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Normal and anomalous diffusion in random potential landscapes

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A relation between the effective diffusion coefficient in a lattice with random site energies and random transition rates and the macroscopic conductivity in a random resistor network allows for elucidating possible sources of anomalous diffusion in random potential models. We show that subdiffusion is only possible either if the mean Boltzmann factor in the corresponding potential diverges or if the percolation concentration in the system is equal to unity (or both), and that superdiffusion is impossible in our system under any condition. We show also other useful applications of this relation.

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A classical particle's diffusion in a random potential or hopping on a lattice with disordered site energies E_i is a versatile theoretical model with a wide range of applications [1]. The particle's motion typically corresponds to normal diffusion, but can get subdiffusive in the presence of deep traps or in the case of infinite contrast when approaching percolation transition. A question arises, whether there can be other cases leading to subdiffusion except for these two (or combinations thereof). In what follows we show that the diffusion coefficient in a discrete disordered lattice is always finite (i.e., that no superdiffusion can be observed) but may vanish (possibly giving rise to subdiffusion). Independently of the particular distribution of *nonzero* transition rates, this is possible either if the percolation threshold in the corresponding network is unity (e.g., in one dimension, on finitely ramified fractals, or when we are *already at percolation threshold*) or if the mean Boltzmann factor $\langle \exp(-E_i/kT)\rangle$ diverges (or both). According to the Arrhenius law, the last situation corresponds to the divergence of the mean sojourn time at a site, pertinent to trapping.

We start from the master equation for the probabilities p_i to find a particle at a site i of a lattice (with lattice spacing a)

$$\dot{p}_i = \sum_j (w_{ij} p_j - w_{ji} p_i), \tag{1}$$

where w_{ij} are transition rates from site j to site i different from zero only for nearest neighbors. Equation (1) can either follow from some microscopic scheme or be obtained by a discretization of the Fokker-Planck equation for the overdamped motion in a continuous potential. The system is taken to be homogeneous and isotropic in the statistical sense. This requirement excludes underdamped cases for which the velocities and coordinates enter differently, thus leading to anisotropy of the state (phase) space. In what follows we consider a d-dimensional lattice with total of $M \gg 1$ sites assigned energies E_i being identically distributed random variables. We assume that the system is isothermic and possesses true thermodynamical equilibrium under appropriate boundary conditions, i.e., that the transition rates fulfill the detailed balance condition $w_{ij} p_j^0 = w_{ji} p_i^0$ at equilibrium (the superscript 0 will denote the corresponding value at equilibrium throughout the work). The transition rates $0 \leqslant w_{ij} < \infty$ are not necessarily bounded from above, and some of them may be put to zero to mimic percolation situations. The values of p_i^0 are given by $p_i^0 \propto b_i = \exp(-E_i/kT)$, where b_i denotes the Boltzmann factor, T is the temperature, and k is the Boltzmann constant.

Our discussion maps the initial problem onto the one for random resistor-capacitor networks. Let g_{ij} be the corresponding conductivities of the bonds, and $\langle g_{ij}\rangle_{EM}$ be the effective conductivity of a corresponding network in the static regime. Then the effective diffusion coefficient in a network follows as

$$D^* = a^2 \frac{\langle w_{ji} \exp(-E_i/kT)\rangle_{EM}}{\langle \exp(-E_i/kT)\rangle}. \tag{2}$$

The statements done in the first paragraph are then demonstrated by using the results from the theory of electric circuits and from the percolation theory. Some other useful applications of Eq. (2) are shown.

Equation (2) by itself is not new, but we give here its physical derivation which stresses its general applicability and its connection with thermodynamics. Thus, the discussion for the case of a barrier model (all E_i are the same, but the transition rates fluctuate) is contained in Ref. [1], Eq. (2.15). Moreover, Eq. (2) naturally appears when applying an effective medium approximation (EMA), like the one of Ref. [2]. A derivation for a continuous case (Langevin description in the Ito interpretation) is given in Ref. [3]. Note that the Ito prescription may correspond to the trap model in the discrete case [4], i.e., to a situation different from the one of Ref. [1]. In our work we confine ourselves to a discrete setup which allows for the application of the theory of electric circuits for the analysis of the results (although we make a limiting transition to continuum to illustrate some outcomes of the approach).

We start by rewriting Eq. (1) as an equation for mean numbers ("concentrations") of noninteracting particles at the corresponding sites, $\dot{n}_i = \sum_j (w_{ij} n_j - w_{ji} n_i)$, connected with probabilities via $n_i = N p_i$ with N being the total number of particles. In equilibrium all n_i^0 are proportional to the Boltzmann factors, $n_i^0 = C b_i$ with prefactor C depending on the number of particles, on the system's size, and on distribution of b_i. Putting the detailed balance condition into the form $w_{ij} n_j^0 = w_{ji} n_i^0$ we denote $w_{ij} n_j^0 = g_{ij}$ where $g_{ij} = g_{ji}$ is now a property of the bond. Using this notation we rewrite Eq. (1) as an equation for the temporal evolution of *activities* $\zeta_i = n_i/n_i^0$ (see the Supplementary Material [6]):

$$\dot{\zeta}_i = \frac{1}{n_i^0}\sum_j (g_{ij}\zeta_j - g_{ji}\zeta_i). \tag{3}$$

Equation (3) is formally equivalent to the evolution equation of node potentials in a random resistor-capacitor model [1], with conductivities g_{ij} and capacitances n_i^0.

Let us now calculate the effective diffusion coefficient provided it exists (i.e., the system homogenizes at large scales). For random resistor networks the homogenization of conductivity is mathematically proved for local conductivities bounded from above and from below; see [7] and references therein. The boundedness from below excludes the conductor-isolator percolation model, but homogenization still holds *provided* the system percolates [8]. Physically, it is known that the conductor-superconductor system homogenizes below the percolation threshold for superconductor [9].

We mimic a stationary experiment on measuring the diffusion coefficient via the first Fick's law: The system, in the form of a membrane of thickness L and of transversal dimension W, separates two reservoirs, the left one with a well-stirred solution of particles at concentration ν_l, the other one with a slightly lower concentration ν_r. The membrane is considered as impermeable for the solvent, and both concentrations are kept constant. The constant particles' current I through the membrane is measured and connected with the mean diffusion coefficient inside it. Since in general a jump of the (free) energy per particle can form on a contact between the membrane and the solution (e.g., when the fluid is a good solvent for diffusing particles and the membrane is, on the average, a bad one, or the other way around), the effective diffusion coefficient *inside* the membrane has to be defined through

$$D^* = \frac{IL}{W^{d-1}(\langle n_l\rangle - \langle n_r\rangle)}, \tag{4}$$

where $\langle n_l\rangle$ and $\langle n_r\rangle$ are the mean particle concentrations in the layers of the membrane in immediate contact with the solution; see Fig. 1. In a stationary state $\dot{\zeta}_i = 0$. Moreover, in the thermodynamical limit $L \to \infty$ the permeability of the membrane and thus the current tend to zero. We will call this situation "quasiequilibrium" in what follows.

The contact with solution is modeled by additional arrays of sites to the left and to the right from the membrane, with constant particles' concentrations and constant energies E_0 which can be chosen arbitrarily (E_0 defines the quality of the solvent). These additional sites are connected to the ones on the membrane's sides via extremely high transition rates fulfilling the detailed-balance condition. In this case a local equilibrium between the surface sites and the solutions persists independently of the particles' distribution inside the bulk. Due to this the activities of the surface sites are all equal to $\zeta_l = A\nu_l$ and $\zeta_r = A\nu_r$ at the left resp. right boundary of the membrane, where the prefactor A depends on E_0. Thus, n_i in the leftmost layer are proportional to $\zeta_l n_i^0 = A\nu_l n_i^0$ and in the rightmost layer to $\zeta_r n_i^0 = A\nu_r n_i^0$ so that the mean concentrations in the layers are $n_l = A\nu_l\langle n_i^0\rangle$ and $n_r = A\nu_r\langle n_i^0\rangle$, where we assume that the distribution of the site energies in the surface layers is the same as in the bulk. We then calculate the corresponding total current I through the system noting that the equations for the currents and activities in a stationary state are the same as the ones given by the Kirchhoff's laws for an electric circuit. Making such a reinterpretation we see that $I = g^*(W^{d-1}/L)(\zeta_l - \zeta_r)$ where $g^* = \langle g\rangle_{EM}$ is the effective conductance (conductivity of a bond in the *effective ordered medium* with the same total conductivity as our heterogeneous one), where the subscript EM denotes the effective medium mean. Therefore $D^* = a^2 g^*/\langle n_i^0\rangle$. The prefactor a^2 is introduced to restore the dimension as follows from Eq. (4), when passing from distances L measured in lattice units to distances measured in centimeters. We note that since n_i^0 are proportional to the Boltzmann factors, and since rescaling of all g_{ij} by a constant factor leads to changing g^* by the same factor, the proportionality factor C cancels out; this gives Eq. (2).

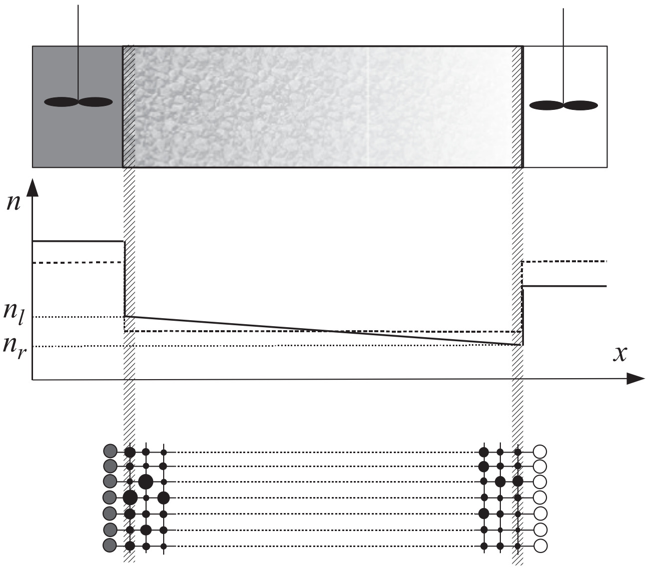
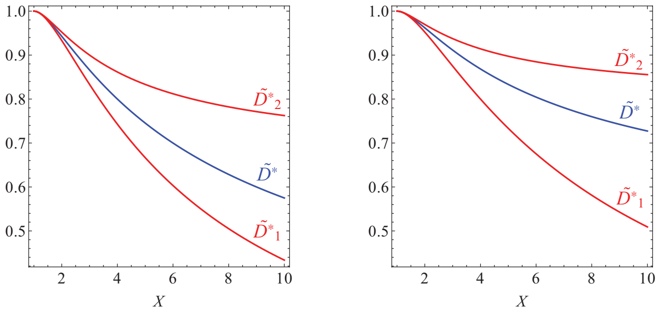


FIG. 1. A schematic illustration of the situation considered in the text: the disordered medium in contact with two reservoirs, the mean concentration at different positions, and the lattice model applied.

The result is rather transparent. If we are able to measure the effective conductivity of the system, we can connect it with the effective mobility μ^* (and thus with the diffusion coefficient) via Nernts-Einstein equation $\sigma^* = n_0 q\mu^* = n_0 q D^*/kT$, where n_0 is the equilibrium concentration of particles with charge q. Reverting this expression we get $D^* \propto \sigma^*/n_0$, which is essentially Eq. (2).

One may argue that the correct way is to define D^* through the gradient of the coarse-grained concentration, and not via the total concentration difference. As we show in Ref. [6] this definition leads to the same result since local concentrations and local activities decouple under quasiequilibrium (but *only* under this condition).

Let us first discuss some applications of Eq. (2) other than discussed earlier. Equation (2) gives the possibility to obtain the universal bounds on the effective diffusion coefficient based on those for the effective conductance, i.e., the universal Wiener bounds [10] and the tighter Hashin-Shtrikman bounds for isotropic systems [11], as well as to generalize some exact results for two-dimensional systems based on duality [12]. In this presentation we concentrate on continuum models where



(a) (b)

FIG. 2. (Color online) EMA result and Hashin-Shtrikman bounds for the symmetric binary case ($p = 1/2$) vs contrast x for $d = 2$ (a) and for $d = 3$ (b).

Eq. (1) arises from discretization of a Fokker-Planck equation for $p(\mathbf{x},t)$: $\dot{p} = D\Delta p + (D/kT)\nabla(\nabla U(\mathbf{x})p)$ with constant diffusion coefficient D and disordered potential $U(\mathbf{x})$. The details of calculations are given in Ref. [6].

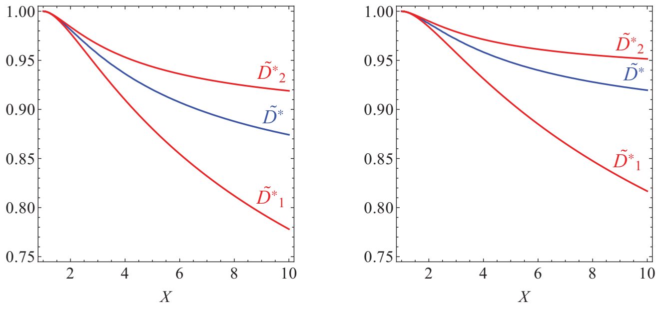
The universal Wiener bounds for the conductance are given by $\langle g_{ij}^{-1}\rangle^{-1} \leqslant \langle g_{ij}\rangle_{EM} \leqslant \langle g_{ij}\rangle$. In our cases this corresponds to

$$\frac{a^2 w_0}{\langle \exp(E_i/kT)\rangle\langle \exp(-E_i/kT)\rangle} \leqslant D^* \leqslant a^2 w_0. \qquad (5)$$

Note that the lower bound reproduces the exact result for the one-dimensional system with random potential and constant diffusion coefficient.

In Figs. 2 and 3 we plot the Hashin-Shtrikman bounds for two cases: the case of the binary disorder $E_i = E_1$ with probability p and $E_i = E_2$ with probability $1 - p$, and the case of E_i possessing an exponential distribution with cutoffs, the one with density $P(E_i) = \beta\, e^{-\beta E_i}[e^{-\beta E_2} - e^{-\beta E_1}]^{-1}$ for $E_2 < E_i < E_1$ and vanishing elsewhere (apart from cutoffs this distribution is reminiscent of the exponential energy distributions leading to CTRWs). As a comparison, the results of the effective medium approximation (EMA), see Refs. [13,14], are shown. The results are plotted as the function of a contrast $x = \exp[(E_2 - E_1)/kT]$ being the ratio of the maximal and the minimal value of g_{ij}.

Note that the result for the effective diffusion coefficient for the symmetric binary case in 2D is essentially exact since in this case $\langle g\rangle_{EM} = \sqrt{g_a g_b}$ due to the duality relation [12].



(a) (b)

FIG. 3. (Color online) EMA result and Hashin-Shtrikman bounds for truncated exponential $P(E_i)$ vs x for $d = 2$ (a) and $d = 3$ (b).

In the limit of very strong disorder D^* may vanish or diverge. In the first case $D = 0$, the system either does not show any transport (does not percolate) or shows anomalous transport slower than diffusion (i.e., shows *subdiffusiom*). In the second case it might show superdiffusion.

If D^* vanishes, it can do so either because the numerator $\langle w_{ji}\exp(-E_i/kT)\rangle_{EM}$ vanishes or because the denominator $\langle \exp(-E_i/kT)\rangle$ diverges, as well as in the cases when both possibilities are realized simultaneously (which may give rise to subdiffusion of mixed origins [5]). We discuss the conditions under which the corresponding behavior may take place. If D^* diverges, it can do so because the numerator diverges, or because the denominator vanishes, or both. As we proceed to show, none of these possibilities can be realized. This excludes not only superdiffusion, but also the "compensated" cases of normal diffusion when both numerator and denominator vanish or diverge simultaneously.

For further discussion we first recapitulate the following properties of percolation systems: (i) The mixture of resistors with given finite conductivity (at concentration p) with insulating bonds (of zero conductivity) at concentration $1 - p$ possesses zero conductance below the percolation threshold p_c and finite conductance above it. The corresponding system homogenizes at scales above the correlation length [1]. This homogenization also takes place for arbitrary distribution of the conductivities of the resistors [8]. Similarly, (ii) the mixture of resistors with given finite conductivity (at concentration p) with superconducting bonds (at concentration $1 - p$) possesses finite conductance below the percolation threshold p_c^s for superconducting bonds, with $1 - p_c^s = p_c$, and infinite conductance above it. These properties do hold not only for the Bernoulli percolation model but also in the case when the short-range correlations in the occupation probabilities of the bond by the corresponding resistors/insulators/superconductors are present. This statement is a (silently assumed) basis of all renormalization group approaches in percolation.

Using the results of the theory of electric circuits, see, e.g., [15], we show that the total conductivity of a resistor network is a nondecaying function of the conductivity of each particular bond. Let us consider the system as placed between two "superconducting" bars considered as a terminal 1 of the system. Let us consider the poles i and j between which g_{ij} is switched as terminal 2. Using the theory of two-terminal circuits we calculate the input impedance (total conductivity) z_{in} as a function g_{ij}: $z_{\text{in}} = z_{11} - z_{12}z_{21}/(z_{22} + g_{ij})$, where $z_{\alpha\beta}$ are the elements of the impedance matrix of the system. For a system of reciprocal passive elements (no batteries, no diodes) this matrix is nonnegatively definite and symmetric as a consequence of nonnegative heat production and of reciprocity theorem. In the case of a pure resistor network the matrix is real. Thus, $z_{11}, z_{22} \geqslant 0$ and $z_{12}z_{21} = (z_{12})^2 \geqslant 0$, so that z_{in} is a nondecaying function of g_{ij}.

Now we show that the numerator never diverges. We fix some $q < 1 - p_c^s = p_c$ and declare the fraction q of bonds (starting from the ones with largest g) to be superconductive. The lowest conductivity of a changed bond is $g_{\min}$. The superconducting bonds are nonpercolating by construction, and the conductance of the remaining system is finite, being smaller than a conductance of the resistor-superconductor mixture where all conductivities are put to $g_{\min}$. Thus the numerator can only diverge if $p_c = 0$, i.e., never in finite dimension.

The numerator does not vanish for a system with percolation concentration $p_c < 1$. Let us remove a portion $q < 1 - p_c$ of bonds with smallest g without destroying percolation and denote the largest removed conductivity by $g_{\max} > 0$. The rest of the system percolates and has a conductance which is larger then the conductance of a two-phase system constructed of resistors with $g = g_{\max}$ and $g = 0$, which is nonzero since we are above percolation threshold. Thus the numerator can only vanish if $p_c = 1$, and no bonds can be removed.

The denominator in Eq. (2) can diverge if the corresponding mean value of the Boltzmann factor diverges. Since $b_i = \exp(-E_i/kT)$ is proportional to the sojourn time at a site i in equilibrium, this corresponds to diverging mean sojourn time at a site, i.e., to a trap model, which in high dimensions is equivalent to CTRW with a broad distribution of waiting times.

The denominator cannot vanish. Let $p(E)$ be the probability density of E_i, and $E_M > -\infty$ its median, $\int_{-\infty}^{E_M} p(E)dE = 1/2$. Since $\langle b \rangle = \langle \exp(-E_i/kT) \rangle = \int_{-\infty}^{\infty} e^{-E/kT} p(E)dE$ where the integrand is nonnegative, we have $\langle b \rangle > \int_{-\infty}^{E_M} e^{-E/kT} p(E)dE > \exp(-E_M/kT) \int_{-\infty}^{E_M} p(E)dE = (1/2)\exp(-E_M/kT)$ since $\exp(-E/kT)$ is monotonically decaying.

Summarizing our findings we state that there exists an exact correspondence between the effective diffusion coefficient in a random potential and macroscopic conductivity in a random resistor model. This simple relation allows us to obtain exact bounds on the effective diffusion coefficient. It also allows for elucidating possible sources of anomalous diffusion in such model. Thus, the subdiffusion is possible either if the mean Boltzmann factor of the corresponding potential diverges (energetic disorder) or if the percolation concentration in a system is equal to unity, i.e., if the system is already at the percolation threshold, in one dimension, or on finitely ramified fractals (structural disorder). Superdiffusion is impossible in our system under any condition.

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