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CURRENT NOISE AROUND STEADY STATES IN DISCRETE TRANSPORT SYSTEMS

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Subject of this paper is the transport noise in discrete systems. The transport systems are given by a number (n) of binding sites separated by energy barriers. These binding sites may be in contact with constant outer reservoirs. The state of the system is characterized by the occupation numbers of particles (current carriers) at these binding sites. The change in time of the occupation numbers is generated by individual "jumps" of particles over the energy barriers, building up the flux matter (for charged particles: the electric current). In the limit $n \to \infty$ continuum processes as e.g. usual diffusion are included in the transport model. The fluctuations in occupation numbers and other quantities linearly coupled to the occupation numbers may be treated with the usual master equation approach. The treatment of the fluctuations in fluxes (current) makes necessary a different theoretical approach which is presented in this paper under the assumption of vanishing interactions between the particles. This approach may be applied to a number of different transport systems in biology and physics (ion transport through porous channels in membranes, carrier mediated ion transport through membranes, jump diffusion e.g in superionic conductors). As in the master equation approach the calculation of correlations and noise spectra may be reduced to the solution of the macroscopic equations for the occupation numbers. This result may be regarded as a generalization to non-equilibrium current fluctuations of the usual Nyquist theorem relating the current (voltage) noise spectrum in thermal equilibrium to the macroscopic frequency dependent admittance.

The validity of the general approach is demonstrated by the calculation of the autocorrelation function and spectrum of current noise for a number of special examples (e.g. pores in membrances, carrier mediated ion transport).

1. Introduction

In the last years the application of noise analysis to biological systems has become an important method [1]. In many cases adequate theoretical concepts for analyzing the noise measurements, e.g. electric noise generated by nerve membrane channels, can be found in older papers concerning fluctuation phenomena in physical and chemical systems, e.g. [2,3], treated with the so-called master equation approach. The master equation approach is an adequate formalism for treating fluctuations in a set of variables representing a Markov process. These Markovian variables may be the occupation numbers of electronic states in a solid or the concentrations in chemical kinetic systems.

In a series of papers [4–6] and in a recent review [7] the master equation approach of van Vliet and Fasset [2] and other authors has been used for noise analysis of kinetic systems and applied to membrane channels. In these systems the observable quantities are linearly coupled to the Markovian variables [7]. E.g. in some models for nerve membrane channels, the channels may be in different states, and one or more states may be "open". Then the current fluctuations are proportional to the fluctuations of the number of channels in the open state. Generally, if the observable fluctuating quantities can be expressed by a linear combination of the Markovian set of variables, the observed fluctuations (correlations and spectra) are simply expressed by the correlation matrix or noise spectrum matrix of the Markov process. Subject of this paper is another type of fluctuations which is of basic importance as well as the fluctuations in occupation numbers but which is basically different. Apart from special trivial cases its theoretical treatment makes necessary a different theoretical approach: Consider a number of binding sites separated by energy barriers. Again the state of the system can be characterized by the occupation numbers of particles at the binding sites. If the set of occupation numbers represents a Markov process, their fluctuations may be treated with the master equation approach. We assume that the change in time of these occupation numbers is generated by individual "jumps" of particles over the energy barriers, building up the *fluxes* of matter. The fluctuations in these fluxes around steady states are the sources of the transport noise (e.g. current noise) generated by the described discrete transport system. And the general treatment of the fluctuations of these fluxes will be presented in this paper. Because the transport system is allowed to be in contact with outer constant reservoirs, fluctuations around non-equilibrium steady states are included.

The fluctuations in fluxes (currents) make necessary a different theoretical approach, because a unique representation of the microscopic fluxes by the occupation numbers in general is not possible. Nevertheless it will be shown that as in the master equation approach to concentration fluctuations the problem of calculating the correlations and noise spectra in fluxes can be reduced to the solution of the macroscopic phenomenological equations, describing the change in time of the occupation numbers.

In an appropriate limit of $n \to \infty$ (n: number of binding sites) and vanishing distance between the binding sites the phenomenological equations become usual (continuum) diffusion equations. Hence the continuum case may be treated as a limit of the discrete transport model. This will be explicitely done for special cases of one-dimensional transport through pores in a later paper.

A most important application of the presented theoretical approach are current fluctuations in electrical systems, because generally the measured current is given by an appropriate linear combination of the individual fluxes. With our general approach the current fluctuations in a number of biological and physical transport systems may be analysed, which at first sight demand different methods or so far have been treated by different methods or which could not yet be treated.

Two important examples are: First, the one-dimensional transport through pores (membrane channels), which are represented by a sequence of binding sites [8,9]. Second, carrier transport systems. The first example has recently been treated by Läuger for the special case of one binding site within the pore [10] and for arbitrary numbers of binding sites in the equilibrium case [11] with the use of the Nyquist theorem. Besides, from our result for the general current noise spectrum the validity of the Nyquist theorem for pore transport systems also far from equilibrium can simply be derived.

The presentation in this paper is arranged as follows: In the second section we describe the general discrete transport model, introduce the necessary notations and conventions and formulate the phenomenological equations for occupation numbers, which determine the macroscopic behaviour of the system. In the third section we derive the general theoretical approach to the fluctuations in fluxes around a (non-equilibrium) steady state starting with an investigation of the time correlation between the individual fluxes. In the fourth section we describe the application to transport noise in pores. Finally in the fifth section we demonstrate the validity of the procedure by application to carrier mediated ion transport far from equilibrium and by explicite discussion of some simple examples: transport noise in pores with one and two binding sites and models for gating current and hydrophobic ions.

A detailed treatment of pores with arbitrary number of binding sites and of carrier noise including the comparison of noise analysis with macroscopic relaxation experiments will be given elsewhere.

2. Discrete transport systems

2.1. The phenomenological equations

The transport system is considered to consist of n binding sites, i.e. possible places for the particles, representing the transported medium. For simplicity the particles are assumed to be identical as far as their transport properties are concerned. In electric systems in this identity is contained the assumption, that all particles carry the same charge. We emphasize that we make this assumption only in order to avoid confusion by introduction of additional parameters. It is not an essential assumption for performing the presented theoretical approach.

Furthermore the binding sites may be in contact with a constant environment (reservoirs). The change in time of the expected occupation numbers $\langle N_i \rangle_{\mathrm{N}(0)}$ (numbers of particles at the ith binding site) is assumed to be given by the following set of phenomenological equations

$$\mathrm{d}\langle N_i\rangle_{\mathbf{N}(0)}/\mathrm{d}t = f_i(\langle N_1\rangle_{\mathbf{N}(0)}, \ldots, \langle N_n\rangle_{\mathbf{N}(0)}, \gamma_k), \qquad (2.1)$$

$i, k = 1, 2, \ldots, n.$

In (2.1) γ_k stands for the interaction with constant reservoirs. A system of the type (2.1) is called a dynamical system. In the equations (2.1) random fluctuations are neglected.

The index $\mathbf{N}(0)$, denoting the initial state, is omitted in the following.

If the system contains a stable time-independent solution (stable point) linearization around this steady state $\mathbf{N}^s$ yields the linearized equations

$$\mathrm{d}\langle N_i\rangle/\mathrm{d}t = \sum_{j=1}^{n} M_{ij}\langle N_j\rangle + y_i \qquad (2.2a)$$

or in matrix notation

$$\mathrm{d}\langle \mathbf{N}\rangle/\mathrm{d}t = \mathbf{M}\langle \mathbf{N}\rangle + \mathbf{y}. \qquad (2.2b)$$

The steady state solution $\mathbf{N}^s$ of (2.2) and (2.1) is given by the linear equations

$$\sum_{j=1}^{n} M_{ij}N_j^s + y_i = 0, \qquad (2.3)$$

which are solved by standard methods.

In the following treatment of fluctuations around the steady state $\mathbf{N}^s$ the linearized equations (2.2) are used. This is a consistent approximation in case the calculated fluctuations are small enough to remain within the region around $\mathbf{N}^s$ where the linearization (2.2) is a good approximation of (2.1). Below we shall specialize to cases where interactions between the transported particles can be neglected.

The justification of this assumption implies the validity of the linearization (2.2). Having solved (2.3) and introduced

$$\alpha_i = N_i - N_i^s \qquad (2.4)$$

we get for $\langle\boldsymbol{\alpha}\rangle$ from (2.2), (2.3) the homogeneous equations

$$\mathrm{d}\langle\boldsymbol{\alpha}\rangle/\mathrm{d}t = \mathbf{M}\langle\boldsymbol{\alpha}\rangle. \qquad (2.5)$$

The system (2.5) of linear first order differential equations may be solved by standard methods extensively described in the literature [e.g. 12]. In this and the following papers we shall derive explicite solutions for special systems.

We now assume to have solved (2.5) and introduce the *fundamental* matrix $\mathbf{\Omega}(t)$ of the system with the elements $\Omega_{ik}(t)$ as solutions

$$\Omega_{ik}(t) = \langle\alpha_i(t)\rangle \qquad (2.6)$$

of (2.5) under the initial condition

$$\begin{aligned} &\alpha_k(0) = 1, \quad \alpha_j(0) = 0 \text{ else}, \quad \text{for } \mathbf{y} \neq 0,\\ &N_k(0) = 1, \quad N_j(0) = 0 \text{ else}, \quad \text{for } \mathbf{y} = 0. \end{aligned} \qquad (2.7)$$

Obviously

$$\lim_{t\to\infty} \mathbf{\Omega}(t) = 0.$$

The fundamental matrix $\mathbf{\Omega}$ represents the solution of (2.5), because for arbitrary initial condition $\mathbf{N}(0)$ the solution of (2.5) is ($\tilde{\boldsymbol{\alpha}}$ transpose of $\boldsymbol{\alpha}$)

$$\begin{aligned} &\langle\boldsymbol{\alpha}(t)\rangle = \mathbf{\Omega}(t)\,\tilde{\boldsymbol{\alpha}}(0), \quad \text{for } \mathbf{y} \neq 0,\\ &\langle\boldsymbol{\alpha}(t)\rangle = \mathbf{\Omega}(t)\tilde{\mathbf{N}}(0), \quad \text{for } \mathbf{y} = 0. \end{aligned} \qquad (2.8)$$

We note that $\mathbf{\Omega}$ in discrete systems is in complete analogy to the Green's function $G(\boldsymbol{r}, \boldsymbol{r}, t)$ in continuous systems, representing the solution $c(\boldsymbol{r}, t)$ of a (linear) partial differential equation under the initial condition $c(\boldsymbol{r}, 0) = \delta(\boldsymbol{r} - \boldsymbol{r})$.

2.2. The flux matrix

In the general case we admit jumps of particles between all binding sites. These jumps build up the individual fluxes, which consist of a sum of δ-functions, i.e. the duration of the jumps is assumed to be very short compared with the characteristic time constants occurring in the fundamental solution for the expected values. We introduce the flux matrix $\mathbf{\Phi}$. The element ϕ_{ik} is the flux from the kth to the ith binding site ϕ_{ii} is set zero.

Microscopically $\phi_{ik}(t)$ consists of a sum of δ-functions. The expected values $\langle\phi_{ik}(t)\rangle$ are given by the expected values $\langle N_i(t)\rangle$ in a way which depends on the special structure of the transport. In this paper we want to restrict to the general case, where interactions between the individual particles are neglected. In this case the probability of "jumps" from the kth binding site is proportional to the occupation number N_k. M_{ik} $(i \neq k)$ is the jump rate from k to i, i.e. the probability (per unit time) that a particle at the kth binding site jumps to the ith site. Hence the expected values $\langle\phi_{ik}\rangle$ are given by

$$\langle\phi_{ik}(t)\rangle = M_{ik}\,\langle N_k(t)\rangle, \quad i \neq k, \tag{2.9}$$

$$\langle\phi_{ii}(t)\rangle = 0.$$

The stationary expected values of the fluxes $\langle\phi_{ik}\rangle$ are indicated by $\langle\phi^{\mathrm{s}}_{ik}\rangle$. The deviations from the stationary expected fluxes are given by $\langle\varphi\rangle$:

$$\langle\varphi_{ik}(t)\rangle = \langle\phi_{ik}(t)\rangle - \langle\phi^{\mathrm{s}}_{ik}\rangle. \tag{2.10}$$

Of central importance for the calculation of the fluctuations will be the "fundamental" expected fluxes

$$\langle\varphi^{k}_{ij}(t)\rangle = M_{ij}\,\Omega_{jk}(t), \tag{2.11}$$

which describe the expected value of flux $\varphi_{ij}(t)$ under the initial condition (2.7).

Up to now we have considered only the internal fluxes between binding sites. If the system is open, i.e. the binding sites are in contact with $(m - n)$ outer reservoirs, we have to regard the fluxes between the reservoirs and the binding sites as well. For this case we extend the $(n \times n)$-flux-matrix to a $(m \times m)$-matrix $(m > n)$ with the components

$$\phi_{\mu\nu} = \phi_{ik} \quad (\mu = i, \nu = k) \quad \text{for } \mu, \nu \leqslant n,$$

$$\phi_{i\mu}, \quad \phi_{\mu i}, \quad \phi_{\mu\nu} \quad \text{for } \mu, \nu > n,\ i \leqslant n. \tag{2.9a}$$

The components $\phi_{\mu i}$ denote the flux from the ith binding site to the $(\mu - n)$th reservoir and $\phi_{i\mu}$ the reverse. Furthermore if there are jumps between the reservoirs themselves, these are the components $\phi_{\mu\nu}(\mu, \nu > n)$. The extension to $\varphi_{\mu\nu}$ is similar.

Naturally the expected values $\langle\phi_{i\mu}\rangle$ and $\langle\phi_{\mu\nu}\rangle$ $(\mu, \nu > n)$ are the time-independent i.e. $\langle\varphi_{i\mu}\rangle = 0$, $\langle\varphi_{\mu\nu}\rangle = 0$, while for $\langle\varphi_{\mu i}\rangle$ in correspondence to (2.10) holds:

$$\langle\varphi_{\mu i}(t)\rangle = \langle\phi_{\mu i}(t)\rangle - \langle\phi^{\mathrm{s}}_{\mu i}\rangle. \tag{2.10a}$$

And the "fundamental" expected fluxes are in extension of (2.11)

$$\langle\varphi^{k}_{\mu i}(t)\rangle = M_{\mu i}\,\Omega_{ik}(t), \tag{2.11a}$$

where $M_{\mu i}$ are the rate constants for jumps from the ith binding site into the reservoir $(\mu - n)$. Obviously the $M_{\mu i}$ are implicitely contained in the diagonal elements M_{ii} of $\mathbf{M}$.

We can extend as well Ω_{ik}. But by the assumption that the reservoirs are constant there is no correlation between jumps into the reservoirs, jumps between the reservoirs and the other fluxes and between the jumps from the reservoirs to the binding sites. Hence the components $\Omega_{\mu i}$, $\Omega_{i\mu}$, $\Omega_{\mu\nu}$ vanish for $\mu, \nu > n$.

2.3. Observable quantities

We assume the observed flux J to be some linear combination of the individual fluxes $\phi_{\mu\nu}$

$$J = \sum_{\mu,\nu=1}^{m} \gamma_{\mu\nu}\,\phi_{\mu\nu}. \tag{2.12}$$

It is not necessary to make specific assumptions about the $(m \times m)$-matrix $\boldsymbol{\gamma}$ at this moment. In electrical systems, where J is the observed current, the contributions of jumps from the ith site to the kth site and reverse differ only in sign: Then $\boldsymbol{\gamma}$ is an antisymmetric matrix

$$\gamma_{\mu\nu} = -\gamma_{\nu\mu}. \tag{2.13}$$

3. Correlation functions and spectra of the fluctuations in fluxes

3.1. The correlation matrix

We introduce a correlation matrix $\mathbf{C}(t)$ of fourth order with the elements $C_{\mu\nu,\kappa\rho}(t)$ representing the usual ensemble averaged correlations between the individual fluxes $\phi_{\mu\nu}$ at one time and $\phi_{\kappa\rho}$ at the same time or later:

$$C_{\mu\nu,\kappa\rho}(t) = \overline{\phi_{\mu\nu}(0)\,\phi_{\kappa\rho}(t)} - \langle\phi^{\mathrm{s}}_{\mu\nu}\rangle\langle\phi^{\mathrm{s}}_{\kappa\rho}\rangle. \tag{3.1}$$

Because we consider steady states, the correlations can be referred to time zero.

We now derive a general expression for $C_{\mu\nu,\kappa\rho}$. Taking the ensemble average at time zero contributions to $\overline{\phi_{\mu\nu}(0)\,\phi_{\kappa\rho}(t)}$ can only occur when at $t = 0$ a particle jumps from the site ν to the site μ. If interactions between the particles can be neglected, (2.9) is valid and the mean rate of such jumps is in the steady state equal to the expected stationary flux $\langle\phi^{\mathrm{s}}_{\mu\nu}\rangle$

$$\langle\phi^{\mathrm{s}}_{\mu\nu}\rangle = M_{\mu\nu}N^{\mathrm{s}}_{\nu}. \tag{3.2}$$

Then the general expression for $C_{\mu\nu,\kappa\rho}(t)$ is simply

$$C_{\mu\nu,\kappa\rho}(t) = M_{\mu\nu}N^{\mathrm{s}}_{\nu}\,[\delta_{\mu\nu,\kappa\rho}\,\delta(t) + M_{\kappa\rho}\,\Omega_{\rho\mu}(t)], \tag{3.3}$$

with

$$\delta_{\mu\nu,\kappa\rho} = \begin{cases} 1 \text{ for } \mu,\nu = \kappa,\rho \\ 0 \text{ else} \end{cases}.$$

The validity of (3.3) may be seen by the following arguments: The δ-like first term in (3.3) is the correlation of the jumps from ν to μ with themselves at $t = 0$. This term can be interpreted as a usual shot noise contribution.

Taking the ensemble average in (3.1) leads to the conditional average for $\phi_{\kappa\rho}(t)$ under the (initial) condition that at $t = 0$ a particle is in the μth binding site as consequence of the jump from ν to μ. And the time dependent contribution of this conditional average to $\mathbf{C}(t)$ is just the expected "fundamental" flux $\phi^{\mu}_{\kappa\rho}$. Hence with (2.11), (2.11a) results the second term in (3.3).

3.2. The spectra

Obviously the fourth order time correlation matrix $\mathbf{C}(t)$ in general is not time reversible ($\mathbf{C}(t) \neq \mathbf{C}(-t)$). The fourth order noise spectrum matrix $\mathbf{G}(\omega)$ is determined by $\mathbf{C}(t)$ through the Wiener–Khintchine relations:

$$G_{\mu\nu,\kappa\rho}(\omega) \tag{3.4}$$

$$= 2\,\mathrm{Re}\left[\int_0^\infty C_{\mu\nu,\kappa\rho}\,\mathrm{e}^{-\mathrm{j}\omega t}\,\mathrm{d}t + \int_0^\infty C_{\kappa\rho,\mu\nu}\,\mathrm{e}^{\mathrm{j}\omega t}\,\mathrm{d}t\right].$$

3.3. Autocorrelation and noise spectrum of the observed flux

The autocorrelation of J, which may be measured in noise experiments, is with (2.12), (3.1) and (3.3)

$$\overline{\Delta J(0)\,\Delta J(t)} = \sum_{\mu,\nu,\kappa,\rho=1}^{m} \gamma_{\mu\nu}\gamma_{\kappa\rho}\,C_{\mu\nu,\kappa\rho}(t) \tag{3.5}$$

$$= \sum_{\mu,\nu,\kappa,\rho=1}^{m} \gamma_{\mu\nu}\gamma_{\kappa\rho}\,M_{\mu\nu}N^{\mathrm{s}}_{\nu}[\delta_{\mu\nu,\kappa\rho}\delta(t) + M_{\kappa\rho}\,\Omega_{\rho\mu}(t)].$$

The noise spectrum $G_J(\omega)$ of J is

$$G_J(\omega) = 4\,\mathrm{Re}\int_0^\infty \overline{\Delta J(0)\,\Delta J(t)}\,\mathrm{e}^{\mathrm{j}\omega t}\,\mathrm{d}t. \tag{3.6}$$

Hence with (3.5)

$$G_J(\omega) = \sum_{\mu,\nu,\kappa,\rho=1}^{m} \gamma_{\mu\nu}\gamma_{\kappa\rho}\,M_{\mu\nu}N^{\mathrm{s}}_{\nu} \times \left[2\,\delta_{\mu\nu,\kappa\rho} + 4M_{\kappa\rho}\int_0^\infty \Omega_{\rho\mu}(t)\cos\omega t\,\mathrm{d}t\right]. \tag{3.7}$$

The first (shot noise) term in (3.7) is white noise. If all eigenvalues of $M_{\kappa\rho}$ are real, $\Omega_{\rho\mu}(t)$ consists of a sum of relaxation terms e^{-t/τ_i}. Then the second part is a sum of usual Lorentz-type spectra.

By the results (3.3)–(3.7) the microscopic fluctuations of the fluxes of matter and linearly coupled quantities as the electric current are related to the phenomenological equations (2.1), (2.2) and hence to the macroscopic properties. This result is valid for steady states also far from equilibrium and may be regarded as an extension of the well known Nyquist formula for current fluctuations in equilibrium.

4. Transport noise in pores

In this chapter we apply the general approach to current noise generated by ion transport through pores in a barrier model. Similarly the described model may be applied also to other transport systems (e.g. superionic conductors).

4.1. The model

The transport model ("pores") is considered to be a sequence of $(n+1)$ activation barriers separated by n energy minima (binding sites). The transport system is assumed to consist of a great number of identical noninteracting pores. The rate constants for jumps from the ith binding site to the right or to the left are denoted by k_i', k_i'' respectively. They are assumed to be independent of the occupation numbers N_j. The macroscopic (phenomenological) equations for the rate of change $\langle \dot{N}_i \rangle$ are then given by:

$$\langle \dot{N}_1 \rangle = k_0' N_0 - (k_1' + k_1'') \langle N_1 \rangle + k_2'' \langle N_2 \rangle,$$

$$\langle \dot{N}_i \rangle = k_{i-1}' \langle N_{i-1} \rangle - (k_i' + k_i'') \langle N_i \rangle + k_{i+1}'' \langle N_{i+1} \rangle, \quad (4.1)$$

$$i = 2, 3, \ldots, n-1$$

$$\langle \dot{N}_n \rangle = k_{n-1}' \langle N_{n-1} \rangle - (k_n' + k_n'') \langle N_n \rangle + k_{n+1}'' N_{n+1}.$$

The concentrations N_0, N_{n+1} at the pore mouths, which determine the influx into the pores, are assumed to be constant and the rate constants k_i', k_i'' form the coefficients of the relaxation matrix **M** in (2.2):

$$M_{ii} = -(k_i' + k_i''), \quad M_{i,i+1} = k_{i+1}'',$$

$$M_{i+1,i} = k_i', \qquad M_{ik} = 0 \text{ else} \qquad (4.2a)$$

and

$$y_1 = k_0' N_0, \quad y_n = k_{n+1}'' N_{n+1}, \quad y_i = 0 \text{ else}. \quad (4.2b)$$

In the limit $n \to \infty$, which can be regarded as the transition to the continuum case, (4.1) becomes a linear diffusion equation [9,13], the special structure of which depends on the special choice of k_i', k_i''. The equations for N_1 and N_n become (homogeneous) boundary conditions.

The system (4.1) can always be symmetrized and the eigenvalues of the relaxation matrix of the system are real and negative [13]. The symmetrization is done by the diagonal matrix **T** with the components:

$$T_{ii} = t_1 t_2 \cdots t_{i-1} t_i$$

$$t_1 = 1, \quad t_i = \sqrt{k_i''/k_{i-1}'}, \quad i = 2, 3, \ldots, n. \qquad (4.3)$$

Under this transformation **N**, **y** and **M** are transformed to

$$\bar{\mathbf{N}} = \mathbf{T}\mathbf{N}, \quad \bar{\mathbf{y}} = \mathbf{T}\mathbf{y}, \quad \bar{\mathbf{M}} = \mathbf{T}\mathbf{M}\mathbf{T}^{-1}, \qquad (4.4a)$$

with

$$\bar{M}_{ii} = M_{ii}, \quad \bar{M}_{i,i+1} = \bar{M}_{i+1,i} = \sqrt{k_i' k_{i+1}''}. \qquad (4.4b)$$

Because **M** may be symmetrized, it can also be diagonalized to $\hat{\mathbf{M}}$ by an appropriate matrix **V** with the transformation

$$\hat{\mathbf{M}} = \mathbf{V}\mathbf{M}\mathbf{V}^{-1}, \qquad (4.5)$$

where $\hat{M}_{ii} = -\lambda_i$ are the real eigenvalues of **M**. The fundamental matrix (see (2.6), (2.7)) is then given by **V** and λ_i through:

$$\Omega_{ik}(t) = \sum_{j=1}^{n} V_{ij}^{-1} \, \mathrm{e}^{-\lambda_j t} \, V_{jk}. \qquad (4.6)$$

According to our model the fluxes are generated by the jumps of the ions over the barriers. Because from a binding site i only jumps to the adjacent sites $(i-1)$ and $(i+1)$ are allowed, the only nonvanishing components of the flux-matrix Φ are $\phi_{i+1,i}$ and $\phi_{i-1,i}$, and it is useful to introduce the following notations

$$\phi_{i+1,i} = \phi_{i+1}', \qquad \phi_{i-1,i} = \phi_i''. \qquad (4.7)$$

Furthermore we define the total flux ϕ_i over the ith barrier by

$$\phi_i = \phi_i' - \phi_i'', \quad i = 1, 2, \ldots, n+1. \qquad (4.8)$$

The expected values for the individual fluxes are according to (2.9), (4.1), (4.2)

$$\langle \phi_i' \rangle = k_{i-1}' \langle N_{i-1} \rangle, \quad \langle \phi_i'' \rangle = k_i'' \langle N_i \rangle. \qquad (4.9)$$

The measured electric current J is represented by a linear combination of the ϕ_i

$$J = \sum_{i=1}^{n+1} \gamma_i \phi_i = \sum_{i=1}^{n+1} \gamma_i (\phi_i' - \phi_i''). \qquad (4.10)$$

The γ_i depend on the geometric properties (e.g. distances between the binding sites) and the dielectric properties of the membrane–pore transport system.

4.2. The correlations

We calculate the correlations in the simplified notations given by the relations (4.1)–(4.10). The time correlation between fluxes ϕ_i and ϕ_k is with the use of (3.1)–(3.3)

$$\overline{\phi_i(0)\,\phi_k(t)} = \overline{(\phi_i' - \phi_i'')_0\,(\phi_k' - \phi_k'')_t} = \langle\phi_i^{\mathrm{S}}\rangle\langle\phi_k^{\mathrm{S}}\rangle$$
$$+\,\delta_{ik}(k_{i-1}'N_{i-1}^{\mathrm{S}} + k_i''N_i^{\mathrm{S}})\,\delta(t)$$
$$+\,[k_{i-1}'N_{i-1}^{\mathrm{S}}(k_{k-1}'\Omega_{k-1,i} - k_k''\Omega_{ki})$$
$$+\,k_i''N_i^{\mathrm{S}}(k_k''\Omega_{k,i-1} - k_{k-1}'\Omega_{k-1,i-1})]. \tag{4.11}$$

With (4.10) we get the autocorrelation function for the observed current J:

$$\overline{\Delta J(0)\,\Delta J(t)} = \sum_{i=1}^{n+1} \gamma_i^2(k_{i-1}'N_{i-1}^{\mathrm{S}} + k_i''N_i^{\mathrm{S}})\,\delta(t)$$
$$+\sum_{i,k=1}^{n+1} \gamma_i\gamma_k\,[k_{i-1}'N_{i-1}^{\mathrm{S}}(k_{k-1}'\Omega_{k-1,i} - k_k''\Omega_{ki})$$
$$+\,k_i''N_i^{\mathrm{S}}(k_k''\Omega_{k,i-1} - k_{k-1}'\Omega_{k-1,i-1})]. \tag{4.12a}$$

Using that $\Omega_{0k}, \Omega_{k0}, \Omega_{n+1,k}, \Omega_{k,n+1}$ are zero and changing the indices in the summations in an appropriate way, this result can be written more simply in the form

$$\overline{\Delta J(0)\,\Delta J(t)} = \sum_{i=1}^{n+1} \gamma_i^2(k_{i-1}'N_{i-1}^{\mathrm{S}} + k_i''N_i^{\mathrm{S}})\,\delta(t)$$
$$+\sum_{i,k=1}^{n} \Omega_{ki}(t)\,[k_{i-1}'N_{i-1}^{\mathrm{S}}(\gamma_i\gamma_{k+1}k_k' - \gamma_i\gamma_k k_k'')$$
$$+\,k_{i+1}''N_{i+1}^{\mathrm{S}}(\gamma_{i+1}\gamma_k k_k'' - \gamma_{i+1}\gamma_{k+1}k_k')] \tag{4.12b}$$

with $\Omega_{ki}(t)$ according to (4.6).

4.3. Noise spectrum and Nyquist relation

The noise spectrum is given by (3.7) and (4.6), (4.12). Because according to (4.6) the solutions of the phenomenological equations are represented by sums of relaxations with time constants

$$\tau_j = 1/\lambda_j, \tag{4.13}$$

the spectrum $G_J(\omega)$ consists of a shot noise (white noise) term and a sum of Lorentz terms. We get

$$G_J(\omega) = 2\sum_{i=1}^{n+1} \gamma_i^2(k_{i-1}'N_{i-1}^{\mathrm{S}} + k_i''N_i^{\mathrm{S}})$$
$$+\,4\sum_{l=1}^{n} \tau_l(1+\omega^2\tau_l^2)^{-1}\sum_{i,k=1}^{n} V_{kl}^{-1}V_{li}$$
$$\times\,[k_{i-1}'N_{i-1}^{\mathrm{S}}(\gamma_i\gamma_{k+1}k_k' - \gamma_i\gamma_k k_k'')$$
$$+\,k_{i+1}''N_{i+1}^{\mathrm{S}}(\gamma_{i+1}\gamma_k k_k'' - \gamma_{i+1}\gamma_{k+1}k_k')]. \tag{4.14}$$

In equilibrium ($k_{i-1}'N_{i-1}^{\mathrm{S}} = k_i''N_i^{\mathrm{S}}$) this result agrees with results obtained by Läuger [11] with the use of the Nyquist relation

$$G_J(\omega) = 4KT\,\mathrm{Re}(Y(\omega)). \tag{4.15}$$

$\mathrm{Re}(Y(\omega))$ = real part of the complex admittance $Y(\omega)$. Calculation of the complex admittance for non-equilibrium stationary states ($\bar{J} \neq 0$) analogously as in [11] yields [13]

$$\mathrm{Re}(Y(\omega)) = \frac{1}{4KT}\,[\text{righthand side of (4.14)}]. \tag{4.16}$$

Hence it follows immediately, that the Nyquist relation (4.15) is valid also for fluctuations around non-equilibrium steady states.

5. Further applications and special examples

5.1. Noise generated by carrier mediated ion transport

An alternative possibility of transport through membranes is the concept of carrier mediated ion transport. In the last ten years especially the valinomycin-mediated transport through lipid bilayers has been extensively investigated by steady-state and macroscopic time-dependent relaxation experiments [14–16]. As a further application of our theoretical approach we briefly describe the analysis of carrier current noise in non-equilibrium steady-states. A detailed presentation comparing the noise analysis with the macroscopic relaxation analysis will be given in an extra paper. Carrier noise in the equilibrium case has recently been investigated by Kolb and Läuger [18].

We refer to the mechanism proposed by Läuger and Stark [15] and Stark et al. [14] for carrier mediated ion transport. In this model the transport takes place in four steps: (a) recombination of ion M^+ and neutral carrier at the left-hand-interface ($'$), (b) translocation of the complex to interface ($''$), (c) dissociation of the complex and release of the ion into the solution and (d) back transport of free carrier. Of course this basic four step mechanism can be extended to n steps. The essential difference between pores and carriers is the closed loop structure of the carrier mechanism. The nth site is in contact with the first one.

The current is generated by the movement of the charged complex MS^+ between the left and right-hand interfaces. The total number N_0 of carriers is constant. In case of an applied voltage the system reaches a non-equilibrium driven steady-state.

Using the notation in [14,15] the electrical current J is simply given by (F = Faraday constant)

$$J = F\phi_{MS}, \tag{5.1}$$

with

$$\phi_{MS} = \phi'_{MS} - \phi''_{MS}. \tag{5.1a}$$

The expected values for the individual fluxes ϕ'_{MS}, ϕ''_{MS} are

$$\langle\phi'_{MS}\rangle = k'_{MS}\langle N'_{MS}\rangle, \qquad \langle\phi''_{MS}\rangle = k''_{MS}\langle N''_{MS}\rangle. \tag{5.2}$$

Then from the general approach described in section 3 the autocorrelation function is

$$\begin{aligned}\frac{1}{F^2}\overline{\Delta J(0)\,\Delta J(t)} &= (k'_{MS}\bar{N}'_{MS} + k''_{MS}\bar{N}''_{MS})\,\delta(t)\\ &\quad + k'_{MS}\bar{N}'_{MS}(k'_{MS}\Omega_{MS',MS''} - k''_{MS}\Omega_{MS'',MS''})\\ &\quad + k''_{MS}\bar{N}''_{MS}(k''_{MS}\Omega_{MS'',MS'} - k'_{MS}\Omega_{MS',MS'})\end{aligned} \tag{5.3}$$

and the fundamental solutions $\Omega_{MS',MS''}$, $\Omega_{MS'',MS''}$ are the solutions of (5.4) for $\langle N'_{MS}\rangle$ and $\langle N''_{MS}\rangle$ under the initial conditions $N''_{MS}(0) = 1$, $N'_{MS}(0)$, $N'_S(0)$, $N''_S(0) = 0$ and $\Omega_{MS'',MS'}$, $\Omega_{MS',MS'}$ correspondingly.

5.2. Pores with one or two binding sites

As simple applications of the general formula (4.12b) and (4.14) we discuss current noise in pores with one or two binding sites, respectively.

One binding site

In this case the phenomenological equation for the expected value of the occupation number $\langle N_1\rangle$ is:

$$\langle\dot{N}_1\rangle = k'_0N_0 - (k'_1 + k''_1)\langle N_1\rangle + k''_2N_2, \tag{5.4}$$

N_0 and N_2 are the constant concentrations on the left and right-hand sides of the pores respectively. The stationary solution is

$$N^s_1 = (k'_0N_0 + k''_2N_2)/(k'_1 + k''_1). \tag{5.5}$$

The fundamental solution Ω_{11} of the homogeneous equation belonging to (5.4) is simply

$$\Omega_{11} = e^{-t/\tau}, \qquad \tau = (k'_1 + k''_1)^{-1}. \tag{5.6}$$

Hence from (4.12b) the autocorrelation function of current J is with (5.5) and (5.6):

$$\begin{aligned}\overline{\Delta J(0)\,\Delta J(t)} &= \delta(t)A_1 + e^{-t/\tau}A_2\\ A_1 &= \gamma_1^2(k'_0N_0 + k''_1N^s_1) + \gamma_2^2(k'_1N^s_1 + k''_2N_2),\\ A_2 &= k'_0N_0(\gamma_1\gamma_2k'_1 - \gamma_1^2k''_1) + k''_2N_2(\gamma_1\gamma_2k''_1 - \gamma_2^2k'_1).\end{aligned} \tag{5.7}$$

The corresponding spectrum $G_J(\omega)$ is

$$G_J(\omega) = 2A_1 + A_2\,4\tau/(1 + \omega^2\tau^2). \tag{5.8a}$$

After some rearrangement we can write (5.8a) in the form

$$\begin{aligned}G_J(\omega) &= \frac{2\tau}{1 + \omega^2\tau^2}\,[(\gamma_1 + \gamma_2)^2\,(k'_1k'_0N_0 + k''_1k''_2N_2)\\ &\quad + \omega^2\tau^2(\gamma_1^2(2k''_2k'_0N_0 + k''_1k''_2N_2 + k'_1k'_0N_0)\\ &\quad + \gamma_2^2(2k'_1k''_2N_2 + k''_1k''_2N_2 + k'_1k'_0N_0))].\end{aligned} \tag{5.8b}$$

In (5.7) and (5.8) we have not yet specified the constants γ_1 and γ_2. According to (4.10), (4.8) γ_i determines the contribution of the flux ϕ_i to the measured current. In many cases γ_1, γ_2 may be (see [11]):

$$\gamma_1 = z e_0\, s_1/d, \quad \gamma_2 = z e_0\, s_2/d, \quad s_1 + s_2 = d, \tag{5.9}$$

where z is the valency of the ions, e_0 the elementary charge, d the membrance thickness (pore length) and $s_1 (s_2)$ the distance of the binding site from the left (right) pore mouth. With (5.9) the spectrum (5.8) agrees with the current noise spectrum recently obtained by Läuger [10,11] with different methods.

Two binding sites

For pores with two binding sites the phenomenological equations are:

$$\langle \dot{N}_1 \rangle = k'_0 N_0 - (k'_1 + k''_1)\langle N_1 \rangle + k''_2 \langle N_2 \rangle,$$

$$\langle \dot{N}_2 \rangle = k'_1 \langle N_1 \rangle - (k'_1 + k''_2)\langle N_2 \rangle + k''_3 N_3. \tag{5.10}$$

N_0, N_3 are the constant reservoirs on the left, right side of the pores respectively. The stationary solutions of (5.10) are:

$$N_1^s = \frac{k'_0 N_0 (k'_2 + k''_2) + k''_3 N_3 k''_2}{(k'_1 + k''_1)(k'_2 + k''_2) - k'_1 k''_2},$$

$$N_2^s = \frac{k''_3 N_3 (k'_1 + k''_1) + k'_0 N_0 k'_1}{(k'_1 + k''_1)(k'_2 + k''_2) - k'_1 k''_2}. \tag{5.11}$$

The fundamental solutions:

$$\Omega_{11} = \frac{b + \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_1} - \frac{b - \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_2},$$

$$\Omega_{12} = -\frac{b + \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_1} + \frac{b + \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_2},$$

$$\Omega_{22} = -\frac{b - \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_1} + \frac{b + \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_2},$$

$$\Omega_{21} = \frac{b - \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_1} - \frac{b - \sqrt{r}}{2\sqrt{r}}\, e^{-t/\tau_2}, \tag{5.12}$$

with [11]

$$\tau_1 = (a + \sqrt{r})^{-1}, \quad \tau_2 = (a - \sqrt{r})^{-1}, \tag{5.13}$$

and

$$a = \tfrac{1}{2}(k'_1 + k''_1 + k'_2 + k''_2), \quad b = \tfrac{1}{2}((k'_1 + k''_1) - (k'_2 + k''_2))$$

$$r = b^2 + k'_1 k''_2. \tag{5.14}$$

With (5.11), (5.12) the autocorrelation and the spectral density of current are given by (4.12), (4.14). We omit the presentation of the explicit lengthly formula.

5.3. Closed pores

The model of closed pores (no contact with outer reservoirs) in the case of two binding sites has recently been applied to the analysis of noise generated by hydrophobic ions [17] and the analysis of gating current noise [17,11]. In closed pores the fluctuations are around equilibrium steady states. Furthermore in this case the microscopic fluxes may uniquely be expressed by the time derivative of the occupation numbers [13]. Hence the case of closed pores is especially interesting for mainly two reasons:

First, it may be treated not only by our general approach to current noise described in this chapter, but also by a number of different methods: e.g. the Langevin method [17], the master equation approach [13] or by application of the Nyquist theorem in the equilibrium case [11]. So the application to the closed pore situation may serve as a test for the validity of the different methods. Second, because the pores are not in contact with outer reservoirs representing uncorrelated noise sources, the long-time correlations are so strong, that the spectral density $G_J(\omega)$ of current noise is $\propto \omega^2$ for small frequencies, i.e. vanishes for $\omega \to 0$.

In the most simple closed pore case of two binding sites the phenomenological equations are in simplification of (5.10) for $k'_0, k''_1, k'_2, k''_3 = 0$:

$$\langle \dot{N}_1 \rangle = -k'_1 \langle N_1 \rangle + k''_2 \langle N_2 \rangle, \qquad \langle \dot{N}_2 \rangle = -\langle \dot{N}_1 \rangle. \tag{5.15}$$

For the occupation numbers holds the conservation relation

$$N_1 + N_2 = N. \tag{5.16}$$

The steady state solutions of (5.15) are

$$N_1^s = \frac{k_2''}{k_1' + k_2''} N, \qquad N_2^s = N - N_1^s = \frac{k_1'}{k_1' + k_2''} N. \tag{5.17}$$

The fundamental solutions of (5.15) are:

$$\begin{aligned} \Omega_{11} &= \tau(k_1' \, e^{-t/\tau}), & \Omega_{12} &= \tau(-k_2'' \, e^{-t/\tau}), \\ \Omega_{22} &= \tau(k_2'' \, e^{-t/\tau}), & \Omega_{21} &= \tau(-k_1' \, e^{-t/\tau}), \end{aligned} \tag{5.18}$$

with

$$\tau = (k_1' + k_2'')^{-1} \tag{5.19}$$

With (5.17)–(5.19) the autocorrelation function of current J becomes:

$$\overline{\Delta J(0)\, \Delta J(t)} = \gamma^2 N k_1' k_2'' (2\tau\, \delta(t) - e^{-t/\tau}). \tag{5.20}$$

The corresponding spectral density is

$$G_J(\omega) = 4N\gamma^2 \frac{k_1' k_2''}{(k_1' + k_2'')} \frac{\omega^2 \tau^2}{(1 + \omega^2 \tau^2)}, \tag{5.21}$$

in agreement with the results obtained by other methods [17,11].

6. Discussion

The aim of this paper has been to develop a unifying formalism for the analysis of current noise around non-equilibrium steady states generated by a number of different transport systems, which so far have not yet been treated or have been treated by different methods. For this case we have started with elementary considerations about the ensemble averaged time correlations between the individual fluxes (see sect. 3.1) forming the correlation matrix **C** and derived the general expression (3.3) for these correlations.

For explicite calculation of the correlations and noise spectra of the observable quantities (e.g. electric current) one needs: (1) The fundamental solutions of the phenomenological equations for the expected values of the occupation numbers. (2) Additional informations about the geometric and dielectric properties of the special transport system, which are not included in the phenomenological equations. These informations are e.g. (a) the coupling constants of the individual fluxes to the measured current and (b) detailed knowledge about the individual fluxes $\phi_{i\mu}$ and $\phi_{\mu i}$ between the ith binding site and the outer reservoirs. The latter information is necessary for a decomposition of the diagonal elements M_{ii} of the relaxation matrix **M** and of the inhomogenities y_i, containing the summarized contributions $\phi_{\mu i}$, $\phi_{i\mu}$ $(\mu > m)$ respectively.

The reduction of the calculation of current noise spectra to the solution of the macroscopic equation may be regarded as an extension to non-equilibrium situations of the usual Nyquist theorem relating the noise spectra to the frequency dependent admittance. For the special pore transport systems discussed in section 4, the validity of the Nyquist relation also for noise around non-equilibrium steady states can explicitely be shown. With our approach it will be possible to investigate the validity of the Nyquist relation in non-equilibrium states for a wide class of transport systems.

The two basic assumptions underlying the general expression (3.3) for the correlations are: (a) the short duration of the individual jumps of particles compared with the relaxation times in the system and (b) the neglection of interactions between the particles. We hope that by an extension of our approach we soon will be able to discuss also the influence of interactions on the noise spectra.

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