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Classical Diffusion in Strong Random Media

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We study classical diffusion of particles in random media. Although many of our results are general, we focus on the case of an ion in a three-dimensional medium with random, quenched charge centers obeying bulk charge neutrality. Within a functional-integral framework, we calculate the effective diffusion coefficients by first-order and second-order self-consistent perturbation theory (with a Gaussian reference in both cases). We also carry out a one-loop order momentum space renormalization group calculation. The self-consistent methods are complicated numerically and fail beyond intermediate disorder strengths. In contrast, the renormalization group calculation gives an analytical result that appears valid even to high disorder strengths. The methodology, generally applicable to a quantitative calculation of effective diffusion coefficients in disordered media, resolves deficiencies in self-consistent perturbation theory approaches to this class of problems.

KEY WORDS: Diffusion; random media; functional integral; perturbation theory; renormalization group.

1. INTRODUCTION

This paper describes quantitative calculations of the effective classical diffusion coefficient of particles in random media. Some of our results are general, but we focus in particular on the three-dimensional classical diffusion of an ion in a medium with charged impurities. The presence of the impurities impedes the motion of the ionic penetrant, thereby reducing the effective diffusion coefficient. The degree of reduction of the diffusion coefficient is, of course, very important in many applications of condensed matter systems, from the diffusion-limited reactions that occur in heterogeneous catalysts, ion-exchangers, and sorbents to the many ionic pro-

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cesses occurring in disordered biological media to the diffusion of gate material across oxide layers in small-scale electronic devices.

Early formulations by Martin *et al.*[1] and De Dominicis and Peliti[2] provide a field-theoretic framework in which to consider problems of diffusion in disordered media. Renormalization group studies of diffusion in random media have shown that for high enough dimensionality or for force–force correlations of short enough range, there is a weak disorder fixed point that is diffusive. Many of the calculations leading to this conclusion are discussed in the recent review by Bouchaud and Georges.[3]

Since the fixed point is diffusive, one might suspect the diffusion problem should be well-modeled by a Gaussian reference system. In fact, this problem has recently been treated by constructing a self-consistent Gaussian reference system for a path integral formulation of the diffusion problem.[4] As noted in ref. 4, the reliability of this approach is restricted to weak and moderate disorder strengths. At strong disorder, it predicts a diffusive to subdiffusive transition, in disagreement with an exact bound known for this problem (*vide intra*).

It seems, therefore, that self-consistent approaches to identifying a Gaussian reference system lead to renormalizations of the diffusion coefficient that are far too dramatic at high disorder strengths. Essentially, these Gaussian reference systems overemphasize short-length-scale features and do not capture the large-length-scale diffusive behavior correctly. Graphically, one expects that the diffusing particle tends to remain trapped in locally deep potential wells, with occasional transitions between trapping sites. The hops between wells leads to overall diffusive behavior, with a diffusion coefficient reduced from the free-space value. If this picture is correct, a renormalization group analysis should capture it.

Mathematically, the problem we treat is the calculation of a diffusion coefficient in a material with a static potential that obeys Gaussian statistics. Physically, one example of a Gaussian potential is that due to the large-length-scale fluctuations in charge density that occur in a medium with ionic disorder. So, for example, we might be considering the diffusion of an ion in sea of fixed, disordered charges. That the Coulomb potential is singular at overlap implies that the potential between the diffusing ion and the disordered ions is not Gaussian on very short length scales. However, on long enough length scales, the potential is likely Gaussian, since the contribution at any point is due to very many ions, and the central limit theorem likely applies. Thus, we can consider imposing a wavevector cutoff while in the process of our calculation, constraining ourselves to the region where the physical potential truly is Gaussian. It will turn out that in the case where the motion is diffusive, we can take the cutoff to infinity at the end of the calculation. Thus, we will proceed as though there were no cutoff.

In Section 2, we describe our model of the random medium in which the particle diffuses. We illustrate our general results by reference to this specific form of disorder. In Section 3 we review the field-theoretic formulation of the classical diffusion problem and discuss simple perturbation theory for the effective diffusion coefficient. We attempt to take into account some of the higher-order terms by constructing self-consistent Gaussian reference systems in Section 4. This approach is not wholly satisfactory, however, and we attempt to incorporate the overall scaling properties of the problem with a renormalization group calculation in Section 5. We discuss the significance and limitations of the calculations in Section 6.

2. RANDOM MEDIUM MODEL

We assume the potential felt by the diffusing ion is caused by a static distribution of charged impurities,

$$V(\mathbf{x}) = \int d\mathbf{y} \, \frac{eq}{|\mathbf{x}-\mathbf{y}|} \rho(\mathbf{y}) \tag{1}$$

The correlation function of the number density of charge centers is assumed to have a finite correlation length and obey bulk charge neutrality. A fairly general form for the susceptibility is therefore

$$\chi_{\rho\rho}(\mathbf{x}) = \rho\delta(\mathbf{x}) - \frac{\rho\kappa^2 e^{-\kappa|\mathbf{x}|}}{4\pi|\mathbf{x}|} \tag{2}$$

In k space, this form is

$$\hat{\chi}_{\rho\rho}(k) = \rho \frac{k^2}{k^2+\kappa^2} \tag{3}$$

The coefficient of the $\exp(-\kappa r)/r$ term in Eq. (2) is chosen so as to make $\hat{\chi}_{\rho\rho}(k)$ vanish in the limit $k \to 0$, thereby satisfying charge neutrality in a bulk sample. Here, the correlation length is given by $1/\kappa$, and the charge centers are considered to have an average number density of ρ. Such a form would result from a simple Debye–Hückel theory for the charged impurities, but we do not make this correspondence and assume no particular relation between κ and ρ. The potential field resulting from the random density field is likely Gaussian in the limit of a large sample due to

the long-range nature of the Coulomb potential and the finite correlation length of Eq. (2). The correlation function of the potential field is given by

$$\hat{\chi}_{VV}(k) = \frac{(4\pi eq)^2 \rho}{k^2(k^2+\kappa^2)} \tag{4}$$

where $\pm e$ is the charge of the impurities and q is the charge of the diffusing ion.

3. FIELD-THEORETIC REPRESENTATION OF THE DIFFUSION EQUATION

The Green's function $G_V(\mathbf{x}, t)$ for diffusion in a particular instance of a quenched random medium is given by the solution of the standard diffusion equation. With D_0 as the free-space diffusion coefficient and $\beta_0 = 1/k_B T$, the diffusion equation is

$$\frac{\partial G_V(\mathbf{x}, t)}{\partial t} = D_0 \nabla^2 G_V(\mathbf{x}, t) + \beta_0 D_0 \nabla \cdot [G_V(\mathbf{x}, t) \nabla V(\mathbf{x})] \tag{5}$$

where $V(\mathbf{x})$ is an instance of the quenched random potential in which the diffusion occurs. The Laplace transform of the Green's function $\tilde{G}_V(\mathbf{x}, s)$ satisfies

$$s\tilde{G}_V(\mathbf{x}, s) = D_0 \nabla^2 \tilde{G}_V(\mathbf{x}, s) + \beta_0 D_0 \nabla \cdot [\tilde{G}_V(\mathbf{x}, s) \nabla V(\mathbf{x})] + \delta(\mathbf{x}) \tag{6}$$

This Green's function can formally be represented by a functional integral over two conjugate fields,[3]

$$\tilde{G}_V(\mathbf{x}, s) = -i \int \mathscr{D}[\bar{\varphi}]\, \mathscr{D}[\varphi]\, \bar{\varphi}_1(\mathbf{x})\, \varphi_1(\mathbf{0})\, e^{L_V[\bar{\varphi}, \varphi]} \Big/ \int \mathscr{D}[\bar{\varphi}]\, \mathscr{D}[\varphi]\, e^{L_V[\bar{\varphi}, \varphi]} \tag{7}$$

where the action is given by

$$L_V[\bar{\varphi}, \varphi] = i \int d\mathbf{x}\, \bar{\varphi}_\alpha(\mathbf{x}) \{(s - D_0 \nabla^2)\, \varphi_\alpha(\mathbf{x}) - \beta_0 D_0 \nabla \cdot [\varphi_\alpha(\mathbf{x}) \nabla V(\mathbf{x})]\} \tag{8}$$

Summation over repeated replica indices is implied in Eq. (8) ($\alpha = 1, \ldots, N$). When the potential is a Gaussian field, as it is assumed to be, the quenched average over the potential results in the effective action

$$L[\hat{\tilde{\varphi}}, \hat{\varphi}] = i \int_{\mathbf{k}} \hat{\tilde{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\alpha(\mathbf{k})[s + D_0 k^2]$$

$$+ \frac{(\beta_0 D_0)^2}{2} \int_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4} (2\pi)^d\, \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)\mathbf{k}_2 \cdot (\mathbf{k}_1 + \mathbf{k}_2)$$

$$\times \mathbf{k}_4 \cdot (\mathbf{k}_1 + \mathbf{k}_2)\, \hat{\chi}_{VV}(|\mathbf{k}_1 + \mathbf{k}_2|)\, \hat{\varphi}_\alpha(\mathbf{k}_1)\, \hat{\tilde{\varphi}}_\alpha(\mathbf{k}_2)\, \hat{\varphi}_\beta(\mathbf{k}_3)\, \hat{\tilde{\varphi}}_\beta(\mathbf{k}_4) \qquad (9)$$

where the notation $\int_{\mathbf{k}}$ stands for the d-dimensional integral $\int d\mathbf{k}/(2\pi)^d$. The function $\hat{\chi}_{VV}(k)$ is the potential–potential correlation function. The average over quenched disorder requires the limit $N \to 0$ be taken in the expression for the Green's function. The disorder-averaged Green's function is thus given by

$$\hat{G}(k, s) = -\frac{i}{\Omega} \lim_{N \to 0} \int \mathscr{D}[\hat{\tilde{\varphi}}]\, \mathscr{D}[\hat{\varphi}]\, \hat{\tilde{\varphi}}_1(\mathbf{k})\, \hat{\varphi}_1(-\mathbf{k})\, e^{L[\hat{\tilde{\varphi}}, \hat{\varphi}]}$$

$$\Big/ \int \mathscr{D}[\hat{\tilde{\varphi}}]\, \mathscr{D}[\hat{\varphi}]\, e^{L[\hat{\tilde{\varphi}}, \hat{\varphi}]} \qquad (10)$$

where Ω denotes the effectively infinite volume of the system. Alternatively, in the thermodynamic limit, Eq. (10) can be written as

$$(2\pi)^d\, \delta(\mathbf{k} + \mathbf{k}')\, \hat{G}(k, s) = -i \lim_{N \to 0} \langle \hat{\tilde{\varphi}}_1(\mathbf{k})\, \hat{\varphi}_1(\mathbf{k}') \rangle \qquad (11)$$

where the angle brackets denote the functional average with weight $\exp(L[\hat{\tilde{\varphi}}, \hat{\varphi}])$.

The action (9) in the disorder-averaged functional integral representation of the Green's function does not have a harmonic form, and the Green's function thus cannot be calculated exactly. We are interested in the effective diffusion coefficient, defined in relation to the mean square displacement averaged over the disorder by

$$D = \lim_{t \to \infty} \int d\mathbf{x}\, |\mathbf{x}|^2\, G(\mathbf{x}, t)/2\, dt = \lim_{k \to 0} \hat{G}^{-1}(k, 0)/k^2 \qquad (12)$$

As detailed in Appendix A, iteration on Eq. (6) using the $V = 0$ free propagator $\hat{G}_{\text{free}}(k, s) = 1/(s + D_0 k^2)$ generates a perturbation series for the effective diffusion coefficient:

$$D/D_0 = 1 - \beta_0^2 \chi_{VV}(0)/d + \beta_0^4 \chi_{VV}(0)^2/2d^2 + O(\beta_0^6) \qquad (13)$$

in d dimensions. The site potential fluctuations are given in the case of model (4) by

$$\beta_0^2\, \chi_{VV}(0) = \frac{\gamma}{4\pi\kappa D_0^2} \qquad (14)$$

where the strength of disorder γ is given by

$$\gamma = (4\pi\beta_0 D_0 eq)^2 \rho \tag{15}$$

Direct perturbation theory on the action (9), discussed in Appendix B, reproduces Eq. (13). To first order, both $N=1$ and $N \to 0$ lead to the same; correct result. The $N \to 0$ limit must be taken to obtain the correct result to second order, however.

4. SELF-CONSISTENT GAUSSIAN REFERENCE SYSTEMS

To make progress on the anharmonic action (9), we require some form of approximation. In this section, we use a self-consistent perturbation theory for the correlation function. That is, we define Gaussian reference systems by requiring either the first-order or the first- plus second-order correction to the correlation function to vanish for a harmonic reference system:

$$\langle \hat{\bar{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\beta(\mathbf{k})(L - L_0) \rangle_{0c} = 0 \tag{16}$$

or

$$\langle \hat{\bar{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\beta(\mathbf{k})(L - L_0) \rangle_{0c} + \tfrac{1}{2} \langle \hat{\bar{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\beta(\mathbf{k})(L - L_0)^2 \rangle_{0c} = 0 \tag{17}$$

where L is the action of Eq. (9). The subscript zero on the brackets indicates an average over the reference system:

$$\langle \cdot \rangle_0 = \lim_{N \to 0} \int \mathscr{D}[\hat{\bar{\boldsymbol{\varphi}}}]\, \mathscr{D}[\hat{\boldsymbol{\varphi}}]\, (\cdot)\, e^{L_0[\hat{\bar{\boldsymbol{\varphi}}}, \hat{\boldsymbol{\varphi}}]} \Big/ \int \mathscr{D}[\hat{\bar{\boldsymbol{\varphi}}}]\, \mathscr{D}[\hat{\boldsymbol{\varphi}}]\, (\cdot)\, e^{L_0[\hat{\bar{\boldsymbol{\varphi}}}, \hat{\boldsymbol{\varphi}}]} \tag{18}$$

The subscript c on the brackets in Eqs. (16) and (17) denotes a connected average. The Gaussian reference action, over which the connected averages are taken, is given by

$$L_0[\hat{\bar{\boldsymbol{\varphi}}}, \hat{\boldsymbol{\varphi}}] = i \int_{\mathbf{k}} \hat{\bar{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\beta(\mathbf{k})\, \hat{G}^{-1}_{0_{\alpha\beta}}(k, s) \tag{19}$$

Equation (16) or (17) determines the Green's function $\hat{G}_{0_{\alpha\beta}}(k, s)$ of the Gaussian reference system. If the partition function generated by the action (9) were real and convergent, Eq. (16) would be the standard variational bound to find the optimal harmonic reference system that mimics the properties of Eq. (9).[5] Note that the effective Green's function $\hat{G}_{0_{\alpha\beta}}(k, s)$ must be real and depends only on $|\mathbf{k}|$ due to the isotropic symmetry of $\hat{\chi}_{VV}(k)$.

Perturbation theory to infinite order in β_0^2 using the diagonal, replica-symmetric free propagator predicts that $\langle \hat{\varphi}_\alpha(\mathbf{k})\, \hat{\bar{\varphi}}_\beta(-\mathbf{k})\rangle_{\text{free}}$ vanishes in the $N \to 0$ limit if $\alpha \neq \beta$. We thus assume a diagonal, replica-symmetric reference system. In this case the resulting self-consistent equation for the real, radially-symmetric, effective propagator for the first-order treatment is

$$\hat{G}_0^{-1}(k, s) = (s + D_0 k^2) + (\beta_0 D_0)^2 \int_{\mathbf{k}_2} \hat{G}_0(k_2, s)\, \hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \tag{20}$$

where

$$\hat{\alpha}(\mathbf{k}, \mathbf{k}_2) = \hat{\chi}_{VV}(|\mathbf{k} - \mathbf{k}_2|)\mathbf{k} \cdot (\mathbf{k} - \mathbf{k}_2)\mathbf{k}_2 \cdot (\mathbf{k} - \mathbf{k}_2) \tag{21}$$

The self-consistent equation arising from the second-order treatment is

$$\begin{aligned}
2\hat{G}_0^{-1}(k, s) = {} & 3(s + D_0 k^2) - \hat{G}_0(k, s)(s + D_0 k^2)^2 \\
& + 4(\beta_0 D_0)^2 \int_{\mathbf{k}_2} \hat{G}_0(k_2, s)\, \hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \\
& - 2(\beta_0 D_0)^2\, \hat{G}_0(k, s)(s + D_0 k^2) \int_{\mathbf{k}_2} \hat{G}_0(k_2, s)\, \hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \\
& - (\beta_0 D_0)^2 \int_{\mathbf{k}_2} \hat{G}_0^2(k_2, s)(s + D_0 k_2^2)\, \hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \\
& - (\beta_0 D_0)^4\, \hat{G}_0(k, s) \left[\int_{\mathbf{k}_2} \hat{G}_0(k_2, s)\, \hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \right]^2 \\
& - (\beta_0 D_0)^4 \int_{\mathbf{k}_2} \hat{G}_0^2(k_2, s)\, \hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \int_{\mathbf{k}_2'} \hat{G}_0(k_2', s)\, \hat{\alpha}(\mathbf{k}_2, \mathbf{k}_2') \\
& - (\beta_0 D_0)^4 \int_{\mathbf{k}_2} \hat{G}_0(k_2, s) \int_{\mathbf{k}_2'} \hat{G}_0(k_2', s)\, \hat{G}_0(|\mathbf{k}_2 + \mathbf{k}_2' - \mathbf{k}|, s) \\
& \times \mathbf{k}_2 \cdot (\mathbf{k}_2 - \mathbf{k})\mathbf{k}_2' \cdot (\mathbf{k}_2 - \mathbf{k})\mathbf{k} \cdot (\mathbf{k}_2' - \mathbf{k})(\mathbf{k}_2 + \mathbf{k}_2' - \mathbf{k}) \cdot (\mathbf{k}_2' - \mathbf{k}) \\
& \times \hat{\chi}_{VV}(|\mathbf{k}_2 - \mathbf{k}|)\, \hat{\chi}_{VV}(|\mathbf{k}_2' - \mathbf{k}|)
\end{aligned} \tag{22}$$

Appendix B gives an outline of the manipulations that lead from Eqs. (16) and (17) to Eqs. (20) and (22). Note that the solutions to Eqs. (20) and (22) exactly satisfy the sum rule $\hat{G}_0(0, s) = 1/s$. These integral equations also satisfy first- and second-order perturbation theory, respectively, as they must.

Equations (20) and (22) apply to any type of Gaussian disorder in any dimension greater than the upper critical dimension, in which case infrared

divergences are avoided for simple analytic forms of $\hat{G}_0(k, s)$. If nonanalytic forms of $\hat{G}_0(k, s)$ are allowed, Eqs. (20) and (22) may also apply below the upper critical dimension and generate nontrivial scaling laws.[3]

When diffusion occurs, the effective diffusion coefficient is given by $D = \lim_{k \to 0} \hat{G}_0^{-1}(k, 0)/k^2$. To analyze the diffusive regime, simpler integral equations for the function

$$\hat{f}(h) = D_0 \kappa^2 h^2 \hat{G}_0(\kappa h, 0) \tag{23}$$

suffice, where h is now a dimensionless variable. The diffusion coefficient is given by

$$D/D_0 = \lim_{h \to 0} \hat{f}^{-1}(h) \tag{24}$$

We solve the integral equations (20) and (22) in the $s \to 0$ limit by a basis set approach. Asymptotic analysis shows $\hat{f}(h) = D_0/D + O(h^2)$ as $h \to 0$ and $\hat{f}(h) \sim 1 + O(1/h^2)$ as $h \to \infty$. Motivated by these constraints, we assume

$$\hat{f}(h) = \sum_{i=1}^{n} \frac{a_i}{1 + (h/b_i)^2} \tag{25}$$

The last coefficient is fixed by $a_n = 1$ and $b_n = \infty$. The half-widths $\{b_i\}$ are distributed in $0 < b_i < h_{\max}$ by the relation $b_i = h_{\max} i^4/(n-1)^4$. The parameters $\{a_i\}$ are determined by insisting the integral equations (20) and (22) are satisfied at h_i, where $h_1 = b_1/2$ and $h_i = (b_i + b_{i-1})/2$. Equations (20) and (22) thus become nonlinear algebraic equations for the $\{a_i\}$. In particular, the equation to be solved in the first-order case is

$$1/(A_{1ij} a_j) = (\gamma/\kappa D_0^2)\, a_j B_{1ij} \tag{26}$$

and in the second-order case the equation is

$$\frac{2}{A_{1ij} a_j} = 3 - A_{1ij} a_j + 4 \frac{\gamma}{\kappa D_0^2} B_{1ij} a_j - \frac{\gamma}{\kappa D_0^2} (2B_{2ijk} + B_{3ijk})\, a_j a_k$$
$$- \frac{\gamma^2}{\kappa^2 D_0^4} (B_{4ijkl} + B_{5ijkl} + B_{6ijkl})\, a_j a_k a_l \tag{27}$$

The summation convention is implied in these equations. The basis set integrals A and B for the specific case of disorder defined by Eq. (4) are

[3] See, for example, the recent self-consistent approach to the Kardar–Parisi–Zhang equation, a nonlinear diffusion equation similar to, but distinct from, Eq. (5), in ref. 6. See also the polymeric swelling case discussed in ref. 7.

listed in Appendix C. We find Eqs. (26) and (27) are efficiently solved by iteration on the $\{a_i\}$ parameters. Convergence is achieved for $n = 16$ and $h_{\max} = 20$. Figure 1 depicts the effective diffusion coefficients predicted by Eqs. (26) and (27) for the specific model of disorder defined by Eq. (4) in $d = 3$.

5. RENORMALIZATION GROUP APPROACH

Renormalization group studies have been applied to the field-theoretic formulation of diffusion in random media. The review of Bouchaud and Georges details some of the scaling predictions that have been made for the mean square displacement, i.e., the exponent in the relation $\langle r^2(t) \rangle \sim t^{2\nu}$.[3] For the case of disorder described by Eq. (4), these RG studies indicate the long-time behavior is diffusive in three dimensions, i.e., $\nu = 1/2$. Quantitative calculation of the diffusion coefficient, however, seems not to have received much attention. Here we present a quantitative RG treatment of the diffusion coefficient for general $\chi_{\nu\nu}(|\mathbf{r}|)$ in any dimension d. The discussion is limited, however, to case where $\chi_{\nu\nu}(0)$ is finite.

We use the standard momentum-space RG algorithm directly in the physical dimension. A general discussion of this approach as applied to the classical diffusion problem can be found in the review by Bouchaud and

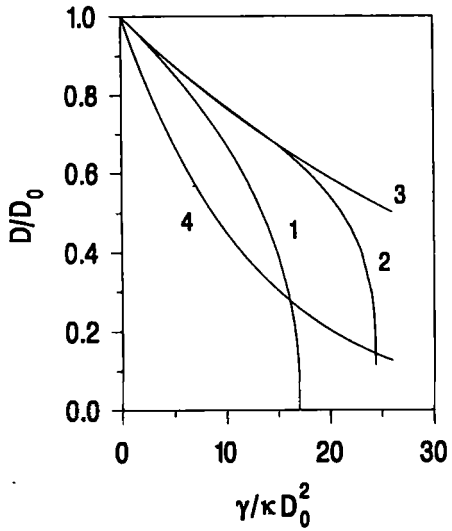

Fig. 1. Diffusion coefficient as a function of disorder strength. Curve 1 is generated from the numerical solution to Eq. (20). Curve 2 is generated from the numerical solution to Eq. (22). Curve 3 is the RG result, Eq. (33), for $d = 3$. Curve 4 is the exact bound, Eq. (34).

George.[3] More general discussions of the simple RG procedure we use can be found in, for example, ref. 8.

The RG procedure will renormalize the parameters s, β_0, D_0, and $\hat{\chi}_{VV}(k)$. We explicitly construct the recursion relation for the renormalized inverse temperature and renormalized diffusion coefficient, which we denote by β and D, respectively. We first introduce an artificial cutoff in the integrations in the action (9) such that $|\mathbf{k}| < k_c$ and $|\mathbf{k}_i| < k_c$. We then integrate out the modes $k_c/b < k < k_c$ from the action (9) to first order in the parameter β^2. The expansion parameter is forced to be β^2 by first scaling the fields in the action (9) by $D^{-1/2}$. These operations transform the action (9) to

$$\begin{aligned} L[\hat{\bar{\varphi}}, \hat{\varphi}] = i \int_{\mathbf{k}} \hat{\bar{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\alpha(\mathbf{k}) \left\{ \frac{s}{D} + \left[1 - \frac{\beta^2}{d} \int_{\mathbf{k}'} \hat{\chi}_{VV}(k') \right] k^2 + O(k^4) \right\} \\ + \frac{\beta^2}{2} \int_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4} (2\pi)^d\, \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)\, \mathbf{k}_2 \cdot (\mathbf{k}_1 + \mathbf{k}_2) \\ \times \mathbf{k}_4 \cdot (\mathbf{k}_1 + \mathbf{k}_2)\, \hat{\chi}_{VV}(|\mathbf{k}_1 + \mathbf{k}_2|)\, \hat{\varphi}_\alpha(\mathbf{k}_1)\, \hat{\bar{\varphi}}_\alpha(\mathbf{k}_2) \\ \times \hat{\varphi}_\beta(\mathbf{k}_3)\, \hat{\bar{\varphi}}_\beta(\mathbf{k}_4) + \text{const} \end{aligned} \tag{28}$$

Here $|\mathbf{k}| < k_c/b$ and $|\mathbf{k}_i| < k_c/b$, but $k_c/b < |\mathbf{k}'| < k_c$. As indicated, integrating out the fields in the momentum shell leads to terms higher order in k^2 in the part of the action quadratic in the fields. We retain in the recursion relations only the lowest order term associated with k^2. This term follows from Eq. (A.2), with the range of $\mathbf{k}'$ restricted to the momentum shell. Also generated by integrating out the fields in the momentum shell are terms independent of the remaining fields. Such terms do not affect the correlation function, and we ignore them. To keep the cutoff at k_c, we rescale the momenta by $k' = bk$. So as to keep the formula for the diffusion coefficient as $D = \lim_{k \to 0} \hat{G}^{-1}(k, 0)/k^2$, with $\hat{G}(k, s)$ given by Eq. (10) and with the fields in the action *not* scaled by $D^{-1/2}$, we rescale the fields by $\hat{\varphi}' = b^{-(d+2)/2} \hat{\varphi}$ and $\hat{\bar{\varphi}}' = b^{-(d+2)/2} \hat{\bar{\varphi}}$. This step prevents trivial scaling from changing the coefficient of the k^2 term in the action. With these rescalings and removal of the primes, the action (9) becomes

$$\begin{aligned} L[\hat{\bar{\varphi}}, \hat{\varphi}] = i \int_{\mathbf{k}} \hat{\bar{\varphi}}_\alpha(-\mathbf{k})\, \hat{\varphi}_\alpha(\mathbf{k}) \left\{ \frac{sb^2}{D} + \left[1 - \frac{\beta^2}{d} \int_{\mathbf{k}'} \hat{\chi}_{VV}(k') \right] k^2 \right\} \\ + \frac{\beta^2}{2b^d} \int_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4} (2\pi)^d\, \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)\, \mathbf{k}_2 \cdot (\mathbf{k}_1 + \mathbf{k}_2) \\ \times \mathbf{k}_4 \cdot (\mathbf{k}_1 + \mathbf{k}_2)\, \hat{\chi}_{VV}(|\mathbf{k}_1 + \mathbf{k}_2|/b)\, \hat{\varphi}_\alpha(\mathbf{k}_1)\, \hat{\bar{\varphi}}_\alpha(\mathbf{k}_2) \\ \times \hat{\varphi}_\beta(\mathbf{k}_3)\, \hat{\bar{\varphi}}_\beta(\mathbf{k}_4) \end{aligned} \tag{29}$$

The ranges of integration are now $|\mathbf{k}| < k_c$, $|\mathbf{k}_i| < k_c$, and $k_c/b < |\mathbf{k}'| < k_c$. It is clear that the action has retained the same form. After scaling the fields by $D^{1/2}$, it is clear that the recursion relations for the parameters are

$$\begin{aligned} \beta'^2 &= \beta^2/b^d \\ D' &= D\left[1 - \frac{\beta^2}{d}\int_{\mathbf{k}'} \hat{\chi}_{VV}(k')\right] \\ \hat{\chi}'_{VV}(k) &= \hat{\chi}_{VV}(k/b) \end{aligned} \tag{30}$$

where the integration over $\mathbf{k}'$ in the expression for D' is restricted to the shell $k_c/b < k' < k_c$. When the scaling b is identified as $b = \exp(l)$ and is taken to be infinitesimally different from unity, the renormalization group equations become

$$\begin{aligned} \frac{d\ln\beta^2}{dl} &= -d \\ \frac{d\ln D}{dl} &= -\frac{\beta^2 S_d k_c^d \hat{\chi}_{VV}(k_c e^{-l})}{(2\pi)^d d} \end{aligned} \tag{31}$$

where S_d is the surface area of a d-dimensional unit sphere. Integration of the flow equations leads to the renormalized coupling constants:

$$\begin{aligned} \beta^2 &= \beta_0^2 e^{-dl} \\ \ln\left(\frac{D}{D_0}\right) &= -\frac{1}{(2\pi)^d d}\int_0^\infty dl\, \beta_0^2 e^{-dl} S_d k_c^d \hat{\chi}_{VV}(k_c e^{-l}) \end{aligned} \tag{32}$$

In the limit that $k_c \to \infty$, this equation yields

$$D = D_0 \exp[-\beta_0^2 \chi_{VV}(0)/d] \tag{33}$$

This result for the specific model of disorder defined by Eq. (4) in $d = 3$ is plotted in Fig. 1.

6. DISCUSSION AND CONCLUSIONS

It is clear that the self-consistent approaches are satisfactory for small $\beta_0^2 \chi_{VV}(0)$. By construction they must satisfy perturbation theory to the appropriate order. The first-order treatment, however, incorrectly predicts a negative curvature of the effective diffusion coefficient for weak disorder. The second-order treatment correctly predicts a positive curvature, and it agrees with the RG answer over a wide range in disorder strength.

The form of the effective diffusion coefficient deduced from the first-order self-consistent treatment is consistent with a recent path integral treatment of this problem.[4] In that reference, an integral equation is derived from a self-consistent, first-order perturbation theory for the propagator. This approximation is somewhat less direct than that of Eq. (20) due to a preaveraging of some of the high-order terms in the action. The results, however, are in qualitative agreement with those of Fig. 1.

For sufficiently large disorder strengths the self-consistent approaches predict that the effective diffusion coefficient drops to zero with an apparently infinite slope. This prediction cannot be correct. As shown in ref. 9,[4] there is an exact lower bound on the effective diffusion coefficient. The bound arises because the one-dimensional effective diffusion coefficient can be calculated exactly, and the value of the d-dimensional diffusion coefficient must be greater than the one-dimensional value. This bound can be expressed as

$$D_{d-\dim} \geqslant D_{1-\dim} = D_0 \exp[-\beta_0^2 \chi_{vv}(0)] \tag{34}$$

The one-loop order renormalization group approach, somewhat surprisingly, provides the exact answer for the effective diffusion coefficient in one dimension. Moreover, the RG result is valid to at least second order in any dimension, as is evident by a comparison of Eqs. (33) and (13). This result never crosses the bound. We speculate that this answer may be valid to rather high disorder strengths. It is of some interest to compare this result with exact numerical results, when they become available.

In conclusion, the reduction in diffusion coefficient due to the disorder occurs as a result of local trapping of the diffusing particle in particularly deep wells in the potential field. The penetrant exhibits diffusive motion between these deep local wells. Self-consistent Gaussian reference systems seem to overemphasize the local behavior, leading to an incorrect prediction of trapping and a vanishing diffusion coefficient. In contrast, the renormalization group method offers a controlled approach to this problem, as it consistently applies perturbation theory only to the high-k modes, where it is valid. If the renormalization group result is indeed valid to high disorder strengths, it means that when the spatial rescaling has driven the momentum shell integration to a region where substantial mode-coupling effects occur, β^2 has been driven to such a small value that perturbation theory is still valid. Whether this is true is worthy of future investigation, by, for example, asymptotic expansion in $1/d$ or in $1/\beta_0$.

[4] The unconventional units chosen in this paper introduce a factor of four in comparison with Eq. (34).

APPENDIX A. PERTURBATION THEORY FOR THE DIFFUSION COEFFICIENT

We describe iteration on Eq. (6) using the $V=0$ form of the propagator $\hat{G}_{\text{free}}(k, s)=1/(s+D_0k^2)$. Specifically, we consider the integral equation for $\hat{g}_V(k)=D_0k^2\hat{G}_V(k, 0)$:

$$\hat{g}_V(k)=1-\beta_0\int_{\mathbf{k}'}\hat{g}_V(k')\,\hat{V}(\mathbf{k}-\mathbf{k}')\mathbf{k}'\cdot(\mathbf{k}-\mathbf{k}')/k'^2 \tag{A.1}$$

We expand the right-hand side (rhs) by iteration, replacing $\hat{g}_V(k')$ by the rhs. We then take the average over the Gaussian potential V and set $\hat{g}(k)=1$. Only terms even in powers of β_0 survive this averaging. The diffusion coefficient is given by $D_0/D=\lim_{k\to 0}\hat{g}(k)$, as in Eq. (24). To first order, for example,

$$\hat{g}(k)=1+\beta_0^2\int_{\mathbf{k}'}\hat{\chi}_{VV}(k')\frac{\mathbf{k}'\cdot(\mathbf{k}'+\mathbf{k})}{k^2}\frac{\mathbf{k}\cdot(-\mathbf{k}')}{|\mathbf{k}'+\mathbf{k}|^2}+O(\beta_0^4)$$

$$=1+\beta_0^2\int_{\mathbf{k}'}\hat{\chi}_{VV}(k')/d+O(k^2,\beta_0^4) \tag{A.2}$$

The $k\to 0$ limit yields the first-order result

$$D_0/D=1+\beta_0^2\chi_{VV}(0)/d+O(\beta_0^4) \tag{A.3}$$

Use is made of averaging over all orientations of $\mathbf{k}$, $\langle\cdot\rangle_{\omega(\mathbf{k})}$, e.g., $\langle\mathbf{k}'\cdot\mathbf{k}\rangle_{\omega(\mathbf{k})}=0$ and $\langle\mathbf{k}'\cdot\mathbf{k}\mathbf{k}''\cdot\mathbf{k}\rangle_{\omega(\mathbf{k})}=k^2\mathbf{k}'\cdot\mathbf{k}''/d$ in d dimensions.

The second-order contribution in Eq. (13) arises from a term in the iteration involving the average

$$\langle V(\mathbf{k}_3-\mathbf{k}_4)\,V(\mathbf{k}_2-\mathbf{k}_3)\,V(\mathbf{k}_1-\mathbf{k}_2)\,V(\mathbf{k}-\mathbf{k}_1)\rangle_V \tag{A.4}$$

over the potential. Three types of terms result from this average: (a) $\mathbf{k}_2=\mathbf{k}_4=\mathbf{0}$, (b) $\mathbf{k}_1=\mathbf{k}_3$ and $\mathbf{k}_4=\mathbf{0}$, and (c) $\mathbf{k}_2-\mathbf{k}_3=\mathbf{k}_1$ and $\mathbf{k}_4=\mathbf{0}$. Term (a) leads to $\beta_0^4\chi_{VV}^2(0)/d^2$. Terms (b) and (c) sum after manipulation to $-\beta_0^4\chi_{VV}^2(0)/2d^2$. The final result is

$$D_0/D=1+\beta_0^2\chi_{VV}(0)/d+\beta_0^4\chi_{VV}(0)^2/2d^2+O(\beta_0^6) \tag{A.5}$$

and inversion gives Eq. (13).

APPENDIX B. THE CONNECTED AVERAGES IN THE SELF-CONSISTENT APPROACH

We consider here the implementation of Eqs. (16) and (17). We first note that

$$\langle Ae^{\Delta L}\rangle_{0c} = \langle A\rangle_{0c} + \langle A\,\Delta L\rangle_{0c} + \tfrac{1}{2}\langle A(\Delta L)^2\rangle_{0c} + \cdots \tag{B.1}$$

gives an asymptotic expansion of the average of A with weighting functional $\exp(L)$ in the reference system with weighting functional $\exp(L_0)$ if $\Delta L = L - L_0$. Thus Eqs. (16) and (17) are the first-order and the first- plus second-order corrections to the correlation function if L is the action of Eq. (9). As discussed in the text, we choose the reference action L_0 of Eq. (19) to be diagonal and replica-symmetric. We denote the diagonal element by $\hat{G}_0(k, s)$. We split the action L into a part quadratic in the fields L_2 and the part quartic in the fields L_4. Since we want a self-consistent equation for the propagator, the quantity we will be averaging is $A = \hat{\bar{\varphi}}_1(\mathbf{k})\,\hat{\varphi}_1(-\mathbf{k})/\Omega$. In this case, Eq. (16) becomes

$$\langle A(L_2 + L_4 - L_0)\rangle_{0c} = 0 \tag{B.2}$$

and Eq. (17) becomes

$$\begin{aligned}\langle A(L_2 + L_4 - L_0)\rangle_{0c} + \tfrac{1}{2}\langle A(L_2^2 + L_4^2 + L_0^2 + 2L_2L_4 \\ - 2L_2L_0 - 2L_4L_0)\rangle_{0c} = 0\end{aligned} \tag{B.3}$$

We can evaluate the connected replica averages appearing in these formulas. After taking the $N \to 0$ limit, we find

$$i\langle AL_0\rangle_{0c} = \hat{G}_0(k, s)$$

$$i\langle AL_2\rangle_{0c} = \hat{G}_0^2(k, s)(s + D_0k^2)$$

$$i\langle AL_4\rangle_{0c} = (\beta_0 D_0)^2\,\hat{G}_0^2(k, s)\int_{\mathbf{k}_2}\hat{G}_0(k_2, s)\,\hat{\alpha}(\mathbf{k}, \mathbf{k}_2)$$

$$i\langle AL_0^2\rangle_{0c} = -2\hat{G}_0(k, s)$$

$$i\langle AL_2^2\rangle_{0c} = -2\hat{G}_0^3(k, s)(s + D_0k^2)^2$$

$$i\langle AL_0L_2\rangle_{0c} = -2\hat{G}_0^2(k, s)(s + D_0k^2)$$

$$i\langle AL_0L_4\rangle_{0c} = -3(\beta_0 D_0)^2\,\hat{G}_0^2(k, s)\int_{\mathbf{k}_2}\hat{G}_0(k_2, s)\,\hat{\alpha}(\mathbf{k}, \mathbf{k}_2)$$

$$\begin{aligned}i\langle AL_2L_4\rangle_{0c} = &-2(\beta_0 D_0)^2\,\hat{G}_0^3(k, s)(s + D_0k^2)\int_{\mathbf{k}_2}\hat{G}_0(k_2, s)\,\hat{\alpha}(\mathbf{k}, \mathbf{k}_2) \\ &-(\beta_0 D_0)^2\,\hat{G}_0^2(k, s)\int_{\mathbf{k}_2}\hat{G}_0^2(k_2, s)(s + D_0k_2^2)\,\hat{\alpha}(\mathbf{k}, \mathbf{k}_2)\end{aligned}$$

$$
\begin{aligned}
i\langle AL_4^2\rangle_{0c} = & -2(\beta_0 D_0)^4\, \hat{G}_0^3(k,s)\left[\int_{\mathbf{k}_2} \hat{G}_0(k_2,s)\,\hat{\alpha}(\mathbf{k},\mathbf{k}_2)\right]^2 \\
& -2(\beta_0 D_0)^4\, \hat{G}_0^2(k,s)\int_{\mathbf{k}_2} \hat{G}_0^2(k_2,s) \\
& \times \hat{\alpha}(\mathbf{k},\mathbf{k}_2)\int_{\mathbf{k}_2'} \hat{G}_0(k_2',s)\,\hat{\alpha}(\mathbf{k}_2,\mathbf{k}_2') \\
& -2(\beta_0 D_0)^4\, \hat{G}_0^2(k,s)\int_{\mathbf{k}_2} \hat{G}_0(k_2,s)\int_{\mathbf{k}_2'} \hat{G}_0(k_2',s) \\
& \times \hat{G}_0(|\mathbf{k}_2+\mathbf{k}_2'-\mathbf{k}|,s) \\
& \times \mathbf{k}_2\cdot(\mathbf{k}_2-\mathbf{k})\mathbf{k}_2'\cdot(\mathbf{k}_2-\mathbf{k})\mathbf{k}\cdot(\mathbf{k}_2'-\mathbf{k})(\mathbf{k}_2+\mathbf{k}_2'-\mathbf{k})\cdot(\mathbf{k}_2'-\mathbf{k}) \\
& \times \hat{\chi}_{VV}(|\mathbf{k}_2-\mathbf{k}|)\,\hat{\chi}_{VV}(|\mathbf{k}_2'-\mathbf{k}|) \qquad \text{(B.4)}
\end{aligned}
$$

Collection and rearrangement of these terms gives the self-consistent equations (20) and (22).

Making the identification $L_0 = L_2$ corresponds to a perturbation theory with the $V=0$ form of the propagator $\hat{G}_{\text{free}}(k,s) = 1/(s+D_0k^2)$. Using Eq. (B.1) with the terms listed in Eq. (B.4) leads directly to the perturbation theory result of Eq. (13) for the diffusion coefficient. The last three terms, proportional to $(\beta_0 D_0)^4$, in Eq. (B.4) give the terms (a), (b), and (c), respectively, discussed in Appendix A. We note that the last term, term (c), acquires an incorrect prefactor of 4 in the limit $N=1$. The prefactor of 2 resulting from the $N\to 0$ limit agrees with the perturbation theory term (c) from Appendix A and is correct.

APPENDIX C. THE BASIS SET INTEGRALS

For the specific case of disorder defined by Eq. (4), the basis set integrals are given by

$$A_{1ij} = \frac{1}{1+h_i^2/b_j^2}$$

$$B_{1ij} = \frac{\hat{v}(h_i,b_j)}{(2\pi)^3}$$

$$B_{2ijk} = \frac{B_{1ik}}{1+h_i^2/b_j^2}$$

$$B_{3ijk} = \int_0^\infty \frac{dk_2}{(2\pi)^3}\,\frac{\hat{u}(h_i,k_2)}{(1+k_2^2/b_j^2)(1+k_2^2/b_k^2)}$$

$$B_{4ijkl} = \frac{B_{1ik}B_{1il}}{1+h_i^2/b_j^2}$$

$$B_{5ijkl} = \int_0^\infty \frac{dk_2}{(2\pi)^6} \frac{\hat{u}(h_i, k_2)\,\hat{v}(k_2, b_l)}{(1+k_2^2/b_j^2)(1+k_2^2/b_k^2)}$$

$$\begin{aligned} B_{6ijkl} = \frac{1}{(2\pi)^5} \int_0^\infty dk_2 \int_0^\infty dk_2' \int_{-1}^{1} dx \int_{-1}^{1} dy \int_{-\pi}^{\pi} d\phi \\ \times b_i^2 b_j^2 b_k^2 k_2 k_2' (k_2^2 + kk_2 x)(-k^2 + kk_2' y) \\ \times z(k_2'^2 - kk_2 x - kk_2' y + k_2 k_2' z) \\ \times [(b_i^2 + k^2 + k_2^2 + 2kk_2 x)(b_j^2 + k_2'^2) \\ \times (b_k^2 + k_2^2 + k_2'^2 + 2k_2 k_2' z)\, k^2 (1 + k_2^2) \\ \times (k^2 + k_2^2 + 2kk_2 x)(k^2 + k_2'^2 - 2kk_2' y) \\ \times (1 + k^2 + k_2'^2 - 2kk_2' y)(k_2^2 + k_2'^2 + 2k_2 k_2' z)]^{-1} \end{aligned}$$

$$z = [(1-x^2)(1-y^2)]^{1/2} \cos(\phi) + xy \tag{C.1}$$

The function $\hat{u}(k, k')$ is given by

$$\begin{aligned} k^2 \hat{u}(k, k') = -\pi - \frac{\pi}{4kk'} \Bigg\{ (k^2 - k'^2)^2 \ln \frac{(k-k')^2}{(k+k')^2} \\ + [(k^2 - k'^2)^2 - 1] \ln \frac{(k+k')^2 + 1}{(k-k')^2 + 1} \Bigg\} \end{aligned} \tag{C.2}$$

The function $\hat{v}(k, k')$ is given by

$$\begin{aligned} \hat{v}(k, b) &= \int_0^\infty dk_2 \frac{\hat{u}(k, k_2)}{1 + k_2^2/b^2} \\ &= -\frac{b\pi^2}{2k^2} + \frac{b^2\pi^2}{2k^2} + \frac{(-b^4 - 2b^2k^2 + k^4)\pi^3}{8k^3} \\ &\quad + \frac{(1 + b^4 + 2b^2k^2 - k^4)\pi^2 \arctan(k)}{4k^3} \\ &\quad + \frac{(b^2 + k^2)^2 \pi^2 \arctan[2bk/(-b^2 + k^2)]}{4k^3} \\ &\quad + \frac{(1 - b^4 - 2b^2k^2 - k^4)\pi^2 \arctan[2bk/(1 - b^2 + k^2)]}{4k^3} \\ &\quad - (1 + b^2 + k^2)(1 - 2b^2 + b^4 - k^4)\pi^2 \\ &\quad \times \frac{\arctan[k(1 + b^2 + k^2)/(1 - b^2 + k^2)]}{4k^3(1 - b^2 + k^2)} \\ &\quad - \frac{(b^2 + k^2)^2 \pi^3 \operatorname{signum}(-b^2 + k^2)}{8k^3} \end{aligned} \tag{C.3}$$

The one-dimensional integrals in Eq. (C.1) are done to a specified tolerance by adaptive Gauss–Legendre integration, and the five-dimensional integral is done by tenth-order Gauss–Legendre integration.[10] The identity

$$\int_0^\infty dx\, f(x) = \int_0^1 [f(x) + f(1/x)/x^2] \tag{C.4}$$

is used in performing the wave vector integrations.

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