Stretched exponential relaxation in a diffusive lattice model

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We studied the single dimer dynamics in a lattice diffusive model as a function of particle density in the high densification regime. The mean square displacement is found to be subdiffusive both in one and two dimensions. The spatial dependence of the self-part of the van Hove correlation function displays as a function of r a single peak and signals a dramatic slow down of the system for high density. The self-intermediate scattering function is fitted to the Kohlrausch-Williams-Watts law. The exponent β extracted from the fits is density independent while the relaxation time τ follows a scaling law with an exponent 2.5.

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I. INTRODUCTION

Lattice-gas models of dense fluids have been explored [1–3] in order to understand the microscopic details of their slow dynamics and to compare them with the behavior of other disordered systems like structural glass formers, spin glasses, and colloids.

Among the lattice models *random sequential adsorption* (RSA) of particles on a substrate is of particular interest. RSA has been invented to mimic many experimental situations like chemisorption on crystal surfaces, reactions on polymer chains, adsorption of macromolecules and colloidal particles, monolayer and multilayer growth processes (for an an extensive review see [4,5]). In particular RSA with added diffusion (RSAD) has been considered a model which captures the main features of the compaction dynamics in granular matter [6]. The description of the relaxation processes in the RSAD model has been investigated through the behavior of the time density correlation function in a limited number of studies and only during the deposition process [7,8].

In this paper we explore by computer simulation the equilibrium dynamical properties of a lattice gas of dimers as a function of density in two dimensions. The starting configurations have been produced with a RSAD model where by deposition and diffusion of particles we reach the desired value for the density. In this way, due to the geometrical frustration, as the dimer density increases trapping configurations that only depend on the local environment [9] are created in the system. The dynamical properties are studied by switching the deposition off.

In Sec. II we describe the model and the details of our Monte Carlo simulation. In Sec. III we present our results for the single dimer dynamics as a function of particle density. In particular we analyze the mean square displacement, the Van Hove self-correlation function and its space Fourier transform, the self-intermediate scattering function. Section IV is devoted to concluding remarks.

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II. MODEL AND COMPUTATIONAL DETAILS

In order to investigate the dynamical properties of dimers on a square lattice with fixed density we have generated the starting configurations through a RSA model of dimers with diffusion in two dimensions (RSAD-2D) [9,10] by Monte Carlo (MC) simulations. We also performed simulations of the same model in one dimension (RSAD-1D) for comparison. We have considered a square lattice of $N=L\times L$ sites, with periodic boundary conditions in both directions. Two kinds of dynamical processes can occur in the system, namely deposition of a dimer on an empty pair of sites and diffusion of a deposited dimer on an empty first neighbor site; no overlap of dimers is allowed. The lattice is initially empty and at each MC step one deposition event (or one diffusion event) is selected with probability p (or $1-p$), where $0<p\leqslant 1$. Dimers can be adsorbed on the lattice in two possible orientations (horizontal and vertical) and can diffuse along their own axis. In the case of deposition, the dimer can occupy a randomly selected pair of sites if they are both empty, otherwise the attempt is rejected. In the case of diffusion the randomly selected horizontal (vertical) particle attempts to move left or right (up or down), with equal probability. A diffusion event to the right (left) or up (down) is possible only if the chosen pair of sites is occupied and the corresponding right (left) or up (down) neighbor site is empty, otherwise the attempt is rejected. As usual the MC time unit corresponds to N deposition and/or diffusion attempts. We checked that finite-size effects are negligible for $L\geqslant 40$, so in the following we analyze a square lattice with $L=40$. We produced 11 starting configurations at densities $\rho=0.60$, 0.70, 0.75, 0.80, 0.88, 0.94, 0.96, 0.98, 0.99, 0.995, 0.998. For each configuration, production runs at constant density have been obtained by switching the deposition events off. In this way we are able to follow the dynamics of the system in an equilibrium situation. In fact, the equilibrium distribution for this system, where all allowed configurations have the same weight, is a constant. Therefore the detailed balance condition reduces to two requirements: transitions to forbidden states are not allowed, and transition from an allowed state to another has the same probability as

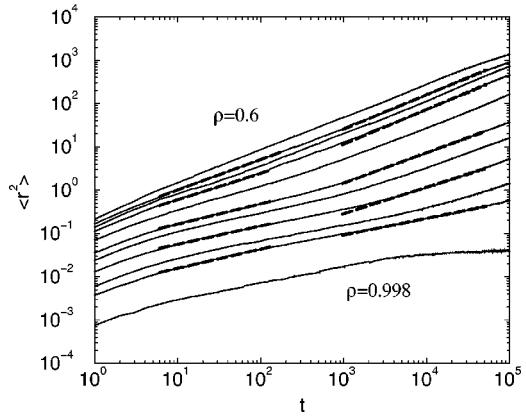

FIG. 1. Log-log plot of the temporal evolution of the MSD for several different densities: $\rho=0.60$, 0.70, 0.75, 0.80, 0.88, 0.94, 0.96, 0.98, 0.99, 0.995, 0.998 from top to bottom. Long-dashed lines are the fits to power law behavior in the two time regions from 5 to 120 MC time steps and from 1000 to 60 000 MC time steps. For the sake of clarity, fits are reported only for even curves. The exponents extracted from the fit are reported in Table I.

the reverse one. Both these requirements are satisfied by the adopted algorithm. A more complete investigation of the irreversible dynamics of these models and discussion of the role of the dimensionality is presented elsewhere [9].

III. SINGLE DIMER DYNAMICS

In this section we investigate the dynamical behavior of this lattice model through the single dimer density correlators. We have chosen relatively large values of the density ($\rho \geqslant 0.60$), since we are interested in the diffusive dynamics of the system in the high densification regime where slow dynamics is more likely to occur. The time over which the diffusive motion of particles has been followed reaches, in most cases, 10^6 MC time units (because of the statistical noise in the last decade only t up to 10^5 is shown in the plots).

A. Diffusion properties

We analyze in the following the mean square displacement (MSD) of the particle, $\langle r^2(t)\rangle$, defined as

$$\langle r^2(t)\rangle = \frac{1}{N_{\text{part}}}\left\langle \sum_{i=1}^{N_{\text{part}}} |\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2 \right\rangle, \qquad (1)$$

where $N_{\text{part}}=N\rho/2$ is the number density, $\mathbf{r}_i$ is the position of particle i at time t, and $\langle\,\rangle$ denotes a time average. In Fig. 1 we show a log-log plot $\langle r^2(t)\rangle$ for RSAD-2D for the different densities investigated. After an initial transient, which is more pronounced at high densities, the temporal behavior of the MSD can be fitted with two power laws. In the first time region $\langle r^2(t)\rangle \sim t^{\delta_1}$. In the intermediate time region for the lower densities the MSD shows a bend followed by a slight increase in the exponent, i.e., $\langle r^2(t)\rangle \sim t^{\delta_2}$ with $\delta_2 > \delta_1$, where the exponents depend upon density. The bend becomes more evident as the density increases. Values of δ_1 and δ_2 are reported in Table I. They are less than 1 for all the densities considered: in particular, δ_1 and δ_2 do not exceed, respectively, 0.75 and 0.80, which are the values found for the lowest density, i.e., $\rho=0.60$. The difference between the two exponents is more marked for intermediate densities ($0.80<\rho<0.96$). For the highest density ($\rho=0.998$) the MSD shows a plateau for large times. In the time region investigated none of the curves shown attains the Brownian diffusive regime, $\delta_2=1$.

TABLE I. Values of the exponents extracted from the fit to the power law of the MSD plotted in Fig. 1.

Density	δ_1	δ_2	δ_2/δ_1
0.60	0.75	0.80	1.07
0.70	0.72	0.80	1.11
0.75	0.67	0.79	1.18
0.80	0.64	0.79	1.23
0.88	0.60	0.74	1.23
0.94	0.54	0.70	1.30
0.96	0.52	0.67	1.29
0.98	0.51	0.60	1.18
0.99	0.51	0.48	0.94
0.995	0.51	0.38	0.75

These findings can be interpreted in terms of the density characterizing the degree of motion of particles like the thermal energy in thermal systems. For low densities single particles can move freely and the diffusive dynamics is almost independent of time. Increasing the density particles remain trapped in local transient configurations [9,10] and diffusion slows down. For very high density the trapping configurations are frozen and the system does not evolve any more on the time scale of our simulations. The existence of trapping configurations and subdiffusive behavior is in general linked to the presence of disorder [11] that in the present case can be ascribed to the random barriers associated with the local environment determined by the geometrical constraints. The particle has to overcome these barriers and spend a long time before detrapping (see [12] for an analogous case in a random walk model).

These dynamical features are not present in the RSAD-1D model, where we have found a MSD with a density independent slope for this case. Nevertheless the behavior is subdiffusive, with an exponent $\delta=0.5$ constant over the whole time window investigated.

B. Density correlator

For a closer analysis of the motion of the dimer we have considered the self-part of the van Hove correlation function (SVHCF) $G_s(r,t)$, defined as

$$G_s(r,t) = \frac{1}{N_{\text{part}}}\left\langle \sum_{i=1}^{N_{\text{part}}} \delta(r-|\mathbf{r}_i(t)-\mathbf{r}_i(0)|) \right\rangle, \qquad (2)$$

which gives the probability of finding a particle around a distance r at time t, given that the same particle was at the origin at time $t=0$. The MSD analyzed in Sec. III A is the

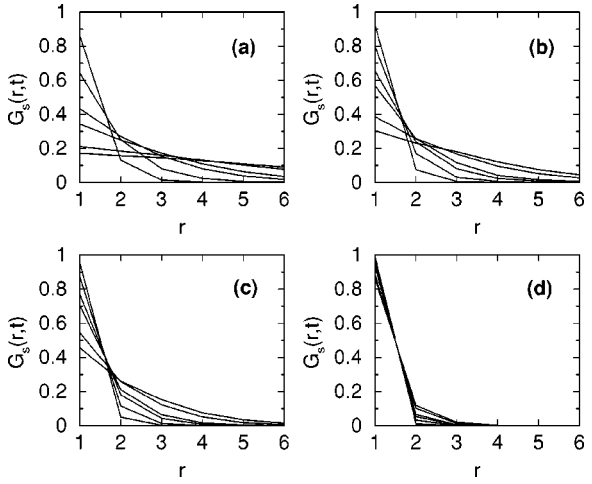

FIG. 2. Spatial dependence of the SVHCF $G_s(r,t)$ for different densities: $\rho=0.60$ (a), $\rho=0.80$ (b), $\rho=0.88$ (c), and $\rho=0.98$ (d). The curves in each graph correspond to various times: $t=3$, 15, 63, 127, 511, 1023 (in MC time units) from top to bottom on the left side of each graph. Distances on the horizontal axis are measured in lattice spacing units.

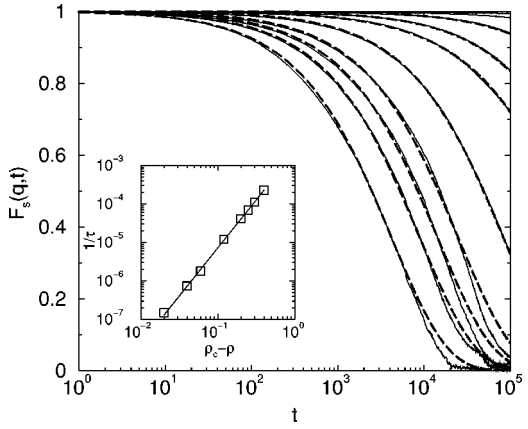

FIG. 3. Temporal evolution of the SISF $F_s(\mathbf{q},\mathbf{t})$ for $\mathbf{q}=(2\pi(L-1)/L,0)$. The solid curves correspond to the result of the simulations for different densities: $\rho=0.60$, 0.70, 0.75, 0.80, 0.88, 0.94, 0.96, 0.98, 0.99, 0.995, 0.998. The long-dashed curves are fits to the data according to Eq. (4). In the inset it is shown the inverse relaxation time vs density: the squares are the parameters obtained from the fit to Eq. (4) for various density, while the solid curve is the best fit according to Eq. (5).

second spatial moment of the SVHCF. Nonetheless, in disordered diffusive systems that do not have a simple behavior, the SVHCF might contain additional information on the microscopic relaxation mechanisms of the system, which could be smeared out in the MSD.

The SVHCF is shown for our system in Fig. 2 for four densities at different times. We have calculated the one dimensional SVHCF along the horizontal or the vertical direction. In Fig. 2 we show the SVHCF averaged over the two directions. The self-correlation function shows a single peak centered around zero for all the times investigated. The appearance of more than one peak at a given time would have evidenced the existence of more than one, well distinct, relaxation mechanism for that time. The single peaked structure confirms the dynamics to be mastered only by a single mechanism related to the existence of high entropic barriers generated by configurations in which a particle is locally trapped. It is also seen that at low density the SVHCF is localized at short distances (typically $1\leqslant r\leqslant 2$) for short times and tends to delocalize for large times, since it is able to explore more configurations. At higher densities we observe a ''clustering'' of the various curves for $1\leqslant r\leqslant 2.5$ [this effect is particularly evident in Fig. 2(d)]: this is the signature of the fact that the movement of particles drastically slows down at such densities.

C. Intermediate scattering function

The space Fourier transform of the SVHCF, i.e., the self-intermediate scattering function (SISF) $F_s(\mathbf{q},t)$, is given by

$$F_s(\mathbf{q},t)=\frac{1}{N_{\rm part}}\sum_{i=1}^{N_{\rm part}}\exp\{i\mathbf{q}\cdot[\mathbf{r}_i(t)-\mathbf{r}_i(0)]\}, \qquad (3)$$

where $\mathbf{q}=(q_x,q_y)$ is the discrete wave vector ($q_{x,y}=2\pi n_{x,y}/L$ with $n_{x,y}$ an integer between 0 and $L-1$). For all the densities considered in the simulations, the smaller q is, the more slowly $F_s(q,t)$ is found to decay. We show in Fig. 3 data for $\mathbf{q}=(2\pi(L-1)/L,0)$ at several different densities. This q value is chosen of the order of the inverse of the typical size of the trapping region, which we estimate to be of the order of 2–3 lattice spacings [9]. As can be seen, the entire dynamical behavior at low-intermediate densities is observed in the time window of our simulations, since the SISF decays to zero for such densities. For high values of the density only a part of the SISF can be observed, due to the very slow dynamical relaxation and the freezing of particles which is also evident in the MSD. The short-intermediate time behavior of SISF can be fitted with a Kohlrausch-Williams-Watts law (KWW)

$$F_s(q,t)\simeq\exp[-(t/\tau)^{\beta}], \quad 0<\beta\leqslant 1. \qquad (4)$$

The curve resulting from this fitting, also shown in Fig. 3, reproduces the data obtained from MC simulations quite accurately for several decades. A deviation of MC results from Eq. (4) is observable only in the tails of the correlators. The collapse of correlators onto a single curve when plotted versus $t/\tau(\rho)$ demonstrates the existence of a well defined scaling law on several decades for this kind of systems. In the range of density considered, the stretching exponent β is essentially constant, with a value $\sim$0.68, the density dependence being reflected only in the relaxation time τ.

Furthermore, we have found that the behavior of τ versus ρ follows the scaling law

$$\tau^{-1}\simeq A(\rho_c-\rho)^{\gamma}. \qquad (5)$$

This fit is shown in the inset of Fig. 3 together with the points determined from the parameters of Eq. (4). As can be seen from the figure, Eq. (5) applies satisfactorily in the entire range of densities considered. Our estimates yield $A\simeq 0.0023$, $\gamma\simeq 2.5$, and $\rho_c\simeq 1.0$. Given the uncertainties in

the fit, this value found for ρ_c cannot be distinguished from the maximal density reachable in this system, which has been found to be ≈ 0.998 in numerical simulations (see [9,10]). This would suggest that there is no dynamical transition in this model, i.e., no critical density (lower than the maximal density) exists at which a structural arrest of the system occurs. It is important to stress that the relaxation time obeys the power law equation (5), which has the same kind of scaling found in many glassy systems and is the signature of a sluggish dynamical behavior. The existence of a power law behavior for τ as a function of density and the validity of the KWW law are novel and interesting points for systems of this kind. It would be interesting to investigate in the future the τ and β dependence on the wave vector to check on the range of validity of both the KWW law and of the power law.

IV. CONCLUSIONS

We presented a Monte Carlo study of the single dimer density correlators for a randomly diffusive model of dimers on a square lattice as function of density. For each density the starting configurations have been generated through a RSAD-2D model. We found that the dynamical behavior is related with the system dimensionality and that the diffusive dynamics is non-Brownian for the time regimes investigated. In spite of its simplicity the model considered shows a quite complex dynamical behavior, and in particular some features resembling that of the slow relaxation of structural glass formers are found.

The most interesting results came from the SISF analysis. We have found that this correlator in the q,t space has a well defined scaling behavior with density that can be described with a high degree of accuracy by the KWW function in most of the time region investigated. This function is well known to reproduce many features of disordered systems, and is connected to fractality in configurational space [13,14]. The exponent of the stretched exponential function β is density independent and the relaxation time follows a power law with an exponent γ in the range of those of structural glass formers [13]. The power law predicts a divergence of the relaxation time for density around 1. From these findings it can be consistently derived that for this nonthermal system the role of thermal energy is played by the density.

We correspondingly find a subdiffusive behavior in the MSD. The slowdown of the system that becomes more significant as density is increased can be attributed to transient trapping configurations. We point out that with respect to lattice-gas models of the kind considered in Ref. [2] we did not introduce any explicit constraint to induce the trapping of the dimers. In our system in fact it naturally arises because of geometrical constraints.

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