

# Non-monotonic temperature evolution of dynamic correlations in glass-forming liquids

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**The viscosity of glass-forming liquids increases by many orders of magnitude if their temperature is lowered by a mere factor of 2–3. Recent studies suggest that this widespread phenomenon is accompanied by spatially heterogeneous dynamics, and a growing dynamic correlation length quantifying the extent of correlated particle motion. Here we use a novel numerical method to detect and quantify spatial correlations that reveal a surprising non-monotonic temperature evolution of spatial dynamical correlations, accompanied by a second length scale that grows monotonically and has a very different nature. Our results directly unveil a dramatic qualitative change in atomic motions near the mode-coupling crossover temperature, which involves no fitting or indirect theoretical interpretation. These findings impose severe new constraints on the theoretical description of the glass transition, and open several research perspectives, in particular for experiments, to confirm and quantify our observations in real materials.**

More than forty years ago Adam and Gibbs<sup>1</sup> put forward the seminal idea that the relaxation dynamics of highly viscous liquids occurs through ‘cooperatively relaxing regions’. Their theory suggested that particle motion occurs in a collective manner in localized domains<sup>1–3</sup>, whose typical size is related to the entropy of the systems and increases with decreasing temperature. This result implied that the relaxation mechanism is controlled by a unique length scale of thermodynamic origin with a direct signature in the dynamics. This approach regained momentum in the 1990s, when novel experimental techniques and large-scale computer simulations established the presence of dynamical heterogeneities, that is, localized regions where dynamics is significantly different from the average<sup>4–8</sup>, although these observations can also be interpreted in terms of a purely dynamical phenomenon<sup>9</sup>.

A qualitatively similar, but much more detailed, theoretical description is obtained within the framework of the random first order transition (RFOT) theory<sup>10</sup>. Within this approach, there exists an ideal glass transition that underlies glass formation, with an associated diverging correlation length scale of entropic origin, related to the existence of a large number of long-lived metastable states. At very low temperatures, the glass-former is described as a ‘mosaic’ of correlated domains that rearrange in a thermally activated, collective manner, such that static and dynamic correlations coincide and grow with the viscosity<sup>11</sup>. However, models with an RFOT (mainly mean-field-like models) also exhibit a ‘spinodal’ singularity at a higher temperature,  $T_c$ , at which metastability is lost and therefore the mosaic picture is no longer useful<sup>10,12</sup>. Thus, above  $T_c$ , a different approach must be used and it is found that the dynamics within mean-field models<sup>13</sup> share profound similarities with the one predicted from mode-coupling theory<sup>14</sup>, where  $T_c$  corresponds to a dynamic critical point associated with a diverging dynamical correlation length<sup>15</sup>. Thus, even at the theoretical level, the physics around  $T_c$  remains ‘mysterious’<sup>16</sup>: How can a dynamical correlation length diverge at two distinct temperatures? The mystery deepens in finite dimensions, for which the mode-coupling singularity is cut off and its existence can be inferred only from fitting relaxation data<sup>14</sup>, a procedure that is prone to criticism. For this reason, the

physical relevance of the ‘avoided’ singularity at  $T_c$  has remained the subject of debate.

Progress is also slow because experiments on molecular systems do not have sufficient resolution to follow atomic motions over long times<sup>4</sup>, and numerical simulations often cannot access low enough temperatures to make definite statements on the size and nature of dynamic heterogeneities (in fact there are so far no numerical studies on the dynamical heterogeneities in equilibrium conditions below  $T_c$ ). At present, most direct measurements<sup>5</sup> seem to indicate that the dynamical correlation length increases from 1–2 particle diameters at moderately supercooled temperatures to 5–10 diameters close to the glass transition temperature, but the interpretation of the experimental data is often rather difficult<sup>8</sup>. In this article we show that the use of a new methodology to characterize bulk dynamic correlations reveals details of their temperature evolution, which were not observed in previous work.

As well as a dynamical length scale, evidence has also been found for an increase of static correlations. However, this information is not captured by standard two-point correlation functions. Recent work has, for instance, suggested the growth of locally favoured geometric structures in some model systems<sup>17,18</sup>, but these methods are not easily generalized to different glass-formers. One possibility to tackle this problem involves using point-to-set correlations, which are an elegant, general method to capture the multi-point static correlations which might characterize the non-trivial structure of viscous liquids<sup>19</sup>. The conceptual idea is to ‘pin’ the position of a number of particles (the ‘set’) in an equilibrated configuration of the fluid, and to measure how the position of the remaining particles is affected. It has recently been argued that in the geometry in which particles outside a spherical cavity are pinned, this point-to-set correlation should detect the typical domain size of the RFOT mosaic state<sup>20</sup>. Numerical simulations qualitatively confirmed the growth of point-to-set correlations in this particular geometry<sup>21</sup>. However, the connection to dynamic correlations and the precise temperature dependence of the various length scales were not studied, and these results did not resolve the ‘mystery’<sup>16</sup> of the  $T_c$  crossover.

Inspired by previous work on confined fluids<sup>22,23</sup>, we have generalized the idea of a point-to-set correlation to a novel geometry. We pin particles in a semi-infinite space and detect the

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resulting effect on the other half-space. The principal advantage is that we can measure simultaneously the static and dynamic profiles induced by the frozen wall. Furthermore, we are able to perform simulations from the high-temperature liquid down to and below  $T_c$  with a realistic molecular dynamics, thus allowing us to resolve simultaneously multi-point static and dynamic correlations in a very broad temperature regime encompassing the (hypothetical) mode-coupling crossover.

We study a binary mixture of quasi-hard spheres<sup>24</sup>, as described in the Methods. The fluid is equilibrated by means of standard molecular dynamics using periodic boundary conditions in all three directions. To simulate particles pinned within a semi-infinite space, with  $z < 0$ , it is enough to freeze at an arbitrary time  $t = 0$  the position of all particles within a slice of thickness  $d_{\text{wall}} = 1.4\sigma$  which is perpendicular to the  $z$ -axis. These particles form our ‘set’. Because we use periodic boundary conditions, we work with a very large system size in the  $z$ -direction, ensuring that bulk behaviour is recovered at the centre of the simulation box (that is, the replicated walls do not interfere with each other).

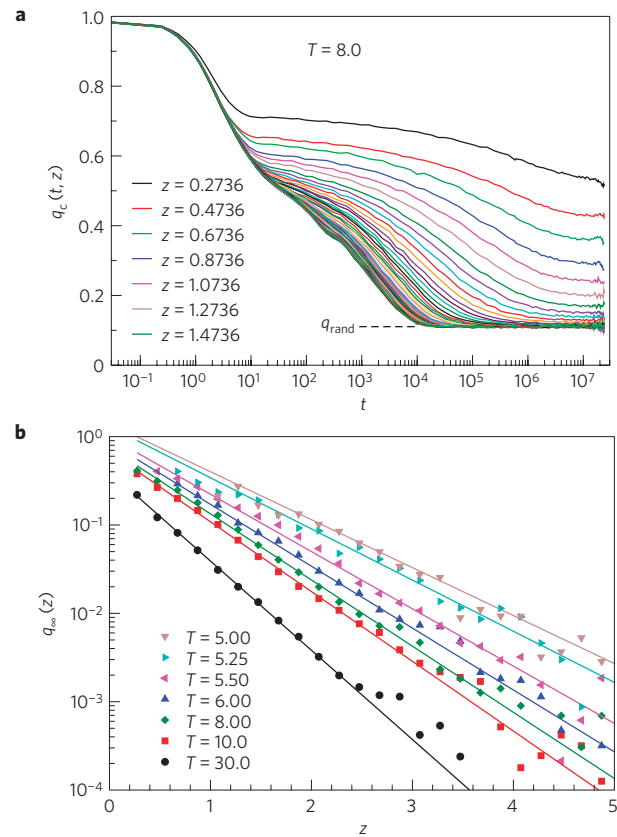
To properly measure a point-to-set correlation it is crucial that the frozen walls have the same structure as the equilibrated liquid at temperature  $T$ , such that the average static properties of the confined liquid are unperturbed<sup>19,22</sup> (see also Supplementary Information). We have measured to what extent (in  $z$ ) the wall influences the static local density field and its dynamics, giving us independent access to static and dynamic correlation length scales. Note that within RFOT theory, the spatial extent of the static profile near a wall is not directly controlled by the mosaic length scale<sup>12</sup>, and a comparison with results obtained with a spherical cavity<sup>21</sup> is not straightforward.

A convenient observable to characterize the influence of the wall is the overlap profile  $q_c(t, z)$ , defined as follows<sup>21</sup>. We discretize space into small cubic boxes of linear size  $\delta \approx 0.55\sigma$ , and define  $n_i(t) = 1$  if box  $i$  is occupied by at least one particle at time  $t$ , and  $n_i(t) = 0$  if not. The overlap profile in the  $z$  direction with respect to the template configuration at time  $t = 0$  is

$$q_c(t, z) = \left[ \frac{\sum_{i(z)} \langle n_i(t) n_i(0) \rangle}{\sum_{i(z)} \langle n_i(0) \rangle} \right]_{\text{wall}} \quad (1)$$

where the sums run over all boxes at distance  $z$  from the wall,  $\langle \dots \rangle$  is the usual thermal average, and  $[\dots]_{\text{wall}}$  is a further average over independent wall realizations. Thus  $q_c(t, z)$  quantifies the similarity of particle configurations separated by a time  $t$  at distance  $z$ , and, by construction,  $q_c(t = 0, z) = 1$ , for all  $z$ . We have also studied  $q_s(t, z)$ , the single particle version of equation (1), obtained by requiring that the box  $i$  is occupied at times 0 and  $t$  by the same particle. We find no relevant difference between these two correlation functions as far as time dependence is concerned.

In Fig. 1a we show the time dependence of  $q_c(t, z)$  at  $T = 8.0$  for different values of  $z$ . For large  $z$  (leftmost curves) the correlators become independent of  $z$  and represent the bulk behaviour. The presence of a shoulder at intermediate times reflects the usual cage motion of particles observed in glassy systems<sup>3</sup>. In the long-time limit,  $t \rightarrow \infty$ , the correlator decays to  $q_{\text{rand}} = 0.110595$ , the probability that a box is occupied, a quantity we measured with high precision from bulk simulations. With decreasing  $z$ , the height of the plateau at intermediate times increases and the time required to reach it decreases. The final decay is much slower near the wall than in the bulk, showing that the  $\alpha$ -relaxation is strongly affected by the frozen wall. Furthermore the long-time limit of the overlap increases from its trivial value,  $q_c(t \rightarrow \infty, z) > q_{\text{rand}}$ , showing that sufficiently close to the wall, the density cannot freely fluctuate. (See Supplementary Information for an illustration.) Thus, the set of frozen particles with  $z < 0$  influences the position of the liquid particles at  $z > 0$  over a non-trivial static length scale. Finally, Fig. 1a



**Figure 1 | Characterization of the static and dynamic properties of the system.** **a**, Time dependence of the overlap  $q_c(t, z)$ , equation (1), for  $T = 8.0$  and various values of  $z$ , increasing from  $z = 0.2736$  (near the wall, rightmost curve) by increments of  $0.2$ . The leftmost curve represents the bulk behaviour. **b**,  $z$ -dependence of the non-trivial part of the static overlap  $q_\infty(z)$  for different temperatures (symbols). The solid lines are fits with the exponential given in equation (3).

shows that there exists a range of  $z$  values for which the long-time limit of the overlap is the trivial bulk value, whereas the relaxation timescale is slower than the bulk. This directly shows, with no further analysis, that dynamic correlations have a longer range than static ones, as we confirm below.

To quantify these observations, we fit the final decay of  $q_c(t, z)$  to the stretched exponential form

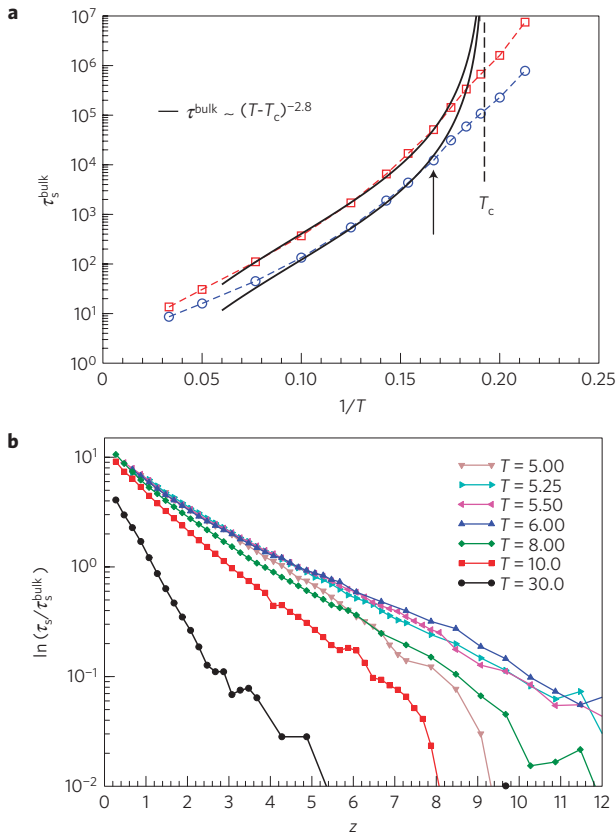
$$q_c(t, z) - q_{\text{rand}} = A \exp[-(t/\tau)^\beta] + q_\infty \quad (2)$$

where  $A$ ,  $\tau$ ,  $\beta$  and  $q_\infty$  are fitted for each  $z$ . The profile of the static overlap,  $q_\infty(z)$ , measures how far from the wall density fluctuations are correlated, whereas  $\tau(z)$  measures to what extent dynamics is affected. We find that equation (2) also describes the single particle overlap,  $q_s(t, z)$ , well with the obvious difference that  $q_s(t \rightarrow \infty, z) = 0$ , because eventually all particles leave the box that they occupy at  $t = 0$ . Thus, we obtain a second, ‘self’ dynamic profile from the study of  $q_s(t, z)$ .

In Fig. 1b, we show the temperature evolution of the static overlap profiles  $q_\infty(z)$ . The semi-log plot indicates these data could be described using an exponential decay<sup>25</sup>

$$q_\infty(z) = B \exp(-z/\xi^{\text{stat}}) \quad (3)$$

which allows us to define a static point-to-set correlation length scale  $\xi^{\text{stat}}(T)$ . From these data it is clear that  $\xi^{\text{stat}}$  grows when temperature decreases, a result in good qualitative agreement



**Figure 2 | Relaxation time of the bulk and confined system.** **a**, Temperature evolution of bulk relaxation time for large (top) and small (bottom) particles. Solid lines represent a power-law fit with  $T_c = 5.2$  (dashed line), the arrow indicates  $T = 6.0$ , where deviations from the fit appear. **b**,  $z$ -dependence of the relaxation time  $\tau_s(z, T)$  at various temperatures. Note the non-monotonic  $T$ -dependence at intermediate and large  $z$ .

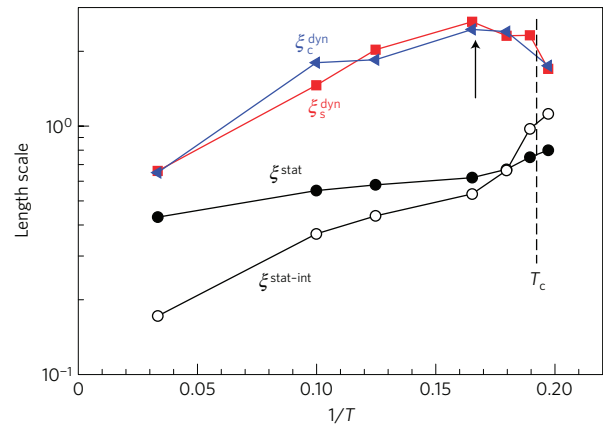
with previous work<sup>21</sup> using a very different geometry. Notice that  $B(T)$  also changes rapidly with  $T$ , which suggests that defining  $\xi^{\text{stat-int}} \equiv B(T)\xi^{\text{stat}}$  would provide a convenient estimate of the integrated profile,  $\xi^{\text{stat-int}} \approx \int_0^\infty q_\infty(z) dz$ .

We now analyse the dynamic profiles. To take into account the fact that the amplitude and stretching of the time-dependent correlations evolve with  $z$  (see Fig. 1a) we have calculated the area under the correlators  $q_c(t, z)$  and  $q_s(t, z)$ , taking into account only the secondary, slowly relaxing part. We denote the resulting times by  $\tau_c(z)$  and  $\tau_s(z)$ , respectively. Previous studies<sup>22</sup> have suggested that for large  $z$  the  $z$ -dependence of  $\tau_s(z)$  can be well described by an exponential functional form,

$$\log(\tau_s) = \log(\tau_s^{\text{bulk}}) + B_s \exp(-z/\xi_s^{\text{dyn}}) \quad (4)$$

where  $B_s(T)$  and, more importantly, the dynamic length scale,  $\xi_s^{\text{dyn}}(T)$ , are adjusted for each  $T$ . The bulk relaxation time  $\tau_s^{\text{bulk}}(T)$  is measured independently with very high precision (see Fig. 2a). Using a power law fit inspired by mode-coupling theory<sup>14</sup>,  $\tau_s^{\text{bulk}}(T) \sim (T - T_c)^{-\nu}$ , we obtain  $T_c \approx 5.2$ , but deviations from the algebraic fit appear above  $T_c$  near  $T = 6.0$  (see Fig. 2a and Supplementary Information for a discussion of this fit).

In Fig. 2b we show that the data at large  $z$  can indeed be fitted well by the ansatz given by equation (4). We have found similar behaviour for  $\tau_c(z)$ , providing us with a second dynamic correlation length scale,  $\xi_c^{\text{dyn}}$ . For high temperatures equation (4) describes the data well over the entire range of distances  $z$ . For intermediate and low temperatures we see the development of a



**Figure 3 | Temperature dependence of static and dynamic length scales identified in this work.** The arrow at  $T = 6.0$  and the dashed line at  $T_c = 5.2$  are as in Fig. 2. Dynamic length scales exhibit a non-monotonic behaviour with a maximum at  $T = 6.0$ , whereas static length scales increase modestly above  $T_c$ .

curvature in a semi-log plot, indicating deviations at small  $z$  from the simple exponential dependence. This might indicate, although very indirectly, the appearance of more than one relaxation process for the relaxation dynamics.

A remarkable behaviour occurs at intermediate and large distances, which has, to our knowledge, previously remained undetected. The dynamic profiles exhibit a striking non-monotonic evolution with temperature. A close inspection of Fig. 2b shows that the dynamic profiles extend to increasingly longer distances when temperature decreases from  $T = 30.0$  down to  $T = 6.0$ , but become shorter-ranged when  $T$  is decreased further, down to  $T = 5.5$ ,  $T = 5.25$  and then  $T = 5.0$ . The maximum occurs near  $T = 6.0$ , which is also the temperature at which deviations from mode-coupling fits appear (see Fig. 2a).

We have carefully checked that this behaviour is not a result of our numerical analysis. A direct visual inspection of the time correlations functions,  $q_s(z, t)$ , shows that the spread of the curves in the slow decay has a maximum at  $T = 6.0$ , so that the non-monotonic temperature behaviour in Fig. 2a is not an artefact of our fits, but is a genuine effect (see Supplementary Fig. SM-2). Furthermore, we found very similar results for the collective relaxation time,  $\tau_c(z, T)$ , which further shows that this non-monotonic behaviour does not sensitively depend on the considered observable. Thus, these results give us direct evidence that the relaxation processes responsible for spatial dynamic correlations have a non-monotonic temperature behaviour. To our knowledge, all previous numerical and experimental studies of spatially heterogeneous dynamics have reported spatial correlations which grow as the temperature is decreased and dynamics slows down<sup>4-8,18</sup>.

In Fig. 3 we summarize the temperature dependence of the static and dynamic length scales identified above. The static length scales show a modest but steady and monotonic growth with decreasing temperature, which seems to become more pronounced below  $T \approx 6.0$ . These are natural findings from the RFOT theory perspective<sup>10,12,16</sup>, in the sense that static correlations should only become prominent below  $T_c$ . We also include in Fig. 3 the dynamic length scales, which have a striking local maximum near  $T = 6.0$ . A comparison with Fig. 2a strongly suggests that we should interpret this maximum in the context of RFOT theory, in which a dynamic critical point at  $T_c$  exists in the mean-field limit (but which is avoided in finite dimensions), whereas activated dynamics governed by growing static correlations appears at low temperatures. Using RFOT theory, Stevenson *et al.* have suggested that around  $T_c$  the cooperative domains should indeed change shape, in that they have an open structure above  $T_c$  and a more

compact structure below  $T_c$  (ref 26). Our findings may be viewed as an indirect confirmation of this scenario. Although a gradual change from ‘flow-like’ to ‘hopping’ motion was often invoked in the past<sup>14</sup>, mainly to rationalize the successes and failures of the mode-coupling theory, our results provide very direct, microscopic evidence of a change of relaxation mechanism, which involves no theoretical fitting or indirect interpretation.

Although the results presented here have been obtained for a system in the presence of pinned disorder, we emphasize that they reflect the behaviour of the liquid in the bulk, because the nature of the boundary condition does not affect averaged static properties. No non-monotonic dynamic length scale has been detected so far in bulk systems (leaving out systems that also show anomalies in their thermodynamics), but we think that this is related to the fact that previous measurements (such as a four-point correlation function  $\chi_4$ ; refs 4,5) only provide a coarse representation of spatial correlations, because they mainly probe the total number of ‘fast relaxing particles’ and not the details of the shape of the relaxing regions<sup>5</sup>. Therefore the present results should not be taken as a contradiction to previous experiments and simulations, but as a new insight into the relaxation mechanism. We hope that in the future new experimental techniques will allow the detection of the non-monotonic  $T$ -dependence of  $\xi^{\text{dyn}}$  also in real molecular systems.

If we naively extrapolate our results to lower temperatures, we find a temperature below which static correlations become longer-ranged than dynamic ones, a situation which is physically not very meaningful. Thus we are led to speculate that at much lower temperatures, dynamic length scales should exhibit an upturn, and perhaps become slaved to the static ones, as in the Adam–Gibbs picture<sup>1</sup> and the scaling regime of RFOT theory<sup>10</sup>. However, studying this final regime numerically is at present too difficult. We suggest that experimental work is needed to resolve these issues further. Our study also suggests that investigations of confined systems should be revisited in both simulations and experiments, and the mode-coupling crossover studied more extensively in glass-formers with different fragility. However, because the model investigated here has no unusual features regarding the relaxation dynamics<sup>24</sup>, we expect our results to apply also to other simple models such as hard spheres, Lennard-Jones-like systems, or soft spheres.

## Methods

We study an equimolar binary mixture of harmonic spheres<sup>24</sup> with diameter ratio 1.4, and interactions between particle  $i$  and  $j$  given by

$$V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{\epsilon}{2} (1 - |\mathbf{r}_i - \mathbf{r}_j|/\sigma_{ij}^2) \quad \text{if } |\mathbf{r}_i - \mathbf{r}_j| < \sigma_{ij}$$

where  $\sigma_{11} \equiv \sigma$  is the unit of length,  $\sigma_{12} = 1.2$ , and  $\sigma_{22} = 1.4$ . The total number of particles is 4,320 and all of them have the same mass  $m$ . Time is expressed in units of  $\sqrt{m\sigma^2/\epsilon}$  and temperature in units of  $10^{-4}\epsilon$ , setting the Boltzmann constant  $k_B = 1.0$ . We have used a rectangular box of size  $L_x = L_y = 13.68$  and  $L_z = 34.2$ , yielding a number density  $\rho = 0.6749715$ . This system size is sufficiently large to avoid finite-size effects. The equations of motion have been integrated with the velocity form of the Verlet algorithm. The longest runs extended over 830 million time steps, which took about 6 weeks of CPU time on a high-end processor. To improve the statistics of the results we have averaged over 10–30 independent walls. The total amount of computer time to obtain the described results was therefore around 7 years. In practice, to prevent particles from penetrating into the frozen half-space, we introduced an infinitely hard wall at the two surfaces of the frozen slice, and have checked that this frozen geometry has negligible influence on the structure of the fluid. (See also Supplementary Information.) Note that here we are investigating a dynamical equilibrium, that is, all fluid particles can leave their initial positions and explore the whole confined space, thus ensuring thermodynamic equilibrium conditions.

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## Author contributions

L.B., W.K. and S.R.-V. contributed to the computer simulations, the analysis of the data, and the writing of the paper.

## Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on [www.nature.com/naturephysics](http://www.nature.com/naturephysics). Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to W.K.