Journal of Statistical Physics, Vol. 20, No. 6, 1979

Distributive Processes and Combinatorial Dynamics

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Received October 12, 1977; revised November 29, 1978

We describe a new family of Markov processes, a prototype for which is in the statistics of a test molecule undergoing "random" energy transfer in collisional complexes with heat-bath particles. Master equations for several versions of this process are constructed and solved exactly under purely statistical prescriptions of the mechanism and degrees of freedom available. Their eigenfunctions, arising through a natural factorization of the transition kernels, prove to be classical polynomials of Laguerre and Jacobi type; the relaxation times are given by simple terminating series in the degree-of-freedom parameters. Moreover, the spectral representations of such kernels prove to be Erdelyi-type bilinear expansion in the respective eigenfunctions, giving these little-known formulas a previously unsuspected physical interpretation. A remarkable property of the solutions is that they are both exact and parametrized over the whole range of behavior from effective "Brownian motion" at one extreme to virtually purely random processes at the other. Autocorrelation functions for equilibrium fluctuations in the same ensembles are also obtained and shown to be strictly exponential. Applications of such "*distributive processes*" are discussed with reference to both the physics of energy transfer and possible alternative realizations, e.g., in operations research. Some related mathematical topics, notably the role of fractional integral-operators in the master equation, are pointed out.

KEY WORDS: Stochastic models; Markov processes; master equation; energy transfer; exact solutions; internal degrees of freedom; Erdelyi expansions; fractional operators.

1. INTRODUCTION

Consider the following statistical thought-experiment. A polyatomic molecule (A) is immersed in a heat bath of dissimilar molecules (B) with which it can exchange energy only through binary collisions. Let the system molecule (A) and heat-bath molecules (B) possess p and q internal degrees of freedom,

The work was financially supported by the Science Research Council (London).

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0022-4715/79/0600-0597$03.00/0

respectively, and make the statistical hypothesis that, upon each binary collision, the internal energy of the two partners is, in an appropriate sense, *randomly distributed* between them. Assuming the notions here introduced to be mathematically definable, if somewhat questionable physically, we may pose a number of problems of increasing difficulty.

(i) What is the probability that the molecule (A), given an internal energy x, will make a transition to an element of energy dy about y upon random collision? How will this depend on the heat-bath temperature and the degree-of-freedom parameters?

(ii) Does the energy distribution of an ensemble of such test molecules approach a Boltzmann equilibrium distribution, and if so, how?

(iii) Given that a stable equilibrium distribution is attained, what are the characteristics of the *equilibrium fluctuations* of such an ensemble, in particular, its energy autocorrelation function and power spectrum?

(iv) How does the same system behave in the presence of an *absorbing barrier* causing the molecules to be removed at some critical upper (or lower) threshold of energy $x^{\dagger}$?

Even informally, we may see that this type of model is rich in statistical interest (see Fig. 1). At the one extreme, that for $q \gg p$, we may expect the system and heat bath to be so strongly coupled that correlation of states before and after collision is virtually absent; at the other, for $q \ll p$, the system undergoes relatively minute changes at each collision and the evolution might be expected to approximate to some form of Brownian motion. The intermediate situation will clearly correspond to a first-order Markov process on continuous states with autocorrelation markedly dependent on the parameters p and q.

Although we have deliberately taken it out of its original context, the problem described here may be recognized as one of a number which have been current in the theory of chemical reactions and intermolecular energy transfer, stimulated largely by the ideas of Kassel.[1,2] While interest in this type of theory has declined somewhat, the original statistical models retain

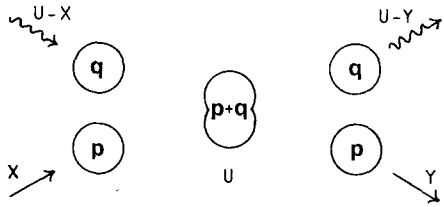

Fig. 1. The distributive process for a p system in a q heat bath. In each collision complex internal energy is conserved and randomly distributed between the p and q available degrees of freedom.

importance, if only because of the near impossibility of writing any sort of dynamical theory of energy transfer between polyatomic molecules that consistently embodies a strong coupling between all degrees of freedom present.[3] In fact the probability scheme originating in answer to question (i) above seems to us to be the only one yet devised which both allows for multiple degrees of freedom and yet is consistent with general conditions of stochasticity, equilibrium stability, and detailed balance. Moreover, it is clear to us that the domain of interest of stochastic processes of "distributive" type extends considerably beyond the physical context we assume here. It is not difficult to envisage applications in fields of applied probability as diverse as storage theory, economic models, and perhaps genetics.

On the mathematical side an unexpected gain has been the discovery of a connection between our solutions for "distributive models" and a variety of lesser known expansion formulas and operator relationships in the theory of special functions. Thus we have obtained for the first time a physical realization of the "Erdelyi-type" bilinear expansions for classical orthogonal polynomials[4,5] as well as, through consideration of the underlying statistical models, extending the list of such expressions by several previously unpublished formulas.[6,7] These and other mathematical aspects are being treated elsewhere,[6,8] but their relationship to the physics of the problem will be indicated briefly as it arises.

1.1. Organization of the Work

This paper is divided as follows: After a general introduction and the setting of notations (Sections 1 and 2) we derive the system of transition probabilities for the problem posed in the opening paragraph (Section 3). A number of properties directly deducible from the transition kernel are then obtained, including the autocorrelation function for equilibrium fluctuations in a "distributive ensemble" (Sections 4 and 5). In Section 6 we solve the eigenvalue problem for the kernel exactly and thence obtain its full relaxation solution and spectral representation. Using this process as a prototype, several extensions to the idea of "distributive processes" over continuous random variables are explored, some of which suggest important applications to energy transfer in molecular systems. (Sections 7–9). A companion paper, to be published elsewhere, extends the present results to the domain of discrete-variable processes.[9]

1.2. Continuous Combinatorics and Occupancy Problems

As a starting point we may take the need to formalize the notion introduced above that in some way a continuous quantity, such as energy, may be considered to be "randomly distributed" among all possible degrees of

freedom of an entity, such as the collision complex of two colliding molecules. The basic formulas we require are quite well known, though often presented in somewhat restricted language. The point of view we take is entirely a stochastic one—that is, we define the state of our physical system in terms of certain random variables whose behavior derives from general statistical assumptions without further reference to any underlying deterministic or quantum mechanics.

In this spirit we begin by examining the level of description in which the state of some small physical system (e.g., a molecule) is specified by the partitioning of some conserved quantity (e.g., its total vibrational energy) into subvariables which are additively, though not individually, conserved. Following common usage, the number of such variables will be termed the *degrees of freedom* of the system and a particular partition $\{\epsilon_1, \epsilon_2, \ldots, \epsilon_s\}$ a *complexion* or *microstate* corresponding to the *macrostate* E, where

$$0 \leqslant \epsilon_i \leqslant E; \qquad \sum_{i=1}^{i=s} \epsilon_i = E$$

If we specify an s-dimensional state space of the variables ϵ_i and associate each complexion with a point in it, then the total volume of state space accessible to systems in dE about E can be specified by a *structure function* $G_s(E)$ defined as

$$G_s(E)\, dE = \int \cdots \int_{\{E \leqslant \epsilon_1 + \epsilon_2 + \cdots \epsilon_s \leqslant E + dE\}} d\epsilon_1 \cdots d\epsilon_s \tag{1}$$

(cf. Kinchine[10]). If no further constraints than those in $\{\cdots\}$ are applied and, in particular, if the variables $\{\epsilon_i\}$ are uncorrelated, then the integral is elementary and gives the well-known result

$$G_s(E) = E^{s-1}/(s-1)! \tag{2}$$

The above, purely geometrical, properties take on additional interest when we consider the *structure function* for subsets of degrees of freedom among the total s. We can then define what is in effect a continuous *occupancy problem* in which the quantity of importance is the probability density $W_{p,q}(x, E)$ defined as

$$W_{p,q}(x, E)\, dx = \Pr\left\{\begin{matrix} p \text{ subsystems of a total } p+q \text{ have a share} \\ \text{in } dx \text{ about } x \text{ when } p+q \text{ contain } E \end{matrix}\right\}$$

If the complexions remain unbiased the result is evidently

$$W_{p,q}(x, E) = \frac{G_p(x) G_q(E-x)}{G_{p+q}(E)}, \qquad 0 \leqslant x \leqslant E$$

$$= \frac{\Gamma(p+q)}{\Gamma(p)\Gamma(q)} \frac{x^{p-1}(E-x)^{q-1}}{E^{p+q-1}} \tag{3}$$

Thus $W_{p,q}(x, E)$ is the Beta distribution normalized on the interval $(0, E)$:

$$\int_0^E W_{p,q}(x, E)\, dx = 1 \tag{4}$$

Putting $p = 1$, we obtain the probability density for a single degree of freedom

$$W_{1,q}(x, E) = q(E - x)^{q-1}/E^q, \qquad 0 \leqslant x \leqslant E \tag{5}$$

while for the special case $p = q = 1$ we see that the whole reduces to a uniform distribution: $W_{1,1}(x, E) = E^{-1}$.

1.3. The Thermodynamic Limit

In order to link up with the problem posed in the introduction, it is interesting at this stage to consider the limiting process $E \to \infty$, $s \to \infty$, $E/s = \beta$, a constant. This clearly corresponds to the required case of a system in thermal equilibrium with a "heat bath" of infinite degrees of freedom, characterized by a temperature β^{-1}. We observe that

$$\lim_{\substack{E\to\infty, q\to\infty \\ q=\beta E}} W_{p,q}(x, E) = \frac{x^{p-1}}{\Gamma(p)} \lim_{\{\cdots\}} \frac{q(q+1)\cdots(q+p-1)}{E^p} \left(1 - \frac{x}{E}\right)^{q-1}$$

from which, under the given constraint,

$$W_{p,\infty}(x, \beta) = [\beta^p/\Gamma(p)]x^{p-1}e^{-\beta x} \tag{6}$$

Thus the Beta distribution converts to a Gamma distribution (Boltzmann distribution in physical contexts).

2. PURE RANDOM SAMPLING DYNAMICS

At the level of simple combinatorics we can do little more than expose the properties of the distributions just given in terms of hypothetical "sampling trials" in which a state variable x is measured over an ensemble, or, equivalently, over an infinite sequence of independent "randomizations." Such thought-experiments formed the basis of early theories of unimolecular reactions,[2] the randomization of energy among vibrational degrees of freedom being imagined as brought about by some ill-defined form of intramolecular "collisions." The conclusions that can be drawn from such experiments are somewhat limited, once we have derived the distributions themselves and their moments. (See Table I.)

A slightly less obvious problem, however, is that of deriving the probability that, on a random trial, the state variable for a *single* degree of freedom

will be found to exceed some threshold value, say E_0. By integration of (5) we arrive at Kassel's formula for this, viz.

$$w_s(E, E_0) = \Pr\left\{\begin{matrix}\textit{one} \text{ degree of freedom of a total } s \text{ has} \\ x > x_0 \text{ when } s \text{ altogether contain } E\end{matrix}\right\}$$

$$= \int_{E_0}^{E} W_{1,s-1}(x, E)\, dx = \left(\frac{E - E_0}{E_0}\right)^{s-1} \tag{7}$$

If we then regard the event in brackets as "success" in a sequence of Bernoulli trials, it is easily shown that the mean number of trials to success is simply $\langle n \rangle = [E_0/(E - E_0)]^{s-1}$ under the conditions stated. If the trials are with random incidence in time, similar to collisions in a dilute gas (i.e., a Poisson process), the mean waiting time to success $\langle t \rangle$ is given by the same expression, provided that time is scaled in units of the mean collision time.

More complicated formulas can be derived if we consider the probability that a group of subsystems together reach a given energy threshold, but, so long as successive outcomes remain statistically independent, the processes are of limited interest.

3. MARKOVIAN MODELS AND TRANSITION PROBABILITIES

3.1. Distributive Transition Probabilities

It is clear that the relaxation problem described in the introduction involves more than the simple occupancy statistics just considered. When the test molecule (the p molecule) collides with one of the heat-bath molecules (the q molecules) it is not instantly equilibrated to the heat-bath temperature, but instead simply shares its energy in an unbiased manner with the q degrees of freedom available. A degree of correlation will thus be present between states before and after collision, this evidently increasing with the ratio p/q. The distribution in the exchange being, nevertheless, independent of the previous collision, the process can clearly be described by a first-order Markov process on a continuous state space $(0, \infty)$. What then are the transition probabilities governing this?

Consider a collision between a particular p molecule, with specified energy x, and a random q molecule having the Gamma energy distribution of the heat bath. We define the *transition kernel* $K(y, x)$ in the usual way as the probability density for the outcome of this collision to be a state with energy in dy about y. For the present we shall imagine a sequence of discrete trials at intervals indexed by n.

The explicit form of $K(y, x)$ is easily written if we notice that the mechan-

ism of "distributive" energy exchange implies a convolution of the (Beta) distribution for the total energy available in a collision complex with the (Gamma) distribution of the heat-bath q molecules entering it. Thus, on integrating over the joint probabilities of formation and breakup of all complexes, we see that

$$K_{p,q}(y, x) = \int_0^\infty W_{p,q}(y, u) W_{q,\infty}(u - x, \beta) H(u - x) H(u - y)\, du \quad (8)$$

where $W_{p,q}(y, u)$ and $W_{q,\infty}(x, \beta)$ are the Beta and Gamma distributions, respectively, and $H(\cdot)$ indicates the unit step function. Thus

$$K_{p,q}(y, x) = \frac{\Gamma(p+q)}{\Gamma(p)\Gamma(q)^2} \beta^q y^{p-1} e^{\beta x} \int_{\max(x,y)}^\infty \frac{(u-x)^{q-1}(u-y)^{q-1} e^{-\beta u}\, du}{u^{p+q-1}} \quad (9)$$

The presence of the step functions, which could be taken as implicit in the two distributions, marks the fact that the collision complex cannot contain less energy than the initial state nor give up more than it contains on division. With the structure of the diagram in Fig. 2 in mind, we shall adopt a notation for the process giving rise to the kernel (9). It will be referred to as the $(p|q, \infty)$ process, the bar indicating the degrees of freedom which interact distributively and the ∞ referring to the infinite degrees of freedom of the heat bath. This system can encompass other interesting cases, such as the $(p|q, r)$ and $(p, q|r, s)$ processes which we treat in Section 9.

The kernel (9), originally derived by Hoare,[11] has both properties to be expected from its method of construction and a number of surprising ones. In particular we may distinguish the following:

3.1.1. Scaling. For most purposes (see, however, Section 3.1.10) we may adopt the scaling $x \to \beta x$, measuring the state variable in units of β^{-1} ($k_B T$ in the physical problem). We can thus suppress the parameter β in the Gamma distribution, writing it as $W_{p,\infty}(x)$ in what follows.

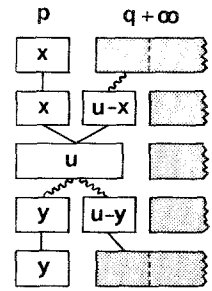

Fig. 2. The probabilistic structure of the $(p|q, \infty)$ distributive process. Here and in subsequent diagrams the wavy lines distinguish the random steps. The heat-bath degrees of freedom are shown shaded. In the notation used above, the vertical bar indicates the division between system and surroundings, the comma indicates the distinction between systems otherwise interacting.

3.1.2. Positivity, Continuity, and Boundedness. Manifestly $0 < K(y, x) < \infty$ for all $x, y \in (0, \infty)$ and p, q positive integers $\geqslant 1$. The $K(y, x)$ diverges at $K(0, 0)$ for the special case $p = q = 1$ but is otherwise bounded in the whole x, y quadrant. The structure of the integral is such that the first $q - 1$ partial derivatives are continuous at the diagonal but that a discontinuity at $x = y$ appears in the derivatives $(\partial^q K/\partial x^q)$ and $(\partial^q K/\partial y^q)$. This Green-function-like property will be seen later to play a crucial role.

3.1.3. Stochasticity. As a convolution of two stochastic kernels, K is itself stochastic, i.e.,

$$\int_0^\infty K_{p,q}(y, x)\, dy = 1 \tag{10}$$

for all $x \in (0, \infty)$. The result, which is evident from (8) and may be checked by partial integrations of (9), corresponds to the existence of a *left* eigenfunction $\psi_0(x) = 1$ with eigenvalue $\lambda_0 = 1$.

3.1.4. Detailed Balance. The symmetry property

$$W_{p,\infty}(x)K_{p,q}(y, x) = W_{p,\infty}(y)K_{p,q}(x, y) \tag{11}$$

is likewise ensured by the method of construction and gives the condition of detailed balance at equilibrium. We may use this to define a new symmetric kernel $G(x, y)$ by the transformation

$$G(x, y) = [W_{p,\infty}(x)/W_{p,\infty}(y)]^{1/2}K_{p,q}(y, x) = G(y, x) \tag{12}$$

3.1.5. Stationarity. The previous two properties together imply that $K(y, x)$ preserves the equilibrium Gamma distribution $W_{p,\infty}(x)$, i.e.,

$$\int_0^\infty K_{p,q}(x, y)W_{p,\infty}(y)\, dy = W_{p,\infty}(x) \tag{13}$$

In other words $W_{p,\infty}(x)$ is necessarily a *right* eigenfunction of K, also with eigenvalue $\lambda_0 = 1$.

3.1.6. Moment Properties. The moments $k_{p,q}^{(n)}(x)$ defined by

$$k_{p,q}^{(n)}(x) = \int_0^\infty y^n K(y, x)\, dy \tag{14}$$

govern in a crucial manner the statistical properties of the kernel. Although they may be obtained by lengthy partial integrations of the expression (9), this is unnecessary, for we may operate directly upon the defining relation (8).

Thus, remembering that $W_{p,q}(x, y)$ and $W_{p,\infty}(x)$ stand for the Beta distribution and the dimensionless Gamma distribution, respectively, we have

$$\begin{aligned} k_{p,q}^{(1)}(x) &= \int dy\, y \int du W_{p,q}(y, u) W_{q,\infty}(u - x) \\ &= \int du\, W_{q,\infty}(u - x) \int dy\, y W_{p,q}(y, u) \\ &= \frac{p}{p + q} \int du\, W_{q,\infty}(u - x) u \\ &= \frac{p}{p + q} \int du\, W_{q,\infty}(u)(u + x) \\ &= \frac{p}{p + q} [x + q] \end{aligned} \tag{15}$$

In these integrations we have left the step functions implicit in the integrands and used the moments of the Beta and Gamma distributions from Table I. We see that, somewhat surprisingly, the first moment of $K(y, x)$ defined by (9) is simply a first-order polynomial in x.

3.1.7. Eigenfunction Properties. As is readily shown (see, e.g., Oppenheim *et al.*[12]) the properties (10) and (11) imply that $K(y, x)$ is positive-definite, having a unique eigenvalue $\lambda_0 = 1$ and an infinite spectrum of real eigenvalues $0 < \lambda_k < 1$. Moreover, these are associated with complete sets of right and left eigenfunctions $\phi_k(x)$ and $\psi_k(x)$, respectively, satisfying the equations

$$\int_0^\infty K(x, y)\phi_k(y)\, dy = \lambda_k \phi_k(x) \tag{16}$$

and

$$\int_0^\infty \psi_k(y) K(y, x)\, dy = \lambda_k \psi_k(y) \tag{17}$$

Table I. Distributions in Continuous Combinatorial Dynamics

Distribution	State space	Form	Mean	Variance	Moments
Beta	$x \in (0, E)$	$B(p, q)^{-1} \times \frac{x^{p-1}(E - x)^{q-1}}{E^{p+q-1}}$	$\frac{pE}{(p + q)}$	$\frac{pqE^2}{(p + q)^2(p + q + 1)}$	$\frac{(p)_n E^n}{(p + q)_n}$
Gamma	$x \in (0, \infty)$	$\Gamma(p)^{-1}\beta^p x^{p-1} e^{-\beta x}$	p/β	p/β^2	$(p)_n/\beta^n$

We know from Sections 3.1.3 and 3.1.5 that the stationary eigenfunctions, corresponding to $\lambda_0 = 1$, can be chosen as

$$\psi_0(x) = 1 \tag{18}$$

and

$$\phi_0(x) = W_{p,\infty}(x) = \Gamma(p)^{-1} x^{p-1} e^{-x} \tag{19}$$

for the present kernel. Combining these with the detailed-balance symmetry, Section 3.1.4, it follows that the left and right eigenfunctions are related through

$$\phi_k(x) = \phi_0(x)\psi_k(x) \tag{20}$$

The determination of the $\psi_k(x)$ for the distributive kernel (9) will be our first objective.

3.1.8. Special Cases. A number of special cases lead to considerable simplification of the kernel. Thus, if $q = 1$ we find

$$K_{p,1}(y, x) = py^{p-1}e^x \int_{\max(x,y)}^{\infty} (e^{-u}/u^p)\, du$$

$$= p(y/x)^{p-1} e^x E_p(\max(x, y)) \tag{21}$$

where $E_p(x)$ is a tabulated function related to the exponential integral (Ref. 13, Item 5.1.4). On further simplification to the case $p = q = 1$

$$K_{1,1}(y, x) = e^x \,\mathrm{ei}[\max(x, y)] \tag{22}$$

This kernel, representing the "distributive" interaction of a single oscillator with a similar heat bath, was originally studied by Hoare.[11] It has the peculiarity that there is divergence at $K(0, 0)$ while at the same time all *down* transitions from a given energy are equally probable.

3.1.9. Limiting Forms. More interesting in certain respects are the asymptotic forms of the kernel for the two cases $q \ll p$ and $q \gg p$. Consider the first.

$q \gg p$: The essence of this case can be seen on examining the general structure of the kernel (9) and observing the behavior of the two factors in the convolution as $q \to \infty$. Under these conditions the main contribution to the integral comes from large values of u near the peak of the shifted Gamma distribution. Replacing u by its value at the maximum, we find that the first factor in the convolution becomes $W_{p,q}(y, q - 1 + x)$. Letting now $q \to \infty$, it is evident that this becomes independent of x as it tends to the scaled Gamma distribution. Thus

$$\operatorname*{Lim}_{q\to\infty} K_{p,q}(y, x) = \operatorname{Lim} \int_0^\infty W_{p,q}(y, q + x - 1)W_{q,\infty}(u - x)\, du$$

$$= W_{p,\infty}(y) \tag{23}$$

The physical content of this is plain. The transition kernel being proportional to its own equilibrium distribution in the final state, an arbitrary ensemble distribution of test molecules will be equilibrated at a single distributive trial. Thus, for any $P(x)$ normalized to unity we have trivially

$$\operatorname*{Lim}_{q\to\infty} \int_0^\infty K_{p,q}(x, y)P(y)\, dy = W_{p,\infty}(x)$$

The Markovian character of the process has vanished and we are left with a pure random process with the Gamma distribution.

Consider now the opposite extreme.

$q \ll p$: An ensemble of test particles having many degrees of freedom now interacts with a heat bath of molecules having relatively few. To a crude approximation we may now replace the Beta distribution in Eq. (8) by a delta function at its very sharp maximum. Thus

$$W_{p,q}(y, x) \approx \delta\{u - [(p + q - 2)/(p - 1)]y,$$

so that qualitatively

$$K_{p,q}(y, x) \underset{p\to\infty}{\simeq} \Gamma(q)^{-1}\beta^q z^{q-1}e^{-\beta z}H(z)$$

where $z = y - [(p + q - 2)/(p - 1)]x$. The interesting energy range near equilibrium being now the vicinity of the Maxwellian mean $\langle x\rangle = p\beta^{-1}$, we can see that, for large p, transitions become restricted to a very narrow peak about the diagonal $y = x$. Though this does not in itself lead to true Brownian motion, the evolution of the system can be expected to have something of the character of a diffusion process.

3.1.10. Relaxation in a "Cold" Heat Bath. Reverting again to the unscaled form of the kernel (8) and (9), we may note that, in the limit of a perfectly "cold" heat bath ($\beta \to \infty$) the transition probability takes the form:

$$K_{p,q}(y, x) = W_{p,q}(y, x)$$

$$= \Gamma(p + q)\Gamma(p)^{-1}\Gamma(q)^{-1}y^{p-1}(x - y)^{q-1}x^{-(p+q-1)}, \qquad y \leqslant x$$

$$= 0; y > x \tag{24}$$

[Note that this is equivalent to taking $W_{q,\infty}(u - x, \beta) \to \delta(u - x)$ in the gamma distribution (6).] The relaxation process remains well defined except that now only *down* transitions are possible and the ensemble will approach the asymptotic distribution $P(x, \infty) = \delta(x)$. This type of problem is interesting in its own right and will be discussed more fully elsewhere.[14]

4. TIME-DEPENDENT PROPERTIES IN GENERAL

The time-dependent properties of stationary Markovian models such as those invented here can be exposed in a number of ways. Common to all these, however, is an essential dependence upon the eigenvalue properties of the transition kernel $K(y, x)$ as expressed in (16) and (17). The formal solutions to the problems posed in the introduction are well enough known that we need only quote them here. Several cases need to be distinguished, however.

4.1. Evolution in Continuous Time: The Master Equation

If $0 \leqslant t < \infty$ is a continuous time scale, with t reduced in terms of some characteristic "collision frequency," then, provided the latter is not a function of the state variable x, and that the kernel K is stationary in time, the evolution of an ensemble distribution $P(x, t)$ will be given by a nonsingular master equation

$$\frac{\partial}{\partial t} P(x, t) = \int_0^\infty K(x, y)P(y, t)\, dy - P(x, t) \tag{25}$$

The solution in eigenfunctions is well known (see, e.g., Ref. 12). We can write

$$P(x, t) = \phi_0(x) + \phi_0(x) \sum_{k=1}^{\infty} a_k \psi_k(x) \exp[-(1 - \lambda_k)t] \tag{26}$$

where $\psi_k(x)$ and $\phi_k(x)$ are left and right eigenfunctions of K with eigenvalues λ_k, and the a_k are constants to be determined from the initial probability distribution $P(x, 0)$. Given the detailed balance condition (11), the eigenfunctions must satisfy an orthogonality property

$$\int_0^\infty \phi_0(x)\psi_i(x)\psi_j(x)\, dx = N_i\, \delta_{ij} \tag{27}$$

with N_i an appropriate normalization function; the coefficients a_k are then determined through the relation

$$a_k = N_i^{-1} \int_0^\infty \psi_k(x)P(x, 0)\, dx \tag{28}$$

Alternatively, the "fundamental" initial condition $P(x, x_0, t) = \delta(x - x_0)$ may be applied to give the coefficients $a_k(x_0) = N_k\psi_k(x_0)$ and the general solution then determined by the superposition principle.

4.2. Evolution in Discrete Time: Iterate Kernels

Evolution in discrete time, i.e., when indexed by the number of consecutive "trials" rather than a continuous timelike parameter with random

incidence of transitions, may be expressed in a manner closely parallel to the above. In the present context we ask for the probability $P(x, n)$ that a test molecule will be in state dx about x at the nth of a series of distributive "collisions" with the heat bath, given its initial condition $P(x, 0)$. This is given by

$$P(x, n) = \int_0^\infty K^{(n)}(x, y)P(y, 0)\, dy \tag{29}$$

where $K^{(n)}(y, x)$ is the nth *iterate kernel* defined recursively through

$$K^{(n+1)}(y, x) = \int_0^\infty K(y, w)K^{(n-1)}(w, x)\, dw$$

$$K^{(1)}(y, x) \equiv K(y, x) \tag{30}$$

Determination of the *n-step transition probability* $K^{(n)}(y, x)$ is likewise possible in terms of the eigenvalue solutions. This time we use a bilinear expansion formula, i.e., the *spectral representation* of $K^{(n)}$ in the form

$$K^{(n)}(y, x) = \phi_0(y) + \phi_0(y) \sum_{k=1}^{\infty} (\lambda_k{}^n/N_k)\psi_k(x)\psi_k(y) \tag{31}$$

with the eigenfunctions $\phi_k(x)$ and $\psi_k(k)$ determined as before. We see that, whereas for continuous time the equilibrium distribution is approached by decay of the exponential transients $\exp(-\lambda_k t)$, for discrete time this results from the vanishing of powers $\lambda_k{}^n$ with $0 < \lambda_k < 1$. [Note that in separating the equilibrium terms above we have used the choice $\psi_0(x) = 1$.]

4.3. Moment Evolution and Autocorrelation: Continuous Time

The evolution of the moments of an initial distribution $P(x, 0)$ may often be determined without knowledge of the full distribution function $P(x, t)$ and the eigenvalue solutions. Special interest attaches to the first moment of the initial delta distribution $P(x, 0) = \delta(x - x_0)$. Let this be designated $\langle x(t); x_0 \rangle$, where

$$\langle x(t); x_0 \rangle = \int_0^\infty xP(x|x_0, t)\, dx \tag{32}$$

and $P(x|\, x_0, t)$ is the evolution of the given delta function.
Forming moments on both sides of Eq. (26), it can be seen that

$$\langle x(t); x_0 \rangle = \langle x(\infty) \rangle + \sum_{k=1}^{\infty} N_k^{-1} X_{0k}\psi_k(x_0) \exp[-(1 - \lambda_k)t] \tag{33}$$

with X_{0k} the "matrix-element"-like quantity

$$X_{0k} = \int_0^\infty x\phi_0(x)\psi_k(x)\,dx \tag{34}$$

The autocorrelation function for equilibrium fluctuations in the variable x is closely related. In the familiar manner this can be written

$$S_x(t) = \int_0^\infty \phi_0(x_0)\{[\langle x(t); x_0\rangle - \langle x(\infty)\rangle][x_0 - \langle x(\infty)\rangle]\}\,dx_0 \tag{35}$$

[noting, of course that $\langle x(0); x_0\rangle = x_0$]. Using the eigenfunction expansion (33) and the orthogonality property, it follows that

$$S_x(t) = \sum_{k=1}^{\infty} N_k^{-1} X_{0k}^2 \exp[-(1 - \lambda_k)t] \tag{36}$$

(cf. Lax[15] and Hoare[16]).

There are nevertheless, as we have indicated, conditions under which the full eigenvalue problem may be bypassed to yield the moment evolution $\langle x(t)\rangle$ and autocorrelation function $S_x(t)$ directly. As Andersen, *et al.*[17] proved:

A sufficient condition for pure exponential relaxation of the moment $\langle x(t)\rangle$ *in a continuous-time process with transition kernel* $K(x, y)$ *is that the latter possess a first moment* $k^{(1)}(x)$ *of the form* $k^{(1)}(x) = a + bx$ *with* a *and* b *constants.* (The AOSW condition.)

It then follows that the mean of x at equilibrium is given by $\langle x(\infty)\rangle = a/(1 - b)$ and that the relaxation solution is explicitly

$$\frac{\langle x(t)\rangle - \langle x(\infty)\rangle}{\langle x(0)\rangle - \langle x(\infty)\rangle} = e^{-(1-b)t} \tag{37}$$

It is a simple step from this to the equilibrium autocorrelation function in the form

$$S_x(t) = \mathrm{Var}(x)_{eq}\, e^{-(1-b)t} \tag{38}$$

with $\mathrm{Var}(x)_{\mathrm{eq}}$ the equilibrium variance

$$\mathrm{Var}(x)_{\mathrm{eq}} = \int_0^\infty \phi_0(x)[x - \langle x(\infty)\rangle]^2\,dx \tag{39}$$

4.4. Moment Evolution and Autocorrelation: Discrete Time

The moment and autocorrelation equations for discrete-time processes follow in similar manner from the bilinear expansion (31). Thus for the first moment of a delta distribution after n trials

$$\langle x(n); x_0 \rangle = \langle x(\infty) \rangle + \sum_{k=1}^{\infty} (\lambda_k{}^n / N_k) X_{0k} \tag{40}$$

and for the autocorrelation of equilibrium fluctuations

$$S_x(n) = \sum_{k=1}^{\infty} (\lambda_k{}^n / N_k) X_{k0}^2 \tag{41}$$

If the ASOW condition applies, there is a corresponding simplification. Forming moments of *any* initial distribution $P(0)$ for this type of kernel, we see from Eq. (29) that

$$\langle x(n+1) \rangle = a + b\langle x(n) \rangle \tag{42}$$

or, in terms of the difference operator Δ,

$$\Delta\langle x(n) \rangle = a + (b-1)\langle x(n) \rangle \tag{43}$$

This is a standard first-order difference equation, which has the solution[18]

$$\langle x(n) \rangle = b^n \langle x(0) \rangle + (1 - b^n)\langle x(\infty) \rangle \tag{44}$$

for given initial moment $\langle x(0) \rangle$. From this it follows that the n-step autocorrelation (autocovariance) function is just

$$S_x(n) = b^n \operatorname{Var}(x)_{\text{eq}} \tag{45}$$

5. MOMENTS AND AUTOCORRELATION FOR THE $(p|q, \infty)$ PROCESS

With the groundwork of the previous section and our result (15) for the first moment of the $(p|q, \infty)$ distributive kernel it is possible to write down the autocorrelation behavior of this model immediately. Thus, using Eqs. (38) and (45) with the property (15) we have for the equilibrium fluctuations

$$S_x(t) = p \exp\{-[q/(p+q)]t\} \tag{46}$$

(continuous time) and

$$S_x(n) = p\left(\frac{p}{p+q}\right)^n \tag{47}$$

(discrete time).

The moment relaxation equations (37) and (44) are expressible with similar transient terms. In these results we see, perhaps more clearly than in the later eigenvalue properties, the essential dependence of the decay of fluctuations upon the parameters p and q. As intuitively forseeable, and indicated by our analysis in Section 3, the condition $p \gg q$ (test molecule much larger than heat-bath molecule) gives a very extended decay of fluctuations

By contrast the condition $q \gg p$ leads to a decay with relaxation time approaching the mean collision time. Note that for $p = q$ the relaxation time is twice this.

In addition to their general interest, these results provide a useful counterexample to the common misconception that the only processes with strictly exponential autocorrelation are "Gaussian" Markov processes of Ornstein–Uhlenbeck type.

6. THE EIGENVALUE PROBLEM FOR THE PROCESS $(p|q, \infty)$

The beauty of the kernel (9) is at its clearest in the eigenvalue properties. We shall show that the integral equation (13) is exactly soluble and thus leads to an explicit result for the relaxation of the $(p|q, \infty)$ model, whether in discrete or continuous time.

A number of solution methods are possible—we choose what seems the most concise and revealing of these. The key to this is the observation that the kernel $K(y, x)$ defined in (9) can be rewritten in such a way that its convolution structure is seen as the "kernel product" of two factors, each factor being itself a "triangular" kernel and vanishing either above or below the diagonal. Thus, in a notation suggestive of the outcome, we may write

$$K_{p,q}(y, x) = (p)_q \int_0^\infty S^{-[q]}_{p+q-1}(y, u) S^{+[q]}_{p-1}(u, x)\, du \tag{48}$$

where

$$S^{+[q]}_{p-1}(u, x) = \Gamma(q)^{-1} x^{p-1} u^{-(p+q-1)} (u - x)^{q-1} H(u - x) \tag{49}$$

and

$$S^{-[q]}_{p+q-1}(y, u) = \Gamma(q)^{-1} e^{y-u} (u - y)^{q-1} H(u - y) \tag{50}$$

and $(p)_q = p(p + 1)(p + 2) \cdots (p + q - 1) = \Gamma(p + q)/\Gamma(p)$ (the Pochhammer function). Now, on writing $\mathscr{S}^{+[q]}_{p-1}$, $\mathscr{S}^{-[q]}_{p+q-1}$, and $\mathscr{K}_{p,q}$ for the integral operators represented by the above kernels, we see immediately that the eigenvalue problem $\mathscr{K}_{p,q}\psi = \lambda\psi$ can be expressed in the form

$$(\mathscr{S}^{-[q]}_{p+q-1}\, \mathscr{S}^{+[q]}_{p-1})\psi = [\lambda/(p)_q]\psi \tag{51}$$

The $\mathscr{S}$ operators being integral operators, we may reasonably seek differential operators $\mathscr{T}^{-[q]}_{p+q-1}$ and $\mathscr{T}^{+[q]}_{p-1}$ inverse to them in the sense that

$$\mathscr{T}^{-[q]}_{p+q-1}\, \mathscr{S}^{+[q]}_{p-1} = \mathscr{T}^{+[q]}_{p-1}\, \mathscr{S}^{-[q]}_{p+q-1} = \mathscr{I} \tag{52}$$

with $\mathscr{I}$ the identity. These would then correspond to the factorized *differential* equation

$$(\mathscr{T}^{-[q]}_{p+q-1}\, \mathscr{T}^{+[q]}_{p-1})\psi = [(p)_q/\lambda]\psi \tag{53}$$

whose solution would be equivalent to that for (51) except for the loss of boundary conditions implicit in the former. The $\mathscr{T}$ operators are not hard to find. Noting the similarity between the implementation of the $\mathscr{S}$ operations and the Riemann–Liouville type integral,[29]

$$D^{-q}f(x) = \frac{1}{\Gamma(q)} \int_x^\infty (u - x)^{q-1} f(u)\, du \tag{54}$$

we can recognize the differential inverses to be

$$\mathscr{T}_{p+q-1}^{-[q]} \equiv x^{-(p-1)} D^q \cdot x^{p+q-1} \tag{55}$$

and

$$\mathscr{T}_{p-1}^{+[q]} \equiv (-1)^q e^x D^q \cdot e^{-x} \tag{56}$$

Consider first the special case $q = 1$. The differential operators are $\mathscr{T}_{p-1}^{+} \equiv -e^x D \cdot e^{-x}$ and $\mathscr{T}_p^{-} \equiv x^{-(p-1)} D \cdot x^p$ and the differential equation (53), which is now of second order, is easily interpreted as

$$(\mathscr{T}_p^{-} \mathscr{T}_{p-1}^{+})\psi = [x^2 D + (p - x)D - p]\psi = -(p/\lambda)\psi \tag{57}$$

or

$$[xD^2 + (p - x)D - p(1 - \lambda^{-1})]\psi = 0 \tag{58}$$

This is recognizable as a confluent hypergeometric equation one of whose solutions can be written

$$\psi(x) = \sum_{\nu=0}^{\infty} \frac{(a)_\nu x^\nu}{(p)_\nu \nu!} = {}_1F_1(a; p; x) \tag{59}$$

where here we can identify $a = -p(\lambda^{-1} - 1)$. The second, logarithmic solution can be disregarded, since the integral operation (13) requires finiteness at the origin. Furthermore, if the same integral operation is to converge at infinity we require that $\psi(x)$ behave as a polynomial. Restoring these boundary conditions to the differential solution (59), we see that the requirement for the ${}_1F_1$ series to terminate is that

$$p(1 - \lambda^{-1}) = -k; \qquad k = 0, 1, \ldots, \infty$$

i.e., that

$$\lambda_k = p/(k + p) \tag{60}$$

The eigenfunctions now become the Laguerre polynomials, conventionally defined

$$L_k^{(p-1)}(x) = \frac{(p)_k}{k!} {}_1F_1(-k; p; x)$$

$$= \sum_{\nu=0}^{k} (-1)^\nu \binom{k + p - 1}{k - \nu} \frac{x^\nu}{\nu!} \tag{61}$$

and having the orthogonality

$$\int_0^\infty x^{p-1}e^{-x}L_i^{(p-1)}(x)L_j^{(p-1)}(x)\,dx = (i+1)_{p-1}\,\delta_{ij} \tag{62}$$

This solves the eigenvalue problem (16) for $q = 1$.

The solution for the case q a general positive integer follows quite easily if we notice that the operators $\mathscr{T}_{p-1}^{+[q]}$ and $\mathscr{T}_{p+q-1}^{-[q]}$ are in effect simple rearrangements of those appearing in the standard differential relationships for the confluent hypergeometric functions. These are usually cited in the forms

$$D^n[x^{c-1}{}_1F_1(a;c;x)] = (-1)^n(1-c)_n x^{c-n-1}{}_1F_1(a;c-n;x) \tag{63}$$

and

$$D^n[e^{-x}{}_1F_1(a;c;x)] = (-1)^n\frac{(c-a)_n}{(c)_n}e^{-x}{}_1F_1(a;c+n;x) \tag{64}$$

[Ref. 25, Vol. 1, Eqs. (6.5.12) and (6.5.13)]. Noting that $(-1)^n(1-c)_n = (c-n)_n$ and replacing c by $c+n$ in the first equation, we can combine these to give the following equation of order $2q$:

$$[x^{-(c-1)}D^n x^{c+n-1}][(-1)^q e^x D^q e^{-x}]\,{}_1F_1(a;c;x)$$

$$= (c-a)_n\,{}_1F_1(a;c;x)$$

The correspondence with the factorization (53) is obvious on making the identifications $c = p$ and $n = q$, and we can see that the latter is satisfied in the form

$$(\mathscr{T}_{p+q-1}^{-[q]}\,\mathscr{T}_{p-1}^{+[q]})\,{}_1F_1(a;p;x) = (p-a)_q\,{}_1F_1(a;p;x)$$

with a at this stage any root of the polynomial equation $\lambda(p-a)_q = (p)_q$. However, we again impose the boundary condition that $\psi(x)$ be a polynomial and restrict a to negative integer values. With this the problem is solved and we can write, to within a normalization,

$$\psi(x) \propto {}_1F_1(-k;p;x) \propto L_k^{(p-1)}(x) \tag{65}$$

$$\lambda_k = (p)_q/(k+p)_q \tag{66}$$

Thus, remarkably at first sight, the eigenfunctions are unchanged, being *independent of* q. We shall adopt the choice $\psi_k(x) = L_k^{(p-1)}(x)$.

Summarizing the above in modern terminology, we can recognize that Eqs. (55) and (56) specify *n-step differential ladder operators*[2] for the confluent hypergeometric function. In acting on the second rather than the first parameter, however, they differ from the better known operators first studied by Schrödinger,[20] Infeld and Hull,[26] and more recently Hadinger *et al.*[32] The operators $\mathscr{S}_{p-1}^{+[q]}$ and $\mathscr{S}_{p+q-1}^{-[q]}$ are correspondingly *n-step integral ladder operators* and act strictly on the polynomials and not the unrestricted CHG function. When written out the raising operation $\mathscr{S}_{p-1}^{+[q]}$ applied to the Laguerre polynomial $L_k^{(p-1)}(x)$ is known as the Kogbetliantz formula.[21] The lowering operation is not usually cited. We note that, like the Riemann–Liouville integral (54), the $\mathscr{S}_{p-1}^{+[q]}$ operation is valid for nonintegral q, this giving rise to a reinterpretation of the whole solution above in terms of the *fractional calculus*. We return to this interesting aspect in Section 10.

With the left eigenfunctions of the operator (9) now known, we can form either the master equation solution (26) or the spectral representation (31) as required. Perhaps the most remarkable feature of these results is the fact that the parameter q is absent from the left eigenfunctions and, in the transient part of the solutions, contributes only through the eigenvalue λ_k. Otherwise the solutions reflect the tendency seen earlier in the autocorrelation functions —i.e., to a long persistence of transients when $p \gg q$ and a compression of the whole spectrum toward the $\lambda_0 = 1$ limit at the opposite extreme $q \gg p$.

Using the orthogonality relation (62) we can distinguish some special cases of the expansion coefficients a_k in the initial-value solution (26). For the delta-function initial condition $P(x, 0) = \delta(x - x_0)$ we find that

$$a_k = \frac{\Gamma(p)}{(k+1)_{p-1}} L_k^{(p-1)}(x_0) \tag{67}$$

For the initial condition in which the distribution $P(x, 0)$ represents a Boltzmann distribution at some temperature T_0 not equal to the heat-bath temperature T we find that

$$a_k = (1 - T_0/T)^k \tag{68}$$

This follows on use of the Laplace transform relation for the Laguerre polynomials [Ref. 25, Vol. 2, Eq. (10.12.32)].

The autocorrelation function (38) may be recovered from the eigenvalue solution on introducing the fact that $x = pL_0^{(p-1)}(x) - L_1^{(p-1)}(x)$ into the evaluation of X_{01} of Eq. (34) and using the orthogonality property. It follows immediately that $X_{01} = p^{1/2}\,\delta_{k1}$ and the autocorrelation series is duly truncated at a single term.

[2] It is implicit in all the above, though we have bypassed the need to use the fact, that the q-step operators for q an integer are equivalent to the iterations $\mathscr{T}_{p+q-1}^{-[q]} \equiv \mathscr{T}_p^- \mathscr{T}_{p+1}^- \cdots \mathscr{T}_{p+q-1}^-$, $\mathscr{S}_{p+q-1}^{-[q]} \equiv \mathscr{S}_p^- \mathscr{S}_{p+1}^- \cdots \mathscr{S}_{p+q-1}^-$ and similarly for the $\mathscr{T}^{+[q]}$ and $\mathscr{S}^{+[q]}$ cases. The $\mathscr{T}^{+[q]}$ and $\mathscr{T}^{-[q]}$ operations are well known. (See Ref. 25, Vol. 1, Section 6.4.)

7. DUALITY AND THE $(p, q|\infty)$ PROCESS

Without considering the detailed form of the distributive kernel (9), it is clear on combinatorial grounds that a second, closely related process must exist with a simple change in the role of the degree-of-freedom subsets p and q.

In physical language the new process can be described thus: A "molecule" of $p + q$ internal degrees of freedom is put into distributive interaction with a heat bath in such a way that now only the q subset interact at each event, these becoming fully equilibrated to the Gamma distribution of an infinite heat bath before being restored to the system of $p + q$. This process, which we denote $(p, q|\infty)$, is illustrated in the diagram of Fig. 3. It might be thought to model a collisional transfer process in which a very large heat-bath molecule exchanges energy during a collision with a subset of internal degrees of freedom, the content of these then redistributing intramolecularly on a longer time scale after the collision is terminated. (However, see Section 9 for an extension of this idea.)

The kernel for this process is again a convolution of type (Beta) $*$ (Gamma) and an accounting of conditional probabilities shows this to be $(\beta = 1)$

$$K'_{p,q}(y, x) = \frac{\Gamma(p + q)e^{-y}}{\Gamma(p)\Gamma(q)^2 x^{p+q-1}} \int_0^{\min(x,y)} u^{p-1}(x - u)^{q-1}(y - u)^{q-1}e^{u}\, du \quad (69)$$

On closer examination it becomes clear that the relation of this kernel to that for the previous process (9) is simply a reversal in the order of factors when it is expressed in terms of the $\mathscr{S}$ operators (51). Thus, denoting the two integral operators by $\mathscr{K}$ and $\mathscr{K}'$, respectively, we may confirm that

$$\mathscr{K}_{p,q} = (p)_q \mathscr{S}_{p+q-1}^{-[q]} \mathscr{S}_{p-1}^{+[q]} \qquad (p|q, \infty) \quad (70)$$

$$\mathscr{K}'_{p,q} = (p)_q \mathscr{S}_{p-1}^{+[q]} \mathscr{S}_{p+q-1}^{-[q]} \qquad (p, q|\infty) \quad (71)$$

Using this and the properties of the $\mathscr{S}$ ladder operators found in the previous section [cf. (49) and (50)], we can write the eigenvalue solution for the kernel $\mathscr{K}'$ immediately. This time we find

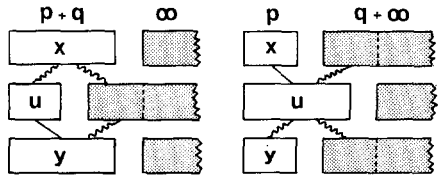

Fig. 3. The dual distributive processes $(p, q|\infty)$ and $(p|q, \infty)$. These diagrams are simplified from the forms in Fig. 2 in an obvious way.

$$\lambda_k' = (p)_q/(k + p)_q \tag{72}$$

$$\phi_0(x) = W_{p+q,\infty}(x) = \Gamma(p + q)^{-1}x^{p+q-1}e^{-x} \tag{73}$$

$$\psi_k(x) = L_k^{(p+q-1)}(x) \tag{74}$$

The eigenvalues are unchanged; the eigenfunctions are modified in becoming orthogonal with respect to the new equilibrium distribution $W_{p+q,\infty}(x)$. The autocorrelation functions are likewise unchanged except that the prefactors become the new equilibrium variance: $\mathrm{Var}(x)_{\mathrm{eq}} = p + q$.

8. SECOND-ORDER DISTRIBUTIVE PROCESSES: THE $(p, q|r, \infty)$ MODEL

The previous examples do not exhaust the possibilities for designing simple distributive models relevant to energy-transfer processes. We shall single out one further type of model from the various extensions possible to the "Laguerre-type" processes of Sections 6 and 7.

Consider the sequence of distributive trials diagrammed in Fig. 4. In molecular language: A test molecule of $p + q$ degrees of freedom is inserted into a heat bath of molecules with r degrees of freedom. On each collision there is a distributive interaction in the manner described previously, but this time only q of the $p + q$ degrees of freedom in the test molecule interact with the r available from the heat bath.

Following the two previous examples, we can recognize the transition kernel for the process to be composed by a double convolution of occupancy distributions of the form (Beta) * (Gamma) * (Beta). When written out it proves to be

$$K_{p,q,r}(y, x) = \int_0^\infty\int^\infty W_{p,q}(u, x)W_{r,\infty}(v - x)W_{q,r}(y - u, v - u) \times H(x - u)H(v - x)H(y - u)H(v - u)\,du\,dv$$

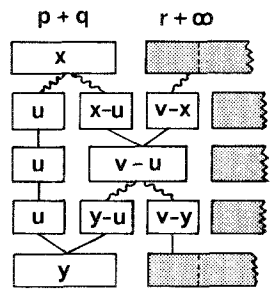

Fig. 4. The second-order distributive process $(p, q|r, \infty)$. Note how the subprocess on the right of the diagram is itself a first-order process of type $(q|r, \infty)$ as shown in Fig. 3. The presence of this "embedded" process is also conspicuous in the form of the transition kernel, Eq. (75).

$$= \frac{\Gamma(p+q)\Gamma(q+r)}{\Gamma(p)\Gamma(q)^2\Gamma(r)^2} e^x x^{-(p+q-1)}$$
$$\times \int_0^{\min(x,y)} u^{p-1}(x-u)^{q-1}(y-u)^{q-1}$$
$$\times \int_{\max(x,y)}^{\infty} \frac{(v-x)^{r-1}(v-y)^{r-1}e^{-v}}{(v-u)^{q+r-1}}\, dv\, du \tag{75}$$

We shall refer to this as a *second-order* distributive kernel reflecting the two convolutions involved.

Although of somewhat forbidding appearance, this kernel [and its near relative Eq. (82) of Section 9] may be of considerable importance in modeling intermolecular energy-transfer processes. Examination of the convolution structure in $K_{p,q,r}(y, x)$ will show that the second-order mechanism supplies a realistic tendency neglected in the first-order models—namely the element of Markovicity due not simply to the aftereffect of high (or low) energy in the collision complex, but also the inhibition of "flow" of energy between the partners in the limited time available.

The solution of the eigenvalue problem for this case is somewhat more difficult than for the "first-order" kernels considered up to now because no comparable factorization of the kernel into "ladder operators" seems possible. However, an exact solution can be found with the help of the addition formula (A2) for the Laguerre polynomials. We shall confine ourselves to a brief statement of the result and an outline of its derivation in the Appendix. As a convolution of normalized distributions $K_{p,q,r}(y, x)$ is automatically stochastic and its detailed-balance symmetry implies the equilibrium distribution $\phi_0(x) \propto W_{p+q}(x)$. The (unnormalized) right eigenfunctions prove to be

$$\phi_k(x) = x^{p+q-1}e^{-x}L_k^{(p+q-1)}(x) \tag{76}$$

with corresponding eigenvalues

$$\lambda_k = {}_3F_2(-k, q, r; p+q, q+r; 1) \tag{77}$$

The autocorrelation function for equilibrium fluctuations is obtainable either via the above or through direct determination of the kernel moment $k^{(1)}(x)$ [cf. Eq. (14)]. This quantity has the first-order polynomial form

$$k^{(1)}(x) = \left[\frac{pr}{(p+q)(q+r)} + \frac{q}{(q+r)}\right]x + \left(\frac{q}{q+r}\right) \tag{78}$$

indicating at once that the moment relaxation is exponential. The autocorrelation functions follow as

$$S_x(t) = (p+q)\exp - [qr/(p+q)(q+r)] \qquad \text{(continuous time)} \tag{79}$$

$$S_x(n) = (p + q)\left[\frac{pr}{(p + q)(q + r)} + \frac{q}{(q + r)}\right]^n \qquad \text{(discrete time)} \qquad (80)$$

Notice how these forms reduce to those for the first-order models *either* on letting $p = 0$ *or* on taking the limit $r \to \infty$. We could write this symbolically as $(0, q|r, \infty) \equiv (q|r, \infty)$ and $\mathrm{Lim}_{r\to\infty}(p, q|r, \infty) = (p, q|\infty)$. This type of correspondence, the physical origin of which is obvious on retracing the derivation of the kernels, is present in the eigenvalue solutions themselves and in all derived properties.

9. FINITE SYSTEMS: THE $(p|q, r)$ AND $(p, q|r, s)$ PROCESSES

Suppose that in the previous models the heat bath is replaced by a further set of subsystems *finite* rather than infinite in number. The system is now characterized by a total energy E rather than a temperature parameter β and its replicas constitute a type of *microcanonical ensemble* rather than the *canonical ensembles* previously considered. However, this change scarcely alters the thought-experiments defining our processes and we can easily retrace the derivations of the new, more general transition kernels.

Thus, forming the convolution (Beta) $*$ (Beta) instead of the (Beta) $*$ (Gamma) of Section 3.1, we immediately arrive at the kernel for the process $(p|q, r)$. This is

$$K_{p,q,r}(y, x) = B(p, q)^{-1}B(q, r)^{-1}y^{p-1}(E - x)^{-(q+r-1)} \times \int_{\max(x,y)}^{E} u^{-(p+q-1)}(E - u)^{r-1}(u - x)^{q-1}(u - y)^{q-1}\, du \qquad (81)$$

Likewise the second-order process analogous to that in Section 8 and having the structure $(p, q|r, s)$ gives a transition kernel through the double convolution (Beta) $*$ (Beta) $*$ (Beta):

$$K_{p,q,r,s}(y, x) = B(p, q)^{-1}B(q, r)^{-1}B(r, s)^{-1}x^{-(p+q-1)}(E - x)^{-(r+s-1)} \times \int_{0}^{\min(x,y)} u^{p-1}(x - u)^{q-1}(y - u)^{q-1} \times \int_{\max(x,y)}^{E} \frac{(E - v)^{s-1}(v - x)^{r-1}(v - y)^{r-1}}{(v - u)^{q+r-1}}\, dv\, du \qquad (82)$$

These kernels clearly reduce to the forms (9) and (75), respectively, on taking the thermodynamic limit $E \to \infty$, $r \to \infty$, $r = \beta E$. As before, there are numerous physical and nonphysical realizations of the above probabilities. A possible use of the kernel (82) would be to model the redistribution of internal energy within a collision complex of given total energy E when only

q and r degrees of freedom from the respective partners are able to communicate energy.

We shall not discuss the solution of the corresponding eigenvalue problems in detail, for they are broadly similar to the $(p|q, \infty)$ and $(p, q|r, \infty)$ cases already treated. In the former, an operator structure leads by entirely analogous steps to Jacobi polynomial eigenfunctions, while the same recur in the second-order case, though the proof is somewhat more difficult than that in the Appendix due to the nonexistence of a Jacobi addition formula analogous to (85). (See Ref. 7 for further details of this case.) The results are given in tabular form in Table III, where it will be seen that all the relevant properties, e.g., the moments and autocorrelation functions, tend like the original kernels to the previous results when the thermodynamic limit is taken. A special case of the kernel (81), that for $q = 1$, was studied some years ago as a problem in unimolecular reaction theory.[22]

The invention of the kernel (82), like its less general form (75), promises important applications to the analysis of experimental measurements. Of particular interest is the case $p = s$, $q = r$, representing energy transfer between limited degree of freedom of identical molecules. Even the peculiar case $p + q = 1$ as a model for single-oscillator transfer would seem worth further investigation. We stress once again that no other transition kernels seem to be known in the literature that represent a Markovian transfer of energy as opposed to a pure randomization within the collision complex of multiple degrees of freedom.

10. MATHEMATICAL IMPLICATIONS

Some forty years ago considerable interest developed around the problem of finding bilinear expansions of the classical orthogonal polynomials, a number of elegant results being derived by Erdelyi, Watson, Koschmieder, and others.[4,5,23,24] None of this work seems to have originated in a physical problem or to have been noticed in the physics or applied probability literature. One of Erdelyi's expansions[4] takes the form

$$\int_0^{\min(x,y)} u^{p-1}(x-u)^{q-1}(y-u)^{q-1}e^u\,du = \Gamma(q)^2(xy)^{p+q-1}\sum_{k=0}^{\infty}\left(\frac{k!\,\Gamma(k+p)}{\Gamma(k+p+q)^2}\right)L_k^{(p+q-1)}(x)L_k^{(p+q-1)}(y) \quad (83)$$

(Re $p > 0$, Re $q > 0$). It is clear that this is none other than the spectral representation of the symmetric part of the transition kernel for the model $(p, q|\infty)$—the "dual Laguerre" process of Section 7. A similar correspondence exists between all the eigenvalue solutions obtained in other sections and

a formula of the Erdelyi type, and these are readily written down on substitution of the quantities λ_k and N_k from Tables II and III into the general expression (31). All these results embody the duality properties inherent in the statistical models and allow the transition from finite to infinite degrees of freedom corresponding to the well-known limiting relationship between the Jacobi and Laguerre polynomials.[25] The latter thus has its counterpart in the "thermodynamic limit" of Section 1.3. None of the resulting formulas, except that quoted above, appear to have been published and some of them, particularly the double-integral results of Sections 8 and 9, were almost certainly unsuspected before the present stochastic interpretation. We have discussed the mathematical aspects of distributive processes in more detail elsewhere[6,8] and Rahman has given an exhaustive account of some Jacobi-type bilinear formulas more general than those considered here.[7] A recent paper by Ismail[27] includes a proof of the Laguerre expansions essentially equivalent to that in Section 6, with additional insights.

It may be noticed, however, that, whereas we have throughout regarded the degree-of-freedom parameters p, q, r, etc. in the models as positive integers, the Erdelyi formulas hold for fractional and even complex values of these under certain restrictions. While not much physical sense can be made of negative or complex degrees of freedom, the idea of fractional values is an interesting one and quite familiar in the interpretation of experimental measurements.[28] Thus, for example, in the $(p, q|\infty)$ and $(p, q|r)$ processes we can allow a fractional q value to parametrize the "effective degrees of

Table II. Continuous First-Order Distributive Processes

	Laguerre type	Jacobi type
Diagram	$(p\|q, \infty)$	$(p\|q, r)$
Structure	(Beta) * (Gamma)	(Beta) * (Beta)
State space	$(0, \infty)$	$(0, E)$
Equilibrium distribution $\phi_0(x)$	$\Gamma(p)^{-1}\beta^p x^{p-1}e^{-\beta x}$	$B(p, q)^{-1}(x^{p-1}(E - x)^{q-1}/E^{p+q-1})$
Transition kernel $K(y, x)$	Eq. (9)	Eq. (81)
Eigenvalues λ_k	$(p)_q/(k + p)_q$	$(p)_q(r)_q/(k + p)_q(k + r)_q$
Eigenfunctions $\psi_k(x)$	$L_k^{(p-1)}(\beta x)$ $= {}_1F_1(-k, p; \beta x)$	$J_k(p, p + q + r - 1; x/E)$ $= {}_2F_1(-k, k + p + q + r - 1, p; x/E)$
Equilibrium mean	p/β	$pE/(p + q + r)$
Equilibrium variance	p/β^2	$p(q + r)E^2/(p + q + r)^2(p + q + r + 1)$
Autocorrelation coefficient $1 - \lambda_1$	$q/(p + q)$	$q(p + q + r)/(p + q)(q + r)$
Normalization coefficients N_k^{-1}	$k!/(p)_k$	$k!\,(q + r)_k(p + q + r - 1)$ $(p)_k(p + q + r - 1)_k(2k + p + q + r - 1)$

Table III. Continuous Second-Order Distributive Processes

	Laguerre type	Jacobi type
Diagram	$(p, q\|r, \infty)$	$(p, q\|r, s)$
Structure	(Beta) * (Beta) * (Gamma)	(Beta) * (Beta) * (Beta)
State space	$(0, \infty)$	$(0, E)$
Equilibrium distribution $\phi_0(x)$	$\Gamma(p+q)^{-1}\beta^{p+q}x^{p+q-1}e^{-\beta x}$	$B(p+q, r+s)^{-1}(x^{p+q-1}(E-x)^{r+s-1}/E^{p+q+r+s-1})$
Transition kernel $K(y, x)$	Eq. (75)	Eq. (82)
Eigenvalues λ_k	${}_3F_2\left[\begin{matrix}-k, q, r \\ p+q, q+r\end{matrix}; 1\right]$	${}_4F_3\left[\begin{matrix}-k, k+p+q+r+s-1\, q, r \\ p+q, q+r, r+s\end{matrix}; 1\right]$
Eigenfunctions	${}_1F_1(-k, p+q; \beta x)$	${}_2F_1(-k, k+p+q+r+s-1, p+q; x/E)$ $= J_k(p+q, p+q+r+s; x/E)$
Equilibrium mean	$(p+q)/\beta$	$(p+q)E/(p+q+r+s)$
Equilibrium variance	$(p+q)/\beta^2$	$(p+q)(r+s)E^2/(p+q+r+s)^2(p+q+r+s+1)$
Autocorrelation	$qr/(p+q)(q+r)$	$(p+q+r+s)qr/(p+q)(q+r)(r+s)$
Normalization coefficients	$k!/(p+q)_k$	$\dfrac{k!\,(r+s)_k(p+q+r+s-1)}{(p+q)_k(p+q+r+s-1)_k(2k+p+q+r+s-1)}$

freedom contributing to energy transfer" provided only that $p + q$ remains integral whenever the equilibrium distribution is meant to correspond to a well-defined Boltzmann case.

The possibility of distributive processes with nonintegral degree-of-freedom parameters sheds further interesting light on the underlying mathematics. Thus the whole derivation of Section 6 can be recast in the language of *fractional calculus* with both the differential and integral ladder operators taking on a more general aspect in this sense.[19] The key integral operators $\mathscr{S}_{p-1}^{+[q]}$ and $\mathscr{S}_{p+q-1}^{-[q]}$ are reinterpreted in terms of Riemann–Liouville-type integrals, the former being directly identifiable with the fractional operator D^{-q}. The differential ladder operators $\mathscr{T}_{p+q-1}^{-[q]}$ and $\mathscr{T}_{p-1}^{+[q]}$ are then interpreted as formal inverses of these and the result is a solution of the eigenvalue problem by *fractional factorization*, a somewhat novel concept, though readily understandable in terms of the $\mathscr{S}$ operators and the basic postulates of fractional calculus.[19,29] We shall take up some of these questions elsewhere,[30] being content here to indicate some signs of increasing interest in the fractional calculus and new aspects of the factorization method in theoretical physics.[19,29,31]

11. DISCRETE DISTRIBUTIVE MODELS

An obvious extension to the models described here is the reconstruction of them in terms of the discrete state-variable $i \in [0, 1, \ldots, N]$ or $i \in [0, 1, \ldots, \infty]$, as appropriate to the redistribution of "quanta" among molecules with multiple degrees of freedom. An early treatment of this idea was that of Hoare,[11] which dealt with the simplest case of "distributive" transfer of quanta between simple oscillators.

The whole structure of results presented in this paper has been generalized to the discrete variable by Hoare and Rahman in work to be published elsewhere.[9] Here we shall cite very briefly the main results of the Hoare–Rahman work in order to establish its close relationship with the present problem.

Consider the opening paragraph of this paper in discrete language, i.e., the interaction of a test molecule containing i "quanta" among p (degenerate) degrees of freedom with the q-molecules of a heat bath. Let the quantum energy be specified in terms of the heat-bath temperature T by $\theta = (h\nu/k_B T)$. The transition matrix $K(j, i)$ giving the probability of a transition $i \to j$ is found to be

$$K(j, i) = \frac{\Gamma(p+q)}{\Gamma(p)\Gamma(q)^2} (j+1)_{p-1}(1 - e^{-\theta})^q e^{i\theta} \times \sum_{k=\max(i,j)}^{\infty} \frac{(k-i+1)_{q-1}(k-j+1)_{q-1} e^{-k\theta}}{(k+1)_{p+q-1}} \tag{84}$$

Here we have used the Pochhammer symbol $(i)_\alpha = i(i+1)(i+2)\cdots(i+\alpha-1)$ to bring out the obvious structural resemblance to the integral kernel in Eq. (9).

The infinite matrix eigenvalue problem $\mathbf{K}\boldsymbol{\phi} = \lambda\boldsymbol{\phi}$ for the above can be solved and yields eigenvalues $\lambda_k = (p)_q/(k+p)_q$ unchanged from those of the continuous model. The right eigenvectors prove to be $\phi_k(i) = \phi_0(i)M_k(i, p, e^{-\theta})$, in which the equilibrium eigenvector $\phi_0(i)$ is the negative binomial distribution, $\phi_0(i) = \Gamma(p)^{-1}(i+1)_{p-1}(1-e^{-\theta})e^{-i\theta}$; and the $M_k(i, p, e^{-\theta})$ are the Meixner polynomials, ${}_2F_1(-i, -k; p; 1-e^{-\theta})$. Thus both spectra and autocorrelation properties are unchanged on discretizing the problem. As to be expected, the discrete results tend to those for the continuous problem on carrying out the limit $h\nu/k_BT \to 0$.

In a similar manner the processes symbolized by $(p, q|\infty)$, $(p|q, r)$, $(p, q|r)$, $(p, q|r, \infty)$, and $(p, q|r, s)$ can all be described and exactly solved in terms of discrete state spaces. We refer to Ref. 9 for full details.

12. GENERAL APPLICATIONS

The idea of a *distributive process* can evidently be restated in quite general terms, having no particular connection with either statistical mechanics or even occupancy problems. Thus we may define general first- and second-order distributive transition probabilities by kernels of the form (8) and (75), respectively, but with the convoluted functions $W(y, u)$, etc. no longer the standard Beta or Gamma distributions. These kernels would inherit some of the simplicity of the present models, though not, of course, the exact spectral representations here derived.

In this framework a number of applications in general applied probability can at least be envisaged. We may retain an aspect of the occupancy problem in using distributive schemes to model the random input/output variables occurring in, for example, the classical problems of storage theory.[33] Thus the fluctuations in *inventories*, *dams*, *queues*, and idealized economic systems might be expressible through transition probabilities having similar structure and some of the characteristics of the kernels for the statistical mechanical problem. The interest of these models would lie not so much in the asymptotic behavior, which is virtually imposed from the start, as in the occurrence of simplified autocorrelation and in the possibility of parametrizing results systematically over the whole range from diffusion-like behavior to the virtually non-Markovian random extreme. Other applications suggest themselves in electrical noise theory and, in the case of discrete systems, genetics.

APPENDIX. SOLUTION OF THE EIGENVALUE PROBLEM FOR THE $(p, q|r, \infty)$ KERNEL (75)

We shall outline the solution of the eigenvalue problem (17)

$$\int_0^\infty \psi_k(y)K(y, x)\,dy = \lambda_k\psi_k(x)$$

in which $K(x, y)$ is the kernel introduced in Section 8 [Eq. (75)]. Knowing from the general considerations in Section 4 that one left eigenfunction $\psi_0(x) = 1$ occurs with $\lambda_0 = 1$, and that $K(y, x)$ satisfies the detailed-balance condition, we know that the eigenfunctions $\psi_k(x)$ will be orthogonal with weight $\phi_0(x) = x^{p+q-1}e^{-x}$ on $(0, \infty)$. It is therefore reasonable to expand the ψ_k in the complete set of Laguerre polynomials $\{L_i^{(p+q-1)}(x)\}$ sharing this property. Thus, writing

$$\psi(x) = \sum_{i=0}^{\infty} c_i L_i^{(p+q-1)}(x) \tag{A1}$$

and entering this into the eigenvalue condition, we obtain

$$x^{p+q-1}e^{-x}\sum_{i=0}^{\infty} c_i L_i^{(p+q-1)}(x)$$
$$= \mu\sum_{i=0}^{\infty} c_i \int_0^x v^{p-1}(x-v)^{q-1}\int_x^\infty \frac{e^{-u}(u-x)^{q-1}I_i(u, v)\,du\,dv}{(u-v)^{p+q-1}}$$

where $I_i(u, v)$ is the integral

$$I_i(u, v) = \int_v^u L_i^{(p+q-1)}(y)(y-v)^{q-1}(u-y)^{q-1}\,dy$$

and μ replaces λ through

$$\lambda = B(p, q)B(q, r)\Gamma(r)\mu$$

The integral can now be reduced by using the series expansion (61) for the polynomials and the appropriate form for the addition theorem [Ref. 25, Eq. (10.12.35)]

$$\sum_{k=0}^{n} L_k^{(d)}(x)L_{n-k}^{(\beta)}(y) = L_n^{(\alpha+\beta+1)}(x+y) \tag{A2}$$

In this way we find that

$$x^{p+q-1}e^{-x}\sum_{i=0}^{\infty} c_i L_i^{(p+q-1)}(x) = \mu\Gamma(r)^2\sum_{i=0}^{\infty} c_i\int_0^x v^{p-1}(x-v)^{q-1}$$
$$\times\sum_{m=0}^{m=i}(m+q)_r^{-1}L_{i-m}^{(p-1)}(v)L_m^{(q-1)}(x-v)e^{-x}\,dv$$

We can now use the orthogonality relation to obtain an infinite set of linear equations for the coefficients c_i. At this point, however, it emerges that the representation (A1) is in fact diagonal because

$$\frac{c_n\Gamma(n+p+q)}{n!} = \Gamma(r)^2\mu \sum_{i=0}^{\infty} c_i \sum_{m=0}^{m=i} \frac{\Gamma(m+q)}{(m+q)_r m!} \times \int_0^{\infty} v^{p-1}e^{-v}L_{i-m}^{(p-1)}(v)L_{n-m}^{(p-1)}(v)\,dv$$

Thus the right-hand side is proportional to c_n itself and cancellation gives the explicit eigenvalue condition we require. Converting from μ back to λ, this proves to be

$$\lambda_k = \frac{1}{(p+q)_k} \sum_{\nu=0}^{\nu=k} \binom{k}{\nu} \frac{(q)_k{}^2(p)_{k-\nu}}{(q+r)_\nu}$$

Noting that $(p)_{k-\nu} = (-1)^\nu(p)_k/(1-p-k)_\nu$ and that

$$\binom{k}{\nu} = (-1)^\nu(-k)_\nu/\nu!,$$

we can rewrite the above in the form

$$\lambda_k = \frac{(p)_k}{(p+q)_k} \sum_{\nu=0}^{k} \frac{(-k)_\nu(q)_\nu{}^2}{(q+r)_\nu(1-p-k)_\nu \nu!} \tag{A3}$$

The summation is evidently a terminating ${}_3F_2$ series with unit argument; in fact,

$$\lambda_k = \frac{(p)_k}{(p+q)_k}\,{}_3F_2\left[\begin{matrix}-k, q, q \\ q+r, 1-p-k\end{matrix}; 1\right] \tag{A4}$$

A theorem exists which enables us to simplify this result. We use the relationship

$${}_3F_2\left[\begin{matrix}-k, a, b \\ c, d\end{matrix}; 1\right] = \frac{(d-b)_k}{(d)_k}\,{}_3F_2\left[\begin{matrix}-k, c-a, b \\ c, 1-b-d-k\end{matrix}; 1\right] \tag{A5}$$

[See Gasper[35] for an explicit statement, and Bailey (Ref. 36, Section 3.2) for details of the method of proof.] Applying this to (A4), we obtain the much neater result

$$\lambda_k = {}_3F_2\left[\begin{matrix}-k, q, r \\ p+q, q+r\end{matrix}; 1\right] \tag{A6}$$

These are thus the eigenvalues of the $(p, q|r, \infty)$ process discussed in Section 8. The corresponding left eigenvalues of the kernel (75) are then precisely the original expansion set, viz.

$$\psi_k(x) = L_k^{(p+q-1)}(x) \tag{A7}$$

to within a normalizing factor.

ACKNOWLEDGMENT

The authors wish to thank Prof. M. Rahman for his considerable assistance, as well as for permission to quote the unpublished results cited in Section 11.

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