Spontaneous Symmetry Breaking in 2D: Kibble-Zurek Mechanism in Temperature Quenched Colloidal Monolayers

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The Kibble-Zurek mechanism describes the formation of topological defects during spontaneous symmetry breaking for quite different systems. Shortly after the big bang, the isotropy of the Higgs-field is broken during the expansion and cooling of the universe. Kibble proposed the formation of monopoles, strings, and membranes in the Higgs field since the phase of the symmetry broken field can not switch globally to gain the same value everywhere in space. Zurek pointed out that the same mechanism is relevant for second order phase transitions in condensed matter systems. Every finite cooling rate induces the system to fall out of equilibrium which is due to the critical slowing down of order parameter fluctuations: the correlation time diverges and the symmetry of the system can not change globally but incorporates defects between different domains. Depending on the cooling rate the heterogeneous order parameter pattern are a fingerprint of critical fluctuations. In the present manuscript we show that a monolayer of superparamagnetic colloidal particles is ideally suited to investigate such phenomena. In thermal equilibrium the system undergoes continuous phase transitions according KTHNY-theory. If cooled rapidly across the melting temperature the final state is a polycrystal. We show, that the observations can not be explained with nucleation of a supercooled fluid but is compatible with the Kibble-Zurek mechanism.

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The Kibble-Zurek mechanism is a beautiful example, how a hypothesis is strengthened if the underlying concept is applicable at completely different scales. Based on spontaneous symmetry breaking, which is relevant at cosmic [1], atomistic (including suprafluids) [2–4], and elementary particle scale [5, 6], the Kibble-Zurek mechanism describes domain and defect formation in the symmetry broken phase.

In big bang theory, the isotropy of a n-component scalar Higgs-field $\Phi_n$ is broken during the expansion and cooling of the universe. Regions in space which are separated by causality can not gain the same phase of the symmetry broken field a priori. The formation of membranes, separating the Higgs fields with different phases [7], strings [8, 9] and monopoles [10, 11] is the consequence [1] [12]. Inflation [13, 14], recently supported by b-mode polarization of the cosmic background radiation (the BICEP2 experiment) [15], explains why such defects are so dilute, that they are not observed within the visible horizon of the universe. A frequently used (but not very precise) analogy is the formation of domains separated by grain boundaries in a ferromagnet below the Curie-temperature. The analogy is not precise since the ground state (or true vacuum) of the Higgs field would be a mono-domain whereas a ferromagnet has to be poly-domain to reduce the macroscopic magnetic energy. The standard Higgs field order parameter expansion is visualized with the 'Mexican-Sombrero' such being compatible with second order phase transition. To slow down the transition (to dilute monopoles and to solve the flatness problem in cosmology [17]) a dip in the central peak (false vacuum) was postulated [1] [13] in the first models of inflation. Due to the dip the 'supercooled' Higgs-field is separated with a finite barrier from the ground state, compatible with a first order scenario. Hence defects easily arise during the nucleation of grains of differently oriented phases being separated by causality.

Zurek pointed out that spontaneous symmetry braking mediated by critical fluctuations of second order phase transitions will equally lead to topological defects in condensed matter physics [4]. While a scalar order parameter (or one component Higgs field $\Phi_1$) can only serve grain boundaries as defects (compare e.g. an Ising model), two component (or complex) order parameters $\Phi_2$ offers the possibility to investigate membranes, strings and monopoles as topological defects depending on the homotopy groups $\mathbb{Z}$ [18]. Examples are liquid crystals and superfluid $^4\text{He}$ and Zurek discussed finite cooling rates [19] as well as instantaneous quenches [20]. For the latter the system has to fall out of equilibrium due to the critical slowing down of order parameter fluctuations close to the transition temperature which is true for every finite but nonzero cooling rate. The symmetry of the order parameter can not change globally since the correlation time diverges. The role of the causality is incurred by the maximum velocity for separated regions to communicate. In condensed matter systems this is the sound velocity (or second sound in superfluid $^4\text{He}$ defining a 'sonic horizon'. The order parameter pattern at the so called 'fall out time' serves as a fingerprint of the frozen out critical fluctuations with well defined correlation length. After the fall out time, the broken symmetry phase will grow on expense of the residual high symmetry phase. The domain size at the fall out time is predicted to grow algebraically as function of inverse cooling rate [19].

Experiments have been done in $^4\text{He}$ for the Lambda-
The large density is due to the fact that the polystyrene beads are doped with iron oxide nano-particles leading to super-paramagnetic behavior of the colloids. After sedimentation particles are arranged in a monolayer at the planar and horizontal water-air interface of the droplet and hence form an ideal 2D system. Particles are small enough to perform Brownian motion but large enough to be monitored with video-microscopy. An external magnetic field \( H \) perpendicular to the water-air interface induces a magnetic moment in each bead (parallel to the applied field) leading to repulsive dipole-dipole interaction between all particles. We use the dimensionless control parameter \( \Gamma \) to characterize this interaction strength. \( \Gamma \) is given by the ratio of dipolar magnetic energy to thermal energy

\[
\Gamma = \frac{\mu_0 (\chi H)^2 (\pi \rho)^{3/2}}{k_B T} \propto T^{-1}
\]

and thus can be regarded as an inverse system temperature. The state of the system in thermal equilibrium - liquid, hexatic, or solid - is solely defined by the strength of the magnetic field \( H \) since the temperature \( T \), the 2D particle density \( \rho \) and the magnetic susceptibility per bead \( \chi \) are kept constant experimentally. In these units the inverse melting temperature (crystalline - hexatic) is at about \( \Gamma_m = 60 \) and the transition from hexatic to isotropic at about \( \Gamma_i = 57 \) \[36\]. Since the system temperature is given by an outer field, enormous cooling rates are accessible compared to atomic systems. Based on a well equilibrated liquid system \[37\] at \( \Gamma \approx 15 \) we initiate a temperature jump with cooling rates up to \( d\Gamma/dt \approx 10^4 \text{ s}^{-1} \) into the crystalline region of the phase diagram \( \Gamma_M \geq 60 \). This temperature quench triggers the solidification within the whole monolayer (the heat transfer is NOT done through the surface of the material as usually in 3D condensed matter systems) and time scale of cooling is \( 10^5 \) faster compared to fastest intrinsic scales, e.g. the Brownian time \( \tau_B = 50 \text{ sec} \), particles need to diffuse the distance of their own diameter. An elaborate description of the experimental setup can be found in \[38\]. The field of view is \( 1160 \times 865 \ \mu m^2 \) in size and contains about 9000 colloids, the whole monolayer contains of \( \sim 300000 \) particles. Each temperature quench is repeated at least ten times to the same final value of the control parameter \( \Gamma_F \) with sufficient equilibration times in between. Fig. 1 shows the monolayer two minutes after the quench from deep in the fluid phase below the melting temperature (above the control parameter \( \Gamma_m \)), (see also movie bondordermagnitude.avi of the supplemental material). The color code of particle \( l \) at position \( \vec{r}_l \) is given by the magnitude \( m_l = m(\vec{r}_l) = \psi_l^* \psi_l \) of the local complex (six-folded) bond order field \( \psi_l = 1/N_j \sum_{k=1}^{N_j} e^{i 6\theta_{ki}} \) given by the \( N_j \) nearest neighbors. Blue particles have low bond orientational order \( m \approx 0 \) (high isotropic symmetry) and red particles indicate domains of broken symmetry \( m \approx 1 \) (high local sixfold order). Note that we in-

FIG. 1. Snapshot of the monolayer with symmetry broken domains, 120 s after a quench from \( \Gamma = 14 \) to a final coupling strength of \( \Gamma_F = 140 \). The color code (from blue \( m = 0 \) over yellow to red \( m = 1 \)) is given by the magnitude \( m \) of the local bond order parameter. Blue particles are disordered (low order = high symmetry phase) and red particles have large sixfold symmetry indicating domains with broken symmetry.
F orientational correlation length \( \xi \) magnitude of the local bond order field \( m \) particle itself and at least one nearest neighbor: i) The define a particle to be part of a symmetry broken do-
terium for locally broken symmetries what furthermore size of individual domains). Therefore we introduce a cri-
m\) is ‘short eyed’ and does not measure the size of individual domains). Therefore we introduce a cri-
ti on the average size of symmetry broken regions. In the supplemental material we show, that the stan-
d standard pair correlation length and the inverse defect den-
vestigate the orientational order and not the translational one, since a) we can hardly distinguish between ‘poly-
nership with zero cooling rates can not be realized during preparation. To analyze the dynamics of locally broken symmetry with respect to Kibble-Zurek mechanism, Figure 2 shows the increase of the bond-order correlation length \( \xi_6(t) \) for low supercooling (\( \Gamma_F = 63 \)), intermediate (\( \Gamma_F = 70 \) and 94), and deep supercooling (\( \Gamma_F = 140 \)). We use \( \xi_6 \) as a measure for the average size of symmetry broken regions. In the early state, we observe an exponential grow of the domain size followed by an algebraic one for all magnitudes of investigated supercoolings. The crossover from exponential to algebraic shifts so shorter times for deeper quenches. For the Lambda-transition of He^4 Zurek proposed an algebraic decrease of the inverse defect density after the quench [19]. For the XY-model a power-law increase of the correlation length with a small logarithmic correction is predicted [28] and in dusty plasma an algebraic increase was found [24]. Whether or not the exponential growing of average domain sizes in the early state is a fingerprint of exponentially diverging correlation length in KTHNY-melting can not be answered at present and should be topic of theoretical investigations. In Fig. 2 the cross-over appears for quite small values of the average correlation length (order of unity), even if individual domain sizes e.g. 120 sec after a quench to \( \Gamma_F = 140 \) are already extend over several particles (comparing Fig. 1 and Fig. 2 \( \xi_6 \) is ‘short eyed’ and does not measure the size of individual domains). Therefore we introduce a cri-
terium for locally broken symmetries what furthermore allows to follow and label individual domains in time: we define a particle to be part of a symmetry broken do-
 the mean size of the nuclei grows monotonically as function of time for all investigated quench depths. The average number of domains (Fig. 3 [left]) first increases but finally decreases in time. As can also been seen in the movies of the supplemental material, fewer but larger domains cover the space as function of time as expected. The maximum sifts to shorter times as function of quench depth - deeper supercooling drives the system faster to the solid variation in bond orientation \( \Delta \Theta = |\psi_k - \psi_l| \) of neighboring particles \( k \) and \( l \) must be less than 2.3° in real space (less than 14^° in sixfolded space). An elaborate discussion of criteria to define crystallinity in 2D on a local scale can be found in [41]. Simply connected domains of particles which fulfill all three criteria are merged to a local symmetry broken domain.

Figure 3 [left] shows the average number of local do-
variation in bond orientation \( \Delta \Theta = |\psi_k - \psi_l| \) of neighboring particles \( k \) and \( l \) must be less than 2.3° in real space (less than 14^° in sixfolded space). An elaborate discussion of criteria to define crystallinity in 2D on a local scale can be found in [41]. Simply connected domains of particles which fulfill all three criteria are merged to a local symmetry broken domain.

FIG. 2. Orientational correlation length as function of time in a log-log-plot for different quench depth. Shortly after the quench, the growing behavior is exponential and switches to algebraic later. The quench depth increases from top to bottom. Note the decreasing cross-over time (red arrows as guide for the eye) for deeper quenches.
After the fall out time, separating critical and classical Zurek mechanism leading to two different time regimes that defect annihilation will alter the classical Kibble-finite cooling rates, G. Biroli et al. have argued [42] that such fluctuations are suppressed in the vicinity of the transition if the domain size $\Delta A$ times the energy-density differences $\Delta \epsilon$ is less than $k_B T$. In equilibrium this is nothing but another argument for critical slowing down. In 2D systems it is well known that fluctuations play a major role. This is obviously the case not only in equilibrium but also in non-equilibrium situations.

In conclusion, we have investigated the Kibble-Zurek mechanism experimentally for a two-dimensional system with complex order parameter given by the local bond order director field. After a sudden quench we resolve two time regimes at an early state (followed by a third regime due to classical coarse graining, see [40]). First, the bond order correlation length grows exponentially un-

FIG. 3. The left image shows the number of symmetry broken domains (SBD) and the average size of the domains (inset) as function of time for different quench depth (the label is valid for all four figures). The error bars are averages about 10 independent quenches with about 9000 particles in the field of view. Whereas the average size of the nuclei grows monotonically as expected, the number of symmetry broken domains first increases to a maximum but then decreases in favor of less but larger domains. The red arrows are a guide to the eye to identify the maxima. The right image shows the same data but plotted as fraction of symmetry broken area (crystallinity, which is implicitly a function of time). The curves almost superimpose as function of crystallinity being independent of the quench depth.

state. Note that the growing of domains starts immediately after the quench such that no lag time known from classical nucleation theory (CNT) is detectable. (Further discussion in the context of CNT can be found in [40].) Figure 3 [left] shows the same data but plotted as function of crystallinity $X$ instead of time. Here, we define crystallinity $X$ (increasing monotonically in time) as the fraction of particles belonging to a symmetry broken domain identified with the three criteria mentioned above. Interestingly all curves almost superimpose as function of crystallinity, re-scaling the time axis to an intrinsic system dependent parameter. Surprisingly, the position and height of average number of symmetry broken domains (in the context nucleation this is called the mosaicity) is independent of the quench depth. It appears when roughly 37% belong to symmetry broken domains. Comparing the maximum on the real time axis (red arrows in Fig. 3 [left]) and the cross-over time in Fig. 2 for different quench depth we propose the following scenario: After a quench, locally symmetry broken domains start to grow exponentially until about 37% of the space is covered. In our 2D system this marks a threshold where domains with different orientation (different phases of the symmetry broken field) start to touch. The following dynamics is dominated by the conversion of the yet untransformed regions of the high symmetry phase marked by an algebraic increase of the bond order correlation length. For finite cooling rates, G. Biroli et al. have argued [42] that defect annihilation will alter the classical Kibble-Zurek mechanism leading to two different time regimes after the fall out time, separating critical and classical coarse graining. In the supplemental material we show [10] that we can resolve the classical coarse graining after an instantaneous quench, too. Large domains grow on the expense of smaller ones with an algebraic increase of the bond-order correlation length with reduced exponent. The latter is due to grain boundary diffusion which was recently described for colloidal mono-layers [13, 44].

In the context of Kibble-Zurek-mechanism one would expect all individual grains to grow after the quench which is surprisingly only the case on average. In the supplemental material we show that the shrinking probability $p_s$ of individually labeled domains is always larger than the of growing probability $p_g$. This again rules out a) critical nucleation with a finite nucleation barrier and b) allows for back and forth fluctuations of the broken symmetry regions in 2D systems below the transition temperatures after a quench. Zurek has argued that such fluctuations are suppressed in the vicinity of the transition if the domain size $\Delta A$ times the energy-density differences $\Delta \epsilon$ is less than $k_B T$. In equilibrium this is nothing but another argument for critical slowing down. In 2D systems it is well known that fluctuations play a major role. This is obviously the case not only in equilibrium but also in non-equilibrium situations.
til roughly 40% of the area belongs to symmetry broken domains with random orientation. While Zurek proposed an algebraic growing for 3D systems, we suggest the exponential behavior being caused by the underlying exponential divergences in KTHNY-melting, being typical for 2D systems. In a second regime an algebraic behavior is observed until no high symmetry phase is left, except grain boundaries separating domains with different phase. The independence of the mosaicity strongly supports the Kibble-Zureck mechanism. We hope our work will stimulate theory and simulations to investigate the phenomena observed in phase transitions far from thermal equilibrium. Further studies in dusty plasma and colloidal mono-layers might shed light on differences and similarities of the Kibble-Zureck mechanism in 2D and 3D systems at sudden quenches or finite cooling rates.

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[36] The transition temperatures correspond to those given in [34, 39, 41]. Recent publications have slightly different values based on new determinations of the magnetic susceptibility of a new batch of particles [35].
[37] The equilibration time to gain a completely flat water/air interface without any gradient of particle number density within the plane is several weeks up to a few months.
[40] Further information can be found in the Supplemental Material
Two-dimensional dusty plasma and colloidal monolayers offer the possibility to investigate structure formation on single particle level. They are complementary in their single particle dynamics in that sense, that colloidal systems are over-damped due to the solvent whereas dusty plasma are not. Under equilibrium conditions this results in exponential relaxation after small local perturbations for colloidal systems whereas in dusty plasma oscillatory behaviour is possible. If the interaction between particles is determined by an outer field, both systems can be quenched almost instantaneously into different regions of the phase diagram. Instantaneously means extremely fast compared to intrinsic time scales which is usually given by the Brownian time, the time a particle need to diffuse it’s own diameter.

For our colloidal monolayer with super-paramagnetic interaction, the outer field is switched on timescales of about 5 ms whereas the Brownian time is of the order of 50 sec, four orders of magnitude larger. This way cooling rates are much larger in colloidal systems or dusty plasma compared to those being accessible in atomic systems. Structure formation and relaxation in dusty plasma has been studied in [1–3].

Peter Hartmann et al. have carefully studied the crystallization dynamics using the bond order orientational correlation length $\xi$, the standard pair correlation length $\xi_g$ and the inverse defect density $1/D$ as measures for the size of crystallites. As in our colloidal system, both correlation functions always decay exponentially and the correlation lengths grow monotonic in time. In [1] a crossover from algebraic to exponential behaviour for the inverse defect density. At the present stage we can not decide if the differences are due to different kinds of kinetics (ballistic in plasma versus Brownian in colloids) or if the exponential increase in time of correlation length and inverse defect density is due to the exponential divergences in KTHNY-melting. Note, that the dust plasma is reported not follow KTHNY-melting but seem to be closer to grain boundary induced melting [1]. The Kibble-Zurek mechanism on the other hand might explain the domain formation for cooling rates different from zero.

Fig. 2 from the main manuscript shows the orientational correlation length $\xi_g$. To complete the picture and to follow Hartmann et al. [1] we analyzed the standard pair correlation function

$$g_g(r) = \frac{1}{2\pi r \rho} \frac{1}{N} \sum_{i \neq j} \delta(r - r_{ij})$$

where $\rho$ is the 2D particle density. Fig. 1 shows the exponential decay of $|g_g(r,t) - 1|$ for different times after the quench. The correlation length $\xi_g(t)$ (left column) and the inverse defect density (right column) is plotted in Fig. 2 for different quench depth in our colloidal system. In all cases, the cross-over from exponential to algebraic is observed. The cross-over times do not match exactly but are of the same order. They show qualitatively identical behaviour, e.g. the decreasing cross-over time with increasing quench depth. Comparing Fig. 1 and Fig. 2 of the main manuscript, the correlation length $\xi_g$ at the cross-over time is still of the order of unity even if the symmetry broken domains are extended over several particles. The correlation length is ‘short eyed’ since it is averaged over all particles and especially at the cross over time 60% of the particles are still in the high symmetry phase. Therefore we introduce a criterion for symmetry broken domains as given in the main text and extensively
discussed in [4].

**LOCAL DOMAINS**

To repeat the criteria we note: individual particles are defined to be part of a symmetry broken domain if the following three conditions are fulfilled for the particle itself and at least one nearest neighbour:

- The magnitude of the local bond order field $m_{kl}$ must exceed 0.6 for both neighboring particles.
- The bond length deviation $\Delta|l_{kl}|$ of neighboring particles $k$ and $l$ is less than 10% of the average particle distance $l_o$.
- The variation in bond orientation $\Delta \Theta = |\psi_k - \psi_l|$ of neighboring particles $k$ and $l$ must be less than $2.3^\circ$ in real space (less than $14^\circ$ in sixfolded space).

The threshold values are defined in comparison with mono-crystalline and isotropic fluid phases under equilibrium conditions and the qualitative results are robust to (moderate) variations (about ±20%) of the threshold values. Simply connected domains of particles which fulfill all three criteria are merged to a crystalline cluster. Fig. 3 and the movie SBD.avi shows such domains. As a side remark: comparing our results with colloidal systems, where an attractive interaction triggers a diffusion limited aggregation from a dilute 'gas' [5, 6] and with simulations and phase field calculations [7, 8], no amorphous precursors (with increased local density) are found in our experiment, where purely repulsive interaction is present.

[FIG. 2. Correlation length $\xi$ from the pair correlation as function of time in a log-log-plot for different quench depth. Shortly after the quench, the growing behavior is exponential and switches to algebraic later. Note the decreasing cross-over time for deeper quenches.]
Crystal nucleation is one of the basic physical phenomena that govern the growth and the structure of crystalline state in three dimensions [9–23]. The most widely used concept, the Classical Nucleation Theory (CNT), attempts to describe this complex process by treating the nuclei as compact spheres that grow if their size exceeds a critical value [9–11]. This critical value is determined by a maximum in the free energy, where the energy gain in the volume $\sim r^2$ overcompensates the surface energy cost $\sim r^3$ of the nucleus. However, experiments on hard sphere colloidal systems [15, 16, 19], where individual particle interactions are sufficiently simple to be modeled theoretically differ from the predictions of critical nucleation theory. In more complex systems, the CNT calculation underestimates the nucleation rate by many orders of magnitude [24]. It is a priori not clear if Classical Nucleation Theory and the concept of supercooled fluids might be applicable for monolayers. Nevertheless, the energy gain in volume of the low symmetry nuclei can be translated into an energy gain of area in two dimensions. Similarly the 3D surface tension might be translated into a 2D line tension such that a critical nucleus size exist in 2D, too. Following Urs Gasser et al. [16] in a 3D colloidal ensemble, we label individual grains in time and compare the size (area) in consecutive time steps. This procedure is published in [? ] and only briefly summarized here. If the crystalline domains are identified for the whole duration of the experiment one can label the domain of consecutive time steps to follow their temporal behaviour. Cluster of time $t_i$ and $t_{i+1}$ are compared by investigating the overlap in area of cluster $A_j$ at $t_i$ with $B_k$ at time $t_{i+1}$. The index $j$ ranges from 1 to $N_t$, and $k$ ranges from 1 to $N_{t+1}$, where $N_t$ and $N_{t+1}$ are the numbers of cluster in the time steps $t_i$ and $t_{i+1}$.

- No passing of Cluster-label $A_j$ to $B_k$ if no overlap in areas exists in the following time step. Cluster $A_j$ has disappeared.
- If cluster $A_j$ has only overlap with one cluster $B_k$, this cluster will become the label of cluster $A_j$ in the previous time step.
- If more than one cluster $B_k$ has overlap with $A_j$, the cluster with the largest overlap in area will become the label of $A_j$.
- If there are cluster $B_k$ which did not get a label after all cluster $A_j$ of time step $t_i$ has run through, they will get a new label.

In Fig. 3 of the main manuscript, where the average size and number of symmetry broken domains is plotted, one can see that the nucleation starts immediately after the quench. Therefore, no lack time of critical nucleation is detectable. Additionally, with the parameters given above about 10% of the particles are identified having low symmetry (large local order) already before the quench, deep in the fluid phase at $\Gamma = 14$. Such domains consists of 2.7 particles on average and the lifetime of the domains is a few seconds. In the context of nucleation such cluster are usually interpreted as ‘precritical nuclei’. In the context of second order phase transitions, those fluctuations should be interpreted as local order parameter fluctuations and are the analogue to quantum or vacuum fluctuations of the Higgs field in the Kibble mechanism. The large amount (compared to 3D systems) of those ‘precritical nuclei’ (or order parameter fluctuations) is due to the fact that the preferred local symmetry in 2D is sixfold, both in the crystalline as well as fluid phase. If the criteria for symmetry broken domain particles are tightened, the amount of ‘precritical nuclei’ decreases but then a monocrystal in equilibrium is not detected as such any more. The latter is due to Mermin-Wagner fluctuations being typical for low dimensional systems [25].

The formation of a nucleus in 2D after a temperature quench is not a rare event and the critical nucleation barrier (if it exist at all) is very low. In this case one would expect all individual nuclei $\geq 2$ particles to grow after the quench which is surprisingly not the case. In Figure 4 the difference of growing $p_g$ and shrinking probability $p_s$ of nuclei is plotted for different time windows after a quench to $\Gamma_F = 93.5$ where $M$ is the size of the nucleus given by the number of the particles which belong to the cluster. The probability for shrinking and growing for individually labeled clusters of size $M$ is given by $p_{g/s} = N_{g/s}/N_M$ where $N_M$ is the number of clusters of size $M$ and $N_g$ or $N_s$ are the numbers of those clusters.
FIG. 4. The shrinking probability after all quenches ($\Gamma_F = 63, 94, 140$ is shown, $\Gamma_F = 70$ is not shown here) for a crystalline domain composed of $M$ particles is always larger than the growing probability. Unlike in 3D systems one can not determine a critical nucleus size on single particle level and hence 2D systems out of equilibrium can not be described with critical nucleation theory.

which are larger $M_r > M$ or smaller $M_r < M$ after a finite waiting time $\tau$.

For all time windows and nucleus sizes the probability of shrinking is larger than the probability of growing. This is true for all quench depths performed, close to melting ($\Gamma_F = 63$) as well as deep into the crystalline phase ($\Gamma_F = 140$). The waiting time was varied over almost two decades from $0.1 - 10$ sec and no qualitative differences were found. Obviously shrinking (often, but small areas) and growing (less often, but larger areas) is quite asymmetric and the solidification far from equilibrium is strongly dominated by fluctuations. Practically all grains which are present shortly after the quench disappear again and those domains which are present at late times were generated in between. Two mechanisms appear to be responsible for this. First, small grains dissolve completely into fluidlike particles and second, at a later stage, grains of intermediate size fluctuate strongly in orientation such that they disrupt into smaller subdomains (looking like Mermin-Wagner fluctuations on a local scale). Such subdomains frequently merge again but then the net contribution to the growing probability is typically zero, since one grain has grown but the other(s) has/have ‘disappeared’. Whereas the latter might be an artefact based on difficulties to define symmetry broken domains on a local scale in a (on average) sixfold background, the disappearance of local order in the early stage is completely unexpected. Interestingly the lifetime of symmetry broken domains shortly after the quench is again a few seconds and comparable to the lifetime of ‘subcritical nuclei’ in the isotropic phase before the quench. Altogether: the absence of a lack time, the large amount of ‘precritical nuclei’ and the dominating shrinking probability for individual grains indicates that the formation of a nucleus in 2D after a temperature quench is not a rare event and a critical nucleation barrier does not exist. Since the underlying equilibrium phase transition is continuous according KTHNY-theory, it is finally not to surprising that the concept of a supercooled fluid and classical nucleation does not fit to our system. This is the reason why we do not use the terminus ‘nuclei’ but ‘symmetry broken domain’ in the main manuscript. Furthermore the ‘subcritical nuclei’ in the isotropic face should be interpreted as local order-parameter fluctuations.

In the context of Kibble-Zurek mechanism the large shrinking probability for individual is still surprising: it indicates that fluctuations of high symmetry and symmetry broken phase is still allowed beyond the fall out time. This might be a special feature of 2D systems where the energy-density differences between high symmetry and symmetry broken phase seem to be small. Furthermore fluctuations in 2D are known to have dramatic effects on the phase behaviour already in equilibrium situations.

**COARSE GRAINING**

In Fig. 2 of the main manuscript and in Fig. 2 we showed the cross-over from exponential to algebraic growing of linear measures of the domain size averaged over at least ten independent quenches for each quench depth. The longest investigated times were $10$ min Fig. 5 we show the bond order correlation length $\xi_6$ of a single quench to a final system temperature $\Gamma_F = 153$ for up to $2$ h after the quench. On this time scale, a third regime is observable which again shows algebraic growing with reduced exponent. In this regime grain boundaries (given as chains of dislocation pairs) as the only high symmetry residuals separate symmetry broken domains with different orientation. The temporal evolution of the system is given by classical coarse graining mediated by grain boundary diffusion [26, 27] recently analyzed in colloidal monolayers.

FIG. 5. On longer time scales a third regime in the growing of the bond order correlation length can be observed. Here the whole sample is covered by symmetry broken domains, except the grain boundaries separating different domains. In this regime coarse graining due to grain boundary diffusion dominates.

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