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# Non-linear dynamic response of glass-forming liquids to random pinning

Walter Kob and Daniele Coslovich

*Laboratoire Charles Coulomb, UMR 5221, CNRS and Université Montpellier 2, Montpellier, France*

We use large scale computer simulations of a glass-forming liquid in which a fraction  $c$  of the particles has been permanently pinned. We find that the relaxation dynamics shows an exponential dependence on  $c$ . This result can be rationalized by means of a simple theoretical Ansatz and we discuss its implication for thermodynamic theories for the glass-transition. For intermediate and low temperatures we find that the slowing down of the dynamics due to the pinning saturates and that the cooperativity decreases with increasing  $c$ , results which indicate that in glass-forming liquids there is a dynamic crossover at which the shape of the relaxing entities changes.

The extensive studies done during the last two decades on the relaxation dynamics of glass-forming liquids have shown that this dynamics is intimately related to a cooperative motion of the particles [1]. In particular it has been found that the number of particles involved in this dynamics increases with decreasing temperature  $T$  [2, 3], thus rationalizing the super-Arrhenius temperature-dependence of the relaxation times [4]. Although these results seem to confirm the old ideas of Adam and Gibbs on the existence of cooperatively rearranging regions (CRRs) [5], other theoretical approaches are compatible with these findings as well [6–8] and hence the question which theoretical description is the right one is still open [4, 9].

Usually this growing cooperativity is expressed via a dynamic four-point correlation function and its associated length scale [1, 3, 10]. Recently, however, evidence has been given that also the *structure* of the CRRs may depend on  $T$  in a non-trivial manner, in agreement with theoretical expectations [11–13], and that this can in turn give rise to a non-monotonic  $T$ -dependence of the dynamic length scale [14]. This shows that it is insufficient to characterize the CRRs just by means of a length scale. While direct measurements of CRRs are still difficult [15], the spatial structure of the CRRs can also be probed indirectly. Indeed, one can study how the relaxation dynamics of the liquid depends on the size of the system [16] or, alternatively, how the dynamics is influenced by the presence of a rigid wall [14, 17].

In this latter type of study, the non-linear response of the liquid to the external field of the rigid wall is used to probe certain multi-point correlations. This is in fact just a special case of a broader class of multi-point correlations functions that can be measured by pinning a subset of particles of the liquid at some instant of time and then measuring the evolution of the remaining, i.e. unpinned, particles. Recent investigations using randomly pinned particles have indeed revealed static and dynamic correlations whose associated length scales grow appreciably with decreasing temperature and hence give insight into the nature of the glass transition [18–25]. However, at present it is not really understood how the presence of such pinned particles affects the relaxation dynamics in

a quantitative manner and to what extent this influence can be captured by theoretical approaches. Since certain theories of the glass-transition, such as the “random first order transition” (RFOT) theory [7, 8, 26, 27], make an intimate connection between the growing *dynamic* length scales and an underlying *static* length scale, it is important to obtain an accurate understanding of this dynamics so that it can be compared with the static order.

In order to advance on this topic we present in the following extensive simulation results on how the relaxation dynamics of a glass-forming liquid is affected by the presence of pinned particles and how thermodynamic theories can rationalize these findings. Such a study allows us to gain insight into the nature of the CRRs in the bulk around and below the dynamic crossover—a temperature regime seldom explored in computer simulations.

The system we consider is a 50:50 binary mixture of harmonic spheres [28] of diameter ratio 1.4 at constant density  $\rho = 0.675$  (more details are given in the SI). This system has been shown to be a good glass-former, i.e. it does not show any sign of crystallization at the temperatures we consider here. To give the relevant temperature scales of this model we recall that its onset temperature is around  $T_{\text{on}} \approx 12$  [29] and its mode-coupling theory (MCT) temperature  $T_{\text{MCT}} \approx 5.2$  [14]. All numbers are expressed in appropriate reduced units (see SI). The number of particles we consider is 20000 for studying the relaxation dynamics and 1000 for the calculation of the variance  $\chi_4(t)$  of the overlap correlation function. The pinning of the particles has been done as in Ref. [25], i.e. the arrangement of the pinned particles is uniform with a well characterized distance between them. More details on this and the simulations can be found in the SI.

To characterize the relaxation dynamics we have calculated the self intermediate scattering function  $F_s(q, t)$  using as wave-vector  $q$  the position of the first peak in the static structure factor, i.e.  $q = 5.52$ . As documented well in the literature [18, 30–32], the relaxation dynamics slows down quickly if the concentration  $c$  of pinned particles increases (Fig. 1 in SI). In Fig. 1a we show an Arrhenius plot of the relaxation time  $\tau(c, T)$ , normalized by the bulk value  $\tau(0, T)$ , for different values of  $c$ . Here

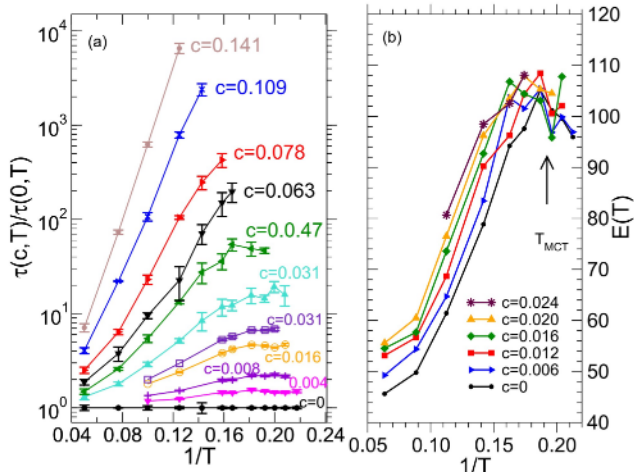


FIG. 1: a) Arrhenius plot of the  $\alpha$ -relaxation time  $\tau(c, T)$ , normalized by the relaxation time of the bulk, for different concentrations of pinned particles. The data for  $c \leq 0.031$  is for  $N = 20000$  particles the other for  $N = 1024$ . b)  $T$ -dependence of the activation energy  $E(T)$  for different values of  $c$  for  $N = 20000$ .

we have defined the relaxation time by the condition that  $F_s(q, \tau) = e^{-1}$ . Also we mention that in the following we will always consider the larger particles but we note that the relaxation dynamics of the small particles is qualitatively very similar.

From the figure we recognize that, for a fixed value of  $c$ , at high and intermediate temperatures the *normalized* relaxation time increases with decreasing  $T$  and then becomes basically flat, i.e.  $\tau(c, T)$  tracks  $\tau(0, T)$ . This can also be clearly seen from the  $T$ -dependence of the activation barrier,  $E(T) = \frac{d \log(\tau)}{d(1/T)}$ , which at low  $T$  becomes essentially constant and independent of  $c$  (Fig. 1b). This change in the relaxation dynamic strongly resembles the dynamic crossover observed experimentally in several supercooled liquids [33, 34]. For small  $c$  this crossover occurs at around  $T = 5.5$ , i.e. slightly above the value of  $T_{MCT}$  of the bulk and as  $c$  is further increased, the crossover slightly shifts to higher temperatures. These results indicate that the dynamic response of the liquid to random pinning changes qualitatively around the ( $c$ -dependent) dynamic crossover: The dynamics at high and intermediate temperatures is increasingly affected by the pinned particles as  $T$  is decreased, whereas the one at low  $T$  is only slowed down (with respect to the bulk) by a constant factor. We emphasize that the  $T - c$ -range we are probing here is far away from the Kauzmann-line  $T_K(c)$  investigated in Refs. [21, 25] and at which  $\tau(c, T)/\tau(0, T)$  can be expected to diverge.

Such a change of the dynamics can be rationalized within the framework of RFOT [11, 12]: We assume that the CRRs are composed of a compact core, whose size grows with decreasing  $T$ , surrounded by a “halo” consist-

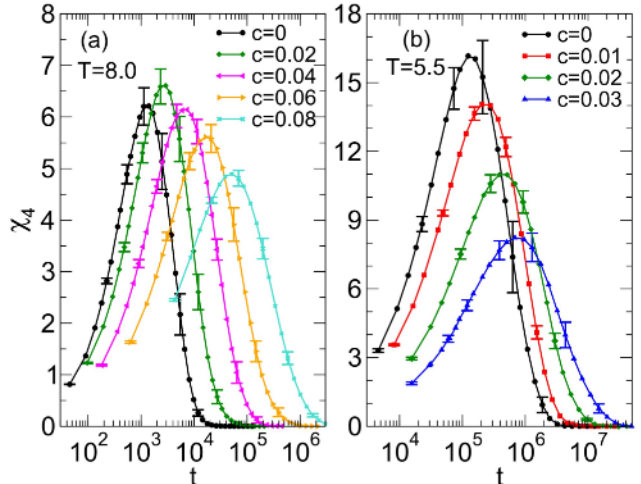


FIG. 2: Time dependence of  $\chi_4$  for different values of  $c$  and  $T$ . a)  $T = 8.0$ , b)  $T = 5.5$ . Note the different scales of the ordinate in the two panels.

ing of string-like excitations connected to this core. The size of these excitations grows if  $T$  is lowered towards  $T_{MCT}$  but once  $T$  is well below  $T_{MCT}$ , these strings are no longer relevant for the relaxation of the system and hence the CRRs consists only of the central core. Thus the increase in  $\tau(c, T)/\tau(0, T)$  we observe at intermediate  $T$  can be explained by the fact that the average length of the string-like excitations is reduced because of the presence of the pinned particles and as a consequence the dynamics slows down faster than  $\tau(0, T)$ . However, once  $T$  is below  $T_{MCT}$  the effective size of the CRRs shrinks and hence  $\tau(c, T)$  tracks  $\tau(0, T)$ , i.e.  $\tau(c, T)/\tau(0, T)$  becomes a constant. This interpretation of the data is also compatible with the results of Refs. [14, 17] for which it has been found that the dynamic length scale shows around  $T_{MCT}$  a local maximum/saturation.

To shed more light on the nature of the relaxation dynamics we have characterized its degree of cooperativity. For this we use the dynamic susceptibility  $\chi_4(t)$ , i.e. the variance of a time correlation function that characterizes the relaxation dynamics [35]. In practice, we have used the self-overlap  $\phi_s(t)$  but it can be expected that the self intermediate scattering function gives qualitatively the same results [29]. Details are given in the SI.

In Fig. 2 we show the  $t$ -dependence of  $\chi_4$  for different values of  $c$  and  $T$ . As usual, this quantity shows a maximum the height of which is related to the degree of cooperativity of the relaxation process [35]. At intermediate temperatures, see Fig. 2a, the height of the peak depends only weakly on  $c$  and its amplitude remains rather small. This shows that at this  $T$  the cooperativity is not very pronounced and only marginally affected by pinning, in agreement with the results shown in Fig. 1. At temperatures close to  $T_{MCT}$ , Fig. 2b, the  $c$ -dependence of  $\chi_4$  is much more pronounced and we see that the cooperativ-

ity *decreases* with increasing  $c$ . This result is reasonable since, as discussed above, the pinned particles reduce the effective size of the CRRs [38]. If we denote by  $\xi(c, T)$  the extent of the CRRs for pinning concentration  $c$  and temperature  $T$ , we can expect that  $\xi(c, T)$  is bounded from above by  $c^{-1/3}$ , i.e. by the typical distance of the pinned particles. If we assume that the CRRs are compact, one expects that  $\chi_4^*$  should scale as  $\xi^3 \propto c^{-1}$  [40]. Note that this estimate holds also if the shape of the CRRs is not spherical. Our data, shown in Fig. 3 of the SI, shows that  $\chi_4^*$  does indeed decrease with growing  $c$  and that there is an upper bound to its value. However, this upper bound is not as expected described by a  $c^{-1}$ -dependence but rather by a  $c^{-2/3}$  law. This suggests that the CRRs have a fractal, rather than compact, structure. Finally we mention that the reduced cooperativity as  $c$  is increased explains why the  $T$ -dependence of the relaxation times becomes Arrhenius-like at high  $c$ , see Fig. 1, a result that is also in qualitative agreement with the ones from Ref. [36].

We now turn our attention to the  $c$ -dependence of the relaxation time. In Fig. 3 we show the ratio  $\tau(c, T)/\tau(0, T)$  as a function of  $c$  for different temperatures. Within the accuracy of the data,  $\tau(c, T)$  has an exponential dependence on  $c$  [41] [42]. We note that the prefactor in the exponent, i.e. the slope of the curves, shows a significant  $T$ -dependence at high and intermediate temperatures, but depends only weakly on  $T$  at low temperatures (see Fig. 4a). Below we will discuss this  $T$ -dependence in the context of thermodynamic theories for the glass-transition. This pronounced change in the  $T$ -dependence occurs at a temperature that is close to  $T_{\text{MCT}}$ , thus giving further indication that at this temperature the nature of the relaxation dynamics changes significantly. Furthermore we mention that we have also determined the  $c$ -dependence of the infinite-time overlap (see Fig. SI4 in SI for details) and found that this static quantity shows a linear dependence on  $c$  with a slope that is basically independent of  $T$ . This shows that non-linearities in the dynamics are found in a concentration regime over which the static response of the liquid is linear.

The exponential  $c$ -dependence of  $\tau(c, T)$  indicates that our simulation probe a concentration regime where pinning linearly affects the activation energy, rather than the bare relaxation times. This “non-local” effect can be easily rationalized within either the Adam-Gibbs or the RFOT theory. To see this we set the Boltzmann constant  $k_B = 1$  and we write the relaxation times as

$$\tau(c, T) = \tau_0(c) \exp[E(c, T)/T] \quad , \quad (1)$$

where  $\tau_0(c)$  is a prefactor that we will assume to be independent of  $c$  and  $T$ , and  $E(c, T)$  can be interpreted as an effective  $c$ -and  $T$ -dependent activation energy. Expanding  $E(c, T)$  around  $c = 0$ , we can write

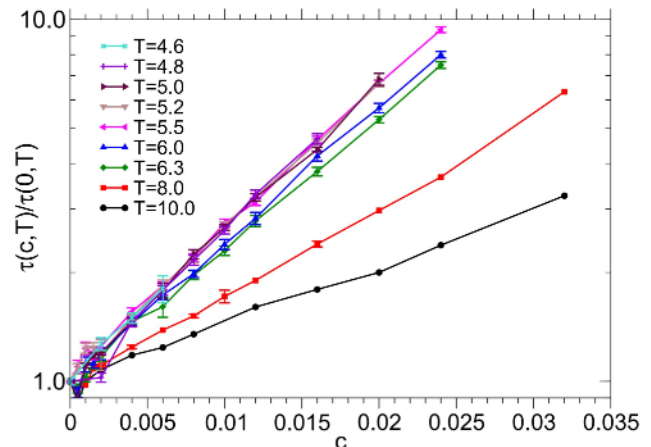


FIG. 3:  $\alpha$ -relaxation time  $\tau(c, T)$ , normalized by the relaxation time of the bulk, as a function of concentration of pinned particles.

$E(c, T) \approx E(0, T) + B(T)c$  from which one obtains immediately an exponential  $c$ -dependence

$$\frac{\tau(c, T)}{\tau(0, T)} = \exp[cB(T)/T] \quad . \quad (2)$$

Within the Adam-Gibbs and RFOT frameworks the bulk relaxation time,  $\tau(0, T) = \tau_0 \exp[E(0, T)/T]$ , can be connected to the thermodynamic properties of the system. In the following we will generalize this connection to the pinned particles case. For this we assume that for small values of  $c$  the pinning leads to a reduction of the configurational entropy  $s_c(c, T)$  via [21]

$$s_c(c, T) = s_c(T) - Y(T)c \quad . \quad (3)$$

Within the Adam-Gibbs theory the activation barrier can thus be written as

$$E_{\text{AG}}(c, T) = A/s_c(c, T) \quad , \quad (4)$$

where  $A$  is a constant, from which one immediately finds

$$B_{\text{AG}}(T) = Y_{\text{AG}} T^2 A^{-1} \ln^2(\tau(0, T)/\tau_0) \quad . \quad (5)$$

Generalizing the expression proposed by the RFOT theory for  $E(0, T)$  [7, 37] to  $c > 0$  one can expect that

$$A_{\text{RFOT}}(c, T) = \frac{3\pi(1.85)^2 T}{s_c(c, T)} \approx \frac{32T}{s_c(c, T)} \quad . \quad (6)$$

Although in the framework of RFOT other expressions for  $E(0, T)$  have been discussed in the literature [37], Eq. (6) is a reasonable approximation. Together with Eq. (3) this leads to

$$B_{\text{RFOT}}(T) = \frac{T Y_{\text{RFOT}}(T)}{32} \ln^2(\tau(0, T)/\tau_0) \quad . \quad (7)$$

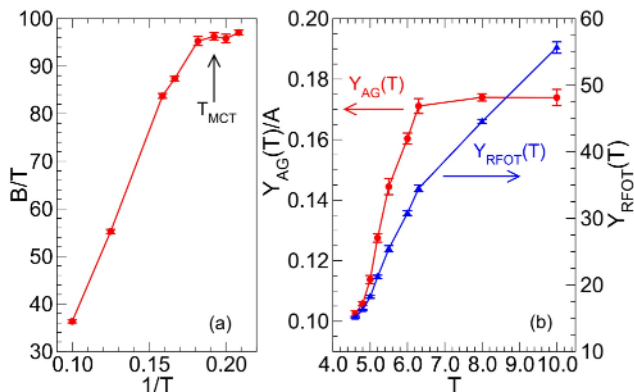


FIG. 4: a)  $T$ -dependence of the slope of the curves in Fig. 3. The  $T$ -dependence of this slope changes significantly at a temperature that is close to the mode-coupling temperature of the system. b)  $T$ -dependence of the ratios  $Y_{AG}(T)/A$  (circles) and  $Y_{RFOT}(T)$  (triangles) from the Adam-Gibbs theory and the RFOT theory, respectively.

Note that in Eqs. (5) and (7) the quantity  $Y(T)$  has a label that refers to the theory considered. In fact, the actual definition of the configurational entropy (and hence the meaning of  $Y(T)$  as defined in Eq. (3)) depends on the theory. These two expressions, together with Eq. (2), are qualitatively consistent with the observed  $c$ -dependence of the relaxation times.

Since the Adam-Gibbs theory is purely phenomenological, it is not possible to predict *a priori* the  $T$ -dependence of  $Y_{AG}$ . In contrast, it should in principle be possible to determine  $Y_{RFOT}$  with RFOT, but so far no explicit expression is known for this quantity. On the other hand, we can use our simulation data for  $\tau(c, T)/\tau(0, T)$  and Eqs. (5) and (7) to extract the  $T$ -dependence of the quantities  $Y_{AG}(T)/A$  and  $Y_{RFOT}(T)$ , respectively and the results are shown in Fig. 4b. From this figure we see that the ratio  $Y_{AG}(T)/A$  is a constant at intermediate and high temperatures, decreases rapidly on approaching  $T_{MCT} \approx 5.2$  before it starts to level off at even lower temperatures. Qualitatively the same  $T$ -dependence is found for  $Y_{RFOT}$ , since basically this quantity differs from  $Y_{AG}(T)$  just by a factor of  $T$ . Thus, in this latter case, a linear  $T$ -dependence is observed at intermediate and high temperatures.

Thus, within the framework of AG or RFOT, the physical origin of the decrease of  $Y(T)$  with decreasing  $T$  is that the size of the CRRs is increasing: At high  $T$ , pinning one more particle is more likely to block the dynamics of an additional CRR, since there are many of them and they are not extended. Hence, increasing  $c$  changes the configurational entropy significantly, i.e.  $Y(T)$  is large. However, at low  $T$  additional pinned particles are likely to be found in regions that are already very slow (since there are only few CRRs and they are extended) and hence the impact of pinning on  $s_c$

is rather weak, i.e.  $Y(T)$  is small. The fact that the slope  $B/T$  shows around  $T_{MCT}$  a marked change in its  $T$ -dependence is thus directly related to a change in the  $T$ -dependence of the dynamic length scales, a change that can be rationalized, at least qualitatively, within RFOT [7, 8].

In summary, the present simulation results show that studying the dynamics of glass-forming liquids with pinned particles allows to gain insight into the nature of the relaxation process *in the bulk*, such as the  $T$ -dependence of the structure of the CRRs. Although this approach remains indirect, it is in principle realizable in experiments using optical tweezers on colloidal suspensions or in granular materials. Therefore it will allow to probe novel details about the dynamics in glass-forming liquids and thus pose a new challenge to microscopic theories like RFOT to rationalize the  $T$ -dependence of  $Y(T)$  on a quantitative level. All this will therefore help in the quest to find the correct theory for the glass-transition.

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- [38] In Ref. [39] it has been found that confinement leads to a *increase* of the cooperativity. However, in that work particles were pinned randomly without additional constraints, thus generating a disordered structure with co-existence of small and large holes. Furthermore, only the mean number of pinned particles was prescribed, thus leading to additional sample-to-sample fluctuation. Therefore, it is not surprising that under those conditions the maximum of  $\chi_4$  behaved differently than in the more homogeneous confinement considered here.
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- [40] Note that this estimate holds also if the shape of the CRRs is not spherical.
- [41] The data shown is for  $N = 20000$  particles and, due to the needed computational effort, we have only data for up to  $c = 0.03$ . However, we have also done simulations for  $N = 1024$  particles and for this smaller system size we have been able to extent the  $c$ -range up to  $c = 0.14$ . The same exponential  $c$ -dependence has been found, thus showing that it holds up to relatively high concentrations. See Fig. SI2 in the SI for more details.
- [42] We mention that we have also carried out simulations of the same system using a Langevin dynamics. Although the absolute time scales for the relaxation are different from the one of the Newtonian dynamics, the *normalized* times are identical, thus showing that the exponential  $c$ -dependence is independent of the microscopic dynamics.

## SUPPLEMENTARY INFORMATION

### Model and details of the simulation

The system we study is a 50:50 mixture of elastic spheres [1]. Both type of particles have the same mass  $m$  and the interaction between a particle of type  $i$  and  $j$  is given by

$$V(r_{ij}) = \frac{\epsilon}{2}(1 - r_{ij}/\sigma_{ij})^2 \quad (8)$$

if  $r_{ij} < \sigma_{ij}$  and zero otherwise. Here  $\sigma_{11} = 1.0$ ,  $\sigma_{12} = 1.2$  and  $\sigma_{22} = 1.4$ . In the following we will use  $\sigma_{11}$  as the unit of distance,  $\sqrt{m\sigma_{11}/\epsilon}$  as the unit of time and  $10^{-4}\epsilon$  as unit of energy, setting the Boltzmann constant  $k_B = 1.0$ . The static and dynamic properties of the system have been obtained via molecular dynamics using the Verlet algorithm with a time step of 0.01. The simulations for the system with 20000 particles have been carried out using the LAMMPS package [2]. In order to improve the statistics we have typically simulated 8 independent samples. The longest simulations were  $3 \cdot 10^9$  time steps. The simulations for intermediate and high values of  $c$  have been done with 1024 particles using typically 4 samples. The data for the four-point susceptibility  $\chi_4(t)$  has been obtained for systems of  $N = 1000$  particles using typically from 6 to 20 samples depending on temperature and pinned particles concentration.

### Relaxation times

We have determined the relaxation time  $\tau(c, T)$  from the self intermediate scattering function  $F_s(q, t)$  by requiring that at  $\tau$  this correlator has decayed to  $e^{-1}$ . The wave-vector used was  $q = 5.52$ , i.e. close to the location of the maximum in the static structure factor. The temperature dependence of  $\tau$  is shown in Fig. SI1 for different values of  $c$  and  $N = 20000$ . As can be seen immediately, an increase of  $c$  leads to a significant increase of  $\tau$ .

In the main text we have shown, see Fig. 3, that the relaxation times show an exponential dependence on  $T$  if  $c$  is small. In Fig. SI2 we show the analogous plot for a system of  $N = 1024$  particles for which we have been able to follow the relaxation dynamics to higher concentrations. From this graph we recognize that the exponential dependence hold also for values that are significantly higher than the ones shown in Fig. 3. We emphasize, however, that the maximum shown value of the concentration,  $c = 0.14$  is still significantly smaller than the critical value at which one expects the ideal glass transition to occur, which, for  $T = 6.3$  is around 0.19 [3] and where a super-exponential  $c$ -dependence can be expected.

### Overlap and $\chi_4(t)$

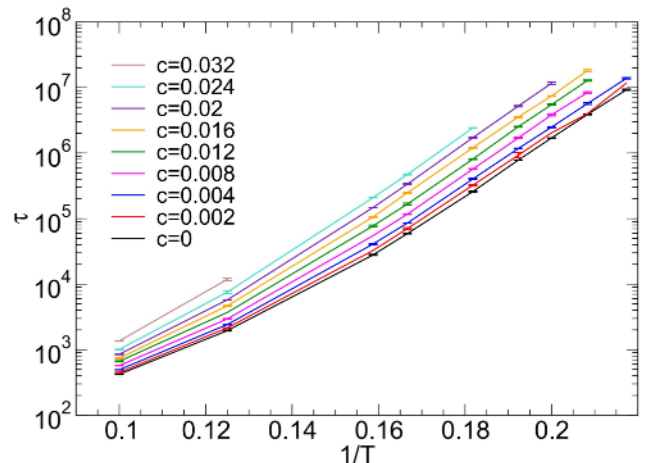


FIG. SI 1: Arrhenius plot of the relaxation time for different values of  $c$ .

To characterize the cooperativity of the dynamics and in order to make contact with previous work, we have studied the fluctuations of the time-dependent overlap function  $Q_s(t)$  which is defined as

$$Q_s(t) = N^{-1} \sum_i \Theta(|\vec{r}_i(t) - \vec{r}_i(0)| - a) \quad (9)$$

Here  $\Theta$  is the Heavyside function and  $a$  is a constant which is typically a fraction of the interparticle diameter (in our case  $a = 0.3$ ). The four-point susceptibility  $\chi_4(t)$  was then evaluated as the variance of the overlap function

$$\chi_4(t) = [\langle Q_s(t)^2 \rangle - \langle Q_s(t) \rangle^2] \quad (10)$$

where  $\langle \dots \rangle$  denotes a thermal average for a fixed realization of pinned particles and  $[\dots]$  is the average over the disorder. Note that our definition of  $\chi_4$  does not account for sample-to-sample fluctuations, which would be included in the quantity

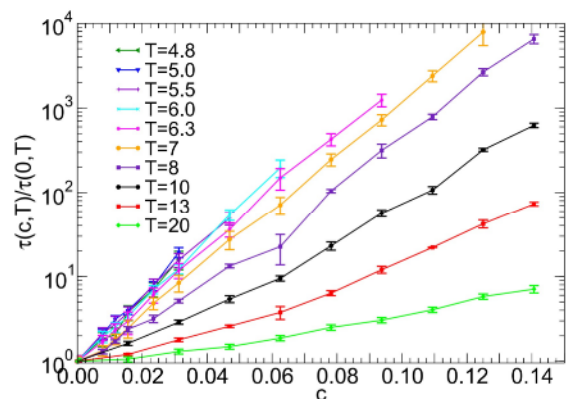


FIG. SI 2: Normalized relaxation time as a function of  $c$  for  $N = 1024$ .

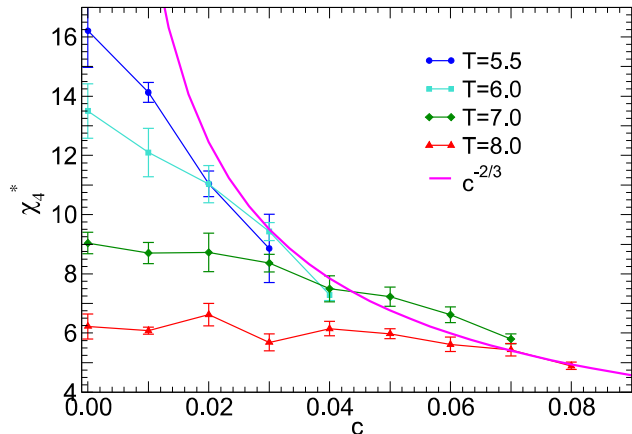


FIG. SI 3: Height of peak in  $\chi_4(t, T)$  as a function of  $c$  for different temperatures. Also show is the function  $c^{-2/3}$  which makes an envelope to the data.

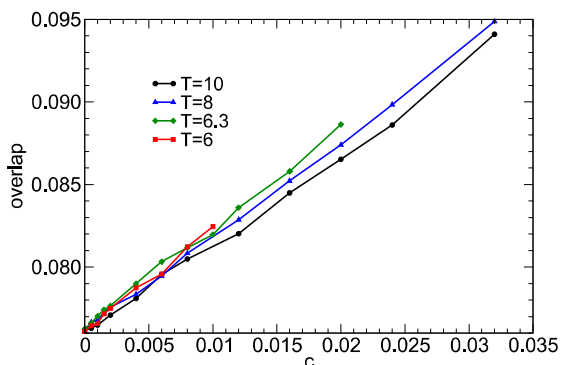


FIG. SI 4: Overlap as a function of  $c$  for different temperatures.

$$\chi_4^{\text{full}}(t) = [\langle Q_s(t)^2 \rangle] - [\langle Q_s(t) \rangle]^2 \quad . \quad (11)$$

We have found that the contribution of sample-to-

sample fluctuations are small compared to the thermal one, at least in the concentration regime we have explored in this work, and for system sizes of  $N = 1000$  particles. The behavior might be different, however, at larger  $c$  and on approaching the putative ideal glass transition. We remark that  $\chi_4^{\text{full}}(t)$  was used in Ref. [4]. The maximum value of  $\chi_4(t)$ ,  $\chi_4^*$ , is shown in Fig. SI3 as a function of  $c$  for different  $T$ 's. From the figure one recognizes that the data is bounded by the function  $c^{-\alpha}$  with  $\alpha \approx 2/3$ , giving evidence for the fractal nature of the CRRs.

We have also considered the collective overlap function  $Q_c(t)$ , defined as

$$Q_c(t) = N^{-1} \sum_i \sum_j \Theta(|\vec{r}_i(t) - \vec{r}_j(0)| - a) \quad . \quad (12)$$

This quantity shows a time dependence that is qualitatively similar to the one of the intermediate scattering function  $F_s(q, t)$  and  $Q_s(t)$ , but at long times it decays on a plateau with a non-zero height. This height is the long time overlap and it characterizes how similar two completely independent configurations are. The  $c$ -dependence of this overlap is shown in Fig. SI4 and one sees that it is a linear function in  $c$ , as expected at low  $c$  where the zone of influence of a given pinning particle is independent of the other frozen particles.

## References

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