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Charge transfer on hierarchical systems

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Abstract. In this paper we present a thermodynamical analysis of charge transport on spatial hierarchical trees with some non-linear and linear barrier height structures. In particular, a discussion of the 'Fibonacci' tree is given. In an ordered m-ary tree (or 'Fibonacci' tree), the rate of charge transport is generation level dependent, except when the barrier height structure is linear (or after a few levels in the 'Fibonacci' tree).

Recently, there has been much interest in natural and artificial systems that possess an underlying hierarchical structure. However, the description and understanding of the complexity of these systems remains an open problem [1–6].

Years of study in this field have provided a number of powerful insights into this subject. Among the studies, most have been devoted to the anomalous diffusion processes in one dimension with a hierarchical potential [1–5], and the spectrum of the Schrödinger equation of such systems [6]. A very appealing concept, namely that complex systems are often nearly decomposable, was articulated some years ago by Simon [7] in his survey of hierarchically organised structures. These hierarchies, which range from the structural layout of matter (the clustering of pieces according to the strengths of their interactions) to the organisation diagrams represented by phylogenies and social organisations, allow for an effective isolation of a given level from both the rapid fluctuations of the lower echelons and the quasi-static constraints of the higher ones. This leads in turn to dynamical processes which bear the imprint of the underlying tree structure and which can also be used for deciding on the complexity of the hierarchical system described by such trees.

As we know, a number of authors have considered diffusive processes on simple hierarchical systems. The first model of this type was due to Huberman and Kerszberg [8] and consists of a particle performing nearest-neighbour hopping over an ordered array of energy barriers in one dimension. This array is assumed to be hierarchical in structure and the particle undergoes dynamical motion in one dimension (real space) [1–5]. Obviously, this model is a simple one for a disordered medium. In order to model actual disorder or a more complex medium, in this paper we present a model for a disordered medium with a hierarchical structure in geometrical space (real space), and at the same time an energy barrier is assumed with some linear or non-linear

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distribution $f(n)$. Here n is the level of the generation of the hierarchical structure of this geometrical configuration for a disordered medium. In this paper, we discuss the charge transport on the hierarchical systems shown in figures 1 and 3. The bonds branching from any intersection point denote spatially separated charge-conducting pathways which may correspond to dislocation lines, grain boundaries, or any other structural imperfections in the solid [9]. This is a geometrical configuration of a disordered medium. The elementary height of the barrier is E for the first level and $f(n)E$ for other levels. Here, we first consider an ordered 2-ary (binary) tree. The charge transfer is from the single segment just preceding the top branching point of the tree to its base. The transport from the segment just preceding the branching point to one of the two available branches is assumed to be an endothermic process.

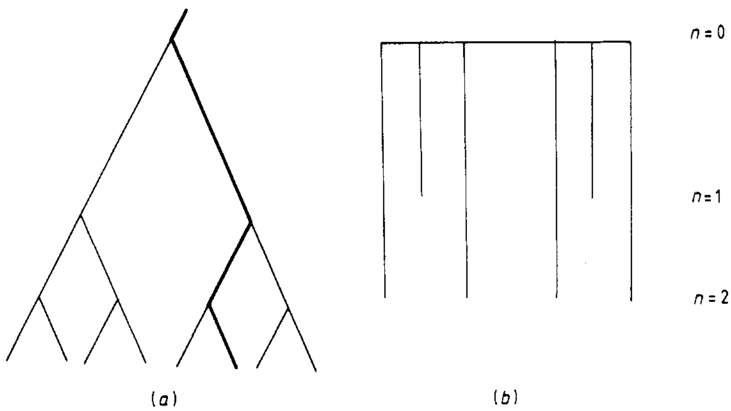

Figure 1. (*a*) A spatial configuration of an ordered 2-ary hierarchical tree extended to the third generation level, $n = 3$. The bold line indicates one of the eight possible charge transport pathways from the top of the tree to its base at level three. (*b*) One type of barrier height structure (case I, a hierarchical binary tree) with respect to the spatial configuration of (*a*). The height from $n = 0$ to $n = 1$ is R^0E, and from $n = 1$ to $n = 2$ is R^1E.

Further we assume that the barrier height increases with the same kind of hierarchical structure (see figure 1(*b*)). For example, when the charge transfer is from the top ($n = 0$) to the second branching point ($n = 1$), the barrier height is R^0E, and to the third branching point ($n = 2$) it is R^1E, and so on.

For the binary tree with n levels, the total energy increment, E_a, and the total number of possible configurational arrangements of conducting pathways, W_n, are

$$E_a = R^{n-1}E \qquad W_n = 2^n. \tag{1}$$

The charge reaching the base of the tree is thermally activated from the ground energy level at the top of the tree to its maximal energy, E_a, through one of the W_n equally probable spatial pathways. Since the charges are transferred from a single spatial position at the top of the tree to any one of the W_n equivalent positions at its base, the entropy gain per unit of charge transport is

$$S_n = K \ln W_n = nK \ln 2. \tag{2}$$

Provided that the charge reaching the base leaves the tree and passes into an irreversible charge sink, the rate of the charge transport, r, is limited by

$$r \propto \exp(S^*/K)\exp(-E^*/KT) \tag{3}$$

where S^* and E^* are the entropy and the energy of activation, respectively. In the present case, $E^* = E_a$ and $S^* = nK\ln 2$. Equation (3) can now be written as

$$r \propto \exp(n\ln 2)\exp(-E_a/KT) = \exp[(-E_a/K)(1/T - 1/T_0)] \tag{4}$$

where

$$KT_0 = R^{n-1}E/n\ln 2 \tag{5}$$

is a temperature.

Generally, we can assume that the barrier height increases functionally with respect to the level of generation, n, as

$$E_a = f(n)E. \tag{6}$$

For instance, if we choose the barrier structure as a hierarchical binary tree (case I), we have the function as equation (1). And if we choose a linear structure (case II), with the barrier height increasing linearly with respect to n, we have $f(n) = n$. And we can also choose the barrier height structure as the Fibonacci sequence (case III):

$$f(n) = f_n = f_{n-1} + f_{n-2} \tag{7}$$

where $f_0 = f_1 = 1$ and $n \geq 2$.

Thus, in general, for a binary tree we have

$$KT_0 = f(n)E/n\ln 2 \tag{8}$$

with various structures, $f(n)E$, of barrier height. In addition, for an ordered m-ary tree, we find $KT_0 = f(n)E/n\ln m$.

In figure 2 we have plotted the numerical results of KT_0/E against n for a binary tree. We can see that for case I, when $R \leq 1$, the limit value of T_0 is zero, and from equation (4) we obtain the rate of charge transport as $r \to \infty$. In physical terms this means the barrier becomes smaller and smaller as the generation level, n, increases; the charge transport is easier and easier, and the tree is a conducting one. However, when $R > 1$ we obtain an opposite result: the larger R is, the faster $r \to 0$, i.e. the higher the barrier the more difficult the charge transfer, and the tree becomes insulated.

For the Fibonacci sequence (case III), equation (7), the $r \to 0$ process is faster than the $R > 1$ process of case I, after only a few generation levels. Finally, we have a completely different consequence for the linear structure (case II). KT_0/E takes a constant value $1/\ln 2$, i.e. an increase in the generation level, n, causes a proportional increase in both the energy and the entropy of activation (see equations (1) and (4)). At $T = T_0$ the rate of charge transport is independent of E_a, and in [10] T_0 is called a glass transition temperature. This effect is the so-called compensation effect [9,10].

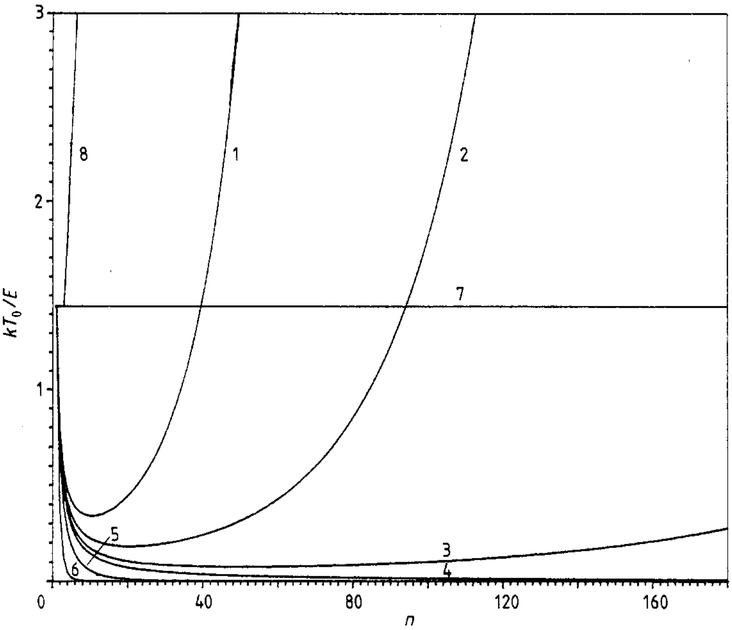

Figure 2. The numerical results for KT_0/E against n, the generation level of the binary trees with the barrier height structures: (case I) $f(n) = R^{n-1}$, (1) $R = 1.1$, (2) $R = 1.05$, (3) $R = 1.02$, (4) $R = 1.0$, (5) $R = 0.9$, (6) $R = 0.5$; (case II) $f(n) = n$, (7); (case III) $f(n) = f_n = f_{n-1} + f_{n-2}$, (8).

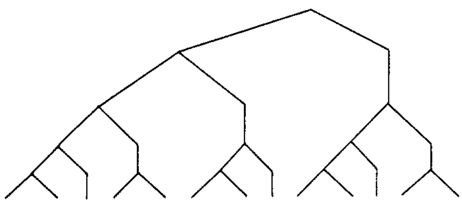

Figure 3. The 'Fibonacci' tree. The tree produced has a population $F_n = F_{n-1} + F_{n-2}$ for $n \geq 2$ with $F_0 = F_1 = 1$. At level n there are F_n pathways for the charge transport.

In figure 3, we show the 'Fibonacci' tree, which is an example of a 'random' tree, i.e. one in which the branching ratio is non-constant, even on a local scale. This tree was first discussed in [2] but not for a spatial configuration. In this paper, we extend this tree to a spatial configuration (real space) in which charge can transfer from one intersection to another. The tree is generated by the following algorithm. At the root there is one parent node. The next generation includes the parent and a single offspring. From then on, any offspring must wait one generation before it becomes a parent; parents, meanwhile, reproduce at every generation. Thus if the tree produced has a population F_n at the nth generation, then

$$F_n = F_{n-1} + F_{n-2} \tag{9}$$

for $n \geq 2$ with $F_0 = F_1 = 1$. Following the method used before for the binary tree, we have

$$T_0 = f(n)E/K \ln F_{n+1} \tag{10}$$

for the 'Fibonacci' tree. For the same three types of barrier structure, we show the results in figure 4. We can see that for case I we have the same conclusions as for a binary tree, and different ones for cases I and III. In case II, for the several initial generation levels T_0 is generation level dependent, and at a generation level, n, less than 30, T_0 takes a constant value KT_0/E=2.073. In case III, we have $r \to 0$, after a few generation levels.

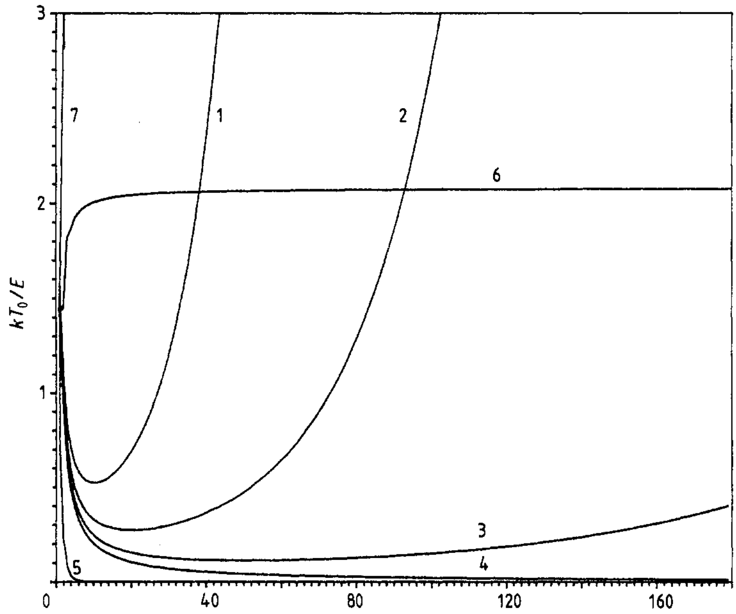

Figure 4. The numerical results for KT_0/E against n, the generation of level of the 'Fibonacci' tree shown in figure 3 with the barrier height structure: case I, $f(n) = R^{n-1}$, (1) $R = 1.1$, (2) $R = 1.05$, (3) $R = 1.02$, (4) $R = 1.0$, (5) $R = 0.5$; case II, $f(n) = n$, (6); case III, $f(n) = f_n = f_{n-1} + f_{n-2}$, (7).

In conclusion, in this paper we first modelled a disordered medium as the n-ary tree and the 'Fibonacci' tree with hierarchical structure in real space. Second, we assumed that the barrier heights had a non-linear and linear structure. We assumed two non-linear structures: a barrier height with the same kind of hierarchical structure as in real space (case II) and a barrier height with the Fibonacci sequence (case III), and one linear structure: a barrier height increasing linearly with respect to n, $f(n) = n$ (case I). A thermodynamical analysis of the charge transport on these spatial hierarchical trees was presented. In particular, a discussion of the 'Fibonacci' tree was presented. In an ordered m-ary tree (or 'Fibonacci' tree), the rate of charge transport is generation level, n, dependent except when the barrier height structure is linear (or after a few levels in the 'Fibonacci' tree).

Although our models are not directly relevant for any particular experimental system, we believe they might be used to describe a disordered medium in some cases, since most of the materials encountered in nature in everyday experience are non-crystalline disordered materials. Some typical examples [1] are the problems of the transport properties in fractured and in porous rock, the anomalous density of states in randomly diluted magnetic systems, silica aerogels and glassy ionic conductors, the anomalous relaxation phenomena in spin glasses and macromolecules, the conductivity of super-ionic conductors such as hollandite and of percolation clusters of Pb on thin films of Ge or Au, and the diffusion-controlled fusion of excitations in porous membrane films, polymeric glasses and isotropic mixed crystals. The charge-conducting pathways used in this paper may correspond to the dislocation lines, grain boundaries, or any other structural imperfections in such a disordered medium. The classical theories of transport valid for crystals do not apply, and the physics of transport, and in particular of diffusion, is anomalous in these disordered systems.

The assumptions for the barrier height made in this paper are made for simplicity. For instance, the Fibonacci sequence is an example of non-linear barrier height structure. On the other hand, the barrier height structure, $f(n)$, could be of some other type; for instance, a probability distribution.

References

[1] Havlin S and Ben-Avraham D 1987 *Adv. Phys.* **36** 695
[2] Keirstead W P and Huberman B A 1987 *Phys. Rev.* A **36** 5392
[3] Havlin S, Kiefer J E and Weiss G H 1987 *Phys. Rev.* A **36** 1403
[4] Ceccatto H A and Huberman B A 1988 *Phys. Scr.* **37** 145
[5] Vilgis T V 1987 *J. Stat. Phys.* **47** 133
[6] Livi R, Maritan A and Ruffo S 1988 *J. Stat. Phys.* **52** 595
[7] Simon H 1962 *Proc. Am. Phil. Soc.* **106** 467
[8] Huberman B A and Kerszberg M 1985 *J. Phys. A: Math. Gen.* **18** L331
[9] Vainas B 1988 *J. Phys. C: Solid State Phys.* **21** L341
[10] Dyre J C 1986 *J. Phys. C: Solid State Phys.* **19** 5655