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Non-Markoffian Diffusion in a One-Dimensional Disordered Lattice

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Recent treatments of diffusion in a one-dimensional disordered lattice by Machta using a renormalization-group approach, and by Alexander and Orbach using an effective medium approach, lead to a frequency-dependent (or non-Markoffian) diffusion coefficient. Their results are confirmed by a direct calculation of the diffusion coefficient.

KEY WORDS: Diffusion; disordered lattice; long time tail.

Considerable attention has been given recently[1] to solutions of the master equation (or continuous time random walk equation)

$$\frac{d}{dt} P_j = W_{j-1}(P_{j-1} - P_j) + W_j(P_{j+1} - P_j) \tag{1}$$

when the transition rates W_j are independent random variables. In particular, Machta[2] has presented a renormalization-group calculation of the effective diffusion coefficient $D(z)$ associated with the long time and large distance solutions of this equation. The variable z is a Laplace transform variable, in time, and may be regarded as a complex frequency. Alexander and Orbach[3] have presented an effective medium calculation of $D(z)$. Their results, which agree with Machta's, are

$$\begin{aligned} D(z) &= D_0 + D_1 z^{1/2} + O(z) \\ 1/D_0 &= \langle 1/W \rangle \\ D_1 &= \frac{1}{2} D_0^{5/2} \left\langle \left(\frac{1}{W} - \frac{1}{D_0} \right)^2 \right\rangle \end{aligned} \tag{2}$$

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The averages are taken with respect to the distribution of a single W_j. If the diffusion coefficient is associated to a "velocity correlation function," then this function has a long time tail proportional to $t^{-3/2}$.

While effective medium and renormalization arguments have great value in circumstances where exact calculations are difficult or impossible, it is sometimes desirable to check them when an exact calculation is possible. In this article I present an explicit derivation of Eq. (2).

The procedure followed here is to transform the master equation from real space (j) to Fourier space (q); to find a "self-energy" expression for the diagonal part of the Green's function in Fourier space; to extract from this an exact expression for $D(z)$ in the long-wavelength limit; and to investigate the small-z behavior of $D(z)$. The procedure is straightforward but algebraically tedious. Although parts of the procedure appear to be arbitrary and unmotivated, the reader who follows it through will see that it was designed to lead as directly as possible to the desired results.

For simplicity, attention is restricted to a finite periodic lattice of N sites. The space index j is always taken modulo N. The Fourier transform of P_j is ρ_q,

$$\rho_q = \frac{1}{N} \sum_j P_j \exp iqj \tag{3}$$

Then the transform of the master equation is

$$\frac{d}{dt} \rho_q = \sum_{q'} V_{qq'} \rho_{q'} \tag{4}$$

where the transition matrix V is given explicity by

$$V_{qq'} = -\left[\exp(iq) - 1\right]\left[\frac{1}{N} \sum_j W_j \exp i(q - q')j\right]\left[\exp(-iq') - 1\right] \tag{5}$$

This matrix is singular. However, it is easy to separate out the "dangerous" parts. Define two new matrices:

$$f_{qq'} = \delta_{qq'}\left[\exp(iq) - 1\right] \tag{6}$$

and

$$U_{qq'} = \frac{1}{N} \sum_j W_j \exp i(q - q')j \tag{7}$$

Then, in matrix form, the transition matrix is

$$V = -f \cdot U \cdot f^* \tag{8}$$

The advantage of this separation is that U is well behaved; in particular, it has an inverse (as long as no $W_j = 0$),

$$(U^{-1})_{qq'} = \frac{1}{N} \sum_j W_j^{-1} \exp i(q - q')j \tag{9}$$

The singular behavior of V is due to f at $q = 0$.

The master equation may be solved formally by means of Laplace transforms,

$$\hat{\rho}_q(z) = \int_0^\infty dt\, \rho_q(t) \exp(-zt) \tag{10}$$

The solution is

$$\hat{\rho}_q(z) = \sum_{q'} G_{qq'}(z) \rho_{q'}(0) \tag{11}$$

This introduces the Green's function G in q space,

$$G = \frac{1}{z1 - V} = \frac{1}{z1 + f \cdot U \cdot f^*} \tag{12}$$

If $q = 0$, G is simply $z^{-1}1$, and is uninteresting. But if $q \neq 0$, which is assumed in all of the following discussion, then G may be rearranged to

$$G = \frac{1}{f^*} \cdot \frac{1}{z1 + f^* \cdot f \cdot U} \cdot f^* \tag{13}$$

which can be verified by, e.g., expanding in powers of U. Further, because U has a well-defined inverse, G may be rearranged to

$$G = \frac{1}{f^*} \cdot U^{-1} \cdot \frac{1}{f^* \cdot f + z \cdot U^{-1}} \cdot f^* \tag{14}$$

Next, the matrix U^{-1} is separated into diagonal and off-diagonal parts,

$$U^{-1} = \frac{1}{D_0} 1 + \Delta \tag{15}$$

$$\frac{1}{D_0} = \frac{1}{N} \sum_j \frac{1}{W_j} \tag{16}$$

$$\Delta_{qq'} = \frac{1}{N} \sum_j \left(\frac{1}{W_j} - \frac{1}{D_0} \right) \exp i(q - q')j \tag{17}$$

By construction, $\Delta_{qq} = 0$.

If fluctuations in the W's are neglected, so that all W_j are replaced by D_0, then one obtains the Green's function for the uniform lattice,

$$\Gamma = \frac{1}{z1 + D_0 f^* \cdot f} \tag{18}$$

or

$$\Gamma_{qq'} = \delta_{qq'} \frac{1}{z + 2D_0(1 - \cos q)} \tag{19}$$

By some algebraic manipulation, G may be expressed in terms of Γ and Δ as follows:

$$G = \Gamma - \frac{1}{f^*} \cdot D_0(z\Gamma - 1) \cdot \Delta \cdot \Gamma \cdot f^* + \frac{1}{f^*} \cdot D_0^2 z(z\Gamma - 1) \cdot \Delta \cdot \frac{1}{1 + D_0 z\Gamma \cdot \Delta} \cdot \Gamma \cdot \Delta \cdot \Gamma \cdot f^* \tag{20}$$

This expression is formally exact.

The first term is diagonal in q. (That is why the factors f^* and f have disappeared.) The second term is strictly off-diagonal, because of the single factor Δ. The third term may have both diagonal and off-diagonal parts. We will focus attention on the diagonal part here; for large N, the off-diagonal terms are expected to be of order $N^{-1/2}$ with respect to the diagonal terms (the law of large numbers). The diagonal part of G is

$$G_{qq} = \Gamma_{qq} + D_0^2 z\Gamma_{qq}(z\Gamma_{qq} - 1) \cdot \left[\Delta \frac{1}{1 + D_0 z\Gamma \cdot \Delta} \cdot \Gamma \cdot \Delta\right]_{qq} \tag{21}$$

As is customary, we write G_{qq} in terms of a "self-energy" function $\sum_q(z)$,

$$G_{qq}(z) = \frac{1}{z + \sum_q(z)} \tag{22}$$

so that

$$\sum_q (z) = 2D_0(1 - \cos q) \cdot \left[1 + \frac{D_0^2 \Phi_q}{1 + D_0^2(z\Gamma_{qq} - 1)\Phi_q}\right] \tag{23}$$

where

$$\Phi_q = \left[\Delta \cdot \frac{1}{1 + D_0 z\Gamma \cdot \Delta} \cdot z\Gamma \cdot \Delta\right]_{qq} \tag{24}$$

In the long-wavelength limit $q \to 0$, the function $\sum_q(z)$ approaches

$$\sum_q (z) \to D(z)q^2 + \cdots \tag{25}$$

$D(z)$ is the effective (non-Markoffian) diffusion coefficient for $q \to 0$. In this limit, using $(z\Gamma - 1)_{00} = 0$, we obtain

$$D(z) = D_0\left[1 + D_0^2 \Phi_0\right] \tag{26}$$

The derivation of this formally exact expression for the effective diffusion coefficient was the reason for all of the preceding tedious algebra. There are, of course, other equivalent expressions for $D(z)$; this one, based on the separation of U^{-1} into diagonal and off-diagonal parts, was chosen because the rest of the discussion is very direct.

Up to this point, the only requirement imposed on the transition rates is that none of them may vanish. The expression for $D(z)$ that was just derived is applicable, for example, if the transition rates are periodically ordered as $ABABABA$ . . . .

When the transition rates are independently distributed random variables, the explicit evaluation of $D(z)$ for small z is almost trivial. The law of large numbers justifies replacement of sums by averages as long as corrections of order $N^{-1/2}$ are of no interest.

The leading term in $D(z)$ is D_0, defined as the harmonic mean of the transition rates. In the limit of large N, we find

$$\frac{1}{D_0} \to \left\langle \frac{1}{W} \right\rangle + O(N^{-1/2}) \tag{27}$$

where $\langle\ \rangle$ denotes the average over the distribution of a single W. If we neglect terms of order $N^{-1/2}$, we must require that the average of $1/W$ does not diverge; this rules out consideration of an interesting class of problems discussed in Ref. 1.

The next step is to expand Φ in powers of Δ,

$$\Phi_0 = \sum_{\nu \geqslant 2} \Phi^{(\nu)} \tag{28}$$

where the first two terms are

$$\Phi^{(2)} = (\Delta z \Gamma \Delta)_{00} \tag{29}$$

$$\Phi^{(3)} = -(\Delta z \Gamma \Delta z \Gamma \Delta)_{00} \tag{30}$$

Discussion of higher terms will be saved for later. Each term contains sums over various q's, and each $\Delta_{qq'}$ is a sum over various j's, for example

$$\begin{aligned}\Phi^{(2)} &= \sum_q \Delta_{0q} z \Gamma_{qq} \Delta_{q0} \\ &= \frac{1}{N^2} \sum_j \sum_k \delta \frac{1}{W_j} \delta \frac{1}{W_k} \sum_q z \Gamma_{qq} e^{-iq(j-k)}\end{aligned} \tag{31}$$

and

$$\begin{aligned}\Phi^{(3)} = &-\frac{1}{N^3} \sum_j \sum_k \sum_l \delta \frac{1}{W_j} \delta \frac{1}{W_k} \delta \frac{1}{W_l} \\ &\times \sum_{q_1} \sum_{q_2} z \Gamma_{q_1 q_1} z \Gamma_{q_2 q_2} e^{-iq_1(j-k)} e^{-iq_2(k-l)}\end{aligned} \tag{32}$$

(In these equations, $1/W_j - 1/D_0$ is abbreviated by $\delta 1/W_j$.) By the law of large numbers, sums over the $\delta 1/W_j$ are well approximated by averages. Some typical averages are

$$\left\langle \delta \frac{1}{W_j} \delta \frac{1}{W_k} \right\rangle = \left\langle \left(\delta \frac{1}{W} \right)^2 \right\rangle \delta_{jk} \tag{33}$$

$$\left\langle \delta \frac{1}{W_j} \delta \frac{1}{W_k} \delta \frac{1}{W_l} \right\rangle = \left\langle \left(\delta \frac{1}{W} \right)^3 \right\rangle \delta_{jk} \delta_{kl} \tag{34}$$

Let us look first at $\Phi^{(2)}$. For large N, it approaches

$$\Phi^{(2)} \to \left\langle \left(\delta \frac{1}{W} \right)^2 \right\rangle \frac{1}{N} \sum_q z\Gamma_{qq} \tag{35}$$

Further, the sum over q may be replaced by an integral,

$$\frac{1}{N} \sum_q z\Gamma_{qq} \to \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{z}{z + 2D_0(1 - \cos\theta)} = \left(\frac{z}{4D_0 + z} \right)^{1/2} \tag{36}$$

Thus, in the limit $z \to 0$, we find

$$\Phi^{(2)} \to \frac{1}{2} \left\langle \left(\delta \frac{1}{W} \right)^2 \right\rangle (z/D_0)^{1/2} + \cdots \tag{37}$$

This contribution to $D(z)$ agrees precisely with Machta's renormalization-group result and Alexander and Orbach's effective medium result. It remains to be shown that the higher-order terms $\Phi^{(\nu)}$ with $\nu \geqslant 3$ do not contribute to order $z^{1/2}$.

Consider next $\Phi^{(3)}$. In the limit of large N, this becomes

$$\begin{aligned} \Phi^{(3)} &= -\sum_{q_1} \sum_{q_2} \langle \Delta_{0q_1} \Delta_{q_1q_2} \Delta_{q_20} \rangle z\Gamma_{q_1q_1} z\Gamma_{q_2q_2} \\ &= -\left\langle \left(\delta \frac{1}{W} \right)^3 \right\rangle \frac{1}{N^2} \sum_{q_1} \sum_{q_2} z\Gamma_{q_1q_1} z\Gamma_{q_2q_2} \end{aligned} \tag{38}$$

On converting the sums to integrals, we find the square of the integral that appeared in $\Phi^{(2)}$, so that $\Phi^{(3)}$ is of order z.

The fourth order term is more complex; the average of Δ^4 is

$$\begin{aligned} \langle \Delta_{0q_1} \Delta_{q_1q_2} \Delta_{q_2q_3} \Delta_{q_30} \rangle &= \frac{1}{N^3} \left[\left\langle \left(\delta \frac{1}{W} \right)^4 \right\rangle - 3 \left\langle \left(\delta \frac{1}{W} \right)^2 \right\rangle^2 \right] \\ &+ \frac{1}{N^2} \left\langle \left(\delta \frac{1}{W} \right)^2 \right\rangle^2 \left[\delta_{0,q_2} + \delta_{q_1,q_2-q_3} + \delta_{q_30} \right] \end{aligned} \tag{39}$$

and contains delta functions in Fourier space. (The number of delta functions in the general term, of order ν, varies from 0 to $[\nu/2] - 1$, where $[x]$ denotes the greater integer contained in x.) Each delta function removes one sum over some q_i, and the number of sums that remain varies from $\nu - 1$ to $[(\nu + 1)/2]$. (The special case where there are no delta functions is included in all of this.) Further, whenever a delta function appears, one factor of $1/N$ is lost, so that each remaining sum is well behaved for large N. When the sums over q_i are converted into integrals over θ_i, the complete integrand of a single term contains a product of $\nu - 1$ factors such as

$$\frac{z}{z + 2D_0[1 - \cos(\theta_i - \theta_j)]} \tag{40}$$

Let us scale each angle by $z^{1/2}$,

$$\theta_i = z^{1/2} x_i \tag{41}$$

Each separate integral over θ_i introduces a factor $z^{1/2}$ times a corresponding integral over x_i. In the limit $z \to 0$, each factor in the complete integrand is independent of z,

$$\to \frac{1}{1 + D_0(x_i - x_j)^2} \tag{42}$$

and the range of integration is $-\infty < x_i < +\infty$. Consequently, the complete integral approaches $z^{\mu/2}$, where μ is the number of variables x_i. Thus, for example, in $\Phi^{(4)}$ the contribution from the term with no delta functions is of order $z^{3/2}$, and the contribution from terms with one delta function is of order z. The leading contribution to the general term $\Phi^{(\nu)}$ is of order $z^{\sigma/2}$, where $\sigma = [(\nu + 1)/2]$.

In conclusion, the only contribution to $D(z)$ that is of order $z^{1/2}$ comes from $\Phi^{(2)}$. This confirms the results of Machta and of Alexander and Orbach. Both the renormalization group and the effective medium arguments work properly in this problem.

REFERENCES

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