocity inside a viscous sublayer. The possibility of probing the flow regions directly adjoining the solid surface makes the electrodiffusion method, not only competitive with, but also preferable to, more conventional thermoanemometric and optical methods.

For the electrodiffusion diagnostics of hydrodynamic characteristics, electrodes placed flush with the solid boundary of the flow have been conventionally used as well as special (e.g. iodine/iodide) electrolytes providing diffusion control of the redox reaction occurring on the electrode surface. If the working electrode length in the flow direction, $L$, is small compared to the size of the diffusion entrance length than the limiting diffusion current, $\bar{I}$, is determined by the time-averaged value of the wall shear stress $\bar{\tau}$ [1, 2]

$$\bar{I} = k_e(\bar{\tau})^{1/3} \quad (1)$$

where $k_e$ is a known coefficient depending on the physico-chemical constants of the electrolyte and the working electrode dimensions.

A quantitative criterion of the smallness of the quantity $L$ was obtained, for example, in [3]:

$$L < 600\, y_\tau \quad (2)$$

where $y_\tau = \nu\sqrt{\rho}/\sqrt{\bar{\tau}}$ is the dynamic length, $\nu$ is the electrolyte kinematic viscosity and $\rho$ is the electrolyte density.

The turbulent pulsations of the electrolyte velocity give rise to fluctuations in the limiting diffusion current. Analysis of the statistical characteristics of these pulsations gives information about the statistical characteristics of wall turbulence. It was traditionally considered [3, 4, 6, 7] that turbulent pulsations of the limiting diffusion current of a microelectrode are determined by wall shear stress pulsations. A more rigorous analysis showed [8–11] that, in fact, the situation is more complicated. The turbulent noise of the microelectrode depends significantly both on pulsations of the longitudinal velocity component (i.e. friction pulsations) and on those of the normal velocity component (i.e. normal pressure gradient pulsations) and also on their cross correlation.

## 2. Theory

The concentration pulsation field $c'(\vec{r}, t) \equiv c(\vec{r}, t) - \bar{c}(x, y)$ satisfies the following simplified equation

$$\frac{\partial c'}{\partial t} + f_\tau y \frac{\partial c'}{\partial x} - D\frac{\partial^2 c'}{\partial y^2} = -v'_x \frac{\partial \bar{c}}{\partial x} - v'_y \frac{\partial \bar{c}}{\partial y}$$

where

$$f_\tau = u_\tau / y_\tau \quad (3)$$

Here $D$ is the molecular diffusivity and the $y$-axis is perpendicular to the electrode surface. All the calculations below are given for the case of a microelectrode, i.e. the average concentration field $\bar{c}(x, y)$ satisfies the Leveque equation [1] and the mean current, $\bar{I}$, satisfies Equation 1. The fluctuation field, $\vec{v}'$, within the viscous sublayer has a considerable length along the stream axis, $x$: $L^{(x)}_{corr} \sim 1000\, y_\tau$ [5]. So, it is possible to consider the fluctuation field as fully correlated along the microelectrode surface ($x$-axis).

A pair of coupled equations for the correlators $\overline{c'(\vec{r}, t)\, c'(\vec{r}_1, t_1)}$ and $\overline{c'(\vec{r}, t)\, \vec{v}'(\vec{r}_1, t_1)}$ can be obtained [8, 11] by using Equation 3. By solving these equations the connection between the power density of microelectrode current pulsations $S_I(\omega)$ and the hydrodynamic characteristics of the flow can be obtained. In particular, for the rectangular electrode this

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connection has the form [8, 11]

$$S_I(\omega, L, H) = \mathscr{P}_{\alpha\beta}(\omega, L) \times \int_{-H}^{H} \mathrm{d}(z - z_1) W_{\alpha\beta}(\omega, z - z_1)\,(H - |z - z_1|) \tag{4}$$

Here $H$ is the electrode dimension in the $z$-direction, $\omega$ is the random frequency, indexes $\alpha$ and $\beta$ are equal to $x$ or $y$.

The functions $W_{\alpha\beta}$ are related to velocity correlators and characterize the magnitude of the longitudinal $v'_x$ and normal $v'_y$ velocity fluctuations at the external boundary of the viscous sublayer ($l_v = 5y_\tau$):

$$\overline{v'_\alpha(t, x, z, y)\, v'_\beta(t; x_1 = x; z_1; y_1)} = \frac{1}{4\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \times \exp\left[-\mathrm{j}\omega(t - t_1)\right] W_{\alpha\beta}(\omega; z - z_1)\,(y/l_v)^{n_\alpha}\,(y_1/l_v)^{n_\beta} \tag{5}$$

for $0 < y < l_v$, $n_x = 1$ and $n_y = 2$.

The transfer functions $\mathscr{P}_{\alpha\beta}$ are equal

$$\mathscr{P}_x = -\frac{1}{15}\frac{\bar{I}}{Hu_\tau}\bar{p}_x(\bar{\omega}); \qquad \mathscr{P}_y = \frac{1}{125}\frac{\bar{I}}{Hu_\tau}\frac{L}{y_\tau}\bar{p}_y(\bar{\omega}) \tag{6}$$

where $\bar{\omega} = \omega L^{2/3} D^{-1/3} f_\tau^{-2/3}$ is dimensionless frequency.

Under quasi steady-state conditions the functions $p_x$ and $p_y$ are unity and, in the high frequency range, they decrease according to the power law, [8, 9, 11]

$$\bar{p}_x(\bar{\omega}) \simeq 3.71\,(-\mathrm{j}\bar{\omega})^{-1} - 4\,(-\mathrm{j}\bar{\omega})^{-3/2} \tag{7}$$

$$\bar{p}_y(\bar{\omega}) \simeq 10\,(-\mathrm{j}\bar{\omega})^{-3/2} \qquad (\bar{\omega} \gg 1) \tag{8}$$

In the frequency range $\bar{\omega} \leqslant 13.5$ the magnitudes of the functions $p_x$ and $p_y$ were obtained by computer simulations [9], see Fig. 1.

We introduce the notion of the critical size of the electrode $L_{\mathrm{crit}}$ [8]. For an electrode of length in the flow direction $L_{\mathrm{crit}}$ the pulsation current is determined equally well both by pulsations of the longitudinal and normal velocity components.

It is possible to estimate numerically the quantity $L_{\mathrm{crit}}$ from Equations 4 and 6. Thus,

$$L_{\mathrm{crit}} \approx (5/3)\,(\overline{v'^2_x}/\overline{v'^2_y})\, l_v \tag{9}$$

that is, the critical size is approximately 10 or 20 times the thickness of the viscous sublayer and one order of magnitude smaller than the diffusion region entrance length.

### 3. Experiment details

The conclusion, based on Equation 4, concerning the influence of the normal component of pulsation velocity on the turbulent pulsations of the limiting diffusion current of the microelectrode can be directly verified experimentally. For this purpose a set of measuring electrodes of different length $L$ are required. Under quasi-steady conditions the magnitude of the normalized spectral density $SO$ ($SO = S_I/\bar{I}^2$ as $\bar{\omega} \ll 1$) does not depend on the electrode length, $L$, if current pulsations are determined by those of the longitudinal velocity component alone. If current pulsations are also related to those of the normal velocity component, the magnitude of the normalized spectral density under quasi-steady conditions, $SO$, is a function depending significantly on the electrode length, $L$.

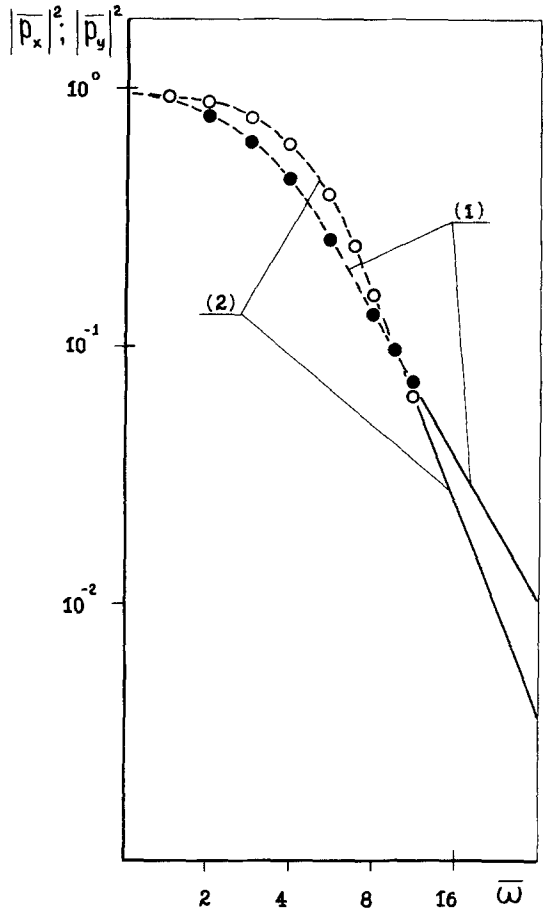


Fig. 1. Transfer functions $\bar{p}_x$ and $\bar{p}_y$. (1) $|\bar{p}_x|^2$, (●) computer calculation, (—) Equation 7; (2) $|\bar{p}_y|^2$, (○) computer calculation, (—) Equation 8.

A suitable set-up for these experiments was made within a collaborative programme between the A. N. Frumkin Institute and the Institute of Theoretical Fundamentals of Chemical Technology (Prague) and was demonstrated at the 1st International Electrodiffusion Diagnostics Workshop held in Prague (August, 1990).

The flow cell, a rectangular channel of dimensions 2 mm × 15 mm was made of Plexiglas. This cell provides a turbulent flow with Reynolds number up to $1.5 \times 10^4$. Rectangular platinum electrodes of width $H = 4.0$ mm ($z$-axis) were used along with the iodine/iodide electrolyte system. The electrode lengths ($x$-axis) were different: $L_1 = 0.1$ mm; $L_2 = 0.4$ mm; $L_3 = 1.0$ mm.

The electrochemical cell was connected to a Commodor PC. This allowed recording of the current pulsations and calculation of their power density. The measured normalized current density pulsations $\bar{S}_I(f) = S_I(f)/\bar{I}^2$ (where $f = \omega/2\pi$) are shown in

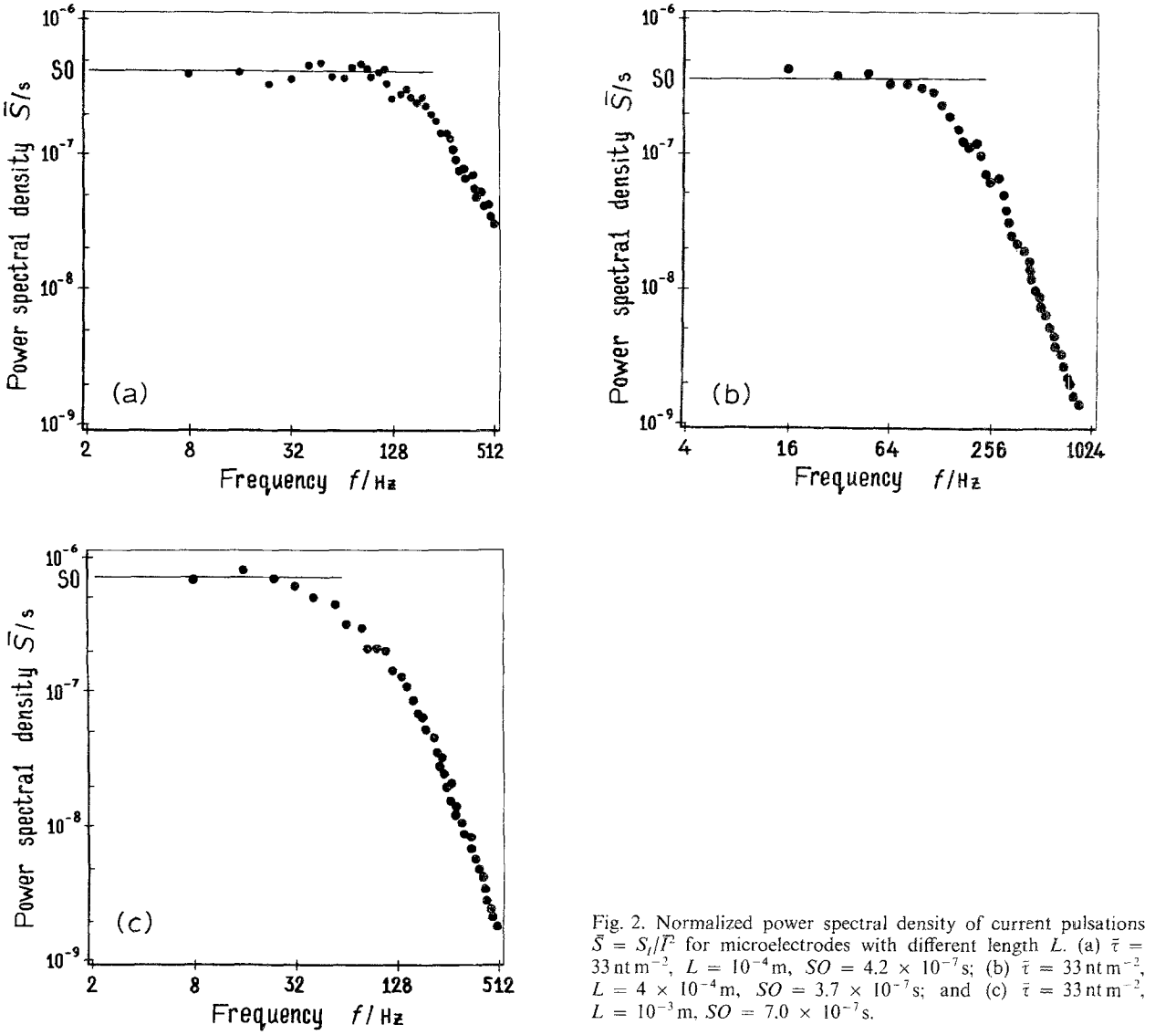


Fig. 2. Normalized power spectral density of current pulsations $\bar{S} = S_I/\bar{I}^2$ for microelectrodes with different length $L$. (a) $\bar{\tau} = 33\,\mathrm{nt\,m^{-2}}$, $L = 10^{-4}\,\mathrm{m}$, $SO = 4.2 \times 10^{-7}\,\mathrm{s}$; (b) $\bar{\tau} = 33\,\mathrm{nt\,m^{-2}}$, $L = 4 \times 10^{-4}\,\mathrm{m}$, $SO = 3.7 \times 10^{-7}\,\mathrm{s}$; and (c) $\bar{\tau} = 33\,\mathrm{nt\,m^{-2}}$, $L = 10^{-3}\,\mathrm{m}$, $SO = 7.0 \times 10^{-7}\,\mathrm{s}$.

Fig. 2a, b and c. The main result of these experiments is that the amplitude of the normalized spectral density under quasi-steady conditions increases significantly for the biggest electrode. It is necessary to emphasize that for all the electrodes the Leveque equation (1) for the mean current was corroborated within 3% accuracy.

## 4. Discussion

For all examined electrodes the mean current was determined by the mean wall shear stress. It may be expected that under these conditions the current pulsations must be determined by the wall shear stress fluctuations. If this point of view is valid than the magnitude of the normalized spectral density $SO$ does not depend on the electrode length, $L$. However, the experiments have shown that the magnitude of $SO$ increases significantly for the biggest electrode. In our opinion this fact is connected with the influence of the normal velocity component fluctuations on the current pulsations in agreement with previous theoretical consideration.

The magnitudes of the mean shear stress, the electrolyte kinematic viscosity and the electrolyte density in our experiments (see Fig. 2a, b and c) were: $\bar{\tau} = 33\,\mathrm{N\,m^{-2}}$, $\nu = 8.4 \times 10^{-7}\,\mathrm{m^2\,s^{-1}}$; $\rho = 1130\,\mathrm{kg\,m^{-3}}$. Using these data and Equation 9 the thickness of the viscous sublayer $l_v$ is $24.6 \times 10^{-6}\,\mathrm{m}$ and the estimated value of the quantity $L_{crit}$ is 0.25–0.5 mm. This is the same order of magnitude for $L_{crit}$ in our experiments. Really, for two electrodes ($L_1 = 0.1\,\mathrm{mm}$ and $L_2 = 0.4\,\mathrm{mm}$) the magnitude of the normalized spectral density, $SO$, is approximately constant and increases significantly for the biggest one ($L_3 = 1\,\mathrm{mm}$). So, it is also possible to estimate the quantity $L_{crit} = 0.4$–$1\,\mathrm{mm}$. In such a way two independent estimations of the quantity $L_{crit}$ are in good agreement.

Strictly speaking, the dependence of magnitude of the normalized spectral density, $SO$, on the electrode length, $L$, is also a parabolic function. But we cannot verify this theoretical prediction because the set of measuring electrodes contains only three electrodes of different length, $L$.

Thus the experiments corroborated the theory qualitatively. Quantitative corroboration of the theory can be obtained using a set of measuring electrodes containing at least six or seven electrodes of different length, $L$.

## 5. Concluding remarks

Using microelectrodes of different length the characteristics of turbulent pulsations, not only of the longitudinal but also the normal component, may be obtained and thus the functional possibilities of the electrodiffusion method are widened.

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