COMMENT

Comment on 'Is there a glassy phase transition in two dimensions?'

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Abstract. Use of the random sequential adsorption (RSA) model to investigate the existence of metastable and glassy phases is discussed. It is argued that, in its simple version, the RSA model is not appropriate for studying such phases. Improved versions are suggested.

In a recent letter [1], Baram and Kutasov discussed the existence of a disordered metastable (glassy) phase at densities $\rho > \rho_c$, where ρ_c is the density at the disorder-order transition, by using data obtained from the analysis of a random sequential adsorption (RSA) process. The central assumption is that the 'quenching procedure' (which for hard objects is rather a 'densification mechanism' [2]) used to obtain glassy states can be adequately described by an RSA process, i.e. by the sequential and random introduction of particles in a volume (or surface, etc) with the prescription that the particles cannot overlap (hard objects) and that once adsorbed, the particles are held fixed. The RSA process is known to reach asymptotically a jamming limit, in which no more particles can be introduced. This jamming limit occurs at a density ρ_r. Then, according to Baram and Kutasov, if $\rho_r > \rho_c$, a glassy phase can be obtained, whereas this is impossible if $\rho_r < \rho_c$. Using lattice models, these authors prove that in three and higher dimensions, $\rho_r > \rho_c$, but that in one and two dimensions, $\rho_r < \rho_c$. They conclude, admittedly with some precautions, that metastable glassy phases may exist in three and higher dimensions but not in lower dimensions.

The main comment we make here is that though we believe using the RSA process may be a fruitful approach to the study of glassy states, a direct transposition RSA ≡ densification mechanism, jamming limit state ≡ glassy state, is questionable. We do not address the lattice models; rather, we consider a continuous description of space (hard-disk fluid, hard-sphere fluid, etc). As a consequence though, it is possible that some of our following comments relative to a continuous picture do not apply to the lattice models studied by Baram and Kutasov.

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That a direct transposition such as that described above is doubtful is illustrated by considering hard-sphere systems (3D). These systems are known to form glasses: 'non-equilibrium' glasses obtained by a kinetic transition and, possibly, 'equilibrium' metastable glasses obtained through a thermodynamic transition [2–5]. However, for hard spheres, the density corresponding to the jamming limit of the RSA process ($\rho_r \simeq 0.4$ [6], when expressed as a packing fraction) is less than the freezing density ($\rho_c \simeq 0.5$ [7]): $\rho_r < \rho_c$! This (counter)example at least reduces the universality of the conclusions drawn by Baram and Kutasov.

Consider first the main features displayed by configurations of particles generated by RSA (at any step of this process): due to the randomness of the filling process and to the assumption of no overlap, they consist of *disordered configurations of hard objects*; however, due to the assumption of no relaxation (the particles once adsorbed are clamped at their positions), they represent '*non-equilibrium*' *configurations* [8, 9]. By 'non-equilibrium' configuration we mean that at a given density and in the thermodynamic limit the typical configuration generated by the RSA is different from the typical configuration of the fluid at equilibrium. From these (known) results, we draw the following two conclusions.

(i) The RSA process is not relevant for studying the existence or properties of metastable states. This is a direct consequence of the fact that RSA configurations are non-equilibrium configurations whereas the metastable states require an equilibrium description. From the RSA process, we may expect to extract information relative only to the 'non-equilibrium' glassy states corresponding to a kinetic glass transition.

(ii) The jamming limit of the RSA is not directly relevant for describing glassy states, even 'non-equilibrium' glasses. A glass may indeed be considered as a 'jammed' state: it is jammed with respect to the dynamics of the ensemble of particles (and, thus, with respect to relaxation toward equilibrium). In contrast, the asymptotic limit of the RSA corresponds to a state which is jammed with respect to the filling process. Since the adsorbed particles are clamped, nothing can then be inferred concerning a potential jamming with respect to the relaxation towards equilibrium. Indeed, the structural properties of the jammed RSA configurations are *a priori* different from those of a typical non-equilibrium glass: compare, for instance, the distribution function $g(r)$ near the jamming limit of the RSA for hard spheres [9] with the $g(r)$ obtained for glassy phases of hard-sphere systems [2, 3]. In the absence of any well defined structural criterion [2–5], the only way to verify that a given configuration is a 'glassy' configuration is to introduce some dynamics into the system, for instance by assigning velocities to the previously clamped particles according to a Maxwellian distribution. The configuration can be considered as 'glassy' if, in the time of the simulation, the system does not equilibrate. Following Baram and Kutasov, we would expect that, if the given configuration has a density higher then ρ_c, it is *likely* that the relaxation to equilibrium will be slow enough for the configuration to be considered as 'glassy'. This must, however, be proven.

In the remainder of this comment, we outline how the RSA process could be used for a better understanding of (non-equilibrium) glasses. Consider first the 'densification mechanism' which is applied in MD simulations of hard-sphere systems to produce equilibrium as well as non-equilibrium glassy states [2, 3]. The mechanism consists of a sequence of successive densification steps. At each step the dynamics are stopped and the spheres are uniformly expanded until the nearest pair comes into contact. By varying the time between two steps, one can vary the compression rate. The initial starting density can be varied as well. At very low compression rates the system can

always equilibrate between two densification steps, but in the opposite limit of infinite compression rates the system may be 'jammed' out of equilibrium between two densification steps. It was mentioned by Woodcock [2] that in the latter limit, two regimes can be identified in the time evolution of the densification mechanism (the second regime corresponds to a marked slowing down of the densification, which becomes less effective) and that the crossover between the two regimes occurs at a density close to that of the jamming limit of the RSA, ρ_r. Notice, however, that in the reported simulations the densification mechanism was initiated at a very low density.

We thus conjecture that the RSA process may be a good description of the densification mechanism at infinite compression rate, *but up to the crossover density only.* Since the RSA process allows no relaxation, it cannot describe the second regime of the densification mechanism and thus, by itself, cannot provide information on the glassy states which are found at densities higher than the crossover density. In particular, in two dimensions, where it is an open question to know whether a glassy phase exists or not (due to the propensity of the hard-disk fluid to crystallise at densities even slightly higher than the freezing density), *a direct application of the RSA does not provide any answer.*

How, then, could the RSA be useful? We suggest two ways.

(i) Instead of starting the RSA with an empty volume (or surface, etc), one can start it with an equilibrium configuration of particles (in the volume) of finite density. According to our above conjecture, the RSA process would then be equivalent to the densification mechanism at infinite compression rate, but initiated at a finite initial density ρ_i. This would hold, of course, up to the density of the new jamming limit $\rho_r(\rho_i) > \rho_r$ ($\rho_i = 0$). If the initial density ρ_i is chosen close to the freezing density, one might expect that 'glassy' configurations would be obtained. In two dimensions, by choosing ρ_i sufficiently less than ρ_c, so as to avoid crystallisation (the configuration obtained at $\rho \simeq \rho_c$ would then be non-equilibrium configurations), but sufficiently close to ρ_c so as to obtain, even before the jamming limit, densities greater than ρ_c, one could investigate the possible existence of glassy states. As we have mentioned, though, a credible test requires the introduction of some dynamics in the RSA configurations.

(ii) A second way is to consider a generalised RSA process in which the assumption of no relaxation is released [10]. This can be done either by allowing the adsorbed particles to diffuse, but the complexity is then as large as in the usual densification mechanism, or by allowing the adsorbed particles to desorb. The process can then be initiated with no particles in the volume (surface, etc). By choosing a small desorption rate (compared with the adsorption rate), the system will first closely follow the simple RSA behaviour. However, it can be shown that the relative influence of the desorption increases as the density (and time) increases and that instead of reaching a jamming limit, the system asymptotically converges towards a steady state and an equilibrium configuration [10]. If the desorption rate is chosen small enough, the final density reached by the system is larger than ρ_c and since the system is out of equilibrium around ρ_c, it may avoid crystallisation. This procedure could lead to glassy states (in contrast to procedure (i), it could lead in principle, to both non-equilibrium and equilibrium glasses). Procedures (i) and (ii) are illustrated in figure 1.

We emphasise that dealing with RSA processes is interesting in that they are relatively easy to implement in simulations (compared with densification mechanisms close to 'infinite' compression rates) and that they can be both exactly and approximately described from a theoretical point of view [10]. More work in this direction (and along some of the lines proposed by Baram and Kutasov) is certainly needed.
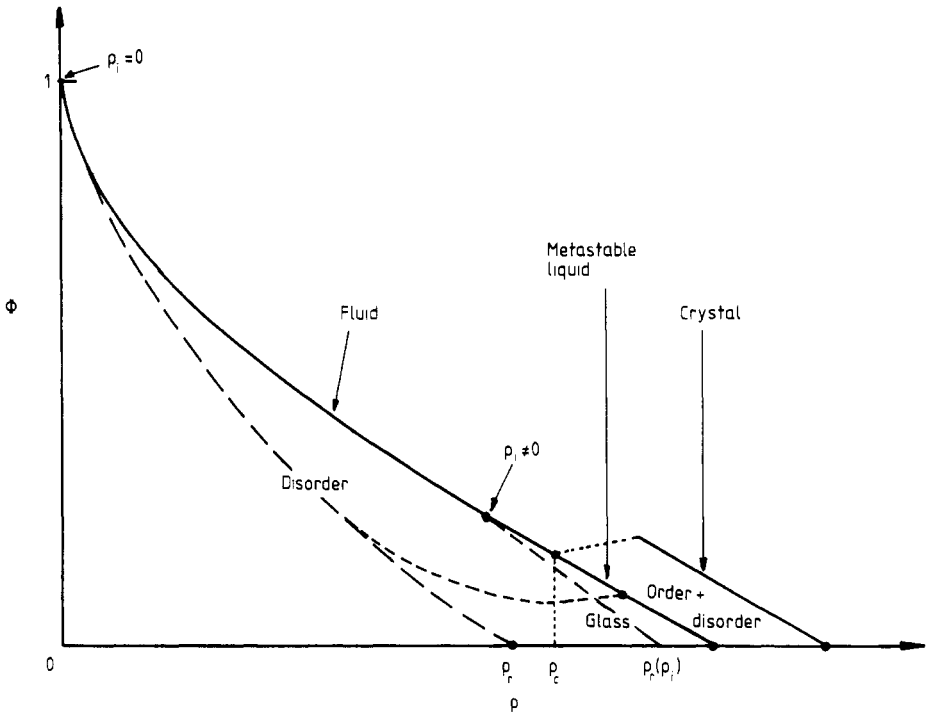
Figure 1. Schematic representation of the density dependence of Φ, the fraction of the total volume to which the centre of a new adsorbing particle would have access. The full curve represents the equilibrium situation (disordered and ordered phases); the long-broken curve represents RSA processes started at an initial equilibrium configuration of density ρ_i (the cases $\rho_i = 0$ and $\rho_i \neq 0$ are illustrated); the short-broken curve represents a generalised RSA process in which desorption of particles is allowed.

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