Correlated Site−Bond Ensembles: Statistical Equilibrium and Finite Size Effects

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This work presents a Monte Carlo analysis of the propagation of correlation strength in site−bond square lattices generated through the dual site−bond model (DSBM), where the values of the property assigned to sites and bonds are sampled from two uniform density distributions that may have some overlapping area with each other. Correlations appear when a construction principle is established. Although this model has been extensively used in many physical applications, such as adsorption and surface diffusion on heterogeneous surfaces and percolation and transport processes in porous media, a careful study of the way correlated topology is settled on through the system was lacking. The dependence of the relaxation time needed to reach equilibrium and of the minimum size of the network to be used is established for different correlation strengths, represented by the overlapping parameter Ω. A more accurate empirical equation, relating the characteristic correlation length l_0, corresponding to the spatial correlation function, and Ω, is found, than the one used in former applications of the DSBM.

Introduction

Many transport and percolation phenomena related to a wide variety of physical problems occurring in surfaces and bulk matter are simulated with the help of a discretized space represented by a regular array of sites or bonds, or by a combined site−bond network.[1−17]

Different physical problems can be treated by association of the elements of the network (sites and bonds) with an appropriate *property*, for example, a porous medium represented by a network of voids (sites) connected by throats (bonds), with the relevant property of each element being its pore size,[18−20] or an heterogeneous adsorptive surface represented by a network of adsorbing potential wells (sites) connected by potential saddle points (bonds) through which an adsorbed particle should jump to migrate from one site to another, with the relevant property of each element being its energy.[13−17] We are interested in the study of disordered media, where the property associated with each element has a probability distribution.

Complexity in these networks may be introduced at different levels as, for instance, a varying connectivity number, the presence of spatial correlations between the property associated with elements separated a certain distance, and the presence of anisotropy, among others.[4,6,11,12] Understanding the influence that complexity has on the physical process to be considered is based on a complete knowledge of the way network topology is affected once this complexity is introduced.

In the present work, we focus on the effects of spatial correlations. To study correlations, it would be desirable to completely know the spatial correlation function, $C(r)$, between two sites (or two bonds) separated by a distance r (in lattice units). $C(r)$ is defined as follows:

$$C(r) = \langle P_S(\vec{R})\, P_S(\vec{R}+\vec{r})\rangle = \langle P_B(\vec{R})\, P_B(\vec{R}+\vec{r})\rangle \quad (1)$$

where P_S (P_B) denotes the value of the evaluated property (energy, size, etc.) for a site (bond) whose position vector is $\vec{R}$ referring to some origin and $\langle\cdots\rangle$ stands for the average over a statistical ensemble of similar systems. This correlation function can be measured by Monte Carlo simulation, using a network of finite size L.

Monte Carlo simulation of such a network involves essentially a model and the generation of a chain of states to reach the desired "equilibrium state". Furthermore, because for finite networks $C(r)$ cannot be measured for arbitrarily large r because finite size effects will always be present, it is important to investigate how large the network must be and how long the chain of states must be, for a given model, to obtain reasonably accurate information about the behavior of this function. Our purpose here is to address these matters for the case of

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two-dimensional networks given by the dual site-bond model (DSBM), introduced in refs 13, 18, and 19 and extensively used in the study of processes occurring on heterogeneous adsorptive surfaces,[16,27−30] in the characterization of disordered mesoporous media,[21,31−34] and in other applications.[35−40] Although the methods to generate DSBM correlated networks have been improved over the years, there has not been a deep study of the way these methods reach statistical equilibrium nor an evaluation of finite size effects in relation to the network correlation length. The results we present in this work will be useful to estimate to what extent the predictions of the model in the many applications it has been used should be modified.

In the following sections, we briefly review the relevant properties of the DSBM and the simulation method, present and discuss our results on the behavior of the correlation function in approaching equilibrium for different network sizes, and finally give the emerging conclusions.

Dual Site−Bond Model

Let $S(P)$ and $B(P)$ be the distribution functions associated with the site and bond property P and let $F_S(P)$ and $F_B(P)$ be the corresponding probability density functions, such that

$$S(P) = \int_0^P F_S(p)\,\mathrm{d}p; \quad B(P) = \int_0^P F_B(p)\,\mathrm{d}p \qquad (2)$$

Let the intervals $s = [s_1, s_2)$ and $b = [b_1, b_2)$ be the support of site and bond measures, i.e., the set of values of P for which F_S and F_B are positively defined. The way in which sites and bonds are connected to form the network is given by the joint probability density function, $F(P_S,P_B)$, of finding a site with property $P_S \in (P_S, P_S + \mathrm{d}P_S)$ connected to a bond with property $P_B \in (P_B, P_B + \mathrm{d}P_B)$. The two basic laws describing the DSBM are

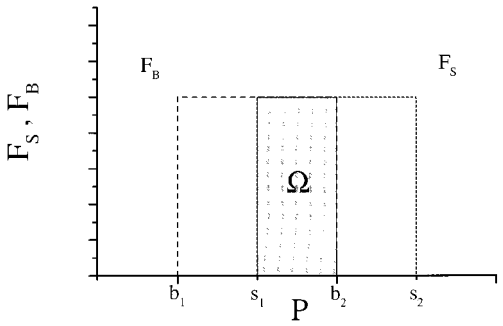

Figure 1. Uniform probability density functions for sites and bonds used to simulate the network.

$$B(P) - S(P) \geq 0 \qquad (3)$$

$$F(P_S,P_B) = 0 \qquad \text{for } P_S < P_B \qquad (4)$$

The first law, eq 3, implies that $b_1 \leq s_1$ and $b_2 \leq s_2$, while the second law, eq 4, called the *Construction Principle* (CP), is of a local nature and expresses the fact that the property P_B of any bond cannot be bigger than that of the two connected sites (for example, in an adsorptive surface, the potential well of a saddle point cannot be deeper than the that of the two connected adsorptive sites or, in a porous medium, the size of a throat cannot be larger than that of the two connected voids).

If the joint probability function is expressed as

$$F(P_S,P_B) = F_S(P_S)\,F_B(P_B)\,\Phi(P_S,P_B) \qquad (5)$$

then the correlation function carries the information about the site−bond assignation procedure in the network. In the simplest case where sites and bonds are assigned to each other in the most random way as allowed by the CP, called the *Self-Consistent* case, then $\Phi(P_S,P_B)$ attains the following expression:

$$\Phi(P_S,P_B) = \frac{\exp\left[-\int_{P_B}^{P_S} \frac{\mathrm{d}B}{B-S}\right]}{B(P_B) - S(P_B)} \qquad (6)$$

If we denote by Ω the overlapping area between the site and bond probability density functions, as shown in Figure 1 for the simple case of uniform distributions, the function Φ has the following properties: (i) $\Phi_{\Omega\to 0}(P_S,P_B) = 1, \forall P_S, P_B$, sites and bonds are distributed completely at random, and (ii) $\Phi_{\Omega\to 1}(P_S,P_B) \propto \delta(P_S - P_B), \forall P_S, P_B$, sites and bonds group together in macroscopic patches, each having a value of P. Then, the overlapping Ω is the fundamental parameter describing the topology of the network in this model.

This behavior also suggests that Ω must be related to some *correlation length* (which would be a physically more meaningful parameter), characteristic of the spatial correlation function defined in eq 1. In fact, it is expected that $C(r)$ decays approximately in an exponential form (this would be the exact behavior for a one-dimensional network generated by a Markov chain of events)

$$C(r) \approx \exp(-r/l_0) \qquad (7)$$

where l_0 is the correlation length (measured in lattice

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constants). This expression has been used extensively in applications of the DSBM[14,16,21,23] together with the ansatz

$$l_0 \approx \Omega/(1 - \Omega) \tag{8}$$

relating the overlapping with the correlation length, in such a way that $l_0 \to 0$ for $\Omega \to 0$ and $l_0 \to \infty$ for $\Omega \to 1$. It will be shown below that eqs 7 and 8 are not generally fulfilled and that a careful study of the approach to equilibrium and of finite size effects in the method used to generate DSBM networks is necessary to obtain accurate results.

The problem of the generation of DSBM networks has been intensively investigated.[18,19,21−25] We employ here the method presented in refs 21 and 22 for the Monte Carlo generation of such networks, which can be resumed in the following very simple terms. An initial network is prepared by sampling the values of P_S and P_B from the corresponding probability density functions F_S and F_B and distributing them completely at random on the lattice. This network will have the correct F_S and F_B but not the correct $\Phi(P_S,P_B)$, in particular the CP is not obeyed everywhere. Then a Markov chain of new states of the network is generated by choosing at random pairs of sites (or bonds) and attempting to exchange them; the exchange is accepted if it does not violate the CP. It has been demonstrated[22] that this procedure leads finally to the equilibrium distribution for the network and that it does not suffer the imperfections introduced by other methods (mainly anisotropy). It will be shown below that the way in which equilibrium is approached depends on the overlapping and the lattice size of the network. In particular, we will find the Markov chain of states needed for equilibrium must be considerably longer than that necessary in order to fulfill the CP everywhere.

Results and Discussion

All of our calculations were performed using the uniform distributions of Figure 1. Different overlappings were attained by keeping the site distribution fixed and shifting the bond distribution.

The central questions to be answered are, when does the network reach statistical equilibrium for a given overlapping and how is the correlation length related to the overlapping? The difficulty is that the number of Monte Carlo steps (MCS) needed to reach equilibrium, the overlapping (or equivalently the correlation length), and the lattice size L used in the simulation are all interdependent quantities. It is expected that, as Ω increase, greater are the size L and the MCS needed to avoid finite size effects and to achieve a well-defined correlation function, respectively.

In the first place, a set of numerical simulations for L running from 200 to 700 was performed for a fixed value of Ω. Then the overlapping was changed and a new set of networks was generated and so on for $\Omega = 0$, 0.5, 0.6, 0.7, 0.8, 0.85, and 0.9. The CPU time needed for each set on a Pentium II-400 MHz processor was just a few minutes for Ω up to 0.7 and around 3 h for Ω close to 0.8 while it rises violently when Ω goes to 0.9 and up, being on the order of 3 days for 0.9.

The convergence to equilibrium for Ω between 0 and 0.6 was achieved for a time t (measured in MCS) on the order of 2×10^5 for all L values employed. Finite size effects were not important for the sizes used, even for $L = 200$. Thus, there was no difference in relaxation times when the size was changed and, consequently, a good statistical equilibrium is expected if the network is thermalized over $t = 2 \times 10^5$ MCS from $L = 200$ on. For

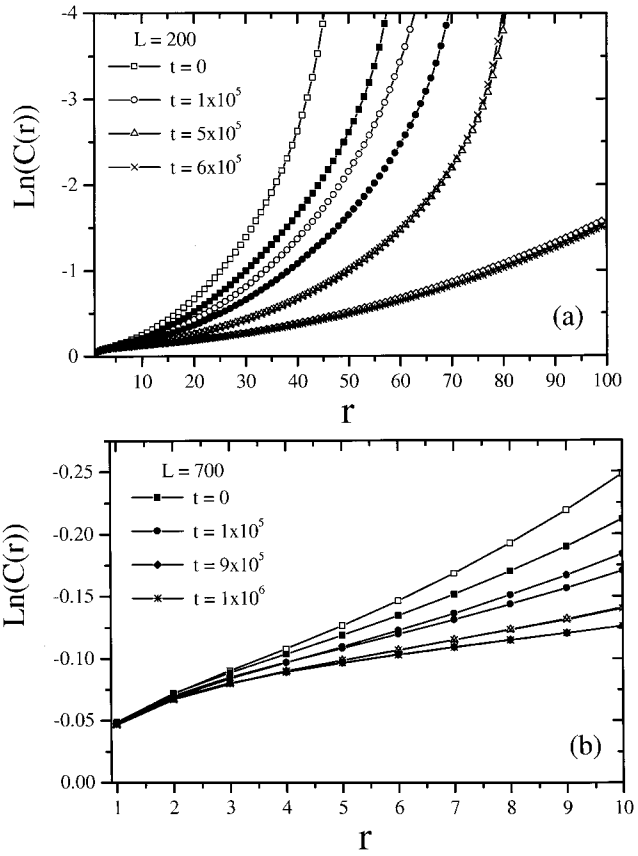

Figure 2. Semilogarithmic plot of the correlation function $C(r)$, defined in eq 1 against r for different MCS and for two different lattice sizes: (a) for the whole range of r; (b) for r up to 10.

Ω greater than 0.6 and up to 0.85, t goes from 2×10^5 to 6×10^5, respectively, until equilibrium is reached. Thus, as a conclusion, $L = 200$ and a relaxation time $t_{eq} = 6 \times 10^5$ MCS are good enough for $\Omega = 0-0.85$.

When the overlapping area increases even more ($\Omega = 0.9$), the size of the network becomes determinant. Figure 2 shows clearly the size effect. In part a the logarithm of the correlation function $C(r)$, defined in eq 1, is plotted against r for different values of t and for two different sizes: empty symbols for $L = 200$ and solid ones for $L = 700$. As can be seen, equilibrium seems to be reached in $t = 6 \times 10^5$ MC steps for $L = 200$, but when L is increased to 700, it is observed that the long-range terms for $C(r)$ (greater values of r) still need more relaxation steps to reach equilibrium. In part b, ln $C(r)$ versus r up to 10 is plotted in order to show that size effects are not so important for $\Omega = 0.9$ for short distance as long as t is greater than 6×10^5. On the other hand, for low t, the size effect must be taken into account.

Performing a linear fit over data up to $r = 10$ on the ln $C(r)$ plots, one can obtain from the corresponding slopes the value for l_0 as a function of t. The results are shown in Figure 3, where part a shows $\Omega = 0.9$ and part b shows $\Omega = 0.7$. These results show the behavior of the correlation length with t until equilibrium is reached. As can be seen, equilibrium is easily achieved for $\Omega = 0.7$ and there is a smooth dependence on the network size; as L increases, the fluctuations in l_0 disappear. For the case $\Omega = 0.9$, equilibrium is harder to reach. Although for $L = 200$ it seems that l_0 does not change with t, when L is increased, the correlation length increases substantially (see the case $L = 400$). Just when $L = 700$, size effects disappear, the curve is smooth, without fluctuations, and there are no important changes in l_0 for larger L.

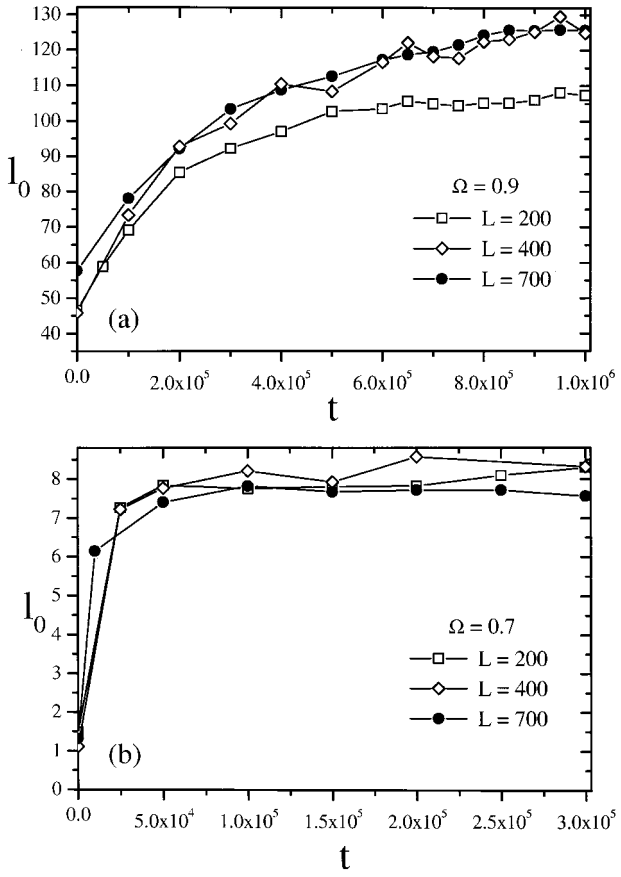

Figure 3. Correlation length l_0 as a function of t until equilibrium is reached (a) for $\Omega = 0.9$ and (b) for $\Omega = 0.7$.

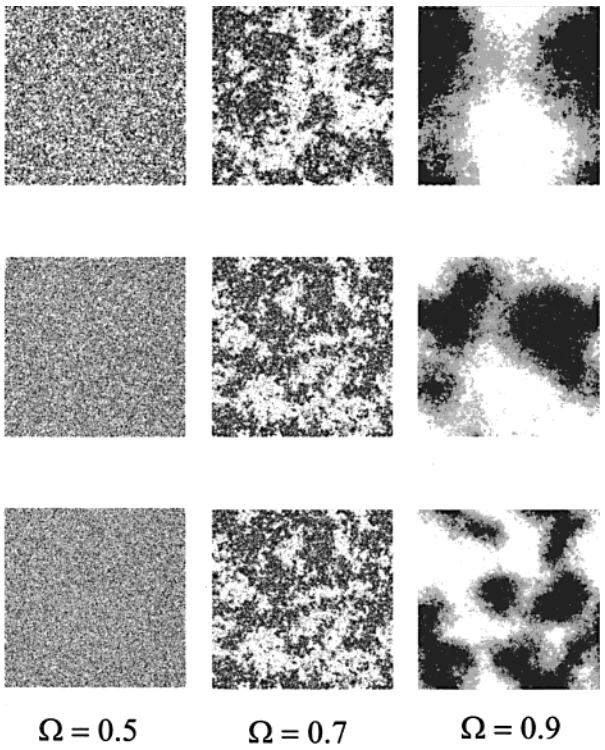

Figure 4. Snapshots showing finite size effects for different overlapping values. Snapshots for the top row are for $L = 200$, those for the middle row are for $L = 400$, and those for the bottom row correspond to $L = 700$.

In Figure 4 size effects on the onset of equilibrium are shown through snapshots representing typical patterns of the network for each selected overlapping. Different darknesses represent an interval for the value of P, for sites or bonds. For the case $\Omega = 0.9$ the role of the network size is far more evident. The features for $L = 200$ can be seen as if they were only a portion of the $L = 700$ sample. One could wrongly deduce that some kind of stratification is spreading through the network because of the presence of correlations among the elements. This effect disappears when greater sizes are used. For the other values of Ω the features for $L = 200$ and $L = 700$ are comparable and the size effects are not important.

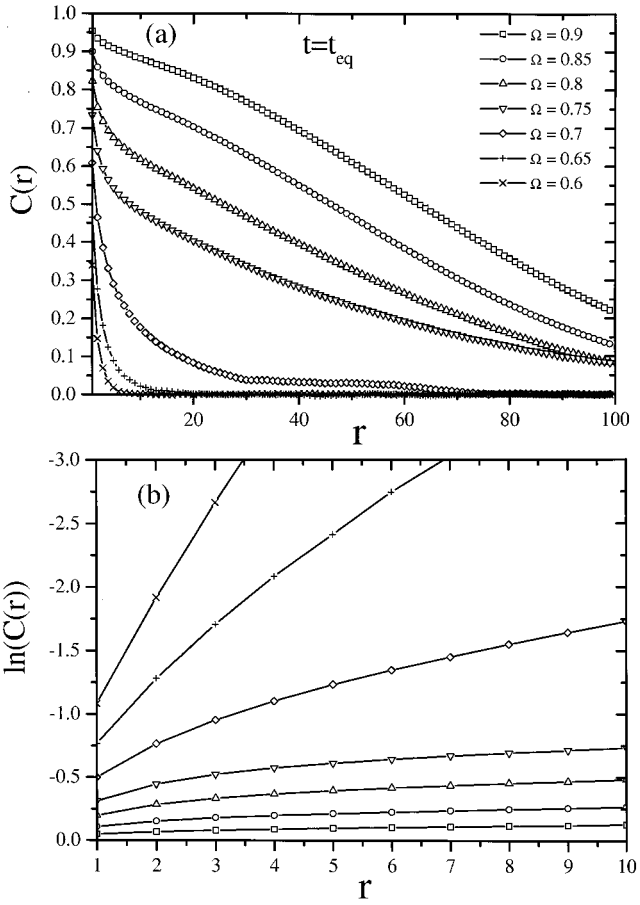

Figure 5. (a) Correlation function for several values of the overlapping and for $L = 700$. (b) Semilog plot for $C(r)$ showing a good linear behavior up to $r = 10$ lattice units.

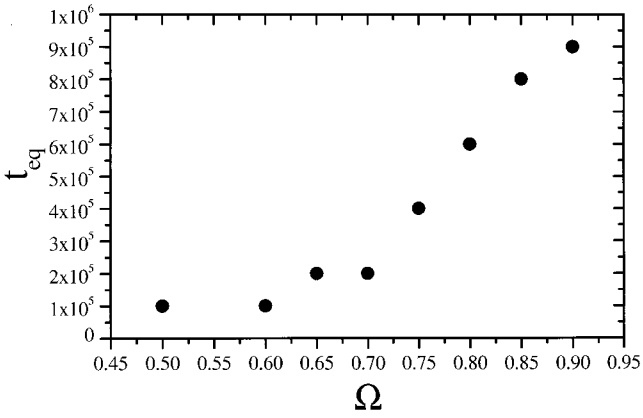

Figure 6. Equilibrium relaxation time for $L = 700$ as a function of the ovelapping area.

In Figure 5a, $C(r)$ versus r is shown for several values of the overlapping and for $L = 700$. The criterion used for the determination of the number of MCS to reach statistical equilibrium, t_{eq}, was such that the change in

l_0 from $t = t_{eq}$ to $t = t_{eq} + 10^5$ was smaller than 1%. As seen in Figure 6 and discussed above, t_{eq} varies for each overlapping considered. The semilog plot in Figure 5b shows a nearly linear behavior of the correlation function up to $r = 10$ lattice units. These curves were fitted with a linear regression whose slope (see eq 3), we take as the correlation length l_0.[26] Through this procedure, the behavior of l_0 as a function of Ω can be determined, and the results are shown Figure 7. The full square symbols represent the simulation results, which are well fitted by the function

$$l_0 = 2\frac{\Omega^2}{(1-\Omega)^2} \tag{9}$$

As can be seen, this function differs substantially from that given by eq 8 at high values of the overlapping Ω.

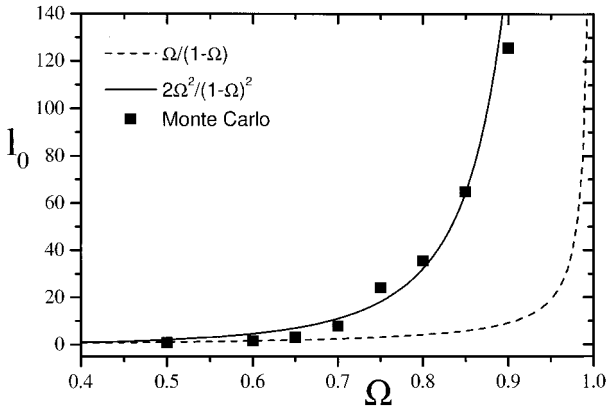

Figure 7. Relation between the correlation length l_0 and the overlapping area Ω.

Conclusions

A thorough study of the correlation properties of site−bond networks generated by the DSBM has been performed by means of MC simulation, demonstrating how these properties are affected by the number of MCS performed in the process toward reaching statistical equilibrium and by finite size effects. As a result, simple rules are established regarding the values of the relaxation time to reach equilibrium, t_{eq}, and the lattice size, L, to be used for a given value of the overlapping Ω.

This study also reveals that the assumed relation between the correlation length l_0 and the overlapping Ω, given in eq 8 and extensively used in many applications of the DSBM, is not accurate at high values of Ω and a more precise relation is obtained as given in eq 9.

At present, efforts are being done to determine the behavior of the correlation length for three-dimensional networks and also for other forms of the site and bond probability density functions, to derive more general features for the DSBM.

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