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## Aging in lattice-gas models with constrained dynamics

J. KURCHAN<sup>1</sup>(\*), L. PELITI<sup>2</sup>(\*\*) and M. SELLITTO<sup>2</sup>(\*\*\*)

<sup>1</sup> *École Normale Supérieure de Lyon, 46, Allée d'Italie - F-69364 Lyon Cedex 07, France*

<sup>2</sup> *Dipartimento di Scienze Fisiche and Unità INFN Università "Federico II" Mostra d'Oltremare, Pad. 19, I-80125 Napoli, Italy*

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**Abstract.** – We investigate the aging behavior of lattice-gas models with constrained dynamics in which particle exchange with a reservoir is allowed. Such models provide a particularly simple interpretation of aging phenomena as a slow approach to criticality. They appear as the simplest three-dimensional models exhibiting a glassy behavior similar to that of mean-field (low temperature mode-coupling) models.

As the temperature of a supercooled liquid is reduced, its dynamics becomes slower and slower and its viscosity increases. The glassy transition is usually located at the temperature  $T_g$  where the viscosity first exceeds the conventional value of  $10^{13}$  Poise [1]. At lower temperatures, the glass is usually assumed to be “solid” in the sense that its molecules rattle within a “cage” formed by their neighbors and do not move away from it, at least within experimental time scales. However, the glassy state is not an equilibrium one since the evolution of the system does not stop altogether, but rather keeps evolving at a slower and slower pace as the time  $t_w$  elapsed since its quench increases. This is the origin of the striking aging effects observed in glasses [2], [3]. Aging corresponds to the property that, if one takes the thermodynamical limit *before* the infinite-time limit, one finds that the Boltzmann-Gibbs distribution is never reached. More precisely, one-time quantities like the average energy, volume, etc., reach a well-defined infinite time limit, whereas two-time correlations and responses at very long times do not depend only on the difference between their arguments [4], [5]. Therefore, there is a region in the two-time plane where time-translation invariance is broken, even at very long times. Similar properties have been observed in spin-glasses [6]. These aging properties have been thoroughly investigated within spin-glass models [7] which are closely related to the mode-coupling theories of structural glasses [1]. Conventional mode-coupling theories,

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(\*) E-mail: Jorge.Kurchan@enslapp.ens-lyon.fr

(\*\*) Associato INFN, Sezione di Napoli. E-mail: luca@turner.pct.espci.fr, peliti@na.infn.it

(\*\*\*) E-mail: Mauro.Sellitto@na.infn.it

which are based on the hypothesis that the initial distribution is the equilibrium one and that time-translation invariance holds, are therefore inconsistent in this limit below  $T_g$ .

The spin-glass models proposed as a description of structural glasses lack, however, a transparent physical interpretation in terms of particles and involve a complex, random Hamiltonian which is hard to justify as a description of a fluid. Their justification is rather *a posteriori* in the sense that the phenomena they exhibit recall the behavior of structural glasses. On the other hand, a class of very simple kinetic models have been introduced to describe the slowing-down of the dynamics [8], [9]. These models are defined by kinetic rules involving a selection of the possible configuration changes (“moves”) and are, therefore, called models with constrained dynamics. The kinetic rules satisfy detailed balance and are compatible with a Boltzmann-Gibbs equilibrium distribution involving a Hamiltonian, usually chosen to be a trivial one. The constraints are alone responsible for the slowing down of the dynamics because, near any allowed configuration, there are only few configurations which satisfy them.

Some out of equilibrium properties in models of this kind have been already discussed in [10]. We shall in this paper refer to the kinetic lattice-gas model studied by Kob and Andersen (KA) [11]. The system consists of  $N$  particles in a cubic lattice of side  $L$ , ( $V = L^3$ ) with periodic boundary conditions. There can be at most one particle per site. At each time step a particle and one of its neighbouring sites are chosen at random. The particle is moved if the three following conditions are all met: i) the neighbouring site is empty; ii) the particle has less than four nearest neighbours; iii) the particle will have less than four nearest neighbours after it is moved. The rule is symmetric in time, detailed balance is satisfied and the allowed configurations have equal probability in equilibrium. In this model the dynamics becomes slower and slower as the particle density  $\rho$  increases. Above a critical value of the density,  $\rho_c$ , particle diffusion stops completely. These investigations are carried on initializing the system in an “equilibrium” configuration, identified by the value of the density. However, the equilibrium dynamics can be different from the dynamics at very long times for an infinite system. Indeed, since the evolution of the system becomes so slow when the density approaches the critical one, it is hard to see how one can force an infinite system, initially at low density, to assume density values higher than  $\rho_c$ .

We show in this paper, by numerical simulation, that it is possible to study aging in these models, if they are provided with a mechanism allowing one to realize a process analog to a quench. We consider the three-dimensional KA model, but we allow the lattice gas to exchange particles on a single two-dimensional layer with a reservoir characterized by the chemical potential  $\mu$  [12]. For each value of  $\mu$  it is trivial to evaluate the equilibrium value of the density  $\rho_{eq}(\mu)$ . If  $\rho_{eq}(\mu) < \rho_c$ , the system rapidly reaches the equilibrium state. There is, therefore, a critical value,  $\mu_c$ , of  $\mu$ , defined by  $\rho_{eq}(\mu_c) = \rho_c$ . A quenching process corresponds to performing a jump of  $\mu$  from below to above  $\mu_c$ . Therefore,  $\mu$  plays a role analogous to the inverse temperature in mode-coupling theories. We then observe that  $\rho$  never exceeds  $\rho_c$ , but rather approaches it like a power law in time, and that the mean squared displacement of the particles and the self-correlation function of the particle violate time-translation invariance, since they explicitly depend on the waiting time,  $t_w$ , after the quench.

One can also perform “annealing” (compression) experiments, where  $\mu$  is increased at a fixed rate. In close resemblance with the behavior of real glasses, we observe that the limit density depends on the compression rate, and tends to  $\rho_c$  as the rate decreases to zero. We can then evaluate, by integration, the entropy variation of the reservoir. The curves remain consistently above the equilibrium curve  $S = S_{eq}(\mu)$ , and seem to reach a critical value,  $S_c$ , as the compression rate decreases to zero. This is reminiscent of the Kauzmann paradox, which is usually considered as an argument for the existence of a thermodynamical phase transition related to the glass one. However, in this case, we know that there is no such transition.

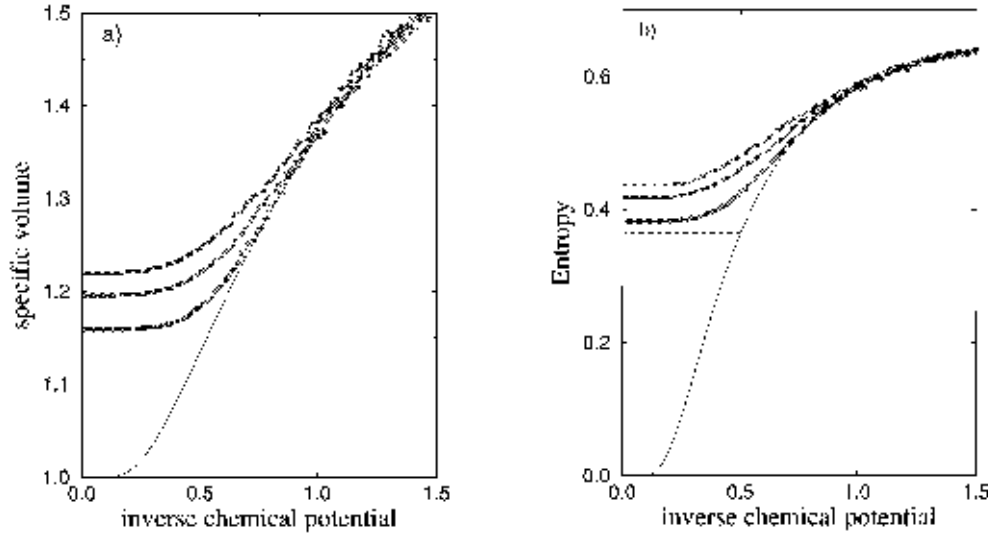


Fig. 1. – a) Compression experiment. The smooth curve is the equilibrium-state equation, while the dashed line is the KA critical value of specific volume. b) “Entropy” as obtained by integration of compression experiment data. The smooth curve is the equilibrium entropy. The dashed line is the KA critical value of entropy. The compression rates are (from top to bottom)  $3 \cdot 10^4, 10^5, 10^6$  sweeps per unit of inverse  $\mu$ . System of size  $20^3$ , averages over five samples.

Hysteresis effects also appear when the reservoir’s chemical potential is varied cyclically.

As mentioned in the introduction, KA studied the diffusion and the decay of the correlation functions evolving at fixed number of particles starting from a random (equilibrium) configuration. They found that correlations decayed to zero with a characteristic time  $\tau(\rho)$  that appears to diverge at  $\rho_c \sim 0.881$ , where also the diffusivity constant goes to zero. For densities above  $\rho_c$ , the correlations did not decay at all.

We modify the KA model by creating and destroying particles on a single slice, say  $(x, y, z) = (1, y, z)$  (the “surface”) with the following Montecarlo rule: We choose a site on that slice at random. If it is empty we add a particle, if it is occupied we remove the particle with probability  $e^{-\mu}$ . We alternate such sweeps of creation/destruction with the ordinary diffusion sweeps. Since the creation/destruction mechanism is very fast, the surface itself is always in equilibrium.

It is easy to calculate the thermodynamical equilibrium quantities (we set the temperature  $k_B T = 1$  throughout):  $1/\rho = 1 + e^{-\mu}$ , where  $\rho$  is the density. The entropy per unit volume is given by  $S = -\rho \ln \rho - (1 - \rho) \ln(1 - \rho)$ .

We first consider compression experiments in which  $1/\mu$  (a quantity analogous to temperature) is slowly lowered from a high value to zero. In fig. 1a) we report the results of the specific volume  $v = 1/\rho$  vs.  $1/\mu$  for several annealing speeds. The smooth curve is the equilibrium state equation and the horizontal dashed line is the critical specific volume of KA  $v_c = 1/\rho_c = 1/0.881$ . In fig. 1b), we show the change in entropy of the reservoir, given by  $S(\mu) = S(\mu_i) - \int_{\mu_i}^{\mu} \mu d\rho$ . The initial value  $\mu_i$  is set to  $1/1.5$ . The smooth curve is the equilibrium curve  $S$  vs.  $1/\mu$ , and the horizontal dashed line is the entropy at the critical density. These curves look quite similar to the energy vs. temperature and entropy vs. temperature curves in the annealing of glasses. As predicted, the system falls off equilibrium around  $\mu_c$ . We have checked that the bulk of the sample does not exhibit density inhomogeneities except very close

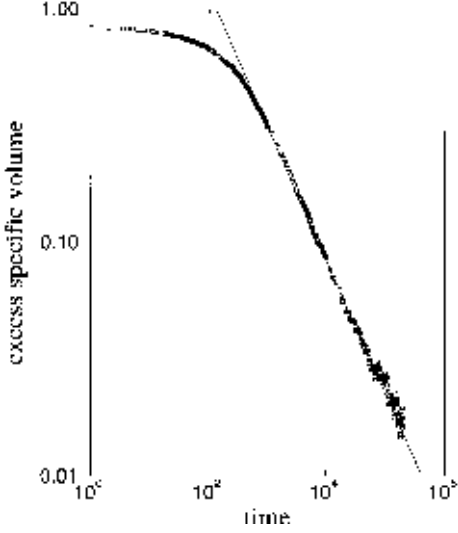


Fig. 2

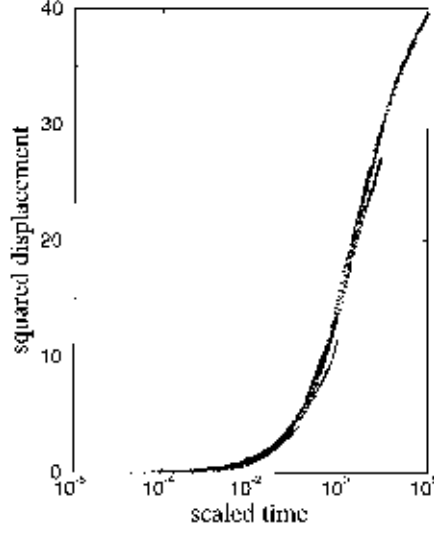


Fig. 3

Fig. 2. – Relaxation of the excess specific volume  $\Delta v = v(t) - v_\infty$  after a quench to the subcritical value  $1/\mu = 1/2.2$  starting from a configuration with density 0.5. The straight line corresponds to  $\Delta v \propto t^{-0.57}$ .

Fig. 3. – Mean-squared displacement  $R^2(t + t_w, t_w)$  vs. scaled time  $t/t_w^{\text{eff}}$  for  $t_w = 10, 10^3, 10^4, 10^5$ , and  $t_0 = 10^3$  ( $t_w^{\text{eff}} = t_w + t_0$ ). Quench at the subcritical value  $1/\mu = 1/2.2$  starting from a configuration with density 0.75. System of size  $20^3$ , average over five samples.

to the “surface”.

We now turn to the behaviour of the system after a quench to the subcritical value  $1/\mu < 1/\mu_c$ . Here we concentrate on the behaviour of a large system at long but finite times. In fig. 2 we plot the specific volume minus its asymptotic value *vs.* time after a quench to the subcritical value  $1/\mu = 1/2.2$ , starting from a configuration with density 0.5. The data can be fitted by a power law of the form  $v(t) - v_\infty \sim t^{-\alpha}$ , where  $\alpha = 0.57 \pm 0.02$ . The asymptotic value of the density  $\rho_\infty = 1/v_\infty = 0.861$  is slightly lower than the KA value  $\rho_c = 0.881$ , suggesting that the critical density might have a weak dependence on the way the particles entered the bulk (although it might also be a finite-size effect).

The mean square displacement  $R^2(t + t_w, t_w)$  of a particle between time  $t_w$  and time  $t + t_w$  must be defined with some care, since the particles may leave or enter the system. We define it by averaging only over the particles which are present at both times. We find that diffusion indeed slows down as the waiting time increases. However, the time  $t(R^2)$  needed to reach a given square distance is roughly proportional to  $t_w$  only for long times. In fact, we find here a phenomenon already encountered by Kob and Barrat [13] in Lennard-Jones systems: one has to consider an effective waiting time that takes into account the relaxation time of the system before the quench. Hence, one should define an effective waiting time  $t_w^{\text{eff}} = t_w + \tau_0$ , where  $\tau_0$  is the relaxation time characteristic of the equilibrium situation [13]. Figure 3 shows that, if one plots  $R^2(t + t_w, t_w)$  *vs.*  $t/t_w^{\text{eff}}$ , the curves lie roughly on top of each other. The deviations are probably due to finite-size effects, *e.g.* to particles that escape from the sample. Indeed, since the contribution of these particles to  $R^2(t + t_w, t_w)$  has not been included, the mean-squared displacement has a tendency to be underestimated at long times. The plot

exhibits the waiting-time dependence of the diffusion constant and is consistent with a simple argument suggesting that diffusion is logarithmic in the presence of aging [14].

One can also easily compute the effective potential of Franz and Parisi [15]. This potential is a purely static quantity, and therefore is independent of the dynamical constraints. Indeed, we have not found any signature for the dynamical transition in the effective potential. However, the “number of neighbors” constraint is an idealization of microscopical (repulsive) energy terms, and as such it *should* be seen by the effective potential. It would be interesting to clarify this point further.

Since the size of the system considered here is finite, equilibrium must eventually be reached, provided that any two allowed configurations can be connected by a path of allowed moves. It is possible to convince oneself that the kinetic rules allow an initially empty lattice to be progressively filled in, leaving only  $O(1/L)$  empty sites per unit volume, and that it is possible to find a path connecting almost any two allowed configurations, if necessary, by letting the particles escape one by one by the way they got in. Therefore, for any value of  $1/\mu$ , the equilibrium density will eventually be reached, but with times which diverge fast as  $L \rightarrow \infty$ . We have verified that a system of size  $5^3$  equilibrates after a time of order  $10^8$  MC sweeps. What this argument implies is that after a quench there is first a power law approach to the critical density  $\rho_c$ , followed by a much slower (size-dependent) increase in density to the equilibrium density.

We have thus shown that the out-of-equilibrium dynamics of kinetic lattice-gas models reproduce the phenomenology of more sophisticated glass models if one endows them with a surface mechanism of particle exchange with a reservoir. The *qualitative* behaviour of this model is similar to that of mean-field spin-glass models, whose dynamical equations are *exactly* (in the infinite-size limit) the “idealised” mode-coupling equations and their correct low-temperature extension. The roles played by the inverse chemical potential and the inverse density (specific volume) in the present model are analogous to the ones played by temperature and energy respectively, in the mean-field case. When quenched below  $T_c$ , mean-field spin-glass models never equilibrate. Their energy relaxes to a “threshold” value  $E_{\text{thres}}(T)$  which is higher than the equilibrium one [5], and can be characterized as the value below which the phase space breaks into disconnected components. In our case, the moves allowed by the kinetic constraints keep the phase space of the system connected only for  $\rho < \rho_c$ . Therefore, the density approaches this threshold value, and the corresponding manifold of allowed states approaches the incipient “percolation” cluster characteristic of  $\rho_c$  [16]. Only for finite sizes the system is able to reach values of  $\rho$  larger than  $\rho_c$ , just as energy values below the threshold can only be reached by finite systems in mean-field spin-glasses [5], [17].

In short: in both cases the system ages because it slowly evolves towards a situation in which the available phase-space becomes completely disconnected [16]. The closer the system to the “phase-space percolation” threshold level, the slower its dynamics becomes. In this sense the system ages because it approaches criticality [18].

To summarize, lattice gas models with constrained dynamics, in spite of their simplicity, capture the essential features of the aging behavior of three-dimensional glasses.

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