

The uses of quantum field theory in diffusion-limited reactions

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The techniques of quantum field theory on a lattice are used to examine the diffusion and reaction processes of particles in a solid, such as vacancies or interstitials, or chemical species of all kinds which move by discrete random hopping processes and react in a prescribed way when they are in proximity. First formulated by Doi in the 1970s, the quantum-field-theoretic solution of the “master equation” of statistical physics allows a systematic investigation of any number of nonequilibrium processes ranging from fluorescence to explosions. By formulating the problem on the points of a space lattice in d dimensions one can control the ultraviolet divergences associated with short-range interactions. For illustrative purposes several models are solved in detail. The authors include as an appendix a chronological list of seminal articles in the field. [S0034-6861(98)00303-1]

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INTRODUCTION

Over the past two decades there has occurred a remarkable development in the many-body theory of “classical objects,” one that has escaped the attention of most of the physics community. We are referring to the use of quantum field theory (QFT) in the study of the motion, diffusion, recombination, and other dynamic manifestations of *non*-quantum-mechanical objects. The

objects in question can be massive particles subject to classical dynamics and/or statistical mechanics, or even entities as small as atoms or molecules, under circumstances in which neither phase coherence nor the uncertainty principle $\Delta p \Delta x \approx \hbar$ are thought to play significant roles. The field theory which at first appears to be just a counting device with which to keep track of the individual particles actually emerges as a useful, powerful, and, to many physicists, familiar tool. It is the purpose of the present paper to review this field-theoretic approach by example and demonstration, all within the context of particles constrained to execute random walks on the vertices of a space lattice in d dimensions. This limitation avoids some of the pitfalls—ambiguities and ultraviolet singularities—associated with motion in the continuum.¹

Only the simplest classical dynamics are both integrable and stable. Integrability implies that a set of initial conditions unambiguously determines the evolution of the system, while stability implies that this evolution is insensitive to initial conditions. However, modern studies of chaotic behavior reveal that most interesting systems behave otherwise. Generally speaking, the equations of motion of numerous interacting particles are *not* integrable,² although upon being averaged over a set of initial conditions they may evolve in an ergodic or quasiergodic manner and require a probabilistic description. Following Wigner (see Mehta, 1967), it is now acceptable to investigate deterministic problems in many-body atomic and nuclear dynamics, using aleatory Hamiltonians to simulate the quantum mechanics that are too difficult to solve directly. Consider how much more natural, compelling, and useful a stochastic approach can be, when used to solve the many-body equations of motion of strongly interacting (and/or reacting) *classical* objects undergoing Brownian motion.

¹But even this limitation can always be lifted by taking the limit of lattice parameter $a \rightarrow 0$ in a prescribed manner.

²With the notable exception of one-dimensional motion, which will be discussed separately.

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The time development of probability is usually found using the solution of a “master equation” that, superficially at least, resembles the time-dependent Schrödinger equation with probability functions taking the place of wave functions and $i\hbar$ replaced by $1/\tau$, with τ some characteristic time (of reaction or diffusion or whatever). And just as Feynman’s path-integral formalism and his diagrammatic methods are used to study the evolution of wave operators satisfying the Schrödinger equation, so can this same formalism and these same methods be adapted for the evolution of probabilities and probability densities governed by the master equation. Natural as it now seems to today’s reader, this extension was in fact a “quantum leap” beyond the ideas of Smoluchowsky (1917) that once informed all of physical chemistry.

The paradigm shift, the fitting of *quantum* algebra to the irreversible motion and chemical reactions of massive *classical* objects, originated in two papers by Masao Doi (1976a, 1976b), although in retrospect some other works, e.g., that of Suna (1970), can be seen as antecedents. The method was a radical departure from the (then standard) hierarchies of equations of motion and could be used to derive them. We shall never know why Doi’s discovery remained such a (loosely kept) secret, ignored by the many and known but to those few researchers who rediscovered it independently or happened on his seminal papers by chance. His two articles are rather complete descriptions of the procedure, the first dealing with the operator representation of classical mechanics and the second with stochastic processes using time ordering, propagators, diagrammatic expansions, vertex functions, and the like. In subsequent times, a dozen authors must have enjoyed an identical epiphany when solving some particular model of a diffusion-limited reaction by an exotic field-theoretic method—ever a *tour de force*—ultimately to find that their methodology, and perhaps even their solution, had been previously discovered and published. Such are the rewards and penalties of working in a largely unreferenced field. At least one author, Peliti (1985), determined this situation to be unacceptable and hoped that, at the very least, his own “. . . expository account of this formalism . . . will make such rediscoveries unnecessary for the future.” But fully a decade has passed since this wish and, still, duplication of methodology and of discoveries remains the rule and not the exception.

For this and other reasons, after laying out some didactic examples in this review, we provide an Appendix that documents the historical development of the field and an annotated bibliography that illustrates its numerous applications in physics and chemistry. These applications have been in the theory of materials growth (aggregation), pattern formation, vacancy-interstitial recombination in damaged solids, delayed fluorescence, and the diffusion and attrition of excitons. In principle, the same method could be applied to activities ranging from the fabrication of diffusion-doped semiconductors to the singular hydrodynamics (Smoluchowsky, 1917) of reacting species—and even to the theory of explosions.

In fact, the examples cited in the bibliography are relatively few and merely scratch the surface of possibilities. Additionally, we should alert the reader to a growing literature on the uses of the Fokker-Planck equation and other purely stochastic methods in the solution of transport-dynamical models. Such approaches are in some respects parallel to the present treatment and are certainly complementary to it. Two fine reviews are currently available (van Kampen, 1984; Gardiner, 1985).

Consider the following simple problems in chemical kinetics, which can usefully be tackled using the QFT approach:

(1) Atomic species A and B diffuse throughout a given volume with diffusion coefficients \mathcal{D}_A and \mathcal{D}_B , but whenever any A and B are at some small distance R from one another, they recombine in a time dt with *a priori* probability $1/\tau(R)dt$. In a unidirectional reaction there results an inert product \emptyset , which does not itself decompose back into $A+B$; in bidirectional reactions the product is not “inert,” but decomposes into $A+B$ at a rate $1/\tau(R) \exp(-\beta U)$, with the parameter τ and the inverse temperature $\beta=1/kT$ both ≥ 0 . Normally $U \geq 0$, but if the reaction is primarily that of decomposition, $U < 0$.

(2) Similar considerations apply to the fluorescence of certain liquid or amorphous semiconductors, in which electrons and holes diffuse separately and independently. When in proximity, these particles have a finite probability of recombining and emitting a photon that immediately disappears from the system; thus the unidirectional model applies. It also applies to the diffusion and decay of excitons at recombination (“scavenger”) sites, an alternative and important mechanism for delayed illumination which involves only a single species.

(3) In a different context, the study of the structure of imperfect solids, one may consider an excess of vacancies (i.e., missing atoms) such as those created by radiation damage. These can either diffuse and ultimately recombine with excess interstitial atoms, or else diffuse to a surface and effectively disappear. Conversely, vacancies or interstitials or other defects created at surfaces can diffuse to the interior of the solid. Among other phenomena that can be treated analogously, diffusion-limited aggregation (whereby certain solids grow from vapor or liquid) has proved a popular object of research.

Although describing diverse physical processes, the above applications all have in common the special challenge arising from the interference between spatial and temporal dependences. So let us first discuss why the most simplistic approximations generally fail.

Consider the mean-field approach to the recombination of two species A and B :

$$\partial_t \rho_A = \partial_t \rho_B = -(1/\tau) \rho_A \rho_B, \quad (0.1)$$

in which the ρ ’s are the particle densities. A moment’s thought shows that this equation could never be valid except in the very special case of a fast-flowing, fast-mixing fluid. For, unless the reaction is initiated under very special conditions, local depletion of the constituents in the regions of maximal reaction requires spatial

diffusion of the species to further fuel the reaction. Thus the one feature common to all diffusion-limited reactions is the need to have the right particles at the right place at the right time.

Depending on the parameters, reactions can asymptotically favor either homogeneity or one of its opposites, such as long-lived turbulence, granularity, separation of species, self-organized singularities, or other inhomogeneities. To distinguish among these various behaviors, it is necessary to bring the spatial dependences into any equation such as (0.1) and identify the relevant control parameters.

However, no sooner do we generalize Eq. (0.1) by writing

$$\begin{aligned} (\partial_t - \mathcal{D}_A \nabla_A^2) \rho_1(r_A, t) &= (\partial_t - \mathcal{D}_B \nabla_B^2) \rho_1(r_B, t) \\ &= -(1/\tau(r_A - r_B)) \rho_2(r_A, r_B, t), \end{aligned} \quad (0.2)$$

than we encounter the magnitude of the difficulties. Such equations are mathematically intractable because the single-particle densities $\rho_1(r, t)$ are connected to two-body correlation functions ρ_2 , which are in turn connected by similar equations to three-body correlation functions ρ_3 , etc. (We shall return to this topic in Sec. II.F.) The equations connecting ρ_n to ρ_{n+1} become increasingly complicated with increasing $n > 1$. Typically such infinite hierarchies of equations are solved approximately, often being truncated from the start in the manner of Eq. (0.1), in which ρ_2 is replaced by $\rho_1(r_A, t) \times \rho_1(r_B, t)$. But even if we could solve the two coupled nonlinear differential equations there would be no inherent way to gauge the errors. This point is reexamined in the next section, once QFT comes to the rescue.

Other reasonably accurate and well-known methods such as molecular dynamics and Monte Carlo have proven useful in analyzing the behavior of the solutions to complex models. In many instances numerical simulations can suggest the correct asymptotic forms of the laws of transport and decay. Additionally, mathematically rigorous analysis yielding upper and lower bounds to the asymptotic rate of recombination have been found in some simple cases, as in the work of Bramson and Lebowitz (1988, 1991a, 1991b). When both bounds carry the same asymptotic power-law dependence of $\rho_1(r, t)$ on t , the problem is essentially solved. But in every such numerical or analytical study of molecular dynamics, the numerical programs or the mathematical analysis have been *ad hoc*, needing to be individually tailored to the particular model at hand.

Clearly a more general framework would serve both practical and theoretical concerns. We shall see that QFT allows the formal solution of the master equation that governs the many-body probabilities. Once found, this solution determines all the correlation functions simultaneously and is not subject to any limitations. A systematic strategy for obtaining this formal solution is what QFT brings to the table. It is well known that many complex models in QFT as well as numerous many-body problems in condensed-matter physics can be “solved”

exactly in one dimension (Mattis, 1994), without approximation, even when similar problems are intractable in higher dimensions. That the same turns out to be true in the study of diffusion-limited reactions is not a coincidence, as the QFT approach easily shows. But there is a surprising twist: a number of dynamic phase transitions can take place in one dimension which have no analogue in three (Kanno, 1988; Zhang, 1987; Lindenberg *et al.*, 1988).

I. WAVE OPERATOR AS A GENERATING FUNCTION

A. Radioactive decay

We seek to communicate the gist of the method in the following few paragraphs; detailed formulations follow in due course. The simplest examples are in zero spatial dimensions, as diffusion operators are required for the more challenging and realistic applications in $d \geq 1$ dimensions. As a start let us consider the prototype unidirectional reaction: radioactive decay with lifetime τ . Whereas the probability per unit time that any given nucleus decays is $1/\tau$, the probability per unit time of the reverse reaction (in which decay products recombine into the original, intact, nucleus) can reasonably be assumed to be essentially zero. There can be no spatial dependence if, as we shall assume, the decay of each nucleus is independent of the others. With these assumptions, we can now formulate a one-body problem in $d=0$ dimensions, which is best solved using the many-body approach.

After a time t has elapsed, m out of an initial set of N nuclei have decayed leaving $n = N - m$ intact. It is obvious that the average number surviving is $\langle n \rangle \equiv n(t) = N \exp(-t/\tau)$. But what is the magnitude of the fluctuations about this average, as measured by the standard deviation σ ? (This question is not often asked, as the answer is much less obvious.) Assuming that we started with precisely N undecayed nuclei, the QFT approach yields, as we shall see,

$$\sigma^2(t) \equiv \langle n^2 \rangle - \langle n \rangle^2 = N e^{-t/\tau} (1 - e^{-t/\tau}) = mn/N$$

(having its maximum at $t = \tau \log 2$). The related quantities

$$\begin{aligned} \sigma^2(t)/n(t) &= (1 - e^{-t/\tau}) \quad \text{and} \\ \sigma(t)/n(t) &= N^{-1/2} \sqrt{e^{t/\tau} - 1} \end{aligned} \quad (1.1)$$

grow monotonically with time. We shall also see that, while different initial assumptions lead to different formulas for $\sigma(t)$, the asymptotic behavior for $t \gg \tau$ is independent of initial conditions. Therefore in a generic treatment it is always the asymptotics that one wishes to examine, even though in actual applications it may be the initial behavior that is the most important. For the simple problem at hand one can obtain all the correlations for arbitrary initial conditions simply by solving—practically by inspection—a master equation for the probability distribution $P(m|t)$.

If $1/\tau$ is the rate at which a single nucleus decays, then, for the set of n noninteracting particles, the rate at

which a single decay occurs is n/τ . The master equation for the probabilities can be immediately written down. It is a linear differential-difference equation,

$$dP(n|t) = \{(n+1)P(n+1|t) - nP(n|t)\} \frac{dt}{\tau}, \quad (1.2)$$

which incorporates the two unidirectional processes: decay *into* the state of occupancy n from $n+1$ and decay *out of* it into $n-1$. After it is solved we can compute any average, or any moment of the distribution, using

$$\langle \chi(n) \rangle = \sum_n P(n|t) \chi(n).$$

Equation (1.2) is solved by indirection, by associating the state of n particles with the n th excited state of an harmonic oscillator. Consider the harmonic-oscillator *raising operator*, a^* and its conjugate operator a . The usual commutation relation $[a, a^*] = 1$ holds.³ With $|0\rangle$ defined as the “particle vacuum” annihilated by a , *i.e.*, $a|0\rangle = 0$, the following relations are either obvious or else can be trivially derived by repeated applications of the commutation relations. We define $|n\rangle$ by

$$a^*|n\rangle = |n+1\rangle, \quad a|n\rangle = n|n-1\rangle.$$

This implies

$$|n\rangle = (a^*)^n |0\rangle \quad (\text{note, the coefficient is } 1),$$

$$\therefore a(a^*)^n |0\rangle = n(a^*)^{n-1} |0\rangle,$$

$$a^*a(a^*)^n |0\rangle = n(a^*)^n |0\rangle.$$

There follow the three important similarity transformations on an arbitrary function F :

$$(1) \quad e^{Aa^*} F(a, a^*) e^{-Aa^*} = F(ae^{-A}, a^*e^A),$$

$$(2) \quad e^{Aa} F(a^*) e^{-Aa} = F(a^* + A), \quad \text{and}$$

$$e^{Aa^*} F(a) e^{-Aa^*} = F(a - A),$$

and a rescaling transformation for arbitrary F and G :

$$(3) \quad (F(a), G(a^*)) \Rightarrow (F(Aa), G(a^*/A)) \quad (1.3)$$

where A is any constant.

The crucial concept here is that of a *probability state vector* in which to imbed the $P(n|t)$:

$$|\Psi(t)\rangle \equiv \sum_{n=0}^{\infty} P(n|t) |n\rangle = \sum_{n=0}^{\infty} P(n|t) (a^*)^n |0\rangle. \quad (1.4)$$

The initial condition $P(n|0) = \delta_{n,N}$ is equivalent to $|\Psi(0)\rangle = (a^*)^N |0\rangle$. (We examine a different set of ini-

tial conditions below.) The right-hand basis states in this vector space (Fock space) are the $(a^*)^n |0\rangle$. Given

$$1/n! \langle 0 | (a^*)^n (a^*)^{n'} | 0 \rangle = \delta_{n,n'}$$

they form a complete orthogonal set. However, the individual states will not be normalized in the conventional manner. Instead, one makes use of a “reference” state denoted $(\mathcal{S}| \equiv \langle 0 | e^a$, a special case of the *Glauber state* $\langle \alpha \mathcal{S} | \equiv \langle 0 | e^{\alpha a}$ (itself an eigenvector of the operator a^* with eigenvalue α).

The *norm* of any *right-hand* state $|\Phi\rangle$ is defined in terms of $(\mathcal{S}|$ by the inner product $(\mathcal{S}|\Phi\rangle$. A normalized state $|\Phi\rangle$ satisfies $(\mathcal{S}|\Phi\rangle = 1$. Given that $(\mathcal{S}|a^{*n} = (\mathcal{S}|$ for all $n \geq 0$, and $(\mathcal{S}|0\rangle = 1$, each of the *right-hand* basis states $(a^*)^n |0\rangle$ is normalized in this fashion—*i.e.*, $(\mathcal{S}|a^{*n} |0\rangle = 1$ for any $n \geq 0$.

Because the probabilities remain normalized at all $t \geq 0$ if the equations of motion conserve probability (and they always do), the state vector $|\Psi(t)\rangle$ remains normalized at all $t \geq 0$. The proof:

$$(\mathcal{S}|\Psi(t)\rangle \equiv \sum_n P(n|t) (\mathcal{S}|(a^*)^n |0\rangle = \sum_n P(n|t) = 1. \quad (1.5)$$

Expectation values are computed as in the following example. Let us evaluate the average number remaining at any given time $t > 0$. With a^*a defined as the number operator, we use Eqs. (1.3) and (1.4):

$$(\mathcal{S}|a^*a|\Psi(t)\rangle \equiv \sum_n n P(n|t) \equiv \langle n \rangle. \quad (1.6)$$

In general,

$$(\mathcal{S}|F(a^*a)|\Psi(t)\rangle \equiv \sum_n F(n) P(n|t) \equiv \langle F \rangle(t). \quad (1.7)$$

Amusingly, by Eq. (1.3), the average of a alone also yields $\langle n \rangle$. But, although a^*a and a have identical expectation values, higher powers of these operators do not. For on the one hand,

$$(\mathcal{S}|(a^*a)^2|\Psi(t)\rangle = \sum_n n^2 P(n|t) = \langle n^2 \rangle,$$

while on the other, the expectation value of a^2 is

$$(\mathcal{S}|a^2|\Psi(t)\rangle = \sum_n n(n-1) P(n|t) = \langle n(n-1) \rangle.$$

Thus it is $(a^*a)^2$ and $a^2 + a$ which here have identical expectation values.

The state vector $|\Psi(t)\rangle$ has all the attributes of a *generating function*. First, it satisfies an elementary differential equation equivalent to Eq. (1.2) (albeit simpler than that satisfied by the individual P 's). Second, it yields the individual $P(n|t)$ by projection onto $1/n! \langle 0 | a^n$. Third, it

³Hence, for most purposes, a can be represented by $\partial/\partial a^*$.

can be used to obtain the various moments, through contractions with $(S|$. The equation in question, in operator language, is

$$\partial_t |\Psi(t)\rangle = \frac{-1}{\tau} \Omega |\Psi(t)\rangle, \quad (1.8)$$

in which $\Omega = a^*a - a$, the dimensionless rate operator for this process, is sometimes referred to as the “quantum Hamiltonian” of the model.⁴ The solution is, straightforwardly,

$$|\Psi(t)\rangle = e^{-t/\tau \Omega} |\Psi(0)\rangle = e^{-t/\tau \Omega} (a^*)^N |0\rangle. \quad (1.9)$$

The right-hand side reflects the chosen, particular, initial condition that at $t=0$ there are precisely N undecayed nuclei.

Next, we take advantage of identities (1) and (2) in Eq. (1.3) to evaluate the average of any arbitrary quantity $F(a, a^*)$ assuming an arbitrary, normalized initial state $\Phi(a^*)|0\rangle = \sum_0^\infty P(n|0) (a^*)^n |0\rangle$:

$$\begin{aligned} \langle F \rangle(t) &= \langle 0 | e^a F(a, a^*) e^{t/\tau (a - a^*a)} \Phi(a^*) |0\rangle \\ &= \langle 0 | F(a, a^*+1) \Phi(a^* e^{-t/\tau} + 1) |0\rangle. \end{aligned} \quad (1.10)$$

For $F =$ either a or a^*a and $\Phi(a^*) = a^{*N}$, Eq. (1.10) yields—by inspection— $n(t) = Ne^{-t/\tau}$. For $F = (a^*a)^2$ with the same Φ , it yields $N(N-1)e^{-2t/\tau} + Ne^{-t/\tau}$. Both results were anticipated in Eq. (1.1).

But consider a different set of initial conditions. While the initial results differ from those above, we shall observe that the asymptotic behavior is unchanged.

B. Effects of initial conditions

Had we set $\Phi(a^*) = e^{N(a^*-1)}$, i.e., had we started with a Poisson distribution peaked at N , the very same calculus would have led us to the following results: $n(t) = Ne^{-t/\tau}$ and $\sigma^2(t) \equiv \langle n^2 \rangle - \langle n \rangle^2 = Ne^{-t/\tau} = n(t)$. The average number is the same function as before, although, at small t , the fluctuations here exceed those we found in the original result (1.1). However, after a time $O(\tau)$ the initial conditions are all “forgotten” and, asymptotically, the two sets of results merge precisely. In more marginal examples, near a critical point (phase transition), initial conditions may play a pivotal role in the asymptotic densities and reaction rates (Cornell, 1992) and may determine such features as whether the species segregate or aggregate in time or whether the mix becomes homogeneous.

The choice of initial conditions is subject only to the twin requirements of normalization and positiveness, the latter ensuring that none of the initial probabilities $P(n|0)$ will be negative. It is not sufficient that some

initial state $|\Psi_A(0)\rangle$ be normalized for an arbitrary parameter A if *even one* of the coefficients in the power-series expansion of $|\Psi_A(0)\rangle$ in powers of a^* is negative, as each coefficient is a $P(n|0)$ and is, by definition, non-negative. As an example of an unacceptable choice of initial state consider $\{1 + \sin A(a^*-1)\}|0\rangle$, which is normalized but obviously fails the non-negative test.⁵ Conversely, any state that satisfies both conditions at $t=0$ will continue to do so at all future times.

C. One-way, one-species, two-body reaction in $d=0$

We return to Eq. (0.1) of the Introduction, in which a unidirectional process eliminates particles one pair at a time. Let there be just a single species, any member of which can annihilate irreversibly with any other, with rate constant $1/\tau$. Initially there are N such particles. The master equation describing this process is

$$\begin{aligned} dP(n|t) &= -\frac{dt}{2N\tau} \{n(n-1)P(n|t) \\ &\quad - (n+2)(n+1)P(n+2|t)\}, \end{aligned} \quad (1.11)$$

subject to initial conditions $\sum P(n|0) = 1$ and $\sum nP(n|0) = N$. The norm $\sum P(n|t) = 1$ is conserved at $t > 0$; we are mainly interested in $\langle n \rangle \equiv N\rho(t)$, subject to the initial condition $\rho(0) = 1$. As the reaction is all consuming, clearly $\rho(\infty) = 0$. Turning to the QFT expression and the harmonic-oscillator raising/lowering operators, one rewrites the master equation (1.11) in the form

$$\partial_t |\Psi(t)\rangle = \frac{-1}{2N\tau} \Omega |\Psi(t)\rangle, \quad (1.12)$$

with $\Omega = \{a^{*2}a^2 - a^2\}$ reproducing the effects of the curly bracket in Eq. (1.11).

Formally, Eq. (1.12) has the solution $|\Psi(t)\rangle = e^{-t/(2N\tau)\Omega} |\Psi(0)\rangle$ once again. With initial state $|\Psi(0)\rangle = e^{N(a^*-1)}|0\rangle$ and the reference state $(S| \equiv \langle 0|e^a$, again $(S|\Psi(t)\rangle = 1$ at all $t > 0$. Next we seek to compute $(S|a/N|\Psi(t)\rangle \equiv \rho(t)$. The rescaling transformation (3) of Eq. (1.3) $a \rightarrow aN$ and $a^* \rightarrow a^*/N$ makes it possible to simplify the expression for ρ ,

$$\begin{aligned} \rho(t) &= \left\langle 0 \left| a \left\{ \exp \frac{-t}{2\tau} \left(2a^*a^2 + \frac{a^{*2}a^2}{N} \right) \right\} e^{a^*} \right| 0 \right\rangle \\ &\Rightarrow \left\langle 0 \left| a \left\{ \exp \frac{-ta^*a^2}{\tau} \right\} e^{a^*} \right| 0 \right\rangle, \end{aligned}$$

by eliminating the quartic term $\propto a^{*2}a^2/N$ in the thermodynamic limit $N \rightarrow \infty$. We can then evaluate $\rho(t)$ as a

⁴Because, unlike the Hamiltonian, Ω is not generally Hermitian, we avoid this terminology here.

⁵Although physically meaningless, such deviant states may occasionally prove useful in the mathematics, e.g., in analyzing the phase space of initial conditions.

power series in t , which sums to the following simple inverse-power-law behavior:⁶

$$\rho(t) = \sum_{p=1}^{\infty} \frac{1}{p!(p-1)!} \left(\frac{-t}{\tau}\right)^{p-1} c_p,$$

where

$$c_p = \langle 0 | a(a^*a^2)^{p-1}a^* | 0 \rangle = p!(p-1)!,$$

i.e.,

$$\rho(t) = \frac{\tau}{t + \tau}. \tag{1.13}$$

D. Finite dimensions: Creation and annihilation processes

In finite dimensions the annihilation process characterized by a rate $1/\tau$ can be on site or it can involve nearest neighbors, next-nearest neighbors, etc. This process competes with generation processes parametrized by a rate g . Here we consider examples for a single species with purely on-site processes.

- (1) One-body decay ($A \rightarrow \emptyset$): $\sum_i 1/\tau_i \{a_i^* a_i - a_i\}$, allowing for different decay rates on different sites, as in Sec. I.A above. The “scavenger” operators are $\{a_i^* a_i - a_i\}$.
- (2) Two-body same-species decay ($A + A \rightarrow \emptyset$): $\sum_i 1/2\tau_i \{a_i^{*2} a_i^2 - a_i^2\}$, as in Sec. I.C above.
- (3) Aggregation: same-species coalescence or coagulation ($A + A \rightarrow A$): $\sum_i 1/2\hat{\tau}_i \{a_i^{*2} a_i^2 - a_i^* a_i^2\}$
- (4) Spontaneous one-particle generation ($\emptyset \rightarrow A$): $\sum_i g_i \{1 - a_i^*\}$, and, finally,
- (5) Spontaneous pair-generation ($\emptyset \rightarrow A + A$): $\sum_i \tilde{g}_i \{1 - a_i^{*2}\}$.

Processes 4 and 5 are omitted in unidirectional reactions but are required for achieving a nontrivial steady state with nonzero concentration of the species. Owing to the different roles played by a and a^* , 4 and 5 are not, in any obvious sense, conjugate to processes 1 and 2, nor are they required to be present for microscopic reversibility.

Operators to simulate any other processes can be similarly constructed using the rules following Eq. (1.2) to ensure that the effect on $|\Psi\rangle$ is the same as the desired effect on P in the master equation. Numerous additional possibilities open up in the phase space of two or more species, as in the following example, for which we can find no closed-form solution.

E. Unsolved: A multispecies two-way reaction in $d=0$

Our third example concerns a bidirectional chemical reaction, again without spatial dependence. As we now include several interacting species, the equations and their solutions reflect more of a many-body character

⁶Amazingly, in this example a simple mean-field approximation also yields the correct power law, albeit with the wrong coefficient. The solution of $\partial_t \rho = -(1/2\tau)\rho^2$ is $\rho(t) = 2\tau/2\tau + t$ instead of Eq. (1.13).

than in the preceding section. That may be the reason we have not found it possible to reduce this problem to quadrature except in steady state.

Assume atom A and atom B combine to form a single molecule C with probability $1/\tau$ per unit time. By detailed balance, the product C can decompose back into A and B at a rate $1/\tau \times \exp(-\beta U)$ per unit time. This reaction is assumed to be exothermic, liberating a quantity of heat U into a heat bath maintained at a nominal temperature $T = 1/k\beta$. Although the master equation in this case has to keep track of three fields, the number of A 's, B 's, and C 's, these are simply related. Numbers are not conserved, but because two particles disappear whenever a C is created we can still write pseudo-number-conservation laws as below. We take as initial conditions

$$n_A = N_A, \quad n_B = N_B, \quad \text{and} \quad n_C = N_C. \tag{1.14}$$

Then

$$\begin{aligned} n_A &= N_A - n_C, \quad n_B = N_B - n_C, \\ n_A + n_B + 2n_C &= N(\text{constant}), \quad \text{and} \\ n_A - n_B &= N_A - N_B(\text{constant}). \end{aligned} \tag{1.15}$$

In the thermodynamic limit (i.e., $N \rightarrow \infty$), all the variables and the equation itself have to remain sensible—in the sense that the densities $\rho_\alpha(t) \equiv \langle n_\alpha \rangle / N$, with $\alpha = A, B$, or C , must approach well-defined limit functions independent of N . The rate equation (master equation) takes the form

$$\begin{aligned} dP(n_A, n_B, n_C | t) &= -\frac{dt}{\tau} \left\{ \left[\frac{n_A n_B}{N} + n_C e^{-\beta U} \right] P(n_A, n_B, n_C | t) \right. \\ &\quad - \left[\frac{(n_A + 1)(n_B + 1)}{N} P(n_A + 1, n_B + 1, n_C - 1 | t) \right. \\ &\quad \left. \left. + (n_C + 1) e^{-\beta U} P(n_A - 1, n_B - 1, n_C + 1 | t) \right] \right\}. \end{aligned} \tag{1.16}$$

If we rewrite this in terms of annihilation and creation operators acting on the probability state vector,

$$|\Psi(t)\rangle = \sum_{n,m,l} P(n,m,l|t) (a^*)^n (b^*)^m (c^*)^l |0\rangle,$$

it once again assumes the canonical form with dimensionless rate operator Ω given by a highly nonlinear expression:

$$\Omega = \left[\frac{a^* a b^* b}{N} + c^* c e^{-\beta U} \right] - \left[\frac{a b c^*}{N} + c a^* b^* e^{-\beta U} \right]. \tag{1.17}$$

Ω is extensive, i.e., proportional to N . The best way to see this is to consider the creation operators as $O(1)$ while the annihilation operators are $\propto N$. Operators $a^* a - b^* b = N_A - N_B$ and $a^* a + b^* b + 2c^* c = N$ commute with Ω , hence they are “constants of the motion.” It follows that a knowledge of $\langle n_C \rangle$ as a function of t

determines the quantities $\langle n_{A \text{ or } B} \rangle$ as well. We take advantage of this information explicitly, setting

$$\rho_A(t) = \langle n_A \rangle / N = \rho_A - f(t), \text{ where}$$

$$\rho_A = N_A / N; \quad \rho_B(t) = \rho_B - f(t) \quad \text{and}$$

$$\rho_C(t) = \rho_C + f(t).$$

Again, we attempt to solve directly for the expectation value $f(t)$ rather than for the P 's. In particular, we shall calculate

$$\rho_C(t) = \frac{1}{N} \langle n_C \rangle = \frac{1}{N} \langle 0 | e^{a+b+c} c e^{-t/\tau \Omega} | \Psi(0) \rangle. \tag{1.18}$$

Note that the generalization of the reference state to three particle fields is just $\langle S | \equiv \langle 0 | e^{a+b+c}$.

A judicious choice of a Glauber or multi-Poisson initial distribution helps with the calculation—without in any way affecting the asymptotic behavior:

$$| \Psi(0) \rangle = e^{N_A(a^*-1) + N_B(b^*-1) + N_C(c^*-1)} | 0 \rangle. \tag{1.19}$$

This distribution evolves more smoothly than does an initial delta-function distribution. The scaling transformations $a, b, c \rightarrow aN, bN, cN$ and $a^*, b^*, c^* \rightarrow a^*/N, b^*/N, c^*/N$ simplify the subsequent expressions while preserving the definition of the vacuum:

$$\begin{aligned} f(t) &= \langle 0 | e^{N(a+b+c)} (c - \rho_C) e^{-t/\tau \Omega'} \\ &\quad \times e^{N_A(a^*/N-1) + N_B(b^*/N-1) + N_C(c^*/N-1)} | 0 \rangle \\ &= \langle 0 | \hat{c}(t) | 0 \rangle = - \langle 0 | \hat{a}(t) | 0 \rangle \\ &= - \langle 0 | \hat{b}(t) | 0 \rangle, \text{ where } \hat{c}(t) \equiv e^{t\hat{\Omega}/\tau} c e^{-t\hat{\Omega}/\tau}, \text{ etc.} \end{aligned} \tag{1.20}$$

The operator Ω' stands for the transformed Ω of Eq. (1.17) after the rescaling transformation. $\hat{\Omega}$ is the transform of Ω' (it is the result of commuting the exponential factor in a, b, c , all the way to the right, and the exponential in a^*, b^* and c^* all the way to the left), and contains terms up to fourth power in the field amplitudes. Explicitly,

$$\begin{aligned} \hat{\Omega} &= \left[a^* + b^* + \frac{a^* b^*}{N} - c^* \right] \\ &\quad \times [\kappa + (a\rho_B + b\rho_A - c e^{-\beta U}) + ab]. \end{aligned} \tag{1.21}$$

The terms in $1/N$ vanish in the thermodynamic limit; $\hat{\Omega}$ is now cubic in field operators—just as it was in the preceding example. We have defined $\kappa \equiv \rho_A \rho_B - \rho_C e^{-\beta U}$ as a lumped “control parameter,” which is positive or negative according to the initial conditions. (Note: if κ is zero, the model is trivially solved, as $f = \langle 0 | \hat{c} | 0 \rangle \rightarrow 0$ by inspection. Physically, this corresponds to an initial steady-state configuration.)

In the thermodynamic limit, the three linearly independent operators, $a + b + 2c$, $a - b$, and $a + c$, all commute with Eq. (1.21) and are therefore constants of the motion, as previously noted. Differentiating Eq. (1.20) with respect to t yields

$$\partial_t f(t) = \frac{1}{\tau} \{ \kappa - (\rho_A + \rho_B + e^{-\beta U}) f(t) + \langle 0 | \hat{a} \hat{b} | 0 \rangle \}. \tag{1.22}$$

Because of the nonlinear term $\langle 0 | \hat{a} \hat{b} | 0 \rangle$, this equation does not appear too promising. If we just ignore the nonlinear term, the solution of Eq. (1.22) is, straightforwardly,

$$f(t) = \frac{\kappa}{\gamma} (1 - e^{-\gamma t/\tau}) \quad \text{and} \quad f(\infty) = \frac{\kappa}{\gamma}, \tag{1.23}$$

with γ denoting a second control parameter ($\rho_A + \rho_B + e^{-\beta U}$). If $|\kappa|$ is not negligible, one might be tempted to replace $\langle 0 | \hat{a} \hat{b} | 0 \rangle$ by its decoupled value, $f^2(t)$, which again allows Eq. (1.22) to be solved in closed form. (This is left as an exercise for the reader.) Nevertheless, at sufficiently large $|\kappa|$, the resulting solution becomes oscillatory and is therefore, in all likelihood, physically unacceptable.

In the preceding model of Eq. (1.12), the density decay satisfied a power law in τ/t and there were no free parameters. In the present instance, the parameter space consists of the half plane (γ, κ) , some regions of which may correspond to exponential decay of concentrations and others to power laws or other behavior. These distinct areas would be separated by phase boundaries (critical lines), which might or might not end in critical or tricritical points. The full richness of this model remains to be explored, together with the tantalizing possibility of solving it exactly.

II. DIFFUSION

In all dimensions $d \geq 1$, it is diffusion (alias Brownian motion) that brings the reactants into contact and nourishes the reactions.⁷ Let us first consider the example of a single entity (particle, vacancy, or whatever) diffusing on the N vertices of a space lattice. For simplicity, we restrict random hopping from any given point \mathbf{R} to just its immediate nearest neighbors, situated at $\mathbf{R} + \delta$. Given $P(\mathbf{R}|t)$ as the probability that \mathbf{R} is occupied at time t , the diffusion equation takes the form

$$\begin{aligned} \partial_t P(\mathbf{R}|t) &= - \mathcal{D} \sum_{\delta} \{ P(\mathbf{R}|t) - P(\mathbf{R} + \delta|t) \} \\ &= - \mathcal{D} \sum_{\delta} \{ 1 - e^{\delta \cdot \partial / \partial \mathbf{R}} \} P(\mathbf{R}|t). \end{aligned} \tag{2.1}$$

⁷In this paper we do not discuss the other transport mechanism: ballistic motion, although this could also be handled by extending the present method slightly.

Here the right-hand side follows from a Taylor-series expansion in δ and is familiar in condensed-matter physics.⁸ The special solution to this equation, which is subject to an initial condition $P(\mathbf{R}|t) = \delta(\mathbf{R} - \mathbf{R}_0)$ at $t = 0$,⁹ is commonly denoted the diffusion Green's function or propagator $G(\mathbf{R} - \mathbf{R}_0|t\mathcal{D})$.¹⁰ If $Q(\mathbf{R}_0)$ is the probability of the particle's being initially at \mathbf{R}_0 , the general solution of Eq. (2.1) is just

$$P(\mathbf{R}|t) = \sum_{\mathbf{R}_0} G(\mathbf{R} - \mathbf{R}_0|t\mathcal{D})Q(\mathbf{R}_0).$$

The dispersion relation is found by solving Eq. (2.1) using a plane wave, i.e., $\exp(-\omega t + ik \cdot \mathbf{R})$,

$$\omega(\mathbf{k}) = \sum_{\delta} (1 - e^{ik \cdot \delta}). \quad (2.2)$$

On hypercubic lattices in d dimensions (the linear chain in 1D, square in 2D, simple cubic in 3D, etc.), the vertices (lattice points) are at $\mathbf{r} = a(n_1, n_2, \dots, n_d)$ where the n 's are integers and the dispersion $\omega(\mathbf{k})$ is separable, i.e., $\omega(\mathbf{k}) = \sum_{j=1}^d \omega(k_j)$, with $\omega(k_j) = 4 \sin^2(k_j a/2)$ on the j th axis.

At long wavelengths, $ka \rightarrow 0$, $\omega(\mathbf{k}) \approx k^2 a^2$, where a is the lattice parameter. In our units, \mathcal{D} has dimensions sec^{-1} . Because the conventional (continuum) diffusion parameter $D \propto a^2$, one recovers the continuum limit by identifying \mathcal{D} with D/a^2 throughout and proceeding to the limit $a \rightarrow 0$.

To construct the hypercubic lattice Green's function at the point $\mathbf{r} = \mathbf{R} - \mathbf{R}_0$, one just sums over all admissible plane waves with the k 's restricted to the first Brillouin zone (BZ) of the lattice. This ensures that G reduces to a Kronecker delta function at $t = 0$. In the large- N limit, the sum over k 's can be replaced by an integral. Recalling the definition of the Bessel function of imaginary argument, $I_n(z)$, one can express G on the hypercubic (linear chain, square, or simple cubic) lattices using just these functions:

$$\begin{aligned} G(\mathbf{R}|t\mathcal{D}) &= \frac{1}{N} \sum_{\mathbf{k} \in \text{BZ}} e^{(i\mathbf{k} \cdot \mathbf{r} - t\mathcal{D}\omega(\mathbf{k}))} \\ &= \prod_{j=1}^d \frac{a}{2\pi} \oint dk_j \cos k_j n_j e^{-t\mathcal{D}\omega(k_j)} \\ &= e^{-2t\mathcal{D}d} \prod_{j=1}^d I_{n_j}(2t\mathcal{D}). \end{aligned} \quad (2.3)$$

At large R and t , Eq. (2.3) smoothly reduces to the familiar $(4\pi t\mathcal{D})^{-d/2} (\exp-(R^2/4t\mathcal{D}a^2))$.

Clearly the probability distribution of a particle within a radius $R \propto \sqrt{t}$ from the origin is $O(t^{-d/2})$, from which it might be inferred that, ultimately, particle density de-

cays as $t^{-d/2}$ owing to various causes such as recombination, etc. But this is not the case. For particles decaying into random "traps," the surviving density decays as a "stretched exponential" (Montroll and Weiss, 1965; Balagurov and Vaks, 1973; Eisenberg, Havlin, and Weiss, 1994). In the interesting case of particle-antiparticle recombination, the correct answer in $d \leq 4$ dimensions, when there are equal numbers of both species, is $t^{-d/4}$ (because, as time progresses, each particle has to diffuse a greater distance to find a partner with which to recombine). Although this exponent, $d/4$, has been verified numerically (Toussaint and Wilczek, 1983) and proved analytically by means of upper and lower bounds (Bramson and Lebowitz, 1988, 1991a, 1991b), no explicit solution of the master equation governing diffusion-limited recombination in arbitrary d has been exhibited in the published literature to date. The example that is discussed explicitly in the present work should prove helpful in this regard.

Note that the one-body diffusion Green's function is directly generalizable to many-body diffusion. For example, in the case of one particle of each of two diffusing species, the two-body Green's function is given by

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'|t\mathcal{D}_1, t\mathcal{D}_2) \\ = \frac{1}{N^2} \sum_{\mathbf{k}, \mathbf{k}' \in \text{BZ}} e^{[i\mathbf{k} \cdot \mathbf{r} + i\mathbf{k}' \cdot \mathbf{r}' - t(\mathcal{D}_1\omega(\mathbf{k}) + \mathcal{D}_2\omega(\mathbf{k}'))]}, \end{aligned}$$

which is just the product of the two respective one-body Green's functions. (Alternatively, this expression is a one-body Green's function on a two-dimensional lattice.) The Green's functions for $n > 2$ particles can be obtained from this, by induction, as higher products of n one-body Green's functions.

A. Two obvious properties of diffusion Green's functions

(i) The Green's functions are normalized, i.e., $\sum_{\mathbf{R}} G(\mathbf{R}|t\mathcal{D}) = 1$, at all $t \geq 0$. Using the Kronecker lattice delta function,

$$\frac{1}{N} \sum_{\mathbf{k} \in \text{BZ}} e^{i\mathbf{k} \cdot \mathbf{R}} = \begin{cases} 1 & \text{for } \mathbf{R} = 0 \\ 0 & \text{for } \mathbf{R} \neq 0. \end{cases}$$

(ii) They satisfy the convolution property:

$$\begin{aligned} \sum_{\mathbf{R}} G(\mathbf{R}_0 - \mathbf{R}'|t_1\mathcal{D}_\alpha) G(\mathbf{R}' - \mathbf{R}_2|t_2\mathcal{D}_\beta) \\ = G(\mathbf{R}_0 - \mathbf{R}_2|t_1\mathcal{D}_\alpha + t_2\mathcal{D}_\beta). \end{aligned}$$

B. Pure diffusion

The field-theoretic expression for the dimensionless operator part of the right-hand side of Eq. (2.1) is the Hermitian operator,

$$\begin{aligned} \Omega &= \sum_{\mathbf{R}} \sum_{\delta} \{a_{\mathbf{R}}^* a_{\mathbf{R}} - a_{\mathbf{R}+\delta}^* a_{\mathbf{R}}\} \\ &= \sum_{\mathbf{R}} \sum_{\delta} (a_{\mathbf{R}}^* - a_{\mathbf{R}+\delta}^*) a_{\mathbf{R}}, \end{aligned}$$

⁸I.e., for any function $f(x)$, $f(x+a) \equiv e^{a\partial/\partial x} f(x)$.

⁹This is the same as requiring, with unit probability, that the particle start out at a specified \mathbf{R}_0 .

¹⁰Anticipating that different species have different diffusion coefficients, we exhibit \mathcal{D} explicitly at every stage.

which graphically expresses the ‘‘hopping’’ of a particle from \mathbf{R} to $\mathbf{R} + \delta$. Diagonal terms in $a_R^* a_R$ are included to ensure that the eigenvalues coincide with the $\omega(\mathbf{k})$'s.

In the absence of reactions, diffusion of particles belonging to $Q \geq 1$ species labeled $s = 1, 2, \dots, Q$ would be the only process affecting the P 's or the state vector $|\Psi\rangle$. In that case,

$$\partial_t |\Psi(t)\rangle = - \sum_{s=1}^Q \mathcal{D}_s \Omega_s |\Psi(t)\rangle \quad (2.4)$$

is the master equation, having the explicit solution

$$|\Psi(t)\rangle = e^{-t \sum_s \mathcal{D}_s \Omega_s} |\Psi(0)\rangle, \quad (2.5)$$

one which, by translational invariance, is best examined in the plane-wave representation. It is useful to Fourier-transform the ‘‘local’’ operators as follows:

$$a(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} \alpha(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}}. \quad \text{The inverse:}$$

$$\alpha(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} a(\mathbf{R}) e^{-i\mathbf{k} \cdot \mathbf{R}}. \quad (2.6)$$

and similarly for the a^* and α^* operators. Upon introducing the number operators $\tilde{n}(k) \equiv \alpha^*(k) \alpha(k)$ for plane-wave states, one finds each Ω is diagonal, i.e., $\Omega_\alpha = \sum_{\mathbf{k}} \omega(\mathbf{k}) \tilde{n}_\alpha(\mathbf{k})$, the only implied assumption for notational convenience being that the dispersion $\omega(k)$ is the same for all the species. It is trivial to generalize to the case of two or more dispersion laws.¹¹

The operator version of the multispecies, many-body diffusion Green's function is the state vector, which evolves after time t from a given initial-state vector in which it is specified that the j th particle of the s th species is located at a given site $R_{0,j,s}$. We write the initial state as $|\mathbf{G}(0)\rangle$, expressed in either of two equivalent forms:

$$|\mathbf{G}(0)\rangle = \prod_{s,j} a_s^*(R_{0,j,s}) |0\rangle$$

$$= \prod_{s,j} \left\{ \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-\mathbf{k} \cdot \mathbf{R}_{0,j,s}} \alpha_s^*(\mathbf{k}) \right\} |0\rangle. \quad (2.7)$$

We use Eq. (2.5), noting that $e^{-Xn(\mathbf{k})} \alpha^*(\mathbf{k}) e^{Xn(\mathbf{k})} e^{-Xn(\mathbf{k})} |0\rangle = e^{-X} \alpha^*(\mathbf{k}) |0\rangle$ (with $X = t\mathcal{D}\omega$), then Fourier transform back to localized operators. Using the original definition of the one-body Green's functions, we obtain

$$|\mathbf{G}(t)\rangle = \prod_{s,j} \left\{ \sum_{\mathbf{R}_j} G(\mathbf{R}_j - \mathbf{R}_{0,j,s} | t\mathcal{D}_s) a_s^*(\mathbf{R}_j) \right\} |0\rangle. \quad (2.8)$$

The norm of this multiparticle wave operator is calculated using $\langle \mathcal{S} | = \langle 0 | \exp\{\sum \alpha_s(\mathbf{R})\}$, in which the sums are

¹¹This might be required in special cases, such as those of vacancies and interstitials, which ‘‘live’’ on conjugate lattices with possibly different coordination numbers.

over all sites \mathbf{R} and species s . [Equivalently, we could have defined $\langle \mathcal{S} | = \langle 0 | \exp\{\sqrt{N} \sum_s \alpha_s(0)\}$, with the sum just spanning the species labels s but restricted to $k=0$.] Then,

$$\langle \mathcal{S} | \mathbf{G}(t) \rangle = \prod_{s,j} \left\{ \sum_{\mathbf{R}_j} G(\mathbf{R}_j - \mathbf{R}_{0,j,s} | t\mathcal{D}_s) \right\} = 1. \quad (2.9)$$

In proving that the many-body Green's function is properly normalized, one uses the first property of the one-body diffusion Green's function, namely, that it is normalized, which ensures that each curly bracket in the product (2.9) is normalized to precisely 1.

C. Rapid diffusion, slow reaction

Let us now consider examples in which the reactions are so slow that the state vector, at times that are not too long, is essentially determined by diffusion alone—a state of affairs which might properly be called ‘‘reaction-limited diffusion.’’ Let us further suppose that when a particle of species α hops onto the same site as a particle of species β there is a probability per unit time $1/\tau_{\alpha\beta}$ of a reaction that eliminates both particles from the system. Such a model lends itself to a perturbation-theoretic treatment in which one approximates the true eigenstates by those of the diffusion operator and treats the reactions to leading order only.

To lowest nontrivial order in $1/\tau$, the rate of disappearance w of α particles is given by $w_\alpha \equiv \sum_{j,\beta} 1/\tau_{\alpha\beta} \langle n_\alpha(\mathbf{R}_j) n_\beta(\mathbf{R}_j) \rangle$, with the state vector given in Eq. (2.8) used to compute the average. Thus

$$-\partial_t \sum_{\mathbf{R}} n_\alpha(\mathbf{R}) \equiv w_\alpha(t)$$

$$= \sum_{i,\beta} 1/\tau_{\alpha,\beta} \langle \mathcal{S} | n_\alpha(R_i) n_\beta(R_i) | \mathbf{G}(t) \rangle$$

$$= \sum_{i,\beta} 1/\tau_{\alpha,\beta} \sum_{j_1} \sum_{j_2} G(\mathbf{R}_{ij_1} | t\mathcal{D}_\alpha)$$

$$\times G(\mathbf{R}_{ij_2} | t\mathcal{D}_\beta) n_\alpha^o(\mathbf{R}_{j_1}) n_\beta^o(\mathbf{R}_{j_2}), \quad (2.10a)$$

in which the superscript o indicates the initial occupation number of each site, at $t=0$. Fourier decomposition affords considerable simplification. Defining the Fourier densities as

$$\rho(\mathbf{q}) = \frac{1}{N} \sum_j n(\mathbf{R}_j) e^{i\mathbf{q} \cdot \mathbf{R}_j}$$

and making use of the definitions at the beginning of Sec. V, we write for the reaction rate in the first Born approximation

$$w_\alpha(t) = \sum_{\beta} 1/\tau_{\alpha,\beta} \sum_{\mathbf{q}} \rho_\alpha^o(\mathbf{q}) \rho_\beta^o(-\mathbf{q}) e^{-t\omega(\mathbf{q})(\mathcal{D}_\alpha + \mathcal{D}_\beta)}, \quad (2.10b)$$

where the superscript o again indicates initial values of the particle densities. It is tempting to dismiss all terms with $q \neq 0$ when $t \rightarrow \infty$, recovering an equation essentially identical to Eq. (0.1), the argument being that the $q \neq 0$ components decay exponentially as all $\mathcal{D}\omega(q) > 0$, while the $q = 0$ component decays only as a power of $1/t$. This is the mean-field result, but it is wrong because ω is a continuous function of q .

Toussaint and Wilczek (1983) were first to point out that the interdependence of the $q = 0$ and $q \neq 0$ components [of which there are $O(N)$] subtly affects the power-law decay of $\rho(0)$. Assuming the fluctuations to be normally distributed, they inferred the correct asymptotic laws for the decay of the ρ_α 's and confirmed these results through their own numerical experiments on a binary system.

Indeed, if the products $\rho_\alpha(q)\rho_\beta(-q)$ are independent of q , the integral in Eq. (2.10b) trivially yields an asymptotic time dependence, $w_\alpha(t) \propto t^{-d/2}$ in d dimensions. As w is also proportional to $\rho\rho$, one might then infer an asymptotic time dependence $\rho(t) \rightarrow t^{-d/4}$ for the densities.

While this is the correct inference for all $d \leq 4$, this "derivation" is not only sketchy, but also patently untrustworthy—since asymptotically $|\Psi(t)\rangle$ cannot be accurately approximated by $|\mathbf{G}(t)\rangle$, however close the two may have been at $t = 0$.

As we shall see, the QFT approach provides us with the systematic formalism required for establishing exact or reliable results in this and other models through the use of the exact $|\Psi(t)\rangle$ or physically satisfactory approximations thereto. In Sec. II.E we develop the theory relying entirely on simple examples. In the first of these we shall consider two physical or chemical processes: the generation of particles at \mathbf{R}_i at a rate g and their demise at \mathbf{R}_j at a rate $1/\tau$. Once again a first-order time-dependent equation has to be solved:

$$\partial_t |\Psi(t)\rangle = -[\mathcal{D}\Omega - \Gamma] |\Psi(t)\rangle \equiv -[H_0 - \Gamma] |\Psi(t)\rangle, \quad (2.11)$$

in which $H_0 = \mathcal{D}\Omega$. Here $\Gamma = \Gamma_1 + \Gamma_2$ treats the one-body birth and death process at \mathbf{R}_1 and \mathbf{R}_2 ,

$$\Gamma_1 = \sum_i g_i \{a^*(\mathbf{R}_i) - 1\} \quad \text{and} \\ \Gamma_2 = - \sum_j \frac{1}{\tau_j} [a^*(\mathbf{R}_j)a(\mathbf{R}_j) - a(\mathbf{R}_j)]. \quad (2.12)$$

If τ_j is finite on some sites and ∞ on others, the sites on which it is finite are denoted "scavenger" sites and Γ_2 the scavenging operator. What makes this process simple is the form of the operator, quadratic and exactly diagonalizable. The many-body problem then factors into sectors labeled by the eigenvectors of $H_0 - \Gamma$. There have been many studies in which the g 's and τ 's are assumed to be randomly distributed. Exact results can be found insofar as the eigenvalue spectra of the random matrix are known (see Mehta, 1967). Below we illustrate with a relatively simple special case. However, prior to doing so, it may be helpful to develop a minimal amount

of formalism, which becomes essential in the case of more general two- and three-body reactions.

D. A little bit of formalism, including time ordering

A special formalism based on "time ordering" is required once Γ contains terms cubic or quartic in the field operators, such that the eigenvalue spectrum of the diffusion-reaction operator $H_0 - \Gamma$ cannot be obtained by straightforward diagonalization. We turn our attention to this procedure and develop some elementary formalism before returning to the example at hand. The solution of the generic master equation can be obtained either by straightforward integration or, alternatively, by use of time ordering (symbol, T). This is a mathematically exact and useful way of exfoliating an exponential form of two operators that do not commute, into the product of an exponential in one of the operators and a quasiexponential series in the other. Thus we can have as the solution either

$$|\Psi(t)\rangle = e^{-[H_0 - \Gamma]t} |\Psi(0)\rangle,$$

or

$$= e^{-tH_0} \mathbf{T}\{e^{\int_0^t dt' \Gamma(t')}\} |\Psi(0)\rangle. \quad (2.13)$$

The two expressions are equal regardless of the initial state $|\Psi(0)\rangle$, because the two operators are identical. While there are different ways of separating the exponentials of noncommuting operators, such as the Baker-Hausdorff expansion, the Trotter formula, etc., all of which have proved useful in some application or other, only the time-ordering procedure leads directly to the formalism of many-body perturbation theory. Symbols have the following meanings:

$$\Gamma(t) = e^{tH_0} \Gamma e^{-tH_0}, \quad \text{hence } \Gamma(0) = \Gamma;$$

$$\mathbf{T}\{e^{\int_0^t dt' \Gamma(t')}\} \equiv 1 + \int_0^t dt' \Gamma(t') \\ + \int_0^t dt' \Gamma(t') \int_0^{t'} dt'' \Gamma(t'') \\ + \int_0^t dt' \Gamma(t') \int_0^{t'} dt'' \Gamma(t'') \\ \times \int_0^{t''} dt''' \Gamma(t''') + \dots \quad (2.14)$$

This time-ordered expansion is defined with the latest operators to the left. Clearly, the decomposition into "unperturbed" and "perturbation" operators is never unique, and it is possible to reappportion them, creating different versions of H_0 and Γ . For instance, in the example below, it will be convenient to associate the quadratic form Γ_2 with H_0 in the solution of Eqs. (2.11) and (2.12) and treat Γ_1 as the perturbation.

But more often it is better to retain in H_0 all terms that are quadratic and/or linear in the field operators and assign higher-order terms to be expanded as in Eq. (2.14). Once the choice of H_0 is made, the time depen-

dence of each operator is known explicitly, and the expansion (2.14) can then be evaluated diagrammatically using Feynman graphs and rules for convoluting the time integrations. The procedure closely follows, *mutatis mutandis*, the exposition and formalism found in numerous standard texts on QFT. An explicit extension of QFT to finite temperature is also available (see Takahashi and Umezawa, 1996). In an attempt to keep this article more or less self-contained, as well as for the benefit of those readers who are unfamiliar with QFT, we now briefly recapitulate the essence of the formalism.

Assume an initial state with $N_0 \equiv \lambda N$ particles, diffusion, and some sort of reaction mechanism denoted Γ . Suppose it is required to calculate a quantity Q for which the operator is \mathbf{Q} . If Q is the total number, the operator \mathbf{Q} can be $\sum a_i^*$ or, simply, $\sum a_i$ [see discussion following Eq. (1.7)]. The expectation value $Q(t)$ is then given by

$$\begin{aligned} Q(t) &= \langle 0 | e^{\sum_j a_j} \mathbf{Q} e^{-tH_0} \mathbf{T} \{ e^{\int_0^t dt' \Gamma(t')} \} e^{\lambda \sum_j (a_j^* - 1)} | 0 \rangle \\ &= \langle 0 | \mathbf{T} \{ e^{\sum_j a_j(t)} \mathbf{Q}(t) e^{\int_0^t dt' \Gamma(t')} \} e^{\lambda \sum_j [a_j^*(0) - 1]} | 0 \rangle. \end{aligned} \tag{2.15}$$

Typically, the quantity Q we wish to compute is the number of particles, $N(t)$:

$$\begin{aligned} N(t) &= \left\langle 0 \left| \mathbf{T} \left\{ e^{\sum_j a_j(t)} \sum_j a_j(t) e^{\int_0^t dt' \Gamma(t')} \right\} e^{\lambda \sum_j [a_j^*(0) - 1]} \right| 0 \right\rangle \\ &= \left. \frac{\partial \log A(\alpha, t)}{\partial \alpha} \right|_{\alpha=0} \end{aligned}$$

in which $A(\alpha, t)$ is

$$A(\alpha, t) = \langle 0 | \mathbf{T} \{ e^{(1+\alpha)\sum_j a_j(t)} e^{\int_0^t dt' \Gamma(t')} \} e^{\lambda \sum_j [a_j^*(0) - 1]} | 0 \rangle. \tag{2.16a}$$

[To obtain the rate of reactions one would differentiate $\log A$ with respect to t instead. Note that $A(0, t) = 1$ by normalization.] In those instances in which the operators are translationally invariant, conservation of momentum k plays an important role. Moreover, if H_0 involves only the diffusion operator, both $\sum a_j$ and $\sum a_j^*$ commute with it, so that it becomes possible to express Eq. (2.16) as a single time-ordered exponential,

$$A(\alpha, t) = \langle 0 | \mathbf{T} \{ e^{\int_0^t dt' \tilde{\Gamma}(\alpha, \lambda, t')} \} | 0 \rangle \tag{2.16b}$$

where

$$\tilde{\Gamma}(\alpha, \lambda, t) = e^{-\lambda \sum_j a_j^*} e^{(1+\alpha)\sum_j a_j} \Gamma(t') e^{-(1+\alpha)\sum_j a_j} e^{\lambda \sum_j a_j^*}.$$

To evaluate this, one expands the exponentials and combines terms with equal numbers of creation and annihilation operators a^* and a [or, in the plane-wave representation of Eq. (2.6), equal numbers of α^* and α operators]. One such typical term is

$$\langle 0 | \mathbf{T} \{ \alpha(k_1, t_1) \cdots \alpha(k_n, t_n) \alpha^*(k'_1, t'_1) \cdots \alpha^*(k'_m, t'_m) \} | 0 \rangle. \tag{2.17}$$

By Wick's theorem this *vacuum expectation value* VEV equals the sum over all (nonvanishing) permutations of the pairings:

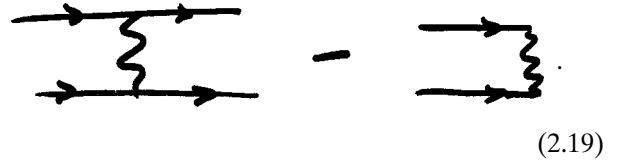
$$\begin{aligned} (2.17) \Rightarrow & \delta_{n,m} \sum_{\text{permut.}} \mathcal{P} \{ \langle 0 | \mathbf{T} \{ \alpha(k_1, t_1) \alpha^*(k_2, t_2) \} | 0 \rangle \cdots \\ & \times \langle 0 | \mathbf{T} \{ \alpha(k_n, t_n) \alpha^*(k_m, t_m) \} | 0 \rangle \} \end{aligned}$$

in which each factor, also a VEV, is called the “bare” propagator

$$\begin{aligned} & \langle 0 | \mathbf{T} \{ \alpha(k, t) \alpha^*(k', t') \} | 0 \rangle \\ & = \begin{cases} \delta_{k,k'} G_k(t-t') & \text{for } t \geq t' \\ 0 & \text{for } t < t'. \end{cases} \end{aligned} \tag{2.18}$$

When H_0 consists of just the diffusion operator, this results in the propagator's being $G_k(t) = \exp -t\mathcal{D}\omega(k)$, i.e., it is the spatial Fourier transform of the diffusion Green's function for $t \geq 0$, and zero otherwise. Its temporal Fourier transform $G(k, \omega) = [\mathcal{D}\omega(k) - i\omega]^{-1}$ is represented by a directed line labeled k . An interaction vertex associated with Γ is represented by a wiggly line.

In the example of two-body recombination $A + A \rightarrow \emptyset$, the “bare” Γ is $1/\tau \sum_i (a_i^{*2} - 1) a_i^2$, i.e.,



The expansion of $\log A$ involves only linked diagrams (those that cannot be separated into two or more distinct parts). As these contribute an amount that is rigorously $O(N)$ in each order of the perturbation expansion, in the thermodynamic limit $\log A$ is a regular, extensive, quantity. In Sec. II.F, where we solve this model in the low-density limit, we actually sum the entire series by solving the differential-integral equation that it satisfies.

At this point, the reader will have no trouble working out and summing the relevant expansion for the example of Eqs. (2.11) and (2.12), in the case when g and τ are independent of position. Therefore, for variety's sake, we illustrate with the algebraic solution to the same problem.

E. One-body generation and recombination

In the following simplified version of the example of Eqs. (2.11) and (2.12) we place a source of particles at the origin. These are subsequently scavenged, homogeneously, throughout the sample. The solution to this model can be considered as a Green's function for arbitrary distributions of sources $Q(\mathbf{R}_0)$ subject to homogeneous decay. (Exercise for the reader: the more general example, in which both sources and scavenging sites are distributed at random.)

In our example it is useful to absorb some of the interaction Γ_2 into H_0 . At time t the average occupation number at any \mathbf{R} is

$$\begin{aligned}
 \langle n(\mathbf{R}) \rangle &= \langle 0 | e^{\sum_{\mathbf{R}'} a(\mathbf{R}')} a(\mathbf{R}) e^{-t[\mathcal{D}\Omega + \Gamma_2]} e^{\int_0^t dt' \Gamma_1(t')} | 0 \rangle \\
 &= \left\langle 0 \left| \frac{1}{\sqrt{N}} \sum_{\mathbf{k}'} \alpha(\mathbf{k}') e^{i\mathbf{k}' \cdot \mathbf{R}} e^{-t[\mathcal{D}\Omega + \Gamma_2']} e^{g/\sqrt{N} \sum_{\mathbf{k}} \alpha^*(\mathbf{k}) \int_0^t dt' e^{t'[\mathcal{D}\omega(\mathbf{k}) + 1/\tau]} \right| 0 \right\rangle \left[\text{where } \Gamma_2' = \frac{1}{\tau} \sum \tilde{n}(\mathbf{R}) \right] \\
 &= \frac{g\tau}{N} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}} \left\{ \frac{1 - e^{-t[\mathcal{D}\omega(\mathbf{k}) + 1/\tau]}}{1 + \tau\mathcal{D}\omega(\mathbf{k})} \right\}. \tag{2.20}
 \end{aligned}$$

Note that time ordering did not play an important role, for in this special case $\Gamma_1(t)$ and $\Gamma_1(t')$ commute. Equation (2.20) yields the steady state at $t \rightarrow \infty$ as a generalized Watson's integral, known to be expressible in terms of elementary functions in dimensions $d \leq 3$ (Glasser and Zucker, 1977). The approach to steady state is given by the even simpler expression, $\partial_t \langle n(\mathbf{R}) \rangle = g e^{-t/\tau} G(\mathbf{R}|t\mathcal{D})$.

If the sources are distributed, we only need specify the Fourier transform of the distribution of sources,

$$\hat{Q}(k) = \sum_{\mathbf{R}_0} e^{-i\mathbf{k} \cdot \mathbf{R}_0} Q(\mathbf{R}_0),$$

and convolute it with Eq. (2.20) to obtain $\langle n(\mathbf{R}) \rangle(t)$. Thus the problem is trivially generalized to arbitrary distribution of sources, assuming a homogeneous distribution of sinks.

F. Solvable model of binary recombination

We now return to the case of binary, on-site, recombination ($A + B \rightarrow \emptyset$) with no spontaneous regeneration. The rate equation for a low density of particles will be reduced to a nonlinear integral/differential equation that can be solved numerically, or even analytically, in the asymptotic regime. Define the initial densities ($N_{A \text{ or } B}(0)/N$) as $\langle n_{A,i} \rangle(0) \equiv \lambda_A$ and $\langle n_{B,i} \rangle(0) \equiv \lambda_B$. We consider a special case, $\lambda_A = \lambda_B = \lambda$. Ultimately there comes a stage in the calculation when, to achieve a closed-form solution, it becomes necessary to proceed to the low-density limit $\lambda \rightarrow 0$.

At arbitrary time and for either species, $\langle n_i \rangle(t) \equiv \lambda(1 - f(t))$, with $f \rightarrow 1$ asymptotically. This is necessarily so, as the only mechanism affecting the diffusing particles is binary recombination, which causes them all ultimately to disappear. (When the initial numbers are unequal, it is only the concentration of the minority constituent which ultimately vanishes, while the majority constituent's concentration tends asymptotically to $\rightarrow \lambda_{>} - \lambda_{<}$.) Using subscript i interchangeably with position \mathbf{R}_i , we write the average occupation number as

$$\begin{aligned}
 \langle n_{A,i} \rangle = \langle n_{B,i} \rangle &= \frac{1}{N} \sum_{\mathbf{R}} \langle 0 | e^{\sum_{\mathbf{R}'} (a_{\mathbf{R}'} + b_{\mathbf{R}'})} a_{\mathbf{R}}^* a_{\mathbf{R}} \\
 &\times e^{-t\mathcal{D}\Omega} e^{\lambda \sum_{\mathbf{R}'} (a_{\mathbf{R}'}^* + b_{\mathbf{R}'}^* - 2)} | 0 \rangle, \text{ for } t > 0, \tag{2.21}
 \end{aligned}$$

where the dimensionless rate operator Ω includes diffusion and recombination. Assuming, again for simplicity, equal diffusion coefficients $\mathcal{D}_A = \mathcal{D}_B = \mathcal{D}$, the dimensionless diffusion-reaction operator is

$$\begin{aligned}
 \Omega &= \sum_{\mathbf{R}} \sum_{\delta} (a_{\mathbf{R}}^* - a_{\mathbf{R}+\delta}^*) a_{\mathbf{R}} + \sum_{\mathbf{R}} \sum_{\delta} (b_{\mathbf{R}}^* - b_{\mathbf{R}+\delta}^*) b_{\mathbf{R}} \\
 &+ \frac{1}{\tau\mathcal{D}} \sum_{\mathbf{R}} \{ a_{\mathbf{R}}^* b_{\mathbf{R}}^* b_{\mathbf{R}} a_{\mathbf{R}} - b_{\mathbf{R}} a_{\mathbf{R}} \} \equiv \Omega_D + \Omega'. \tag{2.22}
 \end{aligned}$$

We first perform two operations that have no effect on Ω_D . First, we commute $e^{\sum_{\mathbf{R}'} (a_{\mathbf{R}'} + b_{\mathbf{R}'})}$ all the way to the right, then $e^{\lambda \sum_{\mathbf{R}'} (a_{\mathbf{R}'}^* + b_{\mathbf{R}'})}$ all the way to the left. This does produce a change in the recombination operator Ω' :

$$\begin{aligned}
 \Omega' \rightarrow \tilde{\Omega}, \text{ where } \tilde{\Omega} &\equiv \frac{1}{\tau\mathcal{D}} \sum_{\mathbf{R}} (a_{\mathbf{R}}^* b_{\mathbf{R}}^* + a_{\mathbf{R}}^* + b_{\mathbf{R}}^*) \\
 &\times (b_{\mathbf{R}} + \lambda)(a_{\mathbf{R}} + \lambda). \tag{2.23}
 \end{aligned}$$

Now upon introducing the quantity $f(t)$, we find that Eq. (2.21) takes the form

$$\langle n_i \rangle = \frac{1}{N} \sum_{\mathbf{R}} \langle 0 | (a_{\mathbf{R}} + \lambda) e^{-t\mathcal{D}(\Omega_D + \tilde{\Omega})} | 0 \rangle,$$

i.e.,

$$f(t) = -\frac{1}{\lambda} \frac{1}{N} \sum_{\mathbf{R}} \langle 0 | a_{\mathbf{R}} e^{-t\mathcal{D}(\Omega_D + \tilde{\Omega})} | 0 \rangle, \tag{2.24}$$

which suggests that we rescale each $a \rightarrow a\lambda$ and $a^* \rightarrow a^*/\lambda$. This, too, leaves Ω_D unaffected, whereas the recombination operator $\tilde{\Omega}$ takes on the form

$$\tilde{\Omega} \rightarrow \hat{\Omega} \equiv \frac{1}{\tau\mathcal{D}} \sum_{\mathbf{R}} [a_{\mathbf{R}}^* b_{\mathbf{R}}^* + \lambda(a_{\mathbf{R}}^* + b_{\mathbf{R}}^*)] (b_{\mathbf{R}} + 1)(a_{\mathbf{R}} + 1) \tag{2.25}$$

and f is given by

$$f(t) = -\frac{1}{N} \sum_{\mathbf{R}} \langle 0 | a_{\mathbf{R}} e^{-t\mathcal{D}(\Omega_D + \hat{\Omega})} | 0 \rangle.$$

We make use of the identity $\langle 0 | = \langle 0 | e^{t\mathcal{D}(\Omega_D + \hat{\Omega})}$ to write

$$f(t) = -\frac{1}{N} \sum_{\mathbf{R}} \langle 0 | a_{\mathbf{R}}(t) | 0 \rangle,$$

where

$$a_{\mathbf{R}}(t) \equiv e^{t\mathcal{D}(\Omega_D + \hat{\Omega})} a_{\mathbf{R}} e^{-t\mathcal{D}(\Omega_D + \hat{\Omega})}. \tag{2.26}$$

This will allow derivatives of the operators w.r. to t to be evaluated as commutators. Then we differentiate Eq. (2.26), recalling that $\Sigma a_{\mathbf{R}}$ commutes with Ω_D :

$$\begin{aligned} \partial_t f(t) &= \frac{D}{N} \sum_{\mathbf{R}} \langle 0 | e^{tD(\Omega_D + \hat{\Omega})} [a_{\mathbf{R}}, \hat{\Omega}] e^{-tD(\Omega_D + \hat{\Omega})} | 0 \rangle \\ &= \frac{\lambda}{\tau} \left\{ [1 - 2f(t)] + \frac{1}{N} \sum_{\mathbf{R}} \langle 0 | a_{\mathbf{R}}(t) b_{\mathbf{R}}(t) | 0 \rangle \right\} \\ &\equiv \frac{\lambda}{\tau} \{ 1 - 2f(t) + g(t) \} \equiv \frac{\lambda}{\tau} \{ \varphi(t) \}. \end{aligned} \quad (2.27)$$

This defines $g(t)$ and the curly bracket $\varphi(t)$, both of them new and as yet unknown functions.

In the evaluation of these functions, we proceed to the limit $\lambda \rightarrow 0$ in the exponent, Eq. (2.25). This allows us to solve for the leading term $g(t)$ [or rather, for $\varphi(t)$] in the limit $\lambda = 0$, using it to pry out the solution, to leading order in λ .

We transform a part of these expressions to the momentum representation, Eq. (2.6). Sums over \mathbf{k} are restricted to the first Brillouin zone. Again using Greek letters to denote the \mathbf{k} operators, we obtain

$$\frac{1}{N} \sum_{\mathbf{R}} b_{\mathbf{R}} a_{\mathbf{R}} \rightarrow \frac{1}{N} \beta(0) \alpha(0) + \sum_{\mathbf{k} \neq 0} \beta(\mathbf{k}) \alpha(-\mathbf{k}),$$

and

$$\frac{1}{N} \beta(0) \alpha(0) = \frac{1}{N^2} \left(\sum_{\mathbf{R}} b_{\mathbf{R}} \right) \left(\sum_{\mathbf{R}} a_{\mathbf{R}} \right)^2. \quad (2.28a)$$

Similarly, the total Ω is Ω_{tot} :

$$\begin{aligned} \Omega_D + \hat{\Omega} &= \sum_{\mathbf{k}} \omega(\mathbf{k}) [\alpha^*(\mathbf{k}) \alpha(\mathbf{k}) + \beta^*(\mathbf{k}) \beta(\mathbf{k})] + \frac{1}{\tau D} \\ &\times \left\{ \left[\alpha^*(0) \beta^*(0) + \sum_{\mathbf{k} \neq 0} \alpha^*(-\mathbf{k}) \beta^*(\mathbf{k}) \right] \frac{1}{N} \right. \\ &\times \left. \sum_{\mathbf{R}} (b_{\mathbf{R}} + 1)(a_{\mathbf{R}} + 1) + \dots \right\}, \end{aligned} \quad (2.28b)$$

where we have shown explicitly only those terms required in the equation of motion. However, it should be emphasized that *all* the other terms (indicated by the ellipsis) are to be retained in the exponent.

Next we evaluate

$$g(t) = \frac{1}{N} \sum_{\mathbf{R}} \langle 0 | e^{tD\Omega_{\text{tot}}} b_{\mathbf{R}} a_{\mathbf{R}} e^{-tD\Omega_{\text{tot}}} | 0 \rangle,$$

inserting Eq. (2.28a) for the sum over \mathbf{R} :

$$\begin{aligned} g(t) &= f^2(t) + \frac{1}{N} \sum_{\mathbf{k} \neq 0} \langle 0 | e^{tD\Omega_{\text{tot}}} \beta(\mathbf{k}) \alpha(-\mathbf{k}) e^{-tD\Omega_{\text{tot}}} | 0 \rangle \\ &\equiv f^2(t) + \frac{1}{N} \sum_{\mathbf{k} \neq 0} \Phi_{\mathbf{k}}(t). \end{aligned} \quad (2.29)$$

This equation defines each fluctuation contribution $\Phi_{\mathbf{k}}(t)$ as a vacuum expectation value. Using Eq. (2.28b) for Ω_{tot} , we solve the individual equation of motion of each $\Phi_{\mathbf{k}}(t)$:

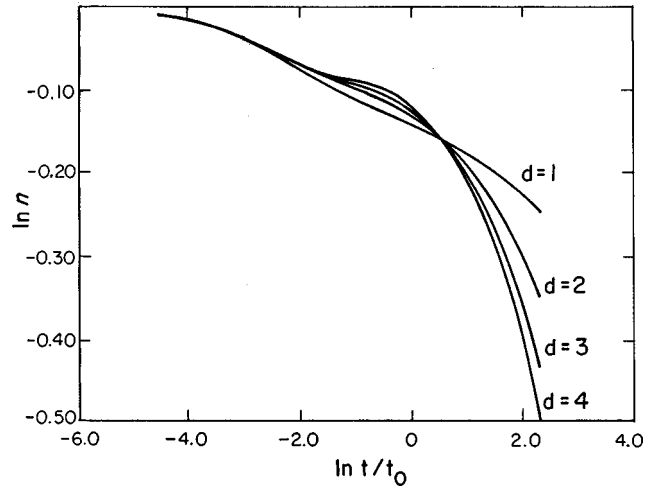


FIG. 1. Log-log plot of density vs time, $\ln n/\lambda$ vs $\ln t/t_0$. The approach to the asymptotic regime in various dimensions d , obtained as the numerical solution of Eq. (2.32) using parameters: $\lambda = 0.1$, $t_0 = 1/8\pi D$, $\tau = 0.1t_0$. Notice that all four curves cross at a common point just above $t = t_0$.

$$\partial_t \Phi_{\mathbf{k}}(t) = -2D\omega(\mathbf{k})\Phi_{\mathbf{k}}(t) - \frac{1}{\tau} \varphi(t),$$

i.e.,

$$\Phi_{\mathbf{k}}(t) = -\frac{1}{\tau} \int_0^t dt' e^{-2(t-t')D\omega(\mathbf{k})} \varphi(t'), \quad (2.30)$$

where we have used $\varphi(t) \equiv \{1 - 2f(t) + g(t)\}$. Each $\Phi_{\mathbf{k}}(t)$ is inserted into the sum in Eq. (2.29). Recalling the definition of $G(\mathbf{R}|tD)$ given in Eq. (2.3), we recognize the sum over \mathbf{k} as G at $\mathbf{R} = 0$, i.e.,

$$g(t) = f^2(t) - \frac{1}{\tau} \int_0^t dt' \{ G(\mathbf{0}|2(t-t')D) \} \varphi(t'). \quad (2.31)$$

On the one hand, φ includes all the fluctuations. On the other, it is related to f (hence to the single-particle density) through $\varphi(t) = \tau/\lambda \partial_t f(t)$. This dichotomy—the equivalence of the derivative of the particle density to the fluctuations in the very same quantity—is reminiscent of the fluctuation-dissipation theorem of equilibrium statistical physics. Here this “theorem” follows directly from the master equation, there being no requirements concerning thermodynamic equilibrium or steady state or any other conditions whatever, beyond the homogeneous initial conditions.

Adding $1 - 2f$ to both sides of Eq. (2.31) reduces the problem to a quadrature:

$$\varphi(t) = \left[(1 - f(t))^2 - \frac{1}{\tau} \int_0^t dt' G(\mathbf{0}|2(t-t')D) \varphi(t') \right], \quad (2.32)$$

subject to $\varphi(0) = 1$ and $\varphi(\infty) = 0$. Nonlinear equations generally require a numerical solution, shown in Fig. 1. But here it is not difficult to uncover the asymptotic nature of the solution analytically.

If $t \rightarrow \infty$ and t' stays finite, $G(\mathbf{0}|2(t-t')D) \rightarrow (8\pi tD)^{-d/2} (1 - t'/t)^{-d/2} \rightarrow (8\pi tD)^{-d/2}$. Recall that f

$\rightarrow 1$ asymptotically, hence its derivative φ is large only at small t and vanishes asymptotically. Let us assume that it vanishes faster than the right-hand side of Eq. (2.32). (We later verify this assumption to be self-consistent in all dimensions $d < 4$.) Under the integral sign in Eq. (2.32), $\varphi(t')$ vanishes at some large but finite t' ($t' \ll t$). Then, if one rewrites the integral in terms of the derivative of f , which varies from 0 to 1, it simplifies enormously. What is more, the left-hand side of Eq. (2.32) vanishes asymptotically—and therefore so must the right-hand side. Setting the right-hand side equal to zero and using $G(\mathbf{0}|2(t-t')\mathcal{D}) \rightarrow (8\pi t\mathcal{D})^{-d/2}$ yields

$$(1-f(t))^2 = \frac{1}{\tau} \int_0^t dt' G(\mathbf{0}|2(t-t')\mathcal{D})\varphi(t') \\ \rightarrow \frac{1}{\tau} \left(\frac{1}{8\pi t\mathcal{D}} \right)^{d/2} \int_0^t dt' \varphi(t') \rightarrow \frac{1}{\lambda} \left(\frac{1}{8\pi t\mathcal{D}} \right)^{d/2}. \quad (2.33)$$

Extracting the square root, we obtain the asymptotic result

$$\langle n \rangle \rightarrow \lambda^{1/2} \left(\frac{1}{8\pi t\mathcal{D}} \right)^{d/4}. \quad (2.34)$$

τ does not figure into this expression, in which the only material parameter is the diffusion coefficient. This supplies graphic proof that in diffusion-limited reactions, ultimately it is only diffusion which plays a significant role. A second surprise concerns the noninteger power of λ , showing that the asymptotic density is not proportional to the initial density but, rather, to its square root. A series expansion of the asymptotic density in powers of the initial density λ would have a zero radius of convergence (Mattis, 1997). Although it is qualitatively correct, Eq. (2.34) is not exact. B. P. Lee and J. Cardy (private communication) have pointed out to the present authors that the exact asymptotic result has been shown to be smaller than what is given here, by a factor $1/\sqrt{\pi}$. They have identified the source of the discrepancy as the seemingly negligible terms which were omitted when we proceeded to the limit $\lambda \rightarrow 0$. Thus, while suggestive, the present derivation is not definitive and a more careful analysis is needed—especially when the diffusion coefficients of the two species are different, or if their initial concentrations are unequal.

Note that the left-hand side of Eq. (2.33) is $O(1)$ or smaller, which implies the asymptotic region starts at some t which satisfies $t\mathcal{D} > \lambda^{-2/d}$. Thus, strictly speaking, instead of proceeding to the limit $\lambda \rightarrow 0$ we should have kept λ small but finite and retained further terms before performing the asymptotic analysis. Note the $-2/d$ power. The greater the dimension d , the sooner is the asymptotic region reached (all other things being equal.)

Nevertheless, the asymptotic power-law behavior predicted in Eq. (2.34) is in fact correct. To see that it is self-consistent, observe that the neglected term [φ on the left-hand side of Eq. (2.32)] decays as $t^{-(1+d/4)}$ while each term on the right-hand side is proportional to $t^{-d/2}$.

Because $1+d/4 > d/2$ for $d < 4$, the neglected term is asymptotically negligible in the limit $t \rightarrow \infty$ (compared with the terms that were retained). This confirms our hypothesis for $d < 4$.

However, in dimension $d \geq 4$ the left-hand side of Eq. (2.32) can no longer be neglected in the asymptotic region where, in fact, it exceeds the contribution of the diffusion integral. Therefore, neglecting this last, one solves the equation $\varphi(t) = \{1-f(t)\}^2$, obtaining asymptotically $\langle n_i \rangle \rightarrow 1/t$.

Is the error in neglecting the integral of any consequence? Both φ and $1-f$ are $O(1/t^2)$, while the diffusion integral remains $O(1/t^{d/2})$. Thus it does indeed vanish faster than $1/t^2$ in all dimensions $d > 4$, and its neglect is justified. Only in the marginal case of $d=4$ dimensions do all terms contribute in the same $O(1/t^2)$ to the equation.¹²

This $1/t$ law of decay, valid for $d > 4$, was first obtained in the preceding section for *zero* dimensions (defined as a space without geometry, hence without diffusion). We see that, strictly speaking, the $1/t$ law follows whenever spatial fluctuations are negligible, whatever the reason.

For $d > 4$ there exists a well-known theorem in QFT, to the effect that local interactions which are quartic in the field operators become trivial in dimension $d > 4$. Then mean-field solutions are essentially exact in $d > 4$, and $d=4$ is the marginal dimension—precisely what was found here.

G. Many-particle correlations

Among those properties specific to many-body systems that can be measured, and that should therefore be calculated, one includes distribution of interparticle distances $P(\mathbf{R}_{ij}|t)$ and the two-particle correlation functions $F(\mathbf{R}_{ij}|t)$. Let us calculate this correlation function, $F(\mathbf{R}|t) \equiv \langle n_{A,\mathbf{r}+\mathbf{R}} n_{B,\mathbf{r}} \rangle - \langle n_{A,\mathbf{r}} \rangle \langle n_{B,\mathbf{r}} \rangle$, with the average being taken over all sites \mathbf{r} . Skipping the details, we find that use of Eqs. (2.25) and (2.26) leads to

$$F(\mathbf{R},t) = \lambda^2 \left\{ \frac{1}{N} \sum_{\mathbf{r}} \langle 0 | (b_{\mathbf{r}+\mathbf{R}}(t)+1)(a_{\mathbf{r}}(t)+1) | 0 \rangle \right. \\ \left. - (1-f(t))^2 \right\}. \quad (2.35)$$

Now, the nontrivial part of this expression is

$$\frac{1}{N} \sum_{\mathbf{r}} b_{\mathbf{r}+\mathbf{R}} a_{\mathbf{r}} \rightarrow \frac{1}{N} \beta(0) \alpha(0) + \sum_{\mathbf{k} \neq 0} \beta(\mathbf{k}) \alpha(-\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}}.$$

The expectation value of each of these operators is already given in Eq. (2.30). After some elementary algebra (a good exercise for the reader), one obtains the asymptotic result at $t \rightarrow \infty$

$$F(\mathbf{R},t) \rightarrow -\lambda G(\mathbf{R}|2t\mathcal{D}) \quad (2.36)$$

¹²Therefore, while in $d=4$ we know the power law in t , the coefficient must still be separately determined.

(note the $(-)$ sign). The negative correlation is characteristic of the depletion caused by the binary reactions.

III. ONE DIMENSION

In one dimension ($d=1$), such as in an extended polymer embedded in the pore of a vycor glass, it is difficult for particles to pass by one another. If the moving entities are atoms, the hard-core potential prevents them from crossing; and if they are vacancies, their mutual exclusion is kinematic. One way to finesse this difficulty in the lattice model is to adopt the pseudo spin representation of the lattice gas using Pauli matrices, as is done below. Generalizations to two species require a spin-1 algebra. The various algebras have been thoroughly examined in a recent paper on the one-dimensional aspects of diffusion-reaction and diffusion-aggregation problems (Alcaraz *et al.*, 1994). Therefore we restrict the present discussion to the simplest examples. In the literature dealing with phase transitions, the remarkable fact transpires that dynamic phase transitions occur only for dimensions $d \leq 2$ and are forbidden for $d \geq 3$, a state of affairs almost diametrically opposite to what is known in thermodynamic equilibrium.

For a single species, we define the vacuum $|0\rangle$ once again as the state with no particles present; a_i (with $a_i|0\rangle=0$) defines the particle annihilation operator at site i . Its Hermitian conjugate is a_i^* , which adds a particle to the site (such that $a_i^*|0\rangle=|1\rangle_i$). If the hard core prohibits two particles at any site, $a_i^{*2}=0$ is required. In the two dimensional Hilbert space that this defines at each site, the Pauli matrices form a complete set. Their algebra is summarized as follows:

$$\begin{aligned} a_i^2 = a_i^{*2} = 0, \quad a_i a_j - a_j a_i &\equiv [a_i, a_j] = 0 \\ &= [a_j^*, a_i^*] \quad \text{for } i \neq j, \\ a_i^* a_i + a_i a_i^* &\equiv \{a_i^*, a_i\} = 1. \end{aligned} \tag{3.1}$$

Such operators satisfy mixed commutation relations, in which commutators are indicated by $[,]$ and anticommutators by $\{, \}$, as usual. In the low-density limit in $d \gg 1$, the hard core is known to be insignificant because of its short range; hence Paulion operators can be replaced by the bosons of the preceding section and nearest-neighbor interactions, or reactions can be approximated by on-site, zero-range interactions and reactions. But in low dimensions, $d=1$ (Schütz, 1995a, 1995b; Stinchcombe and Schütz 1995a, 1995b) and $d=2$, the effects of the hard core cannot be so simply eliminated. Here we consider just $d=1$. The literature shows that little attention has been paid to $d=2$ although there, even more than in $d=1$, most of the research work remains to be done.

The diffusion operator in the language of the operators (3.1) takes the same form as before,

$$\mathcal{D}\Omega_D = \mathcal{D} \sum_{i=1}^N (2a_i^* - a_{i+1}^* - a_{i-1}^*) a_i. \tag{3.2}$$

The one-body reaction operators also mimic the previous expressions, such as Eq. (2.12). However, because two particles cannot occupy the same site, the shortest possible range of the two-body recombination operator is the distance connecting nearest-neighbor sites, i.e.,

$$\Gamma = \sum_i \frac{1}{\tau_i} \{(a_i^* a_{i+1}^* - 1) a_{i+1} a_i\}. \tag{3.3}$$

Consider a master equation in which the time-development operator is $\Omega_{\text{tot}} = \mathcal{D}\Omega + \Gamma$, the sum of Eqs. (3.2) and (3.3), subject to Eq. (3.1). Its solution is once again the usual $|\Psi(t)\rangle = e^{-t\Omega_{\text{tot}}} |\Psi(0)\rangle$.

For the purpose of time ordering, Ω_{tot} can be decomposed into two parts, although it is not clear at the outset which they should be. We remark that the combination of Eq. (3.2) with the particle-conserving part of (3.3),

$$\Gamma_0 = \sum_i \frac{1}{\tau_i} \{a_i^* a_{i+1}^* a_{i+1} a_i\},$$

maps precisely onto the anisotropic Heisenberg spin Hamiltonian (the so-called XXZ model) in an external magnetic field. While the eigenvalues in this model can be solved exactly in 1D by way of Bethe's ansatz (Bethe, 1931), it is quite difficult to use Bethe's eigenstates for the purpose of calculating explicit matrix elements such as those of $\Sigma a_{j+1} a_j$. Modest headway can be made only in special cases.

Assuming that there are initially M particles on N sites, the probability of retaining precisely M particles is

$$\begin{aligned} P_M(t) &\equiv \frac{1}{M!} \left\langle 0 \left| \left(\sum_j a_j \right)^M \right. \right. \\ &\quad \left. \left. \times \exp -t \{ \mathcal{D}\Omega_D + \Gamma_0 \} \right| \Psi(0) \right\rangle. \end{aligned} \tag{3.4}$$

In terms of conventional spin-one-half operators, the exponentiated operator is

$$\begin{aligned} \{ \mathcal{D}\Omega_D + \Gamma_0 \} &= \sum_j \left[\frac{1}{\tau_j} S_j^z S_{j+1}^z - \mathcal{D}(S_j^+ S_{j+1}^- + \text{H.c.}) \right] \\ &\quad + \left[\sum_j S_j^z \left(2\mathcal{D} + \frac{1}{\tau_j} \right) \right] \\ &\quad + \left[N\mathcal{D} + \frac{1}{4} \sum_j \frac{1}{\tau_j} \right]. \end{aligned} \tag{3.4}$$

If $M=N/2$, $\Sigma S^z=0$. Then, if the τ_j are all equal, the first square bracket maps onto the anisotropic XXZ Heisenberg model with an eigenvalue spectrum $Ne_0 + \Delta_\alpha$, and the second expression in square brackets vanishes. Then the lowest eigenvalue of $\{ \mathcal{D}\Omega_D + \Gamma_0 \}$ is $N(e_0 + \mathcal{D} + (4\tau)^{-1}) > 0$. Thus the probability for remaining in the initial state always decays exponentially as $\exp -N/\tau^*$.

For other initial conditions or for $2\mathcal{D}\tau \gg 1$, the first

¹³The $a_i a_{i+1}$ terms can only change $M \rightarrow M-2$.

bracket maps onto the XY model (or onto the anisotropic Heisenberg antiferromagnet with a continuous spectrum $\Delta_1, \Delta_2, \Delta_3 \propto 1/N$). On the other hand, if $2D\tau < 1$, this bracket maps onto an Ising antiferromagnet having a finite energy gap separating the lowest-lying energy levels.

Of course, the effective magnetic field $2D + 1/\tau$ is positive; hence it favors $\Sigma S^z < 0$ (and not $\Sigma S^z = 0$ as we assumed previously). The spectrum of the XXZ model in a finite magnetic field is generally gapless, regardless of the value of the anisotropy parameter $2D\tau$.

Although this analysis by analogy could be extended to any dimension d , the presence of terms that do not conserve particle number renders the comparisons somewhat less than rigorous. Unfortunately, because of the mixed commutation relations, there is no obvious way to take advantage of translational invariance—even when the τ 's are constant. Because of the mixed commutation relations, the Fourier transformation of paulions is not a viable option in any dimension.

A. Normalization

With the reference state remaining formally $\langle 0 | e^{\Sigma i a_i}$, the normalized paulion version of the Glauber state differs from its bosonic counterpart, viz.

$$|\lambda N\rangle = (1 + \lambda)^{-N} e^{\lambda \Sigma_j a_j^*} |0\rangle$$

(see below). In general, definitions such as that of the $\tilde{\Gamma}$ operator remain the same as before [e.g., in (2.16b)], but when evaluated explicitly differ considerably from what was obtained with bosons. Similarity transformations are especially sensitive to the nature of the operator algebra.

B. The Jordan-Wigner transformation

In $d=1$ only, an initial transformation of the paulions into fermion operators—the well-known Jordan-Wigner transformation—can simplify matters. One expresses the paulions a in a one-to-one representation of fermions b ,

$$a_j = b_j e^{\pi i \Sigma_{m < j} \tilde{n}_m} \quad (3.5)$$

where $\tilde{n}_m = b_m^* b_m = a_m^* a_m$ (similarly for the Hermitian conjugate operators). If the b 's anticommute, the a 's satisfy the correct operator algebra—and vice versa. From Eq. (3.5) one deduces

$$a_{j\pm 1}^* a_j = b_{j\pm 1}^* b_j \quad \text{and} \quad a_{j+1} a_j = b_{j+1} b_j \quad (3.6)$$

(similarly for their Hermitian conjugate operators), using the identity, $\exp\{2\pi i a^* a\} \equiv 1$. Thus one can write $\Omega_{\text{tot}} = \mathcal{D}\Omega_D + \Gamma$ entirely in the language of fermions, as

$$\begin{aligned} \Omega_D &= \sum_i (2b_i^* - b_{i+1}^* - b_{i-1}^*) b_i \quad \text{and} \\ \Gamma &= \sum_i \frac{1}{\tau_i} \{(b_i^* b_{i+1}^* - 1) b_{i+1} b_i\}. \end{aligned} \quad (3.7)$$

Unlike the original, this is a bilinear form in fermions, to which the methods of QFT, including Fourier transformation to plane waves, can be usefully applied. However, the effects of the Jordan-Wigner transformation on the reference operator and on the reference state have to be reexamined. For each individual paulion operator the identity $e^a = 1 + a$ holds. In order that the transformation $a \rightarrow b$ not introduce exponentiated strings as in Eq. (3.5), one orders the a 's in ascending order of position for the right-hand side states and descending order of position for the left-hand states. The reference state in the new, Fermionic language is therefore the spatial-ordered product

$$\begin{aligned} \langle 0 | (1 + a_N)(1 + a_{N-1}) \cdots (1 + a_1) \\ \Rightarrow \langle 0 | (1 + b_N)(1 + b_{N-1}) \cdots (1 + b_1), \end{aligned} \quad (3.8a)$$

while each of the complete sets of 2^N right-hand states is similarly written as

$$a_i^* a_{i+p_1}^* \cdots a_{i+\Sigma_j p_j}^* |0\rangle \Rightarrow b_i^* b_{i+p_1}^* \cdots b_{i+\Sigma_j p_j}^* |0\rangle, \quad (3.8b)$$

where the spacings p_1, p_2 , etc. are all > 0 . Because of the exclusion principle, no nearest-neighbor dynamic operator (including Ω) is capable of altering the initial order of the particles that are present—even after some of these particles are made to disappear. The particles simply cannot cross. Thus it is permissible to add to Eq. (3.8b) configurations that differ only by permutations of the b 's and, with their aid, construct plane-wave l.c. of states which are eigenstates of the total momentum operator. The unique high-density state for N particles (one at each site) can be written in two ways: either as $|N\rangle = b_1^* b_2^* \cdots b_N^* |0\rangle$ or as $\Pi_{\text{all } k} \beta^*(k) |0\rangle$, the latter using fermion plane-wave operators

$$\beta^*(k) = \frac{1}{\sqrt{N}} \sum_m e^{ikm} b_m^*.$$

The structure of Ω in Eq. (3.7) allows particle number to change only by multiples of two. In the process of summing the time-ordered series or of solving the equations of motion, the principal (but not the only) contributions are pair scattering and annihilation. If the initial density is high, that is, comparable to $1/2$ particle per site, the method of bosonization (Mattis and Lieb, 1965) should be useful, insofar as it reduces Eq. (3.7) to a quadratic form in density fluctuations for which the eigenstates are well known; but to date it has not been adequately explored in this context.

C. Asymptotic time dependence in 1D

The hard core, resulting in effectively fermionic statistics for what are otherwise classical particles, greatly affects the diffusion. For, qualitatively, when the diffusion operator is expanded about some nonzero Fermi level, its spectrum has linear rather than quadratic dispersion. As a result, the one-dimensional diffusion Green's function $G(0|tD)$ has a $1/t$ rather than $1/\sqrt{t}$ asymptotic dependence. When this G is inserted into Eqs. (2.33) and

(2.34), the asymptotic time dependence of the density becomes $1/t^{1/2}$ (rather than $1/t^{1/4}$ in the absence of the hard core). What is more, it has been found that if there is an initial, systematic drift velocity of the reactants, the limiting behavior changes to $1/t^{1/3}$ (Janowsky, 1995a, 1995b).

D. Nearest-neighbor recombination without diffusion

If \mathcal{D} is zero, the term Γ in Eq. (3.7), subject to the hard-core (no double occupancy) restriction, is the sole surviving operator. Its effect on various localized initial states can be examined. (This process is dual to random sequential absorption of dimers, which can be solved for some choices of initial conditions; see Percus, 1993.) In the simplest case, there are initially only pairs of nearest-neighbor particles separated by any number of vacancies. Clusters of three or more particles are absent. The decay of such states is readily seen to be exponential.

But, more generally, the decay of clusters of three or more particles (in any dimension, not just $d=1$), in the absence of a diffusion mechanism presents a surprisingly complex problem in combinatorics that remains to be completely analyzed. Consider the three decay channels of four contiguous particles on a linear chain with vacancies on either side of them. Ultimately there remain either zero particles or two non-nearest-neighbor “orphans,” as the recombination mechanism is incapable of eliminating all the particles all the time in the absence of diffusion. This points up once again, that the dominant role of diffusion is to take the particles to “where the action is.”

E. Fluctuation-dominated reaction kinetics

Increasingly, the transport properties of physical systems are being explained in terms of fluctuation-dominated reaction kinetics such as were discussed in this Section. Some involve the motion of excitations along linear polymer molecules such as *trans*-polyacetylene (Vardeny *et al.*, 1982; Heeger *et al.*, 1988), others the motion of electronic and lattice excitations along one-dimensional inclusions in higher-dimensional complexes such as the polycarbonate pores in naphthalene (Kopelman, Parus, and Prasad, 1988) and in pseudocyanide (Sündstrom *et al.*, 1988). Details of these studies and references can be found in two chapters of a recent compendium (Kopelman and Lin, 1997; Kroon and Sprik, 1997).

CONCLUSION AND ACKNOWLEDGMENT

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The present paper was written in the belief that the methods of quantum field theory can promote significant

advances in nonequilibrium statistical mechanics and in other areas of “classical” physics and physical chemistry. It follows that popularization of this approach should lead to new and unexpected applications, although only time will tell whether this purpose is achieved. As a secondary goal, we deemed it important to set out an historical record in what was previously an ill-defined area. Below, we list some seminal works in chronological order. We sincerely hope this list gives appropriate credit, where credit is due, to the clever pioneers in the field. If there are any omissions they are unintentional. The bibliography is reasonably representative of the literature up to 1996 and has been annotated for ease of use.

APPENDIX: SELECTED QFT APPROACHES (IN CHRONOLOGICAL ORDER)

Suna (1970). Kinematics of exciton-exciton annihilation in molecular crystals.

Doi (1976a). Second-quantization representation for classical many-particle systems.

Doi (1976b). Stochastic theory of diffusion-controlled reactions.

Siggia (1977). Pseudospin formulation of kinetic Ising models.

Huber, Hamilton, and Barnet (1977). Time-dependent effects in fluorescent line narrowing.

Alexander and Holstein (1978). Lattice diffusion and the Heisenberg ferromagnet.

Zel'dovich and Ovchinnikov (1978). Mass-action law and kinetics of chemical reaction with density fluctuations.

Grassberger and de la Torre (1979). Reggeon field theory and Monte Carlo calculation of critical behavior.

Rose (1979). Renormalized kinetic theory of nonequilibrium many-particle classical systems.

Kimball (1979). Kinetic Ising model.

Cardy and Sugar (1980). Directed percolation and Reggeon field theory.

Alexander *et al.*, (1981). Master equation having random transition probability coefficients.

Mikhailov (1981). Path integrals in chemical kinetics.

Goldenfield (1984). Kinetics of nucleation-controlled polymer crystal growth.

Peliti (1985). Path-integral approach to birth-death processes on a lattice.

Mikhailov and Yashin (1985). QFT in diffusion-controlled reactions.

Kang and Redner (1985). Fluctuation-dominated kinetics.

Peliti (1986). Renormalization of fluctuation effects in $A+A \rightarrow A$ reaction.

Lushnikov (1986). Binary reaction $A+A \rightarrow \emptyset$ in 1D.

Ohtsuki and Keyes (1988). Field-theoretic approach to unstable critical dynamics: initial-stage renormalization.

Grassberger (1989). Kinetic critical phenomena.

Ohtsuki (1991). QFT approach to scaling in diffusion-controlled recombination.

Cornell, Droz, and Chopard (1991). Fluctuations in inhomogeneous diffusion-limited reactions.

Friedman, Levine, and O'Shaughnessy (1992). Renormalization-group study of QFT theory of $A + A \rightarrow \emptyset$.

Jensen and Dickman (1993). Time-dependent perturbation theory.

Sandow and Trimper (1993). Aggregation process.

Stinchcombe, Grynberg, and Barma (1993). Deposition-evaporation: Jamming and broken symmetry.

Droz and Sasvari (1993). Renormalization-group approach to inhomogeneous diffusion-limited reactions.

Alcaraz and Rittenberg (1993). Reaction-diffusion as an Hecke algebra.

Schütz and Sandow (1994). Non-Abelian symmetries of stochastic processes.

Grynberg, Newman, and Stinchcombe (1994). Absorption-desorption and catalysis.

Sandow (1994). Partially asymmetric exclusion process with open boundaries.

Lee and Cardy (1994). Scaling of reaction zones in diffusion-limited recombination.

Cardy (1994). Quantum Hamiltonians and self-organized criticality.

Schütz (1995). Reaction-diffusion of hard-core particles.

Cardy (1995). Proportion of unaffected sites in a reaction-diffusion process.

Howard and Cardy (1995). Fluctuations and multiscaling of reaction-diffusion front.

Hinrichsen, Sandow, and Peschel (1996). On matrix product ground states for the reaction-diffusion process.

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Alcaraz, F. C., and V. Rittenberg, 1993, *Phys. Lett. B* **314**, 377 (Reaction-diffusion as Hecke algebra. Solution in $d=1$ by means of Hecke or Temperley-Lieb algebras).

Aleman, P., and D. ben-Avraham, 1995, *Phys. Lett. A* **206**, 18 (Interparticle distribution functions for one species. For diffusion-limited annihilation reaction $A + A \rightarrow \emptyset$).

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