

Concerning the Validity of the Stochastic Approach to Chemical Kinetics

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A simple argument advanced recently in support of the legitimacy of the stochastic formulation of chemical kinetics has been criticized because it seems to require the imminent collision of widely separated molecules. It is argued here that this criticism is unwarranted because it is based on an incorrect use of probabilities. To illustrate the various probabilistic considerations involved, a detailed analysis is presented of a closely related but mathematically simpler problem: the calculation of the collision probability per unit time for a thermally equilibrated one-dimensional gas of point particles.

KEY WORDS: Chemical kinetics; master equations; collision probabilities; one-dimensional gas; stochastic processes.

1. INTRODUCTION

The stochastic master equation approach to chemical kinetics, in which the time evolution of a chemically reacting system is regarded as a Markovian random walk in the space of the molecular populations of the reacting species, is currently receiving increased attention in the research literature.⁽¹⁻⁷⁾ However, the underlying physical validity of this formulation of chemical kinetics seems to be a moot point.⁽⁸⁻¹²⁾

In a recent paper,⁽¹³⁾ which was aimed primarily at developing a rigorous numerical method for simulating the stochastic time evolution of spatially homogeneous chemical systems, a simple argument was advanced in support of the physical legitimacy of this approach to chemical kinetics. The argument is similar to the elementary gas-kinetic-theory derivation of the rate of reactive molecular collisions,⁽¹⁴⁾ except that instead of trying to calculate the *number* of reactive collisions per unit time, attention is focused on calculating the *probability* of a reactive collision per unit time. It was argued that this

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seemingly semantic modification actually allows one to develop in a rigorous way the stochastic formulation of chemical kinetics for systems that are kept in thermal (as opposed to chemical) equilibrium.

Briefly, the argument in Section 2 of Ref. 13 proceeds as follows: First, physical considerations are employed to obtain an expression for the *probability* that a randomly chosen pair of reactable molecules will undergo a reactive collision in the next small time interval δt . That probability is then multiplied by the total number of distinct reactable pairs, and the product is interpreted as the net probability that such a reaction will occur somewhere inside the system in δt . This is the crucial quantity; using it, one can proceed in a mathematically rigorous way to derive, not only an exact analytical master equation of the type commonly employed,⁽¹⁵⁾ but also an exact numerical simulation algorithm,⁽¹³⁾ to describe the temporal behavior of the system.

In presenting this simple rationale for the stochastic formulation of chemical kinetics to others, the author has frequently encountered misgivings about it on the grounds that it appears to accord the same probability for a collision in the next small time interval to two molecules that are very far apart as it does to two molecules that are very close together. The purpose of this note is to show that these misgivings, though superficially plausible, are in fact not justified, and that the line of reasoning outlined above is sound.

2. A ONE-DIMENSIONAL SYSTEM

The source of confusion on this point and its proper resolution can be exhibited most simply and clearly in the one-dimensional case. Accordingly, we consider now a system of N point particles in thermal equilibrium inside the one-dimensional volume $0 \leq x \leq L$, and we wish to calculate an expression for the quantity

$$p(\delta t) \equiv \text{probability at time } t \text{ that a two-particle collision will occur somewhere inside } 0 \leq x \leq L \text{ in the next vanishingly small time interval } (t, t + \delta t) \quad (1)$$

Implicit in this statement of the problem are two important assumptions concerning our knowledge of the dynamical state of the system at time t , as follows²:

(A) First, it is assumed that the *positions* of the N particles at the chosen time t may be regarded as random variables distributed according to the

² In Section 2 of Ref. 13 it was argued that these two assumptions are valid for *reactive* collisions, *provided* the system is such that nonreactive collisions occur much more frequently than reactive collisions. However, as this point is not at issue here, we simply take these two assumptions as "given."

uniform distribution inside $(0, L)$. This means that the probability of finding a randomly chosen particle inside any subinterval (x_1, x_2) of $(0, L)$ at time t is $(x_2 - x_1)/L$, irrespective of the positions of the other particles.

(B) Second, it is assumed that the *velocities* of the N particles at the chosen time t , and hence also the *relative velocities* of the $N(N - 1)/2$ particle pairs, may be regarded as random variables distributed (roughly) according to Maxwell-Boltzmann distributions. We shall not require the specific forms of these velocity distribution functions here. All that we shall need are the properties that: (i) any particle at time t will be found to be moving in the $+x$ or $-x$ directions with equal probabilities; and (ii) the probability that any pair of particles will have at time t a *relative speed* between v and $v + dv$ can be written as $f(v) dv$, where f is a nonnegative function of v which bounds unit area with the positive v axis and which tends to zero extremely rapidly as $v \rightarrow \infty$.

3. DERIVATION USING UNCONDITIONED PROBABILITIES

A derivation of an expression for $p(\delta t)$ which exactly parallels the arguments in Section 2, Ref. 13 proceeds as follows.

Pick a pair of particles at random at time t , and let v denote the speed of one of them (the "first" particle) relative to the other (the "second" particle). Then in the vanishingly small time interval $(t, t + \delta t)$, the first particle sweeps out relative to the second particle a "collision interval" of length $v \delta t$, in the sense that if the second particle happens to lie inside that interval at time t , then the two particles will collide in $(t, t + \delta t)$. The time interval δt is taken "vanishingly small" for two reasons: First, our subsequent use of $p(\delta t)$ will ultimately require that we pass to the limit $\delta t \rightarrow 0$; and second, only if the interval $v \delta t$ is vanishingly small can we be assured that, if the second particle *does* lie therein at time t , then a collision between the two particles in $(t, t + \delta t)$ will not be prevented by a prior collision of one of them with a third particle.

On the basis of (A), we may infer that the *probability* that the second particle will be found at time t to lie inside the collision interval of the first particle is $v \delta t/L$; therefore, this is the probability at time t that a randomly chosen pair of particles with relative speed v will collide in $(t, t + \delta t)$. If we now average this probability over all pairs—i.e., over all possible relative speeds v in accordance with the specifications of (B)—we evidently obtain the probability that a pair of particles picked at random at time t without regard for their positions or velocities will collide in $(t, t + \delta t)$:

$$\langle v \delta t/L \rangle = \langle v \rangle \delta t/L \quad (2)$$

Here,

$$\langle v \rangle = \int_0^{\infty} v f(v) dv \quad (3)$$

is of course the average relative speed. Now, among N particles there are precisely $N(N - 1)/2$ distinct pairs. Therefore, the addition law for probabilities allows us to conclude that the quantity defined in (1) is given by

$$p(\delta t) = [N(N - 1)/2][\langle v \rangle \delta t/L] + o(\delta t) \quad (4)$$

where $o(\delta t)$ denotes terms of order > 1 in δt , which account for the possibility of more than one collision occurring in $(t, t + \delta t)$.³

Now, to the above derivation of (4) it might be objected that all $N(N - 1)/2$ particle pairs have been accorded the *same* probability, $\langle v \rangle \delta t/L$, of colliding in the next small time interval δt . But this appears to be incorrect: Common sense tells us that two particles that are very far apart at time t , say near opposite ends of the interval $(0, L)$, will surely have *much less* probability of colliding in the next small time interval $(t, t + \delta t)$ than will two neighboring particles.

This objection to the above derivation is fallacious, though, because it fails to properly distinguish between “conditioned” and “unconditioned” probabilities. The quantity in (2) is the *unconditioned* collision probability—i.e., the collision probability for two particles picked at random *without regard for their positions or velocities*. If one wishes to impose the condition that the two particles have certain relative positions at time t , then the collision probability $\langle v \rangle \delta t/L$ no longer applies; in that case an appropriately “conditioned” collision probability must be used, and the probability tallying procedure will have to be modified accordingly.

A calculation carried out in terms of spatially conditioned collision probabilities will be more complicated than one using unconditioned collision probabilities, but if both calculations are done correctly they will necessarily yield the same final result. For the simple one-dimensional system under consideration we can actually demonstrate the validity of this important point by explicit calculation, an exercise which is both interesting and instructive.

4. DERIVATION USING CONDITIONED PROBABILITIES

The derivation of an expression for $p(\delta t)$ that uses spatially conditioned collision probabilities, and which therefore pays careful attention to precisely which pairs of particles are capable of imminent collision, proceeds as follows:

³ All we can or need say about the terms $o(\delta t)$ is that $o(\delta t)/\delta t \rightarrow 0$ as $\delta t \rightarrow 0$.

Let the N particles in $(0, L)$ be numbered at time t from left to right by the index n ($n = 1, \dots, N$). Since we are interested in the probability $p(\delta t)$ that some pair of particles will collide in the next *vanishingly small* time interval $(t, t + \delta t)$, our only concern is with the *first* collision that occurs after time t . Clearly, that collision must be between two *adjacent* particles—i.e., between either particles 1 and 2, or particles 2 and 3, or particles 3 and 4, etc. Therefore, letting

$$p_n(\delta t) \equiv \text{probability at time } t \text{ that particles } n \text{ and } n + 1 \text{ will collide in the next vanishingly small time interval } (t, t + \delta t) \quad (5)$$

then we have by the addition law for probabilities

$$p(\delta t) = \sum_{n=1}^{N-1} p_n(\delta t) + o(\delta t) \quad (6)$$

Here, as before, $o(\delta t)$ denotes terms of order > 1 in δt , which account for the probability of more than one collision in $(t, t + \delta t)$.

To calculate $p_n(\delta t)$, we first observe that particles n and $n + 1$ will collide in $(t, t + \delta t)$ if and only if they are *approaching* each other at time t with speed $v > \xi_n/\delta t$, where ξ_n is the distance between particles n and $n + 1$ at time t . According to (B), the probability for this is

$$\frac{1}{2} \int_{\xi_n/\delta t}^{\infty} f(v) dv$$

provided ξ_n is given. Therefore, letting

$$P_n(\xi_n) d\xi_n \equiv \text{probability at time } t \text{ that particles } n \text{ and } n + 1 \text{ will be separated by a distance between } \xi_n \text{ and } \xi_n + d\xi_n \quad (7)$$

we have by the multiplication and addition laws for probabilities

$$p_n(\delta t) = \int_{\xi_n=0}^L \int_{v=\xi_n/\delta t}^{\infty} P_n(\xi_n) d\xi_n \frac{1}{2} f(v) dv \quad (8)$$

Changing the order of integration in (8) gives

$$p_n(\delta t) = \int_0^{L/\delta t} dv \int_0^{v\delta t} d\xi_n \frac{1}{2} f(v) P_n(\xi_n) + \int_{L/\delta t}^{\infty} dv \int_0^L d\xi_n \frac{1}{2} f(v) P_n(\xi_n) \quad (9)$$

Now, $f(v)$ falls off extremely rapidly as $v \rightarrow \infty$, and in any real situation there will always exist a *finite upper bound* V on the relative speeds v ; e.g., if E is the total energy available to the entire system and m is the mass of each particle, then (classically) no two particles could possibly have a relative speed greater than $V = 2(E/m)^{1/2}$. This means that $f(v)$ can be taken to vanish for $v > V$,

and all v integrations over $f(v)$ can be terminated at $v = V$ instead of $v = \infty$.⁴ Therefore, if we choose δt already small enough so that $L/\delta t \geq V$, then the second term in (9) vanishes and our expression for $p_n(\delta t)$ simplifies to

$$p_n(\delta t) = \frac{1}{2} \int_0^V dv f(v) \int_0^{v\delta t} d\xi_n P_n(\xi_n), \quad \delta t \leq L/V \quad (10)$$

Now we choose δt even smaller; specifically $\delta t \ll L/V$. Then we will have $v \delta t \ll L$ for all v in the interval $(0, V)$, and so we can perform the ξ_n integration in (10) to first order in δt according to

$$\int_0^{v\delta t} P_n(\xi_n) d\xi_n = P_n(0)v \delta t + o(\delta t)$$

Inserting this into (10) and performing the v integration results in

$$p_n(\delta t) = \frac{1}{2} P_n(0) \langle v \rangle \delta t + o(\delta t) \quad (11)$$

where $\langle v \rangle$ is the average relative speed defined in (3).

Evidently, we need to know the value of $P_n(\xi_n)$ at $\xi_n = 0$. In order to obtain an expression for the function $P_n(\xi_n)$, we first construct an expression for $P'_n(x_n, x_{n+1})$, the joint position probability density function for particles n and $n + 1$. Applying the addition and multiplication laws of probability to the hypothesis (A), we have for the probability that particle n will lie between x_n and $x_n + dx_n$ and particle $n + 1$ will lie between x_{n+1} and $x_{n+1} + dx_{n+1}$

$$\begin{aligned} P'_n(x_n, x_{n+1}) dx_n dx_{n+1} \\ = (dx_n/L)(dx_{n+1}/L)(x_n/L)^{n-1} \\ \times [(L - x_{n+1})/L]^{N-n-1} N! / [1! 1! (n-1)! (N-n-1)!] \end{aligned} \quad (12a)$$

where $0 \leq x_n < x_{n+1} \leq L$. Here, the first two factors on the right are the probabilities that two randomly chosen particles will be found in the respective intervals $(x_n, x_n + dx_n)$ and $(x_{n+1}, x_{n+1} + dx_{n+1})$, the third factor is the probability that $n - 1$ randomly chosen particles will be found in $(0, x_n)$, the fourth factor is the probability that $N - (n + 1)$ randomly chosen particles will be found in (x_{n+1}, L) , and the last factor is the number of distinct ways of arranging N like particles into four groups of 1, 1, $n - 1$, and $N - n - 1$ particles. The joint density function $P'_n(x_n, x_{n+1})$ is therefore

$$P'_n(x_n, x_{n+1}) = N! L^{-N} [(n-1)! (N-n-1)!]^{-1} x_n^{n-1} (L - x_{n+1})^{N-n-1} \quad (12b)$$

⁴ It perhaps should be noted that the derivation given in the preceding section likewise assumes the existence of a *finite maximum* for the relative speeds: In order for the probability arguments leading to (2) to be legitimate, it must be true that $v \delta t/L < 1$ for *fixed* δt and *all possible* v . Clearly, this means that δt must initially be chosen smaller than L/v_{\max} , and as we surely want $\delta t > 0$, then we must have $v_{\max} < \infty$.

provided of course that $0 \leq x_n < x_{n+1} \leq L$ [otherwise $P_n'(x_n, x_{n+1})$ vanishes]. If we now change variables according to

$$(x_n, x_{n+1}) \rightarrow (x_n, \xi_n \equiv x_{n+1} - x_n) \quad (13)$$

where ξ_n is the previously defined distance between particles n and $n + 1$, then the joint probability density function $P_n''(x_n, \xi_n)$ for the variables x_n and ξ_n can be obtained by using the transformation rule

$$P_n''(x_n, \xi_n) = P_n'(x_n, x_{n+1}(x_n, \xi_n)) |\partial(x_n, x_{n+1}) / \partial(x_n, \xi_n)| \quad (14a)$$

where on the right x_{n+1} is now the *function* $x_{n+1} = x_n + \xi_n$. The Jacobian in (14a) is easily found to be unity, so inserting (12b), we find for the joint probability density function for the variables x_n and ξ_n

$$P_n''(x_n, \xi_n) = N! L^{-N} [(n-1)! (N-n-1)!]^{-1} x_n^{n-1} (L - \xi_n - x_n)^{N-n-1} \quad (14b)$$

provided that $x_n \geq 0$, $\xi_n \geq 0$, $x_n + \xi_n \leq L$. The desired probability density function for ξ_n alone can now be found simply by integrating $P_n''(x_n, \xi_n)$ over all allowable values of x_n :

$$P_n(\xi_n) = \int_0^{L-\xi_n} P_n''(x_n, \xi_n) dx_n \quad (15a)$$

Upon carrying out this integration,⁵ we obtain

$$P_n(\xi_n) = NL^{-N} (L - \xi_n)^{N-1} \quad (15b)$$

for $0 \leq \xi_n \leq L$. We observe in passing that $P_n(\xi_n)$ is independent of n .

Equation (15b) implies that $P_n(0) = N/L$; when we substitute this into (11) we get

$$p_n(\delta t) = N \langle v \rangle \delta t / 2L + o(\delta t) \quad (16)$$

This, like (15b), is independent of n . Therefore, substituting (16) into (6) immediately yields the result

$$p(\delta t) = (N-1) \langle v \rangle \delta t / 2L + o(\delta t) \quad (17)$$

in exact agreement with (4).

⁵ The integration in (15a) is facilitated by using the formula

$$\int_0^A x^{n_1} (A-x)^{n_2} dx = A^{n_1+n_2+1} n_1! n_2! / (n_1+n_2+1)!$$

The validity of this formula for all nonnegative integers n_1 and n_2 can be proved by using integration by parts and an induction argument. This formula is also helpful in verifying the normalization constants in (12b) and (14b).

5. CONCLUSIONS

It is instructive to compare the arrangement of factors in (4) and (17). In (4), the second factor is the average collision probability per pair *irrespective* of the relative positions of the pair members, and the first factor is the total number of pairs. By simply shifting the quantity $N/2$ from the first factor to the second factor, we obtain (17). Here, the second factor is the collision probability of an *adjacent* pair, and the first factor is the number of such adjacent pairs.

The salient point to be drawn from all this is that the *logic* of the first derivation, which uses unconditioned probabilities, is quite sound, and in particular may *not* be legitimately criticized on the grounds that it calls for the imminent collision of widely separated particles. Consequently, the *logically parallel* derivation given in Section 2, Ref. 13, of the reaction probability per unit time in a spatially homogeneous, three-dimensional system is likewise immune to criticism on these grounds. This lends support to the view that the stochastic formulation of the chemical kinetics of spatially homogeneous systems has a much firmer microphysical basis than seems to be generally acknowledged.

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