Exact Solution for Classical Diffusion on Random Chains

J. Heinrichs
Institut de Physique, Université de Liège, B-4000 Liege 1, Belgium
(Received 16 January 1984)

Classical diffusion is studied on random chains with nearest-neighbor transfer rates having Gaussian distributions about sufficiently large systematic rates. Both the cases of static and dynamical white-noise randomness are considered, for symmetric as well as for asymmetric transfer rates. Probability densities for displacements along the chains are determined exactly in the continuum limit valid at long times, and are found to be Gaussian. The variance increases linearly in time for dynamical disorder and shows a qualitatively new quadratic growth for static disorder.

PACS numbers: 05.40.+j, 05.60.+w, 66.30.Dn

In this Letter I discuss exact analytical results for the long-time diffusion of particles (or excitations) described by classical rate equations with random transfer rates between nearest neighbors on a linear chain. I consider Gaussian fluctuations of the rates over widths that are small compared to fixed, most probable rates. This ensures that unphysical negative rates have a negligible effect in the same sense as, e.g., the Gaussion tails in a properly defined saddle-point approximation to a definite integral. First I analyze the effect of purely dynamical fluctuations correlated over infinitesimal times (white-noise limit). Such dynamical fluctuations may arise, e.g., from incoherent thermal lattice vibrations. Next I study the case of static randomness which corresponds to fluctuations correlated over infinitely long times. I discuss the effects of disorder for symmetric as well as for asymmetric transfer rates and give exact results for the long-time development of the probability of displacements of the particle and of its moments.

In previous work these quantities were studied exactly for the case of a binary distribution of static symmetric rates, W, with a δ-function peak at $W=0$.[1] These results are strongly dependent on the fact that the linear chain breaks up into finite independent segments on which the particle remains localized. On the other hand, for continuous distributions with a finite support, the problem is considerably more complicated.[2] However, Bernasconi and co-workers[3] have obtained expressions for the long-time behavior of the autocorrelation function for several classes of continuous distributions of transfer rates on a linear chain. Their original analysis was later justified in more detail by means of rather involved mathematical arguments.[3] Another aspect discussed more recently concerns the effect of randomness on the drift motion of a particle due to asymmetric transfer rates. However, detailed results for these effects have been presented only for the case of binary (δ-function) distributions.[4]

The Gaussian distribution, which plays a central role in the physics of both thermally and configurationally disordered systems, does not belong to any of the classes considered previously.[1,3,4] This distribution is, in fact, of special interest in the present context since it leads to a qualitatively new asymptotic behavior for the moments of the displacement probability density. Moreover, a qualitative understanding of the effect of a finite correlation time between transfer-rate fluctuations emerges, for the first time, from the present simultaneous analysis of static and dynamical randomness.

The basic rate equations describing classical diffusion on a linear chain have the form

$$dP_n/dt = W_{n+1,n}P_{n+1} + W_{n-1,n}P_{n-1} - (W_{n,n+1} + W_{n,n-1})P_n, \quad P_n(0) = \delta_{n,0}, \tag{1}$$

where P_n is the probability of finding the particle at site n at a time $t \geqslant 0$ and $W_{i,j} \geqslant 0$ is the transition rate for hopping from a site i to a nearest-neighbor site j on the random chain. In the case of *symmetric* transition rates $W_{i,j} = W_{j,i}$, while in the *asymmetric* case all rates in Eq. (1) may be different, as implied by the notation

$$W_{n+1,n} \equiv W_{n+1}^{-}, \quad W_{n,n+1} \equiv W_n^{+}, \quad \text{etc.} \tag{2}$$

For large times the mean square deviation of the position of the particle from its average position on the lattice is much larger than the lattice constant, a, which implies that, within the range of their most probable values, the probabilities $P_n \equiv P(na)$ vary appreciably on a scale large compared to a only. It follows therefore that the long-time behavior of $P_n(t)$ may be obtained from the continuum limit,

$a \to 0$, of Eq. (1). The latter is found by introducing the spatial coordinate $x = na$ and defining

$$P_{n\pm 1} = ap(x \pm a), \tag{3}$$

where $p(x)$ is the probability density associated with the coordinate x.

Considering first the *symmetric* case, we define the continuum limits of the transfer rates,

$$W_{n,n\pm 1} = W(x, x \pm 0^+) \equiv W_\pm(x,t), \qquad a \to 0^+, \tag{4}$$

and expand the probabilities (3) through order a^2. Equation (1) then becomes

$$\frac{\partial p}{\partial t} = a[w_+(x,t) - w_-(x,t)]\frac{\partial p}{\partial x} + a^2 W_0 \frac{\partial^2 p}{\partial x^2}, \tag{5}$$

where

$$w_\pm(x,t) = W_\pm(x,t) - W_0 \tag{6}$$

are random Gaussian fluctuations about a systematic (constant) rate, W_0, and the time variable is included in view of the general case of dynamical disorder. Terms beyond order a in the disorder are ignored.

The continuum limit for the case of *asymmetric* rates follows in a similar way. We again separate the transfer rates into systematic ($W^\pm$) and fluctuating parts described by the random variables $w^\pm(x,t)$ and $w^\mp(x \pm 0^+, t)$ ($a \to 0^+$):

$$W_n^\pm = W^\pm(x,t) = W^\pm + w^\pm(x,t), \tag{7a}$$

$$W_{n\pm 1}^\mp = W^\mp(x \pm 0^+, t) = W^\mp + w^\mp(x \pm 0^+, t). \tag{7b}$$

In general, the continuum transfer rates (7a) and (7b) are not independent. This follows from the fact that, in addition to Eq. (1) (referred to as the forward Kolmogorov equation in the mathematical literature), the occupation probabilities, $P_n(t)$, also obey the so-called backward Kolmogorov equation[5]:

$$dP_{i,n}/dt = W_{i,i-1}P_{i-1,n} + W_{i,i+1}P_{i+1,n} - (W_{i,i-1} + W_{i,i+1})P_{i,n}, \tag{8}$$

where $P_{i,j}(t) \equiv P(i,0|j,t) = P_j(t)$ is the probability for a particle to be at site j at time t given that it was at site i at $t = 0$. Equations (1) and (8) are both consequences of the Chapman-Kolmogorov relation for Markov processes.[5] In particular, the moments of the solution of (1) as a function of final sites, n, coincide with the moments of $P_{i,n}$ considered as a function of initial sites i, with an arbitrarily chosen final site. Now, the comparison of lowest-order terms on the right-hand side of the continuum limits of (1) and (8) readily yields the consistency condition

$$w^-(x + 0^+, t) + w^+(x - 0^+, t) = w^-(x,t) + w^+(x,t), \tag{9}$$

which plays a fundamental role in the case of disordered asymmetric rates while reducing to an identity both for symmetric and for ordered asymmetric rates. Indeed, it is responsible for the existence of a normalizable solution for the configuration average of $p(x,t)$ given by the continuum limit of (1). Finally, using (3), (7a), (7b), and (9) and retaining terms up to order a only, the continuum limit of (1) now reads

$$\partial p/\partial t = a[W^- - W^+ + w^-(x + 0^+, t) - w^+(x - 0^+, t)]\partial p/\partial x, \tag{10}$$

where $w^\mp(x \pm 0^+, t)$ will be treated as independent Gaussian variables.

In the absence of disorder (5) and (10) reduce to the diffusion equation[2] and to the equation describing a uniform drift with the velocity $v = a(W^- - W^+)$, as required. We choose the differences of independent random variables in (5) and (10) as our new Gaussian variables:

$$w(x,t) = w_+(x,t) - w_-(x,t), \tag{11}$$

$$u(x,t) = w^-(x + 0^+, t) - w^+(x - 0^+, t), \tag{12}$$

and assume Gaussian white-noise correlations in both space and time coordinates:

$$\langle r(x,t) r(x',t')\rangle = R_1^2 \delta(x - x') f(t - t'), \tag{13}$$

where $r \equiv w$ or u, $R_1 \equiv W_1$ or U_1, and $f(t) = \delta(t)$ for dynamical white-noise disorder and $f(t) = 1$ for static disorder We are interested in $\rho(x,t) = \langle p(x,t)\rangle$ defining the configurationally averaged probability of finding the particle at x at time t. Exact equations for $\rho(x,t)$ are obtained, with use of Novikov's theorem[6] for averaging functionals of Gaussian random variables such as the random terms in Eqs. (5) and (10). Using (13) with the definitions (11) and (12) we then obtain, both for dynamic and static disorder,

$$\frac{\partial \rho}{\partial t} = aW_1^2 \frac{\partial}{\partial x}\left\langle \frac{\delta p}{\delta w(x,t)}\right\rangle + a^2 W_0 \frac{\partial^2 \rho}{\partial x^2}, \tag{14}$$

$$\frac{\partial \rho}{\partial t} = aU_1^2 \frac{\partial}{\partial x}\left\langle \frac{\delta p}{\delta u(x,t)}\right\rangle + a(W^- - W^+)\frac{\partial \rho}{\partial x}, \tag{15}$$

for symmetric and asymmetric rates, respectively.

We consider first the case of *symmetric rates.* For purely *dynamical disorder* the functional derivative $\delta\rho/\delta w(x,t)$ is readily found from the first integral of Eq. (5), with use of the fact that $p(x,t)$ depends on values of $w(x,t')$ at time instants t' prior to t only. This leads to the diffusion equation

$$\frac{\partial\rho}{\partial t}=a^2(\alpha^2+W_0)\frac{\partial^2\rho}{\partial x^2},\quad \alpha^2=W_1^2\delta(0), \tag{16}$$

which shows that dynamic fluctuations only lead to an enhancement of the diffusion constant. The infinite constant, α^2, may be made finite by smearing out the spatial prefactor in Eq. (13) into a more realistic correlation function of finite width, as discussed elsewhere in a different context.[7]

In the case of *static disorder* the functional derivative in (14) is related to the higher-order derivatives through a hierarchy of equations obtained by successively differentiating (5) with respect to $w(x,t)$ and averaging the resulting equations, using Novikov's theorem together with (13). The important point is that the resulting hierarchy takes the form of a recursion relation which may be solved exactly. Indeed by defining

$$B_n(x,t)=\langle\delta^n p(x,t)/\delta w(x,t)^n\rangle,\qquad B_0(x,t)=\rho(x,t), \tag{17}$$

one finds that the average of the equation obtained by functionally differentiating (5) n times is

$$\frac{\partial B_n}{\partial t}=a\frac{\partial}{\partial x}\left(n\delta(0)B_{n-1}+W_1^2B_{n+1}+aW_0\frac{\partial B_n}{\partial x}\right), \tag{18}$$

for $n=0$ [Eq. (14)], 1, 2,. . . . By introducing spatial Fourier transforms

$$\bar{B}_n(k,t)=\int_{-\infty}^{\infty}dx\, e^{ikx}B_n(x,t), \tag{19}$$

and defining the dimensionless quantities

$$C_n=\frac{\alpha^n}{\delta(0)^n}\bar{B}_n,\quad \tau=\alpha t,\qquad \kappa=ka,\quad \beta=\frac{W_0}{\alpha}, \tag{20}$$

Eq. (18) reduces to

$$\frac{\partial C_n}{\partial\tau}=-i\kappa(nC_{n-1}+C_{n+1}-i\beta\kappa C_n). \tag{21}$$

This recursion relation has been studied by Heinrichs and Kumar[8] in a different context. In order to solve (21) one defines a generating function for the C_n's,

$$G(y)=\sum_{n=0}^{\infty}(n!e^{ny})^{-1}C_n,$$

and converts (21) into a partial differential equation for $G(y)$. The latter is solved subject to the initial condition $C_0(\tau=0)=1$ [$p(x,0)=\delta(x)$] and to the additional relations $C_n(\tau=0)=0$, $n=1,2,\ldots,$ implied by Eq. (5). Further details of the solution of Eq. (21) may be found in Ref. 8. After transforming the exact solution for $C_0(\tau)$ [8] back to x space and to our original parameters we obtain the Gaussian probability density

$$\rho(x,t)=[2\pi a^2(\alpha^2t^2+2W_0t)]^{-1/2}\times\exp\left(-\frac{x^2}{2a^2(\alpha^2t^2+2W_0t)}\right), \tag{22}$$

whose variance is the mean square displacement,

$$\langle x^2(t)\rangle=2a^2W_0t[1+(2W_0)^{-1}\alpha^2t]. \tag{23}$$

Since our model requires $\alpha^2\ll W_0^2$, it follows from (22) that the continuum treatment is valid for $t\gg(2W_0)^{-1}$. In fact, for an ordered lattice, (23) reduces to the exact mean square displacement for any t while (22) coincides with the asymptotic form for $t\gg(2W_0)^{-1}$ of the corresponding exact density. This shows, in particular, that the use of boundary conditions at $t=0$ does not alter the exactness of our asymptotic results. Equations (22) and (23) demonstrate nondiffusive particle motion induced by static randomness, for $t\gg(2W_0)^{-1}$. This behavior contrasts with the diffusive behavior obtained for white-noise dynamical disorder and is a specific property of the infinite correlation time characterizing static fluctuations. The fact that for $t\to\infty$ the initial site occupancy, $\rho(0,t)$, decays faster than in the absence of disorder is related to the presence of a fraction of transfer rates larger than W_0. Compared to the ordered case, our model exhibits enhanced delocalization of the particle, in contrast to the reduced delocalization (quasilocalization) obtained by Bernasconi, Alexander, and Orbach[3] for distributions involving an appreciable fraction of vanishingly small transfer rates. We note that similar nondiffusive behavior has been found recently[8] for different physical systems described by the continous random walk model of Marinari *et al.*[9]

The case of *asymmetric rates* may be discussed along similar lines. For purely *dynamical disorder,* the substitution of the functional derivatives obtained from the first integral of (10), using (12), in

(15) yields

$$\frac{\partial\rho}{\partial t} = a^2\beta^2\frac{\partial^2\rho}{\partial x^2} + a(W^- - W^+)\frac{\partial\rho}{\partial x},$$
$$\beta^2 = U_1^2\delta(0). \tag{24}$$

The solution of (24) with the initial form $\rho(x,0) = \delta(x)$ is

$$\rho(x,t) = (4\pi a^2\beta^2 t)^{-1/2} \times \exp\left(-\frac{1}{4a^2\beta^2 t} \times [x - a(W^+ - W^-)t]^2\right), \tag{25}$$

which leads to

$$\langle x(t)\rangle \equiv \bar{x} = a(W^+ - W^-)t,$$
$$\langle x^2(t) - \bar{x}^2\rangle = 2a^2\beta^2 t. \tag{26}$$

Equations (25) and (26) display a uniform drift motion with a superimposed random diffusive motion which is most significant at the shortest times at which our exact asymptotic results remain valid.

In the case of *static disorder* we successively differentiate Eq. (10) with respect to $u(x,t)$ and average the resulting equations using Novikov's theorem and Eq. (13). This leads to the following hierarchy of coupled recursion relations:

$$\frac{\partial B_n}{\partial t} = a\frac{\partial}{\partial x}[n\delta(0)B_{n-1} + U_1^2 B_{n+1} + (W^- - W^+)B_n],$$
$$B_n = \langle \delta^n p(x,t)/\delta u(x,t)^n\rangle, \quad B_0 = \rho(x,t), \quad n = 0, 1, 2, \ldots. \tag{27}$$

These equations may again be reduced to the form of the recursion relations solved in Ref. 8. The final exact solution for $\rho(x,t)$ differs from (25) only in that the variance is now replaced by

$$\langle x^2(t) - \bar{x}^2\rangle = a^2\beta^2 t^2, \tag{28}$$

which corresponds to a nondiffusive random motion superimposed on the uniform drift, $\langle x(t)\rangle = a(W^+ - W^-)t$.

Finally, for both symmetric and asymmetric rates, we find that the replacement of white-noise dynamical disorder by static disorder leads to the replacement of a linear growth of the variance of $\rho(x,t)$ by a t^2 growth, as a result of the increased correlation time between Gaussian transfer-rate fluctuations.

[1]S. Alexander, J. Bernasconi, and R. Orbach, Phys. Rev. B **17**, 4311 (1978); J. Heinrichs, Phys. Rev. B **22**, 3093 (1980); T. Odagaki and M. Lax, Phys. Rev. Lett. **45**, 847 (1980); J. Heinrichs, Phys. Rev. B **25**, 1388 (1982).

[2]G. H. Weiss and R. J. Rubin, Adv. Chem. Phys. **52**, 363 (1983).

[3]J. Bernasconi, S. Alexander, and R. Orbach, Phys. Rev. Lett. **41**, 185 (1978); S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, Rev. Mod. Phys. **53**, 175 (1981).

[4]B. Derrida and Y. Pomeau, Phys. Rev. Lett. **48**, 627 (1982); J. Bernasconi and W. R. Schneider, J. Phys. A **15**, L729 (1983).

[5]W. R. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1968), Vol. I.

[6]E. A. Novikov, Zh. Eksp. Teor. Fiz. **47**, 1919 (1964) [Sov. Phys. JETP **20**, 1290 (1965)].

[7]J. Heinrichs, Z. Phys. B **53**, 175 (1983).

[8]J. Heinrichs and N. Kumar, J. Phys. C **17**, 769 (1984).

[9]E. Marinari, G. Parisi, D. Ruelle, and P. Windey, Phys. Rev. Lett. **50**, 1223 (1983).