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Reconstruction of Distributions of Nanoparticles or Electroactive Nano-Components in Electrochemical Arrays based on Chronoamperometric Data

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Abstract

The main scope of this work was to elaborate and test a simple mathematical and numerical procedure for reconstructing the probability density distributions \( f(\rho) \) characterizing the distribution of electroactive or electrocatalytic nano-components present or deposited on the electrochemically-inert surface of a planar conductor based on the time-dependent chronoamperometric responses of the corresponding electrochemical array. The mathematical and numerical validity of the procedure was established for three types of arrays (one periodical, two involving random dispersions) involving near-spherical nano-components dispersed on a flat surface. Indeed, altogether, these three types represent most 2D-experimental electrochemical nano-arrays used for analytical or electrocatalytic purposes. This reconstruction procedure is easily implementable using most commercial mathematical programs. Albeit the simplicity of its implementation, it allowed recovering probability densities with an excellent precision, even when the available time-range experimentally accessible was too short for its rigorous application, being thus perfectly adequate to most experimental purposes.

Keywords:

Electrochemical arrays; Chronoamperometry; inverse problem; Micro- and nanodisk electrode arrays; density distribution probability; Voronoi tessellation.

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\(\): Dedicated to Professor Zhao-Wu Tian, our dear, respected and esteemed friend and colleague, in honor of his 90th Birthday.

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1. **Introduction**

Since the development of chemical nanosciences, electrochemical interfaces consisting of electroactive or electrocatalytic nanoparticles or others nano-components dispersed on non-electroactive (or poorly electroactive) electrical conductors have received an increasing importance in the fields of electrocatalysis or (bio)electroanalytical sensors. This is particularly evident for catalysis and chemical energy applications, since using specific metallic nanoparticles, (see, e.g. [1-7]) or faultlessly defined nano-crystals with the adequate amounts of edges and surfaces displaying perfectly designed crystallographic orientations is extremely important for electrocatalysis.[2] Indeed, dispersion of specifically tailored nanoparticles provides a strong control of electrocatalytic efficiency and selectivity when compared to what could be achieved with a macroscopic electrode, while being cost-effective compared to macroscopic single crystals (see, e.g. [8-20]). On the other hand, the growth of applications based on self-assembled monolayers (SAMs) and analytical systems based on them has promoted the development of this field (see, e.g. [21-30]). However, SAMs are seldom perfect and present pinholes that affect the SAMs expected behaviors by acting as nanoelectrodes dispersed in electrochemically-inert layers,[21] or conversely may serve to introduce specific functions in the SAMs.[24,25] Hence, the avenues related in one way or another to the problematics of dispersions of electroactive nano-elements in an inert surface cover a wide range of fundamental and applied researches.

Concerning (bio)electroanalytical applications and sensors, the motivation in using arrays of nanoparticles is quite different. Indeed, electrochemical arrays of nanoparticles or nano-electroactive elements offer great analytical performances compared to macroscopically active electrode surfaces. One origin for such high performance in bioanalytical sensors is that nano-electroactive or conducting elements, such as carbon nanotubes or reduced graphene oxide sheets, facilitate the electrochemical ‘wiring’ of enzymes or other biological molecules with the electrode without altering their structures (hence their biological activities) as would occur if they were directly adsorbed on an electrode surface where they would experience high electrical fields (ca. $10^5$ V/m) prevailing at electrode-electrolyte interfaces. However, this is not the only gain. The most important analytical advantage is that arrays of nanoparticles and nano-electroactive
elements increase the signal-to-noise (S/N) ratio in electrochemical experiments.[31] Indeed, in
 electrochemistry the minimum current noise stems from the electrode capacitance due to the
derivation of small but sharply varying potential fluctuations across the double layer.[32] Hence,
minimizing the electrode surface area directly increases the signal-to-noise ratio and enhances
the analytical performances. Indeed, nanoelectrodes develop convergent diffusional fields so that
the Faradaic current is proportional to its size, \( r_0 \).[31,33] Conversely, the capacitance remains
proportional to its surface area, viz., to \( r_0^2 \), so that the S/N value increases as \( 1/r_0 \).[31] For
example, this property has allowed the detection of extremely low quantities of electroactive
(bio)molecules, down to zeptomoles, even in routine experiments (see e.g.,[34-38]) and to many
bio-electroanalytical applications (see e.g.,[39-54] for recent publications).

Though, at first glance using an electrochemical interface formed of dispersed nano-
components may seem as a non-efficient approach in terms of the total current delivered by the
device. Effectively, would the diffusion layers generated by each nano-electroactive component
remain too small to overlap and interact synergistically such arrays would have no real interest
from an electrochemical point of view. Fortunately, under most analytical conditions these
individual diffusion layers reach sufficiently large sizes to strongly overlap. This overlay produces
a planar uniform diffusion layer expanding towards the solution bulk as if the whole surface of
the array, \( A_{array} \), was active (i.e., including its electroactive and non-electroactive
sections).[31,33,55-57] This occurs when the mean distance, \( d \), between the nanocomponents is
lesser than the extension of the time dependent diffusion layers that expand around each one,
\[ \delta \sim \sqrt{\pi D t} \] where \( D \) is the diffusion coefficient of the electroactive solution
species and \( t \) the duration of the experiment.[63]

When arrays consist of micro-components, they can be designed and manufactured to
respect this constraint, viz., \( d \ll \delta \sim \sqrt{\pi D t} \), in order to ensure that the array may perform in an
optimum way. When such arrays are fabricated through random adsorption / deposition of
electroactive or electrocatalytic micro-components one may check that \( d \ll \delta \sim \sqrt{\pi D t} \) for the
sought time scale by evaluating \( d_{mean} \) values by in situ observations with optical or confocal
microscopy. However, such in situ reports are clearly impossible when the active elements consist
of nanoparticles. On the other hand, quantitative rationalization of the performance of
electrochemical and electrocatalytic devices or sensors and their optimization require a good knowledge of the nano-elements distribution onto the electrochemically-inert supporting conductor surface. Presently, the only possible way to gather such information is to rely on ex situ measurements using electron microscopy (EM). Yet, even if EM is perfectly adequate to investigate the general shape and size of the nanoparticles, it presents a double disadvantage when used to characterize mean separation distances between nano-components in a random array: (i) only too small portions (hence, maybe non-representative?) of the array can be scrutinized and analyzed with special algorithms to have statistical significance; (ii) moreover, the sampled arrays have to be prepared and dried in vacuum before any EM analyses so the nanoparticles may be mechanically displaced during the solvent evaporation, e.g., by Marangoni microscopic flows,[64] if the nanoparticles are not solidly anchored onto their support. STM, AFM and possibly SECM could also be used but in this case the surface range that can be monitored is too small compared to the macroscopic sizes of arrays (see e.g. [65-70]). These difficulties explain why most random arrays are not characterized experimentally, thus leaving interrogations about their real microscopic structures and making quantitative rationalizations of their electrochemical or electrocatalytic performances difficult or even impossible.

We wish therefore to present in this work a theory-based approach to solve this important problem in electrochemical nanosciences without the need of accessing sophisticated instrumentation or specific algorithms for picture recognition and treatment of the data. Yet, to achieve this goal we need first to review the main outcomes of our recently published theoretical works on random electrochemical arrays of nanodisks electrodes,[33,55-62] since the disclosed reconstruction approach strongly relies on their concepts and results. It is thus the purpose of Sections 2.1 and 2.2 to summarize these previously published results, while Sections 2.3 and 2.4 disclose unpublished results.

2. RESULTS AND DISCUSSION

In the following, we only consider arrays of nanodisks since nanodisks capture the main behavior of diffusion at nano-electroactive elements with near-spherical geometries. Furthermore, it is noted that, although beyond the scope of this work, the general principles of the reconstruction
approach presented in Section 2.3 may easily be extended to other geometries (see, e.g., reference [33,55]).

2.1. Modeling random arrays

In order to delineate the main problems at hand when one wishes to predict the electrochemical behavior of such arrays, it is advisable to first consider periodical arrays. As sketched in Figure 1, there are only two possibilities of arranging periodically nano-elements onto a flat conductive support. This leads to squared arrays (Figure 1a) or hexagonal ones (Figure 1b). Following the Voronoi (or Dirichlet) tessellation concept,[71] the edges of the squared or hexagonal unit cells built around each nano-element define linear boundaries equidistant from the center of each nanodisk. By translating these linear segments perpendicularly to the support surface into the solution as in Figure 1c, one defines planar walls that delimit the solution above each unit cell and define diffusional unit cells.[57,58,72-74] Indeed, let us consider one electroactive molecule M located at time \( t \) within the solution above the array inside one such enclosed volume. Whenever M happens to reach one unit cell wall during its diffusional path, its distances to each adjacent nanodisk electrodes centers are equal (Figure 1d). By virtue of Fick’s laws of diffusion this implies that the probabilities of ending up its diffusional trajectory on either electrode are equal, viz., that the normal flux of M across this wall is null. In other words, such molecule behaves mathematically as if it was diffusionaly trapped within the nano- solution volume delimited by the walls elevated above the edges of the Voronoi unit cell. Note that physically, this simply means that if a real molecule located within the unit volume was to cross over such wall its exit from the unit volume would be exactly compensated by the entrance of another one from the adjacent cell as if the molecule M had bounced onto the wall (Figure 1d). This is an important conclusion since it allows to treat the electrochemical behavior of the solution above the whole array as a simple summation of the diffusion-reaction contributions occurring within each of its Voronoi diffusional unit cells.[55,57]
Figure 1. Schematic representation of two regular arrays with (a) a squared or (b) a hexagonal periodical arrangement of the active elements (shown as grey ellipses while the one defining the Voronoi cell is in black). In (a) is shown the construction of a Voronoi polygon for the squared array of microdisk electrodes that is extended into the solution in (c) to define a Voronoi diffusion cell. (d) Apparent diffusional pathway of a molecule M near one planar boundary of a Voronoi unit cell. The horizontal dashed arrow in (d) represents the normal vector to the wall at the point where M “hits” it and “bounces” back.

A second interest of Voronoi construction is that it is perfectly adapted to random arrays. Indeed, the planar surface of the electrochemically-inert support can be partitioned into a series of adjacent polygonal regions such as each of them encloses a single microdisk electrode. As for the squared regular array in Figure 1a, the edges of these ‘elementary’ polygons are defined by the medians of the segments linking the centers of two adjacent microdisks and their apexes marked by the intersections of two such medians that are closer to the center of the microdisk ultimately enclosed in the polygon (Figure 2a). Again, one may translate this Voronoi tessellation diagram into the solution perpendicularly to the support
surface to define a series of adjacent solution elementary volumes limited by zero-normal fluxes across their walls (Figure 2a). In other words, the diffusional behavior of random arrays can again be modeled through a simple superimposition of the independent diffusional behaviors taking place into each elementary cell.[57,58,72-74]

Figure 2. (a) Schematic construction of one Voronoi unit cell around one nanodisk electrode in a random array. (b) Equivalent cylindrical unit cell constructed onto the central Voronoi unit cell shown in (a). (c,d) Representation of two ensembles of Voronoi cells for a uniform (c) or a Gaussian (d) random array (see text for the meaning of uniform and Gaussian randomness). Adapted from [57].

As already evident in Figure 2a one easily remarks that the Voronoi tessellation regions display polygons with widely different shapes (number of edges, angles between two edges, etc.) and sizes (perimeter and surface areas); see Figures 2c,d for more obvious evidences of this fact for full arrays. Hence, the above simplification brought by the Voronoi tessellation concept may
appear as a brilliant conceptualization and yet without a real usefulness from an electrochemical point of view whenever one still would need to evaluate the electrochemical behavior of each single unit cell type and sum their individual current intensities in order to predict the whole array activity. Fortunately, we have recently established on quantitative grounds using sound mathematical modeling supported by Brownian motion simulations that for random and regular (viz., squared and hexagonal ones) arrays, the behavior of each unit cell is equivalent to that of a cylindrical cell whose cross-section surface area is identical.[55-58,72-74] The revolution axis of the cylindrical cell is perpendicular to the array plane and located at the center of the microdisk around which the Voronoi polygon was built (Figure 2b). In fact, this quantitatively validated the central assumption of the seminal model proposed by one of us ca. thirty years ago to model arrays of nanoelectrodes] that received a wide attention from the community since then.[55]. This initial model was recently further implemented by Compton et al. in a series of stimulating contributions on the subject also strongly relying on the Voronoi tessellation concept.[58,72-74] Therefore, in the following we use this fundamental property of diffusion over arrays.

Though, before proceeding one must anticipate that there are two main types of planar random arrays (in the following we consider the general situation in which the array does not contain macroscopic domains with different random distributions of electroactive nano-components). One type, sketched in Figure 2c, can be termed as displaying an ‘uniform’ randomness of the nano-components distribution. In such arrays, the macroscopic density (viz., that over a significant fraction of the array surface) of nano-elements is constant, though their density varies randomly at a microscopic level. In other words, the distance between two adjacent nanodisks fluctuates statistically in an identical way all across the whole array surface. For such array, one can define a probability density, \( f(\rho) \), that characterizes the frequency at which a unit cell of surface area \( A_{cell} = \rho \times \pi r_0^2 \) (where \( \pi r_0^2 \) is the surface area of each of the \( N \) nanodisks of radius \( r_0 \)) appears in the Voronoi ensemble over the whole array (note that \( \rho > 1 \) since by construction no unit cell can be smaller than the nanodisk that defines it). The mean value, \( \rho_{mean} \), of \( \rho \) for \( f(\rho) \), viz., \( \rho_{mean} = \int_1^{\infty} \rho f(\rho) d\rho \), is then constant over macroscopic areas of the array and equal to the macroscopic density value \( A_{array}/(N\pi r_0^2) \). The variations of \( f(\rho) \) with \( \rho \) for such planar uniform random arrays such as that displayed in Figure 2c is shown in Figure 3a for \( \rho_{mean} = \)
35.55. \( f(\rho) \) obeys the approximated general equation in Eqn (1):[75]

\[
f(\rho) = \frac{(\gamma/2)^{\gamma/2}}{\Gamma(\gamma/2)} \times (\rho/\rho_{\text{mean}})^{\gamma/2} \times e^{-\gamma(\rho/\rho_{\text{mean}})^2}
\]

with \( \Gamma(x) \) being the Gamma function (i.e., \( \Gamma(7/2) = 15\sqrt{\pi}/8 \approx 3.3234 \)).

**Figure 3.** Variations of the probability density functions \( f(\rho) \) for a *uniform* (a) or a *Gaussian* (b) random array. Compare (a) and (b) with Figures 2c and 2d respectively for the actual random distributions of the nanodisk electrodes. \( \rho_{\text{mean}}^{\text{uniform}} = 35.55 \) and \( \rho_{\text{mean}}^{\text{Gaussian}} = 33.08 \). Adapted from [57].

A second type of random array is exemplified in Figure 2d, and can be termed a ‘Gaussian’ one because the nanodisk electrodes radial macroscopic density varies along a Gaussian function whose maximum is located at the center of the array. Note that the macroscopic radial density
decreases exponentially with the square of the distance from the array center but the microscopic density remains perfectly random. This situation is encountered, for example, when the distribution of active nano-elements results from the scattered emission from a source located above the center of the array, e.g., as occurs when arrays are prepared by electrochemical filling of the nanopores formed in membranes by irradiation.[76] To the best of our knowledge, there is no general mathematical equation describing the probability density, \( f(\rho) \), of such Gaussian random arrays. Therefore, 1000 different arrays such as that shown in Figure 2d have been generated, each with the same \( \rho_{\text{mean}} = 33.08 \) value, and their individual \( f(\rho) \) probability densities evaluated and averaged.[57] The ensuing average probability density was then fitted by a log-normal distribution, from which it followed that \( f(\rho) \) could be approximated by the general equation (see Figure 3b):

\[
f(\rho) = \frac{1}{\sqrt{2\pi} a_1} \exp \left[ -\frac{(\ln \rho - a_0)^2}{2(a_1)^2} \right]
\]

in which \( a_0 = 3.214 \) and \( a_1 = 0.755 \) for same \( \rho_{\text{mean}} = 33.08 \). Interestingly, the same averaging procedure applied to the above uniform random arrays provided the same result as deduced from application of Eqn (1), evidencing the validity of the method. Finally, for the regular arrays shown in Figures 1a,b, \( f(\rho) \) is a Dirac function centered at \( \rho_{\text{mean}} \), viz.:

\[
f(\rho) = \delta(\rho - \rho_{\text{mean}})
\]

irrespective of their exact squared or hexagonal nature since, by definition, in any regular arrays all unit cells have an identical surface area.

### 2.2. Prediction of the chronoamperometric responses of random and regular arrays

Based on our previous works,[56,57] the chronoamperometric current responses, \( I_{\text{array}}(t) \), of random and regular arrays comprising \( N \) micro- or nanodisk electrodes can be modeled with a very good precision (i.e., better than 5-10%, viz., comparable to or better than the experimental reproducibility of most arrays except when using precise microfabrication techniques for arrays of micro-components) through application of the above Voronoi tessellation concept to a series of cylindrical unit cells with different \( \rho = A_{\text{cell}}/(\pi \rho_0^2) \) values statistically distributed according to the probability density \( f(\rho) \) that characterizes the
considered array, i.e.:

\[ I_{\text{array}}(t) = N \int_{\frac{t_0}{\rho}}^{\infty} i_{\text{cyl}}^\rho(t) f(\rho) \, d\rho \]  

(4)

where \( i_{\text{cyl}}^\rho(t) \) is the time-dependent current intensity characterizing the individual chronoamperometric responses of the cylindrical unit cells having a cross-section surface area \( A_{\text{cell}} = \rho \pi r_0^2 \). Its integration over the whole array weighted by the density probability of the unit cells provides the current time-dependence, \( I_{\text{array}}(t) \), for the whole array.

At very short times, i.e., when the diffusion layer formed in the solution above one nanodisk is much smaller than the nanodisk radius (viz., when \( r_0 \gg \delta \sim \sqrt{\pi D t} \)), the unit cell current response obeys a Cottrell behavior scaled by the surface area \( \pi r_0^2 \) of the nanodisk; let us note this asymptotic limit as \( i_0^\rho(t) \). Conversely, at sufficiently large times, the diffusion layers have expanded laterally to fill up all the cross-section of the unit cell, leading to a planar diffusion propagation towards the solution bulk except within a very narrow solution range near the array surface.[55,56] As a consequence, in chronoamperometry, the current is again Cottrellian but is scaled now by the total surface area \( A_{\text{cell}} \) of the unit cell; let us note this asymptotic limit as \( i_\infty^\rho(t) \).

One may then define a dimensionless current response, \( \varphi_{\text{cyl}}^\rho(t) \), for each unit cell as in Eqn (5):

\[ \varphi_{\text{cyl}}^\rho(t) = \frac{[i_{\text{cyl}}^\rho(t) - i_0^\rho(t)]/[i_\infty^\rho(t) - i_0^\rho(t)]]}{1 + \tanh(b_0^\rho + b_1^\rho \ln t)} \]  

(5)

The interest of this dimensionless definition is that, whatever the value of \( \rho \), \( \varphi_{\text{cyl}}^\rho(t) \) varies from zero to unity when the experimental time varies from zero to infinity. Indeed, the constant factors (i.e., concentration, diffusion coefficient, etc.) involved in the Cottrellian contributions \( i_{\text{cyl}}^\rho(t) \), \( i_0^\rho(t) \) and \( i_\infty^\rho(t) \) are cancelling off. \( \varphi_{\text{cyl}}^\rho(t) \) time variations were thus evaluated for any given \( \rho \) value based on Brownian random walk simulations and shown to obey the general analytical fitting expression in Eqn (6):[57]

\[ \varphi_{\text{cyl}}^\rho(t) = \frac{[1 + \tanh(b_0^\rho + b_1^\rho \ln t)]}{2} \]  

(6)

where \( b_0^\rho \) and \( b_1^\rho \) are two time-independent functions parametrized by \( \rho \):

\[ b_0^\rho = \beta_0^0 + \beta_1^0 / \ln(\beta_2^0 \rho) \]  

(7)

and:

\[ b_1^\rho = \beta_0^1 + \beta_1^1 / \ln(\beta_2^1 \rho) \]  

(8)
in which the values of $\beta_0^0 = -2.866$, $\beta_1^0 = 35.383$, $\beta_2^0 = 11.543$, $\beta_1^1 = 0.204$, $\beta_2^1 = 0.591$, and $\beta_2^2 = 2.534$ could be determined through numerical regressions of the time-dependent $\varphi_{\text{cyl}}^0(t)$ variations obtained for a representative series of individual $\rho$ values ($1 \leq \rho \leq 110$), i.e., covering the whole spectrum of $\rho$ values (compare Figures 3a,b) irrespective of the fact that the array is regular, uniform or Gaussian random. Indeed, $\varphi_{\text{cyl}}^0(t)$ in Eqns (5,6) features an intrinsic characteristics of diffusion in a cylindrical unit cell whatever is the specific probability density $f(\rho)$ value and the unit cells arrangement. Furthermore, it is noted that the dependence of $b_0^\rho$ and $b_1^\rho$ on $\rho$ evidence that the time, $t_{1/2}^\rho$, around which $\varphi_{\text{cyl}}^\rho(t)$ displays its most significant variations, viz., such as $\varphi_{\text{cyl}}^\rho(t_{1/2}) = 1/2$, is a common characteristics for all unit cells having a identical $\rho$ value that increases with $\rho$. This increase reflects the fact that the larger is $\rho$, the larger is the time at which the diffusional wave generated by the nanodisk defining the unit cell needs to reach the wall boundary of the unit cell and develop into a planar diffusion wave.[57] Small unit cells, viz., with small $\rho$ values, reach very soon their plateau value at $\varphi_{\text{cyl}}^\rho = 1$. However, unless $\rho_{\text{mean}}$ is also small (i.e., when most of the array surface is electroactive) they correspond to very small current contributions relative to the global array current. Indeed, the limit of $i_{\text{cyl}}^\rho(t)$ at long times is proportional to the surface area, $A_{\text{cell}}$, of the unit cell cross-section, viz., to $\rho$ since $A_{\text{cell}} = \rho \pi r_0^2$. Meanwhile, within such small time ranges, the unit cells with much larger $\rho$ values, i.e., those that contribute to most the current intensity ultimately delivered at long times by the array do not yet contribute significantly (viz., $\varphi_{\text{cyl}}^\rho \approx 0$) because their diffusion waves have not yet reached the unit cells walls. This is important to recognize owing to the experimental difficulty associated with the measurements of current intensities at very small times in an array (see below).

In conclusion, the chronoamperometric current responses of any array, regular or random, can be predicted through application of Eqn (4) as soon as one independently knows its characteristic probability density function $f(\rho)$. However, as discussed in the Introduction, this is the most critical experimental issue when arrays are composed of submicro- or nano-components since any experimental determination of $f(\rho)$ is then extremely difficult or even impossible. In the following, we will take advantage of the results summarized in this section and the previous
one,[55-57] to propose a simple reconstruction procedure allowing a direct access to the probability density function \( f(\rho) \) of any given array of electrochemically-active nano-components with near-disk geometries.

**2.3. Reconstruction of the unit cell size distribution, \( f(\rho) \), for any random arrays**

We assume hereafter that whatever is the ultimate experimental purpose of the array investigated, one may devise experimental conditions in which it will be able to perform under full diffusional control for chronoamperometric conditions in order to record \( I_{\text{array}}(t) \) time variations over the time range where it matters (see below). This may be performed, for example, by changing the substrate, etc. One may then assume that the time variations of the dimensionless current function defined as:[57]

\[
\Phi_{\text{array}}(t) = \left[ I_{\text{array}}(t) - I_{\text{array}}^0(t) \right] / \left[ I_{\text{array}}^\infty(t) - I_{\text{array}}^0(t) \right] \tag{9}
\]

are experimentally accessible with a sufficient precision over the time range of experimental interest over which \( \Phi_{\text{array}}(t) \) varies from zero (or near zero, viz., \( \Phi_{\text{array}}(t) \ll 1 \)) to unity (see Section 2.4 when this is not achievable experimentally). In Eqn (9), \( I_{\text{array}}^0(t) \) and \( I_{\text{array}}^\infty(t) \) are, respectively, the short and large times asymptotic time variations of \( I_{\text{array}}(t) \). Mathematically, they are defined as \( I_{\text{array}}(t) \) in Eqn (4) but involving now only the short and large times asymptotic current functions of the cylindrical unit cells:

\[
I_{\text{array}}^0(t) = N \int_1^{\infty} i_{\text{cyl}}^0(\rho) f(\rho) \, d\rho \tag{10}
\]

and:

\[
I_{\text{array}}^\infty(t) = N \int_1^{\infty} i_{\text{cyl}}^\infty(\rho) f(\rho) \, d\rho \tag{11}
\]

Note that one has \( I_{\text{array}}^\infty(t) = \rho_{\text{mean}} I_{\text{array}}^0(t) \) by definition of the mean macroscopic density \( \rho_{\text{mean}} \), viz., \( \rho_{\text{mean}} = A_{\text{array}} / (N \pi r_0^2) \). Therefore, whenever the number of nano-active elements \( N \) is known, viz., \( \rho_{\text{mean}} \) is known, the difficultly measurable \( I_{\text{array}}^0(t) \) may then be evaluated through relying on its proportionality to \( I_{\text{array}}^\infty(t) \) (however, see Section 2.4 when \( \rho_{\text{mean}} \) is unknown and \( I_{\text{array}}^0(t) \) not accessible experimentally).

Figures 4a,b exemplify the outcome of this procedure when applied to the random arrays shown in Figures 2c,d for a uniform or a Gaussian case, respectively, and whose corresponding probability density functions \( f(\rho) \) were shown in Figures 3a,b, respectively. As evident by
comparing Figures 4a,b to Figure 4c that features $\Phi_{array}(t)$ time-variations for a regular squared array with a similar $\rho_{\text{mean}}$ value (i.e., $\rho_{\text{mean}}^{\text{squared}} = 35.0$, $\rho_{\text{mean}}^{\text{uniform}} = 35.55$ and $\rho_{\text{mean}}^{\text{Gaussian}} = 33.08$), the three arrays display similar sigmoidal $\Phi_{array}(t)$ functions, though the two random arrays exhibit more sluggish ones that the regular one. This simply reflects the fact that in random arrays the unit cells with $\rho < \rho_{\text{mean}}$ reach their long time asymptotic behavior much sooner than those with $\rho > \rho_{\text{mean}}$ (see above discussion) while for the regular array all unit cells behave identically and in phase.

In the following, we wish to establish that experimentally determined $\Phi_{array}(t)$ time variations can be used to reconstruct with an adequate precision the unknown $f(\rho)$ for a given array. For this purpose, let us approximate the unknown probability density function $f(\rho)$, e.g., such as those in Figure 3, by a discretized one, $H_M(\rho)$, e.g., such as shown in Figure 5. $H_M(\rho)$ may be represented graphically as a histogram consisting of $M$ bins of width $\Delta\rho$ and distributed over the range of $\rho$ values of interest, with the $m^{th}$ bin ($1 \leq m \leq M$) being centered at $\rho_m = m(\Delta\rho)$ and having a height $h_m \geq 0$. Assuming that the reconstruction procedure converges perfectly, $H_M(\rho)$ would actually be a discrete bin-representation of $f(\rho)$ (see e.g., Figures 5) so each $h_m$ coefficient would obey:

$$h_m \times \Delta\rho = \int_{(m-1/2)\Delta\rho}^{(m+1/2)\Delta\rho} f(\rho) d\rho$$  \hspace{1cm} (12)

Since one has $\int_1^\infty f(\rho) d\rho = 1$ by definition, the validity of Eqn (12) under all circumstances imposes that the following constraint applies to $h_m$ values:

$$\sum_{m=1}^M h_m = 1/\Delta\rho$$  \hspace{1cm} (13)

The reconstructing procedure then amounts to determine the optimal series of $h_m$ values that affords the most correct description of the experimental $\Phi_{array}(t)$ dimensionless current. In the practice, since one cannot account for all possible times, the time scale is discretized over the time range over which $\Phi_{array}(t)$ differs from 0 and 1. Let us denote $t_k$ the series ($k = 1,2, \ldots, K$) of selected times and $\Phi_{array}(t_k)$ the corresponding experimental $\Phi_{array}$ values. The convergence criterion consists then in finding the series of $h_m$ values that complies with Eqn (13) while minimizing the sum of the squares of the deviations considering all $t_k$ times:

$$\sum_{k=1}^K [\Phi_{array}(t_k) - \Phi_{array}^{H_M(\rho)}(t_k)]^2$$  \hspace{1cm} (14)
between the set of experimental $\Phi_{\text{array}}(t_k)$ values and those, $\Phi_{\text{array}}^{H_M(\rho)}(t_k)$, predicted upon using $H_M(\rho)$ instead of the unknown $f(\rho)$ function in Eqns (4) and (9-11), viz.: 

$$I_{\text{array}}^{H_M(\rho)}(t_k) = N \int_1^{\infty} i_{\text{cyl}}(t_k) H_M(\rho) \, d\rho$$  \hspace{1cm} (15)$$

and:

$$\Phi_{\text{array}}^{H_M(\rho)}(t_k) = \left[ I_{\text{array}}^{H_M(\rho)}(t_k) - I_{\text{array}}^{H_M(\rho),0}(t_k) \right] / \left[ I_{\text{array}}^{H_M(\rho),\infty}(t_k) - I_{\text{array}}^{H_M(\rho),0}(t_k) \right]$$  \hspace{1cm} (16)$$

where $I_{\text{array}}^{H_M(\rho),0}(t_k)$ and $I_{\text{array}}^{H_M(\rho),\infty}(t_k)$ are the values taken at $t = t_k$ by the asymptotic limits of $I_{\text{array}}^{H_M(\rho)}(t)$ at zero and infinite times.

To evaluate its robustness and performance, this reconstruction procedure was applied to the three arrays whose $\Phi_{\text{array}}(t)$ time-functions were shown in Figures 4a-c, so that the reconstructed $H_M(\rho)$ functions could be compared in each case to the original probability density function, $f(\rho)$, displayed respectively in Figure 3a (uniform random array), Figure 3b (Gaussian random array) or given in Eqn (3) for a regular squared array. A same number, $K = 8$, of $t_k$ values was used in all three cases to allow a straight comparison of the reconstruction qualities as a function of the array type (the $t_k$ values were the time values for which $\Delta \Phi_{\text{array}}(t_k)$ varied between 0.11 and 0.88 in increments of 0.11). Figures 5a,b evidence the spectacular agreement between the $f(\rho)$ functions and their reconstructed discrete versions $H_M(\rho)$ for the two random arrays. Furthermore, the $\rho_{\text{mean}}$ values determined based on the two reconstructed $H_M(\rho)$ functions closely matched those of the original arrays (precision better than 0.5%). Finally, it is clear through comparing Figure 5a to Figure 5b, that the reconstruction procedure successfully distinguishes the two types of random arrays. This and the excellent agreement on $\rho_{\text{mean}}$ values vs. the input ‘experimental’ values demonstrate the high interest of such precise reconstruction procedure for experimental purposes. Indeed, under most circumstances these are the two central information that matter for experimentalists.

For the squared regular array the agreement is not as spectacular (Figure 5c). This is due to the evident fact that a discrete $H_M(\rho)$ histogram-like function described by a series of bins of finite widths $\Delta \rho$ cannot reproduce a Dirac function that has no width at all but an infinite value at $\rho = \rho_{\text{mean}}$. A finite bin-size $\Delta \rho$ necessarily introduces a small filtering effect, although the bin size was reduced compared to those used for the two random arrays (see Figure 5 caption). As a consequence, the reconstructed $H_M(\rho)$ function matches that expected for a narrow Gaussian
function. However, this does not alter significantly the reconstructed $\rho_{\text{mean}}$ value (35.1) compared to that of the original probability density Dirac function ($\rho_{\text{mean}} = 35.0$). A similar filtering is also present in Figures 5a,b due to the same cause though it produces no noticeable effects owing to the significant half-widths of the original $f(\rho)$ functions.

Figure 4. Time variations of the dimensionless current functions $\Phi_{\text{array}}(t)$ as defined in Eqn (9) for the two random arrays in Figures 2c,d: (a) uniform or (b) Gaussian random arrays. In (c) are represented the time variations of $\Phi_{\text{array}}(t)$ for a squared array (see Figure 1a) with a similar $\rho_{\text{mean}}$ value ($\rho_{\text{mean}}^{\text{square}} = 35$ vs. $\rho_{\text{mean}}^{\text{uniform}} = 35.55$ and $\rho_{\text{mean}}^{\text{Gaussian}} = 33.08$). In (a-c) the dashed curves represent the time variations of the three $\Phi_{\text{array}}^*(t)$ functions obtained through the approximation in Eqn (17). Note that the three $\Phi_{\text{array}}^{\text{app}}(t)$ functions approximated using Eqn (19) are also shown but result exactly superimposed onto the exact $\Phi_{\text{array}}(t)$ functions in each case. Adapted from [57].
Figure 5. Comparisons between the original probability density functions, $f(\rho)$, (solid curves) and their reconstructed ones, $H_M(\rho)$, (histogram bins) for the three arrays considered in this work upon using $\Phi_{\text{array}}(t)$ defined in Eqn (9). (a) uniform, (b) Gaussian random or (c) regular arrays. In (c) a dashed Gaussian curve fit is shown to emphasize the filtering effect due to the bin-reconstruction procedure (see text). $\Delta \rho = 8.3$ (a), 8.0 (b) and 2.5 (c); $K = 8$ in all cases (see text).

2.4. Reconstruction of the unit cell size distribution, $f(\rho)$, when $I_{\text{array}}^0(t)$ is unknown

The above section has evidenced the excellent performance of the reconstruction procedure when the array current may be measured over the whole time range of interest so that both $I_{\text{array}}^0(t)$ and $I_{\text{array}}^{\infty}(t)$ can be experimentally determined with a good precision. This is indeed needed to evaluate the current function $\Phi_{\text{array}}(t)$ over its whole [0,1] range of variations.
However, inspection of the $\Phi_{\text{array}}(t)$ functions in Figure 4 evidences that this requires about 6 orders of magnitude in time, which is rarely achievable experimentally. Since most electro(bio)analytical or electrocatalytic arrays are designed to perform close to their maximum current limit, $I_{\text{array}}^\infty(t)$ is generally known experimentally with a good precision, so the main issue concerns the determination of $I_{\text{array}}^0(t)$, viz., of the limit of $I_{\text{array}}(t)$ at sufficiently short times, i.e., over the time range such as $t < r_0^2/D$ (compare Figure 4).

In fact, this problem matters essentially for those arrays with $\rho_{\text{mean}}$ values that largely exceed unity. Indeed, for arrays with $\rho_{\text{mean}}$ values commensurable to unity, viz., for arrays in which the electroactive nano-elements cover altogether almost the whole array surface area, the necessity of determining the probability density functions $f(\rho)$ functions is generally irrelevant in the field of nano-arrays because such arrays behave as near-continuous electrodes (see the Introduction). Furthermore, for such arrays, most unit cells have a surface area comparable to that of their electroactive nano-elements so that $I_{\text{array}}^0(t)$ and $I_{\text{array}}^\infty(t)$ have extremely close values.

Hence, the problem matters essentially for arrays such as those modeled in this work in which most of the array surface is not electroactive, i.e., those characterized by large $\rho_{\text{mean}}$ values ($\rho_{\text{mean}} \gg 1$). Interestingly, this difficulty can be turned into an operational advantage. Indeed, the ratio $I_{\text{array}}^0(t)/I_{\text{array}}^\infty(t)$ is by definition equal to $1/\rho_{\text{mean}}$, hence, is much less than unity for large $\rho_{\text{mean}}$ values (for example, $I_{\text{array}}^0(t)$~3% of $I_{\text{array}}^\infty(t)$ for all arrays investigated here). Similarly, since any $I_{\text{array}}(t)$ value that experimentally matters is a fraction of $I_{\text{array}}^\infty(t)$, $I_{\text{array}}(t)$ values may also be considered as being larger than $I_{\text{array}}^0(t)$. This suggests that $I_{\text{array}}^0(t)$ may be thoroughly neglected in evaluating $\Phi_{\text{array}}(t)$ when using Eqn (9). In other words, $\Phi_{\text{array}}^*(t)$ in Eqn (17) provides a reasonable clue about the real time-variations of $\Phi_{\text{array}}(t)$:

$$\Phi_{\text{array}}^*(t) = I_{\text{array}}(t)/I_{\text{array}}^\infty(t)$$

Yet, to proceed, one needs to envision two possible situations depending on the time range over which $I_{\text{array}}(t)$ is measurable. In the first one, although $I_{\text{array}}^0(t)$ cannot be determined, the experimental time range may be sufficiently wide for $\Phi_{\text{array}}^*(t)$ to reach a near constant limit at short times, $\lim_{t \to 0} \Phi_{\text{array}}^*(t) \ll 1$. In the second one, the experimental time range is too short so that, even for the smallest available times, $\Phi_{\text{array}}^*(t)$ is far from reaching any constant limit. So let
us consider these two situations separately.

2.4.1 Reconstruction when $\Phi_{\text{array}}^*(t)$ reaches a constant limit close to zero at short times

$\Phi_{\text{array}}^*(t)$ current functions were evaluated using Eqn (17) for the same three arrays investigated above ($\rho_{\text{mean}} = 33 - 35$). The results shown in Figures 4a-c (dashed curves) evidence that the three $\Phi_{\text{array}}^*(t)$ current functions reach near constant limits at ca. 0.03 at short times. Though these limits are small, a straight application of the reconstruction procedure did not yield satisfactory results (data not shown). Indeed, the resulting $H_M(\rho)$ histograms exhibited an artefactual maximum at small $\rho$ values. This is a normal consequence from the fact that the non-negligible $\lim_{t \to 0} \Phi_{\text{array}}^*(t)$ value is taken by the reconstruction procedure as indicative of the presence of a second class of unit cells with small $\rho$ values that had already completed their transition towards a synergistic behavior in this small time range. Though this second class of unit cells does not contribute very significantly to the total current (i.e., as indicated by the fact that $\lim_{t \to 0} \Phi_{\text{array}}^*(t) \approx 0.03$), the constancy of the limit is taken by the reconstruction procedure as an indication that their number is high. This led to the presence of the artefactual probability density peak at $\rho \ll \rho_{\text{mean}}$, and to a corresponding decrease of the $H_M(\rho)$ for $\rho$ values close to or larger than $\rho_{\text{mean}}$. In the present theoretical context, such wrong reconstruction outputs may be identified as faulty because one knows the real $f(\rho)$ functions. However, in a true experimental case it may well be that an array exhibits a two-peaked distribution of unit cells sizes. This evidences that $\Phi_{\text{array}}^*(t)$ in Eqn (17) cannot be considered as a valid approximation of the correct $\Phi_{\text{array}}(t)$ current function unless the limit $\lim_{t \to 0} \Phi_{\text{array}}^*(t)$ is less than 0.01 (data not shown), viz., that $\rho_{\text{mean}}$ is ca. 100 or larger.

A non-negligible limit $\lim_{t \to 0} \Phi_{\text{array}}^*(t)$ value (viz., larger than 0.01) at short times specifies that the difference ($l_{\text{array}}(t) - l_{\text{array}}^0(t)$) cannot be neglected in this time range. In other words, the limit of $\Phi_{\text{array}}(t)$ at short times may be used to provide a reasonable estimate of $l_{\text{array}}^0(t)$, viz.:

$$l_{\text{array}}^0(t) \approx l_{\text{array}}(t) \times \lim_{t \to 0} \Phi_{\text{array}}^*(t)$$ (18)

This suggests a better approximation for $\Phi_{\text{array}}(t)$ than the crude one in Eqn (17) may be obtained
through using Eqn (9) while replacing the unknown $I_{array}^0(t)$ values by those in Eqn (18), viz.:

$$
\Phi_{array}^{app}(t) = \left\{\frac{I_{array}(t)}{I_{array}^\infty(t)} - \lim_{t \to 0} \Phi_{array}^*(t)\right\}/\left[1 - \lim_{t \to 0} \Phi_{array}^*(t)\right]
$$

(19)

The validity of this approximation was tested for the three arrays investigated in this work. The ensuing $\Phi_{array}^{app}(t)$ time functions resulted graphically undistinguishable from the correct $\Phi_{array}(t)$ ones as evidenced in Figures 4a-c, the maximum relative deviations being less than 0.1%. Therefore, the reconstruction procedure was applied using the approximated functions $\Phi_{array}^{app}(t)$ obtained by applying Eqn (19) to each of the three arrays investigated in this work. The ensuing $H_M(\rho)$ histograms are compared in Figures 6a-c to those obtained using the exact $\Phi_{array}(t)$ functions that were already shown in Figures 5a-c. The excellent agreement observed between the two sets of histograms for each array evidences that whenever the limit $I_{array}^0(t)$ cannot be measured experimentally with a sufficient precision $\Phi_{array}(t)$ may be correctly approximated through $\Phi_{array}^{app}(t)$ in Eqn (19). This was validated here for arrays with $\rho_{mean}$ values of ca. 35 but it is evident that Eqn (19) would lead to even better results for arrays with larger $\rho_{mean}$ values. Therefore, the reconstruction procedure proposed in this work is applicable experimentally to any array with $\rho_{mean}$ values are larger than a few tens. Note in this respect that, owing to the definition of $\rho_{mean}$, the mean distance between electroactive nano-elements is ca. $2r_0(\rho_{mean})^{1/2}$. Therefore, one may conclude that the reconstruction procedure proposed here is valid for most arrays of (bio)analytical importance provided that $I_{array}(t)/I_{array}^\infty(t)$ displays a plateau in the shortest time range available.
Figure 6. Comparisons between the reconstructed $H_{\text{hy}}(\rho)$ functions for the three arrays considered in this work obtained upon using the exact $\Phi_{\text{array}}(t)$ (Eqn (9); black bins, already shown in Figure 5) or approximated $\Phi_{\text{array}}^{\text{app}}(t)$ (Eqn (19); white bins) functions. (a) uniform, (b) Gaussian random or (c) regular arrays. Note that for the sake of comparison the bins have been split in two parts though $\Delta \rho$ values used in each case were identical to those in Figure 5. The set of $t_k$ values used in the two types of reconstructions was identical to that reported in Figure 5.

2.4.2. Reconstruction when $\Phi_{\text{array}}^{*}(t)$ does not reach any constant limit at short times

To examine this case, we first resorted to the $\Phi_{\text{array}}^{*}(t)$ functions defined as in Eqn (17)
and shown in Figure 4 but voluntarily truncated them by eliminating all values below 0.5. This set of truncated $\Phi_{\text{array}}^*(t)$ functions thus provided a suitable batch to test the performance of the probability density reconstruction procedure when the available experimental time range results too short to explore the short time range in which $\Phi_{\text{array}}^*(t)$ would have approached a near-zero constant limit.[77] As shown in Figures 7a-c the outcome of the reconstruction procedure for the same three arrays investigated above affords results that do not deviate excessively from the original set of $f(\rho)$ functions. Evidently, the absence of values for $\Phi_{\text{array}}^*(t) < 0.5$ has the largest influence onto the reconstruction at small $\rho$ values. This enforces a significant magnification of the probability densities over the range $\rho \ll \rho_{\text{mean}}$ and, by compensation due to the constraint in Eqn (13), decreases those for $\rho \cong \rho_{\text{mean}}$. Interestingly from an experimental perspective, the effect resulted much less marked than when the complete time variations of $\Phi_{\text{array}}^*(t)$ were used (see section 2.4.1). In particular, except for the squared regular array for which a very small maximum is noted around $\rho \approx 2.5$, the resulting $H_M(\rho)$ functions do not exhibit a marked two-peak distribution and yield $\rho_{\text{mean}}$ values close to those of the original set of $f(\rho)$ functions, viz., $\rho_{\text{mean}} = 31.5, 30.9$ and 32.4 for the uniform or Gaussian random arrays and for the squared regular one (compare to 35.55, 33.08, and 35.0, respectively, for the original $f(\rho)$ distributions).

It may be surprising that truncated $\Phi_{\text{array}}^*(t)$ functions provide better results than when their full range of variations is used. However, as discussed in the previous section, this is due in part to the fact that the truncated $\Phi_{\text{array}}^*(t)$ functions do not exhibit any constant limit at short times. This absence makes that the reconstruction procedure cannot be mistaken in trying to enforce the artefactual presence of numerous small unit cells.

On the other hand, it is rather remarkable that the reconstructed distributions correctly track the original $f(\rho)$ functions in the range of large $\rho$ values ($\rho > \rho_{\text{mean}}$). This is due to the fact that the truncation of the $\Phi_{\text{array}}^*(t)$ functions amounts to consider time scales that are larger than ca. $10^2 Dt/r_0^2$ for the $\rho_{\text{mean}}$ values considered here (compare Figures 4a-c). Therefore, the slope of the $\Phi_{\text{array}}^*(t)$ time-variations in this time range reflects mostly the current transitions occurring in the unit cells whose values are larger than $\rho_{\text{mean}}$, leading to more or less correct reconstruction of the probability densities for $\rho > \rho_{\text{mean}}$.

To conclude this section we wish to examine another related situation. Indeed, even if
$I^0_{\text{array}}(t)$ is not measurable, one may have a reasonable estimation of the number $N$ of nanoelements that have been dispersed over the non-electroactive support (see e.g. [78]). As remarked above, then one may estimate $I^0_{\text{array}}(t)$ through its proportionality to $I^\infty_{\text{array}}(t)$, viz., $I^0_{\text{array}}(t) = (N\pi r_0^2 / A_{\text{array}})$. When this is possible, $\Phi_{\text{array}}(t)$ functions may be correctly evaluated through a straight application of Eqn (9) though, due to the limited time range, this results feasible only for $\Phi_{\text{array}}(t)$ values being larger than a given threshold. So we also wished to examine the outcome of using such truncated but otherwise correct $\Phi_{\text{array}}(t)$ functions, by using 0.5 as the lowest determined value. The corresponding results shown in Figures 7d-f are in remarkable agreement with the original $(\rho)$ functions. In particular the extended left tail of the $H_M(\rho)$ histogram for the regular array observed when using truncated $\Phi^*_\text{array}(t)$ functions (Figure 7c) is thoroughly eliminated (Figure 7f).

Therefore, it may be safely concluded that the reconstruction procedure leads to satisfactory results even under the unfavorable situation in which the whole time span required for observing the complete time-variations of $\Phi_{\text{array}}(t)$ over the [0,1] interval is not accessible experimentally. Evidently, the quality of the outcome is lesser than when the full range of $\Phi_{\text{array}}(t)$ time-variations is accessible experimentally, but it remains perfectly adequate for most electroanalytical purposes.

3. CONCLUSION

In a first part of this article (sections 2.1 and 2.2), we had to briefly review the main results and conclusions from the series of our recent works aimed to predict the time-variations of the current delivered by arrays of micro- and nanodisk electrodes.[56,57] Indeed, the concepts introduced in these previous works and the corresponding derivations were central to the development of the main section of this paper. Indeed, the main scope of this work was to establish that one can reconstruct the probability density distributions $f(\rho)$ of the nanocomponents dispersed on the surface of a planar array based on a simple analysis of the chronoamperometric responses of the array.
Figure 7. Reconstructed functions $H_{M}(\rho)$ for the three arrays considered in this work when relying on $\Phi_{array}(t)$ (a-c) or $\Phi_{array}(t)$ (d-f) functions truncated below 0.5. (a,d) uniform, (b,e) Gaussian random or (c,f) regular arrays. $\Delta \rho = 8.3$ (a,d), 8.0 (b,e) and 2.5 (c,f); $K = 8$ in all cases, the $t_k$ values being those for which $\Delta \Phi_{array}(t)$ or $\Delta \Phi_{array}(t)$ varied between 0.56 and 0.94 by increments of $\Delta \Phi_{array}(t) \approx 0.056$.

The mathematical and numerical validity of this simple procedure was tested through considering three types of arrays that cover most of those involving near-spherical nano-components dispersed on a flat surface. It was shown to afford spectacularly good results for random and regular arrays with a precision that is larger than that usually achieved through the combination of Electron Microscopy and sophisticated pattern recognition programs. This was shown to be effective even when the experimental time window is too narrow to determine
simultaneously the short and long times current limits characterizing the arrays. These results and the fact that the reconstruction procedure may easily be implemented using common mathematical programs (e.g., all calculations presented in this work were performed using Mathematica 11®, Wolfram Research, Inc., Mathematica, Version 11.0, (2016) Champaign, IL) should enable most experimentalists to easily characterize the distributions of the electroactive or electrocatalytic nano-components in their arrays when the need occurs especially when the classical approaches based on microscopies cannot be implemented.

Finally, the validity of this procedure was tested and established for regular, i.e., periodic, arrays and for two representative types of random arrays, involving either a uniform macroscopic density of electroactive nano-elements or one in which the density is organized in a Gaussian way around the center of the array. However, it must be stressed that the choice of these three different arrays was only made with the scope of testing and validating the method by comparing the reconstructed distributions to the real ones. In the practice, as shown in this work, the reconstruction procedure does not require any prior hypothesis about the type of distribution. This means that any array can be characterized, e.g., arrays that combine the two type of distributions. The only limit we foresee would concern the situations in which an array consists in the contiguous, but separated, arrangement of two different arrays. Indeed, it is essential for a correct application of the procedure that the macroscopic characteristics of the investigated array are distributed homogeneously (or gaussianly) over its whole surface.

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**Figure Captions**

**Figure 1.** Schematic representation of two regular arrays with (a) a squared or (b) a hexagonal periodical arrangement of the active elements (shown as grey ellipses while the one defining the Voronoi cell is in black). In (a) is shown the construction of a Voronoi polygon for the squared array of microdisk electrodes that is extended into the solution in (c) to define a Voronoi diffusion cell. (d) Apparent diffusional pathway of a molecule M near one planar boundary of a Voronoi unit cell. The horizontal dashed arrow in (d) represents the normal vector to the wall at the point where M “hits” it and “bounces” back.

**Figure 2.** (a) Schematic construction of one Voronoi unit cell around one nanodisk electrode in a random array. (b) Equivalent cylindrical unit cell constructed onto the central Voronoi unit cell shown in (a). (c,d) Representation of two ensembles of Voronoi cells for a uniform (c) or a Gaussian (d) random array (see text for the meaning of uniform and Gaussian randomness). Adapted from [57].

**Figure 3.** Variations of the probability density functions $f(\rho)$ for a uniform (a) or a Gaussian (b) random array. Compare (a) and (b) with Figures 2c and 2d respectively for the actual random distributions of the nanodisk electrodes. $\rho_{\text{mean}}^{\text{uniform}} = 35.55$ and $\rho_{\text{mean}}^{\text{Gaussian}} = 33.08$. Adapted from [57].

**Figure 4.** Time variations of the dimensionless current functions $\Phi_{\text{array}}(t)$ as defined in Eqn (9) for the two random arrays in Figures 2c,d: (a) uniform or (b) Gaussian random arrays. In (c) are represented the time variations of $\Phi_{\text{array}}(t)$ for a squared array (see Figure 1a) with a similar $\rho_{\text{mean}}$ value ($\rho_{\text{mean}}^{\text{squ}} = 35$ vs. $\rho_{\text{mean}}^{\text{Gaussian}} = 33.08$). In (a-c) the dashed curves represent the time variations of the three $\Phi_{\text{array}}^*(t)$ functions obtained through the approximation in Eqn (17). Note that the three $\Phi_{\text{array}}^*(t)$ functions approximated using Eqn (19) are also shown but result exactly superimposed onto the exact $\Phi_{\text{array}}(t)$ functions in each case. Adapted from [57].

**Figure 5.** Comparisons between the original probability density functions, $f(\rho)$, (solid curves) and their reconstructed ones, $H_M(\rho)$, (histogram bins) for the three arrays considered in this work upon using $\Phi_{\text{array}}(t)$ defined in Eqn (9). (a) uniform, (b) Gaussian random or (c) regular arrays. In (c) a dashed Gaussian curve fit is shown to emphasize the filtering effect due to the bin-reconstruction procedure (see text). $\Delta \rho = 8.3$ (a), 8.0 (b) and 2.5 (c); $K = 8$ in all cases (see text).

**Figure 6.** Comparisons between the reconstructed function, $H_M(\rho)$, for the three arrays considered in this work obtained upon using the exact $\Phi_{\text{array}}(t)$ (Eqn (9); black bins, already shown in Figure 5) or approximated $\Phi_{\text{array}}^*(t)$ (Eqn (19); white bins) functions. (a) uniform, (b) Gaussian random or (c) regular
arrays. Note that for the sake of comparison the bins have been split in two parts though $\Delta \rho$ values used in each case were identical to those in Figure 5. The set of $t_k$ values used in the two types of reconstructions was identical to that reported in Figure 5.

**Figure 7.** Reconstructed function, $H_M(\rho)$, for the three arrays considered in this work when relying on $\Phi^*_\text{array}(t)$ (a-c) or $\Phi^*_{\text{array}}(t)$ (d-f) functions truncated below 0.5. (a,c) uniform, (b,e) Gaussian random or (c,f) regular arrays. $\Delta \rho = 8.3$ (a), 8.0 (b) and 2.5 (c); $K = 8$ in all cases, the $t_k$ values being those for which $\Delta \Phi^*_\text{array}(t)$ or $\Delta \Phi_{\text{array}}(t)$ varied between 0.56 and 0.94 by increments of $\Delta \Phi_{\text{array}}(t) \approx 0.056$. 