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Macroscopic glassy relaxations and microscopic motions in a frustrated lattice gas

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We study microscopic and macroscopic dynamical properties of a frustrated lattice gas showing the violation of Stokes-Einstein law. The glassy behaviors are analyzed and related with experimental results in glass former systems. [S1063-651X(97)50908-1]

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In simple liquids the connections between the times of macroscopic relaxations and the properties of microscopic particles motion are elucidated by the Stokes-Einstein relation that links shear viscosity and particle diffusivity. Recent experimental evidence shows how such a relation is violated in supercooled glass forming liquids. In these systems complex dynamical behaviors, which are distributed on many time scales, are supposed to be linked in a nontrivial way to atomic motions of the liquid components [1,2].

We face these questions in the context of a microscopic model recently introduced to describe some general features of glasses [3]. This model, which bridges spin glasses (SG) [4] and site frustrated percolation [5], consists of a lattice gas model in which each particle contains an internal degree of freedom characterized by a spin variable. The spins interact via quenched ferromagnetic and antiferromagnetic interactions randomly distributed like in the SG model. The model is described by the following dilute SG Hamiltonian:

$$\beta\mathcal{H}=-J\sum_{\langle ij\rangle}(\epsilon_{ij}S_iS_j-1)n_in_j-\mu\sum_i n_i, \qquad (1)$$

where $n_i=0,1$ are occupancy variables that have an internal Ising degree of freedom $S_i\pm 1$, the $\epsilon_{ij}=\pm 1$ are quenched random lattice interactions, and μ is an adimensional chemical potential, which plays the role of the inverse of the temperature $1/T$.

When all the sites are occupied ($n_i=1$), i.e., if $\mu\rightarrow\infty$, this model is the standard $\pm J$ Ising spin glass. In the limit $J\rightarrow\infty$ it describes a frustrated lattice gas where two nearest neighbor particles can be occupied only if their internal variables satisfy the constraint $\epsilon_{ij}S_iS_j=1$. Since in a frustrated interaction loop the spins cannot satisfy all the couplings, in this model particle configurations in which a frustrated loop [4] is fully occupied are not allowed.

In a liquid the internal degrees of freedom S_i may be associated, for example, with the internal orientation of particles, but, more generally, they represent microscopic quantities that probe local effects of ''frustration.'' Geometrical hindrance in the liquid implies the existence of loops that cannot be fully occupied, in correspondence with the frustrated loops in the model (see [6]).

In the mean field [7] the static properties of the model show two transitions: one at a value μ_c, which signals the appearance of metastable states, and a second thermodynamic transition at a higher value μ_0 (corresponding to a lower temperature). These properties recall those of the p-spin glass models [8]. These models have received renewed attention, as their dynamical behavior in a mean field is described by the same equation as those of the mode coupling theory for simple liquids [1]. Moreover, the dynamical transition coincides with the first transition from the stable to the metastable state. The similarity in the static properties of the two models suggests that the dynamics may also be the same. Therefore, we expect for the lattice gas model (1) in a mean field a dynamical transition at μ_c with a diffusion coefficient vanishing with a power law.

We have studied the model (1) in $d=3$ dimensions in the limit $J\rightarrow\infty$ by means of Monte Carlo methods. We use a standard Monte Carlo dynamics, in which particles diffuse and spins are updated with Metropolis spin flip. Some results on the static and dynamic properties of the model have been previously reported [3]. Here, we focus mainly on the relation between the diffusion coefficient and the characteristic relaxation time.

Our data are consistent with the following picture: we find a region $\mu<\mu_p$ (high temperature) where the model behaves as a normal fluid characterized by single exponential relaxation and normal diffusion. The value of μ_p is numerically consistent with the percolation threshold for the particles system. For values $\mu_p<\mu<\mu_0$ the density-density time dependent autocorrelation function exhibits a two step relaxation, corresponding to the α and β relaxation times. The value μ_0 corresponds to the spin glass transition characterized by the divergence of the nonlinear susceptibility and moreover, where the diffusion coefficient $D(\mu)$ vanishes [3]. In this region $D(\mu)$ exhibits a net cusp at μ^* ($\mu_p<\mu^*<\mu_0$). Both the diffusion coefficient and the α relaxation time exhibit a power law behavior for $\mu<\mu^*$ with a sharp crossover to an Arrhenius or Vogel-Fulcher law for $\mu>\mu^*$. This crossover can be interpreted in the following way [9]. In a mean field the dynamical transition occurs at the same temperature where the static exhibits a transition from a stable to a metastable state. Once in the metastable state the system is trapped forever due to the infinite lifetime of the mean field metastable state. In finite dimension the metastable state has a finite lifetime, and the system does not reach a full arrest.

The value of μ_p is located roughly where the β relaxation and the α relaxation time starts to separate and where the relation between the α relaxation time and the diffusion coefficient violates the *Stokes-Einstein law*, as observed in real structural glasses [10–14].

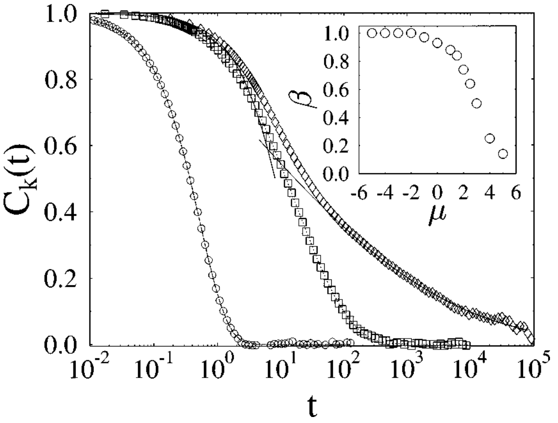

FIG. 1. Fourier transformed density correlation function $C_k(t)$ for $k=L/4$, as a function of time t for several values of the chemical potential μ ($\mu=-2.0,3.0,5.0$), in a system of linear size $L=16$ and coupling constant $J=10$. Superimposed are the short time exponential and the long time stretched exponential fits (see text). Inset: The exponent β of the stretched exponentials of the long time fits of density correlation functions reported in the main frame, as a function of μ.

We have considered a cubic lattice of linear sizes $L=8$, 12, and 16 with periodical boundary conditions, fixing $J=10$ and using μ as a variable. Our results do not change for $J=10\,000$, showing that we are effectively close to the value of $J=\infty$. As stated, the *dynamic* in our model is a standard Monte Carlo (MC) dynamics, in which particle diffuse and spins are updated with Metropolis spin flip. The system is equilibrated after successive thermalization at higher and higher values of μ for about 10^6 MC steps at each fixed value of external parameters. The measures are then taken up to about 10^8 MC steps, for a given random configuration of the couplings ϵ_{ij}. We are aware that in the deep glassy region (above $\mu\sim 5$) our numerical results may be only indicative due to the required very long simulation times, but this does not change the overall picture described above.

We have calculated the density-density time dependent autocorrelation functions,

$$C_k(t)=\langle\rho_k(t)\rho_{-k}(0)\rangle/\langle\rho_k\rho_{-k}\rangle. \qquad (2)$$

Here, ρ_k is the Fourier transform on the lattice of the density $\rho_k(t)=(1/N)\Sigma_{r=0}^{L-1}\rho(r,t)\cos(q_k r)$, where $\rho(r,t)$ is the particle density, at time t and at a distance r from a median plane in our cubic lattice of size L, and $q_k=(2\pi/L)k$, with $k\in\{1,2,\ldots,L/2\}$. Times are measured in such a way that $t=1$ corresponds on average to the time to update once all the degrees of freedom in the system. We have also calculated the square magnetization time dependent autocorrelation function and found that behaves in a similar way.

As anticipated above, the system at low μ (i.e., low density) behaves as a normal liquid, with exponentially decaying time correlation functions (see Fig. 1): $C_k(t)\sim\exp[-t/\tau_0(k)]$. The characteristic time $\tau_0(k)$, excluding finite size effects, is inversely proportional to $k^2, \tau_0(k)\sim 1/D_0k^2+\tau_\infty$.

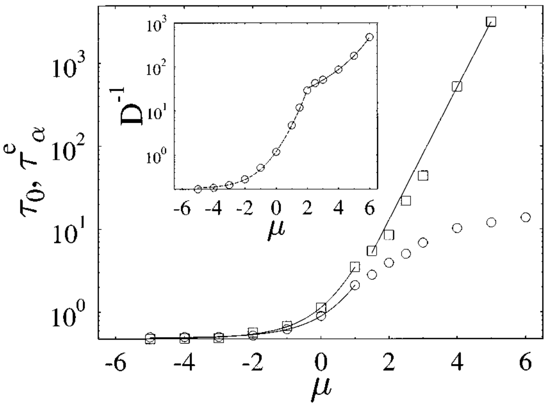

FIG. 2. The short time exponential β-relaxation time $\tau_0(k)$ (circle), and the α relaxation $\tau_\alpha^e\equiv\tau_\alpha/\ln(10)$ (square), of density correlation function (for $k=L/4$), as a function of μ, for a system of linear size $L=16$ and $J=10$. Continuous curves are power law and Arrhenius fit described in the text. The point where the low μ behavior fails is located around $\mu_p\sim 0.75$. Inset: The inverse of diffusivity, $D(\mu)$, as a function of μ for the same system. Superimposed are the power law and Voghel-Tamman-Fulcher fits described in the text. The cusp in $D(\mu)$ individuates a characteristic value $\mu^*\sim 2.0$ ($\mu^*<\mu_0$, where μ_0 is the SG transition).

For larger values of μ (larger density), even if the short time decay ($t\leqslant 1$) is still exponential, the long time relaxation ($t\gg 1$) may be reasonably fitted by the Kohlrausch-Williams-Watt stretched exponential form (see Fig. 1)

$$C_k(t)\sim B\exp\{-[t/\tau(k)]^\beta\}, \qquad (3)$$

with β a function of μ (see Fig. 1), as typically occurs in SG [16]. This implies that the MCT prediction of *time-temperature superposition relation* [1] is verified only in very narrow density intervals.

Close to $\mu_p\sim 0.75$ ($\rho_p\sim 0.38$), we observe the separation of short times (β-process) and long times (α-process) relaxation. For an estimate of the long time relaxation, the α relaxation, in principle we could use $\tau(k)$ from the fit of Eq. (3). However, due to the sensitivity of $\tau(k)$ on the details of the fit, such as for example the region chosen for the fit, following Ref. [15] we define the α relaxation $\tau_\alpha(k;\mu)$ as the time such that $C_k(\tau_\alpha)=10^{-1}$. For $\mu<\mu^*\sim 2$, $\tau_\alpha(k)$ is well fitted with a power law behavior (see Fig. 2) [17]

$$\tau_\alpha(k;\mu)=A_k(\mu_c-\mu)^{-\gamma}+B_k, \qquad (4)$$

with $\gamma=6.8$ and $\mu_c=5.6$ almost independent of k ($A_k=7000$ and $B_k=0.5$ for $k=L/4$). Also the time $\tau_0(k)$ of the initial exponential-like decay follows the same power law dependence up to μ_p, and then saturates to a finite value exponentially with μ.

For $\mu>\mu^*$, while $\tau_0(k;\mu)$ saturates, $\tau_\alpha(k;\mu)$ is reasonably fitted by an Arrhenius behavior divergence (see Fig. 2)

$$\tau_\alpha(k;\mu)=a_k\exp(\mu/\mu_\alpha), \qquad (5)$$

with $a_k=0.7$ and $\mu_\alpha=0.4$ for $k=L/4$.

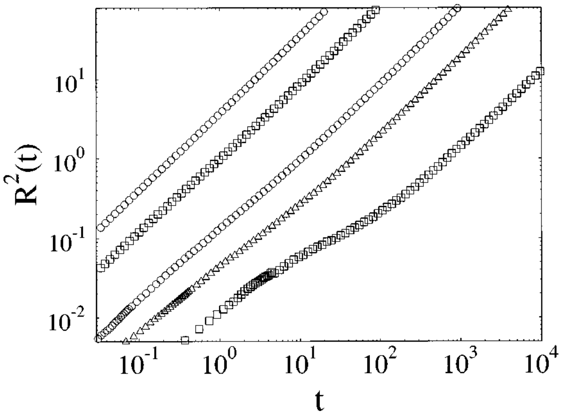

FIG. 3. Particle mean square displacement $R(t)^2$ as a function of time in a system of linear size $L=16$, for $J=10$, and for $\rho=0.088, 0.271, 0.440, 0.581, 0.674$ (higher curves correspond to lower densities).

The crossover from a power law behavior forecasted by MCT or spin glass mean field theory to an Arrhenius (or Vogel-Tamman-Fulcher in fragile liquids) behavior for α relaxation times, is typically observed in real structural glasses, too [2].

It is interesting to compare the anomalies of the autocorrelation functions described above to microscopic particle diffusion. Here, frustration may have a strong effect on particles. We have calculated the particle mean square displacement [3] $R^2(t)=\langle(1/N)\Sigma_i[r_i(t)-r_i(0)]^2\rangle$. For $\mu<\mu_p$ we find a Brownian typical linear time behavior. For $\mu>\mu_p$, in the intermediate time region, we observe a subdiffusive region with an inflection that becomes more evident as μ increases (see Fig. 3).

The linear asymptotic behavior of $R^2(t)$ defines the diffusivity D. This shows an apparent cusp at $\mu^*\sim 2$ ($\rho^*\sim 0.5$) and an abrupt change in behavior, as shown in Fig. 2. Below μ^*, it is possible to fit $D(\mu)$ with the power law given in Eq. (4) with the same γ and μ_c (see Fig. 2) found studying density relaxation times.

The value μ_c from the power law fit corresponds to the characteristic temperature T_c of mode coupling theory [1], or to the ‘‘dynamic transition’’ of the mean-field theory of p-spin glasses [4,8]. Above μ^* the best fit for D is obtained using a Voghel-Tamman-Fulcher (see Fig. 2),

$$D^{-1}(\mu)=A_D\exp[d/(\mu^{-1}-\mu_1^{-1})], \tag{6}$$

with $A_D=17$, $\mu_1=11.4$, and $d=0.3$, for the system of size 16^3. However, an Arrhenius fit (i.e., $\mu_1\rightarrow\infty$), as that found for τ_α of α relaxation, is just slightly worse,

$$D^{-1}(\mu)=A'_D\exp(\mu/\mu_D), \tag{7}$$

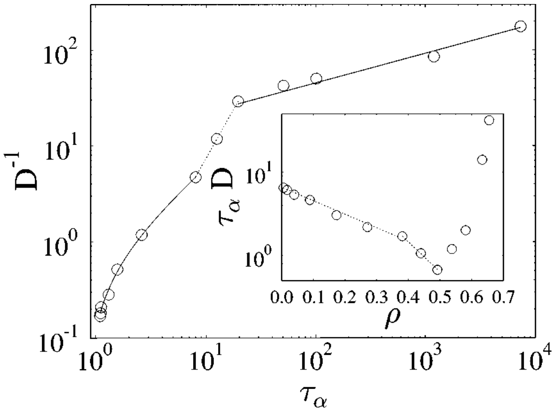

FIG. 4. The diffusivity D as a function of the α-relaxation time τ_α. As in real experiments three different regions appear. The superimposed curves are fit with the generalized fractional Stokes-Einstein law $D^{-1}\sim\tau_\alpha^\xi$. Inset: The product of diffusivity $D(\rho)$ and of α-relaxation time $\tau_\alpha(\rho)$ as a function of density ρ.

where $A'_D=2.72$ and $\mu_D=1.1$. A crossover from power law to Arrhenius (or Voghel-Tamman-Fulcher) behavior is also observed in real experiments [2].

In our model the density ρ^* corresponding to μ^*, where the Arrhenius region sets in, is signaled by a local minimum in the static structure factor $S(k;\rho)$, as a function of ρ. Our observations indicate that the diffusivity D goes to zero in the region where the static SG transition μ_0 should be located as signaled by the divergent nonlinear susceptibility χ_{SG}. However, it is difficult to numerically establish where exactly μ_0 is located ($\mu_0\geqslant 5.5$) [3]. As in real glasses, however, there is no divergence of density fluctuations.

We compare now the diffusion coefficient D and the α relaxation time τ_α. In a normal liquid the diffusion coefficient and the viscosity η are related by the Stokes-Einstein relation (SE): $\eta D=CT$, where T is the temperature in Kelvin and C a constant [19]. In our system it is not possible to directly define a viscosity, but due to the Maxwell relation η is proportional to the time scale of the asymptotic relaxation τ_α. We find that the product $\tau_\alpha D$ is not a constant varying the potential μ, as shown in Fig. 4. Studying $\tau_\alpha(\mu)D(\mu)$, three regions emerge, separated by the values of μ_p and μ^*. A similar separation in three different regions is found in real experiments on colloidal suspensions [14], where, plotting the product ηD as a function of the volume fraction, a behavior is found close to that depicted in the inset of Fig. 4.

It has been suggested that the departure from the Stokes-Einstein relation, in glass forming liquids [10], could be described by the following relation: $D^{-1}=K\eta^\xi$. To check if such relation holds in our model we have plotted (see Fig. 4) $1/D$ as a function of $\tau_\alpha(k=L/4)$. By assuming

$$D^{-1}=K\tau_\alpha^\xi, \tag{8}$$

we find for $\mu\leqslant\mu_p$ $\xi=1$ (as in usual SE), and for $\mu\geqslant\mu^*$ $\xi\sim 0.3$. This last value of ξ for $\mu\geqslant\mu^*$ is consistent with Eqs. (5) and (7) and $\xi=\mu_\alpha/\mu_D$.

Experiments in glass forming liquids [10–13] indicate that the exponent is $\xi \leqslant 1$, ranging in a broad interval depending on the system (for instance, in *o*-terphenyl using the rotational diffusion coefficient, $\xi = 0.28$ is found [10], in PMMA $\xi = 0.69$ [13]). It is striking that the data on *o*-terphenyl [10] not only exhibit the same exponent ξ found here, but the rotational diffusion coefficient also shows a cusp as function of $1/T$ and the appearance of several regions, analogous to those depicted respectively in Figs. 2 and 4.

In conclusion we have studied the macroscopic relaxation and microscopic diffusive properties of the frustrated Ising lattice gas introduced in [3]. Many connections have appeared with the physics of real glass forming liquids ranging from the anomalies in the density relaxations, to those of diffusivity, to violation of Stokes-Einstein law [1,2].

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[17] Actually, other fit functions may be used. We reported the power law fit because it is slightly better than other fits such as exponential or Vogel-Fulcher [18]. Moreover the power law fit is consistent with the mean field picture of a power law behavior at a dynamical transition above the static transition.
[18] M. Nicodemi and A. Coniglio (unpublished).
[19] Note that the Stokes-Einstein law has a general validity only in the hydrodynamical limit, namely, the size of the diffusive particle must be very large compared with the molecular size of the liquid. Experimentally in normal liquids the SE law is verified even for particle sizes of the order of the molecular size. For this range of particle sizes the SE law must be considered a phenomenological law, which seems to break down near the glass transition. This is also the case for our model where the diffusive particle coincides with the particle fluid.