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Maximum information entropy approach to non-markovian random jump processes with long memory: application to surprisal analysis in molecular dynamics

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Abstract

It is shown that non-markovian random jump processes in continuous time and with discrete state variables can be expressed in terms of a variational principle for the information entropy provided that the constraints describe the correlations among a set of dynamic variables at any moment in the past. The approach encompasses a broad class of stochastic processes ranging from independent processes through markovian and semi-markovian processes to random processes with complete connections. Two different levels of description are introduced: (a) a microscopic one defined in terms of a set of microscopic state variables; and (b) a mesoscopic one which gives the stochastic properties of the dynamic variables in terms of which the constraints are defined. A stochastic description of both levels is given in terms of two different characteristic functionals which completely characterize the fluctuations of micro- and mesovariables. At the mesoscopic level a statistic-thermodynamic description is also possible in terms of a partition functional. The stochastic and thermodynamic descriptions of the mesoscopic level are equivalent and the comparison between these two approaches leads to a generalized fluctuation-dissipation relation. A comparison is performed between the maximum entropy and the master equation approaches to non-markovian processes. A system of generalized age-dependent master equations is derived which provides a description of stochastic processes with long memory. The general approach is applied to the problem of surprisal analysis in molecular dynamics. It is shown that the usual markovian master-equation description is compatible with the information entropy approach provided that the constraints give the evolution of the first two moments of the dynamic variables at any time in the past.

1. Introduction

There is an enormous literature dealing with the application of the principle of the maximum information entropy (MIP) in statistical mechanics. This line of research

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started in 1957 with the seminal papers of Jaynes [1] in which classical and quantum equilibrium statistical mechanics were recovered as a consequence of MIP. The first attempts of applying the MIP to non-equilibrium problems were based on the evaluation of the extremum of the informational entropy subject to the constraints that the average values of the relevant macroscopic variables are known at a given time. The result of this optimization procedure is the local equilibrium statistical ensemble of the Mori [2] type. In 1970 Zubarev and Kalashnikov [3] introduced new types of constraints by assuming that the average values of the dynamic variables are given not only at the current time t but also at any moment in the past. By maximizing the informational entropy with respect to these new constraints they recovered the non-local, non-equilibrium statistical ensemble of McLennan [4] and Zubarev [5]. Alternative formulations of the Zubarev–Kalashnikov approach were given by Schlögl [6] and by Grandy [7]. Further developments of the theory deal with the statistical-mechanical implications of the extremal properties of the information gain [7] (Kullback information [8]), the dual distribution and fluctuations of the Lagrange multipliers [9], the analysis of inversion problems [10], etc. Concerning the applications of the theory, the statistical-mechanical information approach has been applied to a broad class of problems [11] ranging from nuclear and solid state physics and physical chemistry to population geography and ecology. Some of these applications have little or nothing to do with statistical mechanics, even though the mathematical formalism is almost the same as in statistical mechanics. A very active field in which the MIP plays a major role is the surprisal analysis in molecular dynamics [12].

Our interest in MIP is mainly related to the problem of fractal random processes with long memory [13–14]. In this context two important problems arise which have been almost ignored in the literature: (a) given a set of constraints, what are the types of stochastic processes generated by the MIP?; and (b) which constraints should be used in order to generate a stochastic process with long memory?.

To answer these questions we introduce a new set of constraints which are a generalization of the constraints of Zubarev and Kalashnikov [3]. The outline of the paper is as follows. In Section 2 we give a formulation of the problem by using the surprisal analysis in molecular dynamics as an example. In Section 3 the new constraints are introduced and the corresponding extremal problem is solved. Sections 4 and 5 deal with the stochastic and the statistic-thermodynamic descriptions of the resulting random process. In Section 6 the comparison between the stochastic and the statistic-thermodynamic formulations of the theory leads to a general dissipation-fluctuation relation. In Section 7 we come back to the problem of surprisal analysis in molecular dynamics, and in Section 8 an alternative approach to the stochastic processes with long memory is suggested, based on a system of age-dependent master equations. Finally in Section 9 some open problems and possible applications of the new approach are outlined.

2. Formulation of the problem

Let us consider a molecule [12] which can exist in a discrete number of states $v = 1, 2, \ldots, M$. Here M is usually assumed to be a possibly very large, but finite, number. Within the framework of the markovian approximation [12] the probability $P(v,t)$ that at time t the molecule is in the state v obeys the master equation

$$dP(v,t)/dt = \sum_{v'} A_{vv'} P(v',t), \tag{1}$$

where

$$A_{vv'} = W_{v'v}(1 - \delta_{vv'}) - \delta_{vv'} \sum_{v'' \neq v} W_{vv''}, \tag{1a}$$

and $W_{vv'}$ is the transition rate from the state v to the state v'. At least in principle the rates $W_{vv'}, W_{vv''}, \ldots$ can be computed by applying the laws of quantum mechanics. For large M, solving the master equation (1) is a very complicated task. The MIP offers an approximate way for evaluating the probabilities $P(v,t)$ known as surprisal analysis [12]. Surprisal analysis is based on the assumption that $P(v,t)$ can be described by an ensemble of the Mori type [2]. If E_v is the energy of the molecule in the state v, and $\langle E(t) \rangle$ is the average energy of a molecule selected from an ensemble of the Mori type, then the probabilities $P(1,t), P(2,t), \ldots$ are estimated by optimizing the informational entropy

$$S = -\sum P_v(t) \ln P_v(t), \tag{2}$$

subject to the constraints

$$\langle E(t) \rangle = \sum E_v P_v(t), \tag{3}$$

$$1 = \sum P_v(t). \tag{4}$$

The optimal values of $P(1,t), \ldots, P(M,t)$ are

$$P_v(t) = Z^{-1}(\lambda(t)) \exp(-\lambda(t) E_v), \tag{5}$$

where $Z(\lambda(t))$ is a time-dependent partition function given by

$$Z(\lambda(t)) = \sum \exp(-\lambda(t) E_v), \tag{6}$$

and the Lagrange multiplier $\lambda(t)$ is determined by the equation

$$\langle E(t) \rangle = -\partial \ln Z(\lambda(t))/\partial \lambda(t). \tag{7}$$

Eqs. (5)–(7) give an exact solution of the master equation (1) only if the molecule can be described by a one-dimensional harmonic oscillator. Otherwise the surprisal analysis is only an approximation. It is surprising that this approximation is fairly good even if the molecule is not described by a harmonic oscillator [12].

In the markovian approximation the master equation (1) determines not only the values of the state probabilities $P(1,t)$, $P(2,t)$, ... at a given time, but also the multitemporal joint probabilities

$$P_m(v_m,t_m;\ \ldots;v_1,t_1)=P_m(\boldsymbol{v}_m,\boldsymbol{t}_m), \tag{8}$$

with

$$\sum_{v_1}\cdots\sum_{v_m}P_m(\boldsymbol{v}_m,\boldsymbol{t}_m)=1, \tag{9}$$

and

$$\boldsymbol{v}_m=(v_1,\ \ldots,v_m),\qquad \boldsymbol{t}_m=(t_1,\ \ldots,t_m). \tag{10}$$

We have

$$P_m(\boldsymbol{v}_m,\boldsymbol{t}_m)=\sum_{v_0}G(v_m,t_m|v_{m-1},t_{m-1})\cdots G(v_1,t_1|v_0,t_0)\,P(v_0,t_0). \tag{11}$$

Here $P(v_0,t_0)$ is the initial value of the state probability and $G(v,t|v',t')$ is the Green function of the master equation (1). That is, $G(v,t|v',t')$ is the solution of

$$\mathrm{d}G(v,t|v',t')/\mathrm{d}t=\sum_{v''}A_{vv''}G(v'',t|v',t'),\qquad \text{with } G(v,t'|v',t')=\delta_{vv'}. \tag{12}$$

The Mori approximation used before cannot be used for the evaluation of the joint probability. Rather, a set of constraints of the Zubarev–Kalashnikov type [3] should be used. For an m-gate joint probability $P_m(\boldsymbol{v}_m,\boldsymbol{t}_m)$ we introduce the information entropy

$$S=-\sum_{v_m}P_m(\boldsymbol{v}_m,\boldsymbol{t}_m)\ln P_m(\boldsymbol{v}_m,\boldsymbol{t}_m), \tag{13}$$

and the constraints

$$\langle E(t_u)\rangle=\sum_{v_m}E_{v_u}P_m(\boldsymbol{v}_m,\boldsymbol{t}_m),\qquad u=1,2,\ \ldots,m, \tag{14}$$

and

$$1=\sum_{v_m}P_m(\boldsymbol{v}_m,\boldsymbol{t}_m). \tag{15}$$

The optimal solution is

$$P_m(\boldsymbol{v}_m,\boldsymbol{t}_m)=\prod_{u=1}^{m}P(v_u,t_u), \tag{16}$$

where $P(v_u,t_u)$, $u=1,\ \ldots,m$, are one-time probabilities, given by Eqs. (5)–(7) of the Mori ensemble. It follows that the Zubarev–Kalashnikov constraints lead to an

independent random process. This result is consistent with the master equation (1) in the case of 'strong collision' systems for which the jump rates $W_{vv'}$, $W_{vv''}$, ... do not depend on the initial state:

$$W_{vv'} = W_{v'} \qquad \text{independent of } v, \tag{17}$$

or for harmonic oscillator systems which are canonically invariant [15]. Otherwise the master equation description leads to a markovian dependence with an m-time joint probability density given by Eq. (11), which contradicts the result (16) obtained by applying the MIP. In order to solve this contradiction we should improve the MIP by using new types of constraints which introduce statistical correlations among the states of the system at different times. To do this, we should specify the average values of a set of dynamic variables $f_u(v_1, t_1; v_2, t_2; \ldots)$ which, unlike the energy, do not only depend on the state v of the molecule at a given time t, but also depend on the different states $v_1, v_2, \ldots$ of the molecule at different times $t_1, t_2, \ldots$. By analogy with the method of Zubarev and Kalashnikov the average values of $f_u(v_1, t_1; v_2, t_2; \ldots)$ are given not only for certain times $t_1, t_2, \ldots$, but also for any times in the past between the current time t and the initial moment t_0; $t_0 \leqslant t_u \leqslant t$, $u = 1, 2, \ldots$.

3. Variational formulation of the theory

We consider a continuous time system described by a set of discrete random variables

$$\boldsymbol{N} = (N_1, N_2, \ldots), \tag{18}$$

and introduce the multiple joint probability

$$P_{m+1}(\boldsymbol{N}_m, t_m; \ldots; \boldsymbol{N}_1, t_1; \boldsymbol{N}_0, t_0), \tag{19}$$

with

$$\sum_{\boldsymbol{N}_m} \cdots \sum_{\boldsymbol{N}_0} P_{m+1}(\boldsymbol{N}_m, t_m; \ldots; \boldsymbol{N}_0, t_0) = 1, \tag{20}$$

and

$$t_u = t_0 + u\Delta t, \qquad \Delta t = (t - t_0)/m, \quad u = 0, 1, \ldots, m. \tag{21}$$

In the limit $m \to \infty$ ($\Delta t \to 0$), P_{m+1} becomes a probability functional which describes the stochastic properties of a random trajectory $\boldsymbol{N}(t')$, $t_0 \leqslant t' \leqslant t$:

$$B[\boldsymbol{N}(t');\ t_0 \leqslant t' \leqslant t] = \lim_{\substack{m \to \infty \\ (\Delta t \to 0)}} P_{m+1}(\boldsymbol{N}_m, t_m, \ldots, \boldsymbol{N}_0, t_0). \tag{22}$$

This random trajectory obeys the normalization condition

$$\underline{\overline{\sum\sum}}\, B[\boldsymbol{N}(t'); t_0 \leqslant t' \leqslant t] = 1, \tag{23}$$

where $\underline{\overline{\sum\sum}}$ stands for a path sum which is a discrete analogue of a path integral:

$$\underline{\overline{\sum\sum}} \cdots = \lim_{\substack{m\to\infty \\ (\Delta t\to 0)}} \sum_{N(t_0)} \cdots \sum_{N(t_m)} \cdots . \tag{24}$$

The information entropy corresponding to $B[\boldsymbol{N}(t'); t_0 \leqslant t' \leqslant t]$, is given by

$$S = -\underline{\overline{\sum\sum}}\, B[\boldsymbol{N}(t')] \ln B[\boldsymbol{N}(t')] . \tag{25}$$

We introduce a set of functions f_{um} which depend on the state vectors $\boldsymbol{N}(t_1), \ldots, \boldsymbol{N}(t_m)$ at different times

$$f_{um}(\boldsymbol{N}(t_1), t_1; \ldots; \boldsymbol{N}(t_m), t_m), \qquad u = 1, 2, \ldots , \tag{26}$$

and the corresponding averages

$$\begin{aligned} \langle F_{um}(\boldsymbol{t}_m)\rangle &= \langle F_{um}(t_1, \ldots, t_m)\rangle = \langle f_{um}(\boldsymbol{N}(t_1), t_1; \ldots; \boldsymbol{N}(t_m), t_m)\rangle \\ &= \underline{\overline{\sum\sum}}\, B[\boldsymbol{N}(t'); t_0 \leqslant t' \leqslant t] f_{um}(\boldsymbol{N}(t_1), t_1; \ldots; \boldsymbol{N}(t_m), t_m) . \end{aligned} \tag{27}$$

Now we formulate the following variational problem: what is the stochastic process for which the information entropy (25) subject to the constraints (23) and (27) is an extremum?. To solve this problem we construct from Eqs. (23), (25) and (27) a Lagrange functional and evaluate its functional derivatives with respect to the probability functional $B[\boldsymbol{N}(t')]$ and with respect to the Lagrange multipliers. All these functional derivatives must be equal to zero. After some standard algebraic manipulations we get the following expressions for the probability functional $B[\boldsymbol{N}(t'), t_0 \leqslant t' \leqslant t]$:

$$\begin{aligned} B[\boldsymbol{N}(t'), t_0 \leqslant t' \leqslant t] = Z^{-1} \exp\Bigg(&- \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(\boldsymbol{t}'_m) \\ &\times f_{um}(\boldsymbol{N}(t'_1), t'_1; \ldots; \boldsymbol{N}(t'_m), t'_m)\, \mathrm{d}t'_1 \ldots \mathrm{d}t'_m \Bigg), \end{aligned} \tag{28}$$

where Z is a partition functional depending on the Lagrange multipliers $\lambda_{um}(t_1, \ldots, t_m) = \lambda_{um}(\boldsymbol{t}_m)$, $\boldsymbol{\lambda}(\boldsymbol{t}) = \| \lambda_{um}(\boldsymbol{t}_m) \|$:

$$Z[\boldsymbol{\lambda}(\boldsymbol{t}')] = \underline{\overline{\sum\sum}} \exp\Bigg(- \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(\boldsymbol{t}'_m) f_{um}(\boldsymbol{N}(t'_1), t'_1; \ldots; \boldsymbol{N}(t'_m), t'_m)\, \mathrm{d}t'_1 \ldots \mathrm{d}t'_m \Bigg). \tag{29}$$

The Lagrange multipliers $\lambda_{um}(t_m)$ are the solutions of the equations:

$$\langle F_{um}(t_m)\rangle = -\frac{\delta \ln Z[\lambda(t')]}{\delta \lambda_{um}(t_m)}, \tag{30}$$

and $\delta \ldots /\delta\lambda_{um}(t_m)$ denotes a functional derivative with respect to the function $\lambda_{um}(t_m)$ at the point $t_m = (t_1, \ldots, t_m)$.

Eqs. (28)–(30) for the probability functional $B[N(t')]$ define a stochastic process with memory which is generally non-markovian. Its main properties are investigated in the following sections.

4. Stochastic description

There are two different levels of description for the stochastic process introduced in the preceding section: (a) A microscopic one which characterizes the fluctuations of the microscopic random vector $N(t')$, $t_0 \leqslant t' \leqslant t$; and (b) a mesoscopic one which deals with the stochastic behavior of the functions $f_{um}(N(t_1), t_1; \ldots; N(t_m), t_m)$ with respect to which the constraints used in Section 3 are defined.

At a microscopic level, the stochastic properties of the vector $N(t')$, $t_0 \leqslant t' \leqslant t$, are completely described by the characteristic functional

$$\mathcal{G}[K(t')] = \left\langle \exp\left(i \sum_l \int_{t_0}^{t} K_l(t') N_l(t') \, dt' \right) \right\rangle$$

$$= \underline{\overline{\sum\sum}} \exp\left(i \sum_l \int_{t_0}^{t} K_l(t') N_l(t') \, dt' \right) B[N(t'); t_0 \leqslant t' \leqslant t], \tag{31}$$

where $K(t') = (K_1(t'_1), K_2(t'_2), \ldots .)$ is a suitable vectorial-valued test function, and the probability functional $B[N(t')]$ is given by Eqs. (28)–(30). The central moments $\langle N_{l_1}(t_1) N_{l_2}(t_2) \ldots \rangle$ and the cumulants $\langle\langle N_{l_1}(t_1) N_{l_2}(t_2) \ldots \rangle\rangle$ of N, if they exist and are finite, are given by two functional expansions of the characteristic functional $\mathcal{G}[K(t')]$:

$$\mathcal{G}[K(t')] = 1 + \sum_{q=1}^{\infty} \sum_{l_1} \cdots \sum_{l_q} \frac{(i)^q}{l_1! \ldots l_q!} \int_{t_0}^{t} \cdots \int_{t_0}^{t}$$

$$\times \langle N_{l_1}(t'_1) \cdots N_{l_q}(t'_q)\rangle K_{l_1}(t'_1) \cdots K_{l_q}(t'_q) \, dt'_1 \ldots dt'_q. \tag{32}$$

and

$$\ln \mathcal{G}[K(t')] = \sum_{q=1}^{\infty} \sum_{l_1} \cdots \sum_{l_q} \frac{(i)^q}{l_1! \ldots l_q!} \int_{t_0}^{t} \cdots \int_{t_0}^{t}$$

$$\times \langle\langle N_{l_1}(t'_1) \cdots N_{l_q}(t'_q)\rangle\rangle K_{l_1}(t'_1) \cdots K_{l_q}(t'_q) \, dt'_1 \ldots dt'_q. \tag{33}$$

From these two equations it follows that the central moments and the cumulants of $\boldsymbol{N}$ can be evaluated by computing the functional derivatives

$$\langle N_{l_1}(t_1) \dots N_{l_q}(t_q)\rangle = (-\mathrm{i})^q \left.\frac{\delta^q \mathscr{G}[\boldsymbol{K}(t')]}{\delta K_{l_1}(t_1) \dots \delta K_{l_q}(t_q)}\right|_{\boldsymbol{K}=\boldsymbol{0}} \tag{34}$$

and

$$\langle\langle N_{l_1}(t_1) \dots N_{l_q}(t_q)\rangle\rangle = (-\mathrm{i})^q \left.\frac{\delta^q \ln \mathscr{G}[\boldsymbol{K}(t')]}{\delta K_{l_1}(t_1) \dots \delta K_{l_q}(t_q)}\right|_{\boldsymbol{K}=\boldsymbol{0}} . \tag{35}$$

At a mesoscopic level we are not interested in the fluctuations of the microscopic variables $\boldsymbol{N} = (N_1, N_2, \dots)$ but rather in the fluctuations of the functions $f_{um}(N_1, t_1; \dots; N_m, t_m)$, $u = 1, 2, \dots$. Denoting a realization of these functions for given values of $N_1, \dots, N_m$ by $F_{um}(t_1, \dots, t_m) = F_{um}(\boldsymbol{t}_m)$ we can introduce the probability density functional:

$$\mathscr{P}[\mathbf{F}(\boldsymbol{t}'),\ t_0 \leqslant t'_u \leqslant t]\, \mathrm{D}[\boldsymbol{F}(\boldsymbol{t}')] , \tag{36}$$

with the normalization condition

$$\overline{\underline{\int\int}}\, \mathscr{P}[\mathbf{F}(\boldsymbol{t}'),\ t_0 \leqslant t'_u \leqslant t]\, \mathrm{D}[\boldsymbol{F}(\boldsymbol{t}')] = 1 , \tag{37}$$

where

$$\mathbf{F}(\boldsymbol{t}') = \| F_{um}(\boldsymbol{t}'_m) \| , \tag{38}$$

$\mathrm{D}[\mathbf{F}(\boldsymbol{t}')]$ is a suitable measure over the space of functions $\mathbf{F}(\boldsymbol{t}')$, $\overline{\underline{\int\int}}$, stands for functional integration and the double bars denote a matrix. A difficulty arises due to the fact that we do not have a suitable definition for the integration measure $\mathrm{D}[\mathbf{F}(\boldsymbol{t}')]$. This difficulty may be overcome by introducing a characteristic functional similar to $\mathscr{G}[\boldsymbol{K}(t')]$:

$$G[\boldsymbol{\sigma}(\boldsymbol{t}');\ t_0 \leqslant t'_u \leqslant t] = \left\langle \exp\left(\mathrm{i} \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \sigma_{um}(\boldsymbol{t}'_m)\, F_{um}(\boldsymbol{t}'_m)\, \mathrm{d}t'_1 \dots \mathrm{d}t'_m \right) \right\rangle$$

$$= \overline{\underline{\int\int}} \exp\left(\mathrm{i} \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \sigma_{um}(\boldsymbol{t}'_m)\, F_{um}(\boldsymbol{t}'_m)\, \mathrm{d}t'_1 \dots \mathrm{d}t'_m \right)$$

$$\times \mathscr{P}[\mathbf{F}(\boldsymbol{t}')]\, \mathrm{D}[\mathbf{F}(\boldsymbol{t}')] , \tag{39}$$

where $\sigma_{um}(t'_1, \dots, t'_m) = \sigma_{um}(\boldsymbol{t}'_m)$ are suitable test functions and

$$\boldsymbol{\sigma}(\boldsymbol{t}') = \| \sigma_{um}(\boldsymbol{t}'_m) \| . \tag{40}$$

Due to the structure of the stochastic process introduced in Section 3, the characteristic functional $G[\boldsymbol{\sigma}(t'_m)]$ is independent of the integration measure $\mathrm{D}[\mathbf{F}(t')]$. To see this, note that the probability density functional $\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]$ is the average of a delta functional

$$\prod_{u,m}\{\delta[F_{um}(t'_m)-f_{um}(\boldsymbol{N}(t'_1),t'_1;\ \ldots;\boldsymbol{N}(t'_m),t'_m)]\}\,\mathrm{D}[\mathbf{F}(t')] \tag{41}$$

over all possible values of the microscopic vectors $\boldsymbol{N}(t_1),\ \ldots,\boldsymbol{N}(t_m)$. We have

$$\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]=\overline{\sum\sum}\,B[\boldsymbol{N}(t')]\prod_{u,m}\{\delta[F_{um}(t'_m)-f_{um}(\boldsymbol{N}(t'_1),t'_1;\ \ldots;\boldsymbol{N}(t'_m),t'_m)]\}\,\mathrm{D}[\mathbf{F}(t')], \tag{42}$$

where $B[\boldsymbol{N}(t')]$ is given by Eqs. (28)–(30). Inserting Eqs. (28) and (42) into the definition (39) of the characteristic functional $G[\boldsymbol{\sigma}(t')]$, and making use of the expression (29), of the partition functional $Z[\boldsymbol{\lambda}(t)]$, we come to

$$G[\boldsymbol{\sigma}(t')]=Z[\boldsymbol{\lambda}(t')-\mathrm{i}\boldsymbol{\sigma}(t')]/Z[\boldsymbol{\lambda}(t')]. \tag{43}$$

Thus the characteristic functional $G[\boldsymbol{\sigma}(t')]$ can be expressed in a closed form in terms of the partition functional $Z[\boldsymbol{\lambda}(t')]$, and the corresponding relation is independent of the integration measure $\mathrm{D}[\mathbf{F}(t')]$.

By expressing $G[\boldsymbol{\sigma}(t')]$ in the form of two functional expansions similar to Eqs. (32)–(33), we can derive expressions for the central moments and the cumulants of the mesoscopic variables $F_{um}(t_m)$, $u=1,2,\ \ldots$. Namely,

$$\langle F_{u_1m_1}(t_{m_1})\cdots F_{u_qm_q}(t_{m_q})\rangle=(-\mathrm{i})^q\left.\frac{\delta^q G[\boldsymbol{\sigma}(t')]}{\delta\sigma_{u_1m_1}(t_{m_1})\ \ldots\ \delta\sigma_{u_qm_q}(t_{m_q})}\right|_{\sigma(t)=0}, \tag{44}$$

and

$$\langle\!\langle F_{u_1m_1}(t_{m_1})\cdots F_{u_qm_q}(t_{m_q})\rangle\!\rangle=(-\mathrm{i})^q\left.\frac{\delta^q\ln G[\boldsymbol{\sigma}(t')]}{\delta\sigma_{u_1m_1}(t_{m_1})\ \ldots\ \delta\sigma_{u_qm_q}(t_{m_q})}\right|_{\sigma(t)=0}. \tag{45}$$

5. Statistic-thermodynamic description

In this section we outline some formal analogies between our approach and the statistic-thermodynamic formalism. First notice that the partition functional $Z[\boldsymbol{\lambda}(t')]$ can be expressed as a multiple functional Laplace transform of the density $g[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]$ of microscopic states compatible with a given set of values $F_{um}(t'_m)$, $u=1,2,\ \ldots$ of the mesoscopic state variables

$$g[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]=\overline{\sum\sum}\prod_{u,m}\{\delta[F_{um}(t'_m)-f_{um}(\boldsymbol{N}(t'_1),t'_1;\ \ldots;\boldsymbol{N}(t'_m),t'_m)]\}\,\mathrm{D}[\mathbf{F}(t')]. \tag{46}$$

From Eqs. (29) and (46) we have

$$Z[\lambda(t')] = \overline{\iint} \exp\left(- \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(t'_m) F_{um}(t'_m) \mathrm{d}t'_1 \ldots \mathrm{d}t'_m \right) g[\mathbf{F}(t')] \mathrm{D}[\mathbf{F}(t')] . \quad (47)$$

By using Eqs. (43)–(46) we can express the moments of $\mathbf{F}(t)$ in terms of the functional derivatives of the partition functional $Z[\lambda(t')]$ with respect to the Lagrange multipliers $\lambda_{um}(t_m)$:

$$\langle F_{u_1 m_1}(t_{m_1}) \cdots F_{u_q m_q}(t_{m_q}) \rangle = (-1)^q Z^{-1}[\lambda(t')] \frac{\delta^q Z[\lambda(t')]}{\delta \lambda_{u_1 m_1}(t_{m_1}) \ldots \delta \lambda_{u_q m_q}(t_{m_q})}, \quad (48)$$

and

$$\langle\langle F_{u_1 m_1}(t_{m_1}) \cdots F_{u_q m_q}(t_{m_q}) \rangle\rangle = (-1)^q \frac{\delta^q \ln Z[\lambda(t')]}{\delta \lambda_{u_1 m_1}(t_{m_1}) \ldots \delta \lambda_{u_q m_q}(t_{m_q})}. \quad (49)$$

In particular, for $q = 1$ Eqs. (48)–(49) reduce to Eqs. (30) derived in Section 3.

The extremal value of the entropy can be computed by inserting Eq. (28) into Eq. (25), to give

$$S_{\mathrm{extr}}[\langle \mathbf{F}(t') \rangle] = \ln Z[\lambda(t')] + \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(t'_m) \langle F_{um}(t'_m) \rangle \mathrm{d}t'_1 \ldots \mathrm{d}t'_m . \quad (50)$$

We evaluate the variations of the extremal entropy $S_{\mathrm{extr}}.\ [\langle \mathbf{F}(t') \rangle]$, and of the logarithm of the partition functional $\ln Z[\lambda(t')]$ due to the variations of the average values of the mesoscopic state variables and of the Lagrange multipliers, through

$$\delta \ln Z[\lambda(t')] = \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \frac{\delta \ln Z[\lambda(t')]}{\delta \lambda_{um}(t'_m)} \delta \lambda_{um}(t'_m) \mathrm{d}t'_1 \ldots \mathrm{d}t'_m$$

$$= - \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \langle F_{um}(t'_m) \rangle \delta \lambda_{um}(t'_m) \mathrm{d}t'_1 \ldots \mathrm{d}t'_m, \quad (51)$$

and

$$\delta S_{\mathrm{extr}}[\langle \mathbf{F}(t') \rangle] = \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \left(\frac{\delta \ln Z[\lambda(t')]}{\delta \lambda_{um}(t'_m)} \delta \lambda_{um}(t'_m) \right.$$

$$\left. + \delta \lambda_{um}(t'_m) \langle F_{um}(t'_m) \rangle + \delta \langle F_{um}(t'_m) \rangle \lambda_{um}(t'_m) \right) \mathrm{d}t'_1 \ldots \mathrm{d}t'_m$$

$$= \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(t'_m) \delta \langle F_{um}(t'_m) \rangle \mathrm{d}t'_1 \ldots \mathrm{d}t'_m, \quad (52)$$

respectively. From Eq. (52) we notice that the functional derivative of the extremal entropy $S_{\text{extr}}[\mathbf{F}(t'_m)\rangle]$ with respect to the average value $\langle F_{um}(t'_m)\rangle$ is equal to the Lagrange multiplier $\lambda_{um}(t_m)$:

$$\lambda_{um}(t_m) = \frac{\delta S_{\text{extr}}[\langle \boldsymbol{F}(t')\rangle]}{\delta \langle F_{um}(t_m)\rangle}. \tag{53}$$

Eqs. (53) are similar to the relationships (30) for the average values $\langle F_{um}(t_m)\rangle$.

6. Fluctuation-dissipation relations

We introduce the compliance functions

$$\eta_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) = \frac{\delta\langle F_{u_1m_1}(t_{m_1})\rangle}{\delta \lambda_{u_2m_2}(t_{m_2})}, \tag{54}$$

and

$$\chi_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) = \frac{\delta \lambda_{u_1m_1}(t_{m_1})}{\delta\langle F_{u_2m_2}(t_{m_2})\rangle}, \tag{55}$$

From Eqs. (30) we have

$$\frac{\delta\langle F_{u_1m_1}(t_{m_1})\rangle}{\delta \lambda_{u_2m_2}(t_{m_2})} = \frac{\delta\langle F_{u_2m_2}(t_{m_2})\rangle}{\delta \lambda_{u_1m_1}(t_{m_1})} = -\frac{\delta^2 \ln Z[\lambda(t')]}{\delta \lambda_{u_1m_1}(t_{m_1})\delta \lambda_{u_2m_2}(t_{m_2})}. \tag{56}$$

By combining Eqs. (49), (54) and (56) we obtain

$$\eta_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) = \eta_{u_2m_2u_1m_1}(t_{m_2}, t_{m_1}) = -\langle\langle F_{u_1m_1}(t_{m_1}) F_{u_2m_2}(t_{m_2})\rangle\rangle. \tag{57}$$

Similarly, from Eqs. (53) we have

$$\frac{\delta \lambda_{u_1m_1}(t_{m_1})}{\delta\langle F_{u_2m_2}(t_{m_2})\rangle} = \frac{\delta \lambda_{u_2m_2}(t_{m_2})}{\delta\langle F_{u_1m_1}(t_{m_1})\rangle} = \frac{\delta^2 S_{\text{extr}}[\langle \mathbf{F}(t')\rangle]}{\delta\langle F_{u_1m_1}(t_{m_1})\rangle \delta\langle F_{u_2m_2}(t_{m_2})\rangle}. \tag{58}$$

Thus the compliance functions $\chi_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2})$ are also symmetric and

$$\chi_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) = \chi_{u_2m_2u_1m_1}(t_{m_2}, t_{m_1}) = \frac{\delta^2 S_{\text{extr}}[\langle \mathbf{F}(t')\rangle]}{\delta\langle F_{u_1m_1}(t_{m_1})\rangle \delta\langle F_{u_2m_2}(t_{m_2})\rangle}. \tag{59}$$

Between the two types of compliance functions introduced before there is a reciprocity relationship which can be easily derived by applying the chain rule for the functional differentiation:

$$\frac{\delta\langle F_{u_1m_1}(t_{m_1})\rangle}{\delta\langle F_{u_2m_2}(t_{m_2})\rangle} = \sum_{u',m'} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \frac{\delta\langle F_{u_1m_1}(t_{m_1})\rangle}{\delta \lambda_{u'm'}(t'_{m'})} \frac{\delta \lambda_{u'm'}(t'_{m'})}{\delta\langle F_{u_2m_2}(t_{m_2})\rangle} \, dt'_1 \ldots dt'_{m'}$$

$$= \delta_{u_1u_2}\delta_{m_1m_2}\delta(t_{m_1} - t_{m_2}). \tag{60}$$

Using the definitions of the compliance functions $\eta_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2})$ and $\chi_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2})$, Eqs. (6) can be rewritten as

$$\sum_{u',m'} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \eta_{u_1m_1u'm'}(t_{m_1}, t'_{m'}) \chi_{u'm'u_2m_2}(t'_{m'}, t_{m_2}) \, dt'_1 \ldots dt'_{m'} = \delta_{u_1u_2} \delta_{m_1m_2} \delta(t_{m_1} - t_{m_2}). \tag{61}$$

Writing the compliance functions as matrices with both discrete (u, m) and continuous labels (t_m), respectively

$$\boldsymbol{\eta} = \| \eta_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) \| \tag{62}$$

and

$$\boldsymbol{\chi} = \| \chi_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) \| , \tag{63}$$

Eqs. (61) can be expressed symbolically as

$$\boldsymbol{\eta}\boldsymbol{\chi} = \mathbf{I}, \qquad \text{with } \mathbf{I} = \| \delta_{u_1u_2} \delta_{m_1m_2} \delta(t_{m_1} - t_{m_2}) \| . \tag{64}$$

That is, $\boldsymbol{\eta}$ is the inverse of $\boldsymbol{\chi}$ and vice versa.

By considering a differential variation $\Delta t \to 0$ of the components of the vector t_m of the time variables,

$$t_m = (t_1, \ldots, t_m) \to (t_1 + \Delta t, \ldots, t_m + \Delta t), \tag{65}$$

in the limit $\Delta t \to 0$, Eqs. (54) lead to a set of evolution equations for the average values $\langle F_{um}(t_m) \rangle$ given by

$$\left(\sum_{u''=1}^{m} \frac{\partial}{\partial t_{u''}} \right) \langle F_{um}(t_m) \rangle = \sum_{u',m'} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \eta_{umu'm'}(t_m, t'_{m'}) \times \left(\sum_{u''=1}^{m'} \frac{\partial}{\partial t'_{u''}} \right) \lambda_{u'm'}(t'_{m'}) \, dt'_1 \ldots dt'_{m'}, \tag{66}$$

where the compliance functions $\eta_{umu'm'}(t_m, t'_{m'})$ play the role of transport coefficients. It follows from this result that the relationships (57) between the compliance functions $\eta_{u_1m_1u_2m_2}$ and the second order cumulants of $\mathbf{F}(t')$ can be viewed as a set of fluctuation-dissipation relations which establish a relationship between the relaxation behavior given by the transport coefficients and the magnitude of fluctuations.

Similarly, by considering the infinitesimal transformation (65), Eqs. (55) lead to a set of reciprocal evolution equations for the Lagrange multipliers $\lambda_{um}(t_m)$:

$$\left(\sum_{u''=1}^{m} \frac{\partial}{\partial t_{u''}} \right) \lambda_{um}(t_m) = \sum_{u',m'} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \chi_{umu'm'}(t_m, t'_{m'}) \times \left(\sum_{u''=1}^{m'} \frac{\partial}{\partial t'_{u''}} \right) \langle F_{u'm'}(t'_{m'}) \rangle \, dt'_1 \ldots dt'_{m'}. \tag{67}$$

Using the reciprocity relationships (61) and (64), we see that Eqs. (66) and (67) are equivalent to each other. By using Eqs. (64) and (57) we can rewrite Eqs. (59) in the symbolic form

$$\chi = \eta^{-1} = -\|\langle\langle F_{u_1 m_1}(t_{m_1}) F_{u_2 m_2}(t_{m_2})\rangle\rangle\|^{-1} = \left\| \frac{\delta^2 S_{\text{extr}}[\langle F(t'_m)\rangle]}{\delta \lambda_{u_1 m_1}(t_{m_1}) \delta \lambda_{u_2 m_2}(t_{m_2})} \right\|. \tag{68}$$

Here the inversion of the matrices is considered both with respect to the continuous (t_m) and discrete (u, m) labels. Eqs. (68) are the fluctuation-dissipation relations for the reciprocal evolution equations (67). Eqs. (57) and (68) are equivalent to each other.

To complete the discussion of the fluctuation-dissipation relation we investigate the relationship between the probabilty of fluctuations and the entropy. We start out by considering the case of gaussian fluctuations, in which we assume that only the first two of the cumulants (45) or (49) are different from zero. This case presents the advantage that the integration measure $\mathrm{D}[\mathbf{F}(t')]$ can be explicitly evaluated. Expanding the characteristic functional $G[\boldsymbol{\sigma}(t')]$ in a cumulant functional series, and keeping the terms up to second order, we obtain

$$G[\boldsymbol{\sigma}(t')] = \exp\Bigg(\mathrm{i} \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \sigma_{um}(t'_m) \langle F_{um}(t'_m)\rangle \, \mathrm{d}t'_1 \ldots \mathrm{d}t'_m$$

$$- \frac{1}{2} \sum_{u_1 m_1} \sum_{u_2 m_2} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \sigma_{u_1 m_1}(t'_{1 m_1}) \sigma_{u_2 m_2}(t'_{2 m_2})$$

$$\times \langle\langle F_{u_1 m_1}(t'_{1 m_1}) F_{u_2 m_2}(t'_{2 m_2})\rangle\rangle \, \mathrm{d}t'_{11} \ldots \mathrm{d}t'_{1 m_1} \, \mathrm{d}t'_{21} \ldots \mathrm{d}t'_{2 m_2} \Bigg). \tag{69}$$

To evaluate the integration measure $\mathrm{D}[\mathbf{F}(t')]$, we return to the discrete-time representation used in Eqs. (20)–(22). For each time vector t_m we attach a vector $\boldsymbol{b} = (b_1, \ldots, b_m)$ according to the following rule:

$$t_m = t_{m\boldsymbol{b}} \to (t_0 + b_1 \Delta t, \ldots, t_0 + b_m \Delta t), \tag{70}$$

with

$$\Delta t = (t - t_0)/m, \qquad b_1, \ldots, b_m = 0, \ldots, m. \tag{71}$$

We introduce a matrix representation of the state variables by attaching to each set

$$(t_{m\boldsymbol{b}}, u, m) \to (\boldsymbol{b}, u, m) \to l, \qquad l = 1, \ldots, L, \tag{72}$$

a label l. We use script letters for the state variables indexed by the label l:

$$F_{um}(t_{m\boldsymbol{b}}) \to \mathscr{F}_l, \qquad \boldsymbol{\mathscr{F}} = (\mathscr{F}_l). \tag{73}$$

The discrete analogue of the probability density functional $\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]$ is the $(m+1)$-gate joint probability density

$$\mathscr{P}_{m+1}(\mathscr{F})\,\mathrm{d}\mathscr{F}, \qquad \text{with } \int \mathscr{P}_{m+1}(\mathscr{F})\,\mathrm{d}\mathscr{F} = 1. \tag{74}$$

We have

$$\mathscr{P}[F(t')]\,\mathrm{D}[F(t')] = \lim_{\substack{m\to\infty \\ (\Delta t\to 0)}} \mathscr{P}_{m+1}(\mathscr{F})\,\mathrm{d}\mathscr{F}. \tag{75}$$

The characteristic function of the probability density $\mathscr{P}_{m+1}(\mathscr{F})\,\mathrm{d}\mathscr{F}$,

$$G_{m+1}(k) = \int \exp\left(\mathrm{i}\sum k_l \mathscr{F}_l\right) \mathscr{P}_{m+1}(\mathscr{F})\,\mathrm{d}\mathscr{F}, \qquad \text{with } \boldsymbol{k} = (k_l), \tag{76}$$

can be obtained from the characteristic functional $G[\sigma(t')]$ for a special choice of the test functions $\sigma'_{um}(t_m)$;

$$\sigma_{um}(t'_m) = \sum_l k_l\,\delta(t_{mb} - t'_m) = \sum k_{umb}\,\delta(t_{mb} - t'_m). \tag{77}$$

From Eqs. (69) and (76) we obtain

$$G_{m+1}(k) = \exp\left(\mathrm{i}\sum_l \langle \mathscr{F}_l\rangle k_l - \frac{1}{2}\sum_{l_1 l_2} \langle\!\langle \mathscr{F}_{l_1}\mathscr{F}_{l_2}\rangle\!\rangle k_{l_1} k_{l_2}\right). \tag{78}$$

The $(m+1)$-gate joint probability density $\mathscr{P}_{m+1}(\mathscr{F})\,\mathrm{d}\mathscr{F}$ can be easily evaluated by means of an inverse Fourier transformation to give:

$$\mathscr{P}_{m+1}(\mathscr{F}) = (2\pi)^{-L/2}\left(\det\langle\!\langle \mathscr{F}\,\mathscr{F}^{\dagger}\rangle\!\rangle\right)^{-1/2} \times \exp\left[-\tfrac{1}{2}(\mathscr{F}^{\dagger} - \langle\mathscr{F}^{\dagger}\rangle)\,\mathscr{M}(\mathscr{F} - \langle\mathscr{F}\rangle)\right], \tag{79}$$

where $\mathscr{M}$ is a symmetric matrix which is the inverse of the covariance matrix

$$\mathscr{M}\langle\!\langle \mathscr{F}\,\mathscr{F}^{\dagger}\rangle\!\rangle = \langle\!\langle \mathscr{F}\,\mathscr{F}^{\dagger}\rangle\!\rangle\,\mathscr{M} = \mathbf{I}. \tag{80}$$

Eq. (80) for $\mathscr{M}$ is similar to the reciprocity equations (61). By using Eqs. (57), Eqs. (61) can be written as

$$-\sum_{u',m'} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \langle\!\langle F_{u_1 m_1}(t'_{m_1})\,F_{u'm'}(t'_{m'})\rangle\!\rangle \chi_{u'm'u_2m_2}(t'_{m'}, t_{m_2})\,\mathrm{d}t'_1 \ldots \mathrm{d}t'_{m'} = \delta_{u_1u_2}\,\delta_{m_1m_2}\,\delta(t_{m_1} - t_{m_2}). \tag{81}$$

In the limit $m\to\infty$ in the scalar transcription of Eq. (80), the sums over $b_1, \ldots, b_m$ become integrals over $t'_1, \ldots, t'_m$ and the structures of Eqs. (80) and (81) become identical; a comparison leads to

$$\chi_{u_1m_1u_2m_2}(t_{m_1}, t_{m_2}) = -\lim_{\substack{m\to\infty \\ (\Delta t\to 0)}} (\mathscr{M})_{l_1 l_2}. \tag{82}$$

Similarly, by comparing Eqs. (75) and (79) and using Eqs. (82) we obtain the following expression for $\mathscr{P}[\mathbf{F}(t')]$ and for the integration measure $\mathrm{D}[\mathbf{F}(t')]$:

$$\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')] = \exp\left(\frac{1}{2}\sum_{u_1 m_1}\sum_{u_2 m_2}\int_{t_0}^{t}\cdots\int_{t_0}^{t}\right.$$
$$\times\left[F_{u_1 m_1}(t'_{1m_1}) - \langle F_{u_1 m_1}(t'_{1m_1})\rangle\right]\chi_{u_1 m_1 u_2 m_2}(t'_{1m_1}, t'_{2m_2})$$
$$\left.\times\left[F_{u_2 m_2}(t'_{2m_2}) - \langle F_{u_2 m_2}(t'_{2m_2})\rangle\right]\mathrm{d}t'_{11}\ldots\mathrm{d}t'_{1m_1}\,\mathrm{d}t'_{21}\ldots\mathrm{d}t'_{2m_2}\right)$$
$$\times\,\mathrm{D}[F(t')]\,, \tag{83}$$

and

$$\mathrm{D}[F(t')] = \lim_{\substack{m\to\infty\\(\Delta t\to 0)}}(2\pi)^{-L/2}\left[\det(\langle\!\langle \mathscr{F}\mathscr{F}^{\dagger}\rangle\!\rangle)\right]^{-1/2}\mathrm{d}\mathscr{F}. \tag{84}$$

Thus, in this case $\mathrm{D}[\mathbf{F}(t')]$ is the usual gaussian measure [16].

The expression (83) for $\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]$ can be written in a simpler form by introducing a fluctuating entropy $S[F(t')]$. $S[\mathbf{F}(t')]$ is defined by the same expressions as S_{extr} (Eqs. (29)–(30) and (50)) with the difference that the average values $\langle F_{um}(t'_m)\rangle$ are replaced by the corresponding fluctuating quantities $F_{um}(t'_m)$. Thus,

$$S[\mathbf{F}(t') = \langle\mathbf{F}(t')\rangle] = S_{\mathrm{extr}}[\langle\mathbf{F}(t')\rangle]. \tag{85}$$

Evaluating the second variation of $S[\mathbf{F}(t')]$ around $\mathbf{F}(t') = \langle\mathbf{F}(t')\rangle$ yields

$$\delta^2 S[\mathbf{F}(t')] = \sum_{u_1 m_1}\sum_{u_2 m_2}\int_{t_0}^{t}\cdots\int_{t_0}^{t}\frac{\delta^2 S_{\mathrm{extr}}[\langle\mathbf{F}(t')\rangle]}{\delta\langle F_{u_1 m_1}(t'_{m_1})\rangle\,\delta\langle F_{u_2 m_2}(t'_{m_2})\rangle}$$
$$\times\left[F_{u_1 m_1}(t'_{m_1}) - \langle F_{u_1 m_1}(t'_{m_1})\rangle\right]\left[F_{u_2 m_2}(t'_{m_2}) - \langle F_{u_2 m_2}(t'_{m_2})\rangle\right]$$
$$\times\,\mathrm{d}t'_{11}\ldots\mathrm{d}t'_{1m_1}\,\mathrm{d}t'_{21}\ldots\mathrm{d}t'_{2m_2}. \tag{86}$$

Using the expressions (59) for the compliance functions $\chi_{u_1 m_1 u_2 m_2}(t_{m_1}, t_{m_2})$, note that the exponent in Eq. (83) for the probability density functional $\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]$ is equal to half of the second variation of the fluctuation entropy:

$$\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')] = \exp\left[\tfrac{1}{2}\delta^2 S[\mathbf{F}(t')]\right]\mathrm{D}[\mathbf{F}(t')]\,. \tag{87}$$

Eq. (87) is a functional analogue of the well known Einstein fluctuation formula from equilibrium statistical thermodynamics [17].

Beyond the gaussian approximation one normally expects that the higher order variations of the fluctuating entropy $[\delta^3 S, \delta^4 S, \ldots]$ should also enter Eq. (87). We conjecture that

$$\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')] = \exp\left[\tfrac{1}{2!}\delta^2 S[\mathbf{F}(t')] + \tfrac{1}{3!}\delta^3 S[\mathbf{F}(t')] + \cdots\right]\mathrm{D}[\mathbf{F}(t')]$$
$$= \exp\left[S[\mathbf{F}(t')] - S_{\mathrm{extr}}[\langle\mathbf{F}(t')\rangle] - \delta S[\mathbf{F}(t')]\right]\mathrm{D}[\mathbf{F}(t')]. \tag{88}$$

Using Eqs. (50)–(52), the conjecture (88) can be written in two different, but equivalent, forms;

$$\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')] = \exp\Bigg(S[\mathbf{F}(t')] - S_{\mathrm{extr}}[\mathbf{F}(t')] - \sum_{um} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(t'_m) \times [F_{um}(t'_m) - \langle F_{um}(t'_m)\rangle]\,\mathrm{d}t'_1 \ldots \mathrm{d}t'_m \Bigg) \mathrm{D}[\mathbf{F}(t')] \tag{89}$$

$$= Z^{-1} \exp\Bigg(S[\mathbf{F}(t')] - \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(t')\,F_{um}(t')\,\mathrm{d}t'_1 \ldots \mathrm{d}t'_m \Bigg) \times \mathrm{D}[\mathbf{F}(t')]\,. \tag{89a}$$

A direct proof of the conjecture contained in Eqs. (88)–(89) is not possible since, in the non-gaussian case, the integration measure $\mathrm{D}[\mathbf{F}(t')]$ is unknown. To circumvent this difficulty, we compute the characteristic functional $G[\boldsymbol{\sigma}(t')]$ by using Eq. (89a) and compare the result with the relation (43) derived in Section 4. Using the normalization condition (37) from Eq. (89a), we obtain the following expression for the partition functional in terms of the fluctuating entropy:

$$Z = \overline{\iint} \exp\Bigg(S[\mathbf{F}(t')] - \sum_{u,m} \int_{t_0}^{t} \cdots \int_{t_0}^{t} \lambda_{um}(t')\,F_{um}(t')\,\mathrm{d}t'_1 \ldots \mathrm{d}t'_m \Bigg) \mathrm{D}[\mathbf{F}(t')]\,. \tag{90}$$

Inserting Eq. (89a) in the definition (39) of the characteristic functional $G[\boldsymbol{\sigma}(t')]$, and noticing that the resulting functional integral has exactly the same form as Eq. (90) where $\boldsymbol{\lambda}(t')$ is replaced by $\boldsymbol{\lambda}(t') - \mathrm{i}\boldsymbol{\sigma}(t')$, we get

$$G[\boldsymbol{\sigma}(t')] = Z[\boldsymbol{\lambda}(t') - \mathrm{i}\boldsymbol{\sigma}(t')]/Z[\boldsymbol{\lambda}(t')]\,. \tag{91}$$

Eq. (91) is identical with Eq. (43), which proves the validity of Eqs. (88)–(89a).

To close this section we point out some formal analogies between the non-gaussian fluctuation equations (88)–(89a) and the theory of thermodynamic fluctuations developed by Greene and Callen [18–19].

Eq. (89) is a functional analogue of the Greene and Callen generalization [18] of the Einstein fluctuation formula for non-gaussian fluctuations. Similarly, Eqs. (48)–(49) for the moments of mesoscopic state variables developed in Section 5 can be viewed as functional generalizations of the Callen equations [19] for the one-time moments of thermodynamic variables at equilibrium, or of the corresponding one-time approach developed by Vlad and Ross [20] for non-equilibrium steady states. These analogies are however rather limited, since the Einstein and Greene–Callen formulas describe the fluctuations at one point in time. In contrast, Eqs. (87)–(89a) contain all information concerning the time development of the fluctuation and relaxation of the mesoscopic state variables $F_{um}(t'_m)$.

7. Application to surprisal analysis in molecular dynamics

Now we use the general theory developed before to return to the problem of molecular dynamics considered in Section 2. In this case, to each microscopic state vector N corresponds a label v which describes the state of a molecule. If we assume that the energy of a molecule is the only relevant dynamic variable, then all constraints (27) should be expressed in terms of it. A stochastic behavior similar to the one given by the master equation (1) can be recovered within the framework of surprisal analysis by assuming that both the first and the second moments of the energy,

$$\langle E(t')\rangle \quad \text{and} \quad \langle E(t'_1)E(t'_2)\rangle, \qquad t_0 \leqslant t', t'_1, t'_2 \leqslant t, \tag{92}$$

are known at all times in the past. The constraints (27) become

$$\langle F_{11}(t')\rangle = \langle E(t')\rangle \tag{93}$$

and

$$\langle F_{12}(t'_1, t'_2)\rangle = \langle E(t'_1)E(t'_2)\rangle = \langle\langle E(t'_1)E(t'_2)\rangle\rangle + \langle E(t'_1)\rangle\langle E(t'_2)\rangle \tag{93a}$$

and the solution of the variational problem is given by

$$B[v(t')] = Z^{-1}\exp\left(-\int_{t_0}^{t}\lambda_1(t')E_{v(t')}\,dt' - \int_{t_0}^{t}\int_{t_0}^{t}\lambda_2(t'_1, t'_2)E_{v(t'_1)}E_{v(t'_2)}\,dt'_1\,dt'_2\right). \tag{94}$$

In Eqs. (94)

$$Z[\lambda_1(t'), \lambda_2(t'_1, t'_2)] = \underline{\overline{\sum\sum}}\exp\left(-\int_{t_0}^{t}\lambda_1(t')E_{v(t')}\,dt' - \int_{t_0}^{t}\int_{t_0}^{t}\lambda_2(t'_1, t'_2)E_{v(t'_1)}E_{v(t'_2)}\,dt'_1\,dt'_2\right). \tag{95}$$

and the Lagrange multipliers $\lambda_1(t')$ and $\lambda_2(t'_1, t'_2)$ are the solutions of the functional equations

$$\langle E(t)\rangle = \frac{\delta \ln Z}{\delta\lambda_1(t)}, \tag{96}$$

$$\langle\langle E(t_1)E(t_2)\rangle\rangle = \frac{\delta \ln Z}{\delta\lambda_2(t_1, t_2)} - \frac{\delta \ln Z}{\delta\lambda_1(t_1)}\frac{\delta \ln Z}{\delta\lambda_1(t_2)}. \tag{96a}$$

Unlike the master-equation approach the surprisal analysis is not based on the assumption of a jump mechanism in the stochastic process. However, at least in principle, the two theories can be made consistent with each other by a suitable choice of the first two moments of the energy of a molecule. We have failed to derive a closed

analytical relationship between the cumulants of energy and the transition rates $W_{vv'}$ entering the master equation (1). Nevertheless, if we compare Eqs. (11) and (94) we see that they display the same type of statistical behavior. If in Eq. (94) we come back to the discrete time description used in Section 2, Eq. (21), and perform a sum over the initial state v_0 of the molecule we see that both for the markovian systems described by the master equation (1) and for the systems described by using the surprisal analysis (Eqs. (94)–(96′)) the joint probability P_m has the same structure. Namely, it can be factored into a sum of products of positive factors depending on two successive states (v_0, v_1), (v_1, v_2), ... In spite of this similar structure the systems described by Eqs. (94)–(96a) may have a more complicated behavior than the markovian jump systems described by Eq. (1). Joint probabilities factorizable into sums of products of positive factors depending on (v_0, v_1), (v_1, v_2), ... may also occur for semi-markovian processes described by a continuous-time random walk (CTRW) [21] or by a system of age-dependent master equations (ADME) [22]. Although we cannot give a formal proof, it is plausible to assume that a suitable choice of the first two moments of the energy would lead to a 'pure' markovian dynamics. In particular, if we drop the constraint (93a) we recover the independent stochastic process of the Zubarev–Kalashnikov type mentioned in Section 2.

Since the constraints (93)–(93a) assign certain values to the first two cumulants of the energy and say nothing about the superior cumulants, it would seem plausible that the fluctuations of energy should be gaussian. However, this is not necessarily the case. The only thing prescribed by the constraints (93)–(93a) is the degree of statistical dependence of the process, i.e. the possible correlations between the successive states of a molecule. To study the fluctuations of energy we use Eq. (43) for the probability density functional $\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[\mathbf{F}(t')]$ of mesoscopic state variables and the expression (44) for the corresponding characteristic functional $G[\boldsymbol{\sigma}(t')]$. As in this case in Eq. (43) we have a product of two delta functionals, depending on $F_{11} = E$ and F_{12} and we can decompose the integration measure $\mathrm{D}[\mathbf{F}(t')]$ into the product of two integration measures

$$\mathrm{D}[\mathbf{F}(t')] = \mathrm{D}[F_{11}(t')]\,\mathrm{D}[F_{12}(t')] = \mathrm{D}[E(t')]\,\mathrm{D}[F_{12}(t')]. \tag{97}$$

As the function $F_{12}(t'_2)$ does not have a direct physical significance, in Eq. (43) we integrate over it, resulting in

$$\mathscr{P}[E(t')]\,\mathrm{D}[E(t')] = \mathrm{D}[E(t')]\,\overline{\iint}\,\mathscr{P}[\mathbf{F}(t')]\,\mathrm{D}[F_{12}(t'_1, t'_2)]$$

$$= Z^{-1}\,\overline{\sum\sum}\exp\left(-\int_{t_0}^{t}\lambda_1(t')\,E(t')\,\mathrm{d}t' - \int_{t_0}^{t}\int_{t_0}^{t}\lambda_2(t'_1, t'_2)\,E(t'_1)\,E(t'_2)\,\mathrm{d}t'_1\,\mathrm{d}t'_2\right)$$

$$\times\,\delta[E(t') - E_v(t')]\,\mathrm{D}[E(t')]. \tag{98}$$

The characteristic functional $G(\sigma(t'))$ corresponding to the probability density functional $\mathscr{P}[E(t')]\mathrm{D}[E(t')]$ is equal to

$$G[\sigma(t')] = \overline{\iint} \exp\left(\mathrm{i}\int \sigma(t')E(t')\,\mathrm{d}t'\right)\mathscr{P}[E(t')]\,\mathrm{D}[E(t')]$$

$$= \frac{Z[\lambda_1(t') - \mathrm{i}\sigma(t'), \lambda_{12}(t'_1, t'_2)]}{Z[\lambda_1(t'), \lambda_{12}(t'_1, t'_2)]}. \tag{99}$$

By combining Eqs. (44)–(45) and (99) we can express all central moments and cumulants of the energy in terms of the partition functional Z. The higher order cumulants are generally different from zero, which confirms the non-gaussian character of energy fluctuations.

8. Random processes with complete connections

The problem of molecular dynamics considered in Sections 2 and 7 shows that the constraints determine the type of statistical dependence of the resulting stochastic process. If in addition to the first two moments (93)–(93') of the energy we require that the moments of order $2, 3, \ldots, M$ have assigned values

$$\langle E_1(t'_1) \ldots E(t'_l)\rangle, \quad l = 1, \ldots, M, \quad t \leqslant t'_1, \ldots, t'_M \leqslant t_0, \tag{100}$$

then the m-gate joint probability density P_m can be factored into a sum of products of positive factors depending at most on M labels $v_{l_1}, \ldots, v_{l_M}$. That is, the memory acts over at most $(M-1)$ steps. In particular, for $M \to \infty$, we have an infinite memory, a situation which can be described by a random process with complete connections [23]. This is also true in the general case. For the constraints (27) with $m = 1, \ldots, M$, and where the functions $f_{um}(\boldsymbol{N}(t_1), t_1, \ldots, \boldsymbol{N}(t_m), t_m)$ cannot be decomposed in additive factors depending on $\boldsymbol{N}(t_i)$; $[\boldsymbol{N}(t_i), \boldsymbol{N}(t_j)]$; $[\boldsymbol{N}(t_i), \boldsymbol{N}(t_j), \boldsymbol{N}(t_k)]$; ..., i.e.

$$f_{um}(\boldsymbol{N}(t_1), t_1; \ldots; \boldsymbol{N}(t_m); t_m) \neq \sum\left[\varphi(\boldsymbol{N}(t_i), t_i) + \varphi(\boldsymbol{N}(t_i), t_i; \boldsymbol{N}(t_j), t_j) + \cdots\right], \tag{101}$$

then the memory acts at most over $(M-1)$ steps. For $M \to \infty$ we have a process with complete connections.

A possible way of describing random processes with complete connections is to generalize the formalism of age-dependent master equations (ADME) [22]. For a discrete random jump system in continuous time described by a state vector $\boldsymbol{N}$ we introduce [22] the age a of the state $\boldsymbol{N}$. By the age a we mean the time interval that has elapsed from the occurrence of the last jump up to the current time. We assume that the transition from the qth state $\boldsymbol{N}_q$ to the $(q+1)$th state $\boldsymbol{N}_{q+1}$ depends on the entire history of the process characterized by the succession of states $\boldsymbol{N}_0, \boldsymbol{N}_1, \ldots, \boldsymbol{N}_q$ as well as by the corresponding ages $a_0, a_1, \ldots, a_q$ of the states at the moments at which the transitions $\boldsymbol{N}_0 \to \boldsymbol{N}_1; \boldsymbol{N}_1 \to \boldsymbol{N}_2; \ldots; \boldsymbol{N}_{q-1} \to \boldsymbol{N}_q$ have taken place. The rate W_{q+1} of the

$(q+1)$th transition depends on the whole history of the process as well as on the final state vector $\boldsymbol{N}_{q+1}$:

$$W_{q+1} = W_{q+1}(\boldsymbol{N}_0, a_0; \ldots; \boldsymbol{N}_q, a_q \to \boldsymbol{N}_{q+1}), \qquad q = 0, 1, 2, \ldots . \tag{102}$$

Now we introduce the m-gate joint probability density

$$\mathscr{B}_q(\boldsymbol{N}_q, a_q; \boldsymbol{N}_{q-1}, a_{q-1}; \ldots; \boldsymbol{N}_0, a_0; t)\, \mathrm{d}a_q\, \mathrm{d}a_{q-1} \ldots \mathrm{d}a_0, \tag{103}$$

with

$$\sum_q \sum_{N_q} \cdots \sum_{N_0} \int_0^\infty \cdots \int_0^\infty \mathscr{B}_q \, \mathrm{d}a_q \cdots \mathrm{d}a_0 = 1 . \tag{104}$$

$\mathscr{B}_q \, \mathrm{d}a_q \ldots \mathrm{d}a_0$ is the probability that, at time t, the state of the system is $\boldsymbol{N}_q$, the age of the state $\boldsymbol{N}_q$ is between a_q and $a_q + \mathrm{d}a_q$ and that at a previous step q' $(q' = 0, \ldots, q-1)$ a transition from the state $\boldsymbol{N}_{q'}$ to the state $\boldsymbol{N}_{q'+1}$ took place and that at the moment of transition the age of the state $\boldsymbol{N}_{q'}$ was between $a_{q'}$ and $a_{q'} + \mathrm{d}a_{q'}$.

By generalizing the ADME formalism [22] we can construct a chain of evolution equations

$$\begin{aligned}(\partial_t + \partial_{a_q})\, \mathscr{B}_q(\boldsymbol{N}_q, a_q; \boldsymbol{N}_{q-1}, a_{q-1}; \ldots; \boldsymbol{N}_0, a_0; t) \\ = -\mathscr{B}_q(\boldsymbol{N}_q, a_q; \boldsymbol{N}_{q-1}, a_{q-1}; \ldots; \boldsymbol{N}_0, a_0; t)\, W_{q+1}(\boldsymbol{N}_0, a_0; \ldots; \boldsymbol{N}_q, a_q \to \boldsymbol{N}_{q+1}), \\ q = 0, 1, 2, \ldots \end{aligned} \tag{105}$$

$$\begin{aligned}\mathscr{B}_q(\boldsymbol{N}_q, 0; \boldsymbol{N}_{q-1}, a_{q-1}; \ldots; \boldsymbol{N}_0, a_0; t) = W_q(\boldsymbol{N}_0, a_0; \ldots; \boldsymbol{N}_{q-1}, a_{q-1} \to \boldsymbol{N}_q) \\ \times \mathscr{B}_{q-1}(\boldsymbol{N}_{q-1}, a_{q-1}; \ldots; \boldsymbol{N}_0, a_0; t), \quad q = 1, 2, \ldots \end{aligned} \tag{106}$$

with the initial condition

$$\mathscr{B}_q(t = 0) = \delta_{q0} \mathscr{B}_0(\boldsymbol{N}_0, a_0), \tag{107}$$

where $\mathscr{B}_0(\boldsymbol{N}_0, a_0)\, \mathrm{d}a_0$ is the initial age-state vector probability density. The ADME semi-markovian dynamics [22] corresponds to

$$W_{q+1} = W(\boldsymbol{N}_q, a_q \to \boldsymbol{N}_{q+1}), \quad \text{independent of } q; \boldsymbol{N}_0, a_0; \ldots; \boldsymbol{N}_{q-1}, a_{q-1}, \tag{108}$$

and the full markovian dynamics to

$$W_{q+1} = W(\boldsymbol{N}_q \to \boldsymbol{N}_{q+1}), \qquad \text{independent of } q; \boldsymbol{N}_0, a_0; \ldots; \boldsymbol{N}_{q-1}, a_{q-1}; a_q . \tag{109}$$

If W_{q+1} depends on the entire history of the process (Eq. (102)), then the stochastic process has infinite memory. This is a situation which can also be described by the maximum entropy formalism with the constraints (27) and (101) for $M \to \infty$. In spite of the physical similarity the mathematical formalism is different for the two models. As in the case of markovian dynamics, we assume that there must be a consistency relationship between the constraints (27) and the rates W_{q+1} (Eqs. (102)); unfortunately we have been unable to prove whether this relationship actually exists or not.

9. Conclusions

We have shown that statistical-temporal correlations can be incorporated into the maximum entropy formalism by a suitable choice of the constraints. In order to describe the memory effects the constraints should fulfill two different conditions: (a) they should be known at any time in the past and (b) they should depend on the values of the microscopic state variables at at least two different times. If the constraints depend only on the state variables at a single moment we obtain an independent random process of the Zubarev–Kalashnikov type. However, for a dependence on the state variables at two different moments a semi-markovian or markovian process results for which the memory acts over a single step. In general, if the constraints are defined in terms of the state variables at M different times, the memory acts over $(M-1)$ different steps and in the limit $M \to \infty$ we get a random process with complete connections.

Our approach leads to a new way of describing a stochastic process with memory. It is not based on the use of stochastic master equations or on the stochastic calculus, but rather on a time-dependent functional generalization of the formalism of equilibrium statistical thermodynamics. Although both this type of MIP and the stochastic equations describe the same type of physical systems, the quantitative relationships between these two descriptions are still unclear.

The MIP itself is not a physical theory but rather a method of inference of the most unbiased stochastic process compatible with a set of constraints. This is both an advantage and a disadvantage of the method. The advantage is that the corresponding mathematical formalism is simpler than in the case of stochastic equations used in the literature, while the disadvantage is that all physical information is contained in the constraints. Thus, a given type of stochastic behavior is an assumption rather than a result of the model.

It is rather surprising that for almost the entire forty years for which the MIP has been used in statistical mechanics, almost no attempts have been made to generate certain types of stochastic processes with memory starting from it. A possible explanation for this omission is that the most general constraints used in the literature are of the Zubarev–Kalashnikov type, and although more general than the constraints of the Mori type they do not describe any type of statistical dependence.

There are at least two possible applications of our approach. A promising field is the study of fractal random processes for which memory effects are important [24]; this is planned to be the subject of future research. Another direction would be the generalization of McLennan–Zubarev formal theory of non-equilibrium processes. In this context the MIP should be combined with the classical or quantum statistical-mechanical description of the system. The constraints should be chosen in such a way that the resulting non-equilibrium statistical operator be a solution of the classical or quantum-mechanical Liouville equation of the system. This is a very difficult project, and at this stage of research the possibilities of carrying it out are uncertain.

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References

[1] E.T. Jaynes, Phys. Rev. 106 (1957) 620; 108 (1957) 171; in: Brandeis University Summer Institute Lectures in Theoretical Physics, Statistical Physics 3, ed. K.W. Ford (Benjamin, New York, 1963).
[2] H. Mori, Phys. Rev. 112 (1958) 1829; 115 (1959) 298;
H. Mori, I. Oppenheim and J. Ross, in: Studies in Statistical Mechanics, eds. J. de Boer and G.E. Uhlenbeck (North-Holland, Amsterdam, 1962) p. 271;
J.W. Dufty, Phys. Rev. 176 (1968) 398.
[3] D.N. Zubarev and V.P. Kalashnikov, Physica 46 (1970) 550.
[4] J.A. McLennan, Phys. Rev. 115 (1959) 1405; Phys. Fluids 3 (1960) 495; Adv. Chem. Phys., 5 (1963) 261; Introduction to Nonequilibrium Statistical Mechanics (Prentice Hall, Englewood Cliffs, 1989) Ch. 9.
[5] D.N. Zubarev, Sov. Phys. Doklady. 6 (1962) 776; 10 (1965) 452; 10 (1966) 850; Fortschr. Phys. 18 (1970) 125; Nonequilibrium Statistical Thermodynamics (Consultants Bureau, New York, 1974).
[6] F. Schlögl, Phys. Rep. 62(4) (1980) 268.
[7] W.T. Grandy, Jr., Phys. Rep. 62(3) (1980) 175; Foundations of Statistical Mechanics, vol. II: Nonequilibrium Phenomena (Reidel, Dordrecht, 1988) Chs. 2–5.
[8] S. Kullback, Ann. Math. Stat. 22 (1951) 79.
[9] Y. Tikochinsky and R.D. Levine, J. Math. Phys. 25(7) (1984) 2160.
[10] R.D. Levine, J. Phys. A.: Math. Gen. 13 (1980) 91.
[11] R.D. Levine and M. Tribus, eds., The Maximum Entropy Formalism (MIT press, Cambridge, MH, 1978) and references therein.
[12] J.L. Kinsey, J. Chem. Phys. 54 (1971) 1206;
A. Ben-Shaul, R.D. Levine and R.B. Bernstein, J. Chem. Phys. 57 (1972)5427;
R.D. Levine, Ann. Rev. Phys. Chem. 29 (1978) 59; Adv. Chem. Phys. 70 (1988) 53;
R.D. Levine and R.B. Bernstein, Molecular Reaction Dynamics and Chemical Reactivity (Oxford University Press, New York, 1987)
J.I. Steinfeld, J.S. Francisco and W.L. Hase, Chemical Kinetics and Dynamics (Prentice Hall, Englewood Cliffs, 1989) Chs. 13–14.
[13] E.W. Montroll and M.F. Shelsinger, in: Nonequilibrium Phenomena II, eds. J.L. Lebowitz and E.W. Montroll (North-Holland, Amsterdam, 1984) Ch. 1, pp. 108–112; J. Stat. Phys. 32(2) (1983) 209–230.
[14] M.O. Vlad, Phys. Lett. A189 (1994) 299; J. Math. Phys. 35(2) (1994) 796; Phys. Rev. E48 (1993) 3406.
[15] H.C. Andersen, I. Oppenheim, K.E. Shuler and G.H. Weiss, J. Math. Phys. 5 (1964) 522.
[16] H. Kleinert, Path Integrals in Quantum Mechanics Statistics and Polymer Science (World Scientific, Singapore, 1990).
[17] A. Einstein, Ann. der Phys. 11 (1903) 170.
[18] R.F. Greene and H.B. Callen, Phys. Rev. 83 (1951) 1231.
[19] H. Callen, in: Nonequilibrium Thermodynamics, Variational Techniques and Stability, eds. R.J. Donnelly, R. Hermann and I. Prigogine (University of Chicago, Chicago, 1966) p. 227.
[20] M.O. Vlad and J. Ross, J. Chem. Phys. 100 (1994) 7295.
[21] G.H. Weiss and R.J. Rubin, Adv. Chem. Phys. 52 (1983) 363 and references therein;
J.W. Haus and K.W. Kehr, Phys. Rep. 150 (1987) 263 and references therein.
[22] M.O. Vlad and A. Pop, Physica A155 (1989) 276; J. Phys. A.: Math. Gen. A 22 (1989) 3845;
M.O. Vlad, J. Phys. A.: Math. Gen. 20 (1987) 3367; Phys. Rev A 45 (1992) 3600.
[23] M. Iosifescu and S. Grigorescu, Dependence with Complete Connections and Applications (Cambridge Tracts, Cambridge, 1989).
[24] M.O. Vlad, J. Phys. A.: Math. Gen. 25 (1992) 749; 26 (1993) 4183; Physica A 197 (1993) 167; 207 (1994) 483; 208 (1994) 167.