nature portfolio

Peer Review File

An equilibrium rotator glass-forming phase for long-ranged repulsive colloidal rods

Corresponding Author: Dr Thijs Besseling

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Report for “An Equilibrium Rotator Glass for Long-Ranged Repulsive Colloidal Rods” by Besseling et al.

This manuscript presents what seem at first glance to be interesting results for an equilibrium rotator glass. The concept involves a re-entrant transition to an amorphous state at high concentration, which the authors interpret as an equilibrium glass. I think that the experiments are quite interesting. However the manuscript in its present form is far from appropriate for Nature Communications.

The dynamical regime accessible to such large colloids is very limited. The authors report they have measured dynamics over 163 times the time for the rod to diffuse its own diameter. Two orders of magnitude change in dynamics though is far from sufficient to term a material a glass.

In the seminal work of Brambilla et al (Phys. Rev. Lett. 102, 085703 (2009)), 7 orders of magnitude of change in relaxation time were recorded, and still the sample was not termed a glass. (I am surprised that the authors do not cite this paper). Now it is true that the particles here are longer, but still the authors lack experimental evidence for a glass by some considerable margin. Of course it is 14 orders of magnitude for a molecular glass.

That in itself, might be OK, as they perform computer simulations to back up their claims. Yet, strangely no details of the relaxation protocols used in the simulations are given. This seems odd, since the simulations surely need to be equilibrated at each step of the thermodynamic integration and some measure must be employed to ensure that this is correctly done. To be clear, mapping the experimental 2 orders of magnitude increase in relaxation time would only correspond to a temperature of perhaps 0.55 in the well-known Kob-Anderson Binary Lennard-Jones model (for example), yet in that community, T=0.55 is only considered a weakly supercooled liquid. Certainly not a glass. It is almost certainly possible technically to perform “thermodynamic integration” with those kinds of dynamics, as there is a separation between the short-time and the full “alpha” relaxation. But that doesn’t make such a material a solid glass. And one would certainly question the meaning of such thermodynamic integration.

With no evidence as to the equilibration of the simulations, it is entirely unclear what the high-density amorphous state is. (Longer experiments would also be more than helpful, but I appreciate that these can be harder to perform than the simulations).

So the authors can either revise their manuscript in line with the evidence they have: that is, evidence for an intriguing retract amorphous state whose dynamics are too slow for their experiments to clarify, ie it might be a glass but (more likely, given the lack of “equilibrium glasses” in nature), a more viscous liquid.

Or if they can perform simulations where they show categorically, that they have obtained an equilibrium free energy for this state then there could be something to discuss. For example SWAP dynamics can be used to probe systems well below the molecular glass transition of 14 orders of magnitude change in relaxation time (eg Ninarello et al Phys. Rev. X 7, 021039 (2017)). So if the states found here can be shown convincing not to decay under SWAP dynamics, then indeed the authors could claim to have identified glass.

Finally a small point. Please remove the comment about volume fraction 0.59 or at least explain exactly what is meant. Is it the mode-coupling value of 0.58 that is referred to? This was shown by the paper mentioned above to be a dynamical crossover. Or are the authors thinking of some limit of the (possible) “true” glass transition, one prediction from the same paper being 0.614, but most lying at a volume fraction above 0.61.

Reviewer #2

(Remarks to the Author)
The physical mechanisms that lead to arrested states of matter, especially gels and glasses, are of paramount importance in several branches of science, such as Physics, Biology, Chemical Engineering, Materials Science, among others.

In this manuscript, authors have reported on the existence of a new “equilibrium” glassy state here defined as rotator glass made up of colloidal spherocylinders that interact with long-ranged repulsive forces. By means of real space measurements and both Monte Carlo and Brownian dynamics simulations, authors provide partial evidence on the role that the anisotropic particle interactions might have on the destabilization of the crystal phase at high volume fractions. Authors discuss how the interplay between translational and rotational degrees of freedom has on the colloidal phase behavior.

I consider that the results obtained by the authors are original and of crucial importance for the understanding of the connection that exists between different types of degrees of freedom on both the structure and dynamics of many-body systems close to dynamical arrest. This topic is appropriated for Nature Communications due to its scientific implications for the vast community of Condensed Matter. Furthermore, I found the paper well written, discussed and organized. However, to recommend the acceptance of the manuscript, authors should properly address the following points:

1. Most of the arguments to understand the appearance of the rotator glassy state is based on the interplay between the translational and rotational degrees of freedom, and that interplay is discussed in terms of the long-time self-diffusion coefficient and the typical rotational and translational trajectories of individual particles when the concentration is increased. However, this information provides partial evidence of the existence of such a glassy state. Nevertheless, it is possible to measure (and calculate) other dynamical observables that will elucidate the particle relaxation and the dynamical coupling between degrees of freedom, see, e.g., Soft Matter 16, 170 (2020). I then suggest the authors to determine, report and discuss the translational and rotational self-correlation functions and from those quantities it is possible to extract the relaxation times, which will elucidate whether this state corresponds or not to a particular class of glassy state.

2. I still do not understand why the colloidal dispersion relaxes back to the rotator glass state from the crystalline-like configuration; the latter is obtained when the electric field is switched on. This is completely physically counterintuitive since the crystal configuration is, in principle, the state of minimum energy. I then wonder whether such a “equilibrium” glassy state is not a dynamical arrested state. This point should be discussed in more detail to clearly state that authors found a new non-equilibrium thermodynamic state.

Reviewer #3

(Remarks to the Author)
Solutions of charged rod-shaped colloids are studied by confocal microscopy. The effective aspect ratio can be changed by varying the screening length which allows the observation of different equilibrium and glassy structures. While liquid crystalline and plastic crystal phases are known, a novel rotational glass is observed, where translations are frozen and disordered while rotations remain liquid-like. With increasing volume fraction of the colloidal rods, the ratio of translational to rotational diffusion coefficients decreases by more than a factor ten. Applying an electric field, the rods can be aligned which enables positional crystalline order to form. Switching off the field, the particles again become disordered and return to the rotational glass state. Brownian dynamics simulations of a simplified model are performed to rationalize the experiments, and observe fluid and plastic crystal states.

This is a very interesting study of a peculiar glass state which, in my opinion, is of broad interest to the Materials Science and Soft Matter community. The study nicely combines experiments and simulations, and the paper is very well written and informative. Still, there are a couple of points that should be addressed before I can recommend publication.

There are theoretical predictions by Schilling and Scheidsteger [1] on orientational glasses and glass transitions of slightly elongated particles. These should be discussed carefully. My impression is that the experiments see the glass states predicted by Schilling and coworkers. Moreover, the predictions could be tested more qualitatively and quantitatively by looking at orientational correlation functions for different angular momenta. It would also be interesting to compare the experimental effective aspect ratio to the value of the critical aspect ratio predicted in [1].

There are detailed simulations by Chong, Kob and colleagues [2,3] testing the orientational glass predictions. These simulations and observations should be discussed carefully including with respect to the present simulations. The present simulations do not observe glassy states in contrast to the experiments, while the older simulation saw the orientational glass formation.

The simulations appear to observe two equilibrium phases, fluid and plastic crystal. The experiments on the other hand find glassy states. This difference should be stated clearly and should be discussed. Why do the simulated states reach equilibrium, while the experimental samples arrest?
Connected with this discussion the presentation of the experimental states as equilibrium solid state (abstract line 22) versus 'rotational glass' (line 26) should be re-assessed. The experiments observe glass states that form upon increasing the density or, at high enough density, upon decreasing an aligning electric field.
Yet, this does not convincingly prove that the rotational glass states are equilibrium states in my opinion. It would require to check. e.g. that these states do not age and are independent of the quench speed or other parameters of the preparation history.

Fig 3 f: One of the g(r) lines is shifted, or? Stating this would be helpful.

In lines around 208 of the main text, it is stated that the rotator glass re-formed upon decreasing the electric field. In the caption of Fig. 4 f the opposite is stated ('crystalline order still persisted'), and Fig 4f itself is inconclusive. The description needs to be corrected, and the Steinhard order measure (Fig 4i) should be discussed in order to quantify the difference between glass and crystal.

[1] R. Schilling and T. Scheidsteger, “Mode coupling approach to the ideal glass transition of molecular liquids: Linear molecules,” Phys. Rev. E 56, 2932 (1997).
[2] S.-H. Chong and W. Kob, “Coupling and decoupling between translational and rotational dynamics in a supercooled molecular liquid,” Phys. Rev. Lett. 102, 025702 (2009).
[3] S.-H. Chong, A. J. Moreno, F. Sciortino, and W. Kob, “Evidence for the weak steric hindrance scenario in the supercooled-state reorientational dynamics,” Phys. Rev. Lett. 94, 215701 (2005).

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Second report for “An Equilibrium Rotator Glass for Long-Ranged Repulsive Colloidal Rods” by Besseling et al.

The authors have done a good job in revising their manuscript in line with the comments made during the first round of reviewing, and I am happy to recommend publication of the revised manuscript. As noted in the first round of reviewing, this is an interesting result that would not be expect a prior and as such, it is suitable for the broad readership of Nature Communications.

Reviewer #2

(Remarks to the Author)
I really appreciate the effort made by the authors to include all the points raised in my previous report. The results obtained by the authors are original and of crucial importance for
the understanding of the connection that exists between different types of degrees of freedom on both the structure and

dynamics of many-body systems close to dynamical arrest. I therefore recommend the publication of the manuscript in its present form.

Reviewer #3

(Remarks to the Author)
In response to the three referee reports, the authors have added further data and analysis, and have extended their discussion. I find the paper now warranting publication in Nature communications as it reports solid insights into an intriguing novel glassy state. The concept of equilibrium amorphous state will certainly motivate theory and simulations. Overall the study shows that anisotropy can lead to novel insights into the formation of amorphous solids with intriguing (de-) coupling of rotational and translational motion which is an actively developing reasearch area.

Response to reviewers:

Reviewer #1:

This manuscript presents what seem at first glance to be interesting results for an equilibrium rotator glass. The concept involves a re-entrant transition to an amorphous state at high concentration, which the authors interpret as an equilibrium glass. I think that the experiments are quite interesting. However the manuscript in its present form is far from appropriate for Nature Communications.

The dynamical regime accessible to such large colloids is very limited. The authors report they have measured dynamics over 163 times the time for the rod to diffuse its own diameter. Two orders of magnitude change in dynamics though is far from sufficient to term a material a glass.

In the seminal work of Brambilla et al (Phys. Rev. Lett. 102, 085703 (2009)), 7 orders of magnitude of change in relaxation time were recorded, and still the sample was not termed a glass. (I am surprised that the authors do not cite this paper). Now it is true that the particles here are longer, but still the authors lack experimental evidence for a glass by some considerable margin. Of course it is 14 orders of magnitude for a molecular glass.

That in itself, might be OK, as they perform computer simulations to back up their claims. Yet, strangely no details of the relaxation protocols used in the simulations are given. This seems odd, since the simulations surely need to be equilibrated at each step of the thermodynamic integration and some measure must be employed to ensure that this is correctly done. To be clear, mapping the experimental 2 orders of magnitude increase in relaxation time would only correspond to a temperature of perhaps 0.55 in the well-known Kob-Anderson Binary Lennard-Jones model (for example), yet in that community, T=0.55 is only considered a weakly supercooled liquid. Certainly not a glass. It is almost certainly possible technically to perform "thermodynamic integration" with those kinds of dynamics, as there is a separation between the short-time and the full "alpha" relaxation. But that doesn't make such a material a solid glass. And one would certainly question the meaning of such thermodynamic integration.

With no evidence as to the equilibration of the simulations, it is entirely unclear what the high-density amorphous state is. (Longer experiments would also be more than helpful, but I appreciate that these can be harder to perform than the simulations).

So the authors can either revise their manuscript in line with the evidence they have: that is, evidence for an intriguing retract amorphous state whose dynamics are too slow for their experiments to clarify, ie it might be a glass but (more likely, given the lack of "equilibrium glasses" in nature), a more viscous liquid.

Or if they can perform simulations where they show categorically, that they have obtained an equilibrium free energy for this state then there could be something to discuss. For example SWAP dynamics can be used to probe systems well below the molecular glass transition of 14 orders of magnitude change in relaxation time (eg Ninarello et al Phys. Rev. X 7, 021039 (2017)). So if the states found here can be shown convincing not to decay under SWAP dynamics, then indeed the authors could claim to have identified glass.

Finally a small point. Please remove the comment about volume fraction 0.59 or at least explain exactly what is meant. Is it the mode-coupling value of 0.58 that is referred to? This was shown by the paper mentioned above to be a dynamical crossover. Or are the authors thinking of some limit of the (possible) “true” glass transition, one prediction from the same paper being 0.614, but most lying at a volume fraction above 0.61.

Response to reviewer #1:

We thank the referee for the thoughtful comments on our manuscript and have revised our manuscript based on additional findings as well as based on the concerns raised by the referee.

Below is a point-by-point explanation and response to the referee’s comments:
We would like to emphasize that our system is extremely soft, evidenced by the extremely large Debye screening length. It is known that there can be up to 7 orders of magnitude difference in the relaxation times for a soft matter system compared to a molecular system, however, even for a soft system our system is extremely soft, resulting in relaxation times increasing much more gradually than typical colloidal systems. Regarding the concern of the orders of magnitude of the relaxation times, (see also the comments by Referee #2), we have, based on additional experimental results, calculated the translational and rotational self-correlation functions and analyzed the resulting relaxation times as a function of density up to the highest packing fraction we could obtain (where both translational motion and rotational motion is completely frozen in), see Figure 2a and SI Figure 2 in the revised manuscript. We have added the details of the calculation of the correlation functions to the method section on page 6, line 518-529.

In the region where most of the experiments were performed (incl the electric-field switching experiments), there is a very strong decoupling of the translational and rotational degrees of freedom, however, there are still limited particle rearrangements taking place (reminiscent of cage escape observed in glassy states of nearly hard-sphere colloids, i.e. particles with much steeper and more short-ranged interactions), resulting in a system that is not completely frozen-in on the timescales of our experiments. However, we also found that these phases are very close to a volume fraction where all motion (translation and rotations) completely freezes in (see Figure 2a and SI Fig. 3), and observe (again in agreement with hard-sphere systems) dynamical heterogeneities, a hallmark of glassy dynamics (see SI Fig. 4). We therefore changed the term ‘equilibrium rotator glass’ and refer to this phase in the paper as an ‘equilibrium rotator glass-forming phase’, or ‘glass-like phase’, indicating an amorphous phase that is close to dynamic arrest. We refrain from using the terminology ‘supercooled liquid’ as this implies an underlying stable crystal phase which, intriguingly, in our system of monodisperse particles was not found and likely does not exist, given also the simulation results. Furthermore, we do not refer to this phase anymore as a ‘solid’.

We would like to emphasize that the conclusion that this glass-forming phase near dynamic arrest is an equilibrium phase still holds and this is in our view an important finding. In our experiments we have found that the rotator glass-forming phase can be crystallized by application of an AC electric field that aligns the particles in the field direction. When the field is turned off again, the particles do not remain on their crystal lattice but return to the translationally disordered (and nearly arrested) phase. This serves as experimental evidence that the induced crystalline state is *not* the equilibrium phase but that it is the glass-like amorphous phase that has lower free energy. This finding is supported with computer simulations of soft rods interacting with simplified interactions but with the same competing tendencies. Furthermore, we observed experimentally strong hysteresis in the system when switching between the crystalline phase and the amorphous phase (Fig. 4), which is indicative of a first-order equilibrium phase transition. We have further clarified this point, by adding an additional sentence in the main paper, see line 220-221.

With respect to how we ensured that the simulations reached equilibrium, in order to study the phase behaviour, we intentionally focused on a system with a slightly shorter interaction range. One consequence of this choice was that the re-entrant phase was disordered, but not strongly glassy. As a result, we were easily able to equilibrate the system and thus obtain the free energies of the system. Therefore, simulation tricks to speed up equilibration were not needed. While we carefully only referred to the re-entrant phase as disordered, it was not clearly stated that this was the case. Hence, we now clarify this both in the main text (line 164) and in the methods section (line 560).

Furthermore, we thank the referee for notifying us about the work of Brambilla et al., which we have added as a reference to the introduction section (line 76, ref 18).

We agree with the referee that the comment about the 0.59 volume fraction is not strongly explained nor supported by further analysis, so we have removed this comment as suggested by the referee (we removed line 272 –276).

All (other) additions or modifications we have made are highlighted in blue in the manuscript, and text that has been removed is crossed out.

Reviewer #2 :

The physical mechanisms that lead to arrested states of matter, especially gels and glasses, are of paramount importance in several branches of science, such as Physics, Biology, Chemical Engineering, Materials Science, among others.

In this manuscript, authors have reported on the existence of a new "equilibrium" glassy state here defined as rotator glass made up of colloidal spherocylinders that interact with long-ranged repulsive forces. By means of real space measurements and both Monte Carlo and Brownian dynamics simulations, authors provide partial evidence on the role that the anisotropic particle interactions might have on the destabilization of the crystal phase at high volume fractions. Authors discuss how the interplay between translational and rotational degrees of freedom has on the colloidal phase behavior.

I consider that the results obtained by the authors are original and of crucial importance for the understanding of the connection that exists between different types of degrees of freedom on both the structure and dynamics of many-body systems close to dynamical arrest. This topic is appropriated for Nature Communications due to its scientific implications for the vast community of Condensed Matter. Furthermore, I found the paper well written, discussed and organized. However, to recommend the acceptance of the manuscript, authors should properly address the following points:

1. Most of the arguments to understand the appearance of the rotator glassy state is based on the interplay between the translational and rotational degrees of freedom, and that interplay is discussed in terms of the long-time self-diffusion coefficient and the typical rotational and translational trajectories of individual particles when the concentration is increased. However, this information provides partial evidence of the existence of such a glassy state. Nevertheless, it is possible to measure (and calculate) other dynamical observables that will elucidate the particle relaxation and the dynamical coupling between degrees of freedom, see, e.g., Soft Matter 16, 170 (2020). I then suggest the authors to determine, report and discuss the translational and rotational self-correlation functions and from those quantities it is possible to extract the relaxation times, which will elucidate whether this state corresponds or not to a particular class of glassy state.

1. We agree with the referee to calculate the translational and rotational self-correlation functions. Based on additional experimental data, for a range of volume fractions, we analyzed the resulting relaxation times as a function of density up to the highest packing fraction we could obtain (where both translation motion and rotational motion is completely frozen in), see Figure 2a and SI Figure 2 in the revised manuscript. We have added the details of the calculation of the correlation functions to the method section on page 6, line 518-529.

It is clear from this analysis, that in the region where most of the experiments were performed (incl the electric-field switching experiments), there is a very strong decoupling of the translational and rotational degrees of freedom, however, there are still limited particle rearrangements taking place (reminiscent of cage escape observed in glassy states of nearly hard-sphere colloids, i.e. particles with much steeper and more short-ranged interactions), resulting in a system that is not completely frozen-in on the timescales of our experiments. However, we also found that these phases are very close to a volume fraction where all motion (translation and rotations) completely freeze in (see Figure 2a and SI Fig. 3), and observe (again in agreement with hard-sphere systems) dynamical heterogeneities, a hallmark of glassy dynamics (see SI Fig. 4). We therefore changed the term ‘equilibrium rotator glass’ and refer to this phase in the paper as an ‘equilibrium rotator glass-forming phase’, or ‘glass-like phase’, indicating an amorphous phase that is close to dynamic arrest. We refrain from using the terminology ‘supercooled liquid’ as this implies an underlying stable crystal phase which, intriguingly, in our system of monodisperse particles was not found and likely does not exist, given also the simulation results. Furthermore, we do not refer to this phase anymore as a ‘solid’.

2. I still do not understand why the colloidal dispersion relaxes back to the rotator glass state from the crystalline-like configuration; the latter is obtained when the electric field is switched on. This is completely physically counterintuitive since the crystal configuration is, in principle, the state of minimum energy. I then wonder whether such a “equilibrium” glassy state is not a dynamical arrested state. This point should be discussed in more detail to clearly state that authors found a new non-equilibrium thermodynamic state.

2. In our experiments we have found that the rotator glass-forming phase can be crystallized by application of an AC electric field that aligns the particles in the field direction. When the field is turned off again, the particles do not remain on their crystalline lattice but return back to the translationally disordered (and nearly arrested) phase. We agree with the referee that this is indeed counterintuitive. However, it serves as experimental evidence that the induced crystalline state is *not* the equilibrium phase but that it is the glassy amorphous phase that has lower free energy. This finding is supported with computer simulations of soft rods interacting with simplified interactions but with the same competing tendencies. Furthermore, we observed strong hysteresis in the system when switching between the crystalline phase and the amorphous phase (Fig. 4), which is indicative of a first-order equilibrium phase transition. To clarify this point, we have added an additional sentence in the main paper, see line 220-221.

All other additions or modifications we have made are highlighted in blue in the manuscript, and text that has been removed is crossed out.

Reviewer #3:

Solutions of charged rod-shaped colloids are studied by confocal
microscopy. The effective aspect ratio can be changed by varying the screening
length which allows the observation of different equilibrium and glassy structures.
While liquid crystalline and plastic crystal phases are known, a novel rotational
glass is observed, where translations are frozen and disordered while rotations remain
liquid-like.
With increasing volume fraction of the colloidal rods, the ratio of translational to
rotational diffusion coefficients decreases by more than a factor ten.
Applying an electric field, the rods can be aligned which enables positional crystalline order
to form. Switching off the field, the particles again become disordered and
return to the rotational glass state. Brownian dynamics simulations of a simplified
model are performed to rationalize the experiments, and observe fluid and plastic
crystal states.

This is a very interesting study of a peculiar glass state which, in my opinion, is
of broad interest to the Materials Science and Soft Matter community.
The study nicely combines experiments and simulations, and the paper is very well written
and informative. Still, there are a couple of points that should be addressed before I can
recommend publication.

There are theoretical predictions by Schilling and Scheidsteger [1]
on orientational glasses and glass transitions of slightly elongated particles.
These should be discussed carefully. My impression is that the experiments see the
glass states predicted by Schilling and coworkers. Moreover, the predictions could
be tested more qualitatively and quantitatively by looking at orientational correlation
functions for different angular momenta. It would also be interesting to compare
the experimental effective aspect ratio to the value of the critical aspect ratio predicted in
[1].

We agree with the referee that this is indeed a very important paper to cite in our manuscript, and have now included it in the discussion (line 309-316, ref 28). Note that we are unable to make a direct comparison to a "critical aspect ratio" from that paper as the critical behaviour was examined for dipolar hard spheres, which is quite different from the system we study in this paper. Nonetheless, as we now write in the discussion, we qualitatively see the same transitions.

There are detailed simulations by Chong, Kob and colleagues [2,3] testing the
orientational glass predictions. These simulations and observations should be
discussed carefully including with respect to the present simulations. The present
simulations do not observe glassy states in contrast to the experiments, while the
older simulation saw the orientational glass formation.

The simulations appear to observe two equilibrium phases, fluid and plastic crystal.
The experiments on the other hand find glassy states. This difference should be stated
clearly and should be discussed. Why do the simulated states reach equilibrium, while
the experimental samples arrest?

To probe whether the disordered phase could be fully an equilibrium phase, we intentionally used a model that was close to the experiments but that was less slow (further from the glass). We found that simply by using a model with a slightly shorter interaction range, the system sped up sufficiently to be able to make fully equilibrium measurements (e.g. of the equation of state and the integration path associated with Einstein integration). As a positive consequence of this choice, we were able to draw an equilibrium phase diagram, however, a more negative consequence was that the simulation model had significantly faster dynamics than the experimental system.

Connected with this discussion the presentation of the experimental states as
equilibrium solid state (abstract line 22) versus 'rotational glass' (line 26) should
be re-assessed.

Based on additional experimental results we calculated the translational and rotational self-correlation functions and analyzed the resulting relaxation times as a function of density up to the highest packing fraction we could obtain (where both translation motion and rotational motion were completely frozen in), see Figure 2a and SI Figure 2 in the revised manuscript. We added the details of the calculation of the correlation functions to the method section on page 6, line 518-529.

In the region where most of the experiments were performed (incl the electric-field switching), there is a very strong decoupling of the translational and rotational degrees of freedom, however, there are still limited particle rearrangements taking place (reminiscent of cage escape observed in glassy states of nearly hard-sphere colloids, i.e. particles with much steeper and more short-ranged interactions), resulting in a system that is not completely frozen-in on the timescales of our experiments. However, we also found that these phases are very close to a volume fraction where all motion (translation and rotations) completely freeze in (see Figure 2a and SI Fig. 3), and observe (again in agreement with hard-sphere systems) dynamical heterogeneities, a hallmark of glassy dynamics (see SI Fig. 4). We therefore changed the term ‘equilibrium rotator glass’ and refer to this phase in the paper as an ‘equilibrium rotator glass-forming phase’, or ‘glass-like phase’, indicating an amorphous phase that is close to dynamic arrest. We refrain from using the terminology ‘supercooled liquid’ as this implies an underlying stable crystal phase which, intriguingly, in our system of monodisperse particles was not found and likely does not exist, given also the simulation results. Furthermore, we do not refer to this phase anymore as a ‘solid’.

The experiments observe glass states that form upon increasing the
density or, at high enough density, upon decreasing an aligning electric field.
Yet, this does not convincingly prove that the rotational glass states are equilibrium
states in my opinion. It would require to check. e.g. that these states do not age and
are independent of the quench speed or other parameters of the preparation history.

In our experiments we found that the rotator glass-forming phase can be crystallized by application of an AC electric field that aligns the particles in the field direction. When the field is turned off again, the particles do not remain on their crystalline lattice but return to the translationally disordered (and nearly arrested) phase. This serves as experimental evidence that the induced crystalline state is *not* the equilibrium phase but that it is the glass-like amorphous phase that has lower free energy. This finding is supported with computer simulations of soft rods interacting with simplified interactions but with the same competing tendencies. Furthermore, we observed experimentally strong hysteresis in the system when switching between the crystalline phase and the amorphous phase (Fig. 4), which is indicative of a first-order equilibrium phase transition. We have further clarified this point, by adding an additional sentence in the main paper, see line 220-221.

Regarding the quench speed, we performed similar experiments as shown in Fig. 4 but with much longer than the 4 min time intervals in between the measurement (results not shown here) as well as much faster quench rates (see SI Fig. 6). In all cases, we observed the same phases at the start and end of the quench procedure, supporting that these phases are independent of quench speed. We have added further clarification about this in the main paper, see line 239 – 243.

Fig 3 f: One of the g(r) lines is shifted, or? Stating this would be helpful.

In Fig. 3f, the g(r) line of the rotator glass-forming phase is indeed shifted upwards for clarity, this is added in the figure caption.

In lines around 208 of the main text, it is stated that the rotator glass re-formed upon decreasing the electric field. In the caption of Fig. 4 f the opposite is stated ('crystalline order still persisted'), and Fig 4f itself is inconclusive. The description needs to be corrected, and the Steinhard order measure (Fig 4i) should be discussed in order to quantify the difference between glass and crystal.

Based on the comment of the referee we changed the text in the caption of Fig. 4 for clarification. We have added in the caption that at zero field strength the system relaxed back to the amorphous glass-like phase (Fig. 4f). The remark 'crystalline order still persisted' was to highlight that the sample was still crystalline for field strength 45 V/m in the down ramp so we changed the text to highlight this comment applies only to panel *d* and *e*.
The fact that the phase in Fig. 4f is no longer in crystalline state can be inferred from the value of the average local hexagonal bond-order parameter which is < 0.4.
While the value of the average local hexagonal bond-order parameter in a perfect hexagonal lattice is 1.0, it is difficult to assign a clear threshold value for a crystal without assessment of the long-ranged order (i.e. bond-order orientation correlation function). Please note that in our case, because we needed to image the system in 3D with high enough frame-rate to follow the rotations of the particles, the view-of-view in Fig. 4 is limited, especially in the z-dimension, which is why we have used a 2D bond-order parameter as an approximation (clearly showing the difference between the phase with and without field, as well as the hysteresis). For a snapshot of the full structure and 3D analysis of the crystalline structure see Fig. 3 and SI Fig. 7, which was recorded at the same field strength as Fig. 4d (90 V/mm).

All (other) additions or modifications we have made are highlighted in blue in the manuscript, and text that has been removed is crossed out.

[1] R. Schilling and T. Scheidsteger, "Mode coupling approach to the ideal glass transition of molecular liquids: Linear molecules," Phys. Rev. E 56, 2932 (1997).
[2] S.-H. Chong and W. Kob, "Coupling and decoupling between translational and rotational dynamics in a supercooled molecular liquid," Phys. Rev. Lett. 102, 025702 (2009).
[3] S.-H. Chong, A. J. Moreno, F. Sciortino, and W. Kob, "Evidence for the weak

steric hindrance scenario in the supercooled-state reorientational dynamics,"
Phys. Rev. Lett. 94, 215701 (2005).