

Dispersive diffusion transport and noise, time-dependent diffusion coefficient, generalized Einstein-Nernst relation, and dispersive diffusion-controlled unimolecular and bimolecular reactions

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(Received 21 November 1980; revised manuscript received 20 February 1981)

Starting from the same fundamental bases as a recently advanced unified theory of low-frequency fluctuation-dissipation properties of condensed matter, we have approached the various problems associated with diffusion phenomena. In this approach the classical Markovian diffusion transport is a limiting case ($n = 0$) of an in-general non-Markovian diffusion transport ($n \neq 0$). The theory involves a single parameter n , the infrared divergent exponent, which ranges from 0 to 1. For any value of n in this range, the form of the diffusion transport equation is completely specified through a universal time correlation function $\psi(t)$ whose form is dependent on n only. Since the present treatment is one branch of the unified theory, the quantity n , although it cannot be easily calculated for a given material and process at this time, can be determined by or inferred from measurements in another low-frequency response provided the same diffusion process governs both phenomena. From the availability of large amounts of experimental data in dielectric, mechanical, and viscoelastic relaxations, in NMR spin-lattice relaxations, in dispersive transient transport, etc., and the already-proven successes of the unified theory when specialized to these subjects, n should not be considered as a free parameter that cannot be cross checked or cannot be determined. The new results on diffusion derived in this work for each n value include (1) the diffusion noise spectra which tend to $1/f$ spectra when n approaches unity; (2) a modified Einstein relation between mean-square displacement and time of diffusion; (3) time-dependent diffusion coefficient and mobility with their ratio now obeying a generalized Nernst-Einstein formula, and (4) the time evolutions of diffusion-controlled unimolecular and bimolecular reactions or recombinations. We have compared these predictions with recent experiments on amorphous Si and achieved good agreement between them. In contrast, the results of our analysis of diffusion in another well-known model due to Scher and Montroll, based on a stochastic-event time distribution function $\psi(t) \equiv t^{-1-\alpha}$ at large times, fail to account for the time dependence of bimolecular recombination of electrons and holes that is controlled by dispersive diffusion.

I. INTRODUCTION

Recently one of us has proposed a physical picture that departs drastically from the conventional one for low-frequency (for example, $\omega \leq 10$ GHz) fluctuation, dissipation, and relaxation behaviors of condensed matter in general.¹⁻¹² The model evolves from a fundamental mechanism that is operative in any condensed matter to govern its low-frequency responses. Since fundamental process is involved, the issues of the model will have some universal features. The new physical picture¹⁻¹⁴ stems from

inquiring into the nature and properties of excitations of arbitrary low energy and the corresponding states that give rise to these excitations. We have adapted the statistical approach to quantum mechanics of Wigner,¹³ known sometimes as random matrices,^{14,15} to condensed matter. Wigner's approach enables us to deduce some general properties of the correlated states¹⁻⁴ that give rise to low-energy excitations. In most if not all considerations⁴ of the low-frequency responses, a primary species can be identified for any particular response. These can be dipolar groups of atoms or molecules,

charged and uncharged particles including electrons, holes, ions, atoms, defects, vacancies, etc. Response and fluctuations are triggered by transitions of the primary species which in turn will cause both excitation and de-excitation of correlated states. We have proposed that the correlated-state excitations and de-excitations that trail the primary transition are infrared divergent.^{1-4,16} This conclusion is arrived at from physical arguments, and a mathematically rigorous treatment has not yet emerged.

The transition rate of the primary species τ_0^{-1} is modified by the infrared-divergent excitations and de-excitation of correlated states to be time dependent according to $\tau_0^{-1} \exp(-n\gamma)(E_c t)^{-n}$, where $\gamma = 0.577$ and E_c is the upper "cutoff" of the correlation-state excitation energy which can be considered as the energy above which the density of correlated-state excitations is no longer linear in E .¹⁻⁴ The transition rate equation for the primary species

$$\frac{dQ}{dt} = \frac{-Q}{\tau_0} \quad (1)$$

is modified by the infrared-divergent phenomenon to

$$\frac{dQ}{dt} = -\tau_0^{-1} e^{-n\gamma}(E_c t)^{-n} Q \quad (2)$$

Of central importance is the function

$$\psi(t) \equiv -\frac{dQ}{dt} \quad (3)$$

which can be obtained explicitly through solution of Eq. (2) as

$$\psi(t) = \tau_0^{-1} e^{-n\gamma}(E_c t)^{-n} \times \exp[-\tau_0^{-1} e^{-n\gamma} t^{1-n}/(1-n)E_c^n] \quad (4)$$

This function will be repeatedly referred to in this work and it is convenient to rewrite Eq. (4) as

$$\psi(t) = (1-n)at^{-n} \exp(-at^{1-n}) \quad (5)$$

with

$$a = e^{-n\gamma}/(1-n)\tau_0 E_c^n \quad (6)$$

For example, in dielectric relaxation² the dielectric polarization correlation function $-\beta \langle P_i(t) \dot{P}_i(t-\tau) \rangle_0$ can be expressed as $\beta p_0^2 \psi(t)$ with p_0 being the dipolar polarization. In carrier hopping transport, $\psi(t)$ is the hopping-time probability density or distribution function, i.e., the carrier being initially at a site will hop between times t and $t + \delta t$ with probability $\psi(t)\delta t$. With $\psi(t)$ being known, predictions of the long-time or low-

frequency (after Fourier transformation) fluctuation and dissipation properties can be worked out.⁴ This has been accomplished⁴ through the use of the fluctuation-dissipation theorem whenever necessary, in a number of areas including dielectric relaxation, mechanical relaxation, internal friction, viscoelastic properties, nuclear-spin relaxation, generation-recombination noise, flicker $1/f$ noise from mobility fluctuations, transient electrical transport, and transient capacitance. We have then arrived at a unified theory of many low-frequency properties of condensed matter. The contribution to dispersion from this mechanism, being universal, will conform to certain predicted forms irrespective of the physical and chemical structure of the material.

The special case of $n = 0$ in Eqs. (4) and (5) recaptures the form for classical Markov processes. For $n \neq 0$, the fundamental mechanism provides a specific "intrinsic" distribution of transition times, Eqs. (4) and (5), even though the transition rate of the primary species τ_0^{-1} has a single value with no distribution. If there is, in addition, a true "extrinsic" distribution of τ_0^{-1} , our intrinsic distribution has to be folded into the extrinsic distribution in order to obtain the observed distribution.

In this present work we present the study of non-Markovian carrier-diffusion transport and diffusion noise, as well as diffusion-controlled unimolecular and bimolecular reactions as modified by the transition-time distribution $\psi(t)$ of Eqs. (4) and (5). For n fixed, $\psi(t)$ has two characteristic time dependences. At earlier times, $t < t_p \equiv a^{-1/(1-n)}$, the pre-exponential function t^{-n} gives the time dependence of $\psi(t)$. At longer times $t > t_p$, $\psi(t)$ is controlled by the exponential function with fractional power of t , and the decay is thus stretched out in a more extended time region. We emphasize both time domains and explore both characteristic time dependences of $\psi(t)$ in the diffusion-related problems. Parallel to the studies of diffusion transport, we consider also the transport of carriers in the presence of an electric field as modified by the hopping-time distribution $\psi(t)$. In diffusion transport we obtain a generalized diffusion coefficient which in a certain time regime is time dependent. Similarly, a generalized mobility can be defined in the case of electric-field-induced carrier transport.^{17,18} The Einstein relation between the generalized diffusion coefficient and mobility still exists, as it should, although its form is modified from the original one due to Einstein.¹⁹

We then turn our attention to diffusion-controlled unimolecular and bimolecular reactions and recom-

binations and treat them in the framework of our present model with $\psi(t)$ of Eqs. (4) and (5). The mathematics of a random walk on lattice,²⁰ its extension to continuous-time random walks (CTRW) of Montroll and Weiss,²¹ and their applications to the master-equation approach²²⁻²⁵ to unimolecular and bimolecular reactions are available in the literature. Earlier applications²³⁻²⁸ of the mathematics of CTRW have implicitly or explicitly assumed that the hopping-time distribution function arises from randomness such as a random array of sites through which the carrier moves, resulting in fluctuations in hopping times. We shall rely heavily on the mathematics of the CTRW (Refs. 20,21) but depart from earlier works in the physics behind $\psi(t)$. Allowing our microscopically derived $\psi(t)$, we calculate the reaction rate $K(t)$ for unimolecular and bimolecular reactions, and the time evolution of the concentration of reacting species. When specialized to bimolecular recombination of electrons and holes generated initially in equal numbers, our $\psi(t)$ leads directly to the result of

$$K(t) = Bt^{-n} \quad (7)$$

and the bimolecular decay-rate equation

$$\frac{dN}{dt} = -Bt^{-n}N^2 \quad (8)$$

Equation (2) has been presaged by Vardeny *et al.*²⁹ and successfully explains their optical studies of excess carrier recombination in hydrogenated amorphous silicon. On the other hand, the rather popular hopping-time distribution function of Scher and Montroll,^{27,28} decaying at large times as

$$\psi_{SM}(t) = t^{-1-\alpha}, \quad 0 < \alpha < 1, \quad (9)$$

which has been employed²⁶⁻²⁸ to describe dispersive transient transport in *a*-As₂Se₃, runs into the difficulty of not being able to arrive at Eq. (8). The paper is organized as follows. In Sec. II and in Appendix A we list only the essential mathematical tools and definitions that are involved in the CTRW formulation of Montroll and Weiss.²¹ This is both necessary and beneficial for clearer exposition of the subject matter to be treated in a later section. The work involved in the later section amounts to the clothing of the body of physics contained in $\psi(t)$ of Eqs. (4) and (5) by the mathematics of CTRW. Section II A deals with a dispersive diffusion transport and noise. Section II B derives the generalized diffusion coefficient and mobility, and II C gives the modified Einstein relation between them. Section III treats the problem of dispersive diffusion-

controlled unimolecular and bimolecular reactions. The results are used to discuss experimental data. We pay special attention to the results of a recent study of electron-hole recombination in amorphous silicon which shows evidence for dispersive diffusion and diffusion-controlled bimolecular recombination. The last section briefly summarizes the essential results.

II. DISPERSIVE DIFFUSION TRANSPORT

In this paper we investigate the problems associated with dispersive non-Markovian diffusion transport with the help of the generalized master equation to formulate the continuous-time random walk (CTRW) processes characterized by the hopping-time distribution function.

CTRW is introduced by Montroll and Weiss to consider the situation when the jumps do not occur at regular time intervals, but are made according to the hopping-time distribution function $\psi(t)$ such as those given by Eqs. (5) and (9). In CTRW we are interested in functions like $\bar{P}(l,t)$ and $\bar{F}(l,t)$, the probability of *being at* l at time t and the probability for *reaching* l for the first time at time t , respectively.

With the help of the generalized master equations to characterize the CTRW processes, $\bar{P}(l,t)$ satisfies³⁰

$$\frac{d\bar{P}(l,t)}{dt} = \int_0^t \phi(t-\tau) \sum_{l'} [p(l,l')\bar{P}(l,\tau) - p(l'l)\bar{P}(l,\tau)] d\tau, \quad (10)$$

where $\phi(t)$ is the memory or relaxation function. The Laplace transform $\phi^*(u)$ of $\phi(t)$ is related to $\psi^*(u)$, the Laplace transform of $\psi(t)$, by^{27,28}

$$\phi^*(u) = u\psi^*(u)/[1 - \psi^*(u)] \quad (11)$$

The master equation (10) for CTRW on a lattice network has a continuum limiting form that will be of interest. In the presence of a constant electric field E in the x direction, at each jump there is a bias for a jump to the right in preference to one to the left. Equal weight is given to jumps in the $\pm y$ and $\pm z$ directions. Passing to the limit of small distance c_0 between jumps, the continuum form of the master equation (10) with $\rho(x,t)$ standing now for $e\bar{P}(l,t)$ is

$$\frac{\partial \rho(x,t)}{\partial t} = \left[\frac{c_0^2}{6} \right] \int_0^t \phi(t-\tau) \left[\frac{\partial^2 \rho(x,\tau)}{\partial x^2} \right] d\tau - 2c_0bE \int_0^t \phi(t-\tau) \left[\frac{\partial \rho(x,\tau)}{\partial x} \right] d\tau \quad (12)$$

The first term in Eq. (12) represents the generalization of diffusion to include non-Markovian processes described by $\phi(t)$. For the particular example of

$$\psi(t) = \lambda_0 e^{-\lambda_0 t} \quad (13)$$

obtainable by taking the limit as $n \rightarrow 0$ of $\psi(t)$ given by Eq. (4) [from Eq. (11)], $\phi(t) = 2\lambda_0\delta(t)$ and the master equation (10) becomes Markovian and has the Pauli's form.³⁰ Correspondingly Eq. (12) reduces to

$$\frac{\partial \rho(x,t)}{\partial t} = D_0 \frac{\partial^2 \rho(x,t)}{\partial x^2} - \mu_0 E \frac{\partial \rho(x,t)}{\partial x} \quad (14)$$

The first term is the conventional diffusion term with diffusion constant D_0 ,

$$D_0 = c_0^2 \lambda_0 / 3, \quad (15)$$

and the second term is the flux in the presence of the electric field. It is worth emphasizing that our microscopic hopping-distribution function $\psi(t)$ given by Eq. (4) reduces to Eq. (13) when $n \rightarrow 0$, which corresponds to the physical situation of negligible density of correlated-state excitations and/or extremely weak coupling of them with the primary species.

A. Diffusion noise

There is a long history in the study of noise spectra resulting from spatially dependent stochastic processes such as transport noise. In particular the noise spectra resulting from diffusion has been a subject of great interest for the last thirty years.²⁸⁻³² These activities in transport noise are motivated by the hope of finding a $1/f$ spectrum over a wide frequency range and explaining the mystery of $1/f$ noise which appears to be a ubiquitous phenomenon. Although in the course of time there have been claims that a $1/f$ spectrum can be derived from specific models³³ of transport, it has been shown by van Vliet *et al.*^{34,35} and by Lax^{36,37} that classical transport of carriers by drift or diffusion, or transport of heat in finite systems, will in general not have a $1/f$ noise spectrum. Specifically for diffusion, one finds always a high-frequency asymptote $\omega^{-3/2}$ (the universal $\omega^{-3/2}$ law of Lax), and for sufficiently low frequencies one finds $f^{-1/2}$, $\ln f$, and f^0 for one-, two-, and three-dimensional diffusion systems, respectively. A $1/f$ range never occurs and the early model of $1/f$ noise from diffusion processes was shown to be elusive.³²⁻³⁷ Despite these conclusions, the model

investigations of transport noise and its connection with $1/f$ noise has not diminished. One notable recent work is by Voss and Clarke.³⁸ They proposed an ad hoc volume noise source called the "P source," and were then able to obtain a $1/f$ diffusion noise spectrum over a range of frequencies. However, van Vliet³² has recently shown rigorously by the Λ theorem that the "P source" implies long-range spatial correlation of the covariance function, which is unphysical and not upheld by statistical mechanisms. Thus classical diffusion transport will not give rise to $1/f$ noise, a conclusion expressed in a most recent review.³²

We have noted that classical diffusion is only a special case ($n = 0$) in our physical model wherein all rate processes are always modified by the infrared-divergent excitations of correlated states to a greater or lesser degree. Specifically, classical diffusion transport equation (14) can be obtained as a special case of a more generally applicable diffusion transport equation (12). In laboratory condensed-matter systems, diffusion transport may be more appropriately described by the set of equations (12), (11), and (4) with $n \neq 0$. Naturally we would like to investigate immediately the noise spectra for diffusion transport with $n \neq 0$ and to see if a $1/f$ spectrum will emerge.

The more direct method of the calculation of noise spectra resulting from diffusion is the Green's-function procedure.³⁵ In this procedure, one calculates the Green's function $G(\vec{r}, \vec{r}', t)$ which is the probability that a carrier will be found at \vec{r} at time t if it is known to be at \vec{r}' at time 0. We shall consider carrier fluctuations although the discussion here is applicable also to other stochastic variables such as temperature or energy. For transport equation (12) that describes diffusion in one dimension, the Green's function satisfies

$$\frac{\partial G(x,t)}{\partial t} = \frac{c_0^2}{2} \int_0^t \phi(t-\tau) \frac{\partial^2 G(x,\tau)}{\partial x^2} d\tau + \delta(t)\delta(x) \quad (16)$$

Taking the Laplace transform in t (denoted by $*$) and Fourier transform in x (denoted by \sim), the transformed Green's function $\tilde{G}^*(k,u)$ can be solved and has the form

$$\tilde{G}^*(k,u) = [u + c_0^2 k^2 \phi^*(u)/2]^{-1} \quad (17)$$

If Ω is the volume of the domain in which the diffusion process takes place one can show that the noise spectrum is

$$S_N(\omega) = \frac{4\langle \Delta N^2 \rangle}{\Omega} \operatorname{Re} \int_{\Omega} \int_{\Omega} G^*(x, x', i\omega) dv dv' , \tag{18}$$

where

$$N(t) = \int_{\Omega} n(\vec{r}) dv \tag{19}$$

is the total number of particles in Ω , $\langle \Delta N^2 \rangle$ is the variance of N , and $G^*(x, x', i\omega)$ is the Laplace transform in t of $G(x, x', t)$ with u the Laplace transform variable written as $i\omega$. Expressed in terms of the Laplace-Fourier transform $\tilde{G}^*(k, u)$, we have

$$S_N(\omega) = \frac{4\langle \Delta N^2 \rangle}{\Omega} \operatorname{Re} \int_{\Omega} dv \int_{\Omega} dv' (1/2\pi) \int dk \tilde{G}^*(k, i\omega) e^{ik(x-x')} . \tag{20}$$

Let us examine first the high-frequency spectrum, for which we know already that when $n = 0$, it has the Lax universal $\omega^{-3/2}$ form. High frequency, or equivalently earlier times, implies that we should emphasize the earlier time dependence of $\psi(t)$, which is

$$\psi(t) = (1 - n)at^{-n} \text{ for } t \ll a^{-1/(1-n)} . \tag{21}$$

The Laplace transform of expression (21) is

$$\psi^*(u) = (1 - n)a \Gamma(1 - n)u^{n-1} \equiv \lambda_n u^{n-1} , \tag{22}$$

where $\Gamma(z)$ is the gamma function. When we substitute Eq. (21) into Eq. (11), the Laplace transform of the relaxation function $\phi(t)$ is

$$\phi^*(u) = \lambda_n u^n / (1 - \lambda_n u^{-1+n}) . \tag{23}$$

This, in turn, when substituted into Eqs. (17) and (2), gives the noise spectrum of

$$S_N(\omega) = \frac{4\langle \Delta N^2 \rangle}{\Omega} \operatorname{Re} \int \frac{dk}{2\pi} (1/\{i\omega + (\lambda_n c_0^2/2)k^2(i\omega)^n/[1 - \lambda_n(i\omega)^{n-1}]\}) \left| \int_{-l}^l dx e^{ikx} \right|^2 . \tag{24}$$

Here the one-dimensional diffusion is in a sample of length $2l$. For frequencies sufficiently high that $|\lambda_n i\omega^{n-1}| \ll 1$, $S_N(\omega)$ simplifies to

$$S_N(\omega) = (8\langle \Delta N^2 \rangle/\pi\Omega) \operatorname{Re} \int dk (\sin^2 kl/k^2)/[i\omega + (\lambda_n c_0^2/2)k^2(i\omega)^n] . \tag{25}$$

The expression can be evaluated by contour integration. The mathematics are detailed in Appendix B. On introducing a natural frequency

$$\omega_n = (\lambda_n c_0^2/4l^2)^{1-n} \tag{26}$$

the noise spectrum is given by

$$S_N(\omega) = 2(\lambda_n c_0^2/2)^{1/2} (\langle \Delta N^2 \rangle/\Omega) [\cos(n\pi/2)/\cos(\phi_n/2)] \omega^{(-3+n)/2} \times (1 - e^{-\theta_n \cos(\phi/2)} \{ \cot(\phi_n/2) \sin[\theta_n \sin(\phi_n/2)] + \cos[\theta_n \sin(\phi_n/2)] \}) , \tag{27}$$

where $\phi_n = (\pi/2)(1 - n)$, $\theta_n = (\omega/\omega_n)^{(1-n)/2}$. This expression is evaluated numerically for several representative values of n between zero and unity and the results are displayed in Fig. 1.

For the $n = 0$ case the result is the same as that of one-dimensional classical diffusion with the high frequency ($\omega \gg \omega_0$) asymptotic $\omega^{-3/2}$ law and the turnover to $\omega^{-1/2}$ behavior at $\omega \ll \omega_0$.³⁵ Note that when $n = 0$, λ_0 in Eq. (26) is the same as that in Eq. (13) and, similar to the result of Eq. (15) for

three dimensions, the one-dimensional diffusion constant $D_0 = \lambda_0 c_0^2/2$. Hence ω_0 in Eq. (26) is just $D_0/2l^2$, identical to the natural frequency of the classical diffusion problem.^{37,39} In fact, not only ω_0 but the entire expression in Eq. (27) reduces to the corresponding one in classical diffusion.^{37,39}

For $n \neq 0$, the high-frequency Lax's $\omega^{-3/2}$ law is modified, as well as the low-frequency $\omega^{-1/2}$ behavior as can be seen from Fig. 1. These modified asymptotic behaviors for $S_N(\omega)$ are given

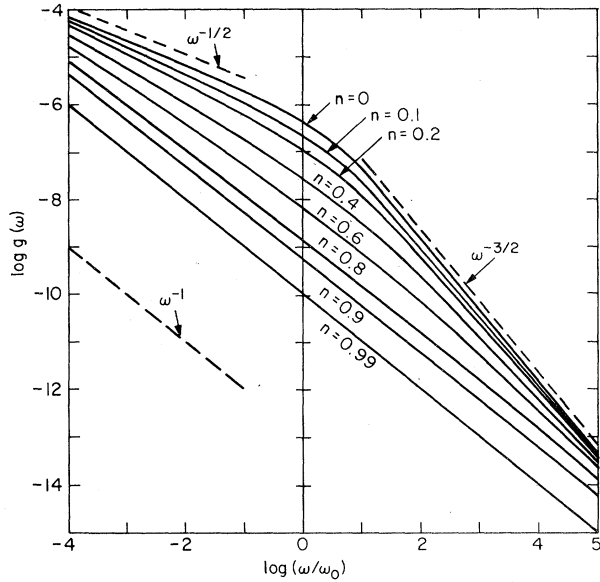


FIG. 1. The noise spectra $g(\omega)$ numerically evaluated for several representative values of n between zero and one. Except for the multiplicative constant $\Omega\tau_0^{1/2}/\langle\Delta N^2\rangle^{1/2}\Delta_0$, $g(\omega)$ is essentially $S_N(\omega)$ given by Eq. (27). We have chosen $E_c = 10^9$ Hz and $\omega_0 = 10^4$ Hz when evaluating $g(\omega)$. Note that $n = 0$ recaptures the classical result and as n increases towards unity, the noise spectrum becomes increasingly $1/f$ -like.

analytically by

$$S_N(\omega) = \begin{cases} \Lambda_n(\omega/\omega_n)^{-(3-n)/2}, & \omega \gg \omega_n \\ (\Lambda_n/2)(\omega/\omega_n)^{-(1+n)/2}, & \omega \ll \omega_n \end{cases} \quad (28a)$$

with

$$\Lambda_n = 2(\lambda_n c_0^2/2)^{1/2} [\cos(n\pi/2)/\cos(\phi/2)] \langle\Delta N^2\rangle/\Omega \quad (28c)$$

It can be seen from Eqs. (28a) and (28b) that starting from zero as n increases towards unity, both the high-frequency and the low-frequency noise power exponents $(n-3)/2$ and $(-1+n)/2$, respectively, approach -1 . This behavior can be seen at a glance from Fig. 1. Thus we have found $1/f$ spectra of many decades in our dispersive diffusion transport model. It is important to emphasize that this dispersive diffusion transport model, Eqs. (12), (11), and (4), is one element among many of a unified theory of low-frequency (long-time) fluctuation-dissipation properties of condensed matter. We have already seen remarkable successes of the unified theory in accounting for experimental data

when applied to several areas other than diffusion, including⁴⁻¹² dielectric relaxation, NMR spin-lattice relaxation, voltage noise, $1/f$ mobility fluctuations, viscoelastic relaxations, and dispersive transient transport. These successes should lend support for our results [Eqs. (27) and (28)] for diffusion noise, which is just another application of the unified theory. Most intimately related to the present subject of dispersive diffusion transport is dispersive transient transport. Evidence of this intimate relationship can be found in Eq. (12) which contains both dispersive diffusion and dispersive transport described by the same memory function whose origin is attributed to the infrared-divergent excitation of correlated states accompanying transitions of a primary species, which in this case is carrier hopping. A brief discussion of dispersive transient transport will be given later in this section. Our earlier works^{4,6,10-12} on dispersive transient transport based on the unified theory not only can account for the time dependences of the transient current, but also predicts a relation between the activation energy of the "transit time" and the microscopic activation energy for hopping. This latter quantitative relation has been verified^{4,6,10-12} in α -As₂Se₃, α -Si, and α -SiO₂. The good agreement between theory and experiment in dispersive transport should give an additional boost to our confidence in the results we derive here for dispersive diffusion, its closest relative in the family of low-frequency responses that have been treated by our unified theory.

Let us examine the noise spectra also in the regime of very long times when the fractional exponential function dominates the time dependence of $\psi(t)$ in Eq. (4). In this case of $t \rightarrow \infty$ ($u \rightarrow 0$) the fractional exponential ensures that the entire $\psi(t)$ has finite moments

$$\langle t^m \rangle = \int_0^\infty t^m \psi(t) dt \quad (29)$$

for any positive nonzero integer m . Then, it follows that

$$\lim_{u \rightarrow 0} \psi^*(u) = 1 - u \langle t \rangle + (u^2/2) \langle t^2 \rangle + (\dots), \quad (30)$$

where the ellipsis indicates higher-order terms in u and, from Eq. (11),

$$\lim_{u \rightarrow 0} \phi^*(u) \cong 1/\langle t \rangle \quad (31)$$

where for $\psi(t)$ of Eq. (5)

$$\langle t \rangle = \Gamma(1 + 1/(1-n)) a^{-1/(1-n)}. \quad (32)$$

If τ_0 in Eqs. (4) and (5) is thermally activated with activation energy E_A , such that $\tau_0 = \tau_\infty \exp(E_A/kT)$, then

$$\langle t \rangle = [(1-n)e^{-n\gamma E_c^n \tau_\infty}]^{1/(1-n)} \times e^{-E_A^*/kT} \Gamma(1 + 1/(1-n)) . \quad (33)$$

Here an apparent activation energy

$$E_A^* = E_A/(1-n) \quad (34)$$

governs the temperature dependence of $\langle t \rangle$. The noise spectrum from Eqs. (17)–(20) is now

$$S_N(\omega) = 4(\langle \Delta N^2 \rangle / \Omega)(c_0^2 / \pi \langle t \rangle) \times \int dk \{ \sin^2 kl / [\omega^2 + (k^2 c_0^2 / 2 \langle t \rangle)^2] \} . \quad (35)$$

Expression (35) can be evaluated with the result

$$S_N(\omega) = 32(\langle \Delta N^2 \rangle / \Omega)(l^3 \langle t \rangle / c_0^2)(\omega / \omega_0)^{-3/2} \times [1 - e^{-\theta}(\cos\theta + \sin\theta)] , \quad (36)$$

where

$$\theta = (\omega / \omega_0)^{1/2} \quad (37)$$

$$\omega_0 \equiv D / 2l^2 = c_0^2 / 4l^2 \langle t \rangle . \quad (38)$$

The noise spectrum as given by Eq. (36) is identical in form to that for the noise spectrum of classical diffusion. In other words, at very long times or very low frequencies, for any n value between 0 and 1 the noise for non-Markovian diffusion [Eqs. (12), (11), and (4) with $n \neq 0$] will have a noise spectrum that is the same as that of classical Markovian diffusion. For a fixed value of $n \neq 0$, the times (or $1/\omega$) should be $\gg t_p = a^{-1/(1-n)}$ and from Eq. (5b) we can see that if $E_c \tau_0 \gg 1$, then t_p can be so long that the result of Eq. (36) holds only at exceedingly low frequencies, especially if n approaches unity. As an example, for $\tau_0 \cong 10^{-6}$ sec, $E_c \cong 10^{11}$ sec $^{-1}$ and $n = 0.7$, then $t_p \cong 10^5$ sec and Eq. (46) starts to hold only for $\omega \ll 10^{-5}$ Hz. In the special case when n is unity, we have seen already (Fig. 1) that a $1/f$ spectrum emerges for many many decades. At the same time $t^p \rightarrow \infty$ if $E_c \tau_0 \gg 1$, and the noise spectrum never returns to the classical result of Eq. (36) for all practical purposes.

B. Modification of Einstein's formula $\langle r^2 \rangle = 6D_0 t$

In condensed matter one often has the occasion to consider diffusive transport or migration of particles or electronic excitations. In our physical picture the

diffusive transport that involves carrier hopping from site to site or electronic excitation jumping from one molecule to another (such as the Förster mechanism⁴⁰) will inevitably excite correlated states in an infrared-divergent manner and lead to a distribution of event times as given by Eqs. (4) and (5). Thus necessarily, if $n \neq 0$, the diffusion transport becomes non-Markovian and one can expect that the classical results of diffusion such as the Einstein's^{19,39} formula $\langle r^2 \rangle = 6D_0 t$ may be modified. We shall investigate what this modification will be for our $\psi(t)$.

The mathematical details are relegated to Appendix C. The result given by Eqs. (C9) and (C10), is

$$\langle r^2(t) \rangle = 6D_n t^{1-n} \quad (39)$$

with

$$D_n = \lambda_n c_0^2 / 6\Gamma(2-n) . \quad (40)$$

Note that when $n \rightarrow 0$, $D_n \rightarrow D_0 = \lambda_0 c_0^2 / 6$ is the classical diffusion constant in three dimensions [see the discussions following Eq. (27)], and Eq. (39) reduces to the original Einstein's equation of $\langle r^2(t) \rangle = 6D_0 t$. However, when $n \neq 0$ the Einstein equation does not apply but is modified to the form given by Eq. (39). When n approaches unity, the modification is so severe that $\langle r^2(t) \rangle$ is no longer dependent on time.

For very long time $t \gg t_p$ when the fractional exponential dominates the time dependence of $\psi(t)$, we follow the developments and results from Eq. (26) to Eq. (31). The Fourier-Laplace transform of the Green's function now is

$$\tilde{G}^*(\vec{k}, u) = [u + (c_0^2 / 6 \langle t \rangle) k^2]^{-1} \quad (41)$$

and

$$\langle r^2(t) \rangle = (c_0^2 / \langle t \rangle) t . \quad (42)$$

If we rewrite it in the standard form of

$$\langle r^2(t) \rangle = 6C_n t , \quad (43)$$

then C_n can be expressed in terms of λ_n through Eqs. (22) and (32) and has the form

$$C_n = \{ [(1-n)\Gamma(1-n)]^{1/(n-1)} / \Gamma(1 + 1/(1-n)) \} \times (\lambda_n^{1/(1-n)} c_0^2 / 6) . \quad (44)$$

The diffusion coefficient C_n has the apparent activation energy E_A^* of Eq. (34) if the hopping process is thermally activated with activation energy E_A . C_n should be contrasted with D_n in Eq. (39) which has activation energy E_A . The important result is that at very long times, the original Einstein equation

holds again, although the diffusion constant C_n is no longer $\lambda_0 c_0^2/6$. This behavior of the return at very long times of the validity of the description of diffusion by a conventional Markovian diffusion equation, is consistent with a conjecture made by Haan and Zwanzig.⁴¹ It is pleasing that we can derive this from our $\psi(t)$.

C. Generalized Nernst-Einstein relation

The Nernst-Einstein relation between the diffusion constant D_0 and mobility μ_0 is given by³⁹

$$\mu_0/D_0 = e/kT \quad (45)$$

In our physical picture, to encompass the diffusion process in all forms of condensed matter one must necessarily consider the $n \neq 0$ non-Markovian transport Eq. (12) caused by $\psi(t)$ of Eq. (4). We have seen in Sec. II B that the t^{-n} dependence of $\psi(t)$ modifies the Einstein formula in accordance with Eq. (39) which, in one dimension, is rewritten here as

$$\langle x^2 \rangle = 2D_n t^{1-n} \equiv 2\hat{D}_n(t)t \quad (46)$$

The last identity formally rewrites the result in the original form of Einstein, but now the new diffusion constant \hat{D}_n is time dependent, corresponding to the transient situation and given by

$$\begin{aligned} \hat{D}_n(t) &= [\lambda_n c_0^2 / 2\Gamma(2-n)]t^{-n} \\ &\equiv [D_0(1-n)e^{-n\gamma}\Gamma(1-n)/\Gamma(2-n)]t^{-n} \end{aligned} \quad (47)$$

The corresponding $n \neq 0$ non-Markovian transient transport in the presence of an electric field E is derived in Appendix D. Again the mathematical details are relegated to Appendix D where we have derived the result of

$$\langle x(t) \rangle = 2c_0 b E \lambda_n t^{1-n} / \Gamma(2-n) \quad (48)$$

We can then define a generalized transient mobility by

$$\begin{aligned} \mu_n(t) &\equiv \left[\left[\frac{d\langle x(t) \rangle}{dt} \right] / E \right] \\ &= \left[\frac{2(1-n)c_0 b \lambda_n}{\Gamma(2-n)} \right] t^{-n} \end{aligned} \quad (49)$$

When $n = 0$, infrared divergence is suppressed and the result (49) reduces to the classical time-independent mobility μ_0 which is

$$\mu_0 = 2c_0 b \lambda_0 / \Gamma(2) \quad (50)$$

Hence we have

$$\mu_n(t) = \mu_0 [(1-n)^2 e^{-n\gamma} \Gamma(1-n) / \Gamma(2-n)] t^{-n} \quad (51)$$

With the results for $\hat{D}_n(t)$ and $\mu_n(t)$ as given by Eqs. (47) and (51), we readily see through Eq. (44),

$$\mu_n(t) / \hat{D}_n(t) = (1-n)\mu_0 / D_0 = (1-n)e / kT \quad (52)$$

Equation (52) is the generalized Nernst-Einstein relation between mobility and diffusion coefficient. Except for the factor $(1-n)$, it is identical in form to the original Nernst-Einstein relation, but now the transient diffusion coefficient \hat{D}_n is introduced formally.

III. DIFFUSION-CONTROLLED REACTION AND RECOMBINATION

In various areas of physics, biophysics, and chemical physics, reaction or recombination occurs through diffusion of one reactant or both reactants to some special sites, or to encounter each other. The reaction or recombination rate and its time dependence are controlled by the diffusion process.^{42,43} There has been a continued interest in this class of problems²⁰⁻²⁵ which is most appropriately handled by the mathematics of random walks²⁰ or continuous-time random walks on lattices.²¹ However, the physics behind the mathematics without exception is attributed to some randomness of one kind or another, including intersite hopping distance and trap depths. The assumed randomness will then introduce a broad distribution of event times, which for hopping diffusion motions is characterized by the probability function $\psi(t)$ defined earlier. In this section we reconsider these problems in the light of our universal $\psi(t)$ as given by Eq. (4).

Unimolecular and bimolecular reactions are best treated by a stochastic master equation⁴⁴ obeyed by the probability P of the random variable number (numbers) of reactant (reactants) in the system at time t . Shlesinger²³ has given a clear exposition of the problems involved in the calculations of the reaction rate $K(t)$, a conditional probability distribution, which is related to an unconditional one, $F(t)$. Both $K(t)$ and $F(t)$ are first-encounter distributions appropriate for irreversible reaction, but $F(t)$ is immediately amenable to calculation by the continuous-time random-walk (CTRW) formalism

of Montroll and Weiss²¹ once the jump-time distribution is specified. A detailed discussion of the mathematics involved can be found in Appendix E. This has been carried out for unimolecular (UM) and pseudounimolecular (PUM) reaction.²³ We have rederived the result [see Eq. (E18) in Appendix E], which in the notation of Montroll is^{20,22} (Laplace transform):

$$F(t) = [1/(V-1)] \{ [1 - \psi_n^*(u)] \times G(\vec{0}, z = \psi_n^*(u)) \}^{-1} - 1, \quad (53)$$

where $G(\vec{0}, z)$ for $\vec{1} = \vec{0}$ that has already been

$$G(0, z = \psi^*(u)) = [V(1 - \psi^*(u))]^{-1} + \frac{1}{V} \sum_{k_1=0}^{N-1} \sum_{k_2=0}^{N-1} \sum_{k_3=0}^{N-1} \{ [1 - \psi^*(u)] [\cos(2\pi k_1 N) + \cos(2\pi k_2 N) + \cos(2\pi k_3 N)] \}^{-1}, \quad (54)$$

where the prime at the summation signs means that the origin $k_1 = k_2 = k_3 = 0$ is to be omitted.

We consider first a bimolecular reaction $A + B \rightarrow C$ where $N_A(t=0) = N_B(t=0)$ and the A 's diffusing so slowly compared with the B 's that the A 's can be considered stationary at the origins of their unit cells. This is appropriate for electron-hole recombination²⁹ in a -Si:H where, although both electrons and holes diffuse, they have very different mobilities. The stochastic master equation approach leads to the equation for bimolecular decay (see Appendix E):

$$\frac{d \langle N_A(t) \rangle}{dt} = -K(t) \langle N_A(t) \rangle^2. \quad (55)$$

From the mathematics of CTRW it is more direct to calculate $F(t)$. $K(t)$ can be obtained once $F(t)$ is known through the relation [see Eq. (E7)]

$$K(t) = F(t) / \int_t^\infty F(\tau) d\tau. \quad (56)$$

At very long times $t \rightarrow \infty$ ($u \rightarrow 0$) we can readily obtain $\psi_n^*(u)$ by the expansion

$$\psi_n^*(u) = 1 - u \langle t \rangle + \frac{1}{2} u^2 \langle t^2 \rangle + \dots,$$

where $\langle t^p \rangle \equiv \int t^p \psi_n(t) dt$. Substitution into Eq. (5) yields

$$F(t) = [1/(VW)^{1-n}] (1-n) a_n t^{-n} \times \exp(-\{ [1/(VW)^{1-n}] a_n t^{1-n} \}). \quad (57)$$

evaluated for various lattices, extending it to consider bimolecular (BM) reaction, which has not been done before. Here we follow Shlesinger²³ and divide the system into $N_A(t=0)$ identical unit cells each containing V sites, one A reactant at its origin and one B reactant which at $t=0$ has equal probability of occupying all sites in the unit cell except the origin.

The random-walk-generating function $G(\vec{0}, z)$ as it appeared in Eq. (2) has already been evaluated by Montroll^{20,22} for various lattices in different dimensions. Hence we can obtain $F(t)$ by substitution of the Laplace transform $\psi^*(u)$ of our model $\psi_n(t)$ into Eq. (2). For a simple cubic lattice it has been shown that

Here W is the Watson integral which for a simple cubic lattice has the value of 1.516. It then follows from Eq. (56),

$$K(t) = [1/(VW)^{1-n}] (1-n) a_n t^{-n}. \quad (58)$$

This is exactly the same as the time-dependent bimolecular recombination rate $K(t) = Bt^{-n}$ as assumed by Vardeny *et al.*²⁹ which gives, as they have already shown, a good account of the time dependence of the electron-hole recombination decay in a -Si:H.

The rate equation for $a_n t^{1-n} \gg 1$ is

$$\frac{d \langle N_A(t) \rangle}{dt} = - \frac{1}{(VW)^{1-n} N_B(0)} (1-n) a_n t^{-n} \langle N_A(t) \rangle^2 \quad (59)$$

Solution to Eq. (59) is given by

$$\langle N_A(t) \rangle \sim N_A(0) (VW)^{1-n} / a_n t^{1-n} \quad (60)$$

for $t \rightarrow \infty$.

In contrast, the Scher and Montroll^{27,28} form of $\psi(t) \propto A [\Gamma(1-\alpha)]^{-1} t^{-1-\alpha}$ at large times gives

$$F(t) = [\alpha A W V / \Gamma(1-\alpha)] t^{-1-\alpha} \quad (61)$$

and, from Eq. (E7)

$$K(t) = \alpha t^{-1}. \quad (62)$$

For pseudounimolecular reaction it follows then

$$\langle N_A(t) \rangle = N_A(0) \{ [A W V / \Gamma(1-\alpha)] t^{-\alpha} \}^M. \quad (63)$$

This result has been obtained by Shlesinger.²³ For bimolecular reaction, the expression (62) for $K(t)$ implies that

$$\langle N(t) \rangle \propto [\alpha \ln(t/t_i)]^{-1} \quad (64)$$

with t_i a constant. These differences between the predictions of our $\psi(t)$ and that of Scher and Montroll's²⁷ will now be discussed in conjunction with experimental data of dispersive diffusion²⁹ and dispersive transient transport in *a*-Si:H.

In amorphous Si dispersive transient transport has been observed⁴⁵⁻⁴⁷ in time-of-flight drift-mobility experiments. The observed transient current $I(t)$ has the characteristic t^{-n} dependence for $t \ll t_\tau$ where t_τ is the "transit time" and the $t^{-(2-n)}$ dependence for $t \gg t_\tau$ in accordance with the CTRW theory of Scher and Montroll³⁰ based on their $\psi(t)$. This same characteristic of $I(t)$ follows also from our $\psi(t)$. A derivation of the t^{-n} dependence for $t \ll t_\tau$ has been given in Sec. II C (see also Ref. 12). The absorbing electrode boundary will give the $t^{-(2-n)}$ behavior for $t \gg t_\tau$. Thus both our $\psi(t)$ of Eq. (4) and that of Scher and Montroll can account for the dispersive transient transport. There is one important difference. Our prediction on the transit time t_τ is that its activation energy is given by an apparent activation energy E_a^* related to the microscopic activation energy E_A via Eq. (34). This prediction is in agreement^{4,6,10-12}

with experimental data on *a*-SiO₂ and *a*-As₂Se₃.

Recently, evidence for dispersive diffusion of electrons in *a*-Si:H has been found in diffusion-controlled electron-hole (bimolecular) recombination studies by Vardeny *et al.*²⁹ They found that the observed time evolution of the photoinduced midgap absorption can be explained by bimolecular recombination [Eq. (E6)] with time-dependent rate $K(t)$ of the form Bt^{-n} and that n has the same value as that determined by transient transport measurements.^{45,46} The latter strongly suggests that both dispersive diffusion and transient transport are due to the same cause. Thus one expects that any model which can describe transient transport must also be able to derive the dispersive diffusion-controlled bimolecular recombination rate $K(t) = Bt^{-n}$. We have seen that our model based on $\psi(t)$ of Eq. (4) fulfills this expectation while Scher and Montroll's model based on their $\psi(t) \propto t^{-1-\alpha}$ does *not*. Their model gives $K(t) = \alpha t^{-1}$ and the decay follows Eq. (64) which is different from the observed time dependence by Vardeny *et al.*²⁹ In actual experiments²⁹ the $N_A(0)$ depends on the distance x from the sample surface due to the attenuation $e^{-\alpha_L x}$ of the exciting laser light in a sample of thickness d such that $N_A(0, x) = N_A(0) \exp(-\alpha_L x)$. Then the bimolecular reaction Eq. (60) must be integrated over x as well. This being taken into account and in terms of a reduced time $\tau = t a_n^{1/(1-n)}/VW$, the $\psi_n(t)$ model predicts that

$$\langle N_A(t) \rangle = [N_A(0)/(1-n)\tau^{1-n}] \ln\{ (1 + \tau^{1-n})/[1 + \tau^{1-n} \exp(-\alpha_L d)] \} ,$$

in agreement with the results of Vardeny *et al.*²⁹ and their experimental data of excess carrier recombination in *a*-Si:H. On the other hand, the ψ_{SM} model with $\psi_{SM} = t^{-1-\alpha}$ gives

$$N_A(t) = [\alpha_L \alpha \ln(t/t_0)] \ln\{ [1 + \alpha N_0 \ln(t/t_0)]/[1 + \alpha N_0 \ln(t/t_0) \exp(-\alpha_L d)] \} ,$$

where $N_0 = N_A(t = t_0)$ and t_0 is a reference time. This prediction of the ψ_{SM} model is in contradiction with experimental data.

The failure to derive both transient transport and dispersive diffusion-controlled bimolecular recombination from Scher and Montroll's $\psi(t)$ will cast doubt on the general applicability of their assumption of $\psi(t) \propto t^{-1-\alpha}$ for $t \rightarrow \infty$. This remark applies also to an exponential-distribution-of-traps model⁴⁸ which uses a distribution of release times of the form $t^{-1-\alpha}$.

For pseudomolecular reaction, it follows from Eqs. (E10)–(E12) and the expression for $F(t)$ as given by Eq. (57) that the reaction rate at long times according to the ψ_n model is given by

$$K_M(t) = [M/(VW)^{1-n}](1-n)a_n t^{-n} \quad (65)$$

and

$$\langle N_A(t) \rangle = N_A(0) \exp(-\{ [M/(VW)^{1-n}] a_n t^{1-n} \}) . \quad (66)$$

These results for pseudomolecular reaction have been obtained earlier by Shlesinger.²³ Shlesinger²³ was motivated by the same ideas of Scher and Montroll²⁷ that randomness such as intersite hopping distance will introduce a distribution of event times. Previously it has been proposed that the hopping-time distribution $t^{-1-\alpha}$ of Scher and Montroll [see Eq. (9)] is rather universal for randomness as evidenced by the successes of Eq. (9) when applied to dispersive transient transport. However the use of $t^{-1-\alpha}$ distribution in pseudomolecular (and also in

bimolecular) reaction fails to obtain $K(t) = Bt^{-n}$, a result which is required in order to explain the electron scavenging data in glasses of Miller⁴² and of Baxendale and Sharpe.⁴³ These are pulse radiolysis experimental results on the decay of trapped electrons in aqueous glasses by reaction with impurity molecules whose concentration is much larger than that of the electrons ($M \gg 1$). Apparently this is the reason for Shlesinger²³ to seek another trial hopping-time distribution function. It is a happy coincidence that he has chosen the fractional exponential form that we have derived from our fundamental physical picture. In another example of photoluminescence decay in *a*-Si:H, this prediction is also in accord with the short-time decay data. This has been pointed out by Vardeny *et al.*²⁹

IV. SUMMARY AND CONCLUSIONS

In this work we have extended our unified theory of low-frequency (long-time) fluctuation-dissipation properties of condensed matter to the consideration of several problems that are connected with diffusion. The entire consideration is based on the same universal correlation function $\psi(t)$ that has been derived microscopically and applied successfully in several areas of low-frequency responses. The important results we have derived here include (1) the emergence of $1/f$ spectrum for diffusion transport; (2) a modification of Einstein's formula $\langle r^2 \rangle = 6D_0t$; (3) time-dependent diffusion coefficient and time-dependent transient mobility; (4) a generalized Nernst-Einstein relation between the time-dependent diffusion coefficient and transient mobility; and (5) diffusion-controlled unimolecular and bimolecular reaction rate and its time dependence that is in accord with experimental data. We have also contrasted these results with the corresponding ones that follow from Scher and Montroll's model with their $\psi(t)$ of $t^{-1-\alpha}$ for large times. Somewhat surprisingly, Scher and Montroll's $\psi(t)$ fails to reproduce the observed behavior of both the bimolecular electron-hole recombination decay and the unimolecular photoluminescence decay in *a*-Si:H which shows also dispersive transient transport. Reinterpretation⁴⁸ of the dispersive transient transport in *a*-Si:H by thermalization of electrons in an exponential distribution of traps has arrived at a $\psi(t)$ of $t^{-1-\alpha}$, and hence it cannot account for the recombination decay.²⁹ On the other hand, our $\psi(t)$ can reproduce all these three features.

This paper is intended for the presentation of the derivations of the results of our unified model when specialized to diffusion. Needless to say, there is a large amount of experimental data on various aspects of diffusion. We shall make contact with the experimental data in the future. It is expected that analyses of diffusion, with the unreserved belief in the validity of the classical diffusion equation and its consequences such as the original Einstein's formula, may have to be reexamined in the framework of our present theoretical predictions. Diffusion is a very common phenomenon in condensed matter. It occurs in metal, semiconductors, insulators, polymers, liquids, biochemical, and organic substances. Our predictions are characterized by a single parameter n , the infrared-divergence exponent, and $0 \leq n < 1$. Starting from $n = 0$ which recaptures the classical diffusion phenomena, as n increases and at each n we have well-defined predicted modifications of the classical results. Such easy access to the theoretical results will facilitate the comparison between theory and experiments in the future.

ACKNOWLEDGMENT

This work was supported in part by ONR.

APPENDIX A: MATHEMATICAL TOOLS OF CTRW

In this appendix we collect only the mathematics of the CTRW description of Montroll and Weiss^{20,21} that we use throughout the remainder of this paper. These mathematical results are stated without proof or derivation. The purpose of this is to help the reader for easy access to the necessary mathematics and for accurate reference to the specific results we invoke from the CTRW literature.

Random walk at regular time intervals on a periodic lattice $\{l\}$ can be handled through the random-walk generating function $G(l, z)$ defined as^{20,21}

$$G(l, z) = \sum_{n=0}^{\infty} z^n P_n(l) , \quad (\text{A1})$$

where $P_n(l)$ is the probability that a walker is at lattice site l after n steps. $G(l, z)$ satisfies

$$G(l, z) - z \sum p(l, l') G(l', z) = \delta_{l,0} , \quad (\text{A2})$$

where $p(l, l')$ = probability for walk from l' to l (independent of time). The form for $G(l, z)$ on an s -dimensional finite lattice of N^s lattice points with periodic boundary conditions is

$$G_N(l, z) = N^{-s} \sum_{\vec{k}} \exp \left[\frac{-2\pi i \vec{k} \cdot \vec{l}}{N} \right] / \left[1 - z \lambda \left[\frac{2\pi \vec{k}}{N} \right] \right] , \quad (\text{A3})$$

where $\vec{k} = \{k_1, \dots, k_j, \dots, k_s\}$ with k_j being integers and $0 \leq k_j \leq N-1$. The structure function $\lambda(2\pi\vec{k}/N) = \sum_l p(l) \exp(i\vec{k} \cdot \vec{l})$. $G_N(l, z)$ can be expressed as a sum of a singular and nonsingular part^{20,22}

$$G_N(l, z) = 1/N^s(1-z) + \phi(l, z) . \quad (\text{A4})$$

For infinite unit cell or lattice ($N \rightarrow \infty$), the singular part vanishes as N^{-s} but $\phi(z, l)$, which then becomes identical to $G(z, l)$, develops new singularity of a weaker type such as in one dimension and in three dimensions it even converges as $z \rightarrow 1$. For example, in one dimension $G(0, z) = (1-z^2)^{-1/2}$, and in a simple cubic lattice

$$G(0, z) \cong 1.516 - (3/\pi)(3/2)^{1/2}(1-z^2)^{1/2} + \dots$$

We will also be interested in the concept of first-passage time. If $F_n(l)$ is the probability that random walker reaches the point l for the first time after step n , the generating function of the $F_n(l)$ is²⁰⁻²²

$$F(l, z) = \sum_{n=1}^{\infty} F_n(l) z^n . \quad (\text{A5})$$

The generating functions $G(l, z)$ and $F(l, z)$ satisfy

$$F(l, z) = [G(l, z) - \delta_{l,0}]/G(0, z) . \quad (\text{A6})$$

The generating function $F(l, z)$ for the special case of an s -dimensional finite lattice of N^s lattice points will be denoted by $F_N(l, z)$.

CTRW is introduced by Montroll and Weiss to consider the situation when the jumps do not occur at regular time intervals, but are made according to the hopping-time distribution function $\psi(t)$ such as those given by Eq. (5) and Eq. (9). In CTRW we

are interested in functions like $\bar{P}(l, t)$ and $\bar{F}(l, t)$, the probability of *being at* l at time t and the probability for *reaching* l for the first time at time t , respectively. Montroll and Weiss have shown^{21,22}

$$\bar{P}(l, t) = \int_0^t Q(l, \tau) \Psi(t - \tau) d\tau , \quad (\text{A7})$$

where $\Psi(t) = \int_t^{\infty} \psi(\tau) d\tau$ is the probability that walker remains fixed in time interval $(0, t)$, and $Q(l, t)$ is the probability density for the random walk to *reach* l at time t (not necessarily for the first time). The Laplace transform $Q^*(l, u)$ is related to the generating function $G(l, z)$ defined by Eq. (A1) as

$$Q^*(l, u) = G(l, z = \psi^*(u)) \quad (\text{A8})$$

where

$$\psi^*(u) = \int_0^{\infty} e^{-ut} \psi(t) dt . \quad (\text{A9})$$

It then follows from Eqs. (A7) and (A8) that the Laplace transforms of $\bar{P}(l, t)$ are simply related to $G(l, z)$ by

$$\bar{P}^*(l, u) = G(l, z = \psi^*(u)) [1 - \psi^*(u)] / u . \quad (\text{A10})$$

Similarly the Laplace transform of $\bar{F}(l, t)$ can be expressed in terms of the generating function $F(l, z)$ of Eqs. (A5) and (A6) as

$$\bar{F}^*(l, u) = F(l, z = \psi^*(u)) . \quad (\text{A11})$$

Again, whenever specialized to an s -dimensional unit cell or lattice of N^s lattice points, the functions \bar{P} , Q , and \bar{F} will be denoted by \bar{P}_N , Q_N , and \bar{F}_N for clarity because we shall have to distinguish the cases for N finite and for N infinite in the long-time behavior in later sections.

APPENDIX B

We have the following:

$$S_N(\omega) = (8\langle \Delta N^2 \rangle / \pi \Omega) \text{Re} \int dk [(\sin^2 kl) / k^2] / [i\omega + (\lambda_n c_0^2 / 2) k^2 (i\omega)^n] . \quad (\text{B1})$$

Taking the real part of the integrand and letting $A = \lambda_n c_0^2$, one can obtain

$$S_N(\omega) = (8\langle \Delta N^2 \rangle / \pi \Omega) [\cos(n\pi/2) / A \omega^n] \int dk (\sin^2 kl) / \{ k^4 + k^2 \omega^{1-n} [\sin(n\pi/2) / A + (\omega^{1-n} / A)^2] \} . \quad (\text{B2})$$

The roots of the denominator of the integrand are

$$k = \pm i (\omega^{1-n} / A)^{1/2} e^{\pm i\phi/2} . \quad (\text{B3})$$

Applying the residue theorem and defining $\omega_n = (A/2l^2)^{1-n}$, one can obtain Eq. (27).

APPENDIX C

In three dimensions the non-Markovian diffusion equation from Eq. (12) is

$$\frac{\partial \rho(\vec{r}, t)}{\partial t} = \frac{c_0^2}{6} \int_0^t \phi(t - \tau) \nabla^2 \rho(\vec{r}, \tau) d\tau . \quad (C1)$$

The Green's function for Eq. (C1) satisfies

$$\frac{\partial G(\vec{r}, t)}{\partial t} = \frac{c_0^2}{6} \int_0^t \phi(t - \tau) \nabla^2 G(\vec{r}, \tau) d\tau + \delta(t) \delta(x) . \quad (C2)$$

In the same manner as in going from Eq. (16) to Eq. (17), we get

$$\tilde{G}^*(\vec{k}, u) = [u + c_0^2 k^2 \phi^*(u)/6]^{-1} . \quad (C3)$$

In the earlier-time regime when $\psi(t) \propto t^{-n}$,

$$\tilde{G}^*(\vec{k}, u) \cong [u + (\lambda_n c_0^2 / 6) k^2 u^n]^{-1} \quad (C4)$$

provided that $\lambda_n u^{-1+n} \ll 1$. By definition

$$\tilde{G}^*(\vec{k}, u) = \int_0^\infty dt e^{-ut} \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} G(\vec{r}, t) \quad (C5)$$

which, when the factor $\exp(-i\vec{k} \cdot \vec{r})$ is expanded in powers of $(\vec{k} \cdot \vec{r})$, gives the term that is proportional to $(\vec{k} \cdot \vec{r})^2$ as

$$\begin{aligned} I_2 &= \frac{k^2}{6} \int_0^\infty dt e^{-ut} \int d\vec{r} r^2 G(\vec{r}, t) \\ &= -\frac{k^2}{6} \int_0^\infty dt e^{-ut} \langle r^2(t) \rangle . \end{aligned} \quad (C6)$$

The last equality follows from the physical meaning of the Green's function $G(\vec{r}, t)$. To solve for $\langle r^2(t) \rangle$ we expand in powers of k^2 the result (39) for $\tilde{G}^*(\vec{k}, u)$ which gives

$$\tilde{G}^*(\vec{k}, u) = u^{-1} [1 - (\lambda_n c_0^2 / 6) u^{n-1} k^2 + \dots] . \quad (C7)$$

On comparing Eq. (C7) with Eq. (C6) for the k^2 term, we obtain

$$\frac{1}{6} \int_0^\infty dt e^{-ut} \langle r^2(t) \rangle = \frac{\lambda_n c_0^2}{6} u^{n-2} . \quad (C8)$$

Inverse Laplace transform of Eq. (C6) gives

$$\langle r^2(t) \rangle = 6D_n t^{1-n} \quad (C9)$$

with

$$D_n = \lambda_n c_0^2 / 6\Gamma(2 - n) . \quad (C10)$$

APPENDIX D

We consider the Green's-function equation

$$\begin{aligned} \frac{\partial G(x, t)}{\partial t} &= -2c_0 b E \int_0^t d\tau \phi(t - \tau) \frac{\partial G(x, \tau)}{\partial x} \\ &+ \delta(t) \delta(x) \end{aligned} \quad (D1)$$

and its Fourier-Laplace transform $\tilde{G}^*(k, u)$ which can be solved by the same transforms of Eq. (D1) and is given by

$$\tilde{G}^*(k, u) = [u + 2c_0 b E i k \phi^*(u)]^{-1} . \quad (D2)$$

In the time domain where $\psi(t) \propto t^{-n}$ and its expression together with its Laplace transform is given as in Eqs. (21) and (22), then ϕ^* as given by Eq. (23) can be approximated for $\lambda_n u^{-1+n} \ll 1$ to give

$$\tilde{G}^*(k, u) = (u + 2c_0 b E i k \lambda_n u^n)^{-1} . \quad (D3)$$

By definition,

$$\tilde{G}^*(k, u) = \int_0^\infty dt e^{-ut} \int_{-\infty}^{+\infty} dx e^{-ikx} G(x, t) . \quad (D4)$$

Expanding e^{-ikx} in powers of (ikx) , the term linear in k is

$$\begin{aligned} I_1 &= \int_0^\infty dt e^{-ut} \int dx (-ikx) G(x, t) \\ &= -ik \int_0^\infty dt \langle x(t) \rangle e^{-ut} . \end{aligned} \quad (D5)$$

Correspondingly from Eq. (D3) another expression for I_1 is

$$I_1 = -2c_0 b E i k \lambda_n u^{-2+n} . \quad (D6)$$

On comparing Eq. (D5) with Eq. (D6), we get

$$\int_0^\infty dt e^{-ut} \langle x(t) \rangle = 2c_0 b E \lambda_n u^{-2+n} . \quad (D7)$$

Inverse Laplace transform of Eq. (D7) yields

$$\langle x(t) \rangle = 2c_0 b E \lambda_n t^{1-n} / \Gamma(2 - n) . \quad (D8)$$

Another way of arriving at the result of Eq. (D8) is by the CTRW method. The result which has already been given is²⁶

$$\langle x(t) \rangle = \bar{L}^{-1} \{ \psi^*(u) / u [1 - \psi^*(u)] \} , \quad (D9)$$

where \bar{L} the mean displacement for a single hop is $2c_0 b E$. Substituting the expression (17) for $\psi^*(u)$ into Eq. (64), one can obtain the result (D8).

APPENDIX E

The master equation obeyed by the $P(N, t)$, the probability that the number N (a random variable)

of unreacted molecules in the system at time t for a unimolecular reaction, is⁴⁴

$$\frac{dP(N,t)}{dt} = K(t)[(N+1)P(N+1,t) - NP(N,t)] \quad (E1)$$

It has been emphasized by Shlesinger²³ that the rate $K(t)$ is the conditional probability of the reaction to occur in the time interval $(t, t+dt)$, given that no reaction occurred in the interval $(0, t)$ assuming that the stochastic process starts at $t=0$. Solution of the problem requires the calculation of

$$\frac{dP(N_A,t)}{dt} = K'(t)\{ (N_A+1)[N_B(0) - N_A(0) + N_A + 1]P(N_A+1,t) - N_A[N_B(0) - N_A(0) + N_A]P(N_A,t) \} \quad (E3)$$

where the $K'(t)$ is the conditional probability of the bimolecular reaction. From Eq. (E3) it follows that the mean $\langle N_A(t) \rangle$ satisfies⁴⁴

$$\begin{aligned} \frac{d\langle N_A(t) \rangle}{dt} &= -K'(t)[N_B(0) - N_A(0)] \\ &\quad \times \langle N_A(t) \rangle - K'(t)\langle N_A(t) \rangle^2 \end{aligned} \quad (E4)$$

If the initial ($t=0$) number of B molecules $N_B(0)$ is much larger than that of A molecules $N_A(0)$, then Eq. (E4) reduces to a pseudounimolecular rate equation

$$\begin{aligned} \frac{d\langle N_A(t) \rangle}{dt} &= -K'(t)N_B(0)\langle N_A(t) \rangle \\ &\equiv -K(t)\langle N_A(t) \rangle \end{aligned} \quad (E5)$$

On the other hand if $N_A(0) = N_B(0)$, we have the genuine bimolecular rate equation

$$\begin{aligned} \frac{d\langle N_A(t) \rangle}{dt} &= \frac{d\langle N_B(t) \rangle}{dt} \\ &= -K'(t)\langle N_A(t) \rangle^2 \end{aligned} \quad (E6)$$

From the mathematics of CTRW it is more direct to calculate $F(t)$, the unconditional probability density for the first coincidence^{21,22} at time t , than the conditional probability density $K(t)$. $K(t)$ can be obtained once $F(t)$ is known, through

$$K(t) = F(t) / \int_t^\infty F(\tau) d\tau \quad (E7)$$

It can be shown from Eqs. (E2) and (E7) that

$K(t)$ for given $\psi(t)$ which can be carried out by CTRW mathematical techniques as summarized in Appendix A. From the knowledge of $K(t)$, the mean number $\langle N(t) \rangle$ of unreacted molecules is^{44,23}

$$\langle N(t) \rangle = N_0 \exp \left[- \int_0^t K(\tau) d\tau \right], \quad (E2)$$

where N_0 is the initial number of molecules. For irreversible bimolecular reaction⁴⁴ $A + B \rightarrow C$, the master equation satisfied by $P(N,t)$ has the form

$$\langle N(t) \rangle = N(0) \int_t^\infty F(\tau) d\tau \quad (E8)$$

The lattice network is divided into $N_A(0)$ identical units,²³ each having V lattice points and containing one A molecule. For pseudounimolecular reaction [Eq. (E5)], each unit cell contains M B molecules where necessarily $1 \ll M < V$. For genuine bimolecular reactions [Eq. (E6)], each unit cell contains one A molecule and one B molecule. Periodic boundary conditions are employed.

Shlesinger,²³ in his consideration of pseudounimolecular reactions, places each A molecule at the origin and considers the M B molecules as independent and initially having equal probability $1/(V-1)$ of being located at any of the $V-1$ lattice positions in the unit except the origin. For $M \gg 1$ pseudounimolecular reaction, Shlesinger²³ has emphasized for M -independent B molecules that the relevant quantity to calculate is when the first B molecule arrives at the A -molecule site. This first-passage time density $F_M(t)$ is given by

$$F_M(t) = MF(t) \left[1 - \int_0^t F(\tau) d\tau \right]^{M-1}, \quad (E9)$$

where $F(t)$ is the probability per unit time for a particular B molecule to reach the A -molecule site for the first time. Substituting $F_M(t)$ for $F(t)$ in Eq. (E8) and Eq. (E7) and performing the integration in Eq. (E8) yields

$$\langle N_A(t) \rangle = N_A(0) \left[\int_t^\infty F(\tau) d\tau \right]^M, \quad (E10)$$

and the reaction rate defined in Eq. (E5) is given by

$$K_M(t) = F_M(t) / \int_t^\infty F_M(\tau) d\tau \quad (E11)$$

When $M = 1$, $F_M(t)$ and $K_M(t)$ are identical to $F(t)$ and $K(t)$, respectively. It is interesting to note a simple relation between $K_M(t)$ and $K(t)$, which can be derived by direct substitution of Eq. (E11) into Eq. (E9), and has the form

$$K_M(t) = MK(t) . \quad (\text{E12})$$

In a genuine bimolecular-reaction process [Eq. (E6)], if one molecular species says the A 's have a diffusion constant much smaller than that of the B 's, then to a good approximation we can consider that the A 's are fixed at the origin of each unit cell and one B molecule per unit cell is diffusing. This is similar to the $M = 1$ case of the pseudounimolecular-reaction model of Shlesinger.²³ If we consider a system in which there are $N_A(0)$ A molecules and $N_B(0)$ B molecules at time $t = 0$, we can deduce the reaction rate $K'(t)$ of Eq. (E6) from Eqs. (E5) and (E12) for $M = 1$ as

$$K'(t) = K_m(t)/N_B(0) = K(t)/N_B(0) . \quad (\text{E13})$$

The genuine bimolecular reaction, Eq. (E6), is solved to give

$$\langle N_A(t) \rangle = N_A(0) / \left[1 + N_A(0) \int_0^t K'(\tau) d\tau \right] . \quad (\text{E14})$$

Hence if we calculate $F(t)$ by the CTRW method as has been done by Shlesinger,²³ we can solve the pseudounimolecular problem for $M \gg 1$; and the bimolecular reaction through Eqs. (E7), (E12), and (E14).

Shlesinger obtains an expression for the Laplace transform $F^*(u)$ of $F(t)$. $F(t)$ is the sum of the probability densities for reaching the origin from any of the $V - 1$ lattice points, each weighted by $1/(V - 1)$. In the notations and definitions of CTRW functions given in Appendix A,

$$F(t) = \sum_{\vec{l} \neq \vec{0}} (V - 1)^{-1} L^{-1} \bar{F}^*(\vec{l}, u) . \quad (\text{E15})$$

$$\begin{aligned} F(t) &= \left[\frac{1}{(V - 1)} \right] L^{-1} \sum_{\vec{l} \neq \vec{0}} G(\vec{l}, z = \psi^*(u)) / G(\vec{0}, z = \psi^*(u)) \\ &= \left[\frac{1}{(V - 1)} \right] L^{-1} \sum_{\vec{l} \neq \vec{0}} Q^*(\vec{l}, u) / Q^*(\vec{0}, u) . \end{aligned} \quad (\text{E20})$$

The last expression is Shlesinger's result²⁶ if we identify his $R(\vec{l}, t | \vec{l}_0)$ with our $Q(\vec{l}, t)$. Of course the expressions (E19) and (E20) are equivalent. Here is an example that through the self-contained summary of CTRW mathematical

One should note that any quantity in Appendix A is for random walk starting out from the origin $\vec{0}$ to \vec{l} ; however, this is the same as that for the reverse direction random walk from \vec{l} to $\vec{0}$ of interest here. We observe that from Eq. (A11), Eq. (E15) can be rewritten as

$$LF(t) = \frac{1}{(V - 1)} \sum_{\vec{l} \neq \vec{0}} F(\vec{l}, z = \psi^*(u)) . \quad (\text{E16})$$

The right-hand side of Eq. (E16) is related to the generating function $G_k(z)$ (in Montroll's²² notation), the probability that a walker originally not at the origin and randomly placed in the $(V - 1)$ lattice positions will arrive at the origin for the first time in a given number of steps [see Eq. (4) of Ref. 22], given by

$$G_k(z) = \frac{1}{(V - 1)} \sum_{l \neq 0} F(l, z) . \quad (\text{E17})$$

Montroll has already evaluated this, which, in our notations is [see Eq. (6) of Ref. 22]

$$G_k(z) = 1/(V - 1) \{ [(1 - z)G(0, z)]^{-1} - 1 \} . \quad (\text{E18})$$

Then from Eqs. (E18) and (E16) we get the result first obtained by Shlesinger²³:

$$\begin{aligned} F(t) &= L^{-1} [1/(V - 1)] \\ &\quad \times \{ [1 - \psi^*(u)] G(0, z = \psi^*(u)) \}^{-1} - 1 \} . \end{aligned} \quad (\text{E19})$$

Note that $G(0, z)$, as given by Eqs. (A3)–(A6), have already been evaluated by Montroll²² for various lattices in different dimensions. Hence we can at once obtain $F(t)$ by substitution of our model $\psi(t)$ into Eq. (E19). Alternatively from Eqs. (A11), (A6), and (A8) we see that

tools in Appendix A, the much earlier result of Montroll^{20–22} can be identified with the recent rederivations by Shlesinger,²⁶ notwithstanding the fact that the notations of these authors are very different.

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