Perturbation theory for the effective diffusion constant in a medium of random scatterers

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Abstract

We develop perturbation theory and physically motivated resummations of the perturbation theory for the problem of a tracer particle diffusing in a random medium. The random medium contains point scatterers of density ρ uniformly distributed throughout the material. The tracer is a Langevin particle subjected to the quenched random force generated by the scatterers. Via our perturbative analysis, we determine when the random potential can be approximated by a Gaussian random potential. We also develop a self-similar renormalization group approach based on thinning out the scatterers; this scheme is similar to that used with success for diffusion in Gaussian random potentials and agrees with known exact results. To assess the accuracy of this approximation scheme, its predictions are confronted with results obtained by numerical simulation.

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1. Introduction

The bulk transport properties of quenched random media play an important role in engineering sciences such as hydrology [1]. Calculational techniques to evaluate bulk transport properties such as effective diffusivities, mobilities, conductivities and permeabilities thus have far reaching applications. In systems such as zeolites, disorder modifies the diffusion of reacting chemical species and thus plays a crucial role in diffusion-limited chemical reactions [2]. The study of such systems is also relevant to the evaluation of short-time transport properties in non-quenched random media, where the time scale on which a tracer diffuses over the typical correlation scale of the advecting field is much shorter than the time scale controlling the temporal evolution of the advecting field. Systems with quenched disorder may also be used

as paradigms for systems with temporal disorder and may sometimes be used to obtain bounds on the transport properties of non-quenched fields.

Recently there has been much interest in the nature of the glass transition, in particular as to whether it is a purely dynamical or a static transition. Consider a tracer particle diffusing and interacting with other identical particles as could be the case in a liquid or gas. If inertial effects are not important, we can assume that the motion of the particle is controlled by over-damped Langevin dynamics. In the liquid, or ergodic, phase, we expect the tracer particle to have a non-zero self-diffusion constant κ. Now consider a situation in which the same particle diffuses in a quenched background where all the other particles have been frozen in a particular configuration, possibly chosen from a Gibbs–Boltzmann equilibrium ensemble. Let the diffusion constant in this quenched system be κ_e. It has been shown [3] that $\kappa_e < \kappa$; a result that seems physically plausible since, if the background particles can move about, the cages which could trap the tracer in the quenched background will break up on some time scale and free it to disperse more quickly than in the quenched case. This consideration recently led Szamel [4] to study this problem as a test of the mode-coupling theory for interacting particle systems.

A Langevin particle diffusing in a random potential is often invoked to describe, at a suitably coarse grained level, the transport properties of certain random media. Often the first choice of statistics for the potential is Gaussian. If the potential has a finite correlation length, then we can subdivide the system into uniform blocks whose size is larger than that correlation length. Consequently, the diffusion processes within each of these blocks will be independent of one another. The particle will stay within each block for a random time τ, that will be distributed similarly but independently for each block. For Gaussian statistics, we expect the mean value of τ to be finite. Thus, viewed as coarse grained hopping process between blocks, the motion of the tracer will appear to be an uncorrelated random walk and thus asymptotically exhibit normal diffusion.

The calculation of the diffusion constant of a Langevin particle in a Gaussian potential, specified therefore solely by its two-point correlation function $\Delta(\mathbf{x})$, has been attempted via a wide variety of approximation schemes [5]. The most successful to date is the self-similar renormalization group (RG) scheme of [5]. Other approximation schemes such as self-consistent perturbation theory, and the Hartree–Fock approximation perform poorly when confronted with known exact results and numerical simulations. The modification of the diffusion constant in the presence of inertial effects [6] can also be well explained using a Gaussian closure scheme, within the Martin–Siggia–Rose path integral formalism [7]. This closure approximation is rather reminiscent of certain aspects of mode-coupling theory [8] and is related to the dynamics of mean field spin glasses [9] (the approximation becomes exact in the limit of infinite spatial dimension and when the field strength is suitably scaled). This Gaussian closure predicts a glass transition [6] (signalled by a vanishing of the diffusion constant and ageing in correlation and response functions) for a Langevin process diffusing in a short range correlated, finite variance Gaussian random potential; however from our previous discussion we do not expect such a transition in finite dimensions.

In this paper, we shall consider the diffusion constant of a Langevin tracer particle diffusing in a system of quenched random scatterers which are independently and uniformly dispersed throughout the volume. This corresponds to the situation found in zeolites where the scatterers are usually charged ionic sites. We draw attention to the fact that this model is distinct from that of the Lorentz gas in which an undamped Newtonian particle is scattered by hard spheres in three dimensions or hard discs in two dimensions (overlapping or non-overlapping) [10].

We develop a double expansion for the self-diffusion constant in interaction strength and the density of scatterers and determine the range of validity of the Gaussian approximation

for the random field statistics. We then evaluate the density expansion to first order and use renormalization group ideas to resum this expansion. This strategy leads to a result which agrees with known exact results for diffusion in the presence of scatterers in one and two dimensions [11]. We identify the situations where this approximation appears to be accurate by comparison with numerical simulations of diffusion in the presence of hard and soft sphere scatterers. A distinct trend appears from our study; a renormalization group calculation based on the weak density expansion appears to work very well in problems where the scatterers attract the tracer particle, but is considerably less effective where the scatterers are repulsive.

A number of useful mathematical results for Langevin particles diffusing in random potentials, which we shall make use of in this paper, are given straightforward derivations in the appendix, thus making the paper self-contained.

2. The model

The position $\mathbf{X}_t$, of the Langevin tracer particle subject to a white noise, $\eta(t)$ and a force generated by a potential $\phi(\mathbf{x})$, satisfies the stochastic differential equation

$$\frac{\mathrm{d}\mathbf{X}_t}{\mathrm{d}t} = \sqrt{\kappa}\eta(t) - \lambda\nabla\phi(\mathbf{X}_t), \tag{1}$$

where

$$\langle\eta_i(t)\eta_j(t')\rangle = 2\delta_{ij}\delta(t-t'), \tag{2}$$

and $\langle\cdots\rangle$ denotes an average over the white noise. The Einstein relation implies that the local, or bare, diffusivity κ and the coupling to the potential gradient λ are related by the equation

$$\frac{\lambda}{\kappa} = \beta = \frac{1}{T}, \tag{3}$$

where T is the absolute temperature in appropriate units. The probability density, $p(\mathbf{x}, t)$, for the position of the particle obeys

$$\frac{\partial p}{\partial t} = \kappa\nabla^2 p + \lambda\nabla\cdot(p\nabla\phi) \tag{4}$$

$$= -Hp, \tag{5}$$

where equation (5) defines the positive operator H. The effective diffusivity, κ_e, describing the dispersion of the particle at large times and distances is defined by

$$\kappa_e = \frac{1}{2D}\lim_{t\to\infty}\frac{\langle\mathbf{X}_t^2\rangle}{t}, \tag{6}$$

where D is the dimension of space. The mean squared displacement of the particle is calculated via

$$\langle\mathbf{X}_t^2\rangle = \int \mathrm{d}\mathbf{x}\,\mathbf{x}^2 p(\mathbf{x}, t). \tag{7}$$

In this paper, we will consider potentials of the type

$$\phi(\mathbf{x}) = \sum_{n=1}^{N} V(\mathbf{x} - \mathbf{x}_n), \tag{8}$$

generated by N scatterers frozen in the volume $\mathcal{V}$. Here $\mathbf{x}_n$ is the position of scatterer n and in what follows all the $\mathbf{x}_n$ will be taken to be independently and uniformly distributed in the volume $\mathcal{V}$. This situation where the scatterers are uniformly and independently distributed could arise in circumstances where the medium is formed by the rapid quench of a very high

temperature liquid or gas to a solid phase, the scatterers then becoming frozen in the high temperature configuration. The density of scatterers is $\rho = N/\mathcal{V}$. The thermodynamic limit is $\mathcal{V} \to \infty$ at fixed ρ.

The potential $V(\mathbf{x})$ for a scattering particle at the origin will be taken to be rotationally invariant that is $V(\mathbf{x}) = V(|\mathbf{x}|)$. The quenched disorder in this problem is therefore completely specified by the positions, $\mathbf{x}_n$, of the scatterers and the disorder average is given by

$$\langle \mathcal{O} \rangle_d = \prod_n \frac{1}{\mathcal{V}} \int d\mathbf{x}_n \, \mathcal{O}. \tag{9}$$

The Green's function for the problem is $G'(\mathbf{x}, \mathbf{x}') = H^{-1}(\mathbf{x}, \mathbf{x}')$. It satisfies the equation

$$\kappa \nabla^2 G' + \lambda \nabla \cdot (G' \nabla \phi) = -\delta(\mathbf{x} - \mathbf{x}'). \tag{10}$$

The Fourier transform $\tilde{G}'(\mathbf{k})$, may be defined to be

$$\tilde{G}'(\mathbf{k}) = \int d\mathbf{y} \exp(-i\mathbf{k} \cdot \mathbf{y}) G'(\mathbf{y} + \mathbf{x}', \mathbf{x}'). \tag{11}$$

Because the system is statistically homogeneous in space, we may for most purposes set $\mathbf{x}' = 0$ in the above without loss of generality. From equation (10) we have in Fourier space

$$\tilde{G}'(\mathbf{k}) = \frac{1}{\kappa \mathbf{k}^2} - \frac{\lambda}{\kappa \mathbf{k}^2} \int \frac{d\mathbf{q}}{(2\pi)^D} \mathbf{k} \cdot \mathbf{q} \, \tilde{\phi}(\mathbf{q}) \tilde{G}'(\mathbf{k} - \mathbf{q}). \tag{12}$$

The effective diffusion constant κ_e can now be obtained from the long distance behaviour of the Green's function [5]. In Fourier space we have

$$\tilde{G}'(\mathbf{k}) \sim \frac{1}{\kappa_e \mathbf{k}^2} \qquad \text{as} \quad |\mathbf{k}| \to 0. \tag{13}$$

One can calculate κ_e exactly for this problem in one dimension [11] and one finds

$$\kappa_e = \kappa \exp\left(-2\rho \int dx (\cosh(\beta V(x)) - 1)\right). \tag{14}$$

Remarkably the expression (14) is independent of the sign of β. For positive β, the particle is attracted to the minima of the potential ϕ and for negative β it is attracted to the maxima. To disperse however, the particle must visit both minima and maxima, due to the absence of saddles in one dimension, and so one could argue that, in some sense, both minima and maxima were equally important for determining the dispersion. The result is still, however, rather intriguing from a physical point of view. Another interesting property of the one-dimensional result is that if one considers a system with two types of scatterers, types a and b, one type of density ρ_a with potential V_a and the other of density ρ_b with potential V_b one finds that

$$\kappa_e(a + b) = \frac{\kappa_e(a)\kappa_e(b)}{\kappa}, \tag{15}$$

where $\kappa_e(a + b)$ is the effective diffusivity for system with both scatterer types and $\kappa_e(a)$ and $\kappa_e(b)$ are the effective diffusivities for the system with only particles of types a and b respectively.

An exact result was also recently found in two dimensions. If one considers a system of charged scatterers where

$$\phi(x) = \sum_{n=1}^{N} q_n V(\mathbf{x} - \mathbf{x}_n), \tag{16}$$

Figure 1. Diagrammatic expansion for $\tilde{G}'(\mathbf{k})$.

and where q_n is the charge of the scatterer at x_n which takes the (quenched) value $q_n = \pm 1$ with probability $1/2$ so that the system is statistically electro-neutral, then it was shown that

$$\kappa_e = \kappa \exp\left(-\rho \int d\mathbf{x}\,[\cosh(\beta V(\mathbf{x})) - 1]\right). \tag{17}$$

The interesting feature in this case is again that the multiplicative structure seen in equation (15) in the case of two families of independent charged scatterers still holds.

3. Weak disorder expansion

In the non-neutral case in two and higher dimensions, one must revert to approximate methods to calculate κ_e. We consider the perturbation expansion generated by iterating equation (12) and which is shown diagrammatically in figure 1.

The Feynman rules for this perturbation theory (before averaging over the disorder) are:

- The total momentum at each vertex is conserved.
- Each solid horizontal line with momentum $\mathbf{k}$ flowing through it is the bare propagator $1/\kappa \mathbf{k}^2$.
- Each wavy line with momentum $\mathbf{q}$ flowing into it carries a factor $-\lambda \mathbf{k} \cdot \mathbf{q}\,\tilde{\phi}(\mathbf{q})$ where $\mathbf{k}$ is the incoming (from the horizontal left) momentum.
- Each wavy line momentum $\mathbf{q}$ in the diagram is integrated with the measure $d\mathbf{q}/(2\pi)^D$.

One now has to average over the disorder to obtain

$$G(k) = \langle \tilde{G}'(\mathbf{k}) \rangle_d, \tag{18}$$

where $k = |\mathbf{k}|$, as the averaged Green's function is clearly isotropic. We now note that the Fourier transform of ϕ is given by

$$\tilde{\phi}(\mathbf{q}) = \sum_n \tilde{V}(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{x}_n). \tag{19}$$

Therefore each vertex contains n terms of the form $\tilde{V}(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{x}_n)$. If one considers a diagram coming from the expansion of all the sums at each vertex containing the particle index i, k times at the vertices $v_1 \ldots v_k$, then the contribution depending on the position $\mathbf{x}_i$ of scatterer i is given by the prefactor

$$P = \exp\left(-i\sum_{m=1}^{k} \mathbf{x}_i \cdot \mathbf{q}_{v_m}\right). \tag{20}$$

Now, the disorder average with respect to $\mathbf{x}_i$ yields

$$\langle P \rangle_d = \frac{(2\pi)^D}{\mathcal{V}} \delta\left(\sum_{m=1}^{k} \mathbf{q}_{v_m}\right). \tag{21}$$
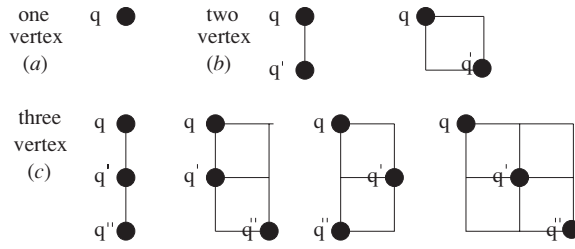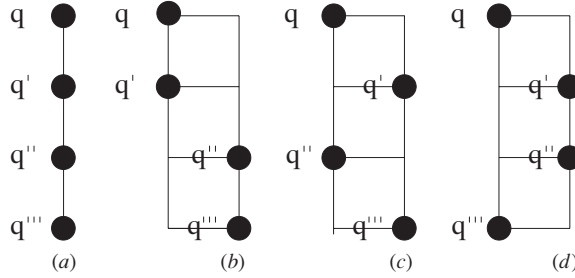
Figure 2. Blob diagrams to order λ^3.

Figure 3. Non-zero blob diagrams of order λ^4.

Hence the total momentum flowing up into vertices with the same scatterer index is zero. We also note that in the unaveraged Feynman rules, any vertex with upward flowing momentum $\mathbf{q}_\nu = 0$ causes the diagram containing it to be zero. In each diagram, one has N choices for the scatterer index at the first vertex. Every distinct scatterer in each diagram carries a factor of $1/\mathcal{V}$ from averaging over its position. A diagram with r distinct scatterer indices at its vertices (but with the positions of each index fixed) therefore carries a factor ρ^r because there is a factor N^r for the number of ways to choose the scatterers plus a factor of $1/\mathcal{V}^r$ from the averaging over the r distinct scatterer positions. We can represent this ordering graphically as is shown in figure 2 where the one-, two- and three-vertex contributions are shown; the first column represents the first scatterer chosen in the first vertex, the momentum at each blob is the momentum flowing into that vertex. We continue this development where the νth row corresponds to the νth vertex. In each of these diagrams, the sum of the momentum down each column is zero due to equation (21). Also, from the Feynman rules, any diagram with a blob containing zero momentum must be zero; along with momentum conservation this means that any non-zero diagram must contain each scatterer zero times or at least twice. The diagram in figure 2(a) is thus zero as are all but the first of the diagrams in figures 2(b) and (c). The order of each diagram written this way is $\rho^c \times \lambda^r$, where c is the number of columns, corresponding to distinct particles, and r is the number of rows, corresponding to the number of vertices.

In figure 3, we show the non-zero four-vertex contributions: figure 3(a) has only one column (scatterer) and figures 3(b)–(d) represent the two scatterer diagrams.

We note that for large ρ, the dominant diagrams with an even number $2n$ of rows are those where each column has only two blobs and that this diagram, in units where $\kappa = 1$, is of order $(\rho \lambda^2)^n$. Note that these diagrams are formed by pairing the vertices and reproduce the diagrams for a particle diffusing in a Gaussian random field [5], where the field ψ has the correlation function given by

$$\langle \psi(\mathbf{q}) \psi(\mathbf{q}') \rangle_d = (2\pi)^D \rho \lambda^2 \delta(\mathbf{q} + \mathbf{q}') \tilde{V}(\mathbf{q}) \tilde{V}(-\mathbf{q}). \tag{22}$$

For diagrams with an odd number of vertices $2n + 1$, the dominant diagrams in ρ are those with $n - 1$ pairs of blobs with a single column containing three blobs and the order of these diagrams is, in units where $\kappa = 1$, $\rho^{n-1}\lambda^{2n+1} = (\rho\lambda^2)^n\lambda/\rho$. Thus in the limit $\lambda \to 0$ whilst keeping $\rho\lambda^2 = $ constant, one recovers the limit where a system of scatterers generates a potential which can be treated as Gaussian for the purposes of calculating κ_e. This limit can also be seen in exactly soluble one-dimensional and two-dimensional models [11].

The modified Feynman rules leading to systematic expansion of $G(\mathbf{k})$ in terms of λ are thus:

- At order λ^r draw all distinct blob diagrams with r rows.
- Each blob diagram carries a factor of ρ^c where c is the number of columns.
- Each blob diagram has a corresponding Feynman diagram with the same rules as before except it is $\tilde{V}(\mathbf{q})$ at each vertex instead of $\tilde{\phi}(\mathbf{q})$.
- The total momentum down each line is zero and each independent remaining momentum is integrated with the measure $d\mathbf{q}/(2\pi)^D$.

Finally the series can be Dyson resummed in terms of one-particle irreducible diagrams by writing

$$G(k) = \frac{1}{\kappa k^2 - \Sigma(k)}, \tag{23}$$

where Σ is given by the summed one-particle irreducible blob diagrams multiplied by $\kappa^2 k^4$, that is to say the corresponding diagram with the first in going and the last out going bare propagators amputated. As usual a one-particle irreducible diagram is one that does not factorize. All the diagrams of order ρ are clearly one-particle irreducible. Figure 3(b) is clearly reducible and the others are irreducible.

In terms of the one-particle irreducible diagrams

$$\kappa_e = \kappa - \lim_{k \to 0} \frac{\Sigma(k)}{k^2}. \tag{24}$$

In what follows we shall use the spherical symmetry of the potential V to set $\tilde{V}(\mathbf{q}) = \tilde{V}(q)$ where $q = |\mathbf{q}|$. Using the perturbation theory rules developed here we find that to order β^4

$$\frac{\kappa_e}{\kappa} = 1 - \frac{\rho\beta^2}{D} \int \frac{d\mathbf{q}}{(2\pi)^D} \tilde{V}^2(q) + \frac{\rho\beta^3}{D} \int \frac{d\mathbf{q}}{(2\pi)^D} \frac{d\mathbf{p}}{(2\pi)^D} \left(1 - \frac{(\mathbf{p}\cdot\mathbf{q})^2}{p^2 q^2}\right) \tilde{V}(q)\tilde{V}(q)\tilde{V}(|\mathbf{p} + \mathbf{q}|)$$

$$+ \frac{\rho^2\beta^4}{2D^2} \left[\int \frac{d\mathbf{q}}{(2\pi)^D} \tilde{V}^2(q)\right]^2 + \beta^4\rho R. \tag{25}$$

The principal difficulty with the above-perturbation theory is the identification of the $O(k^2)$ term in each one-particle irreducible diagram. The term R not written explicitly in the above suffers from this problem and it is not clear how the resulting integral should be expressed for efficient evaluation. Also expansion as a power series in β is presumably not very accurate where κ_e deviates significantly from its bare value, as the first term is $O(\beta^2)$.

4. Weak density expansion

One of the principal technical difficulties with the weak disorder expansion as presented in the previous section is that its convergence can be expected to be poor, and it may possess divergences for singular potentials. In addition, as the interested reader may verify, the identification of κ_e by extracting the terms $O(k^2)$ in the expansion of $\Sigma(k)$ is algebraically

rather difficult. In the case of scatterers it is natural to examine the expansion of κ_e in terms of the density ρ of the scatterers. The small density expansion was pioneered by Maxwell [16] in the context of effective dielectric constants. We shall develop this analysis for the problem of the scatterers in a compact and direct manner. We start with the formal expression for the diffusion constant which is given in terms of the Green's function by

$$\frac{\kappa_e}{\kappa} = 1 - \frac{\kappa\beta^2}{DZ} \int d\mathbf{x} \, d\mathbf{x}' G'(\mathbf{x}, \mathbf{x}') \nabla\phi(\mathbf{x}) \cdot \nabla\phi(\mathbf{x}') \exp(-\beta\phi(\mathbf{x}')), \tag{26}$$

where Z is the one-particle partition function for a particle in the potential ϕ given by

$$Z = \int_{\mathcal{V}} d\mathbf{x} \exp\left(-\beta\phi(\mathbf{x})\right). \tag{27}$$

This result does not appear to be widely known (or at least used) in the physics literature. It can be derived from static considerations [12] or via the stochastic differential equation for the diffusion process [13]. For a proof based on the stochastic approach, we refer the reader to the appendix of this paper.

The expression equation (26) may be used to reformulate the weak disorder expansion by exploiting the perturbation expansion for G'. We see that to order ρ, the effective diffusion constant is the result of independent contributions from N scatterers, that is

$$\frac{\kappa_e^{(1)}}{\kappa} = 1 - \sum_n \frac{\kappa\beta^2}{DZ_{1,n}} \int d\mathbf{x} \, d\mathbf{x}' G_1(\mathbf{x}, \mathbf{x}', \mathbf{x}_n) \nabla\phi_{1,n}(\mathbf{x}) \nabla\phi_{1,n}(\mathbf{x}') \exp(-\beta\phi_{1,n}(\mathbf{x}')), \tag{28}$$

where $\kappa_e^{(1)}$ denotes κ_e calculated to first order in ρ. In the above $\phi_{1,n}(\mathbf{x}) = V(\mathbf{x} - \mathbf{x}_n)$ is the potential due to the scatterer at $\mathbf{x}_n$ and $Z_{1,n}$ the corresponding one-particle partition function. We have denoted by $G_1(\mathbf{x}, \mathbf{x}', \mathbf{x}_n)$ the diffusion Green's function for a tracer particle in the presence of only one scatterer at $\mathbf{x}_n$. Note that without loss of generality we may take all the $\mathbf{x}_n = 0$ and in the limit of large $\mathcal{V}$ and N, when $V(\mathbf{x})$ goes to zero sufficiently quickly as $|\mathbf{x}| \to \infty$ so that the integral

$$F = \int d\mathbf{x}'[1 - \exp(-\beta V(\mathbf{x}'))] \tag{29}$$

is finite, then

$$\frac{\kappa_e^{(1)}}{\kappa} = 1 - \rho\frac{\kappa\beta^2}{D} \int d\mathbf{x} \, d\mathbf{x}' G_1(\mathbf{x}, \mathbf{x}', 0) \nabla V(\mathbf{x}) \cdot \nabla V(\mathbf{x}') \exp(-\beta V(\mathbf{x}')). \tag{30}$$

We note here that to order ρ, the value of κ_e is independent of the nature of the correlations between the $\mathbf{x}_n$ and the formula equation (30) relies only on the fact that the distribution of scatterers is homogeneous and isotropic. We now define

$$\mathbf{w}(\mathbf{x}) = \beta\kappa \int d\mathbf{x}' G_1(\mathbf{x}, \mathbf{x}', 0) \nabla V(\mathbf{x}') \exp(-\beta V(\mathbf{x}')), \tag{31}$$

and by the definition of G_1, the Green's function for diffusion in the presence of a single scatterer taken to be at the origin, we have that

$$\nabla^2\mathbf{w}_i(\mathbf{x}) + \beta\nabla \cdot \mathbf{w}_i(\mathbf{x})\nabla V(\mathbf{x}) = -\beta\nabla_i V(\mathbf{x}) \exp(-\beta V(\mathbf{x})). \tag{32}$$

Using the spherical symmetry of the problem we write $\mathbf{w} = \exp(-\beta V(r))g(r)\mathbf{x}/r$ where $r = |\mathbf{x}|$ and g obeys

$$\frac{d^2}{dr^2}g + \frac{D-1}{r}\frac{d}{dr}g - \frac{D-1}{r^2}g - \beta\frac{d}{dr}g\frac{d}{dr}V + \beta\frac{d}{dr}V = 0. \tag{33}$$

In terms of g we thus have

$$\frac{\kappa_e^{(1)}}{\kappa} = 1 + \frac{\rho S_D}{D} \int_0^\infty r^{D-1} dr \left[\frac{\partial}{\partial r} \exp(-\beta V(r)) \right] g(r), \tag{34}$$

where S_D is the area of a unit sphere in D dimensions. The behaviour of g at large r needs to be determined. Note that if V decays sufficiently quickly at large r then we can write equation (32) as

$$\nabla^2 \mathbf{w}_i(\mathbf{x}) \approx -\beta \nabla_i V(\mathbf{x}) \exp(-\beta V(\mathbf{x})), \tag{35}$$

for large r. The effect of the source term must die away as $r \to \infty$ for rapidly decaying potentials and so at large r we may write $\mathbf{w} = \nabla \psi$ where ψ obeys

$$\nabla^2 \psi = \exp(-\beta V) - 1, \tag{36}$$

which has the solution

$$\psi(\mathbf{x}) = \int d\mathbf{x}' \Delta_D^{-1}(\mathbf{x}, \mathbf{x}')[1 - \exp(-\beta V(\mathbf{x}'))], \tag{37}$$

where

$$\Delta_D^{-1} = \frac{C_D}{|\mathbf{x} - \mathbf{x}'|^{D-2}} \tag{38}$$

is the inverse of the Laplacian in D dimensions (the case $D = 2$ is to be interpreted as a logarithm). Now at large $|\mathbf{x}|$

$$\mathbf{w}(\mathbf{x}) \approx \nabla \psi(\mathbf{x}) \approx C_D' \frac{\mathbf{x}}{|\mathbf{x}|^D} \int d\mathbf{x}'[1 - \exp(-\beta V(\mathbf{x}'))], \tag{39}$$

when the integral F defined in equation (29) is finite. For F to be finite we must have that $V(r)$ decays quicker than $1/r^D$ to ensure convergence as $r \to \infty$. In this case we see that equation (39) then implies that $g(r) \sim 1/r^{D-1}$ for large r.

The boundary conditions on g are that $g(r) \to 0$ as $r \to \infty$ (for $D \geqslant 2$) from the previous discussion and, if the potential V is sufficiently well behaved, we expect that $g(0)$ is finite. In greater than one dimension equation (33) is difficult to solve explicitly. However for the case of soft sphere potentials of the form $V_s(r) = \epsilon$ for $r < a$ and $V_s(r) = 0$ for $r > a$, one can solve equation (33) explicitly. In this case it is useful to rewrite equation (33) as

$$\frac{d}{dr}\left(\exp(-\beta V(r)) r^{D-1} \frac{d}{dr} g \right) + \exp(-\beta V(r)) r^{D-3}(1-D)g - r^{D-1}\frac{d}{dr}\exp(-\beta V(r)) = 0. \tag{40}$$

This gives

$$\frac{d}{dr}\left(r^{D-1}\frac{d}{dr}g \right) + r^{D-3}(1-D)g = 0, \tag{41}$$

for all $r \neq a$, supplemented by the conditions for matching the discontinuity at $r = a$ which are

$$g(a^-) = g(a^+) \tag{42}$$

$$a^{D-1}\left(\frac{dg}{dr}(a^+) - \exp(-\beta\epsilon)\frac{dg}{dr}(a^-) \right) - a^{D-1}(1 - \exp(-\beta\epsilon)) = 0. \tag{43}$$

The general solution to equation (41) is

$$g(r) = \frac{A}{r^{D-1}} + Br, \tag{44}$$

and the boundary conditions at $r = 0$ and as $r \to \infty$ along with the continuity and jump condition across $r = a$ give

$$
\begin{aligned}
g(r) &= -\frac{1 - \exp(-\beta\epsilon)}{D - 1 + \exp(-\beta\epsilon)} r; & r < a \\
&= -\frac{1 - \exp(-\beta\epsilon)}{D - 1 + \exp(-\beta\epsilon)} a \left(\frac{a}{r}\right)^{D-1}; & r > a.
\end{aligned} \tag{45}
$$

We thus obtain

$$
\begin{aligned}
\frac{\kappa_e^{(1)}}{\kappa} &= 1 + \frac{\rho S_D}{D} a^{D-1} (1 - \exp(-\beta\epsilon)) g(a) \\
&= 1 - \frac{\rho S_D a^D}{D} \frac{(1 - \exp(-\beta\epsilon))^2}{(D - 1 + \exp(-\beta\epsilon))}.
\end{aligned} \tag{46}
$$

In the limit of hard spheres, that is to say as $\epsilon \to \infty$, we obtain

$$
\frac{\kappa_e^{(1)}}{\kappa} = 1 - \frac{\rho S_D a^D}{D(D-1)}. \tag{47}
$$

This result is divergent at all ρ for $D = 1$ as it is clear that in the presence of hard scatterers, the tracer particle will be confined between its nearest right and left neighbour for all time and thus will not diffuse.

5. Self-similar renormalization group schemes

The basic idea of self-similar renormalization group schemes is to resum the original perturbation expansions available to us in a physically motivated way. Consider the general problem of diffusion in a random potential where the potential is parametrized by Λ such a way that when $\Lambda = 0$ the potential vanishes and the resulting diffusion is free. For example, we could use a Fourier-based parametrization where we write

$$
\phi_\Lambda(\mathbf{x}) = \int_{|q| < \Lambda} \frac{d\mathbf{q}}{(2\pi)^D} \tilde{\phi}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{x}). \tag{48}
$$

Now we define a perturbation $\delta\phi_\Lambda(\mathbf{x})$ to the potential so that

$$
\phi_{\Lambda + \delta\Lambda} = \phi_\Lambda + \delta\phi_\Lambda. \tag{49}
$$

In the case of the Fourier parametrization we have therefore

$$
\delta\phi_\Lambda(\mathbf{x}) = \int_{\Lambda < |q| \Lambda + \delta\Lambda} \frac{d\mathbf{q}}{(2\pi)^D} \tilde{\phi}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{x}), \tag{50}
$$

which is the usual slicing technique in Fourier space.

One then integrates the high momentum component $\delta\phi_\Lambda$ perturbatively to find an effective theory where the effects of $\delta\phi_\Lambda$ have been taken into account on the running diffusion constant denoted by $\kappa(\Lambda)$ and the coupling to the remaining gradient field denoted by $\lambda(\Lambda)$. This is a self-similarity ansatz which means only keeping interactions that were in the original problem and hence the only parameters which change are κ and λ (as well as the potential which just has the term $\delta\phi_\Lambda$ removed). One therefore has a running diffusion constant $\kappa(\Lambda)$ and a running coupling to the gradient field $\lambda(\Lambda)$. The effective diffusion constant is then given by $\kappa_e = \kappa(0)$. In addition, it can be shown by general arguments [12] that

$$
\frac{\kappa(\Lambda)}{\lambda(\Lambda)} = \frac{\kappa}{\lambda} = T, \tag{51}
$$

that is to say that the Einstein relation, or fluctuation dissipation relation, is satisfied by the renormalized theory at each step of the renormalization. This renormalization is only valid for the low-momentum component of the remaining drift and a possible improvement to the calculation here would be to functionally renormalize the remaining field ϕ_Λ, which amounts to introducing new interactions generated by the renormalization procedure (this approach has been applied to diffusion in an incompressible quenched Gaussian velocity field [14]). If $\nabla \phi = \mathbf{u}$ were a constant applied field then λ would be the local conductivity coupling the particle to this external field.

We remark that one may verify from the results on the weak disorder perturbation theory in section 2 that the Fourier space-based renormalization group method does not reproduce the exact results for scattering generated potentials in one and two dimensions. The Fourier-based renormalization group does, however, reproduce known exact results in one and two dimensions for Gaussian potentials [5]. However, the Fourier space slicing of the potential is not the only decomposition possible. It was noted that in the case of diffusion in a Gaussian field, a so-called t-slicing renormalization group procedure [15] gave identical results to the Fourier space renormalization group. In the case of anisotropic potentials, these two renormalization group schemes give different but numerically very close results. The basic idea behind the t-slicing approach is to write

$$\phi_\Lambda = (\Lambda - \delta\Lambda)^{\frac{1}{2}} \phi' + \delta\Lambda^{\frac{1}{2}} \phi'', \tag{52}$$

where ϕ' and ϕ'' are two independent Gaussian fields with the same correlation function as the original field ϕ. In the above prescription, Λ is integrated down from one to zero, by perturbatively calculating, and averaging over, the effect of term ϕ''. The corresponding flow equations for $\kappa(\Lambda)$ and $\lambda(\Lambda)$ are then integrated. The physical argument for the Fourier-based renormalization group scheme is that at length scales $1/\Lambda$, the effective diffusion constant and effective 'conductivity' λ are determined by fluctuations in the field on length scales shorter than this. In the case of the scatterers, one can apply a self-similar renormalization group approach based on thinning out the density and which has the advantage of agreeing with known exact results. Concretely, one assumes that the effect of a density ρ of scatterers is to generate an effective diffusion process described by an effective diffusion constant $\kappa(\rho)$ and coupling $\lambda(\rho)$ on length scales bigger that the inter-particle separation. We now throw in more scatterers of the same type of small density $\delta\rho$. As $\delta\rho$ is small we may use the results of the previous section along with the self-similarity ansatz here to write

$$\frac{\delta\kappa(\rho)}{\kappa(\rho)} = \frac{\delta\rho S_D}{D} \int_0^\infty r^{D-1} \, dr \left[\frac{\partial}{\partial r} \exp(-\beta V(r)) \right] g(r), \tag{53}$$

which integrates to give

$$\kappa(\rho) = \kappa \exp\left(\frac{\rho S_D}{D} \int_0^\infty r^{D-1} \, dr \left[\frac{\partial}{\partial r} \exp(-\beta V(r)) \right] g(r) \right). \tag{54}$$

We see that the effect of the renormalization group procedure is to exponentiate the small ρ expansion equation (34). Immediately we see from its multiplicative form that the result equation (34) agrees with the known results in one and two dimensions referred to previously. Note it is important that the scatterers are uniformly and independently distributed as the added scatterers at each step have no information about those already integrated out. Let us also note that on adding an additional $\delta\rho$ of scatterers, the characteristic length between these scatterers is $l^* \sim 1/\delta\rho^{\frac{1}{D}}$ which is strictly infinite as $\delta\rho \to 0$, hence a diffusing particle will, on average, have acquired the effective diffusion constant $\kappa(\rho)$ and conductivity $\lambda(\rho)$ before encountering a newly added scatterer. For a system of soft spheres we have in the RG approach

$$\frac{\kappa_e}{\kappa} = \exp\left[-\frac{\rho S_D a^D}{D} \frac{(1 - \exp(-\beta\epsilon))^2}{(D - 1 + \exp(-\beta\epsilon))} \right]. \tag{55}$$

Despite its agreement with known exact results in one and two dimensions, the expression equation (54) will not be exact in general. Indeed, if one considers a system of hard spheres, one expects that there is a percolation transition at a density ρ_c above which the diffusion constant vanishes, the formula equation (55) is clearly insensitive to any such transition; we see that in the hard sphere limit $\epsilon \to \infty$ that $\kappa_e = \exp(-\rho S_D a^D / (D(D-1)))$. It is inevitable that this approximate result will be inaccurate at high densities. In the following section, we shall compare the results obtained by the various techniques used here with numerical simulations.

A related problem to the one studied here is the problem of calculating the effective diffusivity of a medium with locally varying diffusivity. The diffusion equation for this system is

$$\frac{\partial p}{\partial t} = \nabla \cdot (\kappa(\mathbf{x}) \nabla p). \tag{56}$$

The effective diffusion constant in this model also corresponds to the effective dielectric permeability of a medium with local permeability $\kappa(\mathbf{x})$ and thus we shall denote it by $\kappa_e^{(p)}$. In the case where

$$\kappa(\mathbf{x}) = \kappa \exp(-\beta \phi(\mathbf{x})), \tag{57}$$

one can relate the diffusion constant for a particle diffusing in the potential ϕ at inverse temperature β with the bare diffusion constant κ, to that of the effective diffusion constant of the process defined by equation (56) by the remarkably simple formula

$$\kappa_e^{(p)} = \frac{\kappa_e \overline{\kappa}}{\kappa}. \tag{58}$$

We denote by $\overline{\kappa}$ the spatial average of the local diffusivity or permeability

$$\overline{\kappa} = \frac{1}{\mathcal{V}} \int_V d\mathbf{x} \, \kappa(\mathbf{x}). \tag{59}$$

This result was shown in [12] via an algebraic approach but it has a simple probabilistic derivation which we include in the appendix. In the case considered here, of uniform scatterers, we have

$$\overline{\kappa} = \kappa \exp\left[\rho \int d\mathbf{x}(\exp(-\beta V) - 1)\right]. \tag{60}$$

The study of the effective dielectric constants of a mixture of dielectric spheres suspended in an otherwise uniform medium dates back to Maxwell [16]. If the spheres have dielectric constant κ' and the background medium has dielectric constant κ, then the local dielectric constant may be written as

$$\kappa(\mathbf{x}) = \kappa \exp(-\phi(\mathbf{x})), \tag{61}$$

where

$$\phi = \sum_i V(\mathbf{x} - \mathbf{x}_i), \tag{62}$$

with $V(r)$ given by the soft sphere potential: $V(r) = \ln(\kappa/\kappa')$ for $r < a$ and $V(r) = 0$ for $r > a$, with a being the radius of the spheres. This formulation clearly works when the positions of the spheres are chosen to be non-overlapping. However, to order ρ the spheres do not overlap and thus from the calculations developed here, using equation (46) with $\epsilon = \ln(\kappa/\kappa')$, equation (58) and equation (60) to order ρ, we find

$$\frac{\kappa_e^{(p)}}{\kappa} \approx \left(1 - \frac{\rho S_D a^D}{D} \frac{\left(1 - \frac{\kappa'}{\kappa}\right)^2}{\left(D - 1 + \frac{\kappa'}{\kappa}\right)}\right) \times \left(1 + \frac{\rho S_D a^D}{D}\left(\frac{\kappa'}{\kappa} - 1\right)\right)$$

$$\approx 1 + \frac{cD(\alpha - 1)}{(D-1) + \alpha}, \tag{63}$$

Table 1. Calculations of $\kappa_e^{(p)}/\kappa$ for $\alpha = \infty$.

c	Numerical	$O(c^2)$ result	Maxwell	RG
0.00	1.000	1.000	1.000	1.000
0.10	1.352 ± 0.030	1.345	1.333	1.349
0.20	1.821 ± 0.081	1.780	1.750	1.822
0.30	2.529 ± 0.168	2.306	2.236	2.459
0.40	3.590 ± 0.230	2.923	3.000	3.320
0.50	4.967 ± 0.339	3.628	4.000	4.482

Table 2. Calculations of $\kappa_e^{(p)}/\kappa$ for $\alpha = 10$.

c	Numerical	$O(c^2)$ result	Maxwell	RG
0.00	1.000	1.000	1.000	1.000
0.10	1.247 ± 0.011	1.240	1.243	1.252
0.20	1.545 ± 0.028	1.511	1.529	1.568
0.30	1.944 ± 0.046	1.812	1.871	1.964
0.40	2.443 ± 0.046	2.144	2.286	2.460
0.50	3.080 ± 0.053	2.507	2.800	3.080

where $c = \rho S_D a^D/D$ is the volume fraction of the spheres and $\alpha = \kappa'/\kappa$. In three dimensions this result gives

$$\frac{\kappa_e^{(p)}}{\kappa} \approx 1 + \frac{3c(\alpha - 1)}{2 + \alpha}, \tag{64}$$

which agrees with Maxwell's result, which he gives as [16]

$$\frac{\kappa_e^{(p)}}{\kappa} = \frac{\alpha + 2 + 2c(\alpha - 1)}{\alpha + 2 - c(\alpha - 1)}, \tag{65}$$

to first order in c. Note that the Maxwell result is only accurate to order c and equation (65) is a physically motivated resummation of the order c result; it is sometimes referred to in the literature as the Clausius–Mosotti equation. The correction at order c^2 was calculated many years later by Jeffrey [17]. Despite the fact that the calculation carried out in this paper is for spheres which can overlap, it is interesting to compare the full renormalization group result for overlapping spheres with results obtained for the effective dielectric constant for a system of non-overlapping spheres via numerical calculation. The renormalization group calculation for overlapping spheres gives

$$\kappa_e^{(p)} = \kappa \exp\left(3c\frac{\alpha - 1}{\alpha + 2}\right). \tag{66}$$

Brady and Bonnecaze [18] numerically computed the effective dielectric constant for non-overlapping dielectric spheres in a background medium. In tables 1–3, we compare their results with equation (66), the Maxwell formula equation (65) and Jeffrey's result which is correct to $O(c^2)$. For $\alpha = \infty$ and $\alpha = 10$, the RG result is surprisingly close to the numerically obtained values and performs better than the Maxwell formula and the $O(c^2)$ result. For $\alpha = 0.01$ it performs less well than the other two results.

The effective potential for the scatterers in the potential diffusion problem was $\epsilon = -\ln(\alpha)$. Hence if $\alpha > 1$ then the potential ϵ is negative and thus attractive to a particle diffusing in that potential. The diffusion of the particle is clearly slowed down by trapping inside the scatterers, and it appears that the RG is picking up this dominant effect; correlations between scatterers give a small effect.
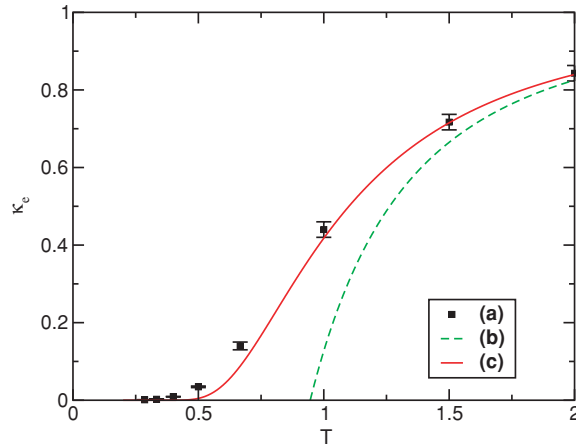
Figure 4. Effective diffusion constant as a function of the temperature, for $\epsilon = -1$ and $\rho = 0.35$: from numerical simulations (a), low density approximation (b) and density RG (c).

Table 3. Calculations of $\kappa_e^{(p)}/\kappa$ for $\alpha = 0.01$.

c	Numerical	$O(c^2)$ result	Maxwell	RG
0.00	1.000	1.000	1.000	1.000
0.10	0.859 ± 0.004	0.858	0.859	0.862
0.20	0.729 ± 0.005	0.727	0.731	0.744
0.30	0.600 ± 0.007	0.608	0.614	0.641
0.40	0.504 ± 0.010	0.501	0.506	0.554
0.50	0.406 ± 0.012	0.455	0.407	0.478

If we consider the case where $\alpha < 1$, then the potential ϵ is positive and repels the tracer. The slowing down of the diffusion is now mainly induced by another, much more subtle, effect: a memory effect which is much more sensitive to the correlations between the scatterers.

6. Simulation results

The values of the effective diffusion constant as predicted by equations (46) and (55) have been compared to the effective diffusion constant measured in Monte Carlo simulations of two-dimensional systems of soft spheres. The system is a square of linear size $L = 20$, with the spheres of radius, as defined by equation (46), $a = 1$ uniformly distributed in the area. As usual periodic boundary conditions are imposed. The simulations consisted of 2000 independent runs of a single tracer particle during a total time $t_{\max} = 10^5$, with an elementary time increment $\delta t = 0.0025$. Each particle was evolved in an independent realization of the disorder. The value of κ_e was evaluated by fitting the ensemble average of $\mathbf{X}_t^2/t$ to $4\kappa_e + A \ln(t)/t$ at late times (see equation (A.12)). The errors were then estimated from the typical late time fluctuation of the ensemble averaged curve about the fitting curve. In figure 4, κ_e is plotted as a function of T, for $\rho = 0.35$ and $\epsilon = -1$, i.e. a case where the scatterers attract, and tend to trap, the tracer. The agreement with the RG calculation is extremely good; the RG calculation correctly predicts the behaviour of κ_e across a range where it varies almost by a factor of 5. In this case, the accuracy of the RG is comparable to that when it is applied to the problem of diffusion in a Gaussian random potential in three dimensions [5].
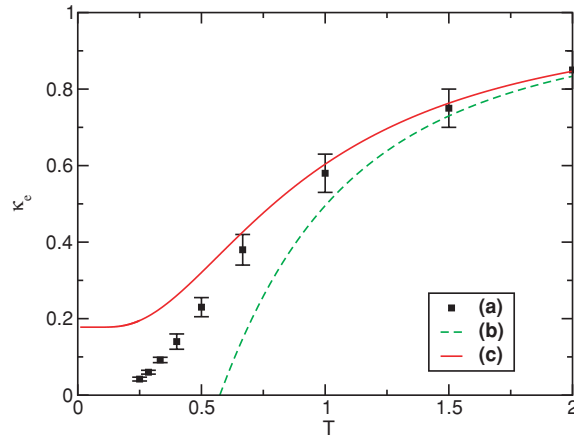
Figure 5. Effective diffusion constant as a function of the temperature, for $\epsilon = 1$ and $\rho = 0.55$: from numerical simulations (a), low density approximation (b) and density RG (c).
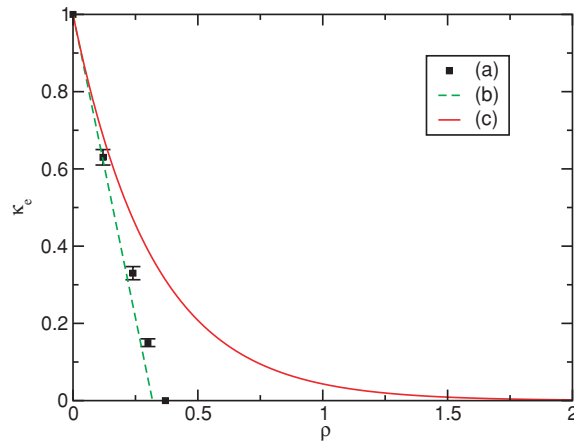

Figure 6. Effective diffusion constant as a function of the density for $\epsilon = \infty$ (overlapping hard spheres): from numerical simulations (a), low density approximation (b) and density RG (c).

In figure 5, κ_e is plotted as a function of T, for $\rho = 0.55$ and $\epsilon = 1$, thus the scatterers repel the tracer. In this case, the RG works notably less well and the numerical curves appear to be bounded above by the RG and bounded below by the order ρ result.

Finally in figure 6, κ_e is plotted as a function of ρ for $\epsilon = \infty$, the case of hard sphere scatterers. Here the perturbative order ρ result performs extremely well and is superior to the RG result. This may be expected as the ratio λ_0/κ_0 in this case is effectively infinite and the renormalization in the zero temperature case may not make sense.

The comparisons here are in accordance with those seen in the last section; the RG seems to perform well when the slowing down of the diffusion is due to trapping centres. It performs significantly less well in the case of repulsive scatterers where the slowing down of the diffusion is due to more subtle correlation effects and presumably needs a higher order treatment of terms in the expansion in ρ.

7. Conclusion

In this paper, we have considered the problem of a Langevin process diffusing in a quenched random potential. The random potential is generated by uniformly and independently distributed scatterers. We developed a weak coupling or high temperature perturbation theory which can be used to determine the validity of the Gaussian approximation to the random field distribution. As expected from the central limit theorem, one of the conditions needed to validate the Gaussian approximation is that there is a high density of scatterers so that the potential at each point is the sum of a large number random variables. However, this condition is only sufficient at high temperatures. Physically this can be understood as follows: even though, due to the central limit theorem, at a randomly chosen point the potential will be Gaussian, at low temperatures the diffusion will be dominantly near the minima of the potential which by definition belong to the tails of the distribution where the central limit theorem does not apply as they are at the extreme points of the distribution. We have also seen that the self-similar RG resummation of the weak disorder expansion does not reproduce known exact results. In addition the weak disorder expansion is destined to fail for singular potentials, where the potential contains a divergence. We thus formulated the self-similar RG resummation in terms of a decimation or thinning procedure in terms of the particle density. Direct and indirect comparison with numerical results for hard and soft sphere potentials show that the density-based RG resummation gives reasonable predictions for the bulk diffusivity and agrees with known exact results. It appears to work best in cases where the scatterers have a potential which is attractive to the tracer and thus act as trapping centres. In the case where the scatterers are not trapping but are repelling, diffusion is again slowed down but by a more subtle correlation mechanism, this effect is less well described by the RG result.

Acknowledgments

Appendix A. Expression for κ_e

Here we derive the representation equation (26) for the effective diffusion constant. The basic idea of the proof in much more mathematical terms may be found in the book of Spohn [13]. Consider the process in equilibrium in a large volume $\mathcal{V}$ at the time $t = 0$. Let the initial position be $\mathbf{X}_0$ distributed according to the equilibrium measure $p_{eq}(\mathbf{x}_0) = \exp(-\beta\phi(\mathbf{x}_0))/Z$ where Z is the one-particle partition function normalizing the distribution. Integrating the stochastic differential equation (1) between 0 and t we obtain

$$\mathbf{X}_t - \mathbf{X}_0 = \sqrt{\kappa}\mathbf{B}_t - \lambda \int_0^t \mathrm{d}s \, \nabla\phi(\mathbf{X}_s), \tag{A.1}$$

where $\mathbf{B}_t$ is a standard D-dimensional Brownian motion with $\langle \mathbf{B}_t^2 \rangle = 2Dt$. Squaring the above and taking its average yields

$$2D\kappa t = \langle (\mathbf{X}_t - \mathbf{X}_0)^2 \rangle + 2\lambda \left\langle (\mathbf{X}_t - \mathbf{X}_0) \cdot \int_0^t \mathrm{d}s \, \nabla\phi(\mathbf{X}_s) \right\rangle$$
$$+ 2\lambda^2 \left\langle \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \, \nabla\phi(\mathbf{X}_s) \cdot \nabla\phi(\mathbf{X}_{s'}) \right\rangle. \tag{A.2}$$

Defining a time-dependent diffusion constant of $\kappa^*(t) = \langle (\mathbf{X}_t - \mathbf{X}_0)^2 \rangle / 2Dt$, so that $\lim_{t \to \infty} \kappa^*(t) = \kappa_e$ this yields

$$\kappa^*(t) = \kappa - \frac{\lambda}{Dt} \left\langle (\mathbf{X}_t - \mathbf{X}_0) \cdot \int_0^t \mathrm{d}s \nabla \phi(\mathbf{X}_s) \right\rangle - \frac{\lambda^2}{Dt} \left\langle \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \nabla \phi(\mathbf{X}_s) \cdot \nabla \phi(\mathbf{X}_{s'}) \right\rangle.$$
(A.3)

Using the property of detailed balance, which ensures time translation invariance at equilibrium, we have for any two functions A and B that

$$\langle A(\mathbf{X}_t) B(\mathbf{X}_s) \rangle = \langle A(\mathbf{X}_{t-s}) B(\mathbf{X}_0) \rangle,$$
(A.4)

and the symmetry relation

$$\langle A(\mathbf{X}_t) B(\mathbf{X}_s) \rangle = \langle B(\mathbf{X}_t) A(\mathbf{X}_s) \rangle.$$
(A.5)

Using this it is easy to verify that the second term on the right-hand side of equation (A.3) is zero. The third term may be simplified using

$$
\begin{aligned}
I(t) &= \left\langle \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \nabla \phi(\mathbf{X}_s) \cdot \nabla \phi(\mathbf{X}_{s'}) \right\rangle \\
&= \left\langle \int_0^t \mathrm{d}s \int_0^s \mathrm{d}u \nabla \phi(\mathbf{X}_u) \cdot \nabla \phi(\mathbf{X}_0) \right\rangle \\
&= \int \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}_0 \int_0^t \mathrm{d}s \int_0^s \mathrm{d}u \nabla \phi(\mathbf{x}) p(\mathbf{x}, \mathbf{x}_0, u) \cdot \nabla \phi(\mathbf{x}_0) p_{\mathrm{eq}}(\mathbf{x}_0),
\end{aligned}
$$
(A.6)

where $p(\mathbf{x}, \mathbf{x}_0, u)$ is the transition density to go from $\mathbf{x}_0$ to $\mathbf{x}$ in time u and we have used the fact that the density for the starting point $\mathbf{x}_0$ is the equilibrium density. We now use the fact that formally

$$p(\mathbf{x}, \mathbf{x}_0, u) = \exp(-u H(\mathbf{x}, \mathbf{x}_0)),$$
(A.7)

to obtain

$$
\begin{aligned}
I(t) &= \int \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}_0 \int_0^t \mathrm{d}s \nabla \phi(\mathbf{x}) H^{-1} (1 - \exp(-sH)) \cdot \nabla \phi(\mathbf{x}_0) p_{\mathrm{eq}}(\mathbf{x}_0) \\
&= t \int \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}_0 \nabla \phi(\mathbf{x}) H^{-1} \cdot \nabla \phi(\mathbf{x}_0) p_{\mathrm{eq}}(\mathbf{x}_0) \\
&\quad - \int \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}_0 \nabla \phi(\mathbf{x}) H^{-2} (1 - \exp(-tH)) \cdot \nabla \phi(\mathbf{x}_0) p_{\mathrm{eq}}(\mathbf{x}_0),
\end{aligned}
$$
(A.8)

where in the above the notation of multiplication by H^{-1} corresponds to operator composition. Using the definition of G' and putting this altogether we find, keeping the dominant terms in the large t expansion, that

$$\kappa_e = \kappa - \frac{\lambda^2}{D} \int \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}_0 \nabla \phi(\mathbf{x}) \cdot G(\mathbf{x}, \mathbf{x}_0) \nabla \phi(\mathbf{x}_0) p_{\mathrm{eq}}(\mathbf{x}_0),$$
(A.9)

which is the desired result. Note that all the above derivation depends on the fact that H is a positive definite operator. In a finite volume this is clearly not the case as there is an equilibrium distribution. The result should be understood for long times but such that the system has not encountered the boundary of $\mathcal{V}$. If in the above the limit $t \to \infty$ is taken before $|\mathcal{V}| \to \infty$ one finds that $\kappa_e = 0$ which is to be expected for a finite system. A more detailed discussion of this subtlety can be found in [12].

Another interesting consequence of equation (A.8) is that using the zeroth order (or free diffusion) result for H^{-2} and $\exp(-tH)$ in the finite time correction in equation (A.8), we

obtain the expected finite time correction [13] to the long time diffusive behaviour, i.e.

$$\langle \mathbf{X}_t^2 \rangle = 2\kappa_e t + O(\sqrt{t}); \qquad D = 1 \tag{A.10}$$

$$= 4\kappa_e t + O(\ln(t)); \qquad D = 2 \tag{A.11}$$

$$= 2D\kappa_e t + O(1); \qquad D \geqslant 3. \tag{A.12}$$

Appendix B. Relationship between κ_e and $\kappa_e^{(p)}$

The diffusion equation (56) corresponds to a process which in the Ito prescription of the stochastic calculus obeys

$$d\mathbf{X} = \sqrt{\kappa \exp(-\beta\phi(\mathbf{X}))}\eta(t)\, dt - \kappa\beta \exp(-\beta\phi(\mathbf{X}))\nabla\phi(\mathbf{X})\, dt, \tag{B.1}$$

where $\kappa(\mathbf{x}) = \kappa \exp(-\beta\phi(\mathbf{x}))$. We bear in mind that the equilibrium distribution of this process can be readily seen from equation (56) to be flat, i.e. $p_{eq}(\mathbf{x}) = 1/\mathcal{V}$. Now define a random time variable

$$\tau = \int_0^t ds \, \exp(-\beta\phi(\mathbf{X}_s)), \tag{B.2}$$

which is clearly a monotonic proper, though random, change of time scales. Clearly we may write equation (B.1) as

$$d\mathbf{X} = \sqrt{\kappa \exp(\beta\phi(\mathbf{X}))}\eta(t)\, d\tau - \lambda\nabla\phi(\mathbf{X})\, d\tau, \tag{B.3}$$

and we have used $\kappa\beta = \lambda$. Formally we may write

$$\eta(t) = \sigma/\sqrt{dt}, \tag{B.4}$$

where σ is a normal random variable of zero mean and variance 2. We can therefore write equation (B.3) entirely in terms of the time variable τ

$$d\mathbf{X} = \sqrt{\kappa}\eta(\tau)\, d\tau - \lambda\nabla\phi(\mathbf{X})\, d\tau. \tag{B.5}$$

This equation is just that for a particle diffusing in the potential ϕ at inverse temperature β. Thus by definition

$$\langle \mathbf{X}_\tau^2 \rangle = 2\kappa_e D\tau \tag{B.6}$$

but also

$$\langle \mathbf{X}_t^2 \rangle = 2\kappa_e^{(p)} Dt. \tag{B.7}$$

Comparing the two expressions which must be the same one finds

$$\kappa_e^{(p)} = \kappa_e \frac{\tau}{t}$$

$$= \kappa_e \frac{1}{t} \int_0^t ds \, \exp(-\beta\phi(\mathbf{X}_s)). \tag{B.8}$$

We now use the fact that $\mathbf{X}$ has a flat equilibrium distribution to give that (for large times)

$$\frac{1}{t} \int_0^t ds \, \exp(-\beta\phi(\mathbf{X}_s)) \to \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{x} \, \exp(-\beta\phi(\mathbf{x})), \tag{B.9}$$

which thus leads to the desired result, equation (58).

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