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Microscopic Derivation of a Markovian Master Equation in a Deterministic Model of Chemical Reaction

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We consider a (deterministic, conservative) one-dimensional system of colored hard points, changing color each time they hit one another with a relative velocity above a threshold. In the limit of rare reactions, the N-particle color distribution follows a Markovian birth-and-death process. Using the reaction rate as an intrinsic time scale, we also obtain the reaction-diffusion equation for a test particle in this hydrodynamic limit. Explicit results are given for a discrete and a Maxwellian velocity distribution.

KEY WORDS: Master equation; Markovian limit; hard points in one dimension; irreversibility; reaction-diffusion kinetics.

1. INTRODUCTION

One of the most intriguing questions of theoretical physics is the connection between our reversible description of microscopic processes and the irreversible evolution observed in macroscopic systems. The early formulation of nonequilibrium statistical mechanics adopts a probabilistic picture of microscopic processes, related heuristically to the deterministic dynamics: Boltzmann equations, Langevin equations, or master equations stand among the most popular examples.(20) These stochastic descriptions, Markovian or not, naturally entail an irreversible evolution of macrovariables.

A first step toward a more satisfactory (eventually rigorous) justification of these stochastic equations was initiated by the introduction of weak-coupling or low-density limits, playing a role similar to the thermodynamic limit of equilibrium statistical mechanics.(3,9,19) In this scheme, one

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is concerned with the evolution of some test particles in a larger system: such a method was first applied rigorously for hard points on the infinite real line.(11,24) On this general "hydrodynamic scaling limit" procedure for mechanical systems, we refer the reader to the review(25) by Spohn.

The mathematical theory of dynamical systems and ergodic theory also lead to a complementary approach to irreversible phenomena. Dynamically unstable systems (like hyperbolic ones) seem to naturally lend themselves to a statistical-mechanical description: much progress was recently made in the analysis of physical models like the Lorentz gas,(4) planar billiards,(22) and geodesic flows(2) at a high level of mathematical rigor. The one-dimensional hard rod system also benefited from these works.(1,23) From another point of view, dynamical instability has also been used to propose a general technique for deriving a microscopic Markov process from a deterministic picture without resorting to projections or coarse graining in "mesoscopic" cells: this nonunitary transformation formalism(18) may also be applied to the hard rod gas,(5) and its results will be compared to the hydrodynamic limit in a future publication.

The aim of the present paper is to present a derivation of a Markovian description from a fully deterministic, time-reversible dynamics modeling chemical reactions. To allow for as simple a discussion as possible, we consider the one-dimensional motion of colored hard points undergoing elastic collisions. The reaction is a simple change of color (A to B or conversely), which occurs only at collisions with a high relative velocity of the particles involved. As we are mainly concerned with the chemical evolution of M test particles ($M \ll N$), the initial state of the whole system is a thermal equilibrium with an arbitrary distribution of the colors. The reaction rate is determined by the number of collisions above the velocity threshold, and may thus be taken as an intrinsically defined small parameter. This will enable us to take a suitably defined hydrodynamic limit in which the Markovian description will emerge.

The model is defined in Section 2, where we also recall some properties of the hydrodynamic limit for the process of self-diffusion. Our main results are stated in Section 3, where we discuss their physical interpretation. We obtain in the hydrodynamic limit a Markovian birth-and-death master equation for an "elementary" reaction scheme, for an arbitrary finite number of test particles. We also obtain for a single test particle the reaction-diffusion equation characteristic of the macroscopic phenomenological description.

Section 4 is devoted to the statement and proof of some lemmas and the theorems. Two applications are presented in Section 5, namely, a simplified discrete velocity distribution and a Maxwellian distribution. Conclusions are summarized in Section 6.

2. THE MODEL

2.1. Definitions

We consider a system of point particles on the line. Particle k has position $q_k \in \mathbb{R}$, velocity $v_k \in \mathbb{R}$ and color $\eta_k \in I = \{-1, 1\}$; -1 stands for white (A) and $+1$ for black (B). The phase space of one particle in $\Omega_1 = \mathbb{R} \times \mathbb{R} \times I$; the state of particle k is $\omega_k = (q_k, v_k, \eta_k)$. The phase space of the infinite system is $\Omega = \Omega_1^{\mathbb{Z}}$ modulo permutations; the configuration space Ω_p is the space $\mathbb{R}^{\mathbb{Z}}$ of sequences (q_k) modulo permutations; the velocity space is $\Omega_v = \mathbb{R}^{\mathbb{Z}}$; the color space is $\Omega_c = I^{\mathbb{Z}}$. The state of the infinite system is written as $\boldsymbol{\omega} = (\mathbf{q}, \mathbf{v}, \boldsymbol{\eta})$.

The evolution is given by the following "reactive hard points" dynamics. Particles move freely up to a collision; at a collision they rebound elastically:

$$\dot{q}_k(t) = v_k(t) \tag{2.1}$$

$$\begin{aligned} \dot{v}_k(t) &= 0 \text{ [iff] } \forall i \neq k: q_i(t) \neq q_k(t) \\ v_k(t+0) &= v_i(t-0) \text{ [iff] } q_k(t) = q_i(t) \text{ for some } i \neq k \end{aligned} \tag{2.2}$$

Three-body collisions are excluded. We use the permutation freedom in Ω_p to order all positions according to the index ($k \leqslant i$ iff $q_k \leqslant q_i$); this ordering is preserved in time. The color does not change except at *reactive collisions*, in which the relative velocity exceeds some threshold $2c$:

$$\dot{\eta}_k(t) = 0 \tag{2.3a}$$

$$\eta_k(t+0) = -\eta_k(t-0) \text{ iff for some } i \neq k \begin{cases} q_k(t) = q_i(t) \\ |v_k - v_i| \geqslant 2c \end{cases} \tag{2.3b}$$

Thus the colour variable η_k only counts the number G_k of reactive collisions during lapse $[0, t[$:

$$\eta_k(t) = \eta_k(0)(-1)^{G_k(t)} \tag{2.4}$$

The whole set of evolution laws (2.1)–(2.3) is deterministic, time reversible, and invariant for space-time translations.

Except for the labels k, the motion of hard points cannot be distinguished from the free motion of the ideal gas on $\mathbb{R}$. We define *trajectory* (k) as

$$x_k(t) = q_k(0) + v_k t \tag{2.5}$$

in contradistinction with *position* (k), which follows the physical location of particle k in the hard-point model. The data of all trajectories are equivalent to that of the positions, but trajectories cross when particles collide.

We consider states of the system where the particles are in *thermal equilibrium*, i.e., where the measure on the mechanical space $\Omega_p \times \Omega_v$ is invariant. These states are characterized by a uniform Poisson measure μ_p on Ω_p (with constant density ρ) and a product measure μ_v on Ω_v, all positions and velocities being independent. Since ρ simply scales the lengths, setting $\rho = 1$ implies no loss of generality. The common velocity distribution $F(v)$ need not be specified, provided

$$\begin{aligned} &\mathscr{E}\,|v| = \int_{\mathbb{R}} |v|\, dF(v) = \mu_0, \qquad 0 < \mu_0 < \infty \\ &\mathscr{E} v = \int_{\mathbb{R}} v\, dF(v) = 0 \end{aligned} \tag{2.6}$$

Given a mechanical configuration $(\mathbf{q}, \mathbf{v})$, the color state of the gas is given by a measure $P(\boldsymbol{\eta} \mid \mathbf{q}, \mathbf{v})$ on $I^{\mathbb{Z}}$, so that $P(d\boldsymbol{\omega}) = P(\boldsymbol{\eta} \mid \mathbf{q}, \mathbf{v})\, \mu_v(d\mathbf{v})\, \mu_p(d\mathbf{q})$ determines the probability measure on the phase space. This measure evolves according to the deterministic, reversible equation induced by the dynamics (2.1)–(2.3). In this paper, we mainly focus on the evolution of one-particle distributions

$$P(d\omega_0) = \int_{d\omega_0 \times (\Omega/\Omega_1)} P(d\boldsymbol{\omega}) \tag{2.7}$$

where the choice $k_0 = 0$ is arbitrary. The initial state being given up to a free translation, we assume $q_0(0) = 0$.

The neglected particles ($k \neq 0$) now play the role of a bath modifying the motion and color of our test particles at random; the resulting stochastic process $(q_0, v_0, \eta_0)(t)$ is generally not Markovian.

2.2. Reaction Schemes

The reaction equations (2.3) correspond to the deterministic isomerization scheme

$$\begin{aligned} \mathrm{A} + \mathrm{B} &\rightleftharpoons \mathrm{B} + \mathrm{A} \\ \mathrm{A} + \mathrm{A} &\rightleftharpoons \mathrm{B} + \mathrm{B} \end{aligned} \tag{2.8}$$

where the transition $\mathrm{A} \rightleftharpoons \mathrm{B}$ of a particle does not depend on the other particles' colors. As the essential feature of our model is that particles react with their neighbors only, we define the right reaction number $N_k(t)$ of particle k,

$$N_k(t+0) = 1 + N_k(t-0) \qquad \text{iff} \quad \begin{cases} q_k(t) = q_{k+1}(t) \\ |v_k(t) - v_{k+1}(t)| \geqslant 2c \end{cases} \tag{2.9}$$

with $N_k(0) = 0$; this number corresponds to the elementary (symmetric and reversible) reaction scheme

$$\begin{gathered} \mathrm{A} + \mathrm{X} \rightleftharpoons \mathrm{B} + \mathrm{X} \\ (\mathrm{X} = \mathrm{A} \text{ or } \mathrm{B}, \text{ does not change}) \end{gathered} \tag{2.10}$$

from which more complex schemes can be constructed by combination. For instance, our model allows for both left and right reactions:

$$G_k(t) = N_k(t) + N_{k-1}(t) \tag{2.11}$$

2.3. The Hydrodynamic Limit

The isomorphism of the hard-point system with the ideal gas greatly simplifies its analysis. As Volkovysskii and Sinai proved,$^{(23,27)}$ these systems are K flows. In particular, they exhibit mixing of all multiplicities:

Theorem 2.1. For any finite subset $K \subset \mathbb{Z}$, and for any sequence of times (t_i), the distributions of $(q_k(t_i), v_k(t_i))$, $k \in K$, become independent as $\min_{i,j} |t_i - t_j| \to \infty$.

This is reminiscent of a Markov property on an infinitely long timescale. Spitzer$^{(24)}$ has in a sense specified this result by the explicit definition of a "hydrodynamic limit", using a scaling parameter ε. Let

$$q_k^\varepsilon(t) = \varepsilon q_k(\varepsilon^{-2} t) \tag{2.12}$$

and denote by $x_B(t)$ the Brownian motion on the line:

$$\begin{gathered} x_B(0) = 0, \qquad \mathscr{E} x_B(t) = 0 \\ \mathscr{E}(x_B(t)\, x_B(s)) = D \min(s, t) \end{gathered} \tag{2.13}$$

with diffusion coefficient

$$D = \mu_0 / \rho \tag{2.14}$$

Theorem 2.2 (Spitzer). The stochastic processes $q_0^\varepsilon(t)$ converge weakly to the Brownian motion process $x_B(t)$ as $\varepsilon \to 0$.

Observing that only μ_0 matters in Spitzer's proof straightforwardly yields (cf. Section 4.2) the following:

Corollary 2.3. If the velocity distributions $F_\sigma(v)$ converge uniformly to $F_0(v)$ as $\sigma \to 0$, the following limits commute for any finite interval $[0, T]$ of time:

$$\begin{tikzcd}
q^\varepsilon(t; \sigma) \arrow[r, "w", "(\varepsilon \to 0)"'] \arrow[d, "w"', "(\sigma \to 0)"] & x_B(t; D_\sigma) \arrow[d, "w"', "(\sigma \to 0)"] \\
q^\varepsilon(r; 0) \arrow[r, "w", "(\varepsilon \to 0)"'] & x_B(t; D_0)
\end{tikzcd}$$

where D is given by Spitzer's formula.

Though Spitzer's theorem holds for general velocity distributions, the microscopic motion $q(t)$ is usually a non-Markov process,(14) except for the special (discrete) velocity distribution(17,21) $P(v = \mu_0) = P(v = -\mu_0) = 1/2$.

As the distribution function $f(x, t)$ for the position of a Brownian particle satisfies the diffusion equation

$$\partial_t f = \frac{D}{2} \partial_x^2 f \tag{2.15}$$

one may consider Spitzer's theorem as a rigorous derivation of the self-diffusion equation for the hard-point system.(15) Unifortunately, Theorem 2.2 does not imply diffusion in its ordinary sense, for particles always remain in the same order (given by their indices). Moreover, the scaling (2.12) entails a blockwise diffusion process(26): the motions of particles k, i are independent in the "hydrodynamic limit" $\varepsilon \to 0$ provided that $\lim_{\varepsilon \to 0} \varepsilon \, |q_k^\varepsilon(t) - q_i^\varepsilon(t)| = \infty$. Thus even "macroscopically" separated particles undergo joint motion in this one-dimensional model.

3. COLLISIONS AND REACTIONS

3.1. Definitions

As the mechanical state is stationary, the expected number of crossings undergone during $[0, t[$ by a trajectory of velocity v with faster trajectories (coming from its left) is(24)

$$\rho t \mu_l(v) = \rho t \int_v^\infty (v' - v) \, dF(v') \tag{3.1a}$$

and similarly for slower trajectories:

$$\rho t \mu_r(v) = \rho t \int_{-\infty}^{v} (v - v')\, dF(v') \tag{3.1b}$$

The expected total number of intersections per unit time (with $\rho = 1$)

$$\mu(v) = \mu_l(v) + \mu_r(v) \tag{3.2}$$

is a differentiable convex function with a positive minimum $\mu_m = \mu(v_m)$ and an average

$$\bar{\mu} = \int_{\mathbb{R}} \mu(v)\, dF(v) \tag{3.3}$$

We also introduce the symmetry parameter for collisions

$$\lambda(v) = \min \left(\frac{\mu_r(v)}{\mu(v)}, \frac{\mu_l(v)}{\mu(v)} \right) \in \left[0, \frac{1}{2} \right] \tag{3.4}$$

which is maximum for $v = v_m$.

The expected number of reactions per unit time occurring on a trajectory of velocity v, is given by the analogous integrals

$$\begin{aligned} \mathscr{R}(v) &= \mathscr{R}_l(v) + \mathscr{R}_r(v) \\ \mathscr{R}_l(v) &= \int_{-\infty}^{v-2c} (v - v')\, dF(v') \\ \mathscr{R}_r(v) &= \int_{v+2c}^{\infty} (v' - v)\, dF(v') \end{aligned} \tag{3.5}$$

which incorporate the restriction (2.3). Let

$$\bar{\mathscr{R}} = \int_{\mathbb{R}} \mathscr{R}(v)\, dF(v) \tag{3.6}$$

Because trajectories are independent and intersect only once, the probability for the next intersection of one trajectory to be reactive is

$$s(v) = \mathscr{R}(v)/\mu(v) \tag{3.7}$$

whatever happened before on this trajectory. By symmetry, this is also the probability that the last intersection was reactive.

We determine in Section 4.1 the probability

$$b(v) = \frac{2\lambda(v)\, s(v)}{1 - 2\lambda(v) + 2\lambda(v)\, s(v)} \tag{3.8}$$

for a particle to undergo at least one reaction at one of its later returns on a trajectory with velocity v. The same arguments allow one to define

$$\begin{aligned} s_r(v) &= \mathscr{R}_r(v)/\mu(v) \leqslant s(v) \\ b_r(v) &= \frac{2\lambda s_r}{1-2\lambda+2\lambda s_r} \leqslant b(v) \end{aligned} \tag{3.9}$$

and similarly s_l and b_l.

3.2. Colliding and Reacting Pairs

In one dimension, a particle can only react with its two neighbors. Since the mechanical state is stationary, the parameters μ_r, $\mathscr{R}_r$ determine the expected numbers of collisions $Q_k(t)$ and reactions $N_k(t)$ occurring between particles k and $k+1$ during $[0, t[$; for instance,

$$\mathscr{E} N_k(t) = t\bar{\mathscr{R}}/2 \tag{3.10}$$

As successive collisions may not be independent, the distributions of $Q_k(t)$ and $N_k(t)$ are generally not Poissonian and one cannot compute

$$\langle \eta_k(0)\, \eta_k(t) \rangle = \mathscr{E}(-1)^{G_k(t)} \tag{3.11}$$

directly from $\bar{\mathscr{R}}$. Yet, as the particle's evolution is a K-mixing process, we may expect that reactions separated by long durations be quite independent, so that a simple chemical evolution is possible on a time scale of order $\bar{\mathscr{R}}^{-1}$. Consider thus a scaling parameter ε such that $\rho\bar{\mathscr{R}} = \varepsilon^2 g$. This can be achieved physically, e.g., by fixing a threshold c and reducing the proportion of faster particles, or by letting $c \to \infty$ with a fixed distribution $F_\varepsilon(v) = F(v)$. We define the scale-dependent processes

$$\begin{aligned} N_k^\varepsilon(t) &= N_k(\varepsilon^{-2} t) \\ \eta_k^\varepsilon(t) &= \eta_k(\varepsilon^{-2} t) \end{aligned} \tag{3.12}$$

Both stochastic processes are non-Markovian, with no discontinuities of the second kind.(10) We denote by $\nu(t; g)$ the (Markovian) Poisson process with rate g:

$$P(\nu(t) = n) = P(\nu(-t) = -n) = e^{-gt} \frac{(gt)^n}{n!} \tag{3.13}$$

and by $\gamma(t; g)$ the Markov birth-and-death process on I with rate g:

$$\gamma(t) = (-1)^{\nu(t)} \tag{3.14}$$

For any subset $K \subset \mathbb{Z}$, $(\nu_k(t;\, g))$, $k \in K$, denotes the vector Poisson process with independent identically distributed components defined as $\nu(t;\, g)$, and $\tau K = \{k \mid k-1 \in K\}$.

Theorem 3.1. If the velocity distributions $F_\varepsilon(v)$ converge uniformly to $F_0(v)$ as $\varepsilon \to 0$ and are such that (with the dependence on ε implicit in all these expressions)

(a) $\lim\limits_{\varepsilon \to 0} \varepsilon^{-2} \bar{\mathscr{R}} \rho = \bar{g} < \infty$

(b) $\lim\limits_{\varepsilon \to 0} \displaystyle\int_{\mathbb{R}} b(v) \frac{\mathscr{R}(v)}{\bar{\mathscr{R}}}\, dF(v) = 0$

(c) $\lim\limits_{\varepsilon \to 0} \displaystyle\int_{\mathbb{R}} \frac{\mathscr{R}_r(v)\, \mathscr{R}_l(v)}{\mu(v) \bar{\mathscr{R}}}\, dF(v) = 0$

(d) $\lim\limits_{\varepsilon \to 0} \displaystyle\int_{-v_0}^{v_0} \frac{\mathscr{R}(v)}{\bar{\mathscr{R}}}\, dF(v) = 0 \qquad$ for some $v_0 > 0$

then for any finite subset $K \subset \mathbb{Z}$, the vector process $(N_k^\varepsilon(t))$, $k \in K$, converges weakly to the vector process $(\nu_k(t;\, \bar{g}/2))$.

Color evolution itself for the particles is described by the subsequent corollaries:

Corollary 3.2. With the hypotheses (a)–(d), the color process $\eta_k^\varepsilon(t)$ converges weakly to $\gamma(t)$ for any particle k.

Corollary 3.3. Under hypotheses (a)–(d), the vector process $(G_k^\varepsilon(t))$, $k \in K$, converges weakly to the vector compound Poisson process with components $\nu_k(t) + \nu_{k-1}(t)$, whose components are independent iff $K \cap \tau K = \phi$.

3.3. Physical Considerations

The physical motivation behind the scaling in Theorem 2.2 is the difference in magnitude between the scale at which the (deterministic) process of motion occurs and the scale at which this motion is observed as a Brownian process. On these grounds one would relate ε to the ratio of a mean free path to a macroscopic length. However, no such macroscopic length, like one related to a density gradient, can be defined for self-diffusion in the equilibrium "bath" of Spitzer's canonical ensemble: this leaves us with some indetermination on the status of the parameter ε.

By contrast, for the reacting model, the scaling parameter should be taken as the fraction $\bar{\mathscr{R}}/\bar{\mu}$ of reactions with respect to all collisions: as both quantities are well defined from the microscopic dynamics, this ratio is *intrinsic* to the model. The macroscopic time scale so defined by the reaction rate may also determine a spatial scale via the diffusion constant D.

The main role of the scaling by ε, in all these models, is to allow for "many" collisions between successive observations of the particles. Then the details of the microdynamics are smoothed out and one is left with their average effect. Moreover, as the non-Markovianity of the microscopic process is due to correlated collisions or reactions, our sampling at macroscopically separated times allows for these correlations to fade away: we do not see the "transient" perturbation of the environment and the relaxation of a test particle's velocity just after a reaction.

In view of this separation of scales, the irreversible nature of the macroscopic evolution is not surprising; and the disconnection of future from past—reflected by the independence of increments—also follows directly. It may be worth emphasizing that we are not looking here at the whole set of variables (q_k, v_k, η_k), $k \in \mathbb{Z}$, and their evolution: our Markov process is a "projection" of the general evolution onto a chosen subset of variables. However, we may take the finite subset $K \subset \mathbb{Z}$ as large as we wish: if one assumes that all observables relate to a finite number of particles, this argument justifies the Markovian description of macroscopic chemical reactions in our model.

The role of each condition in Theorem 3.1 is to implement the ideas behind the "decorrelation of collisions" mentioned above. Condition (a) expresses that ε^2 is the right scaling for $\bar{\mathscr{R}}$. Conditions (b)–(c) avoid "chain reactions": even shortly after a reactive collision, when it may have a high velocity, a particle is not likely to find a reactive companion and it thus "thermalizes" with its new color. Condition (d) is a purely technical requirement, intended to eliminate reactions from the slow-velocity trajectories which the test particles visit an infinite number of times; this condition (d) is natural (see Section 5), but its loosening might be harmless to our conclusions.

3.4. Multivariate and Reaction-Diffusion Stochastic Models

Theorem 3.1 and its corollaries immediately matter to the physical description of reactions in the hard-point gas. Indeed, the Markov processes $v(t; g)$ and $\gamma(t; g)$ are described by the Chapman–Kolmogorov (master) equations,

$$P(v(t) = n) = gP(v(t) = n - 1) - gP(v(t) = n) \tag{3.15a}$$

$$P(\gamma(t) = 1) = g - 2gP(\gamma(t) = 1) \tag{3.15b}$$

Corollary 3.3 therefore implies the validity of a multivariate master equation for the elementary process $(N_k(t))$, $k \in K \cup \tau K$, underlying the M-particle reactions process $(G_k(t))$, $k \in K$, and the corresponding color process $(\eta_k(t))$, $k \in K$. However, as (G_k) appears as a *combination* of these independent Poisson processes, the multivariate master equation does *not* hold for $(G_k(t))$ itself unless $K \cap \tau K = \phi$.

Similarly, the relaxation equation (3.15b) extends as $\varepsilon \to 0$ to the vector $((-1)^{N_k(t)})$, $k \in K$, with independent components for any finite K, but not to the corresponding vector $(\eta_k(t))$, $k \in K$, in general. Indeed, a convenient way to express a distribution function on the space I^K of colors of M test particles is to give the 2^M expectations $\mathscr{E}(\prod_{k \in \mathbf{k}} \eta_k)$ for all subsets $\mathbf{k} \subset K$. In view of Corollary 3.3, one factorizes

$$\mathscr{E}\left(\prod_{k \in \mathbf{k}} \eta_k \prod_{i \in \mathbf{i}} \eta_i\right) = \mathscr{E}\left(\prod_{k \in \mathbf{k}} \eta_k\right) \mathscr{E}\left(\prod_{i \in \mathbf{i}} \eta_i\right) \tag{3.16}$$

if $(\mathbf{k} \cup \tau\mathbf{k}) \cap (\mathbf{i} \cup \tau\mathbf{i}) = \phi$, so that we may consider only intervals $\{1,..., M\}$ and find all other expectations by translations and products. Now

$$\mathscr{E} \prod_{k=1}^{M} \eta_k(t)\, \eta_k(0) \to \mathscr{E}(-1)^{\nu_0(t) + \nu_M(t)} = e^{-2gt} \tag{3.17}$$

If the M test particles had independent colors, the product would decay as $\exp(-2Mgt)$ by (3.16): neighboring particles are not independent. Of course, one may also interpret our model as describing the isomerization (A, B) of a family of M particles in a bath of "colorless" (X) particles [see the model (2.10)].

In this context, even more physical would be the derivation of a reaction-diffusion (multivariate) master equation,(16) which would describe the whole phenomenology of the M particles in our dynamical model. But here the rigid ordering limits us to a blockwise diffusion. So from Theorems 2.2 (or its extension 2.3) and 3.1 we deduce the following:

Theorem 3.4. Under hypotheses (a)–(d), the one-particle joint process $(q_k^\varepsilon(t), G_k^\varepsilon(t))$ converges weakly to the independent Markov process $(x_B(t), \nu(t))$ with diffusion coefficient $D = \mu_0/\rho$ and reaction rate $\bar{g}$.

Hence, in the scaling limit $\varepsilon \to 0$, the one-particle position-color probability density $f(x, \eta, t)$ is factorized:

$$f(x, \eta, t) = \psi(x, t)\, h(\eta, t) \tag{3.18}$$

where ψ and h satisfy the diffusion and reaction equations

$$\begin{aligned} \partial_t \psi &= \frac{D}{2} \partial_x^2 \psi \\ \partial_t h &= \bar{g}(1 - 2h) \end{aligned} \tag{3.19}$$

The probability density $f(x, \eta, t)$ can also be related to "concentrations"

$$f^{\pm}(x, t) = f(x, \pm 1, t) \tag{3.20}$$

which satisfy the coupled reaction-diffusion phenomenological equations

$$\begin{aligned} \partial_t f^+ &= \frac{D}{2} \partial_x^2 f^+ + \bar{g}(f^- - f^+) \\ \partial_t f^- &= \frac{D}{2} \partial_x^2 f^- + \bar{g}(f^+ - f^-) \end{aligned} \tag{3.21}$$

corresponding to the isomerization model (2.8) in ideal conditions. As the functions $f^{\pm}$ refer to a single particle, the phenomenological equations describe a self-diffusion-reaction process.

4. PROOFS

4.1. Lemmas

Before proving the theorems, we must discuss a few physical events related to the evolution of a test particle after a time at which its velocity is known.

Lemma 4.1. If a particle is on trajectory $x_0(t) = q_0 + v_0 t$ at time $t = 0$, the probability for its coming back exactly n times on this trajectory later is $K^n(1 - K)$ with $K = 2\lambda(v_0)$.

Proof. Denote by $L_k(t)$ (resp. $R_k(t)$) the number of trajectories x_i crossing x_k from the left (resp. right) in the time interval $[0, t[$. The event $q_0(t) = x_k(t)$ is identical to the event $L_k(t) - R_k(t) = k$, and L_k and R_k are independent Poisson processes with rates $\rho\mu_l(v_k)$ and $\rho\mu_r(v_k)$. Therefore $L_0 - R_0$ is a (biased) random walk, whose returns to the origin have a negative binomial distribution, with the return probability $2\lambda(v_0)$. ∎

Consequently, the probability for this particle to undergo a reaction when leaving x_0 after a return on it, is

$$b(v) = \frac{2\lambda s}{1 - 2\lambda + 2\lambda s}$$

The same argument holds for the reaction probability when coming back on x_0, and for determining b_l and b_r.

Lemma 4.2. If a particle is on trajectory x_0 at time $t=0$ and on some other trajectory at time t, its conditional velocity distribution has a bounded Radon–Nikodym derivative $dF(v, t \mid v_0)/dF(v) \leqslant Q$.

The proof (mainly technical) is in the appendix. Inserting this result in the definition of $\mathscr{R}(v)$ shows that the reaction number of particle 0 conditioned by its velocity v_0 at time 0, is majorized by the stationary Poisson process with rate $Q\bar{\mathscr{R}}$.

These last results restrict the non-Markovianity of the velocity and reaction processes: the v_0-conditioned evolution cannot differ from the unconditioned evolution by more than a factor Q.

4.2. Proof of Corollary 2.3

The least obvious part is the limit $\sigma \to 0$ for $\varepsilon \neq 0$. However, the joint distributions $f(q(t_1),..., q(t_n); \sigma)$ are directly obtained from the time-displaced self-distribution functions, which may be expressed as continuous functionals of the velocity distribution $F(v)$ (the two-time function is given explicitly by Lebowitz and Percus$^{(14)}$): the joint distributions $f(q(\cdot); \sigma)$ converge pointwise to the joint distribution $f(q(\cdot); 0)$ if the distribution functions F_σ converge uniformly to F_0.

Weak convergence is then obtained by verifying the tightness condition$^{(10)}$

$$\lim_{\delta \to 0} \limsup_{\sigma \to 0} A(\lambda, \delta, \sigma; \varepsilon, T) = 0$$

for every $\lambda > 0$, with

$$\begin{aligned} A(\lambda, \delta, \sigma; \varepsilon, T) &= P\left(\sup_{|s-t|<\delta} |q^\varepsilon(s;\sigma) - q^\varepsilon(t;\sigma)| > \lambda\right) \\ &\leqslant P\left(\sup_{0<t<T} v(t) > \frac{\lambda}{\delta}\right) + P\left(\inf_{0<t<T} v(t) < -\frac{\lambda}{\delta}\right) \end{aligned}$$

Consider the first term on the right-hand side. The test particle can reach a velocity $v > \lambda\delta^{-1}$ during $[0, T[$ only if there is such a fast particle within the interval $]-(v+\lambda\delta^{-1})T, 0[$ at initial time, or if it starts with such a high velocity:

$$P\left(\sup_{0<t<T} v(t) > \lambda\delta^{-1}\right) \leqslant 1 - F_\sigma(\lambda\delta^{-1}) + \int_{\lambda/\delta}^{\infty} \rho T(v + \lambda\delta^{-1})\, dF_\sigma(v)$$

Thanks the uniform convergence of F_σ, the right-hand side converges to the same expression with F_0. Then both terms vanish in the limit $\delta \to 0$ by (2.7).

The infimum part is treated in the same way.

4.3. Proof of Theorem 3.1

To prove weak convergence for the vector integer-valued processes $(N_k^\varepsilon(t))$, we first show convergence in probability for n-times joint distribution functions of one component $N_k(t)$, which reduces by stationarity to demonstrating independence of the increments for $t > 0$ versus $t < 0$. The condition on successive increment of $N_k^\varepsilon(t)$ warranting weak convergence is then obtained. Finally we prove that the components of the vector $(N_k^\varepsilon(t))$ converge weakly to independent processes.

Convergence in Probability for N_k^ε. As $k = 0$, we omit the index in this section. Using ε^{-2} as scaling parameter for $\bar{\mathscr{R}}$, we must prove that the increments of the limit $N^*(t)$ of $N^\varepsilon(t)$, for $t > 0$, are (a.s.) independent of its increments for $t < 0$.

Consider a time $\theta > 0$. For $\varepsilon \to 0$, the number of reactions within $]0, \theta[$ almost surely vanishes as $\theta \to 0$ because of condition (a) and (3.10). Thus we may subtract from $\mathbb{R}$ an interval $]0, \theta[$ without modifying the evolution of the process $N^*(t)$, provided that $\theta \to 0$ as $\varepsilon \to 0$.

Moreover, K mixing in velocity space (Theorem 2.1) implies that a particle's velocity at time $t = \theta$ be independent of its velocities at any finite number of instants $t < 0$, if $\varepsilon^{-2}\theta \to \infty$ as $\varepsilon \to 0$. Therefore reactions after $t = 0$ will not be affected by the insertion or deletion of reactive trajectories (modifying N^* arbitrarily), provided the particle does not cross them after $t = \theta$. By condition (d), a reactive trajectory must have a finite velocity in the scaling limit; it now suffices to show that the particle cannot recross after $t = \theta$ a reactive trajectory it followed before $t = 0$. This follows from Spitzer's theorem and from the law of the iterated logarithm for the Brownian motion.

Now, the two requirements $\varepsilon^{-2}\theta \to \infty$, $\theta \to 0$ are compatible, and the proof is completed. Thus, since N^ε has stationary increments, a.s. equal to unity, it converges in probability to the Poisson process with rate $\bar{g}/2$ determined by the expectation (3.10).

Weak Convergence. Let $T > 0$, $\theta > 0$, $\varepsilon > 0$ and define the functionals

$$\Delta'_\theta(N^\varepsilon) = \sup_{\theta \leqslant t \leqslant T - \theta} \min(N^\varepsilon(t) - N^\varepsilon(t - \theta), N^\varepsilon(t + \theta) - N^\varepsilon(t))$$

$$\Delta_\theta(N^\varepsilon) = \Delta'_\theta(N^\varepsilon) + N^\varepsilon(\theta) + N^\varepsilon(T) - N^\varepsilon(T - \theta)$$

Weak convergence of the integer process $N^\varepsilon(t)$ to $\nu(t)$ on $[0, T]$ is given by the tightness condition

$$\lim_{\theta\to 0}\ \limsup_{\varepsilon\to 0} P(\Delta_\theta(N^\varepsilon) \neq 0) = 0$$

But $P(\Delta_\theta(N^\varepsilon) \neq 0) \leqslant P' + P''$, with $P' = P(\Delta'_\theta(N^\varepsilon) \neq 0)$ and

$$P'' \leqslant \mathscr{E}N^\varepsilon(\theta) + \mathscr{E}(N^\varepsilon(T) - N^\varepsilon(T-\theta)) \to \bar{g}\theta$$

vanishing for $\theta \to 0$.

The probability P' that two reactions of $(k, k+1)$ occur in $[0, T]$ with a separation shorter than 2θ, is easily estimated using the stationarity of the reaction process:

$$P' \leqslant \varepsilon^{-2}\frac{\bar{\mathscr{R}}T}{2} P(N^\varepsilon(2\theta) \neq 0 \mid \text{reaction at } t = 0)$$

The reaction during $]0, 2\theta]$ conditioned by the initial reaction (at $t = 0$), can be triggered by two processes: it may occur on the same reactive trajectory x_0 which the particle $k = 0$ followed just before the initial reaction, or on x_1 followed just after the reaction, or it occurs on another trajectory:

$$P' \leqslant \varepsilon^{-2}\frac{\bar{\mathscr{R}}T}{2}\iint_{\mathbb{R}^2} (P'_0(v_0, v_1) + P'_1(v_0, v_1) + P'_2(v_0, v_1))\, d^2\varphi(v_0, v_1)$$

where P'_0 and P'_1, respectively, are the probabilities for reactions on x_0 and x_1, and P'_2 is the probability for a reaction on another trajectory. The joint velocity distribution function $\varphi(v_0, v_1)$ for reactions, with $v_0 > v_1$, is known:

$$d^2\varphi(v_0, v_1) = \frac{|v_0 - v_1|}{\bar{\mathscr{R}}/2}\chi(v_0 \geqslant v_1 + 2c)\, dF(v_0)\, dF(v_1)$$

Let

$$dF_r(v_0) = \int_{v_1=-\infty}^{v_1=\infty} d^2\varphi(v_0, v_1) = 2\frac{\mathscr{R}_r(v_0)}{\bar{\mathscr{R}}}\, dF(v_0)$$

We first examine P'_0. The next collision on x_0 may be a second reaction of (0, 1), which has probability $s_l(v_0)$; and a reaction of the pair (0, 1) may also occur again on x_0 if these particles later come back on it. Thus

$$\begin{aligned} P'_0(v_0, v_1) &\leqslant s_l(v_0) + b_l(v_0) + b_r(v_0) \\ &\leqslant s_l(v_0) + 2b(v_0) \end{aligned}$$

$$\iint_{\mathbb{R}^2} P'_0\, d^2\varphi \leqslant \int_{\mathbb{R}} (s_l(v) + 2b(v))\, dF_r(v)$$

A similar argument can be given for P'_1, so that the first two terms in the integral majorising P' are independent of θ and vanish for $\varepsilon \to 0$ by conditions (b), (c).

Finally, the probability P'_2 for another reaction of the pair (0, 1) on other trajectories during $]0, 2\theta]$ is easily majorized, using Lemma 4.2, in terms of the stationary reaction rate:

$$\int_{\mathbb{R}^2} P'_2(v_0, v_1)\, d^2\varphi(v_0, v_1) \leqslant Q\varepsilon^{-2} \frac{\bar{\mathscr{R}}}{2} 2\theta\rho$$

vanishing as $\theta \to 0$ uniformly in ε.

Independence. Let us now give all reaction times for M pairs $(k, k+1)$, $k \in K$, and show that reactions at $k = 0 \notin K$ are independent of them as $\varepsilon \to 0$. First, the distances $|q_0 - q_k|$ $(k \in K)$ are finite because of the Poisson distribution of positions. Thus a trajectory with velocity $|v| > v_0$ must cross the set $\{0\} \cup K$ in a finite lapse of microscopic time: as $\varepsilon \to 0$, this becomes instantaneous. Hence only reactions of K in $[t_1 - \theta, t_2 + \theta]$ can affect the reactions of $k = 0$ during the lapse $[t_1, t_2]$, $\theta \to 0$.

The only information provided by a reaction occurring is that two trajectories cross with a high relative velocity. Each such trajectory has a velocity distributed according to either F_l or F_r, so that it causes a reaction of any given particle $k \in \mathbb{Z}$ with a probability smaller than

$$2\int_{\mathbb{R}} (b(v) + s(v))\, dF_r(v)$$

(or similarly with 1), vanishing as $\varepsilon \to 0$. Since the pairs of K have only a finite number of reactions during the lapse, these reactions do not affect the reactions at $k = 0$.

Thus reactions at $k = 0$ (almost surely) do not occur on the same trajectories as reactions at $k \in K$ as $\varepsilon \to 0$. Since trajectories are independent, so are the reaction processes (N^*_k), $k \in K$, and N^*_0. By translation invariance, this implies independence for any finite $K \subset \mathbb{Z}$.

4.4. Proof of Theorem 3.4

Since (N^*_k) converges weakly to (v_k), we only need prove that, given any realization of (N^ε_k), the conditioned process $q^\varepsilon(t) \mid N^\varepsilon$ converges weakly to the independent Brownian motion $x_B(t)$. But the only information contained in $(N^\varepsilon_k(t))$ is that the trajectories just before and after each reaction have a large relative velocity. Let us delete some of these trajectories: the particle now crosses them instead of reacting. At time t, the index k of the trajectory on which our test particle now travels, differs from the original index k' by at most the number (n) of deleted trajectories—which is finite. This deletion of reactive trajectories induces a shift in spatial motion by an (a.s.) finite distance (at most $\sim n/\rho$) close to the original one, so that they both converge to the same motion $q(t)$. This proves the independence of $q^{\varepsilon}(t)$ with respect to $(N_k^*(t))$ in the scaling limit. Spitzer's theorem can then be applied directly.

5. EXAMPLES

5.1. The 4-Velocity Gas

As a first example, consider the following family of velocity distributions F_σ:

$$\frac{d}{dv}F(v)=\frac{1-\sigma}{2}(\delta(v+1)+\delta(v-1))+\frac{\sigma}{2}(\delta(v+c)+\delta(v-c)) \quad (5.1)$$

with Dirac distributions δ. This is the simplest discrete even velocity distribution for which reactions may be described deterministically as high-energy collisions $(c>1)$. The average collision velocity is distributed as

$$\mu(\pm c)=c, \qquad \mu_0=\mu(\pm 1)=1+(c-1)\sigma \quad (5.2)$$

Reactions only occur between particles moving at $\pm c$:

$$\mathscr{R}(\pm c)=\sigma c, \qquad \mathscr{R}(\pm 1)=0 \quad (5.3)$$

with the average reaction rate

$$\rho\bar{\mathscr{R}}=\sigma^2 c\rho \quad (5.4)$$

Since reactive trajectories have the highest velocity, a particle never returns on them $(b(v)=0)$ and double reactions are rare:

$$\int_{\mathbb{R}}\frac{\mathscr{R}_l(v)\,\mathscr{R}_r(v)}{\bar{\mathscr{R}}\mu(v)}\,dF(v)=0$$

Conditions (b)–(d) are fulfilled for any σ, and condition (a) is satisfied with the following scaling of σ by ε:

$$\sigma=\varepsilon \quad (5.5)$$

The reaction rate $\bar{g}$ after scaling and the diffusion coefficient D_0 are

$$\bar{g} = \rho c = \rho^2 c D_0, \qquad D_0 = 1/\rho \tag{5.6}$$

Note that for $\sigma = 0$ the microscopic motion also becomes a Markov process.(21)

5.2. The Maxwellian Gas

As a second example, we choose a normal distribution of velocities:

$$dF(v) = F'(v)\, dv = \left(\frac{m}{2\pi T}\right)^{1/2} e^{-mv^2/2T}\, dv \tag{5.7}$$

where T is the temperature ($k_B = 1$) and m the mass of the particles. The mean velocity

$$\mu_0 = \mathscr{E}\,|v| = \left(\frac{2T}{\pi m}\right)^{1/2} \tag{5.8}$$

determines the diffusion coefficient D, whose square-root dependence on the temperature must be traced to the restrictive nature of one-dimensional motion.

The average relative velocity for collisions from the left is

$$\mu_l(v) = \mu_r(-v) = \frac{1}{2}\mu_0\, e^{-w^2} - \frac{v}{2}\operatorname{erfc} w \tag{5.9}$$

with the dimensionless velocity $w = (m/2T)^{1/2} v$. The average collision frequency is

$$\rho\bar{\mu} = \rho\mathscr{E}\mu(v) = \sqrt{2}\,\mu_0\rho \tag{5.10}$$

The average reaction rate

$$\bar{\mathscr{R}} = \bar{\mu} e^{-mc^2/T} \tag{5.11}$$

is just the Arrhenius expression, with the kinetic energy mc^2 in the center-of-mass frame. We define for simplicity the dimensionless velocity threshold

$$\gamma = \left(\frac{m}{T}\right)^{1/2} c \tag{5.12}$$

Since the Maxwellian distribution allows for arbitrarily large velocities, we maintain its parameters in the hydrodynamic limit and only scale the reaction threshold:

$$\gamma \to \infty$$

Such a scaling is physically justified for thermal (i.e., collisional) isomerization reactions by the high values of the activation energy.(8) For instance,(6) the *cis–trans* isomerization of CDH=CHD (which has no heat of reaction) require 2.82 eV per molecule (272 kJ mol^{-1}) around 750 K, so that $\gamma^2 = 43.6$ and $\exp(-\gamma^2) = 10^{-19}$ for the twisting of one molecule. Twisting two molecules simultaneously (as in our model) would require $2\gamma^2 = 87.3$.

Conditions (b)–(c) are readily verified, with bounds in powers of the Arrhenius factor; let then

$$c^2 = \frac{2T}{m} \ln(2^{-1/4}\varepsilon^{-1}) \tag{5.13}$$

The microscopic reaction rate scales as $\rho\bar{\mathscr{R}} = \varepsilon^2 \bar{g}$ with the macroscopic rate

$$\bar{g} = \rho\mu_0 \tag{5.14}$$

The rescaled reaction rates

$$g_l^*(-u) = g_r^*(u) = \lim_{\varepsilon \to 0} \varepsilon^{-2} \mathscr{R}_r(uc)\rho$$

are easily found:

$$\begin{aligned} &\text{for } u < 2 - \sqrt{2}: \quad g_r^*(u) = 0 \\ &\text{for } u = 2 - \sqrt{2}: \quad g_r^*(u) = g \\ &\text{for } u > 2 - \sqrt{2}: \quad g_r^*(u) = \infty \end{aligned} \tag{5.15}$$

so that condition (d) is satisfied for any finite $v_0 > 0$. In the scaling limit ($c \to \infty$), almost all reactions involve particles with velocities larger than $(2 - \sqrt{2})c$; slow particles nearly never meet partners for reaction. As very fast particles are very rare, most reactions occur at $v \simeq \pm c$:

$$\lim_{c \to \infty} \rho\varepsilon^{-2} \mathscr{R}(uc)\, cF'(uc) = \tfrac{1}{2}[\delta(u+1) + \delta(u-1)] \tag{5.16}$$

6. CONCLUDING REMARKS

We have shown on an explicit (though simplistic) example how one can derive an exact Markovian master equation for the populations involved in a chemical reaction. As in all arguments involving hydrodynamic types of limits, the only statistical element injected in the description is the initial ensemble. The Markov property is obtained on the macroscopic time scale (by tuning an intrinsic small parameter) for the distributions of an arbitrary subset of an infinite population. The basic elements in our analysis are indeed the N-particle distributions.

Thus the reacting hard-point model presents in the hydrodynamic limit the best stochastic properties one can expect from a one-dimensional model: for better diffusion in space, one must resort to either stochastic dynamics(12) or higher dimensionality.(13,15) Moreover, poorer dynamics do not lead to such a Markovian behavior: with the same reaction conditions, ideal gas dynamics does not lead to a Markovian reaction scheme for even two particles, for a particle always preserves its velocity and its (corresponding) reaction rate $\mathscr{R}(v)$. And since particles always keep the same relative velocities, their reactions are finally correlated.(7)

As our whole discussion rests on the effective use of the correlation-decay properties of the hard-points model, we should investigate more deeply the connections between the hydrodynamic limit and the abstract theory of K flows, which applies to this model.(1) In particular, a general abstract technique has been devised for such systems to derive exactly Markov processes equivalent to deterministic dynamics.(18) We are presently performing such an analysis, though of course chemical processes need not always be described by K systems at the microscopic level!

Finally, it would be sensible to extend our results to more complex reaction schemes; however, any such improvement would be unrealistic as long as the particles of various species cannot diffuse to react with farther particles. Therefore one should first investigate generalizations to higher dimensionalities. In this framework, the only case for which some rigorous results are known is the low-density gas in the Boltzmann–Grad limit(13): there one may hope deriving the Markovian master equation together with the (linear) reactive Boltzmann equation for the macroscopically ideal mixture. The extension of these works to nonideal systems is still an open problem.

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APPENDIX: CONDITIONAL VELOCITY DISTRIBUTION

Lemma 4.2 is completely independent of the notion of reaction we use through this paper: it simply expresses a uniform bound on the velocity distribution at any time, given the velocity at some time. For a differentiable distribution function F, it may be stated as

$$h_1(v, t \mid v_0) \leqslant Q h_0(v)$$

if

$$dF(v) = h_0(v)\,dv$$
$$dF(v, t \mid v_0) = h_1(v, t \mid v_0)\,dv + A(v, t)\,\delta(v - v_0)\,dF(v)$$

where $A(v_0, t)$ is the probability(14) for the particle to be at time t on the same trajectory (of velocity $v = v_0$). A straightforward calculation from the self-correlation function(14) yields

$$Q(v, t \mid v_0) = \frac{h_1(v, t \mid v_0)}{h_0(v)} = \rho t \int_{\mathbb{R}} e^{-\rho\mu t - n\varphi} I_n(\rho t \psi)\,dy$$

where we omit the dummy variable y in the notations

$$\mu = \mu(y)$$
$$\psi = (\mu^2 - y^2)^{1/2} = \mu - \frac{y^2}{\mu + \psi}$$
$$\varphi = \ln \frac{\mu + y}{\psi}$$
$$n = \chi(y > v) - \chi(v_0 > y)$$

and I_n is the modified Bessel function of nth order.

(1) If $v_0 < 0 < v$ or $v < 0 < v_0$, one easily sees that

$$Q(v, t \mid v_0) \leqslant \rho t \int_{\mathbb{R}} e^{-\rho t \mu} I_0(\rho t \psi)\,dy$$

We part the real line in four regions:

(a) For $y \geqslant y_0 \geqslant 0$, assuming $\mu + \psi \leqslant \gamma y$:

$$\rho t \int_{y_0}^{\infty} e^{-\rho t \mu} I_0(\rho t \psi)\,dy \leqslant \gamma$$

with the standard majorization of I_0 by the exponential and the definition of ψ.

(b) For $0 \leqslant y \leqslant y_0$, assuming $\psi \geqslant s$ and $\mu + \psi \leqslant m$:

$$\rho t \int_0^{y_0} e^{-\rho t \mu} I_0(\rho t \psi)\, dy \leqslant \left(\frac{\pi m}{s}\right)^{1/2} \operatorname{erf}\left(\frac{\rho t}{m} y_0^2\right)^{1/2}$$

by similar arguments.

As analogous majorizations hold for $y \leqslant 0$, the ratio $Q(v, t \mid v_0)$ is bounded by some constant Q_0.

(2) If $0 < v < v_0$, the previous majorizations cannot be used on the interval $[0, v]$, but hold everywhere else. Now, for $y_0 \leqslant y \leqslant v$, assuming $\mu + \psi \leqslant \gamma y$:

$$\rho t \int_{y_0}^{v} e^{-\rho t \mu} \frac{\mu + y}{\psi} I_1(\rho t \psi)\, dy \leqslant \gamma^3$$

and for $0 \leqslant y \leqslant y_0$, assuming $\psi \geqslant s$ and $\mu \leqslant m$:

$$\rho t \int_0^{y_0} e^{-\rho t \mu} \frac{\mu + y}{\psi} I_1(\rho t \psi)\, dy \leqslant \left(\frac{\pi m}{s}\right)^{1/2} \frac{m + y_0}{s}$$

so that $Q(v, t \mid v_0)$ is again majorized by a constant Q_1.

(3) The other cases are treated similarly.

We must now justify our majorizations and minorizations of ψ and μ. Write $F_0 = F(0)$.

(1) For $y \geqslant 0$: $\mu(y) \geqslant y F_0 + (1/2)\mu_0$ and if $0 \leqslant y \leqslant y_0$: $\psi^2(y) \geqslant (F_0^2 - 1) y^2 + \mu_0 F_0 y + (1/4)\mu_0^2$. The right-hand side is minimum either for $y = 0$ or for $y = y_0$; choosing $y_0 = \mu_0/2$, $s = \mu_0 F_0/2$ and $m = 3y_0$ leads to our inequalities.

(2) For $y \geqslant y_0$, the convexity of μ and the inequality $\psi \leqslant \mu$ allow one to choose $\gamma = 2\mu(y_0)/y_0$.

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