Network of characterizing functions for stationary populations

C. Rödenbeck,[1,*] J. Kärger,[1] H. Schmidt,[2] T. Rother,[3] and M. Rödenbeck[4]

[1]Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik I, Universität Leipzig, Linnèstraße 5, D-04103 Leipzig, Germany

[2]Fakultät für Physik und Geowissenschaften, Institut für Geographie, Universität Leipzig, Johannisallee 19a, D-04103 Leipzig, Germany

[3]Zentrum für innere Medizin, Klinik und Poliklinik 1, Abteilung für Kardiologie und Angiologie, Universität Leipzig, Johannisallee 32, D-04103 Leipzig, Germany

[4]Medizinische Fakultät, Institut für Medizinische Physik und Biophysik, Universität Leipzig, Liebigstraße 27, D-04103 Leipzig, Germany

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A variety of open systems in nature and society exist under dynamic equilibrium, maintained by statistical counterbalance between the entering and leaving of individuals and the stationarity of the exchange processes. A network of functions characterizing the dynamics of such a stationary population is established and discussed, which allows the mutual transference of system properties without the need of any explicit information about the microdynamic processes. In order to illustrate the potential benefit of these interdependence relations, examples taken from diverse branches of research (adsorption and reaction kinetics, demographic analysis, and coronary blood flow diagnosis) are given. [S1063-651X(99)11409-0]

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I. INTRODUCTION

Let us consider a population of individuals within a confined system. Suppose that there are stationary processes continuously exchanging individuals between this population and the system's surrounding. Depending on the application, one may think of molecules temporarily adsorbed to some surface, people entering and leaving a public building or a social group, the volume elements of the fluid flowing through a biological tissue or a chemical device, advected particles temporarily trapped in the vortices of a fluid, or various other situations. For many questions, one is interested in the statistics of the time spent among the population, in the evolution of the ratio between different species of individuals, in the interplay between the exchange processes and transitions from one species into another, etc.

II. THE NETWORK OF CHARACTERIZING FUNCTIONS

In order to describe the dynamics of the stationary exchange of the individuals between the system and its surroundings, two basic probability density functions may be introduced, the *residence time distribution* $\varphi(\tau)$ and the *transit time distribution* $\chi(\tau)$. Per definition, $\varphi(\tau)d\tau$ denotes the probability that an arbitrary individual within the system has entered it a time between τ and $\tau+d\tau$ ago, while $\chi(\tau)d\tau$ is the probability that an individual just leaving the system has spent a time between τ and $\tau+d\tau$ in its interior. These functions may uniquely be transferred into each other [1] by expression (1) in Fig. 1. As a conventional means for experimentally determining the exchange dynamics, one may, starting from time $t=0$, label the individuals entering the system (in the case of molecules, e.g., by applying isotopes). The *tracer exchange curve* $\gamma(t)$ is defined as the relative amount of labeled individuals within the system at time t [in the medical literature, $\gamma(t)$ is referred to as the accumulation curve]. Since all individuals with residence times smaller than the observation time t surely have been labeled, the tracer exchange curve follows from the residence time distribution by simple integration [expression (3) in Fig. 1]. In a more general sense, $\gamma(t)$ gives the relative amount of individuals which were, as a consequence of the system's exchange dynamics, replaced during a time span t. Finally, the individuals within the system may be assumed to be converted irreversibly from one species into another (for molecules, e.g., by a chemical reaction) without changing their exchange statistics. If the probability of such a transition within a small time interval dt is kdt (as in a first-order reaction), then the probability that after a residence time τ a given individual still belongs to its initial species is $\exp(-k\tau)$. Averaging over the residence time distribution yields the mean relative amount of the initial species within the system, $\eta(k)$, as given by expression (4) in Fig. 1. (In heterogeneous catalysis, this is the famous *effectiveness factor*.) Mathematically, expression (4) in Fig. 1 is simply a Laplace transform.

Although the four functions introduced so far describe quite different features of a stationary population, they turn out, thanks to their one-to-one relations summarized in Fig. 1, to be equivalent in their information about the system. For this reason we refer to them as ‘‘characterizing functions.’’ Their importance is also due to the fact that they can be used to predict the system's response to external changes. If the relative amount of a certain species among the individuals *entering* the system is given by an arbitrary time function $\varrho_E(t)$, then the time evolution of the relative amount $\varrho(t)$ of

*Present address: Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, D-01187 Dresden, Germany. Electronic address: roeden@mpipks-dresden.mpg.de

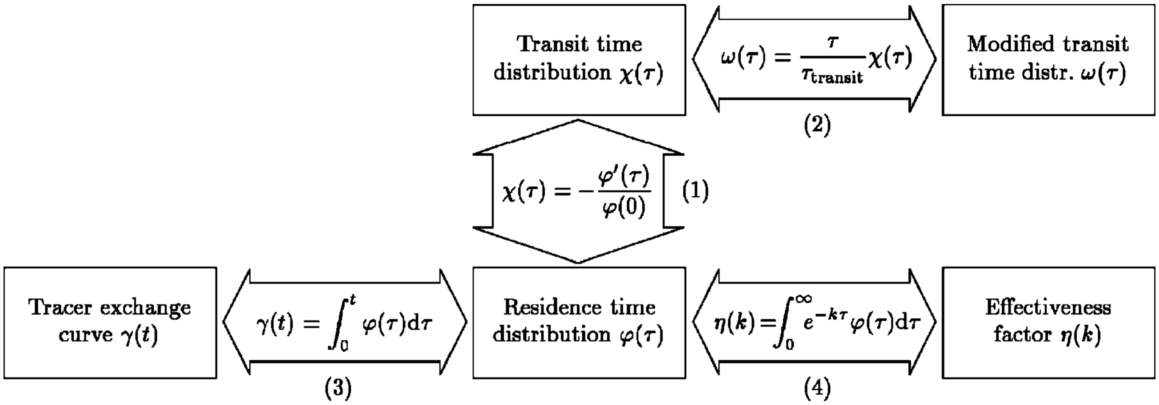

FIG. 1. The network of characterizing functions, interdependent by one-to-one relations (for definitions, see text).

this species among the population *within* the system is found to be

$$\varrho(t) = \int_0^\infty \varrho_E(t-\tau)\varphi(\tau)d\tau. \tag{1}$$

This is in fact a generalization of expression (3) in Fig. 1. Analogously, for the relative amount of the considered species among the *leaving* individuals, one has

$$\varrho_A(t) = \int_0^\infty \varrho_E(t-\tau)\chi(\tau)d\tau. \tag{2}$$

These equations can, in turn, be used to calculate important mean quantities. This shall be illustrated with the mean transit time τ_{transit}, defined as

$$\tau_{\text{transit}} = \int_0^\infty \tau\chi(\tau)d\tau. \tag{3}$$

Independently of the distribution $\chi(\tau)$, this quantity relates the (constant) mean number V of individuals within the system (if volume elements are considered, this is the total volume) and the (constant) mean flow I through the system via

$$\tau_{\text{transit}} = V/I. \tag{4}$$

To determine τ_{transit} experimentally, one may ''inject'' a small number of labeled individuals into the entering ones and measure the response functions $\varrho(t)$ and $\varrho_A(t)$. From Eqs. (1)–(3) it then follows that

$$\tau_{\text{transit}} = \frac{\int_t^\infty \varrho_A(\tau)d\tau}{\varrho(t)}. \tag{5}$$

Here, t is an arbitrary observation time after the injection is complete. Since thus t only refers to the measurement while τ_{transit} is, of course, time-independent, Eq. (5) offers the advantageous possibility to easily check for measuring errors by varying t.

A similar quantity is the mean residence time, originally defined for adsorbate-adsorbent systems via the tracer exchange curve as the mean intracrystalline lifetime [2]:

$$\tau_{\text{intra}} = \int_0^\infty [1-\gamma(t)]dt. \tag{6}$$

At closer view, this quantity has a much more general meaning since it can be expressed as the first moment of the residence time distribution,

$$\tau_{\text{intra}} = \int_0^\infty \tau\varphi(\tau)d\tau, \tag{7}$$

or as the second moment of the transit time distribution $\chi(\tau)$ [1]. Thus, τ_{intra} not only describes a tracer exchange process but provides, like τ_{transit}, an intrinsic time scale of an open stationary system.

There is an interesting link with Feller's famous *waiting time paradox* [3]. Transit times correspond to Feller's interarrival times (the time intervals between subsequent events of a stochastic point process) while the residence time corresponds—up to unimportant time reversal—to Feller's waiting time (the time interval between a given process-independent observation time t and the next arrival). Indeed, if one substitutes the interarrival time distribution of the Poisson process considered by Feller into the transit time distribution, $\chi(\tau) = \alpha e^{-\alpha\tau}$ $(\alpha = \tau_{\text{transit}}^{-1})$, then from expression (1) in Fig. 1 and Eqs. (3) and (7) one easily obtains the surprising result for the ''mean waiting time'' $\tau_{\text{intra}} = \tau_{\text{transit}}$. Feller had explained it by the fact that the observation time is more probable to fall into a *longer* interval between arrivals. Consistently, if all interarrival times are identical, $\chi(\tau) = \delta(\tau - \tau_{\text{transit}})$, the intuitive result $\tau_{\text{intra}} = \tau_{\text{transit}}/2$ becomes correct.

III. EXAMPLES OF APPLICATION

Three special examples shall illustrate ways in which the general relations presented above (or similar ones, respectively) can be exploited to answer concrete questions of research. At first, consider a finite array of particles which are able to diffuse along one dimension without having the possibility to pass each other [5]. An example of such a ''single-file system'' is zeolitic adsorbate-adsobent systems of a one-dimensional channel structure (e.g., tetraflouromethane in zeolite $AlPO_4$-5) [6]. Since there is still no satisfactory analytical solution modeling the exchange dynamics, one has to resort to the more empirical results of Monte Carlo computer

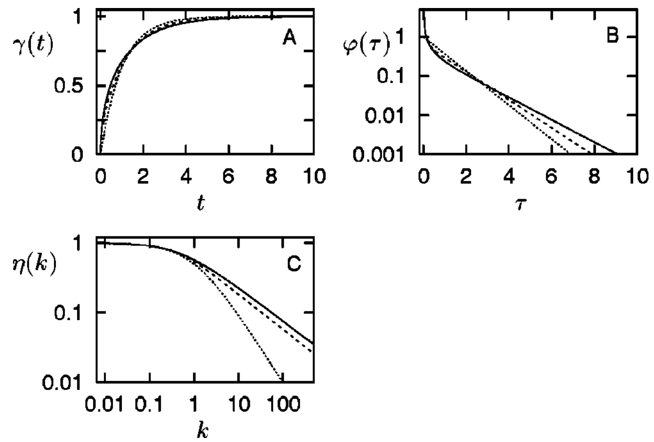

FIG. 2. Residence time distributions (b) and effectiveness factors (c) as calculated from simulated tracer exchange curves (a) for three different adsorbate-adsorbent systems: normal diffusion (----), single-file diffusion (——), and barrier-limited exchange ($\cdots\cdots$). [All times are given in units of the mean intracrystalline lifetime τ_{intra} as expressed by Eq. (7).]

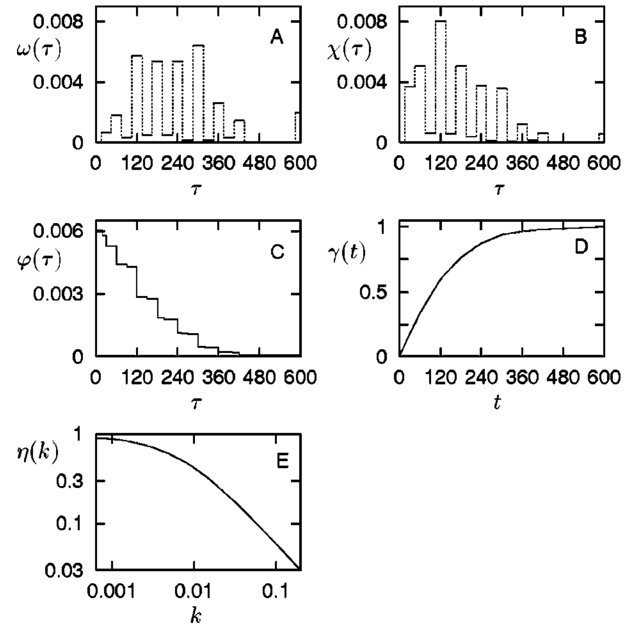

FIG. 3. Transit time distribution (b), residence time distribution (c), relative amount of new customers (d), and relative amount of strolling customers with empty trolleys in dependence on the assumed ''buying rate'' (e), calculated from the modified transit time distribution (a), which was obtained from interviews with the customers of a shopping center (all times are given in minutes). The mean time the customers spend within the center is approximately $\tau_{\mathrm{transit}}=170$ min as obtained from $\chi(\tau)$ via Eq. (3).

simulations. Figure 2(a) shows a tracer exchange curve typical for a single-file system [7], compared with the analytical curves for systems ruled by normal diffusion or by transport resistances at the surface. The residence time distributions and the effectiveness factors for the same cases are presented in Figs. 2(b) and 2(c), this time calculated by the network equations without the need of further time-expensive computer simulations. Similarly, a dramatic reduction of computation expense was possible on calculating τ_{intra}. Instead of using its definition, Eq. (6), which requires simulating a complete curve $\gamma(t)$ and averaging over a large number of systems, one may calculate τ_{intra} via Eq. (7) as a time average of residence times of just a single system [8].

A special tracer exchange experiment is the tracer desorption ZLC (zero length column) technique [9], measuring the *time derivative* of $\gamma(t)$ of an adsorbate-adsorbent system. According to a hypothesis coined in Ref. [10], one should be able to discriminate between normal and single-file diffusion by whether the logarithmic long-time tail of this response curve is straight or bent (as suggested by the different time behavior of the mean square displacement of tagged particles). Since, however, due to expression (3) in Fig. 1, the time derivative of $\gamma(t)$ is merely $\varphi(\tau)$, Fig. 2(b) clearly disproves this hypothesis: Identically, *all* curves tend asymptotically to single exponentials.

The second example demonstrates that the relevance of the network reaches beyond typical physics. Figure 3(a) shows the result of interviews with the customers of one of the largest shopping centers in Germany [11], representing their estimates of the duration of their stay in the center (i.e., their estimated ''transit times''). For simplicity, we assume that these estimates reflect the true situation with sufficient precision (and that the population is sufficiently stationary). Interestingly, although referring to transit times, this curve does not give $\chi(\tau)$ since it reflects the distribution among the customers *within* the center. In contrast, the conversion of this *modified transit time distribution* $\omega(\tau)$ into the function $\chi(\tau)$ [Fig. 3(b)] by expression (2) in Fig. 1 yields the fictive result if the interviews would have taken place *at the exit doors*. The ''tracer exchange curve'' [Fig. 3(d)] gives the relative amount of customers which have newly entered the center within the time t. If the interest focuses on the strolling customers, even the ''effectiveness factor'' [Fig. 3(e)] allows an interpretation. As a crude approximation of the rather complex behavior of customers, one might assume that they buy, stimulated by some display, incidentally with an (unknown) rate k (i.e., on average once in time $1/k$). The quantity $\eta(k)$ would then give the (observable) relative amount of customers with a still empty shopping cart.

Our final example concerns the blood flow in the coronary arteries, being of high diagnostic value. As a well validated method, digital subtraction coronary angiography [12] (injecting a small bolus of a contrast medium into the influx blood and measuring its concentration within the perfused myocardium via x-ray extinction) determines the ratio of maximal coronary flow (stimulated by vasodilatatory drugs) to resting flow, known as *coronary flow reserve* [13]. The *absolute* flow, however, can only be measured by methods such as intracoronary Doppler-ultrasound catheters, which are expensive and involve additional risks. Further, the densiometric method determines the vascular volume by only an approximative method, which is generally criticized [14]. The network of characterizing functions inspired a new way of data processing [15], yielding both the absolute volume flow I and the total volume V just from the angiographic extinction curves, which give ϱ_E, $V\varrho$, and ϱ_A. It represents an application of general equations like Eqs. (4) and (5) and makes use of the fact that τ_{transit} can be calculated in several different ways. This enabled a better exploitation of the information contained in the measured data.

IV. CONCLUSION

The presented equations with the involved functions can be applied quite universally in the analysis of the exchange dynamics of open stationary systems, to be encountered numerously in nature and society. Although individual ones of these relations are in daily use in several branches of science (see, e.g., [4]), so far the remarkable generality of the network of interrelated characterizing functions is not, to our knowledge, commonly appreciated. Being a comfortable tool if the internal dynamics allows a mathematical treatment, it even offers means of analysis if the underlying mechanisms are too difficult to be handled mathematically or if explicit models of the internal processes do not even exist. Without requiring any additional knowledge about the inherent mechanisms, each of the characterizing functions may be used to determine any other of them, as well as the system response to changes in the surrounding. Thus it turns out that a particular feature of the system may be inferred from another, seemingly completely different one. In each of the three presented examples of current research interest, the network of interrelated characterizing functions was, in quite different ways, most helpful to provide new insights.

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