January 25th, 2012

**Dear Joerg,**

First I would like to thank you again for your e-mail concerning our paper ([NM11092386](http://mts-nm.nature.com/cgi-bin/main.plex?form_type=view_ms&ms_id=32418&ms_rev_no=0&ms_id_key=V6WvyD5WQgwW4826G9llfw&j_id=3) ) with the comments of the reviewers.

We took seriously the comments of your Reviewers and revised our manuscript, following their valuable comments. The details are explained below.

We have newly added Supplementary Information to explain several issues, which include (1) our novel method for particle localisation and sizing, (2) the estimation of polydispersity, (3) difference between MRCO and crystal nuclei, (4) icosahedral percolation and its insignificance, and (5) an explanation for the details of the quantities characterizing dynamical heterogeneity.

The revisions made are now highlighted by using blue characters in the revised manuscript.

We believe that the revisions made following the valuable comments of Reviewers have made the physical message of our paper much clearer and more convincing.

We sincerely hope that you and your reviewers would find that our revised paper has an impact large enough to warrant publication in Nature Materials.

**Sincerely yours,**

**Hajime Tanaka**

**Institute of Industrial Science**

**University of Tokyo**

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**Replies to the comments of Reviewer #2:**

First we would like to thank the reviewer for having carefully read our manuscript and provided valuable comments and suggestions.

**This manuscript presents a structural and dynamical analysis of dense and hard-sphere-like colloidal suspensions whose trajectories have been recorded with unprecedented accuracy - the technical details are sadly left to a future unspecified publication. The authors' interpretation is that the dynamical slowdown in the dense fluid they study is related to local crystal-like order, while the presence of local icosahedral order is presented as contingent. The latter may be unexpected for some, but, if true, the former suggests that the glass problem is really one of hidden (micro-) crystallization, which would be of broad interest for the glass-forming and materials science communities. There are, however, possibly serious flaws in the analysis, which cast a doubt on this interpretation. Note that it is not clear whether a revised version that takes account of these problems would have the impact expected of Nature Materials publications.**

**The authors claim that the system's polydispersity is sufficient to prevent crystallization, and that they therefore do not have to worry about this effect interfering the dynamical slowdown. Recent analysis by Zaccarelli et al. [Phys. Rev. Lett. 103 135704 (2009) - not cited in the text], however, indicate that even for a polydispersity of 6% (as is measured here), hard spheres crystallize on a time scale similar to the structural relaxation time. It is therefore quite likely that the dynamical heterogeneity reported is related to a trivial structural heterogeneity resulting from the system being partially crystallized. Because diffusion in a crystal is much slower than even in the dense fluids studied here, the correlation is thus far from surprising. Whether dynamical heterogeneity in Refs 16-18 is also due to a partial crystallization or to a general propensity for crystal-like domains to form remains open.**

First, thanks to the kind comment, we have decided to include a brief description on our novel particle tracking method and its power. It is this method that allows us to extract not only the coordinate but also the size of a particle without missing particles even in very polydisperse samples. All of these issues are not addressed by previous methods. We also note that the careful analysis of bond orientational order described in Methods and Supplementary Information is essential and prerequisite for extracting both icosahedral and fcc-like bond orientational order properly. We believe this raises the impact of our paper as an experimental paper.

To answer the main concern of the reviewer about the possibility of trivial crystallisation of our samples, we performed the standard analysis of Frenkel and co-workers (Pieter Rein ten Wolde, Maria J. Ruiz-Montero, and Daan Frenkel, J. Chem. Phys. 104, 9932 (1996)) (used among others by Zaccarelli et al.) to detect crystal nuclei. In this way we confirm that our samples have a very low amount of truly crystalline particles (1%, corresponding to the very end of the high Q\_6 tail). These tiny crystal nuclei are embedded in regions of high crystal-like bond orientational order we focus on in the paper, but their sizes are much smaller than the critical nucleus size and thus crystals appear just as ‘fluctuations’. This means that these small crystals may be regarded as the extreme of bond orientational order fluctuations. To explain this, a discussion about the relationship between crystal nuclei and crystal-like order is now included as Supplementary Information.

We see two possible reasons to explain this lack of crystallisation, at odds with Zaccarelli et al. results (now cited).

1) Our size distribution is not Gaussian and slightly asymmetric, which may influence the nucleation barrier.

2) We actively discarded the samples that crystallised. Zaccarelli et al. did the opposite: they labelled as "unstable to crystallisation" the state points that crystallised at least once out of 5 simulations.

As a summary, the sample presented here are metastable to the crystal (i.e., supercooled) but not crystallised. It is evident that crystals exhibit only very slow diffusion, however the correlation we demonstrate between very imperfect ordering and dynamic heterogeneities is, to our point of view, ‘not’ trivial.

Furthermore, the most important finding of this paper is the lack of importance of the icosahedral order in glassy slow dynamics. After the seminal argument by Frank and also the discovery of quasicrystals, in the late 80's and 90's, icosahedral order was conjectured as a possible cause of the glass transition. This explanation has continued to be the basis of major theories on glass transition and quite often been used in recent metallic glass publications. We thus think that clarifying the role of icosahedral order is of major importance for a broad audience. Secondly, we showed the first ‘experimental’ confirmation of the correlation between crystal-like order and dynamic heterogeneity in 3D glass-forming systems. Combining these, we have shown that ‘medium-range’ ordering (or correlation) is crucial for causing slow dynamics, which is one of the major findings of our work. Finally, our work also demonstrated hat ‘amorphous order’, which is a key to the Random First Order Transition (RFORT) theory of glass transition, does not play an important role in slowing down of the dynamics at least in our colloidal glass.

We made more explicit our analysis of the icosahedral percolation into the Supplementary information to show much clearer that short-range icosahedral ordering is not responsible for glassy slow dynamics. .

To our knowledge our paper is the first to bring a proof of the lack of importance of the icosahedral or exotic amorphous order, while exhibiting a more solid-like structural cause.

**Other points:**

**1) Although the structural relaxation time may not need to be carefully defined for a knowledgeable audience, quantities such as the non-Gaussianity of the dynamics (presumably the time at which the non-Gaussian parameter \alpha\_2(t) peaks), the dynamical heterogeneity length xi\_u (??), and the structural correlation length xi\_6 (presumably the decay length of q\_6.q\_6(r)) ought to be.**

1) We agree that the quantities the reviewer cited ought to be defined. We included the definitions in Supplementary Information, following the valuable advice.

**2) The authors use a definition for the coarse-grained tensorial BOO in Eq. 6 that is different from Ref. 32's. It is not clear what additional information the self-contribution brings to the measure, nor what is the j=0 nearest neighbor. A clarification is in order.**

2) Our definition of the coarse-grained BOO is the same as in Lechner & Dellago's paper. They wrote their definition as follows: "Here, the sum from k=0 to N~\_b(i) runs over all neighbors of particle i plus the particle i itself." However we needed coherent sums over the neighbours to explain our point about the neighbours selection, so we developed the self-contribution.

**3) On p. 4, the authors should specify what is surprising about the fact that icosahedra are present even at a relatively low volume fraction. Anikeenko and Medvedev [Phys. Rev. Lett. 98, 235504 (2007) - not cited in the text] find that hard spheres packings at those densities contain 5-10% of tetrahedral and decays relatively slowly with packing fraction. And some of these tetrahedra are likely to assemble into icosahedra. Similar conclusions could also be gleaned from a recent preprint by Charbonneau et al. [arXiv:1108.2494 - not cited in the text].**

3) We thank Reviewer for bringing our attention to Anikeeko and Medvedev work, that we included in our bibliography. However they claim in their introduction that "icosahedra per se are rarely found" and that is seemingly the main reason why they extended their search to other polytetrahedral structures. However we agree that the word "surprise" was overstated and we removed it from the manuscript. We also cited the very recent paper by Charbonneau et al., which seeks more dynamical than static origin for slow dynamics.

Charbonneau et al. (published in Phys. Rev. Lett. in the interval) also showed that there is no static growing length in supercooled liquids including polydisperse hard spheres (8.5% polydispersity). This is at odds with our finding. It is the major current issue in the glass transition physics whether there is a growing static length or not. We show convincing 'experimental' evidence for the presence of such static order in 3D typical glass formers for the first time. We believe that this would contribute to our understanding on the role of static order in glassy slow dynamics. However, we could not find an obvious origin of the discrepancy between our results and those by Charbonneau et al. without access to their data or more precision on their bond order correlation method than what was provided in the PRL. We have added a brief comment in Supplementary Information on this issue.

**4) Along with Refs. 3 and 4, the authors should cite Sadoc and Mosseri's book about Geometrical Frustration [Cambridge University Press (1999)]. The pair was working on the problem contemporaneously to Nelson and coworkers.**

4) We thank the Reviewer for pointing out this. We agree that these two groups contributed a lot to the development of the concept of Geometrical Frustration. We have added the book of Sadoc and Mosseri to our bibliography.

We think that thanks to the valuable comments, the physical messages have become much clearer and more convincing in te revised manuscript. We hope that the reviewer would think that the revised manuscript is now suitable for publication in Nature Materials.

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**Replies to the comments of Reviewer #3 :**

First we thank the Reviewer for having carefully read our manuscript and provided useful comments.

**Leocmach and Tanaka have investigated the relationship between structure and dynamics in a colloidal glass transition experiment, where confocal microscopy is used to examine the direct local connection between structure and dynamics. This follows in the spirit of lots of prior work by the Tanaka group. The key question studied here is whether icosohedral ordering or crystalline ordering is more relevant for determining dynamics. The answer is that crystalline ordering has a stronger influence over the slowing dynamics. This addresses long-standing conjectures that icosahedral ordering is important. The link between local structures and local dynamics is not the new result, but rather, the specific examination of the two types of order. This paper is clearly written and I recommend accepting it for publication, although there are points below that should be addressed.**

We are very glad to see the positive comments of the Reviewer. Below we reply to the comments of the Reviewer one by one.

**1. I think that calling their analysis method the iso-bond order ensemble and the x-propensity (where x=w\_6, Q\_6, etc.) is a bit of a stretch. People have been looking at links between structure and mobility for quite a while [Perera and Harrowell, J. Chem. Phys. 111, 5441 (1999): psi\_6 and mobility; Donati et al., Phys. Rev. E 60, 3107 (1999): potential energy and mobility; Weeks and Weitz, Phys. Rev. Lett. 89, 095704 (2002): crystalline order and mobility; Conrad, Starr, and Weitz, J. Phys. Chem. B 109, 21235 (2005): voronoi volume and mobility; lots of work by the Tanaka group]. Plotting the mean mobility as a function of a parameter may be the iso-parameter ensemble, but it's not really of the same power as the iso-configurational ensemble. I mostly dislike the implication that the authors have invented a way to do iso-configurational ensembles when rather, they have renamed a technique that has been often used in the past, that has some similarity to iso-configurational ensembles.**

1) We agree on the opinion of the Reviewer: calling our quantity "propensity" was improper. We renamed it "mobility", following the advice. We added a few lines to clarify the link between the bond order mobility and the iso-configurational propensity in the revised manuscript.

**2. On page 7, the sentence "This suggests that the structural origin of the dynamical arrest is linked to the avoided crystallisation..." reminds me of a lot of van Megen's recent papers. For example, Phys. Rev. Lett. 102, 168301 (2009) discusses a link to crystallisation and vitrification in its intorductory paragraph. Perhaps this would be relevant or interesting to cite, although it is up to the authors.**

2) We thank the Reviewer for pointing out this important pioneering paper and others by van Megen and his coworkers. We have added the van Megen's PRL paper to our bibliography (now cited in the introduction).

We hope that the reviewer would think that the revised manuscript is now suitable for publication in Nature Materials.