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The kinetic glass transition

Mauro Sellitto

Laboratoire de Physique de l'École Normale Supérieure de Lyon, 46 Allée d'Italie, 69007 Lyon, France

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Abstract. Kinetic lattice-gas models display fragile-glass behaviour, in spite of their trivial Gibbs–Boltzmann measure. This suggests that the nature of glass transition might be, at least in some cases, understood in purely kinetic or dynamical terms.

1. Introduction

A long-debated problem in glass physics concerns the nature of the dynamical ergodicity breaking and its relation with the existence of an underlying equilibrium phase transition [1,2]. In mode-coupling theory the glass transition appears as a purely dynamic effect due to an instability of the equation governing the time correlation of density fluctuations [3,4]. In particular, mean-field disordered models of structural glasses show that glassy features are associated with a rugged free-energy landscape and that the origin of the dynamical transition is the existence of a large number of metastable states which trap the system for an infinite time [5,6]. On the other hand, the lifetime of metastable states in finite-dimensional short-range models is finite, since it is always possible to nucleate, by a thermally activated process, a droplet of the stable phase. Therefore the dynamical transition appears as an artifact of the mean-field approximation, and in real glasses this transition would be just a *finite-time* kinetic effect, at least on timescales much smaller than the lifetime of metastable states. Recently, the close connection between the non-trivial structure of Gibbs equilibrium states and the appearance of a persistent glassy dynamics has been established for a certain class of systems [8]. However, since the dynamical universality classes are smaller than the static ones [9,10], and since salient features of glasses are essentially of dynamical nature [11], it is important to understand to what extent glassy behaviour depends on the details of microscopic kinetics. A generic microscopic mechanism leading to slow relaxation phenomena was suggested some time ago by Fredrickson and Andersen [12]. It is based on kinetic rules involving only a selection of the possible configuration changes compatible with the detailed balance and the Boltzmann distribution. A kinetic rule can be so effective that there is no need to introduce an energetic interaction between the particles. Although they are physically motivated (e.g. by the cage effect mechanism), these kinetic models are not intended to describe the realistic dynamics of glasses, but rather to show that the glass transition could be, at least in principle, a purely kinetic or dynamical phenomenon. Taking advantage of this idea we have explored the limit case of a three-dimensional lattice-gas model defined only by short-range kinetic constraints and by a trivial equilibrium measure [13]. Remarkably, this finite-dimensional model exhibits a *fragile*-glass behaviour unrelated to the existence of a thermodynamic phase transition [13–15] (for another case and the related experimental

situation, see [16], [17] and [18]). It provides a simple example of how the distinction between the *ideal* (static or dynamic) and the *laboratory* (i.e. kinetic) glass transition can be very subtle and elusive. In the following we present some numerical results showing that this model reproduces qualitatively some aspects of the glassy phenomenology, such as history dependence, irreversibility effects, power-law approach to the asymptotic state, and simple aging behaviour. Some related works on constrained lattice-gas models are [19–22].

2. The model

Our starting point is a kinetic lattice-gas model introduced by Kob and Andersen [13]. The system consists of N particles in a cubic lattice of size L^3 , with periodic boundary conditions. There can be at most one particle per site. Apart from this hard-core constraint there are no other static interactions among the particles. At each time step a particle and one of its neighbouring sites are chosen at random. The particle moves if the three following conditions are all met:

- (a) the neighbouring site is empty;
- (b) the particle has fewer than m nearest neighbours;
- (c) the particle will have fewer than m nearest neighbours after it has moved.

The rule is symmetric in time, detailed balance is satisfied, and the allowed configurations have the same statistical weight in equilibrium. Significant results are obtained when the value of m is set to 4. With this simple definition one can proceed to study the dynamical behaviour of the model at equilibrium. One observes that the dynamics becomes slower and slower as the particle density ρ increases; in particular, the diffusion coefficient of the particles, D , vanishes as the density ρ approaches the critical value $\rho_c \simeq 0.88$, with a power law

$$D(\rho) \sim (\rho_c - \rho)^\phi \quad (1)$$

with an exponent $\phi \simeq 3.1$ [13]. Since we are interested in the dynamical approach to the putative equilibrium state we allow the system to exchange particles with a reservoir characterized by a chemical potential μ . Therefore, we alternate the ordinary diffusion sweeps with sweeps of creation/destruction of particles on a single layer with the following Monte Carlo rule: we randomly choose a site on the layer; if it is empty, we add a new particle; otherwise we remove the old particle with probability $e^{-\beta\mu}$. The number of particles is no longer fixed and the external control parameter is $1/\mu$, which plays the role of the temperature. The equilibrium equation of state $\rho = \rho_{\text{eq}}(\mu)$ is then trivially calculated. There is therefore a critical value μ_c of μ defined by $\rho_{\text{eq}}(\mu_c) = \rho_c$ corresponding to the ideal glass transition of the model. In this way we can prepare the system in a non-equilibrium state by a process analogous to a quench, which is represented by a jump in $1/\mu$ from above to below $1/\mu_c$. Or, we can let $1/\mu$ decrease or increase smoothly like in cooling or heating experiments. The situation becomes analogous to the *canonic* case in which one controls the temperature, and the energy endeavors to reach its equilibrium value.

3. Thermodynamics

Before studying the non-equilibrium regime let us consider the static properties. This point is relevant for the question of whether the possible ideal glass transition is purely dynamical or is a consequence of an equilibrium transition of some sort. The Hamiltonian of the model is

$$\mathcal{H} = -\mu \sum_{i=1}^N n_i \quad (2)$$

where $n_i = 0, 1$ are occupation site variables and μ is the chemical potential. The corresponding partition function, for a system of volume $V = L^3$,

$$Z = (1 + e^{\beta\mu})^V \tag{3}$$

would describe correctly the thermodynamics of the system provided that the measure of configurations made inaccessible by the kinetic constraints vanishes in the thermodynamic limit. It is possible to convince oneself that the kinetic rules, which satisfy detailed balance, allow an initially empty lattice to be progressively filled in, leaving only $O(1/L)$ empty sites per unit volume. Indeed, it is always possible to find a path connecting almost any two allowed configurations, if necessary by letting the particles escape one by one in the way in which they got in. Therefore the Markov process generated by the dynamical evolution rule is irreducible on the full manifold of particle configurations and the static properties of the model are described by (3). In particular the state equation and the entropy are respectively given by

$$\rho = 1/(1 + e^{-\beta\mu}) \tag{4}$$

$$S = -\rho \log \rho - (1 - \rho) \log(1 - \rho). \tag{5}$$

Since the static properties of the system are regular as a function of the density or the chemical potential, the possible ideal glass transition should appear as a purely dynamical effect. The critical value of μ and S corresponding to the threshold density, ρ_c , can be estimated from the previous equations and they are given by

$$\mu_c \simeq 2.0 \quad S_c \simeq 0.36. \tag{6}$$

4. History dependence

Initial insight into the nature of the relaxational processes can be gained by studying the behaviour of one-time observables (energy, specific volume, etc) in a slow annealing procedure. We consider a compression experiment in which the inverse chemical potential of the reservoir, $1/\mu$, is slowly decreased at fixed rate from a value corresponding to a low-density equilibrium configuration up to zero. The simulation results presented in the following refer to a system of size 20^3 . In figure 1 the numerical results for the specific volume $v = 1/\rho$ versus $1/\mu$ are compared, for several annealing rates, r , with the equilibrium state equation of the system (the smooth curve). In close resemblance with the behaviour of real glasses these curves exhibit the characteristic annealing dependence of one-time observables: after a certain value of the inverse chemical potential, $1/\mu_g(r)$, is reached, the dynamics becomes so sluggish that the system is no longer able to follow the annealing procedure; the faster the compression, the sooner the system falls out of equilibrium. The limit value of v reaches a plateau that depends on the compression rate and never seems to cross the critical value $v_c = 1/\rho_c$ (the horizontal dashed line). In the inset of figure 1 we also show the same plot for a compression experiment, but this time removing the dynamical constraints. We see that the ordinary lattice gas has no problem in equilibrating at each value of the chemical potential μ ; therefore our ‘experimental’ set-up (the way in which the particle reservoir and its connection with the system is realized) provide a suitable representation of the equilibrium properties of the model.

4.1. Kauzmann’s paradox

Once we have obtained the experimental equation of state, we can evaluate the entropy variation of the reservoir by numerical integration; it is given by

$$S(\mu_f) = S(\mu_i) - \int_{\mu_i}^{\mu_f} \mu \frac{d\rho}{d\mu} d\mu. \tag{7}$$

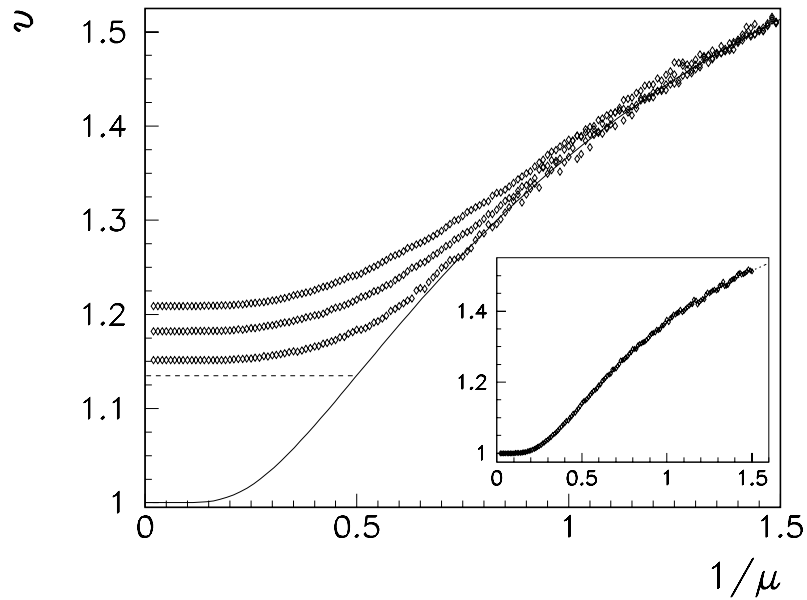


Figure 1. The compression experiment. The smooth curve is the equilibrium state equation $v = v(1/\mu)$, while the dashed line shows the critical value of the specific volume $v_c \simeq 1.13$. The compression rates are (from top to bottom) $r = (1/3) \times 10^{-4}, 10^{-5}, 10^{-6}$ in units of $(\mu \cdot \text{MC sweep})^{-1}$. Inset: the same experiment in a system without kinetic constraints; here the rate is $r = 10^{-4}$.

This ‘calorimetric entropy’ in the presence of irreversible effects will be different from the thermodynamical entropy S_{eq} . Indeed, in figure 2 we see that when the relaxation time exceeds the inverse of the annealing rate the numerical data remain consistently above the equilibrium curve $S = S_{\text{eq}}(\mu)$. If one were given only the *dynamical* data of figures 1 and 2, one would feel tempted to extrapolate the equilibrium specific volume and entropy to lower values of $1/\mu$. Then, given that both these quantities are bounded, one could conclude that the Kauzmann ‘temperature’, defined here as

$$\frac{1}{\mu_K} = \lim_{r \rightarrow 0} \frac{1}{\mu_g(r)} \quad (8)$$

is different to zero and therefore that there *has* to be a static transition. This is the usual argument, known as Kauzmann’s paradox, according to which the glassy state is related to the existence of a thermodynamic phase transition. Of course, here there is no such static transition: in this simple case we have access to the complete equilibrium curves, which are perfectly analytical though they change in concavity rather sharply. Irreversibility effects are also evident when we let $1/\mu$ perform a cycle: in this case the specific volume appears to follow a hysteresis loop whose area decreases as the compression speed decreases (figure 3).

5. Structural relaxation

We now turn to the behaviour of the system after a sudden quench to a subcritical value $1/\mu < 1/\mu_c$. In order to allow the system to reach the asymptotic regime more rapidly we perform a ‘gentle’ quench, i.e. starting from a configuration with density 0.75 corresponding to a chemical potential closer to μ_c .

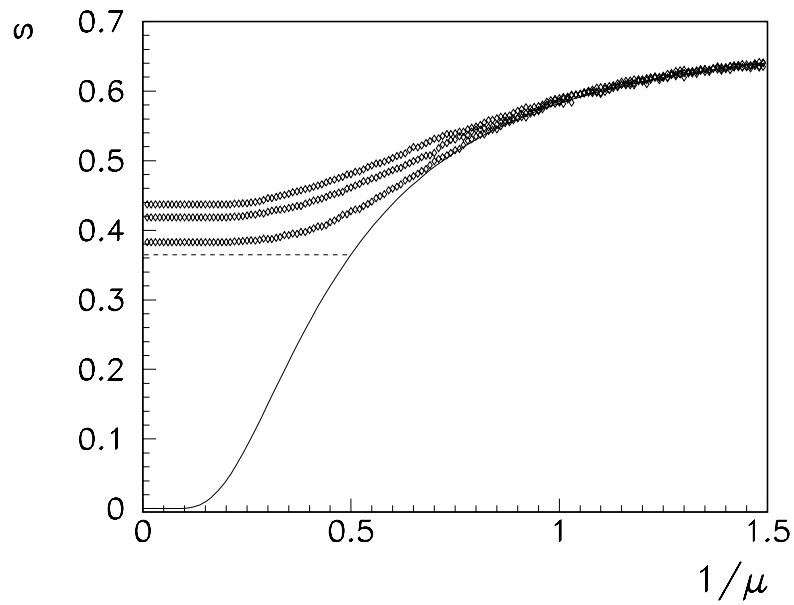


Figure 2. The calorimetric entropy as obtained by integration of compression experiment data. The smooth curve is the equilibrium entropy $S = S(1/\mu)$ while the dashed line shows the critical value of the entropy $S_c \simeq 0.365$. The compression rates are (from top to bottom) $r = (1/3) \times 10^{-4}, 10^{-5}, 10^{-6}$.

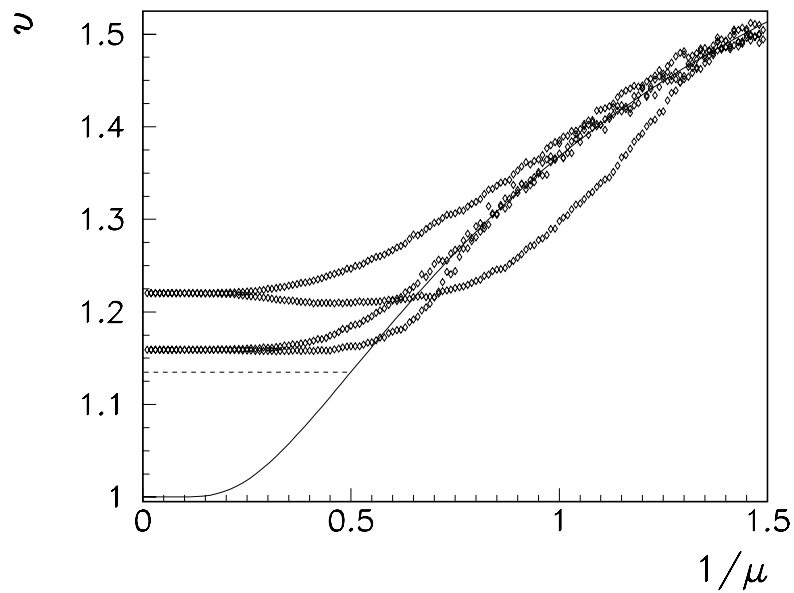


Figure 3. Hysteresis cycles in a ‘cooling–heating’ experiment. The lower branch of the cycles represents the decompression. The annealing rates are (from top to bottom) $r = (1/3) \times 10^{-4}, 10^{-6}$.

Figure 4 shows the time relaxation of the particle density after a subcritical quench at $1/\mu = 1/2.2$. We see that ρ never exceeds the threshold ρ_c , but rather approaches it like a

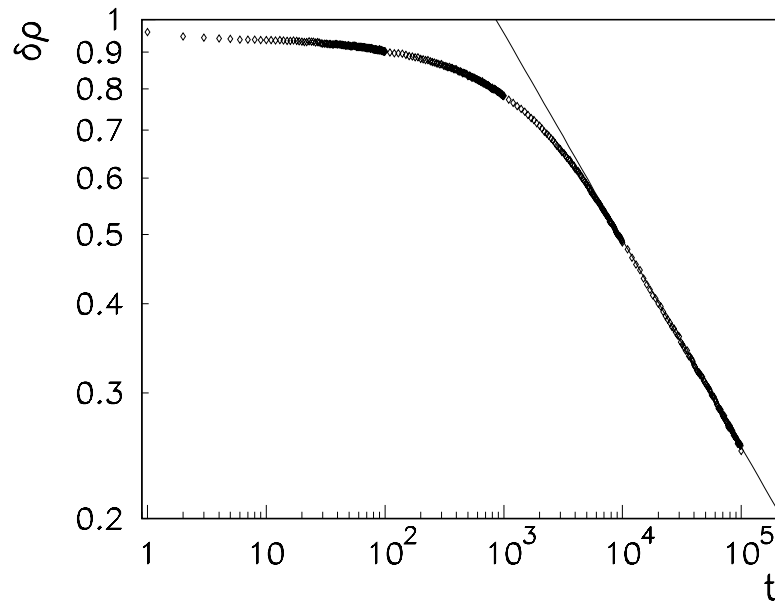


Figure 4. Time relaxation of the excess density after a subcritical quench, $\delta\rho = (\rho_c - \rho)/(\rho_c - \rho_0)$. The straight line is $\delta\rho \sim t^{-z}$ with $z \simeq 0.3$.

power law in time:

$$\rho_c - \rho(t) \sim t^{-z} \quad (9)$$

where t is the time elapsed after the quench and where the exponent $z \simeq 0.3$. Therefore the diffusion coefficient D of particles after a subcritical quench vanishes as

$$D(t) \sim t^{-\zeta} \quad (10)$$

with the exponent $\zeta = z\phi$ quite close to one. This is closely related to the aging behaviour observed in the two-time mean squared displacement of particles, $B(t, s)$. Indeed, in a simple-minded approach such a quantity would be given by

$$B(t, s) = \int_s^t d\tau D(\tau) \quad (11)$$

from which follows the simple logarithmic aging

$$B(t, s) \sim \log(t/s) \quad (12)$$

in good agreement with the numerical results and the analytical solution of the associated singular diffusion model [15]. Since the size of the system considered here is finite, equilibrium will eventually be reached (since almost any two allowed configurations can be connected by a path of allowed moves), but with times which grow quickly as $L \rightarrow \infty$.

5.1. Activated processes

It is interesting to investigate the role of activated hopping processes in the low-temperature phase of glassy systems since they are responsible for restoring the ergodicity broken at the glass transition, and it is important to know the characteristic timescale on which this equilibration process takes place. As pointed out in reference [13], the activation processes can be simply

implemented in this model by allowing the violation of the kinetic constraint with a given probability p . Figure 5 shows an example of a v versus $1/\mu$ plot in a compression experiment at fixed annealing rate for several values of the activation probabilities, p . As expected, in this case the system becomes able to cross the threshold and, after a certain value of p , p^* , it follows the full equilibrium curve; we can also see that, for p below p^* , the dependence of the relaxation time on $1/\mu$ is not affected by p , since the annealing curves depart from the equilibrium one at approximately the same point. The relation between the activation probability p^* and the equilibration time is better characterized by looking at behaviour of the density after a sudden quench. In figure 6 the relaxation curves in the presence of activated processes are compared with the one obtained previously for $p = 0$ (figure 4). If we conventionally define the ergodicity time, $\tau_{\text{erg}}(p)$, as the time at which the curves with $p \neq 0$ depart from the one at $p = 0$, it appears that this characteristic time follows a power law, $\tau_{\text{erg}}(p) \sim p^{-\alpha}$, with an exponent $\alpha \simeq 1$. A similar result was obtained by Castellano and Franz [23]. This seems to provide further evidence of the existence of a purely dynamical glass transition in this model.

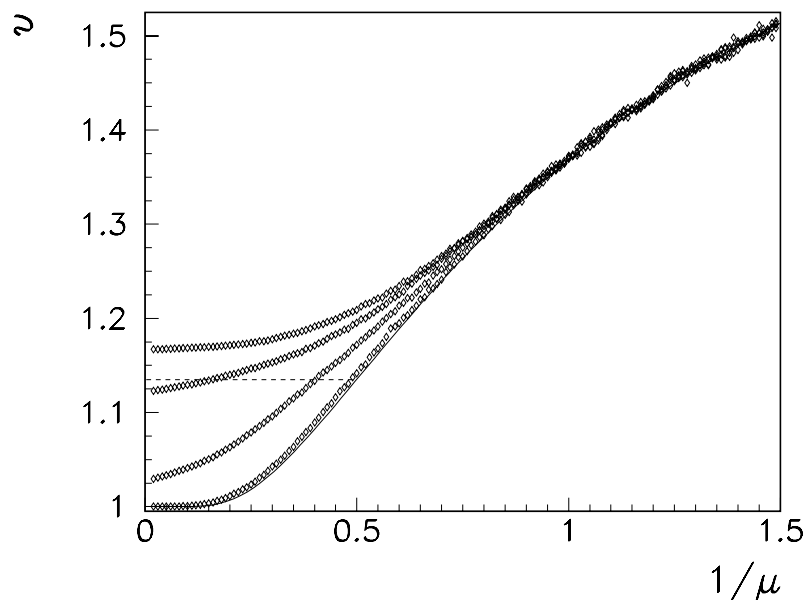


Figure 5. The compression experiment in the presence of activated hopping processes for a fixed annealing rate, $r = 10^{-5}$, and different activation probabilities $p = 10^{-k}$ with $k = 1, 2, 3, 4$.

6. Conclusions

To summarize, we have shown that three-dimensional lattice-gas models defined by short-range kinetic constraints and trivial equilibrium Boltzmann–Gibbs measures display many features of the fragile-glass behaviour. Glassy phenomena may therefore have a purely dynamical or kinetic origin unrelated to an underlying equilibrium phase transition, even in finite dimensions and in the absence of metastable states. If this kinetic model exhibits a true dynamical transition it would provide a microscopic realization, in finite dimensions, of the mechanism invoked by the ideal mode-coupling theory for the glass transition. Of course, it is hard to establish the existence of such a dynamical transition from numerical simulations. Indeed, a comparison with the backbone percolation problem shows that the linear size dependence of the critical

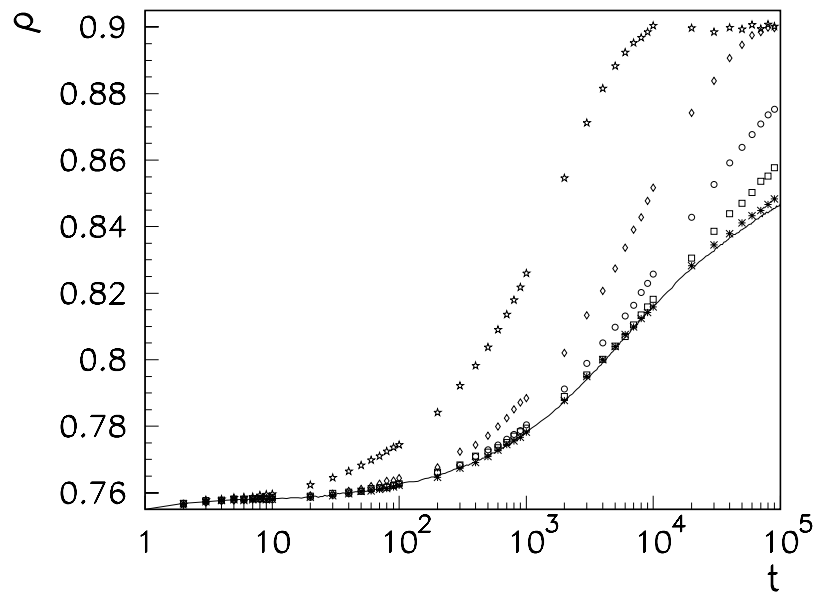


Figure 6. Density relaxation in the presence of activated hopping processes: $p = 10^{-k}$, $k = 1, 2, 3, 4, 5$ (from left to right); the continuous line represents the data with $p = 0$. The subcritical value of the quench, $1/\mu = 1/2.2$, corresponds to an equilibrium density $\rho \simeq 0.9$.

threshold cannot be faster than [13]

$$1 - \rho_c(L) \sim 1/\log(\log L). \quad (13)$$

Therefore, even if $\lim_{L \rightarrow \infty} \rho_c(L) = 1$ (i.e. there is no ideal dynamical glass transition), the length scale over which such a value would be observable is not experimentally accessible. In this respect, the emergence in purely kinetic models of a well defined macroscopic effective temperature [24] associated with the violation of the fluctuation-dissipation theorem appears quite surprising [25]. Indeed, given the non-holonomic nature of kinetic constraints and the trivial Hamiltonian of the model, it would be interesting to understand whether a statistical mechanics approach based on the calculation of some restricted partition function is able to predict the features of the glassy phase and in particular the value of the so-called fluctuation-dissipation ratio. A first step in this direction would consist in defining a *kinetic* analogue of the metastable states by considering, for example, as metastable those system configurations where all particles are blocked by the kinetic constraint, and then finding a way to count them.

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