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Fluctuation dynamics, thermodynamic analogies and ergodic behavior for nonequilibrium-independent rate processes with dynamical disorder

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Abstract

The stochastic properties of the sojourn times attached to a Markov process in continuous time and with a finite number of states are described by using a statistical ensemble approach. This approach is applied for investigating the large time behavior of independent rate processes with dynamical disorder. The large time behavior of the system is described in terms of an effective transport operator which can be expressed as a static average with respect to the stochastic properties of the sojourn times. The method is illustrated by the generalization of the Van den Broeck approach to the generalized Taylor diffusion. Explicit formulas for the effective transport coefficients and for the fluctuations of the concentration fields are derived. The results are used for extending the non-equilibrium generalized thermodynamic formalisms suggested by Keizer and by Ross, Hunt and Hunt to systems with dynamical disorder. It is shown that the logarithm of the probability density functional of concentration fluctuations is a Lyapunov functional of the effective transport equation. This Lyapunov functional plays the role of a generalized nonequilibrium thermodynamic potential which may serve as a basis for a thermodynamic description of the average behavior of the system. The existence and stability of a steady state can be expressed as an extremum condition for the Lyapunov functional. For Taylor diffusion in an external electric field different from zero the generalized potential has a structure similar to the Helmholtz free energy rather than to the entropy. A generalized chemical potential is derived as the functional derivative of the Lyapunov functional with respect to the concentration field; the gradient of this generalized chemical potential is the driving force which determines the structure of the effective transport equation.

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1. Introduction

In the preceding article, herein called I [1], we have developed a new method of describing the dynamics of Markov processes in continuous time with a finite number of states. This method is based on the use of the total sojourn times and of the total number of transition events attached to the different states of the system as additional stochastic variables. The stochastic properties of these random variables can be computed in terms of the Green function attached to the master equation of the process. In the limit of large times the sojourn times become Gaussian random variables and their cumulants of first and second order increase linearly in time. This linear increase of the cumulants ensures the ergodicity of the Markov process.

In this article we use the general results developed in paper I for developing a systematic approach for computing transport coefficients and effective rate coefficients for rate and transport processes in systems with dynamical disorder. The study of dynamical disorder is of interest in connection with the analysis of line shape in spectroscopy [2–9], of catastrophic earthquakes [10] of the Taylor problem in hydrodynamics [11,12], of the transport processes with dynamical percolation [13] of very fast chemical processes without activation barriers [14] the description of fluorescence depolarization [15] of the collective orientational relaxation in liquids [16] and of protein dynamics [17–19]. The evaluation of the time dependence of the average state variables for these systems is a difficult problem which can be solved only in a few particular cases. In this article we show that the formalism developed in paper I is a useful tool in studying some rate processes with dynamical disorder.

The structure of the paper is as follows. In Section 2 the results derived in paper I serve as a basis for constructing some thermodynamic analogies for nonequilibrium systems. In Section 3 the analogies developed in Section 2 are used for developing a general approach for investigating the large time behavior of Markov transport processes with dynamical disorder. In Sections 4 and 5 the method of studying the rate processes with dynamical disorder is illustrated in the particular case of Taylor diffusion in an external force field. Finally, the main results of our approach are summarized in Section 6.

2. Ensemble description for the statistics of sojourn times

In paper I [1], we have studied a Markov process in continuous time with M discrete states. For such a system the probability $P_j(t)$ that at time t the state of the system is j is the solution of the master equation

$$\frac{dP_j(t)}{dt} = \sum_{j' \neq j} P_{j'}(t)W_{j'j} - P_j(t)\Omega_j, \quad j, j' = 1, \dots, M, \quad (2.1)$$

with

$$\Omega_j = \sum_{j' \neq j} W_{jj'}, \quad j = 1, \dots, M, \quad (2.2)$$

where $W_{jj'}$ is the transition rate from the state j to the state j' and Ω_j is the total transition rate from the state j to other any other states and $P_j(t)$ is the probability that at time the state of the system is j . For a given time interval of length t for each possible state of the system, $j = 1, \dots, M$, we have introduced two different random variables: the total sojourn time θ_j of the system in the state j and the total number q_j of transition events from the state j to other states in the time interval considered. We have shown that for large times the cumulants of first and second order of these random variables are proportional to the length of the time interval considered. Moreover, we have shown that in this limit the sojourn times are Gaussian random variables characterized by the probability distribution

$$\mathcal{R}(\boldsymbol{\theta}; t) \sim (2\pi t)^{-M/2} [\det|\mathbf{bC} + \mathbf{C}^+ \mathbf{b}|]^{-1/2} \times \exp\left\{-\frac{1}{2}(\boldsymbol{\theta} - t\mathbf{P}^{st})[t(\mathbf{bC} + \mathbf{C}^+ \mathbf{b})]^{-1}(\boldsymbol{\theta} - t\mathbf{P}^{st})^+\right\} \quad \text{as } t \rightarrow \infty, \quad (2.3)$$

where the matrices \mathbf{b} and \mathbf{C} are given by

$$\boldsymbol{\theta} = [\theta_j], \quad \mathbf{P}^{st} = [P_j^{st}], \quad \mathbf{b} = [P_j^{st} \delta_{jj'}], \quad \mathbf{C} = [C_{jj'}]; \quad (2.4)$$

the steady-state probabilities P_j^{st} , $j = 1, \dots, M$, are given by the stationary solution of the master equation (2.1) and the matrix elements $C_{jj'}$ are given by the nontrivial solution of the linear equations

$$P_j^{st} - \delta_{jj'} = \sum_{u \neq j} C_{ju} W_{uj'} - C_{jj'} \Omega_j, \quad j, j' = 1, \dots, M, \quad (2.5)$$

$$\sum_{j'} C_{jj'} = 0, \quad j = 1, \dots, M. \quad (2.6)$$

The cumulants of first and second order of the distribution (2.3) are linear functions of time:

$$\langle \theta_u(t) \rangle \sim P_u^{st} t \quad \text{as } t \rightarrow \infty, \quad (2.7)$$

$$\langle \Delta \theta_{u_1}(t) \Delta \theta_{u_2}(t) \rangle \sim (P_{u_1}^{st} C_{u_1 u_2} + P_{u_2}^{st} C_{u_2 u_1}) t \quad \text{as } t \rightarrow \infty. \quad (2.8)$$

This linear dependence of time ensures the ergodicity of the Markov process considered.

In this section we study the statistical properties of the sojourn times in the limit $t \rightarrow \infty$ by using a statistical ensemble description. Instead of studying a single system, we consider a large number \mathcal{N} of identical replicas of it and investigate the statistical behavior of their ensemble. We express the number \mathcal{N} of systems as a sum (or rather as an integral) of the densities $\eta(\boldsymbol{\theta}; t)$ attached to the different sets of sojourn times:

$$\mathcal{N} = \int \eta(\boldsymbol{\theta}; t) d\boldsymbol{\theta}. \quad (2.9)$$

Here $\eta(\boldsymbol{\theta}; t)d\boldsymbol{\theta}$ is the number of replicas with the sojourn times between θ_u and $\theta_u + d\theta_u$, $u = 1, \dots, M$, corresponding to the total time interval of length t . We are interested in the evaluation of the stochastic properties of the density of states $\eta(\boldsymbol{\theta}; t)$.

We introduce the characteristic functional

$$\Xi[K(\boldsymbol{\theta}; t)] = \left\langle \exp \left\{ i \int K(\boldsymbol{\theta}; t) \eta(\boldsymbol{\theta}; t) d\boldsymbol{\theta} \right\} \right\rangle, \tag{2.10}$$

where the average is taken over all possible random functions $\eta(\boldsymbol{\theta}; t)$. For evaluation of the characteristic function $\Xi[K(\boldsymbol{\theta}; t)]$, we express the density of states $\eta(\boldsymbol{\theta}; t)$ as a sum of delta functions, each delta function corresponding to a different replica of the system:

$$\eta(\boldsymbol{\theta}; t) = \sum_{\ell=1}^{\mathcal{N}} \delta(\boldsymbol{\theta} - \boldsymbol{\theta}_\ell), \tag{2.11}$$

where the statistics of the vector $\boldsymbol{\theta}_\ell$, $\ell = 1, \dots, \mathcal{N}$ of the sojourn times attached to the different replicas are described by the Gaussian probability density $\mathcal{R}(\boldsymbol{\theta}; t)$ given by Eq. (2.3). Since by definition all replicas are independent, the vectors $\boldsymbol{\theta}_\ell$, $\ell = 1, \dots, \mathcal{N}$ are independent random variables selected from the probability density $\mathcal{R}(\boldsymbol{\theta}; t)$. It follows that the characteristic functional $\Xi[K(\boldsymbol{\theta}; t)]$ can be evaluated by inserting Eq. (2.11) into Eq. (2.10) and by computing the average in terms of \mathcal{N} probability densities of the type (2.3), $\mathcal{R}(\boldsymbol{\theta}_1; t), \dots, \mathcal{R}(\boldsymbol{\theta}_{\mathcal{N}}; t)$ attached to the different replicas of the system:

$$\begin{aligned} \Xi[K(\boldsymbol{\theta}; t)] &= \int \dots \int \prod_u \{ \mathcal{R}(\boldsymbol{\theta}_u; t) \} \exp \left\{ i \sum_u K(\boldsymbol{\theta}_u; t) \right\} d\boldsymbol{\theta}_1 \dots d\boldsymbol{\theta}_{\mathcal{N}}, \\ &= \left\{ 1 + \int \{ \exp[iK(\boldsymbol{\theta}; t)] - 1 \} \mathcal{R}(\boldsymbol{\theta}; t) d\boldsymbol{\theta} \right\}^{\mathcal{N}}. \end{aligned} \tag{2.12}$$

The cumulants $\langle\langle \eta(\boldsymbol{\theta}_1; t) \dots \eta(\boldsymbol{\theta}_m; t) \rangle\rangle$, $m = 1, 2, \dots$ of the density of states are defined by a functional Taylor expansion of the logarithm of the characteristic functional $\Xi[K(\boldsymbol{\theta}; t)]$

$$\ln \Xi[K(\boldsymbol{\theta}; t)] = \sum_{m=1}^{\infty} \frac{i^m}{m!} \langle\langle \eta(\boldsymbol{\theta}_1; t) \dots \eta(\boldsymbol{\theta}_m; t) \rangle\rangle K(\boldsymbol{\theta}_1; t) \dots K(\boldsymbol{\theta}_m; t) d\boldsymbol{\theta}_1 \dots d\boldsymbol{\theta}_m. \tag{2.13}$$

By expanding the r.h.s of Eq. (2.12) in a functional Taylor series in $K(\boldsymbol{\theta}; t)$ and comparing the coefficients of the resulting expansion with Eq. (2.13) we get the following expressions for the cumulants:

$$\begin{aligned} \langle\langle \eta(\boldsymbol{\theta}_1; t) \dots \eta(\boldsymbol{\theta}_m; t) \rangle\rangle &= \sum_{n=1}^m \sum_{\beta_1 \geq 1} \dots \sum_{\beta_n \geq 1} \delta_{n(\sum_u \beta_u)} \mathcal{N}^{-(n-1)} \\ &\times \frac{(-1)^{n-1}}{n} \int \dots \int \langle \eta(\boldsymbol{\theta}'_1; t) \rangle \dots \langle \eta(\boldsymbol{\theta}'_n; t) \rangle \dots d\boldsymbol{\theta}'_1 \dots d\boldsymbol{\theta}'_n \frac{m!}{\prod_u \beta_u!} \delta(\boldsymbol{\theta}_1 - \boldsymbol{\theta}'_1) \dots \\ &\times \delta(\boldsymbol{\theta}_{\beta_1} - \boldsymbol{\theta}'_1) \dots \delta(\boldsymbol{\theta}_{\beta_1 + \dots + \beta_{n-1} + 1} - \boldsymbol{\theta}'_n) \dots \delta(\boldsymbol{\theta}_{\beta_1 + \dots + \beta_n} - \boldsymbol{\theta}'_n), \end{aligned} \tag{2.14}$$

where

$$\langle \eta(\boldsymbol{\theta}; t) \rangle = \mathcal{N} \mathcal{R}(\boldsymbol{\theta}; t) \tag{2.15}$$

is the average density of states.

By considering a limit of the thermodynamic type for which the number of replicas tends to infinity but the average density of states remains constant

$$\mathcal{N} \rightarrow \infty \quad \text{with} \quad \langle \eta(\boldsymbol{\theta}; t) \rangle = \text{constant} , \tag{2.16}$$

the expressions (2.14) for the cumulants of the density of states take a form characteristic for a Poissonian process

$$\langle \langle \eta(\boldsymbol{\theta}_1; t) \dots \eta(\boldsymbol{\theta}_m; t) \rangle \rangle = \langle \eta(\boldsymbol{\theta}_1; t) \rangle \delta(\boldsymbol{\theta}_2 - \boldsymbol{\theta}_1) \dots \delta(\boldsymbol{\theta}_{m-1} - \boldsymbol{\theta}_m) , \tag{2.17}$$

and the characteristic functional $\Xi[K(\boldsymbol{\theta}; t)]$ has a Poissonian form

$$\Xi[K(\boldsymbol{\theta}; t)] = \exp \left\{ \mathcal{N} \int \{ \exp[iK(\boldsymbol{\theta}; t)] - 1 \} \mathcal{R}(\boldsymbol{\theta}; t) d\boldsymbol{\theta} \right\} . \tag{2.18}$$

In particular, if we consider small but finite cells in the $\boldsymbol{\theta}$ -space and denote by

$$\Delta \mathcal{N}(\boldsymbol{\theta}_u; t) \quad \text{with} \quad \sum_u \Delta \mathcal{N}(\boldsymbol{\theta}_u; t) = \mathcal{N} , \tag{2.19}$$

the numbers of replicas attached to these cells, then the corresponding probability distribution of $\Delta \mathcal{N}(\boldsymbol{\theta}_u; t)$ is a multivariate Poissonian:

$$P(\Delta \mathcal{N}(\boldsymbol{\theta}_1; t), \Delta \mathcal{N}(\boldsymbol{\theta}_2; t), \dots) = \prod_u \left\{ \frac{[\langle \eta(\boldsymbol{\theta}_u; t) \rangle \Delta \boldsymbol{\theta}_u]^{ \Delta \mathcal{N}(\boldsymbol{\theta}_u; t) }}{\Delta \mathcal{N}(\boldsymbol{\theta}_u; t)!} \right. \\ \left. \times \exp[-\langle \eta(\boldsymbol{\theta}_u; t) \rangle \Delta \boldsymbol{\theta}_u] \right\} , \tag{2.20}$$

from which, by using Stirling's formula we get

$$P(\Delta \mathcal{N}(\boldsymbol{\theta}_1; t), \Delta \mathcal{N}(\boldsymbol{\theta}_2; t), \dots) = \prod_u \left\{ \frac{\Delta \mathcal{N}(\boldsymbol{\theta}_u; t)}{\sqrt{2\pi \langle \eta(\boldsymbol{\theta}_u; t) \rangle \Delta \boldsymbol{\theta}_u}} \right\} \\ \times \exp \{ -\mathcal{N} \Phi[\Delta \mathcal{N}(\boldsymbol{\theta}; t)] \} , \tag{2.21}$$

where

$$\Phi[\Delta \mathcal{N}(\boldsymbol{\theta}; t)] = \sum_v \frac{\Delta \mathcal{N}(\boldsymbol{\theta}_v; t)}{\mathcal{N}} \ln \left\{ \frac{\Delta \mathcal{N}(\boldsymbol{\theta}_v; t)}{\langle \eta(\boldsymbol{\theta}_v; t) \rangle \Delta \boldsymbol{\theta}_v} \right\} , \tag{2.22}$$

is a potential function which characterizes the strength of fluctuations of the density of states. In the continuous limit $\Delta \boldsymbol{\theta}_v \rightarrow 0$ the expression (2.22) for the potential $\Phi[\Delta \mathcal{N}(\boldsymbol{\theta}; t)]$ becomes

$$\Phi[\xi(\boldsymbol{\theta}; t)] = \int \xi(\boldsymbol{\theta}; t) \ln \{ \xi(\boldsymbol{\theta}; t) / \mathcal{R}(\boldsymbol{\theta}; t) \} d\boldsymbol{\theta} , \tag{2.23}$$

where

$$\xi(\theta; t) = \lim_{\mathcal{N} \rightarrow \infty} \lim_{\Delta\theta \rightarrow 0} \frac{\Delta\mathcal{N}(\theta; t)}{\mathcal{N} \Delta\theta} \quad \text{with} \quad \int \xi(\theta; t) d\theta = 1 \tag{2.24}$$

is the relative frequency of states with sojourn times between θ_u and $\theta_u + d\theta_u$, $u = 1, \dots, M$, respectively. Note that the fluctuation potential $\Phi[\xi(\theta; t)]$ has the structure of the information gain (Kullback information [20–22]) acquired when for a Markov process characterized by the theoretical probability density of the sojourn times $\mathcal{R}(\theta; t)$ we measure an observed frequency function $\xi(\theta; t)$. The structure of the stochastic potential $\Phi[\xi(\theta; t)]$ given by Eq. (2.23) outlines the analogies with the nonequilibrium thermodynamic theories of Keizer and of Ross et al. The fluctuation formula (2.21) is the analogue of Einstein’s fluctuation formula from equilibrium thermodynamics and is similar to its nonequilibrium analogs suggested by Keizer [23] and by Ross et al. [24]. The stochastic potential $\Phi[\xi(\theta; t)]$ is analogous to a generalized thermodynamic state function. In terms of the fluctuating potential $\Phi[\xi(\theta; t)]$, we can give the following variational formulation for the existence and stability of the probability density $\mathcal{R}(\theta; t)$:

$$\delta\Phi[\xi(\theta; t) = \mathcal{R}(\theta; t)] = 0, \tag{2.25}$$

$$\delta^2\Phi[\xi(\theta; t)] > 0, \tag{2.26}$$

which corresponds to a minimum of the fluctuating potential $\Phi[\xi(\theta; t)]$ and to a maximum of the probability $P(\Delta\mathcal{N}(\theta_1; t), \Delta\mathcal{N}(\theta_2; t), \dots)$ for $\xi(\theta; t) = \mathcal{R}(\theta; t)$. Eqs. (2.25) and (2.26) are similar to the conditions for the existence and stability of nonequilibrium steady states in the thermodynamic theories of Keizer [23] and of Ross et al. [24]. The analogies with these theories can be further developed by noticing that we can write down an effective Fokker–Planck evolution equation for the average frequency density $\bar{\xi}(\theta; t)$ of the sojourn times

$$\begin{aligned} \partial_1 \bar{\xi}(\theta; t) = & - \sum_u P_u^{st} [\partial \bar{\xi}(\theta; t) / \partial \theta_u] \\ & + \frac{1}{2} \sum_{u_1, u_2} [P_{u_1}^{st} C_{u_1 u_2} + P_{u_2}^{st} C_{u_2 u_1}] [\partial^2 \bar{\xi}(\theta; t) / \partial \theta_{u_1} \partial \theta_{u_2}]. \end{aligned} \tag{2.27}$$

This Fokker–Planck equation for the frequency density $\bar{\xi}(\theta; t)$ has the normal solution

$$\bar{\xi}(\theta; t) = \mathcal{R}(\theta; t), \tag{2.28}$$

where $\mathcal{R}(\theta; t)$ is given by Eq. (2.1). However, not all solutions of Eq. (2.27) have this form; for small to moderately large times the solutions of Eq. (2.27) are convolutions of the initial condition for $\bar{\xi}(\theta; t)$ with the normal solution (2.28) which is also the Green function of Eq. (2.27). For large times, however, all transient solutions of Eq. (2.27) depending on different initial conditions tend towards the normal form (2.28) which is independent of the initial conditions. An important difference in comparison with the theories of Keizer [23] and the Ross et al. [24] is that these theories investigate the

eventual emergence of a nonequilibrium steady state in the long run. In contrast, the normal solution (2.28) is time-dependent and thus in our case the process is non-stationary even in the limit $t \rightarrow \infty$

$$\bar{\xi}(\theta; t) \rightarrow \mathcal{R}(\theta; t) \text{ time-independent as } t \rightarrow \infty. \quad (2.29)$$

Despite the time dependence of the probability $\mathcal{R}(\theta; t)$ the development of a thermodynamic theory is still possible because for large time all information concerning the initial state of the system has been lost. The asymptotic behavior (2.29) is ensured by the fact that the fluctuation potential $\Phi[\xi(\theta; t)]$ is a Lyapunov function of the Fokker-Planck equation (2.27), that is, it fulfills the conditions:

$$\Phi[\xi(\theta; t) \neq \mathcal{R}(\theta; t)] > 0, \quad \Phi[\xi(\theta; t) = \mathcal{R}(\theta; t)] = 0, \quad (2.30)$$

$$\dot{\Phi}[\xi(\theta; t) \neq \mathcal{R}(\theta; t)] < 0, \quad \dot{\Phi}[\xi(\theta; t) = \mathcal{R}(\theta; t)] = 0. \quad (2.31)$$

The proof of Eqs. (2.30)–(2.31) is lengthy but standard. For saving space and avoiding repetition the detailed derivation is not given here; for similar proofs see Refs. [25]–[27] and Section 5. The derivation is based on the fact that the probability diffusion tensor in Eq. (2.27), $P_{u_1}^{st} C_{u_1 u_2} + P_{u_2}^{st} C_{u_2 u_1}$, is given, up to a positive proportionality factor, by a covariance matrix (see Eqs. (2.8)) and it is therefore positive definite for fluctuations different from zero. The Lyapunov property (2.30)–(2.31) of the fluctuating potential $\Phi[\xi(\theta; t)]$ is closely related to the variational conditions (2.25)–(2.26) and may serve as a basis for the development of a thermodynamic formalism similar to the formalisms suggested by Keizer [23] and by Ross, Hunt and Hunt [24]. Some aspects of this formalism are presented in Section 5.

3. General approach to independent transport processes with dynamical disorder

A simple application of the ergodic property of Markov processes is the investigation of the large time behavior of rate or transport processes with dynamical disorder. Our method of analysis is very simple: we express a realization of the random function which describes the behavior of the system in terms of the total sojourn times attached to the different states and then we evaluate the probability density functional of the random function or the corresponding mean value by averaging a given realization over all possible random variations of the sojourn times in the limit $t \rightarrow \infty$.

In this section we consider a general transport mechanism with dynamical disorder which includes Van den Broeck's approach to Taylor diffusion [11,12] as a particular case. We investigate the spreading of a large number of noninteracting particles initially placed in the vicinity of the origin of a coordinate system in d_s -dimensional space ($d_s = 1, 2, 3$). The particles may exist in different M states $j = 1, 2, \dots, M$. Throughout time the state of the particles change, the dynamics of this change being described by a Markov process. For each different state the motion of the particle is described by a different transport equation and by different transport coefficients. Our

goal is to investigate the main features of the spreading process in the limit of large times.

For a given state j of a particle we introduce the probability $g_j(\mathbf{r}; t)d\mathbf{r}$ that the position of the particle at time t is between $d\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ provided that at time $t = 0$ its position was $\mathbf{r} = 0$. This probability is the solution of a partial differential or integral transport equation of the type

$$\partial_t g_j(\mathbf{r}; t) = \mathbb{T}_j g_j(\mathbf{r}; t) \text{ with } g_j(\mathbf{r}; t = 0) = \delta(\mathbf{r}), \tag{3.1}$$

where \mathbb{T}_j is a translationally invariant linear differential or integral operator. For example, \mathbb{T}_j can have the form of a master or of a Fokker–Planck operator

$$\mathbb{T}_j g_j(\mathbf{r}; t) = \int \mathcal{W}_j(\mathbf{r} - \mathbf{r}') g_j(\mathbf{r}'; t) d\mathbf{r}' - g_j(\mathbf{r}; t) \int \mathcal{W}_j(\mathbf{r}' - \mathbf{r}) d\mathbf{r}', \tag{3.2}$$

$$\mathbb{T}_j g_j(\mathbf{r}; t) = -\nabla \cdot [\mathbf{v}_j g_j(\mathbf{r}; t)] + \sum_u \sum_{u'} D_{uu'}^{(j)} [\partial^2 g_j(\mathbf{r}; t) / \partial r_u \partial r_{u'}], \tag{3.3}$$

where $\mathcal{W}_j(\mathbf{r} - \mathbf{r}')$, \mathbf{v}_j and $[D_{uu'}^{(j)}], j = 1, \dots, M$ are transition rates, drift velocity vectors and diffusion tensors attached to the different states of a particle.

The dynamics of the process can be described in terms of the joint probability distribution

$$\rho_j(\mathbf{r}; t) d\mathbf{r} \quad \text{with} \quad \sum_j \int \rho_j(\mathbf{r}; t) d\mathbf{r} = 1, \tag{3.4}$$

that at time t the state of the particle is j and that its position is between $d\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$. The probability density $\rho_j(\mathbf{r}; t)$ obeys a compound evolution equation

$$\partial_t \rho_j(\mathbf{r}; t) = \mathbb{T}_j \rho_j(\mathbf{r}; t) + \sum_{j' \neq j} \rho_{j'}(\mathbf{r}; t) W_{j'j} - \rho_j(\mathbf{r}; t) \Omega_j, \tag{3.5}$$

with the initial condition

$$\rho_j(\mathbf{r}; t = 0) = \delta(\mathbf{r}) P_j(t = 0). \tag{3.6}$$

For studying the asymptotic behavior of $\rho_j(\mathbf{r}; t)$ as $t \rightarrow \infty$ we take advantage of the translational invariance of Eq. (3.5) and use the Fourier transformation technique. Eqs. (3.5) and (3.6) become

$$\partial_t \bar{\rho}_j(\mathbf{k}; t) = \bar{\mathbb{T}}_j(\mathbf{k}) \bar{\rho}_j(\mathbf{k}; t) + \sum_{j' \neq j} \bar{\rho}_{j'}(\mathbf{k}; t) W_{j'j} - \bar{\rho}_j(\mathbf{k}; t) \Omega_j, \tag{3.7}$$

$$\bar{\rho}_j(\mathbf{k}; t = 0) = P_j(t = 0), \tag{3.8}$$

where

$$\bar{\rho}_j(\mathbf{k}; t) = \int \exp(ik \cdot \mathbf{r}) \rho_j(\mathbf{r}; t) d\mathbf{r}$$

is the Fourier transform of the joint probability density $\rho_j(\mathbf{r}; t)$, \mathbf{k} is the wave vector in the Fourier space conjugate to the position vector \mathbf{r} and $\bar{\mathbb{T}}_j(\mathbf{k})$ is the Fourier transform

of the transport operator \mathbb{T}_j . Usually, $\bar{\mathbb{T}}_j(\mathbf{k})$ is no longer an operator but rather a function of the wave vector \mathbf{k} .

In Appendix A we show that Eqs. (3.7) and (3.8) have exactly the same structure as the evolution equations

$$\partial_t \bar{R}_j(\boldsymbol{\omega}; t) = i\omega_j \bar{R}_j(\boldsymbol{\omega}; t) + \sum_{j' \neq j} \bar{R}_{j'}(\boldsymbol{\omega}; t) W_{jj'} - \bar{R}_j(\boldsymbol{\omega}; t) \Omega_j, \quad (3.9)$$

$$\bar{R}_j(\boldsymbol{\omega}; t) = P_j(t = 0), \quad (3.10)$$

for the Fourier transform of joint probability density $R_j(\boldsymbol{\theta}; t)$ of the sojourn times and the state of the particle

$$\bar{R}_j(\boldsymbol{\omega}; t) = \int \exp(i\boldsymbol{\theta} \cdot \boldsymbol{\omega}) R_j(\boldsymbol{\theta}; t) d\boldsymbol{\theta},$$

where $\boldsymbol{\omega}$ is the Fourier frequency vector conjugate to the vector $\boldsymbol{\theta}$ of sojourn times. The isomorphism of Eqs. (3.7) and (3.8) with Eqs. (3.9) and (3.10) allows us to express the Fourier transform of the joint probability density $\rho_j(\mathbf{r}; t)$ in terms of the Fourier transform of the marginal probability density $R_j(\boldsymbol{\theta}; t)$:

$$\bar{\rho}_j(\mathbf{k}; t) = \bar{R}_j(i\omega_u = \bar{\mathbb{T}}_u(\mathbf{k}), u = 1, \dots, M; t) = \int \exp\left[\sum_u \bar{\mathbb{T}}_u(\mathbf{k})\theta_u\right] R_j(\boldsymbol{\theta}; t) d\boldsymbol{\theta}. \quad (3.11)$$

The joint probability density $\rho_j(\mathbf{r}; t)$ can be computed from Eq. (3.11) by means of an inverse Fourier transformation

$$\begin{aligned} \rho_j(\mathbf{r}; t) &= (2\pi)^{-d_s} \int \exp(-i\mathbf{k} \cdot \mathbf{r}) \bar{\rho}_j(\mathbf{k}; t) d\mathbf{k} \\ &= (2\pi)^{-d_s} \int \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{k} \int \exp\left[\sum_u \bar{\mathbb{T}}_u(\mathbf{k})\theta_u\right] R_j(\boldsymbol{\theta}; t) d\boldsymbol{\theta}. \end{aligned} \quad (3.12)$$

Now we take the Fourier transform of the individual evolution equations (3.1) attached to the different states of the particle:

$$\partial_t \bar{g}_j(\mathbf{k}; t) = \bar{\mathbb{T}}_j(\mathbf{k}) \bar{g}_j(\mathbf{k}; t) \quad \text{with } \bar{g}_j(\mathbf{k}; t = 0) = 1, \quad (3.13)$$

where

$$\bar{g}_j(\mathbf{k}; t) = \int \exp(i\mathbf{k} \cdot \mathbf{r}) g_j(\mathbf{r}; t) d\mathbf{r}. \quad (3.14)$$

By integrating Eqs. (3.13) we arrive at

$$\bar{g}_j(\mathbf{k}; t) = \exp(t \bar{\mathbb{T}}_j(\mathbf{k})), \quad j = 1, \dots, M, \quad (3.15)$$

and thus Eq. (3.12) for the joint probability density $\rho_j(\mathbf{r}; t)$ can be expressed as

$$\begin{aligned} \rho_j(\mathbf{r}; t) &= \int R_j(\boldsymbol{\theta}; t) g_1(\mathbf{r}; \theta_1) \odot g_2(\mathbf{r}; \theta_2) \odot \cdots \odot g_M(\mathbf{r}; \theta_M) d\boldsymbol{\theta} \\ &= \int \cdots \int \delta\left(\mathbf{r} - \sum_{u=1}^M \mathbf{r}_u\right) g_1(\mathbf{r}_1; \theta_1) g_2(\mathbf{r}_2; \theta_2) \cdots g_M(\mathbf{r}_M; \theta_M) R_j(\boldsymbol{\theta}; t) d\boldsymbol{\theta} d\mathbf{r}_1 \dots d\mathbf{r}_M, \end{aligned} \tag{3.16}$$

where \odot denotes the space convolution product

$$f(\mathbf{r}) \odot g(\mathbf{r}) = \int f(\mathbf{r} - \mathbf{r}') g(\mathbf{r}') d\mathbf{r}', \tag{3.17}$$

and

$$\begin{aligned} g_1(\mathbf{r}; \theta_1) \odot g_2(\mathbf{r}; \theta_2) \odot \cdots \odot g_M(\mathbf{r}; \theta_M) \\ = \int \cdots \int \delta\left(\mathbf{r} - \sum_{u=1}^M \mathbf{r}_u\right) g_1(\mathbf{r}_1; \theta_1) g_2(\mathbf{r}_2; \theta_2) \cdots g_M(\mathbf{r}_M; \theta_M) d\mathbf{r}_1 \dots d\mathbf{r}_M \end{aligned} \tag{3.18}$$

is the M -fold space convolution product of the probability densities $g_1(\mathbf{r}; \theta_1)$, $g_2(\mathbf{r}; \theta_2)$, ..., $g_M(\mathbf{r}; \theta_M)$. Here we have taken into account that the product of many Fourier transforms corresponds to the multiple convolution product of the originals.

The physical significance of Eq. (3.16) is simple: the probability density $\rho_j(\mathbf{r}; t)$ of the state and position of a particle at time t is the average of a delta function

$$\delta\left(\mathbf{r} - \sum_{u=1}^M \mathbf{r}_u\right), \tag{3.19}$$

which expresses the contributions of the total displacements $\mathbf{r}_1, \dots, \mathbf{r}_M$ of a given particle corresponding to the different time intervals $\theta_1, \dots, \theta_M$ spent in the states $j = 1, \dots, M$, respectively, the average being taken over all possible values of the displacement vectors $\mathbf{r}_1, \dots, \mathbf{r}_M$ and of the sojourn times $j = 1, \dots, M$.

Since we are not interested in the state of a particle but only on its position we introduce the marginal probability density $\rho(\mathbf{r}; t)$ of the position of a particle, irrespective of its state. We have

$$\rho(\mathbf{r}; t) = \sum_j \rho_j(\mathbf{r}; t) = \int \cdots \int \delta\left(\mathbf{r} - \sum_{u=1}^M \mathbf{r}_u\right) \left[\prod_{u=1}^M g_1(\mathbf{r}_u; \theta_u) \right] \mathcal{R}(\boldsymbol{\theta}; t) d\boldsymbol{\theta} d\mathbf{r}_1 \dots d\mathbf{r}_M. \tag{3.20}$$

From Eq. (3.20) we can derive an effective evolution equation for $\rho(\mathbf{r}; t)$. We write down an effective transport equation similar to Eq. (3.5):

$$\partial_t \rho(\mathbf{r}; t) = \mathbb{T}_{\text{eff}} \rho(\mathbf{r}; t), \tag{3.21}$$

with the initial condition

$$\rho(\mathbf{r}; t = 0) = \delta(\mathbf{r}), \tag{3.22}$$

where \bar{T}_{eff} is a translationally invariant differential or integral effective transport operator. For evaluating the Fourier transform $\bar{T}_{\text{eff}}(\mathbf{k})$ we take the Fourier transforms of Eqs. (3.20)–(3.22), resulting in

$$\partial_t \bar{\rho}(\mathbf{k}; t) = \bar{T}_{\text{eff}}(\mathbf{k}) \bar{\rho}(\mathbf{k}; t) \quad \text{with } \bar{\rho}(\mathbf{k}; t = 0) = 1, \tag{3.23}$$

and

$$\begin{aligned} \bar{\rho}(\mathbf{k}; t) &= \int \cdots \int \left[\prod_{u=1}^M g_1(\mathbf{k}_u; \theta_u) \right] \mathcal{R}(\boldsymbol{\theta}; t) d\boldsymbol{\theta} = \int \cdots \int \exp \left[\sum_{u=1}^M \theta_u \bar{T}_u(\mathbf{k}) \right] \mathcal{R}(\boldsymbol{\theta}; t) d\boldsymbol{\theta} \\ &= \mathfrak{C}(i\omega_u = \bar{T}_u(\mathbf{k}), u = 1, \dots, M) \\ &\rightarrow \exp \left\{ t \left[\sum_u P_u^{st} \bar{T}_u(\mathbf{k}) + \frac{1}{2} \sum_u \sum_{u'} (P_u^{st} C_{uu'} + P_{u'}^{st} C_{u'u}) \bar{T}_u(\mathbf{k}) \bar{T}_{u'}(\mathbf{k}) \right] \right\} \\ &\text{as } t \rightarrow \infty. \end{aligned} \tag{3.24}$$

Here we have taken into account that for large time the multiple Fourier transform

$$\mathfrak{C}(\boldsymbol{\omega}; t) = \int \exp(i\boldsymbol{\theta} \cdot \boldsymbol{\omega}) \mathcal{R}(\boldsymbol{\theta}; t) d\boldsymbol{\theta}$$

of the probability density $\mathcal{R}(\boldsymbol{\theta}; t)$ of the sojourn times is a Gaussian given by the relationship

$$\mathfrak{C}(\boldsymbol{\omega}; t) = \exp \left\{ it \mathbf{P}^{st} \boldsymbol{\omega}^+ - \frac{t}{2} \boldsymbol{\omega} (\mathbf{bC} + \mathbf{C}^+ \mathbf{b}) \boldsymbol{\omega}^+ \right\} \quad \text{as } t \rightarrow \infty$$

(see Eq. (4.41) from paper I). By integrating Eq. (3.23) and comparing the result with Eq. (3.24) we get the following asymptotic expression for the effective transport operator $\bar{T}_{\text{eff}}(\mathbf{k})$:

$$\bar{T}_{\text{eff}}(\mathbf{k}) = \sum_u P_u^{st} \bar{T}_u(\mathbf{k}) + \frac{1}{2} \sum_u \sum_{u'} (P_u^{st} C_{uu'} + P_{u'}^{st} C_{u'u}) \bar{T}_u(\mathbf{k}) \bar{T}_{u'}(\mathbf{k}). \tag{3.25}$$

The stochastic properties of the fluctuations of the numbers of particles can be studied by using the statistical ensemble approach developed in the preceding section. Since the particles are assumed to be non-interacting the fluctuating concentration field $c(\mathbf{r}; t)$ at a position between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ at time t can be expressed as a sum of delta functions similar to Eq. (2.3):

$$c(\mathbf{r}; t) = \sum_{u=1}^{\mathcal{N}} \delta(\mathbf{r} - \mathbf{r}_u(t)),$$

where $\mathbf{r}_u(t)$ are independent random variables selected from the probability density $\rho(\mathbf{r}; t)$ of the position of a particle at time t given by Eq. (3.20); the vectors $\mathbf{r}_u(t)$ describe the positions of the \mathcal{N} particles at time t , ($u = 1, \dots, \mathcal{N}$). Note that in this case the replicas making up the statistical ensemble have a straightforward statistical significance: they correspond to the \mathcal{N} particles making up the system. The computation of the stochastic properties of the concentration field $c(\mathbf{r}; t)$ follows exactly the same

pattern as in Section 6. In the following we give the main results. The characteristic functional of the concentration field and the corresponding cumulants are given by

$$A[K(\mathbf{r}); t] = \left\langle \exp \left\{ i \int K(\mathbf{r}) c(\mathbf{r}; t) d\mathbf{r} \right\} \right\rangle = \left\{ 1 + \int [\exp[iK(\mathbf{r})] - 1] \rho(\mathbf{r}; t) d\mathbf{r} \right\}^{\mathcal{N}}, \tag{3.26}$$

$$\begin{aligned} \langle\langle c(\mathbf{r}_1; t) \dots c(\mathbf{r}_m; t) \rangle\rangle &= \sum_{n=1}^m \sum_{\beta_1 \geq 1} \dots \sum_{\beta_n \geq 1} \delta_{n(\sum_u \beta_u)} \mathcal{N}^{-(n-1)} \\ &\times \frac{(-1)^{n-1}}{n} \int \dots \int \langle c(\mathbf{r}'_1; t) \rangle \dots \langle c(\mathbf{r}'_n; t) \rangle \dots d\mathbf{r}'_1 \dots d\mathbf{r}'_n \frac{m!}{\prod_u \beta_u!} \delta(\mathbf{r}_1 - \mathbf{r}'_1) \dots \\ &\times \delta(\mathbf{r}_{\beta_1} - \mathbf{r}'_1) \dots \delta(\mathbf{r}_{\beta_1 + \dots + \beta_{n-1} + 1} - \mathbf{r}'_n) \dots \delta(\mathbf{r}_{\beta_1 + \dots + \beta_n} - \mathbf{r}'_n), \end{aligned} \tag{3.27}$$

where

$$\langle c(\mathbf{r}; t) \rangle = \mathcal{N} \rho(\mathbf{r}; t) \tag{3.28}$$

is the average concentration of particles at a position between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ at time t . In a limit of the thermodynamic type similar to the limit (2.16):

$$\mathcal{N} \rightarrow \infty \quad \text{with} \quad \langle c(\mathbf{r}; t) \rangle = \text{constant}, \tag{3.29}$$

the fluctuations of the concentration field are Poissonian and the characteristic functional $A[K(\mathbf{r}); t]$ and the cumulant $\langle\langle c(\mathbf{r}_1; t) \dots c(\mathbf{r}_m; t) \rangle\rangle$ become

$$A[K(\mathbf{r}); t] = \exp \left\{ \mathcal{N} \int [\exp[iK(\mathbf{r})] - 1] \rho(\mathbf{r}; t) d\mathbf{r} \right\}, \tag{3.30}$$

$$\langle\langle c(\mathbf{r}_1; t) \dots c(\mathbf{r}_m; t) \rangle\rangle = \langle c(\mathbf{r}_1; t) \rangle \delta(\mathbf{r}_2 - \mathbf{r}_1) \dots \delta(\mathbf{r}_m - \mathbf{r}_{m-1}). \tag{3.31}$$

The probability density functional of the concentration fluctuations

$$\mathfrak{D}[c(\mathbf{r}; t)] \mathscr{D}[c(\mathbf{r}; t)] \quad \text{with} \quad \int \int \mathfrak{D}[c(\mathbf{r}; t)] \mathscr{D}[c(\mathbf{r}; t)] = 1, \tag{3.32}$$

is given by an expression similar to Eq. (2.21):

$$\mathfrak{D}[c(\mathbf{r}; t)] \mathscr{D}[c(\mathbf{r}; t)] \sim \exp \{ -F[c(\mathbf{r}; t)] \} \mathscr{D}[c(\mathbf{r}; t)], \tag{3.33}$$

where $F[c(\mathbf{r}; t)]$ is an extensive fluctuating potential given by an expression of the Kullback information type similar to Eq. (2.23):

$$F[c(\mathbf{r}; t)] = \int c(\mathbf{r}; t) \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}; t) \rangle] d\mathbf{r}. \tag{3.34}$$

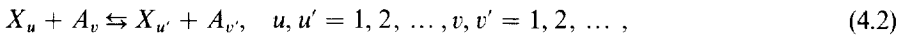
4. Generalized Taylor diffusion

As an application of the general approach developed in Section 3 we study a generalized version of Van den Broeck approach to the Taylor’s diffusion problem

[11,12]. We assume that the individual transport operators \mathbb{T}_u are of the Fokker–Planck type (3.3) and thus the corresponding Fourier transforms $\mathbb{T}_u(\mathbf{k})$ are square functions of the wave vector \mathbf{k} :

$$\mathbb{T}_k(\mathbf{k}) = i\mathbf{k} \cdot \mathbf{v}_u^+ - \mathbf{k} \cdot \mathbb{D}_u \cdot \mathbf{k}^+, \quad \mathbb{D}_u = [D_{\ell_1 \ell_2}^{(u)}], \quad u = 1, \dots, M, \quad \ell_1, \ell_2 = 1, \dots, d_s, \tag{4.1}$$

which corresponds to an anisotropic convection–diffusion process characterized by the individual drift velocities \mathbf{v}_u and by the individual diffusion tensors \mathbb{D}_u attached to the different states of a particle. Due to the random fluctuations of the drift velocity generated by the random fluctuations of the state of a particle, for a model described by Eqs. (4.1) a supplementary diffusion of the turbulent type emerges which can outweigh the intrinsic (molecular) diffusion described by the individual diffusion tensors attached to the different states of a particle. A variety of experimental situations can be described by this type of model, for example, the turbulent diffusion [28], the description of line shape in spectroscopy [5–8], the electrodiffusion [29–30]. Such a description has been used for the measurement of reaction rates in fast chemical processes of the type



where $X_u, X_{u'}$ are species with different electric charges and variable concentrations and the concentrations of the species $A_v, A_{v'}$ are kept constant by buffering [29,30]. A further application is the study of chromatographic separation processes [29,30].

By applying the general approach developed in Section 3 we get the following expression for the Fourier transform $\bar{\rho}(\mathbf{k}; t)$ of the marginal probability density $\rho(\mathbf{r}; t)$ of the position of a particle:

$$\bar{\rho}(\mathbf{k}; t) = \mathfrak{C}(\omega_u = \mathbf{k} \cdot \mathbf{v}_u^+ + i\mathbf{k} \cdot \mathbb{D}_u \cdot \mathbf{k}^+; u = 1, \dots, M; t). \tag{4.3}$$

Now we use the asymptotic expression (4.41) from paper 1 for the characteristic function $\mathfrak{C}(\omega; t)$ and notice that $\bar{\rho}(\mathbf{k}; t)$ is the characteristic function of the probability density $\rho(\mathbf{r}; t)$. After lengthy calculations we can express $\bar{\rho}(\mathbf{k}; t)$ in the standard form of a cumulant expansion

$$\bar{\rho}(\mathbf{k}; t) = \exp \left\{ \sum_{m=1}^{\infty} \frac{t^m}{m!} \sum_{\ell_1} \dots \sum_{\ell_m} k_{\ell_1} \dots k_{\ell_m} \langle\langle r_{\ell_1}(t) \dots r_{\ell_m}(t) \rangle\rangle \right\} \quad \text{as } t \rightarrow \infty, \tag{4.4}$$

where the cumulants $\langle\langle r_{\ell_1}(t) \dots r_{\ell_m}(t) \rangle\rangle$ of the position vector are given by

$$\langle\langle r_{\ell}(t) \rangle\rangle \sim \langle v_{\ell} \rangle t, \quad t \rightarrow \infty, \tag{4.5}$$

$$\langle\langle r_{\ell_1}(t) r_{\ell_2}(t) \rangle\rangle \sim \left[2\langle D_{\ell_1 \ell_2} \rangle + \sum_{u, u'} (P_u^{st} C_{uu'} + P_{u'}^{st} C_{u'u}) v_{\ell_1}^{(u)} v_{\ell_2}^{(u')} \right] t \quad \text{as } t \rightarrow \infty, \tag{4.6}$$

$$\langle\langle r_{\ell_1}(t)r_{\ell_2}(t)r_{\ell_3}(t)\rangle\rangle \sim \left[3 \sum_{u,u'} (P_u^{st}C_{uu'} + P_{u'}^{st}C_{u'u}) (v_{\ell_1}^{(u)}D_{\ell_2\ell_3}^{(u')} + D_{\ell_1\ell_2}^{(u')}v_{\ell_3}^{(u)}) \right] t \quad \text{as } t \rightarrow \infty, \tag{4.7}$$

$$\langle\langle r_{\ell_1}(t)r_{\ell_2}(t)r_{\ell_3}(t)r_{\ell_4}(t)\rangle\rangle \sim \left[12 \sum_{u,u'} (P_u^{st}C_{uu'} + P_{u'}^{st}C_{u'u}) D_{\ell_1\ell_2}^{(u')}D_{\ell_3\ell_4}^{(u')} \right] t \quad \text{as } t \rightarrow \infty, \tag{4.8}$$

$$\langle\langle r_{\ell_1}(t) \dots r_{\ell_{2m}}(t)\rangle\rangle \sim 0, \quad m > 4 \quad \text{as } t \rightarrow \infty, \tag{4.9}$$

where

$$\langle v_{\ell} \rangle = \sum_u P_u^{st} v_{\ell}^{(u)}, \quad \langle D_{\ell\ell'} \rangle = \sum_u P_u^{st} D_{\ell\ell'}^{(u)}. \tag{4.10}$$

For large times all cumulants of the position vector of order higher than four tend to zero. If the intrinsic molecular diffusion coefficients $D_{\ell\ell'}^{(u)}$ are different from zero then the cumulants of the third and fourth order of the displacement vector are different from zero and the probability distribution $\rho(\mathbf{r}; t)$ has the skewness and kurtosis coefficients different from zero. If however the process of intrinsic molecular diffusion is negligible in comparison with the macroscopic diffusion due to the random variations of the state of the particle, then from Eqs. (4.7)–(4.9) we have

$$\langle\langle r_{\ell_1}(t) \dots r_{\ell_{2m}}(t)\rangle\rangle \sim 0, \quad m > 2 \quad \text{as } t \rightarrow \infty, \tag{4.11}$$

and as $t \rightarrow \infty$, $\rho(\mathbf{r}; t)$ is a Gaussian characterized by the cumulants of first and second order given by Eqs. (4.5) and (4.6).

Following Van den Broeck [11,12], in terms of the cumulants of the second order $\langle\langle r_{\ell_1}(t)r_{\ell_2}(t)\rangle\rangle$, we can introduce the effective diffusion tensor

$$\mathbb{D}_{\text{eff.}} = \lim_{t \rightarrow \infty} (\langle\langle r_{\ell_1}(t)r_{\ell_2}(t)\rangle\rangle)/(2t) = \langle \mathbb{D}_u \rangle + \frac{1}{2} \sum_{u,u'} (P_u^{st}C_{uu'} + P_{u'}^{st}C_{u'u}) v_{\ell_1}^{(u)} v_{\ell_2}^{(u')}. \tag{4.12}$$

Eqs. (4.3)–(4.12) for the cumulants of the position vector of the moving particle at time t , $\mathbf{r}(t)$ and for the effective diffusion tensor are new. If the process of intrinsic molecular diffusion is isotropic:

$$\mathbb{D}_{\text{eff.}} = [D_{\ell\ell'} \delta_{\ell_1\ell_2}], \tag{4.13}$$

and if the jump rates $W_{uu'}$ are different from zero only if $u' = u \pm 1$

$$W_{uu'} = 0 \quad \text{for } u' \neq u \pm 1, \tag{4.14}$$

then the stationary solution of the master equation P_i^{st} as well as the solutions of Eqs. (2.5) and (2.6) for $C_{uu'}$ can be evaluated explicitly. By inserting the resulting expressions for P_u^{st} and $C_{uu'}$ into Eqs. (4.5)–(4.12) we recover, as a particular case of our approach, the equations for the cumulants and for the effective diffusion coefficients derived by Van den Broeck [11,12] by applying a different approach.

5. Thermodynamic analogies for generalized Taylor diffusion in an external potential field

Although the thermodynamic analogies can be analyzed in the case of the free-field system for which a cloud of particles initially placed at $\mathbf{r} = \mathbf{0}$ spread to infinity, the corresponding results are rather trivial. In this section we try to apply the results derived before for translationally invariant systems for the more complicated case of the systems with a position-dependent weak potential field. For such a system the equations are no longer translationally invariant. We consider a force field derived from a scalar potential $U(\mathbf{r})$ which generates an additional position-dependent velocity field which is dependent of the state u of the particle considered:

$$(\mathbf{v}_{\text{add}})_r = - \sum_{r''} \mathbf{b}_{r''} [\nabla U(\mathbf{r})]_{r''}, \quad (5.1)$$

where $\mathbf{b} = [\mathbf{b}_{r''}]$ is a mobility tensor independent of the state u of the particle. The evolution equations (3.5) and (3.6) for the position-state joint probability density $\rho_j(\mathbf{r}; t)$ become

$$\partial_t \rho_j(\mathbf{r}; t) = \mathbb{T}_j \rho_j(\mathbf{r}; t) + \mathbb{T}_j^{(1)} \rho_j(\mathbf{r}; t) + \sum_{j' \neq j} \rho_{j'}(\mathbf{r}; t) W_{j'j} - \rho_j(\mathbf{r}; t) \Omega_j, \quad (5.2)$$

$$\rho_j(\mathbf{r}; t = 0) = \delta(\mathbf{r}) P_j(t = 0), \quad (5.3)$$

where the additional transport operator $\mathbb{T}_j^{(1)}$ generated by the external field is given by

$$\begin{aligned} \mathbb{T}^{(1)} \dots &= \mathbf{b} : (\nabla U(\mathbf{r})) \nabla \dots + \mathbf{b} : (\nabla \nabla U(\mathbf{r})) \dots \\ &= \sum_{r''} \mathbf{b}_{r''} [(\partial_{r'} U(\mathbf{r})) \partial_{r''} \dots + (\partial_{r''}^2 U(\mathbf{r})) \dots]. \end{aligned} \quad (5.4)$$

By using an interaction representation suggested by Van Kampen [28,31], we search for a solution of Eqs. (5.2) and (5.3) of the type:

$$\rho_j(\mathbf{r}; t) = \varphi(\mathbf{r}; t) \rho_j^{(0)}(\mathbf{r}; t), \quad (5.5)$$

where $\varphi(\mathbf{r}; t)$ is the solution of

$$\partial_t \varphi(\mathbf{r}; t) = \mathbb{T}^{(1)} \varphi(\mathbf{r}; t). \quad (5.6)$$

The solution (5.5) has the form

$$\rho_j(\mathbf{r}; t) = \left[\exp(t \mathbb{T}^{(1)}) \left\{ \vec{\mathbb{E}} \exp \left\{ \int_0^t dt' [\varphi^{-1} \mathbb{F} \varphi + [\delta_{jj'} \mathbb{T}_a^{(1)}]] \right\} \right\} \right]_j \delta(\mathbf{r}), \quad (5.7)$$

where $\vec{\mathbb{E}}$ is Dyson's time-ordering operator, \mathbb{F} is a matrix differential operator defined by writing the field-free evolution equation (3.5) in the matrix form

$$\partial_t \boldsymbol{\rho}^+(\mathbf{r}; t) = \mathbb{F} \boldsymbol{\rho}^+(\mathbf{r}; t),$$

that is

$$\mathbb{F} = [\delta_{jj'}\mathbb{T}_j + W_{j'j} + \delta_{jj'}\Omega_j], \tag{5.8}$$

and $\mathbb{T}_a^{(1)}$ is the first-order differential part of the operator $\mathbb{T}^{(1)}$:

$$\mathbb{T}_a^{(1)} \dots = \mathbf{b}: (\nabla U(\mathbf{r}))\nabla \dots = \sum_{r''} \mathbf{b}_{r''} [(\partial_{r'} U(\mathbf{r}))\partial_{r''} \dots +]. \tag{5.9}$$

If the external field is weak the non-commutativity effects in Eq. (5.6) can be neglected and we have

$$\rho_j(\mathbf{r}; t) \cong \exp(t\mathbb{T}^{(1)})[\exp(t\mathbb{F})]_j\delta(\mathbf{r}),$$

and therefore

$$\rho(\mathbf{r}; t) = \sum_j \rho_j(\mathbf{r}; t) \cong \exp(t\mathbb{T}^{(1)})\exp(t\mathbb{T}_{\text{eff}})\delta(\mathbf{r}) \cong \exp[t(\mathbb{T}^{(1)} + \mathbb{T}_{\text{eff}})]. \tag{5.10}$$

Eq. (5.10) is the solution of the effective transport equation

$$\partial_t \rho(\mathbf{r}; t) = (\mathbb{T}^{(1)} + \mathbb{T}_{\text{eff}})\rho(\mathbf{r}; t). \tag{5.11}$$

For simplicity, we limit ourselves to the case where the intrinsic (molecular) diffusion described by the diffusion tensors attached to the different states of a particle is smaller than the turbulent diffusion generated by the random fluctuations of the drift velocity. In this case the effective transport operator \mathbb{T}_{eff} is approximately of the Fokker–Planck type and characterized by an average drift velocity $\langle \mathbf{v} \rangle$ given by the first equation (4.10) and by an effective diffusion tensor $\mathbb{D}_{\text{eff}} = [D_{r''r''}^{\text{eff}}]$ given by Eq. (4.12). The inertial component of the motion given by the average velocity field $\langle \mathbf{v} \rangle$ is non-dissipative and thus uninteresting from the thermodynamic point of view. Without loss of generality, we consider that the fluctuating velocity field has an average value zero

$$\langle \mathbf{v} \rangle = \mathbf{0}, \tag{5.12}$$

and thus the effective transport equation (5.11) becomes

$$\partial_t \rho(\mathbf{r}; t) = \mathbb{T}_{\text{eff}}^* \rho(\mathbf{r}; t), \tag{5.13}$$

where

$$\mathbb{T}_{\text{eff}}^* \dots = \sum_{r''} \left\{ D_{r''r''}^{\text{eff}} \partial_{r''}^2 \dots + \mathbf{b}_{r''} \left[\left(\partial_{r'} U(\mathbf{r}) \right) \partial_{r''} \dots + \left(\partial_{r''}^2 U(\mathbf{r}) \right) \dots \right] \right\}. \tag{5.14}$$

By analogy with equilibrium statistical mechanics we assume that, due to the presence of the external field, a stationary solution of Eq. (5.13) eventually emerges which is an exponential function of the potential $U(\mathbf{r})$:

$$\rho^{\text{st}}(\mathbf{r}) \sim \exp(-\beta U(\mathbf{r})), \tag{5.15}$$

where β is a positive constant. By requiring that Eq. (5.15) is a stationary solution of the effective transport equation (5.14) we come to a fluctuation–dissipation relation of

the Einstein type

$$\mathbf{b}_{i'j'} = \beta D_{i'j'}^{\text{eff}}. \quad (5.16)$$

In particular, for equilibrium systems, β is proportional to the reciprocal value of the absolute temperature of the system, T :

$$\beta = (k_B T)^{-1}, \quad (5.17)$$

and Eq. (5.16) reduces to the Einstein's relation generalized to anisotropic diffusion

$$\mathbf{b}_{i'j'} = D_{i'j'}^{\text{eff}} / (k_B T). \quad (5.18)$$

For investigating the analogies with the nonequilibrium thermodynamic formalisms suggested by Keizer [23] and by Ross et al. [24] we write the effective evolution equation (5.13) in terms of the concentration field $c(\mathbf{r}; t)$,

$$\partial_t c(\mathbf{r}; t) = \mathbb{T}_{\text{eff}}^* c(\mathbf{r}; t), \quad (5.19)$$

and try to make a connection between the asymptotic solutions of Eq. (5.19) and fluctuation dynamics. We notice that the derivation of the expressions (3.26)–(3.35) for the characteristic functional, the cumulants, the probability density functional of concentration fluctuations and for the fluctuating potential is based on the assumption that the particles are non-interacting and it is independent of the form of the probability density $\rho(\mathbf{r}; t)$ of the position of a particle. Since in the presence of an external field the particles do not interact with each other but only with the field Eqs. (3.26)–(3.35) remain valid. In particular, we can compute the fluctuating potential $F[c(\mathbf{r}; t)]$ for the particular case when the reference concentration has the form

$$\langle c(\mathbf{r}) \rangle^{\text{st}} = [\mathcal{N} \exp(-\beta U(\mathbf{r}))] / \left[\int \exp(-\beta U(\mathbf{r})) d\mathbf{r} \right], \quad (5.20)$$

which corresponds to the stationary probability density given by Eq. (5.15). From Eqs. (3.34) and (5.20) we arrive at

$$F[c(\mathbf{r}; t)] = \tilde{\mu}^0 \int c(\mathbf{r}; t) d\mathbf{r} + \int c(\mathbf{r}; t) [\beta^{-1} \ln c(\mathbf{r}; t) + U(\mathbf{r})] d\mathbf{r}, \quad (5.21)$$

where

$$\tilde{\mu}^0 = \ln \left\{ \left[\int \exp(-\beta U(\mathbf{r})) d\mathbf{r} \right] / \mathcal{N} \right\}. \quad (5.22)$$

The fluctuating potential (5.21) has a structure typical for a free energy functional made up of an energetic contribution

$$E = \int c(\mathbf{r}; t) U(\mathbf{r}) d\mathbf{r}, \quad (5.23)$$

which gives the total potential energy of the external field and by an entropic contribution

$$s = - \int c(\mathbf{r}; t) \ln c(\mathbf{r}; t) \, d\mathbf{r}. \tag{5.24}$$

We have

$$F = \tilde{\mu}^0 \mathcal{N} + E - \beta^{-1} S. \tag{5.25}$$

According to its definition (5.21), (5.22), the fluctuating potential F is an extensive state function which is homogeneous function of the first order of the volume of the system. By evaluating its functional derivative with respect to the concentration field $c(\mathbf{r}; t)$, we get a zeroth-order homogeneous function which plays the role of a generalized ‘field-chemical potential’

$$\tilde{\mu}[c(\mathbf{r}; t)] = \delta F[c(\mathbf{r}; t)] / \delta c(\mathbf{r}; t) = U(\mathbf{r}) + \tilde{\mu}^0 + \beta^{-1} \ln c(\mathbf{r}; t). \tag{5.26}$$

$\tilde{\mu}[c(\mathbf{r}; t)]$ has a structure typical for a partial molar function in an external field which is made up of the contribution of a function of the chemical potential type, $\tilde{\mu}^0 + \beta^{-1} \ln c(\mathbf{r}; t)$ and of the potential field $U(\mathbf{r})$. The thermodynamic analogies can be further developed by noticing that, if the fluctuation dissipation relation (5.16) holds, then the effective transport equation (5.19) for the concentration field can be expressed in the form of a continuity equation

$$\partial_t c(\mathbf{r}; t) + \nabla \cdot \mathbf{J} = 0, \tag{5.27}$$

where the components of the particle flux vector \mathbf{J} are proportional to the components of the gradient of the ‘field-chemical potential’ $\tilde{\mu}[c(\mathbf{r}; t)]$:

$$[\mathbf{J}]_{i'} = - c(\mathbf{r}; t) \sum_{i''} D_{i'i''}^{\text{eff}} \cdot [\nabla \tilde{\mu}[c(\mathbf{r}; t)]]_{i''}. \tag{5.28}$$

Eq. (5.28) has a form typical for an anisotropic force–flux relationship in nonequilibrium thermodynamics showing that the gradient of the ‘field–chemical potential’ is the driving force of the transport process.

We can also prove that the fluctuating potential $F[c(\mathbf{r}; t)]$ given by Eq. (5.21) is a Lyapunov function of the transport equations (5.27) and (5.28), corresponding to the stationary solution $\langle c(\mathbf{r}) \rangle^{\text{st}}$, that is, it fulfills the conditions

$$F[c(\mathbf{r}; t) \neq \langle c(\mathbf{r}) \rangle^{\text{st}}] > 0, \quad F[c(\mathbf{r}; t) = \langle c(\mathbf{r}) \rangle^{\text{st}}] = 0, \tag{5.29}$$

$$\dot{F}[c(\mathbf{r}; t) \neq \langle c(\mathbf{r}) \rangle^{\text{st}}] < 0, \quad \dot{F}[c(\mathbf{r}; t) = \langle c(\mathbf{r}) \rangle^{\text{st}}] = 0. \tag{5.30}$$

If Eqs. (5.29) and (5.30) hold then in the long run all time-dependent transient solutions $c(\mathbf{r}; t)$ of Eqs. (5.27) and (5.28) tend towards the stationary solution $\langle c(\mathbf{r}) \rangle^{\text{st}}$.

$$c(\mathbf{r}; t) \rightarrow \langle c(\mathbf{r}) \rangle^{\text{st}} \quad \text{as } t \rightarrow \infty. \tag{5.31}$$

The derivation of Eq. (5.29) is based on the conservation of the total number of particles which leads to:

$$\int c(\mathbf{r}; t) d\mathbf{r} = \int \langle c(\mathbf{r}) \rangle^{st} d\mathbf{r} = \mathcal{N} = \text{constant}, \quad (5.32)$$

which allows us to express Eqs. (3.34) and (5.21) in the form:

$$F[c(\mathbf{r}; t)] = \int \{ c(\mathbf{r}; t) \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}) \rangle^{st}] - c(\mathbf{r}; t) + \langle c(\mathbf{r}) \rangle^{st} \} d\mathbf{r}. \quad (5.33)$$

By making use of the well-known identity

$$x \ln x + 1 - x > 0 \quad \text{for } x \neq 1, x > 0, \quad x \ln x + 1 - x = 0 \quad \text{for } x = 1, \quad (5.34)$$

Eq. (5.33) leads to the inequality (5.29).

The proof of Eq. (5.30) is based on the assumption that the effective diffusion tensor $\mathbb{D}_{\text{eff.}} = [D_{i'j'}^{\text{eff.}}]$ is positive definite, that is, on the assumption that the square form attached to $\mathbb{D}_{\text{eff.}}$ has the property

$$f(\mathbf{y}) > 0 \quad \text{for } \mathbf{y} \neq \mathbf{0} \quad \text{and} \quad f(\mathbf{y}) = 0 \quad \text{for } \mathbf{y} = \mathbf{0}, \quad (5.35)$$

where

$$f(\mathbf{y}) = \mathbf{y} \cdot \mathbb{D}_{\text{eff.}} \cdot \mathbf{y}^+. \quad (5.36)$$

Note that the property (5.36) is consistent with Eqs. (4.6) and (4.12) which show that, up to a proportionality factor $(2t)^{-1}$, the components of the diffusion tensor are proportional to the components of a covariance matrix. By taking the time derivative of Eq. (5.21) and using the evolution equations (5.27) and (5.28) we obtain

$$\begin{aligned} dF/dt = & \int [dc(\mathbf{r}; t)/dt] \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}) \rangle^{st}] d\mathbf{r} \\ & + \beta^{-1} \int c(\mathbf{r}; t) \sum_{i'j'} D_{i'j'}^{\text{eff.}} \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}) \rangle^{st}] \partial_{r_{i'}}^2 \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}) \rangle^{st}] d\mathbf{r}, \end{aligned} \quad (5.37)$$

from which, by assuming vanishing conditions and performing a partial integration, we arrive at

$$dF/dt = -\beta^{-1} \int c(\mathbf{r}; t) \sum_{i'j'} D_{i'j'}^{\text{eff.}} \{ \partial_{r_{i'}} \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}) \rangle^{st}] \} \{ \partial_{r_{j'}} \ln [c(\mathbf{r}; t) / \langle c(\mathbf{r}) \rangle^{st}] \} d\mathbf{r}. \quad (5.38)$$

From Eqs. (5.35) and (5.38) we get the second inequality (5.30).

The Lyapunov properties (5.29) and (5.30) of the fluctuating potential $F[c(\mathbf{r}; t)]$ are closely related to the variational formulation of the conditions of existence and

stability of the stationary solution $\langle c(\mathbf{r}) \rangle^{st}$:

$$\delta F[c(\mathbf{r}; t) = \langle c(\mathbf{r}) \rangle^{st}] = 0, \quad (5.39)$$

$$\delta^2 F[c(\mathbf{r}; t) > 0, \quad (5.40)$$

which correspond to a minimum of the fluctuating potential $F[c(\mathbf{r}; t)]$ and are analogous to the similar stationarity and stability conditions suggested by Keizer and by Ross et al.

We emphasize that the Taylor diffusion in an external field is a typical nonequilibrium process and, thus, even though the stationary solutions (5.15) and (5.20) are similar to an equilibrium solution, their properties may be very different from the ones corresponding to an equilibrium solution. In particular, the condition of microscopic reversibility is generally not fulfilled and thus the components of the effective diffusion tensor \mathbb{D}_{eff} do not satisfy a set of reciprocity conditions of the Onsager type.

6. Conclusions

In this article a statistical ensemble approach has been introduced for the study of stochastic properties of sojourn times attached to the different states of a Markov process. The suggested approach makes possible the systematic evaluation of the effective transport equations and of the transport coefficients for Markov rate and transport processes with dynamical disorder. The technique has been illustrated by the study of a generalization of the Van den Broeck model of Taylor diffusion [11,12]. For this problem explicit expressions for the transport operators and for the effective diffusion tensors have been derived. It has been shown that for generalized Taylor diffusion it is possible to construct a nonequilibrium thermodynamic formalism which is a generalization to a process with dynamical disorder of the theories suggested by Keizer [23] and by Ross et al. [24]. The thermodynamic formalism has been developed starting from a fluctuating potential which is proportional to the logarithm of the probability density functional of concentration fluctuations. This fluctuating potential is a Lyapunov function of the effective transport equations. For Taylor diffusion in an external potential force field the fluctuating potential has a structure similar to that of a free energy functional and its functional derivative with respect to the concentration field is a generalized ‘field-chemical potential’; its gradient is the driving force of the diffusion process. Explicit conditions for the existence and stability of a nonequilibrium concentration field have been given in terms of the fluctuating potential; these conditions are similar to the conditions of equilibrium and stability derived from the second law of thermodynamics.

The study of rate processes with dynamical disorder does not exhaust the possibilities of application of the suggested approach. Other applications are related to the stochastic description of the nonlinear reaction-diffusion systems far from equilibrium. In this field the theory leads to a stochastic measure for the relative stability of

two different steady and makes possible to predict the behavior of propagating fronts. Work on this problem is in progress.

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Appendix A

The reduced joint probability density $R_j(\boldsymbol{\theta}; t)$ of the state j of the system and of the total sojourn times $\theta_j, j = 1, \dots, M$ at time t obeys the stochastic Liouville equation

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial \theta_j} \right) R_j(\boldsymbol{\theta}; t) = \sum_{j' \neq j} W_{j'j} R_{j'}(\boldsymbol{\theta}; t) - \Omega_j B_j(\boldsymbol{\theta}; t), \quad (\text{A.1})$$

with the initial and boundary conditions

$$R_j(\boldsymbol{\theta}; t = 0) = P_j(t = 0) \delta(\boldsymbol{\theta}), \quad (\text{A.2})$$

$$R_j(\text{at least one } \theta_j \leq 0 \text{ or } \sum \theta_j > t; t \neq 0) = 0, \quad (\text{A.3})$$

Eqs. (A.1)–(A.3) can be derived from the evolution equations for the joint probability density $B_j(\boldsymbol{\theta}, \mathbf{q}; t)$ of the state of the system, of the sojourn times $\theta_j, j = 1, \dots, M$, and of the numbers $q_j, j = 1, \dots, M$, of transition events at time t . (Eqs. (2.12)–(2.14) from paper I). The relations between the probability densities $R_j(\boldsymbol{\theta}, t)$ and $B_j(\boldsymbol{\theta}, \mathbf{q}; t)$ is given by:

$$R_j(\boldsymbol{\theta}, t) = \sum_{\mathbf{q}} B_j(\boldsymbol{\theta}, \mathbf{q}; t). \quad (\text{A.4})$$

By summing in Eqs. (2.12)–(2.14) from paper I over \mathbf{q} and by using Eqs. (A.4) we arrive at Eqs. (A.1)–(A.3). By introducing the Fourier transform

$$\bar{R}_j(\boldsymbol{\omega}; t) = \int \exp(i\boldsymbol{\theta} \cdot \boldsymbol{\omega}) R_j(\boldsymbol{\theta}; t) d\boldsymbol{\theta}, \quad (\text{A.5})$$

Eqs. (A.1)–(A.3) lead to Eqs. (3.9)–(3.10). By comparing Eqs. (3.7) and (3.8) with Eqs. (3.9) and (3.10) we notice the complete isomorphism of these two sets of equations.

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