Journal of Statistical Physics, Vol. 42, Nos. 5/6, 1986

On the Relation Between a Fluctuating Diffusion Equation and Long Time Tails in Stationary Random Media

Alan K. Harrison and Robert Zwanzig[1]

Received August 2, 1985; revision received September 30, 1985

Ernst, Machta, Dorfman, and van Beijeren [*J. Stat. Phys.* **34**:477 (1984); **35**:413 (1984)] have proposed that diffusion in a stationary random medium is described by a fluctuating diffusion equation involving a coarse-grained local diffusion coefficient $\mathsf{K}(\mathbf{r})$ and free volume fraction $\psi(\mathbf{r})$. We show that for a particular class of models [lattice diffusion with random transition rates and constant $\psi(\mathbf{r})$], their prediction for the long time tail in the velocity autocorrelation function is the correct asymptotic limit.

KEY WORDS: Long time tails; disordered materials; diffusion.

In two recent papers,[1] Ernst, Machta, Dorfman, and van Beijeren (EMDvB) proposed a generalized diffusion equation to describe diffusion in statically disordered media. In their intuitively appealing picture, each realization of such a medium was characterized by a spatially varying coarse-grained diffusion tensor $\mathsf{K}(\mathbf{r})$ and free volume fraction $\psi(\mathbf{r})$. The particle current $\mathbf{J}$ and the concentration c were related by a generalized form of Fick's law, as follows:

$$\mathbf{J} = -\mathsf{K} \cdot \nabla(c/\psi) \tag{1}$$

This equation, combined with the usual continuity equation, gave their generalized diffusion equation

$$\frac{\partial c}{\partial t} = \nabla \cdot \mathsf{K} \cdot \nabla(c/\psi) \tag{2}$$

[1] Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742.

This approach led to predictions for the long-time properties of the system, such as the long time tail in the velocity autocorrelation function (VAF), in terms of the fluctuations of the spatial averages of K and ψ about their expected values. The authors then applied this apparatus to several specific models, with good agreement with previously known results.

In the present paper we present a derivation of EMDvB's VAF result for a class of models. We consider Markovian diffusion on a lattice with statically disordered transition rates. The equilibrium concentration is taken to be uniform, so in this case $\psi(\mathbf{r}) = 1$.

Let the concentration C_j at site j of a regular d-dimensional lattice diffuse according to

$$\frac{\partial}{\partial t}\mathbf{C} = \mathsf{W}\cdot\mathbf{C} \tag{3}$$

where $\mathbf{C}$ is an N-dimensional vector and W is an $N\times N$ matrix of random transition rates W_{jk}. We impose the constraints

$$\sum_j W_{jk} = \sum_k W_{jk} = 0 \tag{4}$$

in order to conserve total concentration and guarantee uniform concentration at equilibrium. We exclude models where the W_{jk} can be arbitrarily small. A distribution of W's with too much weight near zero may give rise to an extra term in the long time tail; an example is given by Machta.[2] In order that the system evolution be dominated by diffusion rather than drift, we also require sufficient statistical isotropy that for each dimension α,

$$\left|\sum_{j,k} W_{jk}\left(\frac{R_j^\alpha - R_k^\alpha}{L_\alpha}\right)\right| \ll \sum_{j,k} W_{jk}\left(\frac{R_j^\alpha - R_k^\alpha}{L_\alpha}\right)^2 \tag{5}$$

where L_α is the sample length in the α direction. This inequality is satisfied automatically if $W_{jk} = W_{kj}$, as for instance in the familiar random bond case with $W_{jk} = w_{jk} - \delta_{jk}\sum_l w_{jl}$, $w_{jk} = w_{kj}$. [In the thermodynamic limit $(L_\alpha \to \infty)$ (5) reduces to the requirement that the first moment $\sum_{j,k} W_{jk}(\mathbf{R}_j - \mathbf{R}_k)$ vanish, and we must also stipulate that the second moment $\sum_{j,k} W_{jk}(\mathbf{R}_j - \mathbf{R}_k)^2$ exists.]

The Fourier transform of any $N\times N$ matrix A is

$$A_{\mathbf{q}\mathbf{q}'} = \frac{1}{N}\sum_{jk} A_{jk}\, e^{i\mathbf{q}\cdot\mathbf{R}_j - i\mathbf{q}'\cdot\mathbf{R}_k} \tag{6}$$

The Green's function corresponding to the equation of motion (3) is

$$\mathsf{G}(z) = (z\mathsf{1} - \mathsf{W})^{-1} \tag{7}$$

where z is the Laplace transform variable. Then the diagonal part of the Fourier-transformed Green's function is, to second order in q,

$$G_{\mathbf{qq}}(z) = \frac{1}{z + \mathbf{qq}:K_0(z) + \cdots} \tag{8}$$

The term linear in q can be neglected due to inequality (5). Our fluctuating diffusion tensor K_0 can be obtained from

$$\mathsf{K}_0(z) = -\frac{z^2}{2} \nabla_{\mathbf{q}} \nabla_{\mathbf{q}} G_{\mathbf{qq}}(z) \,|_{\mathbf{q}=0} \tag{9}$$

We will see later that K_0 is the spatial average of $\mathsf{K}(\mathbf{r})$.

When averaged over some statistically homogeneous and isotropic ensemble, the Green's function has the form

$$\langle \mathsf{G}(z) \rangle = [z\mathsf{1} + \mathbf{\Psi}(z)]^{-1} \tag{10}$$

for some $\mathbf{\Psi}(z)$ which is related to the *average* diffusion coefficient $D(z)$ by the relation

$$\Psi_{\mathbf{qq}}(z) = q^2 D(z) + \text{higher order in } q \tag{11}$$

We assume that $D(z)$, and hence $\mathbf{\Psi}(z)$, has a well-defined zero-frequency limit. The diffusion constant can be found from

$$D(z) = -\frac{z^2}{2d} \nabla_{\mathbf{q}}^2 \langle G_{\mathbf{qq}}(z) \rangle \,|_{\mathbf{q}=0} \tag{12}$$

and it is indeed the ensemble average of the fluctuating diffusion tensor K_0:

$$\langle \mathsf{K}_0(z) \rangle = D(z)\mathsf{1} \tag{13}$$

In order to elucidate the properties of $\langle \mathsf{G} \rangle$, it will be useful to express G in terms of the related matrix in which $\mathbf{\Psi}(z)$ is replaced by $\mathbf{\Psi}(z = 0+)$,

$$\mathsf{g}(z) = [z\mathsf{1} + \mathbf{\Psi}(0+)]^{-1} \tag{14}$$

and a fluctuation matrix

$$\mathsf{V} = \mathsf{W} + \mathbf{\Psi}(0+) \tag{15}$$

which contains the random parts of G. Then the Green's function can be expanded as a series in terms of g and V. Using the T matrix of the entire lattice (not that of a single defect),

$$\mathsf{T}(z) = \mathsf{V} \cdot [\mathsf{1} - \mathsf{g}(z) \cdot \mathsf{V}]^{-1} \tag{16}$$

we sum the series and write

$$\mathsf{G} = \mathsf{g} + \mathsf{g} \cdot \mathsf{T} \cdot \mathsf{g} \tag{17}$$

Since g is translationally invariant, its Fourier transform is diagonal. Averaging the last equation gives us

$$\langle G_{\mathbf{qq}} \rangle = g_{\mathbf{qq}} + g_{\mathbf{qq}}^2 \langle T_{\mathbf{qq}} \rangle \tag{18}$$

Then it follows readily that the $z \to 0+$ limit of $\langle T_{\mathbf{qq}} \rangle$ vanishes, so that

$$\langle T_{\mathbf{qq}}(0+) \rangle = 0 \tag{19}$$

This is the point at which it is important to exclude models where the W's can be arbitrarily small. The limit $z \to 0+$ in (19) implies that for each lattice realization in the average, $T_{\mathbf{qq}}$ is evaluated at a frequency z small compared to the rate W_{jk} of any bond of the lattice. On the other hand, if the W's could be arbitrarily small, then for any positive z the realization average $\langle T_{\mathbf{qq}}(z) \rangle$ could include contributions from lattices for which some W's were small compared to z. Thus the zero-frequency limit of the realization average might not equal the average of the limit.

Now according to Eq. (12), the average diffusion coefficient is

$$D(z) = D(0+) - \frac{z^2}{2d} \nabla_{\mathbf{q}}^2 \, g_{\mathbf{qq}}^2(z) \langle T_{\mathbf{qq}}(z) \rangle \,|_{\mathbf{q}=0} \tag{20}$$

It is easily shown from the sum rule (4) and equation (11) that for any q,

$$T_{0\mathbf{q}} = T_{\mathbf{q}0} = 0 \tag{21}$$

Therefore the Laplacian must act on $\langle T_{\mathbf{qq}} \rangle$. We are free to subtract $\langle T_{\mathbf{qq}}(0+) \rangle$, which was shown to be zero, so that

$$D(z) = D(0+) - \frac{1}{2d} \nabla_{\mathbf{q}}^2 \langle T_{\mathbf{qq}}(z) - T_{\mathbf{qq}}(0+) \rangle \,|_{\mathbf{q}=0} \tag{22}$$

By writing the definition of T as

$$[1 - \mathsf{g}(z) \cdot \mathsf{V}] \cdot \mathsf{T}(z) = \mathsf{V} \tag{23}$$

and subtracting from this equation its $z \to 0+$ limit, we see that

$$\begin{aligned} \mathsf{T}(z) - \mathsf{T}(0+) = \{ &[\mathsf{T}(z) - \mathsf{T}(0+)] \cdot \mathsf{g}(z) + \mathsf{T}(0+) \\ &\cdot [\mathsf{g}(z) - \mathsf{g}(0+)] \} \cdot \mathsf{V} \end{aligned} \tag{24}$$

We rearrange, using (16) again, to derive the identity

$$\mathsf{T}(z)-\mathsf{T}(0+)=\mathsf{T}(0+)\cdot[\mathsf{g}(z)-\mathsf{g}(0+)]\cdot\mathsf{T}(z) \tag{25}$$

We would like to determine the asymptotic form of the VAF for long times, which is equivalent to the leading singular behavior of the diffusion coefficient $D(z)$ for small z. By substituting identity (25) into itself, it is apparent that for small z,

$$\mathsf{T}(z)-\mathsf{T}(0+)=\mathsf{T}(0+)\cdot[\mathsf{g}(z)-\mathsf{g}(0+)]\cdot\mathsf{T}(0+)+O(z^2) \tag{26}$$

According to Eq. (17), the effect of the disorder on the system is embodied in the T matrix. In the limit $z\to 0+$, T gives fluctuations in the random diffusion tensor $\mathsf{K}_0(0+)$ about its ensemble average, and its small-z behavior is ultimately equivalent to the disorder-induced long time tail in the VAF. Equation (26) leads to the proportionality between the VAF and the squared fluctuations in $\mathsf{K}_0(0+)$ with a known nonrandom coefficient depending on z.

We put (26) into expression (22) for the diffusion coefficient; we find that

$$D(z)=D(0+)-\frac{1}{d}\sum_{\mathbf{q}_1\neq 0}[g_{\mathbf{q}_1\mathbf{q}_1}(z)-g_{\mathbf{q}_1\mathbf{q}_1}(0+)] \times\langle\nabla_{\mathbf{q}}T_{\mathbf{q}\mathbf{q}_1}(0+)\cdot\nabla_{\mathbf{q}}T_{\mathbf{q}_1\mathbf{q}}(0+)\rangle\,|_{\mathbf{q}=0} \tag{27}$$

We know that $g_{\mathbf{q}\mathbf{q}}(z)=[z+q^2D(0+)]^{-1}$, so that most singular part of $D(z)$ comes from the terms of small q_1 in the sum. We are therefore justified in imposing an upper cutoff q_c on the sum and neglecting the contribution of terms with $q_1>q_c$. We may now use the small-wave-number expression (11) to evaluate $g_{\mathbf{q}_1\mathbf{q}_1}$. For small q and q_1 the leading behavior of $T_{\mathbf{q}\mathbf{q}_1}(0+)$ is

$$T_{\mathbf{q}\mathbf{q}_1}(0+)=\mathbf{q}\cdot\boldsymbol{\tau}\cdot\mathbf{q}_1+O(q^2q_1)+O(qq_1^2) \tag{28}$$

due to (21), for appropriate choice of $\boldsymbol{\tau}$. Therefore to leading order,

$$D(z)-D(0+)\sim\frac{1}{d}\sum_{\mathbf{q}_1\neq 0}^{q_c}\frac{z\langle\mathbf{q}_1\cdot\boldsymbol{\tau}\cdot\boldsymbol{\tau}\cdot\mathbf{q}_1\rangle}{q_1^2D(0+)[z+q_1^2D(0+)]} \tag{29}$$

But $\langle\mathbf{q}_1\cdot\boldsymbol{\tau}\cdot\boldsymbol{\tau}\cdot\mathbf{q}_1\rangle$ can be replaced by $(q_1^2/d)\langle\boldsymbol{\tau}:\boldsymbol{\tau}\rangle$, as may be seen by summing over orientations of $\mathbf{q}_1$ before magnitudes. Therefore we find that the leading behavior of $D(z)$ for small z is

$$D(z)-D(0+)\sim\frac{z}{d^2D(0+)}\langle\boldsymbol{\tau}:\boldsymbol{\tau}\rangle\sum_{\mathbf{q}_1\neq 0}^{q_c}\frac{1}{z+q_1^2D(0+)} \tag{30}$$

We now convert the sum to an integral and invert the Laplace transform. Since $D(z)$ is the Laplace transform of the velocity autocorrelation function $\phi_2(t)$, we find the long time tail behavior

$$\phi_2(t) \sim -\frac{2\pi V}{d} \langle \tau : \tau \rangle [4\pi D(0+)t]^{-(d+2)/2} \tag{31}$$

where V is the volume of the system. Note that this asymptotic result does not depend on q_c.

In order to identify τ, we put the Green's function (17) into expression (9) for the diffusion tensor. Eliminating $g_{\mathbf{qq}}$ as before, we find that

$$\mathbf{K}_0(z) = D(0+)\mathbf{1} - \tfrac{1}{2}\nabla_{\mathbf{q}}\nabla_{\mathbf{q}} T_{\mathbf{qq}}(z)\,|_{\mathbf{q}=0} \tag{32}$$

Then in the limit $z \to 0+$, we have

$$\mathsf{K}_0(0+) - \langle \mathsf{K}_0(0+) \rangle = -\tfrac{1}{2}\nabla_{\mathbf{q}}\nabla_{\mathbf{q}} T_{\mathbf{qq}}(0+)\,|_{\mathbf{q}=0} \tag{33}$$

We identify the left-hand side of this equation as $\delta\mathsf{K}_0$, so Eq. (28), which defines τ, leads to

$$\delta\mathsf{K}_0 = \tau \tag{34}$$

Then the VAF may be written as

$$\phi_2(t) \sim -\frac{2\pi V}{d} \langle \delta\mathsf{K}_0 : \delta\mathsf{K}_0 \rangle [4\pi D(0+)t]^{-(d+2)/2} \tag{35}$$

for large t. This is in complete agreement with Eq. (4.22) of the first paper of EMDvB, when our K_0 is identified as the spatial average of $\mathsf{K}(\mathbf{r})$.

We have not derived the generalized diffusion equation of EMDvB, but we have established the correctness of its prediction for the asymptotic behavior of the VAF for our class of models. We have also given a precise (but formal) specification of the fluctuating diffusion tensor K_0. Our identity [Eq. (26)] relating the small-z T matrix to the square of its static limit would possibly be useful in other problems involving long time tails as well.

ACKNOWLEDGMENTS

We acknowledge helpful discussions with J. Machta, T. R. Kirkpatrick, and J. R. Dorfman. This work was supported by a National Science Foundation research grant.

REFERENCES

1. M. H. Ernst, J. Machta, J. R. Dorfman, and H. van Beijeren, *J. Stat. Phys.* **34**:477 (1984); J. Machta, M. H. Ernst, H. van Beijeren, and J. R. Dorfman, *J. Stat. Phys.* **35**:413 (1984).
2. J. Machta, *J. Stat. Phys.* **42**: (1986).