[45]See C. Freed and H. A. Haus, Ref. 1; F. T. Arecchi, M. Giglio, and A. Sona, Ref. 37; F. Davidson and L. Mandel, Ref. 12.

[46]H. Haken, *Handbuch der Physik* (Springer-Verlag, Berlin, 1970), Vol. XXV/2c.

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Fluctuation Spectra and Quasithermodynamics of a Linearized Markov Process*

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An n-dimensional linear Markov process with parameters $\alpha_i (i=1, \ldots, n)$ and $\dot{\underline{\alpha}} = -\underline{M}\,\underline{\alpha}$ is considered. Criteria for stationarity of the process and spectral properties of the fluctuations around the stationary state $\underline{\alpha} = \underline{0}$ are derived. When the stationary state is a thermodynamic equilibrium state, the spectra are proven to be monotonic functions of the frequency. Positive-definiteness of the matrix $\underline{M}^3 \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ turns out to be the necessary and sufficient condition for the absence of local maxima in the spectra. A process with $\underline{M}^3 \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ positive-definite also has the property that $\underline{M}^2 \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ is positive-definite, which guarantees the absence of external driving forces, and corresponds to a pure relaxation process. $\underline{M} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ positive-definite is a necessary condition for stationarity. Moreover, it is a necessary and sufficient condition for the existence of spectra and transport coefficients. Positive-definiteness of $\underline{M} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$, $\underline{M}^2 \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$, and $\underline{M}^3 \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ is linked to properties of the excess-entropy production.

I. INTRODUCTION

We shall derive some properties of fluctuation spectra ("noise") and the excess-entropy production during those fluctuations from equilibrium, as well as from stationary nonequilibrium states of systems with n-coupled macroscopic variables.

As an example, one may think of an n-"level" semiconductor with the electron occupancy numbers of each level as the variables. In the equilibrium state there are only thermal transitions between the levels. A stationary nonequilibrium state may result when we continuously "pump" electrons from one level to another by means of a steady light source. Spectra can be obtained experimentally through a Fourier decomposition of the temporal history of the fluctuations in the conduction current: The conductivity is a linear combination of these occupancies, with the mobilities as coefficients.

The time dependence of the n macroscopic variables a_i $(i=1, \ldots, n)$ of this and many other kinetic processes is assumed to behave like a Markov process and thus to be governed by a first-order differential equation in time[1-4]:

$$\dot{\underline{a}} = \underline{f}(\underline{a}), \quad \underline{a} \equiv (a_1, \ldots, a_n)^T . \tag{1a}$$

For the semiconductor example discussed before, the explicit form of Eq. (1a) may be obtained[1,5] by assuming that the transition current p_{ij} from the ith level to the jth level is proportional to the occupation a_i of the ith level and to the number of vacancies in the jth level, the "mass-action" laws: $p_{ij} = \gamma_{ij} a_i (N_j - a_j)$, where N_j is the total number of states in the jth level. This gives

$$\dot{a}_i = -\sum_{j=1}^{n} (p_{ij} - p_{ji})$$

$$= -\sum_{j=1}^{n} [\gamma_{ij} N_j a_i - \gamma_{ji} N_i a_j + (\gamma_{ji} - \gamma_{ij}) a_i a_j] . \tag{1b}$$

In many cases the energy gap between the valence band, defined as $i=n$, and the higher levels, defined as $i=1$ or 2, is equal to the energy of photons in the optical spectrum. In the case of steady light absorption there results a current U_{nk}, for example, from the nth level to the kth level. One has $U_{nk} = a_n q E$ with q, the quantum efficiency, and E, the constant number of incident photons per second. For all practical cases, however, the net decrease in a_n is negligible compared to the large number a_n of electrons in the valence band. Hence, one takes $a_n \approx N_n$ and U_{nk} a constant as a result. This is incorporated in Eq. (1b) by adding U_{nk} to the equation for $\dot{a}_k$ and $-U_{nk}$ to the equation for $\dot{a}_n$.

We solve each model for its stationary state $\underline{a}_0$, i.e., $\underline{f}(\underline{a}_0) = \underline{0}$. We linearized Eq. (1a) defining $\underline{\alpha}(t) \equiv \underline{a}(t) - \underline{a}_0$ and find

$$\dot{\underline{\alpha}} = -\underline{\tilde{M}}\,\underline{\alpha}, \quad \underline{\tilde{M}}_{ij} \equiv -\left.\frac{\partial f_i(\underline{a})}{\partial a_j}\right|_{\underline{a}=\underline{a}_0} \quad (i, j = 1, \ldots, n) . \tag{2}$$

We now remove any dependent equations and variables. We therefore obtain a reduced matrix $\underline{M}$ with dimension $\leq n$, $\det\underline{M} \neq 0$, and $\underline{\alpha} = \underline{0}$ as the only point where $\dot{\underline{\alpha}} = \underline{0}$:

$$\underline{\dot{\alpha}} = -\underline{M}\,\underline{\alpha}\,,\quad \det\underline{M} \neq 0\,,\quad \dim\underline{\alpha} \leq n\,. \tag{3}$$

In the semiconductor example, a first reduction would have been the elimination of one α_i because of the over-all charge neutrality of the material.

The solution of Eq. (3) is

$$\underline{\alpha}(t) = e^{-\underline{M}t}\,\underline{\alpha}(0)\,. \tag{4}$$

It seems reasonable on physical grounds that $\underline{M}$ can be diagonalized by a similarity transformation. Thus, we assume that

$$\underline{M} = \underline{c}^{-1}\,\underline{\Lambda}\,\underline{c} \quad \text{with } \Lambda_{ij} = \delta_{ij}\lambda_i\,. \tag{5}$$

(If $\underline{M}$ could not be diagonalized, $\underline{M}$ would not have a complete set of eigenvectors and some identical eigenvalues. In the semiconductor case, for example, this is not likely to happen due to the many different submicroscopic perturbations that affect the relaxation times $1/\lambda_i$.) The solution of Eq. (4) then becomes

$$\underline{\alpha}(t) = \underline{c}^{-1} e^{-\underline{\Lambda}t}\,\underline{c}\,\underline{\alpha}(0)$$

or (6)

$$\alpha_i(t) = \sum_{j,k} (\underline{c}^{-1})_{ij}\, e^{-\lambda_j t} c_{jk}\alpha_k(0)\,.$$

In order to ensure asymptotic stability of the stationary solution $\underline{a}_0$, i.e., that any orbit finally comes back or that $\underline{\alpha}(\infty) = \underline{0}$, also in the original Eq. (1b), we require $\mathrm{Re}\lambda_i > 0$.[6] The last condition does not imply that $\underline{M}$ is positive-definite.[7] [An arbitrary real matrix $\underline{A}$ is called positive-definite if $(\underline{A}\underline{x}, \underline{x}) > 0$ for all real $\underline{x} \neq \underline{0}$, using the real scalar product.] For example, the matrix $\underline{M}$ for curve II in Ref. 8 is not positive-definite. $\mathrm{Re}\lambda_i > 0$ is not a sufficient condition for positive-definiteness of $\underline{M}$ unless $\underline{M}$ is symmetric. However, even for an equilibrium stationary state $\underline{M}$ need not be symmetric and not be positive-definite as a result.

Fluctuations

Equation (6) shows the smooth return from a measurable macroscopic initial deviation $\underline{\alpha}(0)$. The return is smooth because $\underline{\alpha}(0)$ is so large that we neglected any fluctuations in this case. In order to use Eqs. (1)–(6) for the description of fluctuations we must, as is well known,[1–4] identify $\underline{\alpha}(t)$ with an average over some appropriate ensemble of the fluctuating microscopic variable, at a time t, after a given initial $\underline{\alpha}(0) = \underline{\alpha}_0$. It is not obvious in the case where the $\underline{\alpha}_0$ are caused only by fluctuations that this conditional average $\underline{\alpha}(t)$ exists and still satisfies the previous macroscopic Eq. (3). The last condition is the so-called "regression hypothesis." The equivalence between processes obeying the regression hypothesis and Markov processes was established by Lax[4] and used to define a quantum-mechanical Markov process. For a stationary process, the initial deviations are determined by a probability distribution $P(\underline{\alpha}_0)$. We have $\langle \underline{\alpha} \rangle = 0$ and assume the matrix $\langle \underline{\alpha}\underline{\alpha}^T \rangle$, i.e., $\{\langle \alpha_i \alpha_j \rangle\}$, to be given. We will only use these two moments of $P(\underline{\alpha}_0)$.

All previous assumptions together do not necessarily guarantee that $P(\underline{\alpha}_0, t) = P(\underline{\alpha}_0, t + t_1)$ as is the case for a stationary process. We prove in Sec. III that $\underline{M}\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ positive-definite is a necessary condition for stationarity. Moreover, it is a necessary and sufficient condition for the existence of the time-displaced correlation matrix $\langle \underline{\alpha}_0\,\underline{\alpha}(t)^T \rangle$, fluctuation spectra, and transport coefficients for all linear combinations of the $\alpha_i(t)$. This requirement implies that $\mathrm{Re}\lambda_i > 0$ but not that $\underline{M}$ is positive-definite.

We define a relaxation process in Sec. IV as a process for which the matrix $\underline{M}^2\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ is positive-definite. We make a linear transformation to new variables $\underline{\beta}(t)$ such that $\langle \underline{\beta}\,\underline{\beta}^T \rangle = \underline{I}$, the identity matrix. In this new space of equal variances in all directions, the impulsive fluctuation "forces" apparently are $\underline{0}$ on the average. Any remaining accelerations $\ddot{\underline{\beta}}(t)$, in this space, will either slow down the return in the direction of $\underline{0}$ as for a dissipative process or will drive $\underline{\beta}(t)$ towards $\underline{0}$, depending on whether $\underline{M}^2\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ is positive-definite or not. In the last case, some components of $\underline{\beta}(t)$ may become 0 and change sign in the time evolution of $\underline{\beta}(t)$.

Thus, when $\underline{M}^2\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ is not positive-definite we expect damped periodic solutions for some linear combination of the $\beta_i(t)$, in the case of a complex λ_j, or solutions with one 0 (quasiperiodic), in the case of real λ's. Hence, its time-displaced correlation function has a negative part and the Fourier transform of this, the spectrum $S(\omega)$, may, as will be demonstrated, have a local maximum as a result of this. In Sec. V it is shown that a necessary and sufficient condition to have a spectral maximum in a linear combination $z(t) = (\underline{p}, \underline{\alpha}(t)) = (\underline{q}, \underline{\beta}(t))$ is that $(\underline{M}^{-3}\langle \underline{\alpha}\,\underline{\alpha}^T \rangle \underline{p}, \underline{p}) < 0$. Thus, there are no spectral maxima at all if and only if we have $\underline{M}^3\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ positive-definite. If there are no maxima, the process also turns out to be a relaxation process as defined before. It is proven in Sec. II that processes satisfying time reversibility, i.e., $\langle \underline{\alpha}_0\,\underline{\alpha}(t)^T \rangle = \langle \underline{\alpha}_0\,\underline{\alpha}(-t)^T \rangle$, among which are the equilibrium processes,[1–4] do not have spectral maxima. In Sec. VI we show the excess entropy production $\mathcal{P}(t)$ to be positive, monotonically decreasing, and concave depending on the positive-definiteness of, respectively, $\underline{M}\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$, $\underline{M}^2\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$, and $\underline{M}^3\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$. Each of these three properties restricts the λ_i to smaller sectors of the complex plane.

II. SPECTRA

One defines the time-displaced correlation matrix[1,3] as

$$\underline{\phi}(t) \equiv \langle \underline{\alpha}_0 \, \underline{\alpha}(t)^T \rangle = \int d\underline{\alpha}_0 \, P(\underline{\alpha}_0) \, \underline{\alpha}_0 \, \underline{\alpha}(t)^T \; .$$

One easily checks that $\underline{\phi}(-t) = \underline{\phi}(t)^T$. Given a vector $\underline{b}$, every matrix $\underline{b}\,\underline{b}^\dagger$ is Hermitian and positive-semidefinite as $[\underline{b}\,\underline{b}^\dagger \underline{x}, \underline{x}] = [\underline{b}^\dagger \underline{x}, \underline{b}^\dagger \underline{x}]$ under the complex scalar product. $\mathrm{Re}\,\underline{b}\,\underline{b}^\dagger$ is symmetric and, moreover, positive-semidefinite under both the real and complex scalar product. Hence, $\underline{\phi}(0)$ is symmetric and positive-definite. If it were not for the averaging $\underline{\phi}(0)$ would only be positive-semidefinite.[9] From Eq. (4) one finds[3]

$$\begin{aligned} \underline{\phi}(t) &= \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \, e^{-\underline{M}^T t} \qquad \text{for } t \geq 0 \; , \\ &= e^{+\underline{M}t} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \qquad \text{for } t \leq 0 \; . \end{aligned} \tag{7a}$$

Replacing the ensemble average over $\underline{\alpha}_0$ with the time average, we rewrite the definition of $\underline{\phi}(-t)$ for all t as

$$\underline{\phi}(-t) = \lim_{T\to\infty} T^{-1} \int_{-T/2}^{+T/2} \underline{\alpha}(u) \, \underline{\alpha}(u-t)^T \, du \; ,$$

a convolution integral of $\underline{\alpha}(z)$ with $\underline{\alpha}(-z)^T$. One defines the spectral noise density $\underline{S}(\omega)$ as

$$\underline{S}(\omega) \equiv \lim_{T\to\infty} (2/T) \, \hat{\underline{\alpha}}_T(\omega) \, \hat{\underline{\alpha}}_T(\omega)^\dagger \; ,$$

with

$$\hat{\underline{\alpha}}_T(\omega) \equiv \int_{-T/2}^{+T/2} \underline{\alpha}(u) \, e^{-j\omega u} \, du \; .$$

It is important to notice that $\underline{S}$ is Hermitian and positive-definite whenever stationarity allows us to define an $\underline{S}$ or a $\underline{\phi}$.[9]

The convolution (or Faltung) theorem of Fourier analysis connects $\underline{S}$ and $\underline{\phi}(-t)$ and results in

$$\underline{S}(\omega) = \hat{\underline{\phi}}(\omega) = 2 \int_{-\infty}^{+\infty} \underline{\phi}(+t) \, e^{+j\omega t} \, dt \; . \tag{7b}$$

For the $\underline{\phi}$ of Eq. (7a) we rewrite this as

$$\underline{S}(\omega) = \hat{\underline{\phi}}_-(\omega) + \hat{\underline{\phi}}_-(\omega)^\dagger \; ,$$

with

$$\hat{\underline{\phi}}_-(\omega) \equiv 2 \int_0^\infty e^{-\underline{M}t} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \, e^{-j\omega t} \, dt \; . \tag{7c}$$

After partial integration we find

$$\hat{\underline{\phi}}_-(\omega) = \frac{2}{j\omega} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle - \frac{1}{j\omega} \underline{M} \, \hat{\underline{\phi}}_-(\omega) \; .$$

Solving for $\hat{\underline{\phi}}_-(\omega)$ we get the general expression for all spectra:

$$\underline{S}(\omega) = 2(\underline{M} + j\omega \underline{I})^{-1} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle + 2 \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \left[(\underline{M} + j\omega \underline{I})^{-1} \right]^\dagger \; . \tag{8}$$

The properties of the spectra now are completely determined by the properties of $\underline{M}$ and $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$.

Time Reversibility

We defined time reversibility in Sec. I as $\underline{\phi}(t) = \underline{\phi}(-t)$. Hence $\underline{\phi}^T = \underline{\phi}$. From Eq. (7b) we see that $\underline{S}$ is real now. Also $\mathrm{Re}\hat{\underline{\phi}}_- = \mathrm{Re}\hat{\underline{\phi}}_-^\dagger$. Therefore, [see Eq. (7c)] the real parts of the two terms in the right-hand side of Eq. (8) are equal. The spectra now become

$$\underline{S}(\omega) = 2\underline{S}_r(\omega) \; , \tag{9a}$$

when "time reversibility" applies with

$$\begin{aligned} \underline{S}_r(\omega) &\equiv 2\mathrm{Re}\big((\underline{M} + j\omega \underline{I})^{-1} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \big) \\ &= 2(\underline{M}^2 + \omega^2 \underline{I})^{-1} \, \underline{M} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \; . \end{aligned} \tag{9b}$$

By $\mathrm{Re}\underline{A}$, for an arbitrary complex matrix $\underline{A}$, we mean the matrix with elements $\mathrm{Re}A_{ij}$. Using the nonequilibrium values of $\underline{M}$ and $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle$, the matrix $\underline{S}_r(\omega)$ may just as well be defined for a nonequilibrium stationary state. This will be done in Sec. V. However, then $\underline{S} = 2\underline{S}_r$ obviously is no longer valid. Applying Eq. (5), we decompose $\underline{S}_r$ in normal modes:

$$\underline{S}_r(\omega) = 2\underline{c}^{-1} \underline{N}(\omega) \underline{c} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \; ,$$

with

$$N_{ij} \equiv \delta_{ij} \left[\lambda_j / (\lambda_j^2 + \omega^2) \right] \; . \tag{10}$$

Since $\underline{S}$ is Hermitian it is symmetric now that it is real. Applied to Eq. (9) this gives, after some rearranging,

$$\underline{M} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle = \langle \underline{\alpha}\,\underline{\alpha}^T \rangle \underline{M}^T \; , \tag{11}$$

necessary and sufficient for time reversal. Substituting $\omega = 0$ in Eq. (9) shows this condition to be necessary. We will now prove that it is sufficient. Put $\underline{L} \equiv \underline{M} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$, then $\underline{L} = \underline{L}^T$ and $\underline{M} = \underline{L} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{-1}$. From this we see that $\underline{M}^n \langle \underline{\alpha}\,\underline{\alpha}^T \rangle$ is symmetric for all $n \geq 0$. Therefore, all coefficients in the series definition of $\underline{\phi}$ in Eq. (7) are symmetric, QED.

In Eq. (7a), we saw that $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{1/2}$ is symmetric and positive-definite. Hence, we may define $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{1/2}$. (It is always possible here to write $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{1/2} = \underline{Q}^T \underline{D}^{1/2} \underline{Q}$, $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle = \underline{Q}^T \underline{D}\,\underline{Q}$, where $\underline{D}$ is diagonal with positive elements and where $\underline{Q}$ is orthogonal.) $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{-1/2}$ is positive-definite and symmetric. We prove that the matrix of eigenvectors $\underline{c}^{-1}$ defined in Eq. (5) may be written as

$$\underline{c}^{-1} = \langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{1/2} \underline{O}_r \; , \tag{12}$$

where $\underline{O}_r$ is orthogonal and diagonalizes $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{-1/2} \underline{M} \times \langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{1/2}$ in the case of time reversibility.

Proof. We have $\langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{-1/2} \underline{M} \langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{1/2} = \langle \underline{\alpha}\,\underline{\alpha}^T \rangle^{-1/2}$

$\times \underline{L}\langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{-1/2}$. The latter is symmetric because $\underline{L}$ was symmetric. Hence, it can be diagonalized by a particular orthogonal $\underline{O}_r$. Comparison of the left-hand side after that with Eq. (5) gives Eq. (12), QED.

The eigenvectors and eigenvalues of $\underline{M}$ are real now as we see from Eqs. (5) and (12). [As mentioned before $\mathrm{Re}\lambda_i > 0$ follows from stationarity; see result (20), etc.] Equation (12) considerably simplifies the expression for the time-reversible spectra. Using Eq. (12), we have $\underline{c}\langle \underline{\alpha}\, \underline{\alpha}^T \rangle = \underline{O}_r^T \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2} = (\underline{c}^{-1})^T$. Substituting in Eqs. (9) and (10) we find

$$\underline{S}(\omega) = 2\underline{S}_r(\omega) = 4\underline{c}^{-1}\underline{N}(\omega)(\underline{c}^{-1})^T \; . \tag{13}$$

In this form it is clear that $\underline{S}$ is symmetric and positive-definite. We compute the autocorrelation spectrum for the ith variable itself

$$S(\omega)_{ii} = 2S_r(\omega)_{ii} = 4\textstyle\sum_j (\underline{c}^{-1})_{ij} N_{jj} (\underline{c}^{-1})^T_{ji}$$

$$= 4\textstyle\sum_j (\underline{c}^{-1})^2_{ij} N_{jj}(\omega) \; . \tag{14}$$

This is a "positive" combination of the normal modes which are monotonic functions of ω [see Eq. (10)]. Therefore, we already see that the spectra of the $\alpha_i(t)$ are monotonic functions of ω when time reversibility applies. One easily proves that all linear combinations of the $\alpha_i(t)$ have this property Also it follows directly [see result (23)] from the theory in Sec. V.

This refutes the explanations given for some maxima found experimentally in equilibrium.[10] An equation similar to (14) has been derived earlier by van Kampen,[2] using the master equation and "detailed balance." It has been assumed however by several authors[10,5] that the conditions he used were not applicable to the system considered here.

III. INEQUALITIES FOLLOWING FROM STATIONARITY

We want to find the cross-correlation functions and spectra for the following arbitrary real-linear combinations of the $\alpha_i(t)$, $y(t) \equiv (\underline{q}, \underline{\alpha}(t)) = \underline{q}^T \underline{\alpha}(t)$ and $z(t) \equiv (\underline{\alpha}(t), \underline{p})$. Their time-displaced cross-correlation function is $\phi_{yz}(t) \equiv \langle y(0) z(t) \rangle \equiv \langle \underline{q}^T \underline{\alpha}(0)\, \underline{\alpha}(t)^T \underline{p} \rangle = \underline{q}^T \underline{\phi}(t) \underline{p} = (\underline{q}, \underline{\phi}(t)\underline{p})$. After Fourier transforming we find their "cross spectrum" $S_{yz}(\omega) = 2\int_{-\infty}^{\infty} (\underline{q}, \underline{\phi}(t)\underline{p}) \times e^{j\omega t}\, dt = (\underline{q}, \underline{S}(\omega)\underline{p})$. Note that in general this is a complex number. Directly from stationarity we prove

$$(\underline{\phi}(t)\underline{p}, \underline{q})^2 \leq (\underline{\phi}(0)\underline{p}, \underline{p})\, (\underline{\phi}(0)\underline{q}, \underline{q}) \; . \tag{15}$$

This gives $|(\underline{\phi}(t)\underline{p}, \underline{p})| \leq (\underline{\phi}(0)\underline{p}, \underline{p})$ but not $|(\underline{\phi}(t)\underline{p}, \underline{q})| \leq |(\underline{\phi}(0)\underline{p}, \underline{q})|$.

Proof. Take $x(u) \equiv z(u+t)$ in the definitions above. x, z, and y are functions of the time through the variable $\underline{\alpha}(t)$, which itself is a stochastic variable in $\underline{\alpha}(0)$. Because of stationarity the same distribution $P(\underline{\alpha}_0)$ applies to all. One has $\mathrm{covar}^2(x;y) \leq \mathrm{var}(x)\, \mathrm{var}(y)$, i.e., the Schwartz inequality applied to a new scalar product $\{x, y\} \equiv \int\int \cdots \int x(\underline{\alpha}_0) y(\underline{\alpha}_0) P(\underline{\alpha}_0)\, d\underline{\alpha}_0$. Here it gives $\langle yx \rangle \leq \langle x^2 \rangle \langle y^2 \rangle$. From stationarity one also sees $\langle yx \rangle \equiv \langle y(0) x(0) \rangle = \langle y(0) z(t) \rangle$ and $\langle x^2 \rangle = \langle z^2 \rangle$. Substitution yields $\langle y(0) z(t) \rangle^2 \leq \langle y^2 \rangle \langle z^2 \rangle$. Using the definitions above Eq. (15), we find Eq. (15), QED. Applying this to our $\underline{\phi}(t)$ in Eq. (7) we find for real vectors that

$\underline{M}\langle \underline{\alpha}\, \underline{\alpha}^T \rangle$ positive-definite is necessary and sufficient for inequality (15) to hold. (16)

Proof. Necessity: We substitute the $\underline{\phi}(t)$ in $(\underline{p}, \underline{\phi}(t)^T \underline{q})^2$, take $\underline{q} = \underline{p}$ and expand for small $t (\geq 0)$:

$$|(\underline{p}, \underline{\phi}^T \underline{p})| \approx |(\underline{p}, \langle \underline{\alpha}\, \underline{\alpha}^T \rangle \underline{p}) - t(\underline{p}, \underline{M}\langle \underline{\alpha}\, \underline{\alpha}^T \rangle \underline{p})|$$

$$\leq (\langle \underline{\alpha}\, \underline{\alpha}^T \rangle \underline{p}, \underline{p})\,? \; ;$$

certainly not if not $\underline{M}\langle \underline{\alpha}\, \underline{\alpha}^T \rangle$ positive-definite.[9] Sufficiency: we substitute our $\underline{\phi}(t)$ in Eq. (15) and rearrange it for $t \geq 0$ to read

$$(\langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{-1/2} \underline{r}, e^{-\underline{M}t} \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2} \underline{s})^2 \leq (\underline{r}, \underline{r})(\underline{s}, \underline{s})\,? \, ,$$

with

$$\underline{r} \equiv \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2} \underline{p}, \qquad \underline{s} = \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2} \underline{q}$$

because $\langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2}$ was symmetric and positive-definite. We further rewrite it as $(\underline{r}, e^{-\underline{K}t} \underline{s})^2 \leq (\underline{r}, \underline{r}) \times (\underline{s}, \underline{s})?$, with $\underline{K} \equiv \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{-1/2} \underline{M} \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2}$. Schwartz's inequality show that the left-hand side is $\leq (\underline{r}, \underline{r}) \times (e^{-\underline{K}t} \underline{s}, e^{-\underline{K}t} \underline{s})$. The inequality then is certainly true if we can prove

$$(\underline{s}, \underline{s}) \geq (e^{-\underline{K}t} \underline{s}, e^{-\underline{K}t} \underline{s}) \equiv g(t) \; .$$

If $\underline{M}^n \langle \underline{\alpha}\, \underline{\alpha}^T \rangle$ is positive-definite, then $\underline{K}^n$ is positive-definite and vice versa, as

$$(\underline{K}^n \underline{r}, \underline{r}) = (\underline{M}^n \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{1/2} \underline{r}, \; \langle \underline{\alpha}\, \underline{\alpha}^T \rangle^{-1/2} \underline{r})$$

$$= (\underline{M}^n \langle \underline{\alpha}\, \underline{\alpha}^T \rangle \underline{p}, \underline{p}) \; .$$

The case with $n = 1$ is sufficient to prove $g(t) \leq (\underline{s}, \underline{s})$. We see that $\dot{g}(t) = -2\, (\underline{K} e^{-\underline{K}t} \underline{s}, e^{-\underline{K}t} \underline{s}) < 0$ for $\underline{s} \neq \underline{0}$, because $\underline{K}$ positive-definite and $\det \underline{K} = \det \underline{M} \neq 0$.[9] Then $g(t)$ is monotonically decreasing, $g(0) = (\underline{s}, \underline{s})$ and $g(t) > 0$. Hence $g(t) \leq (\underline{s}, \underline{s})$, QED. For negative t one uses $\underline{\phi}(-t) = \underline{\phi}(t)^T$, QED.

We could generally derive that the existence of an $\underline{S}(\omega)$ is necessary and sufficient for inequality (15). Here we only prove it for our particular $\underline{\phi}(t)$, through result (16):

$\underline{M}\langle \underline{\alpha}\, \underline{\alpha}^T \rangle$ positive-definite on real vectors is necessary and sufficient for $\underline{S}(\omega)$ positive-definite under the complex scalar product. (17a)

Proof. Before and in Eq. (7c) we found $\underline{S}(\omega) = \hat{\underline{\phi}}_-(\omega) + \hat{\underline{\phi}}_-(\omega)^\dagger$ and $[\underline{S}\underline{f}, \underline{f}] > 0$ for $\underline{f} \neq \underline{0}$. Hence we have[9]

$$2\,\mathrm{Re}[\hat{\underline{\phi}}_-\underline{f}, \underline{f}] > 0,$$

i.e.,

$$2\,\mathrm{Re}[(\underline{M} + j\omega\underline{I})^{-1}\langle\underline{\alpha}\,\underline{\alpha}^T\rangle\underline{f}, \underline{f}] > 0 .$$

We now need

$\underline{A}^{-1}\underline{H}$ positive-definite is equivalent to $\underline{A}\underline{H}$ positive-definite when $\underline{H}$ is Hermitian and $\underline{A}$ an arbitrary matrix. (17b)

This can be seen from

$$[\underline{A}^{-1}\underline{H}\underline{b}, \underline{b}] = [\underline{h}, \underline{H}^{-1}\underline{A}\underline{h}] = [\underline{H}^{-1}\underline{h}, \underline{A}\underline{h}] = [\underline{d}, \underline{A}\underline{H}\underline{d}] ,$$

with $\underline{h} \equiv \underline{A}^{-1}\underline{H}\underline{b}$ and $\underline{d} \equiv \underline{H}^{-1}\underline{h}$. In our case then we have, equivalently,

$$\begin{aligned}\mathrm{Re}[(\underline{M} + j\omega\underline{I})\langle\underline{\alpha\alpha}^T\rangle\underline{f}, \underline{f}] &= \mathrm{Re}\{[\underline{M}\langle\underline{\alpha\alpha}^T\rangle\underline{f}, \underline{f}] - j\omega[\langle\underline{\alpha\alpha}^T\rangle\underline{f}, \underline{f}]\} \\ &= \mathrm{Re}[\underline{M}\langle\underline{\alpha\alpha}^T\rangle\underline{f}, \underline{f}] > 0 .\end{aligned}$$

One easily checks that this is so, if and only if, $\underline{M}\langle\underline{\alpha\alpha}^T\rangle$ is positive-definite on real vectors, QED.

We now change to the variables used in the proof of result (16):

$$\dot{\underline{\beta}} = -\underline{K}\underline{\beta} \;\text{ with }\; \underline{\beta}(t) \equiv \langle\underline{\alpha\alpha}^T\rangle^{-1/2}\underline{\alpha}(t), \qquad (18)$$
$$\underline{K} = \langle\underline{\alpha\alpha}^T\rangle^{-1/2}\underline{M}\langle\underline{\alpha\alpha}^T\rangle^{1/2}, \;\text{ and }\; \langle\underline{\beta\beta}^T\rangle = \underline{I} .$$

$\underline{K}$ has the same eigenvalues λ_i as $\underline{M}$ and is positive-definite as we found in the proof of result (16). The reason that $\underline{M}\langle\underline{\alpha\alpha}^T\rangle$ should be positive-definite is more apparent in $\underline{\beta}$ space. If $\underline{K}$ was not positive-definite there would be a $\underline{\beta}_0$, and a neighborhood of $\underline{\beta}_0$, for which $(\dot{\underline{\beta}}_0, \underline{\beta}_0) = -(\underline{K}\underline{\beta}_0, \underline{\beta}_0) > 0$. All multiples of vectors in this neighborhood have this property. So there is a "cone" in $\underline{\beta}$ space where the conditional average $\underline{\beta}(t)$ always moves away from $\underline{0}$. In $\underline{\beta}$ space the fluctuations are isotropic because $\langle\underline{\beta\beta}^T\rangle = \underline{I}$. Hence, in a first approximation, fluctuations away from the $\underline{\beta}(t)$ orbit are equally probable in all directions as for a "random-walk" process. A random walk all by itself already has a finite probability of "drifting" off to infinity and a smaller one of doing so while staying within a given cone in space, in particular the cone where $(\dot{\underline{\beta}}, \underline{\beta}) > 0$. In this cone the conditional average does not move back to $\underline{0}$. Because of the "drift" property of the random walk this is not consistent with stability of the stationary point $\underline{0}$.

In thermal equilibrium moreover, $\underline{K}$ is symmetric as we can see from the formula under Eq. (12). Therefore $\underline{K}^n = \underline{O}_r\underline{\Lambda}^n\underline{O}_r^T$, with $\underline{O}_r$ defined in Eq. (12), and $\underline{K}^n$ symmetric and positive-definite for all $n \geq 0$, whenever time reversibility applies. Hence $\underline{M}^n\langle\underline{\alpha\alpha}^T\rangle$ is symmetric and positive-definite as we saw in the proofs of results (11) and (16).

Introducing the fluctuations through a Langevin source term $\underline{\xi}(t)$ in the right-hand side of Eq. (3) rather than specifying $\langle\underline{\alpha\alpha}^T\rangle$, one finds (see the Appendix)

$$\underline{M}\langle\underline{\alpha\alpha}^T\rangle + \langle\underline{\alpha\alpha}^T\rangle\underline{M}^T = \tfrac{1}{2}\underline{S}_{\xi}(\omega) = \underline{\Xi} = \underline{B} = 2\underline{D} \approx k(\underline{L} + \underline{L}^T) ,$$

with $\underline{B}$ the matrix of second-order Fokker-Planck moments, $\underline{D}$ the matrix of diffusion constants, and $\underline{L}$ the matrix of "Onsager coefficients" when it exists (see Sec. VI). $\underline{\Xi}\delta(t)$ turns out to be the time-displaced correlation matrix of $\underline{\xi}(t)$. All of them are positive-definite by definition. These relations and $\underline{M}\langle\underline{\alpha\alpha}^T\rangle$ positive-definite thus allow us to define all these transport coefficients. For the semiconductor case the matrix $\langle\underline{\alpha\alpha}^T\rangle$ can now also be derived from the "mass action" laws as there exists an expression for the $\underline{\Xi}$ (see the Appendix) and $\underline{M}$ could be found from Eq. (1b).

IV. RELATION PROCESSES AND DAMPED PERIODIC SOLUTION

From Eqs. (3) and (18) we find the *accelerations* of the conditional averages:

$$\ddot{\underline{\alpha}} = \underline{M}^2\underline{\alpha}, \quad \ddot{\underline{\beta}} = \underline{K}^2\underline{\beta} . \qquad (19)$$

The eigenvalues of $\underline{M}^2$ and $\underline{K}^2$ are $\{\lambda_i^2\}$ and do not necessarily satisfy $\mathrm{Re}\lambda_i^2 > 0$. Moreover, $\underline{K}^2$ might not be positive-definite. A relaxation process is defined here as a process with $\underline{M}^2\langle\underline{\alpha\alpha}^T\rangle$ positive-definite. If $\underline{K}^2$ is not positive definite, there is a cone in $\underline{\beta}$ space with $(\ddot{\underline{\beta}}, \underline{\beta}) < 0$. The conditional average $\underline{\beta}(t)$ has an acceleration component towards $\underline{0}$ there. In this space all velocities $\dot{\underline{\beta}}$ have a component towards $\underline{0}$ and the fluctuation "forces" average out to zero. Accelerations of the conditional averages then come from external driving forces. (Decelerations are due to friction or dissipation.) In that case one would rather introduce *one* fluctuation source term (Langevin) into the second- or higher-order equations than *one into each* first-order equation as we do here (see the Appendix). An example of this is the fact that one introduces "noise" into the second-order equation for the electric "LRC" (or harmonic) oscillator so as to preserve the formal relation $i \equiv dq/dt$.[9]

$\underline{K}$ positive-definite and $\underline{K}^2$ positive-definite each impose additional restrictions on the domain of the λ_i in the complex plane as we will see from the following:

$\underline{K}^n$ is positive-definite in the real plane defined by the complex eigenvectors $\underline{e}_i$ and $\underline{e}_i^*$, if and only if $\mathrm{Re}\lambda_j^n/|\mathrm{Im}\lambda_j^n| \gtrless \cot(\psi_0)$; with $n = 0, 1, 2, 3, \cdots,$

$\cos(\psi_0) \equiv (\underline{a}, \underline{b})/|\underline{a}|^2$, $\underline{a} \equiv \underline{e}_j + \underline{e}_j^*$, $\underline{b} \equiv (\underline{e}_j - \underline{e}_j^*)/j$, such that $|\underline{a}| = |\underline{b}|$ and $0 \le \psi_0 < \frac{1}{2}\pi$. (20)

Proof. $\underline{e}_i$ is an eigenvector of $\underline{K}$ and $\underline{K}^n$. Hence $\gamma\underline{e}_i$ and $\gamma^*\underline{e}_i^*$, with γ arbitrary-complex, are also eigenvectors. We choose γ such that $|\underline{a}| = |\underline{b}|$ and $\underline{K}^n\underline{e}_i = (R + jJ)\underline{e}_i$ with $J > 0$. Then $\underline{K}^n\underline{a} = R\underline{a} - J\underline{b}$ and $\underline{K}^n\underline{b} = J\underline{a} + R\underline{b}$. We want $(\underline{K}^n(f\underline{a} + g\underline{b}), f\underline{a} + g\underline{b}) > 0$ for all f and $g \ne 0$. Working out the quadratic equation in f and g we find the conditions

$$R^2/J^2 \ge (\underline{a}, \underline{b})^2/(|\underline{a}|^4 - (\underline{a}, \underline{b})^2), \quad R > 0, \quad \text{QED} .$$

Writing $\lambda_i = |\lambda_i| e^{j\varphi}$ we see that $\underline{K}$ positive-definite restricts all eigenvalues to the sector of the right half-plane with $|\varphi| \le \psi_0 < \frac{1}{2}\pi$ as the other real λ_j's are positive for a positive-definite $\underline{K}$. Hence $\mathrm{Re}\lambda_i > 0$ follows from $\underline{M}\langle\underline{\alpha\alpha^T}\rangle$ positive-definite. A "relaxation" process, i.e., $\underline{K}^2$ positive-definite restricts the same eigenvalues λ_i to a sector with $|\varphi| \le \frac{1}{2}\psi_0 < \frac{1}{4}\pi$ guaranteeing $R_i/|J_i| > 1$. In the next paragraph the spectra are proven to be monotonic if $\underline{K}^3$ is positive-definite. It will result in $|\varphi| \le \frac{1}{3}\psi_0 < \frac{1}{6}\pi$ guaranteeing $R_i/|J_i| > \sqrt{3}$ for this type of process. This class of processes apparently is a subset of the "relaxation" processes here in the plane defined by $\underline{e}_i$ and $\underline{e}_i^*$. This may be incorporated in the general theorem:

If $\underline{M}^3\langle\underline{\alpha\alpha^T}\rangle$ positive-definite,

then $\underline{M}^2\langle\underline{\alpha\alpha^T}\rangle$ positive-definite. (21)

Proof. We prove that if $\underline{K}^2$ is not positive-definite then $\underline{K}^3$ is not positive-definite. If a matrix $\underline{A}$ is not positive-definite, then $(\underline{A} + \underline{A}^T)$ has an eigenvector with a negative eigenvalue as

$$(\underline{A}\underline{q}, \underline{q}) = \tfrac{1}{2}((\underline{A} + \underline{A}^T)\underline{q}, \underline{q}) = \tfrac{1}{2}(\underline{O}^T\underline{\Xi}\underline{O}\underline{q}, \underline{q}) = \tfrac{1}{2}(\underline{\Xi}\underline{r}, \underline{r}) = \tfrac{1}{2}\sum \xi_i r_i^2 ,$$

with $\underline{O}$ orthogonal, $\Xi_{ij} = \delta_{ij}\xi_i$, and $\underline{r} = \underline{O}\underline{q}$. (Numerically this often is a fast method to determine whether a matrix is positive-definite.) Then under our assumption there exists a $\underline{p}$ with $(\underline{K}^2 + \underline{K}^{T2})\underline{p} = -\mu\underline{p}$ and $\mu > 0$. Applying $\underline{K}$ once again we find $(\underline{K}^3\underline{p}, \underline{p}) + (\underline{K}^T\underline{r}, \underline{r}) = -\mu(\underline{K}\underline{p}, \underline{p}) < 0$ with $\underline{r} = \underline{K}^T\underline{p}$. This is only possible when $(\underline{K}^3\underline{p}, \underline{p}) < 0$, QED.

These accelerations in $\underline{\beta}$ space when $\underline{K}^2$ is not positive-definite will result in (quasi-) periodic solutions for a certain linear combination of the $\beta_i(t)$ as discussed in Sec. I. This combination has a negative part in its time-displaced correlation function and a local maximum in its spectrum, as we will see.

V. CRITERION FOR LOCAL MAXIMA IN THE NONEQUILIBRIUM SPECTRA

We limit ourselves to maxima in the nonequilibrium autocorrelation spectrum $S_{zz}(\omega)$ of any real linear combination $z(t) = (\underline{p}, \underline{\alpha}(t))$. Using the results above inequality (15) we find

$$S_{zz}(\omega) = (\underline{p}, \underline{S}(\omega)\underline{p}) = (\underline{p}, \mathrm{Re}(\underline{S})\underline{p}) + j(\underline{p}, \mathrm{Im}(\underline{S})\underline{p}) .$$

We prove that $\mathrm{Im}(\underline{S})$ is an antisymmetric real matrix. $\underline{S}$ was Hermitian by definition. Hence $\underline{S} = \underline{S}^\dagger = (\underline{S}^T)^*$ and $\mathrm{Im}\underline{S} = (1/2j)(\underline{S} - \underline{S}^*) = (1/2j)(\underline{S} - \underline{S}^T)$. Therefore, we have $[\mathrm{Im}\underline{S}]^T = -\mathrm{Im}\underline{S}$, QED.

As a result we have $(\underline{p}, \mathrm{Im}(\underline{S})\underline{p}) = 0$ and the autocorrelation spectrum $S_{zz}(\omega) = (\underline{p}, \mathrm{Re}[\underline{S}(\omega)]\underline{p})$ is real as it should be by definition.

For our general nonequilibrium $\underline{S}$, we write the expression in Eq. (8), $\mathrm{Re}[\underline{S}(\omega)] = \underline{S}_r(\omega) + \underline{S}_r(\omega)^T$, with $\underline{S}_r$ defined in Eq. (9), using however the nonequilibrium values of $\underline{M}$ and $\langle\underline{\alpha\alpha^T}\rangle$. We have $(\underline{p}, (\underline{S}_r + \underline{S}_r^T)\underline{p}) = 2(\underline{p}, \underline{S}_r\underline{p})$ and thus

$$S_{zz}(\omega) = 2(\underline{S}_r(\omega)\underline{p}, \underline{p}) \text{ for } z = (\underline{p}, \underline{\alpha}(t)) , \tag{22a}$$

with $\underline{S}_r$ defined in Eq. (9). We can use the nonequilibrium $\underline{S}_r$ only to determine the *auto*correlation spectra. We now prove the following:

The variable $z(t) \equiv (\underline{p}, \underline{\alpha}(t))$ generates a local maximum in $S_{zz}(\omega)$ if and only if $(\underline{M}^{-3}\langle\underline{\alpha\alpha^T}\rangle\underline{p}, \underline{p}) < 0$. There is no linear combination of the $\alpha_i(t)$ with a spectral maximum if and only if $\underline{M}^{+3}\langle\underline{\alpha\alpha^T}\rangle$ is positive-definite. (22b)

Proof. Sufficiency: We have $\underline{S}_r = (\underline{M}^2 + \omega^2\underline{I})^{-1} \times \underline{M}\langle\underline{\alpha\alpha^T}\rangle$ [see Eq. (9)], using the nonequilibrium values of $\underline{M}$ and of $\langle\underline{\alpha\alpha^T}\rangle$. Note that $(\underline{M}^2 + \omega^2\underline{I})^{-1}$ is real also. We find

$$\frac{dS_{zz}}{d\omega} = 2(\underline{S}_r'(\omega)\underline{p}, \underline{p}) = -8\omega((\underline{M}^2 + \omega^2\underline{I})^{-2}\underline{M}\langle\underline{\alpha\alpha^T}\rangle\underline{p}, \underline{p}) .$$

We have $S_{zz}'(0) = 0$ because $S_{zz}(\omega)$ is even. Hence, if S_{zz}' would be positive for small $\omega > 0$, there would certainly be a spectral maximum. For small ω we have

$$S_{zz}'(\omega) \approx -8\omega(\underline{M}^{-3}\langle\underline{\alpha\alpha^T}\rangle\underline{p}, \underline{p}) \quad \text{as} \quad \omega \to 0 . \tag{22c}$$

Therefore, a sufficient condition for at least one maximum would be $(\underline{M}^{-3}\langle\underline{\alpha\alpha^T}\rangle\underline{p}, \underline{p}) < 0$. Necessity: $S_{zz}(\omega)$ only has a maximum if $S_{zz}'(\omega)$ is not negative-definite for all $\omega > 0$. This means that there only is a maximum if $(\underline{M}^2 + \omega^2\underline{I})^{-2}\underline{M}\langle\underline{\alpha\alpha^T}\rangle$ is not positive-definite for $\omega > 0$. Result (17b) for a real scalar product and a symmetric $\underline{H}$ shows $\underline{A}\langle\underline{\alpha\alpha^T}\rangle$ positive-definite to be equivalent to $\underline{A}^{-1}\langle\underline{\alpha\alpha^T}\rangle$ positive-definite. Hence we only have a maximum if $\underline{M}^{-1}(\underline{M}^2 + \omega^2\underline{I})^2\langle\underline{\alpha\alpha^T}\rangle$ is not positive-definite for all $\omega > 0$. We write this out as

$$\underline{M}^3\langle\underline{\alpha\alpha^T}\rangle + 2\omega^2\underline{M}\langle\underline{\alpha\alpha^T}\rangle + \omega^4\underline{M}^{-1}\langle\underline{\alpha\alpha^T}\rangle .$$

The middle term is positive-definite; see result (16). According to result (17b) the third term is positive-definite also. Therefore, the first term $\underline{M}^3\langle\underline{\alpha\alpha}^T\rangle$ is the decisive term which dominates for small $\omega > 0$. According to result (17b) again, there *only* is a maximum if $\underline{M}^{-3}\langle\underline{\alpha\alpha}^T\rangle$ is not positive-definite, QED.

From the derivation it is apparent that the second derivative at $\omega = 0$, i.e., $\underline{S}''(0) = -8\underline{M}^{-3}\langle\underline{\alpha\alpha}^T\rangle$, completely determines the presence or absence of maxima at any ω. A negative ith diagonal element in $\underline{M}^{-3}\langle\underline{\alpha\alpha}^T\rangle$ apparently means a maximum in $S_{ii}(\omega)$, the spectrum of $\alpha_i(t)$, due to the coupling with the other $\alpha_j(t)$'s. Maxima are always the result of coupling effects because for a single variable process we have $\underline{M}^3\langle\underline{\alpha\alpha}^T\rangle = \lambda^3\langle\alpha^2\rangle > 0$. From result (21) we see that every process which is not a relaxation process, as defined in Sec. IV, has a spectral maximum for some linear combination of its variables.

When *time reversibility* applies we found $\underline{K} = \underline{K}^T$ and $\underline{K}^n$ positive-definite for all $n \geq 0$. In that case $\underline{M}^2\langle\underline{\alpha\alpha}^T\rangle$ and $\underline{M}^3\langle\underline{\alpha\alpha}^T\rangle$ were shown to be positive-definite. Hence, equilibrium fluctuations are a relaxation process and

> there is no linear combination of the $\alpha_i(t)$ with a spectral maximum in the case of thermodynamic equilibrium. (23)

From $S'_{ii}(0) = 0$ and result (22c) it is obvious that

> if a linear combination of the $\alpha_j(t)$ has a spectral maximum, the slope of the spectrum is positive from $\omega = 0+$ till the first maximum. (24)

The experimental nonequilibrium maximum in the Cd-Se photoconductor of Ref. 8 is found at ≈ 0.005 Hz. Most of the spectra for Au-Si-4 in Ref. 10 with maxima certainly do not have positive slopes for small ω. This may be attributed to additional "$1/f$ noise" or a maximum at even lower ω.

We show that $\phi_{ii}(t_0) < 0$ for a certain t_0, is a necessary condition for the existence of a maximum in $S_{ii}(\omega)$. The necessary and sufficient condition is

$$\int_0^\infty dt(\underline{\phi}(t)t^2\underline{p}, \underline{p}) < 0$$

as we may see from the expression for $(\underline{S}''(0)\underline{p}, \underline{p})$ found by two partial integrations of Eq. (7b).

VI. RELATION WITH EXCESS-ENTROPY PRODUCTION

One expands the linear laws [(see Ref. 11, Chap. 5] $\dot{\underline{a}} = \underline{L}(\partial S/\partial \underline{a})$, with $S(\underline{a})$ the entropy of the system, for small deviations from the entropy maximum:

$$\dot{\underline{\alpha}} = -\underline{L}\,\underline{s}\,\underline{\alpha} \quad \text{with} \quad s_{ij} \equiv -\left.\frac{\partial^2 S(\alpha)}{\partial\alpha_i\,\partial\alpha_j}\right|_{\underline{\alpha}=\underline{0}} . \qquad (25)$$

As a result $\underline{s}$ is symmetric and positive-definite. Comparison with Eq. (3) gives

$$\underline{M} = \underline{L}\,\underline{s} . \qquad (26)$$

Inverting $S(\underline{\alpha}) = k \ln P(\underline{\alpha})$ and expanding it one arrives at

$$\langle\underline{\alpha\alpha}^T\rangle = k\underline{s}^{-1} . \qquad (27)$$

Therefore, $\langle\underline{\alpha\alpha}^T\rangle$ is indeed symmetric and positive-definite in equilibrium here and $\underline{L} = \underline{M}\langle\underline{\alpha\alpha}^T\rangle/k$. Thus $\underline{L}$ is positive-definite because of stationarity. Our $\underline{L}$ here is equal to the $\underline{L}$ under Eq. (11), apart from Boltzmann's constant. Hence, in equilibrium Eq. (11) holds and expresses the Onsager relations

$$\underline{L} = \underline{L}^T, \text{ when time reversibility holds.} \qquad (28)$$

The change in entropy during a deviation from $\underline{\alpha} = \underline{0}$, i.e., the excess entropy, here is $\nabla S \equiv S(\underline{\alpha}) - S(\underline{0}) \approx -\frac{1}{2}(\underline{s}\,\underline{\alpha}, \underline{\alpha})$ which is $\propto -\frac{1}{2}k(\langle\underline{\alpha\alpha}^T\rangle^{-1}\underline{\alpha}, \underline{\alpha})$. We then find for the excess-entropy production $\mathcal{P} \equiv d\Delta S/dt$ using Eqs. (16) and (18):

$$k^{-1}\mathcal{P} = (\langle\underline{\alpha\alpha}^T\rangle^{-1}\underline{\alpha}, \underline{M}\,\underline{\alpha}) = (\underline{\beta}, \underline{K}\underline{\beta}) \geq 0. \qquad (29)$$

The minimum excess-entropy production is 0 as a result of the entropy maximum and stationarity. The $\mathcal{P}$ serves as a Liapunov function of stability theory.[6] It is also equal to Onsager's dissipation function because $-k(\langle\underline{\alpha\alpha}^T\rangle^{-1}\underline{\alpha}, \dot{\underline{\alpha}}) = (\underline{L}^{-1}\dot{\underline{\alpha}}, \dot{\underline{\alpha}})$.[12] Its time derivative is

$$\frac{1}{k}\frac{d\mathcal{P}}{dt} = -(\underline{K}\underline{\beta}, \underline{K}\underline{\beta}) - (\underline{K}^2\underline{\beta}, \underline{\beta}) . \qquad (30)$$

If time reversibility applies we have $\underline{K}^2$ positive-definite and $d\mathcal{P}/dt < 0$ at all moments during the time evolution of $\underline{\beta}(t)$ or $\underline{\alpha}(t)$. Hence $\mathcal{P}(t)$ decreases monotonically to its equilibrium value 0 then. Its second derivative is

$$\frac{1}{k}\frac{d^2\mathcal{P}}{dt^2} = +3(\underline{K}^2\underline{\beta}, \underline{K}\underline{\beta}) + (\underline{K}^3\underline{\beta}, \underline{\beta}) . \qquad (31)$$

The first term on the right-hand side is always positive. If time reversibility applies $\underline{K}^3$ is positive-definite also and $\mathcal{P}(t)$ is a concave-monotonically decreasing function during the time evolution of $\underline{\beta}(t)$. Hence $(\underline{K}\underline{p}, \underline{p})$ has potential-like properties here.

For a nonequilibrium stationary state one often still finds the two proportionalities expressed in Eqs. (25) and (27).[1,3,13] One may easily define a nonequilibrium entropy from $\langle\underline{\alpha}\,\underline{\alpha}^T\rangle$ in the neighborhood of the stationary state using $P(\alpha) \propto \exp[-\frac{1}{2}(\langle\underline{\alpha}\,\underline{\alpha}^T\rangle^{-1}\underline{\alpha}, \underline{\alpha})]$. The problem however is to find a general nonequilibrium entropy from which one could get the stationary state $\underline{a}_0$ and the same $P(\underline{\alpha})$.

For our fluctuations here we never used higher moments than the second one. Replacing the $P(\underline{\alpha})$

by the above-mentioned Gaussian distribution has no effect on any previous results.[12] It makes Eq. (27) a tautology and allows us to define an $\underline{L}$ for a nonequilibrium stationary state, through Eqs. (3) and (26), as suggested directly from Eq. (25) by Ref. 1.

Whatever name one gives to $(\underline{K}\underline{\beta}, \underline{\beta})$ outside equilibrium it still retains many of these potential-like properties. For our relaxation processes $\mathcal{P}(t)$ still is a monotonically decreasing function as we see from Eq. (30). When $\underline{K}^2$ is *not* positive-definite $\mathcal{P}(t)$ need no longer be monotonic. At the end of Secs. I and IV we saw that "$\underline{K}^2$ not positive-definite" resulted in damped periodic solutions. Some of those might indeed give temporary increases in $\mathcal{P}(t)$ if $(\underline{K}\underline{\beta}, \underline{\beta})$ were a potential. One might even "explain" the maxima in the spectra by noticing from Eq. (31) that, for example, $d\mathcal{P}/dt$ may have a local maximum, or come close to that, if $\underline{K}^3$ is not positive-definite. This would disturb the monotonic rate of change of $\mathcal{P}$ and result in an overrepresentation of some frequencies in the Fourier decomposition of $\underline{\beta}(t)$ and $\underline{\alpha}(t)$ as compared to the case that $\underline{K}^3$ *is* positive-definite.

VII. THE SEMICONDUCTOR EXAMPLE

Charge neutrality gives $\alpha_n = -\sum_{i=1}^{n-1} \alpha_i$ hence $M_{ij} = \tilde{M}_{ij} - \tilde{M}_{in}$ and $\sum_{i=1}^{n} \tilde{M}_{ij} = 0$, for the $\underline{\tilde{M}}$ and $\underline{M}$ defined in Eqs. (2) and (3). $\underline{\tilde{M}}$ has the same eigenvalues as $\underline{M}$ plus $\lambda_n = 0$. If the transition current p_{ij} is an increasing function of a_i, a decreasing function of a_j and of no other a_k, as for the "mass-action" laws, one easily checks from Eqs. (1b) (first part) and (2) that

$$\text{sign}\tilde{M}_{ij} = \text{sign}\tilde{M}_{ji} < 0 \quad (i \neq j)$$

and

$$\tilde{M}_{ii} > 0 \ .$$

Therefore $\underline{\tilde{M}}$ is "sign symmetric" and

$$\underline{A} \equiv -\underline{\tilde{M}}^T + \max_i (\tilde{M}_{ii})\, \underline{I}$$

is non-negative, i.e., all $A_{ij} \geq 0$. From the theory of positive and non-negative matrices[14] and $\sum_{i=1}^{n} \tilde{M}_{ij} = 0$ we find that all λ_i lie within a circle with radius equal to $\max\tilde{M}_{ii}$ and center at $\max\tilde{M}_{ii}$; hence $\text{Re}\lambda_i > 0$. Wessels and van Vliet[5] proved this differently. Carrying one of their arguments one step further one finds

$$(\underline{\tilde{M}}^2)_{ii} = \sum_{j\neq i}^{n} (\tilde{M}_{ij}\tilde{M}_{ji}) + \tilde{M}_{ii}^2 \geq \tilde{M}_{ii}^2$$

or

$$\text{Tr}\underline{\tilde{M}}^2 \geq \sum \tilde{M}_{ii}^2 \geq n^{-1}[\text{Tr}\underline{\tilde{M}}]^2 \quad ,$$

with Schwartz's inequality. Using $\text{Tr}\underline{\tilde{M}}^2 = \sum\lambda_i^2$ and $\text{Tr}\underline{\tilde{M}} = \sum\lambda_i$ this would be obvious for any matrix with real eigenvalues. It now also applies to the complex eigenvalues of a sign symmetric $\underline{\tilde{M}}$ and its reduced version $\underline{M}$. Therefore, one has for the $\underline{M}$ of the semiconductor case:

$$\sum_{i=1}^{n-1} \lambda_i^2 \geq \frac{1}{n}\left(\sum_{i=1}^{n-1} \lambda_i\right)^2 , \quad \dim\underline{M} = n-1. \qquad (32)$$

Applied to the three-level semiconductor this gives $2(R^2 - J^2) \geq \frac{1}{3}(2R)^2$ or $|R/J| \geq \sqrt{3}$. From above Eq. (21), we see that the periodic orbits, when the λ's are complex, certainly do not *guarantee* maxima in any spectra because of the damping, also expressed by Eq. (32).

Realistic nonequilibrium examples have a separation between the three levels which is large compared to kT because the largest separation is of the order of the optical energy $h\nu$. With level 2 in between 3 and 1 and pumping from 3 to 1, the currents due to γ_{31}, γ_{21}, and γ_{32} then are negligible. It further restricts the $\underline{M}$, and shotnoise $\underline{\Xi}$ (see the Appendix). Either $\gamma_{12} < \gamma_{13} < \gamma_{23}$ or $\gamma_{23} < \gamma_{13} < \gamma_{12}$ is necessary for λ_i complex. Numerically we have only found $R/|J| \gtrsim 4.8$ in this case.

VIII. SUMMARY

We assumed the *regression* of our parameters α_i from fluctuations $\underline{\alpha}(0)$ back to the stationary state $\underline{\alpha} = \underline{0}$ to be governed by $\dot{\underline{\alpha}} = -\underline{M}\,\underline{\alpha}$. The $\underline{\alpha}(t)$ here stand for a conditional ensemble average of the actual values of the parameters at a time t after a given initial $\underline{\alpha}_0$ at $t = 0$. Usually, the process is believed to be stable when $\underline{M}$ has positive eigenvalues λ, or $\text{Re}\lambda > 0$. This is indeed so for the solution $\underline{\alpha}(t) = e^{-\underline{M}t}\,\underline{\alpha}_0$ of the differential equation. However the stochastic properties of the process, i.e., the probability distribution $P(\underline{\alpha}_0, t)$, determine the *existence* of such conditional averages and the overall stochastic stability of the process as a result. In Sec. III, we showed that the required stationarity of $P(\underline{\alpha}_0, t)$, i.e., $P(\underline{\alpha}_0, t+t_1) = P(\underline{\alpha}_0, t)$ for all t and t_1, results in the requirement that the matrix $\underline{M}\langle\underline{\alpha}\underline{\alpha}^T\rangle$ should be positive-definite. Therefore, not every combination of $\underline{M}$, with $\text{Re}\lambda > 0$, and a positive-definite covariance matrix $\langle\underline{\alpha}\underline{\alpha}^T\rangle$ is allowed in a model of stationary process.

In Sec. II we saw that $\underline{M}^n\langle\underline{\alpha}\underline{\alpha}^T\rangle$ for a thermal equilibrium process is positive-definite for all $n \geq 0$. In the Appendix we show that $\underline{M}\langle\underline{\alpha}\underline{\alpha}^T\rangle$ is positive-definite for a *nonequilibrium* process when the probability distribution of the fluctuations in the $\dot{\alpha}_i$ consists of sums of Poisson distributions, i.e., shotnoise in the transition currents.

The rest of the paper is concerned with the power spectra of the fluctuations, the "spectral noise density" $\underline{S}(\omega)$. In Sec. V necessary and sufficient conditions to find a local maximum in the spectrum of any quasilinear Markov process were derived.

It turns out that the absence of spectral maxima in any linear combination of the α_i depends on positive-definiteness of $\underline{M}^3\langle\underline{\alpha}\underline{\alpha}^T\rangle$. Therefore, the fluctuation spectra of an equilibrium process are monotonic functions of the frequency ω (Secs. II and V). This implies that experimental spectra exhibiting these maxima may not be explained by means of a quasilinear Markov process.

A process with $\underline{M}^2\langle\underline{\alpha}\underline{\alpha}^T\rangle$ positive-definite is defined as a "relaxation" process in Sec. IV, because of the absence of accelerations towards the stationary state $\underline{\alpha}=\underline{0}$, i.e., other than the stochastic ones. Also we prove there that a process with only monotonic spectra, i.e., $\underline{M}^3\langle\underline{\alpha}\underline{\alpha}^T\rangle$ positive-definite, is necessarily a "relaxation" process, i.e., $\underline{M}^2\langle\underline{\alpha}\underline{\alpha}^T\rangle$ positive-definite.

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APPENDIX: LANGEVIN SOURCES; FOKKER-PLANCK MOMENTS

In practice it is often easier to introduce the fluctuations by adding Langevin-source terms;

$$\dot{\underline{\alpha}} = -\underline{M}\,\underline{\alpha}+\underline{\xi}(t) \quad \text{with } \langle\underline{\xi}\rangle = 0. \tag{A1}$$

We take the $(-j\omega t)$-Fourier transform of Eq. (A1) and find $\underline{S}(\omega)$ using its definition[1,8]:

$$\underline{S}(\omega) = (\underline{M}+j\omega\underline{I})^{-1}\,\underline{S}_\xi(\omega)[(\underline{M}+j\omega\underline{I})^{-1}]^\dagger . \tag{A2}$$

Equating this to the $\underline{S}$ found before, in Eq. (8), we get

$$\underline{S}_\xi(\omega) = 2\underline{M}\langle\underline{\alpha}\,\underline{\alpha}^T\rangle + 2\langle\underline{\alpha}\underline{\alpha}^T\rangle\,\underline{M}^T . \tag{A3}$$

Wang and Uehlenbeck[15] already proved the right-hand side to be equal to $4\underline{D}$, the matrix of diffusion constants which is equal to $2\underline{B}$, the matrix of second-order Fokker-Planck moments.[1,3] The relation with $\underline{D}$ may be found here from

$$\underline{M}\langle\underline{\alpha}\underline{\alpha}^T\rangle = \int_{0+}^{\infty}\langle\dot{\underline{\alpha}}(0+)\dot{\underline{\alpha}}(t)^T\rangle dt.$$

We have to use 0+ rather than 0 as the expectation value of $\dot{\underline{\alpha}}(0)\dot{\underline{\alpha}}(0)^T$ does not exist because $\underline{\alpha}(t)$ is nondifferentiable at $t=0$. Our $\underline{S}(\omega)$ in Eq. (8) is the sum of two Cauchy distributions of ω and does not have any moments beyond the first. Therefore,

$$\langle\dot{\underline{\alpha}}(0)\dot{\underline{\alpha}}(0)^T\rangle = \int_{-\infty}^{+\infty}\omega^2\underline{S}(\omega)\,df$$

does not exist $(f=\omega/2\pi)$.

It is obvious from Eq. (A3) that $\underline{S}_\xi$ can only be independent of ω, i.e., white noise sources only. So Eq. (7b) only allows $\underline{\Xi}\,\delta(t)$, with a constant $\underline{\Xi}$, positive-definite and symmetric, as the correlation matrix of the $\xi(t)$. Thus we have $\underline{S}_\xi = 2\,\Xi$. Using Eqs. (26) and (27) we find

$$\underline{\Xi} = \underline{M}\langle\underline{\alpha}\underline{\alpha}^T\rangle + \langle\underline{\alpha}\underline{\alpha}^T\rangle\,\underline{M}^T = \tfrac{1}{2}\underline{S}_\xi = 2\underline{D} = \underline{B} \approx k(\underline{L}+\underline{L}^T), \tag{A4}$$

a form of the so called "Λ theorem." We now find $\langle\underline{\alpha}\underline{\alpha}^T\rangle$ and make the connection with the rest of the paper. Using $\underline{M}$ in its diagonalized form Eq. (5) we rewrite Eq. (A4) and get

$$\langle\underline{\alpha}\underline{\alpha}^T\rangle = \underline{c}^{-1}\,\underline{E}\,\underline{c}^{-1^T} \qquad \text{with } E_{ij} \equiv \frac{1}{\lambda_i+\lambda_j}(\underline{c}\,\underline{\Xi}\,\underline{c}^T)_{ij} . \tag{A5}$$

We have $\underline{E}=\underline{E}^T$ and positive-definite only under the complex scalar product. It also shows that $\langle\underline{\alpha}\underline{\alpha}^T\rangle$ is uniquely determined by a given symmetric positive-definite $\underline{\Xi}$ and $\underline{M}$ with $\mathrm{Re}\lambda_i>0$. That the $\langle\underline{\alpha}\underline{\alpha}^T\rangle$ thus found is positive-definite indeed is more easily seen from[6,3]

$$\langle\underline{\alpha}\underline{\alpha}^T\rangle = \int_0^\infty e^{-\underline{M}t}\,\underline{\Xi}\,e^{-\underline{M}^Tt}\,dt . \tag{A6}$$

Equation (A6) is easily proven by partial integration or by diagonalization. Essential for convergence is $\mathrm{Re}\lambda_i>0$, which is so for the semiconductor model (see Sec. VII).

We notice that $\underline{M}^k\langle\underline{\alpha}\underline{\alpha}^T\rangle$ positive-definite is equivalent to $\underline{\Lambda}^k\,\underline{E}$ positive-definite, which provides the connection with the previous paragraphs.

van Vliet and Blok[16] assuming one-particle transitions per interval dt only, expressed the elements of $\underline{B}$ in terms of the p_{ij}. This assumption (see Ref. 16) is the same as used for obtaining a Poisson distribution. [Here for the "1 sec$\underline{\xi}(t)$" the currents are expressed in "number of electrons per second."] Thus, we obtain "shot noise" in the transition currents as a first approximation. And as a result we have

$$\Xi_{ij} = -p_{ij}-p_{ji} \quad \text{for } i\neq j,$$

(a negative correlation because a current p_{ij} causes an increase of $\dot{\alpha}_j$ and a decrease of $\dot{\alpha}_i$) and

$$\Xi_{ii} = \sum_{j=1}^{n} p_{ij}+p_{ji}.$$

Note that the dimension of $\underline{\Xi}$ is $n-1$. The previous equations allow one also to compute the noise from the mass-action laws.[8] Therefore, this $\underline{\Xi}$ has the properties

$$\underline{\Xi}=\underline{\Xi}^T, \qquad \sum_{j=1}^{n-1}\Xi_{ij} = 2(p_{in}+p_{ni})>0.$$

Using this and again applying the theory of non-negative matrices[14] this time to $[-\underline{\Xi}+\max_i(\Xi_{ii})\underline{I}]$, we find that all eigenvalues of $\underline{\Xi}$ are positive. Our $\underline{\Xi}$ is positive-definite indeed because $\underline{\Xi}=\underline{\Xi}^T$.

Therefore, $\underline{M}\langle\underline{\alpha}\underline{\alpha}^T\rangle$ is positive-definite in this case as required in Sec. III [use first part of the proof of result (21)].

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Binding of Two Closed-Shell Atoms on a Solid Surface*†

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The interaction of two noble-gas atoms on a solid surface is studied with a view to finding conditions under which they form a bound state. Two limiting models for the surface are considered – a flat surface which constrains the atoms to move in two dimensions and imposes no further restriction on their motion, and a surface consisting of a periodic arrangement of potential wells separated by large barriers, to which the tight-binding method is applicable. A curious feature of the result for the binding energy is shown to be a consequence of the fact that the problem is two dimensional.

I. INTRODUCTION

Experimental work by Dash and collaborators[1–3] on He^3 and He^4 adsorbed on a solid surface has opened up interesting questions on phase transitions and the formation of a condensed state in the two-dimensional film of a noble gas. The major forces that operate on such a film adsorbed on a surface are the attraction of the substrate and the mutual interaction of the closed-shell atoms. The attraction of the solid constrains the atoms to move largely in two dimensions parallel to the surface. Any possible phase transition, on the other hand, can come only from the mutual interaction of the atoms themselves. This interaction is modified by properties of the substrate, its geometry for example, which may help or hinder the formation of a condensed state.

The study of the behavior of two inert atoms on a surface may be regarded as a useful preliminary step to an eventual exploration of the many-particle system. Such a study is interesting for two main reasons. First, if two closed-shell atoms form a bound state on a surface, it would strongly suggest the possibility of the film of such atoms having a condensed phase. Second, the information gathered from a study of the two-inert-atom system may be used for computing bulk thermodynamic parameters, as for example in a virial expansion. For the two-inert-atom system, interesting questions relate to the existence of a bound state and the magnitude of the binding energy. In this paper we study the prob-