

Supplemental Material for “Phase behavior and crystal nucleation of hard triangular prisms”

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This Supplementary Material includes additional information on the fluid–crystal order parameter discussed in the main paper, as well as the time evolutions of the local parameters of some additional nucleation events.

I. ORDER PARAMETER FOR FLUID–CRYSTAL CLASSIFICATION

In order to identify the crystal nuclei in our systems, we use an order parameter which classifies a particle as either fluid or crystal. In the main paper, we define an order parameter based on the positional ordering of a particle, and use this for the umbrella sampling. Here, we first provide some additional information to validate our choices in certain threshold values. Second, we show that an order parameter based on the orientational ordering results in very similar classifications for this system.

The order parameter used throughout this work is based on the 3-fold symmetric Ten Wolde bond¹ $d_3(i, j)$, which provides a measure for the 3-fold positional symmetry of a bond between particles i and j (see Eq. (9) of main paper). In Fig. S1a, we show the probability distribution of $d_3(i, j)$ for all pairs of neighboring particles inside a (metastable) fluid phase and a (thermal) honeycomb crystal. We clearly see that $d_3(i, j)$ has a very broad distribution in the fluid, whereas its distribution exhibits well-defined peaks near ± 1 in the crystal. We, therefore, chose to classify bonds with $|d_3(i, j)| > 0.7$ as crystal-like, and define the parameter ξ^d as the number of crystal-like bonds per particle. In Fig. S1b, we show the probability distribution of ξ^d . We clearly see that the fluid phase mostly contains particles with $\xi^d < 5$ and the crystal phase mostly contains particles with $\xi^d > 5$. Hence, we chose to classify a particle as crystal when $\xi^d \geq 5$.

Next, we define, in a similar fashion, an order parameter based on the orientational ordering of a particle. We base this order parameter on long-axis alignment of neighboring particles, which is captured by $(\hat{\mathbf{u}}_z^{(i)} \cdot \hat{\mathbf{u}}_z^{(j)})^2$. In Fig. S2a, we show the probability distribution of this value for a (metastable) fluid phase and a (thermal) crystal. The crystal phase has a sharp and well-defined peak at $(\hat{\mathbf{u}}_z^{(i)} \cdot \hat{\mathbf{u}}_z^{(j)})^2 \simeq 1$. We, therefore, chose to classify bonds between neighboring particles as crystal-like when $(\hat{\mathbf{u}}_z^{(i)} \cdot \hat{\mathbf{u}}_z^{(j)})^2 > 0.75$, and define the parameter ξ^u as the number of crystal-like bonds per particle. In Fig. S2b, we show the probability distribution of ξ^u . We clearly see that the fluid phase mostly contains particles with $\xi^u < 7$ and the crystal phase mostly contains particles with $\xi^u > 7$. Hence, we chose to classify a particle as crystal when $\xi^u \geq 7$.

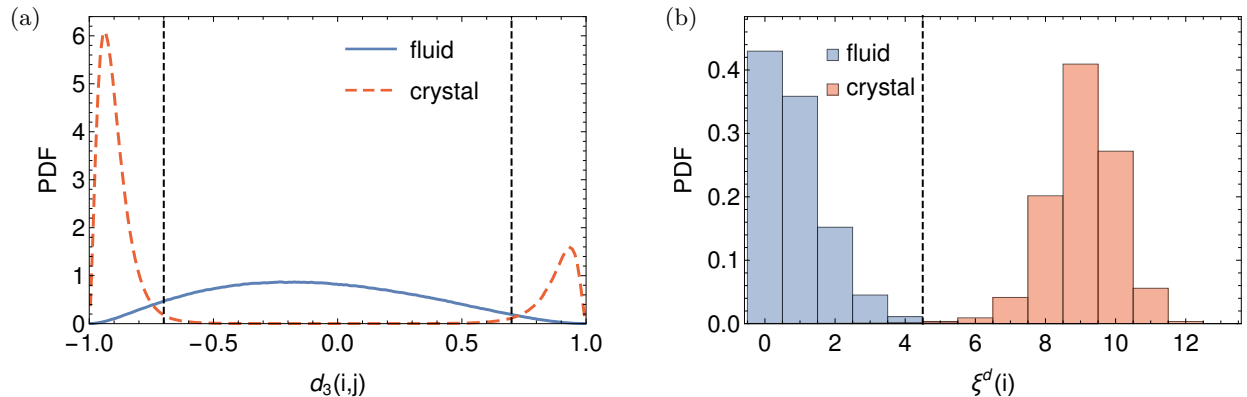


FIG. S1. Probability distribution of (a) the 3-fold symmetric Ten Wolde bond $d_3(i, j)$ and (b) the number of crystal-like bonds per particle (i.e. when $|d_3(i, j)| > d_c$) for the bulk fluid ($\eta = 0.501$) and the crystal ($\eta = 0.6344$) phases. The vertical dashed lines indicate the cutoff parameters $d_c = 0.7$ and $\xi_c^d = 5$.

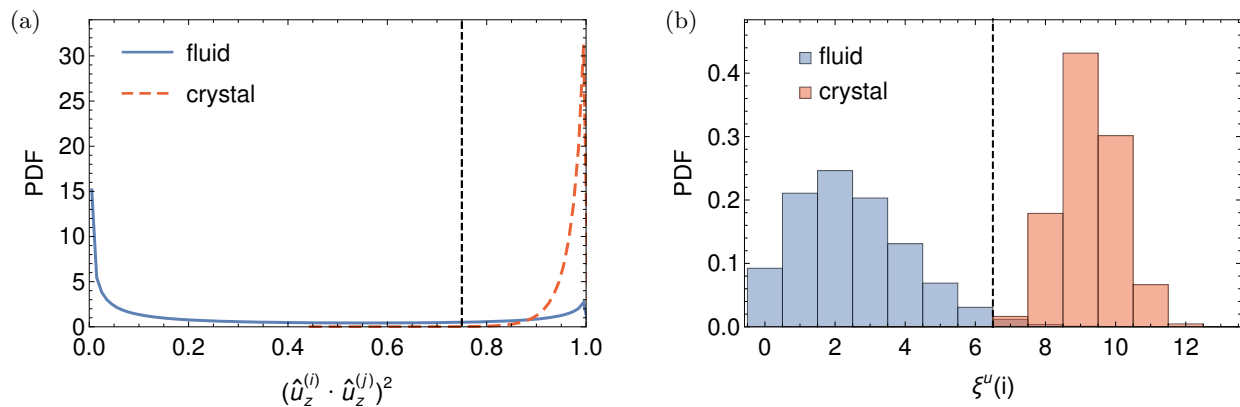


FIG. S2. Probability distribution of (a) the long-axis alignment $(\hat{\mathbf{u}}_z^{(i)} \cdot \hat{\mathbf{u}}_z^{(j)})^2$ and (b) the number of crystal-like bonds per particle (i.e. when $(\hat{\mathbf{u}}_z^{(i)} \cdot \hat{\mathbf{u}}_z^{(j)})^2 > u_c$) for the bulk fluid ($\eta = 0.501$) and the crystal ($\eta = 0.6344$) phases. The vertical dashed lines indicate the cutoff parameters $u_c = 0.75$ and $\xi_c^u = 7$.

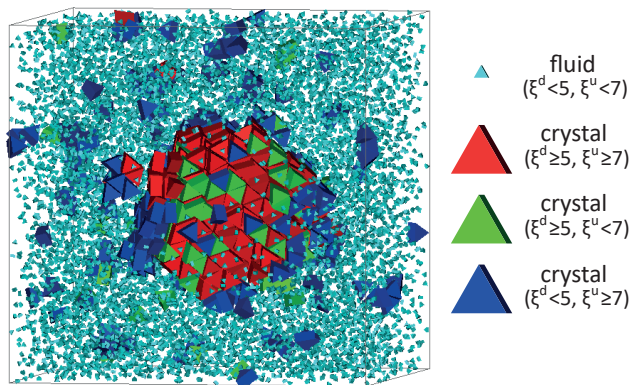


FIG. S3. Snapshot of a fluid containing a crystal nucleus. Fluid particles are displayed at a quarter of their actual size to make the nucleus visible. Particles classified as crystal by both positional ordering ($\xi^d \geq 5$) and orientational ordering ($\xi^u \geq 7$) are colored red, particles only classified as crystal by positional ordering are colored green, and particles only classified as crystal by orientational ordering are colored dark blue.

In order to compare both classifications, in Fig. S3 we show a snapshot of a system containing a crystal nucleus and color the particles according to their classification. Particles classified as crystal by both ξ^d and ξ^u are colored red, particles classified as crystal by ξ^d but not by ξ^u are colored green, and particles classified as crystal by ξ^u but not by ξ^d are colored dark blue. We clearly see that the majority of the nucleus is classified as crystal by both ξ^d and ξ^u . Only some surface particles are classified differently by ξ^d and ξ^u .

As a last remark, we want to stress that there are many more options for classifying particles as either crystal or fluid. One could also, e.g., use an order parameter which classifies particles based on a certain threshold for q_3 or S_2 . However, the choice of order parameter does not influence our results, as any reasonable choice for the order parameter will result in nucleation barriers with the same height².

II. ADDITIONAL ANALYSIS AND NUCLEATION EVENTS

In the main paper, we discuss our observations and results using two typical nucleation events. Here, we show for one of these events the time evolution of some additional bond orientational order parameters (BOPs), as well as the results on some additional nucleation events. As in the main paper, all figures show the average values of the local order parameters inside the spherical region coinciding with the birthplace of the crystal nucleus. In each figure, the vertical dashed line indicates the start of nucleation t_0 and the horizontal dashed lines indicate the reference values of that specific order parameter in the bulk crystal and fluid phases. Note that the left vertical axis of each figure is scaled in such a way that they all depict the same relative range with respect to these bulk values.

Figure S4 shows, for the event depicted in Fig. 8 of the main paper, the time evolution of some additional BOPs. As for the order parameters discussed in the main paper, we observe that all BOPs depicted in Fig. S4 increase simultaneously, and in a similar fashion, as soon as nucleation starts. That we can observe the simultaneous increase in these BOPs this clearly is quite astonishing, as the reference values of the bulk crystal and fluid phases for some of these BOPs differ only by $\sim 10\%$.

The remaining figures of this document show the time evolution of the local order parameters of three additional nucleation events. Figure S5 shows an event for $\eta = 0.505$ and Figs. S6 and S7 show two events for $\eta = 0.501$. As for the events in the main text, we observe a simultaneous and abrupt increase in all order parameters. Note that, for the event of Fig. S6, the initial nucleus largely melts before it resumes to grow again. However, as it resumes its growth at a slightly shifted location, the location \mathbf{r}_0 of the birthplace of the initial crystal nucleus no longer coincides with the center of mass of the growing nucleus. This causes the drop in the values of the local properties at later times (Fig. S6a1-d1). Nonetheless, the initial start of nucleation (Fig. S6a2-d2) behaves the same as for other nucleation events. Events like the one in Fig. S6 demonstrate why it is impractical to average the time evolution of multiple nucleation events together.

¹P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, *J. Chem. Phys.* **104**, 9932 (1996).

²L. Filion, M. Hermes, R. Ni, and M. Dijkstra, *J. Chem. Phys.* **133**, 244115 (2010).

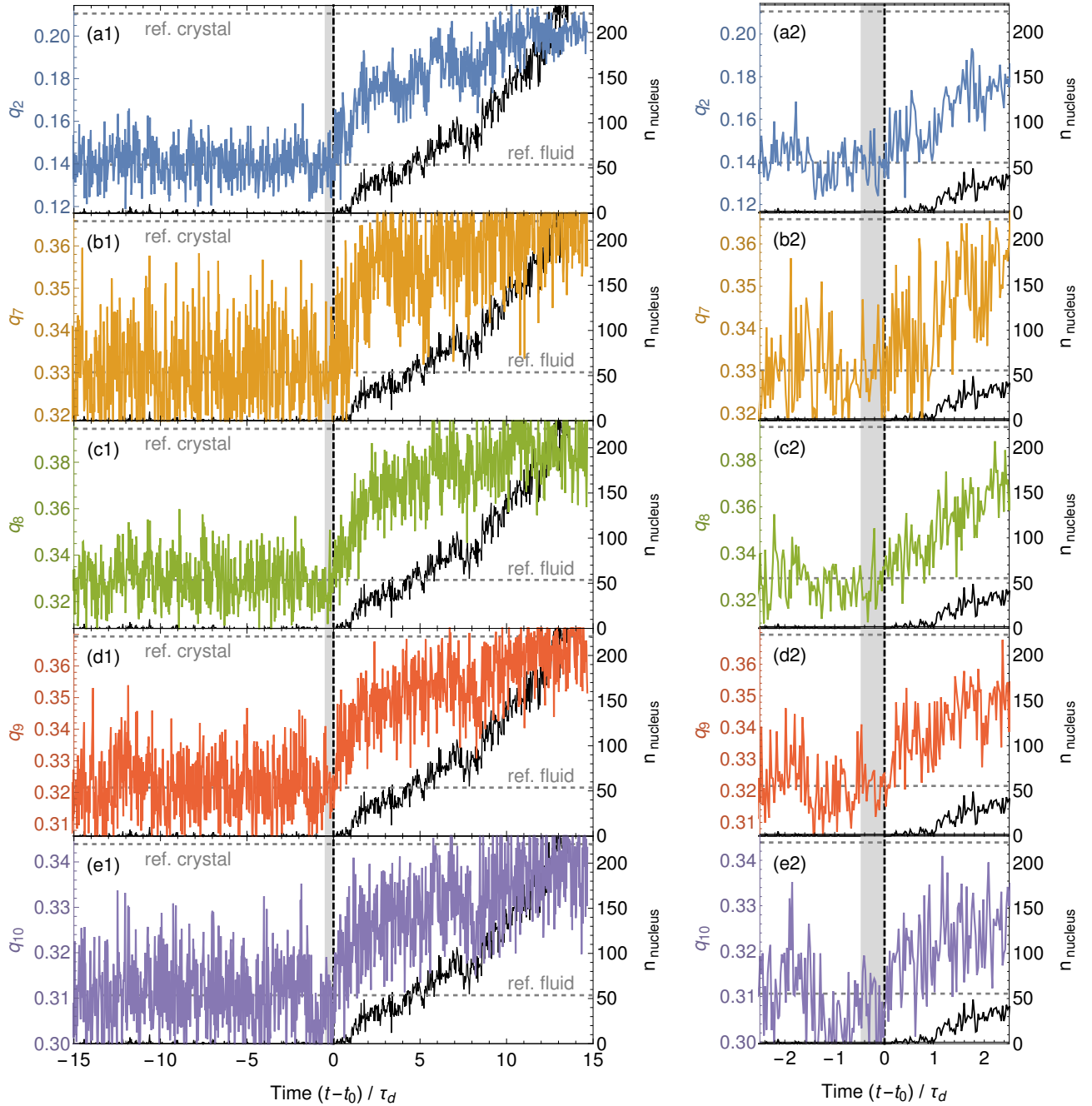


FIG. S4. For the same event as in Fig. 8 of the main paper ($\eta = 0.505$), the time evolution of some additional BOPs at the birthplace of the crystal nucleus, in (a) q_2 , (b) q_7 , (c) q_8 , (d) q_9 , and (e) q_{10} . The vertical dashed line in each figure indicates the start of nucleation t_0 , and the shaded area indicates the time window before t_0 for which $\text{ACF}(S_2) > 0.05$. The left panels, (a1-e1), show the evolution of the parameters over a long time interval, and the right panels, (a2-d2), show the same evolutions but now zoomed in on the short time interval around the start of nucleation. In each figure, the black line indicates the number of particles in the crystal nucleus. The horizontal dashed lines indicate the reference value of each parameter in the bulk fluid and crystal phases. The left vertical axis of each figure is scaled in such a way that they all depict the same relative range with respect to these bulk values.

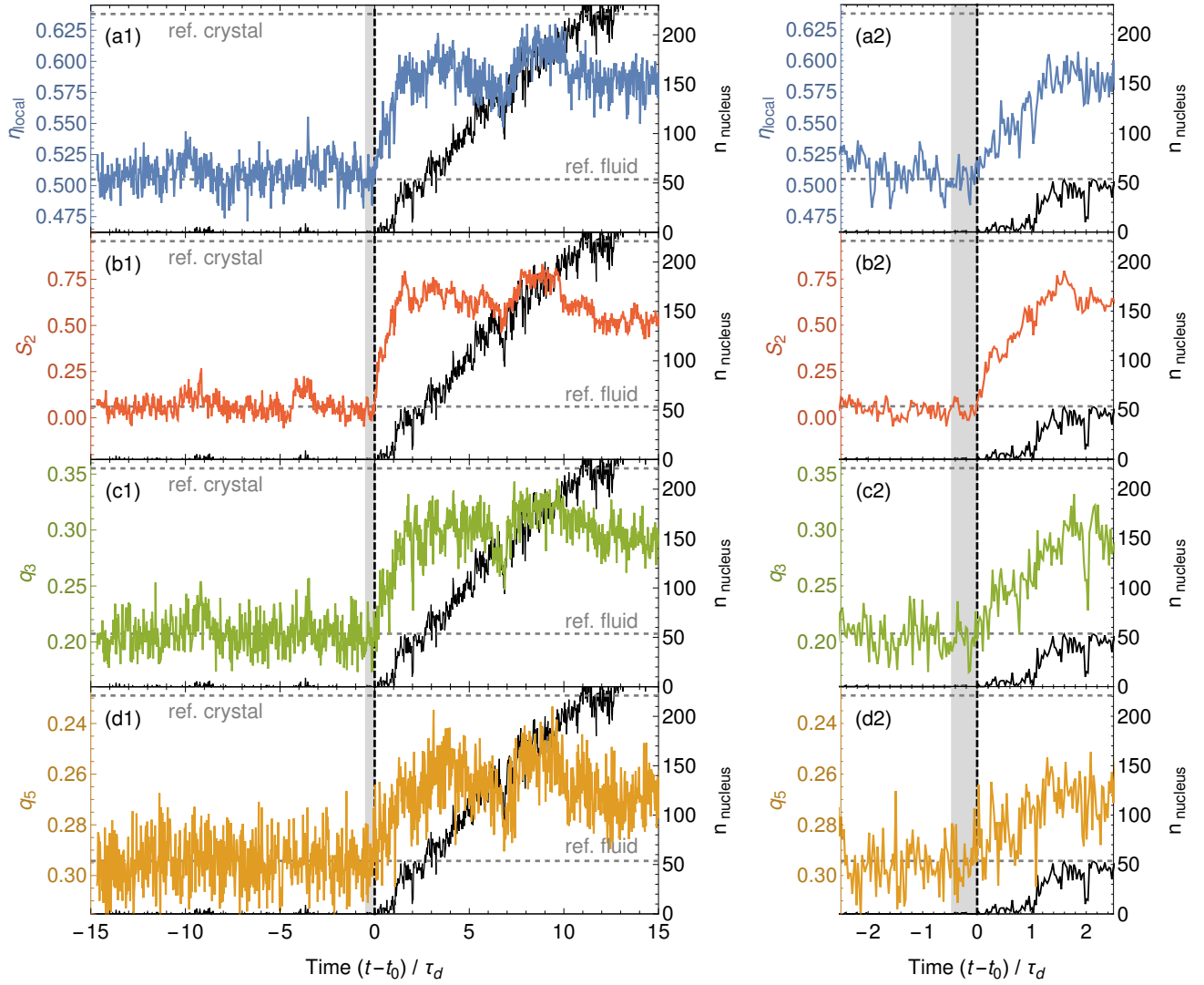


FIG. S5. Time evolution of the average local order parameters at the birthplace of the crystal nucleus for another typical nucleation event at packing fraction $\eta = 0.505$. The vertical dashed line in each figure indicates the start of nucleation t_0 , and the shaded area indicates the time window before t_0 for which $\text{ACF}(S_2) > 0.05$. The left panels, **(a1-d1)**, show the evolution of the parameters over a long time interval, and the right panels, **(a2-d2)**, show the same evolutions but now zoomed in on the short time interval around the start of nucleation. In each figure, the black line indicates the number of particles in the crystal nucleus. The colored lines indicate **(a)** the local packing fraction, **(b)** the nematic order parameter, and the **(c)** 3-fold and **(d)** 5-fold symmetric BOPs. Note that the vertical axis of **(d)** is inverted such that, even though q_5 is decreasing as nucleation progresses, the inverted trend shows a similar increase as for the other order parameters. The horizontal dashed lines indicate the reference value of each parameter in the bulk fluid and crystal phases. The left vertical axis of each figure is scaled in such a way that they all depict the same relative range with respect to these bulk values.

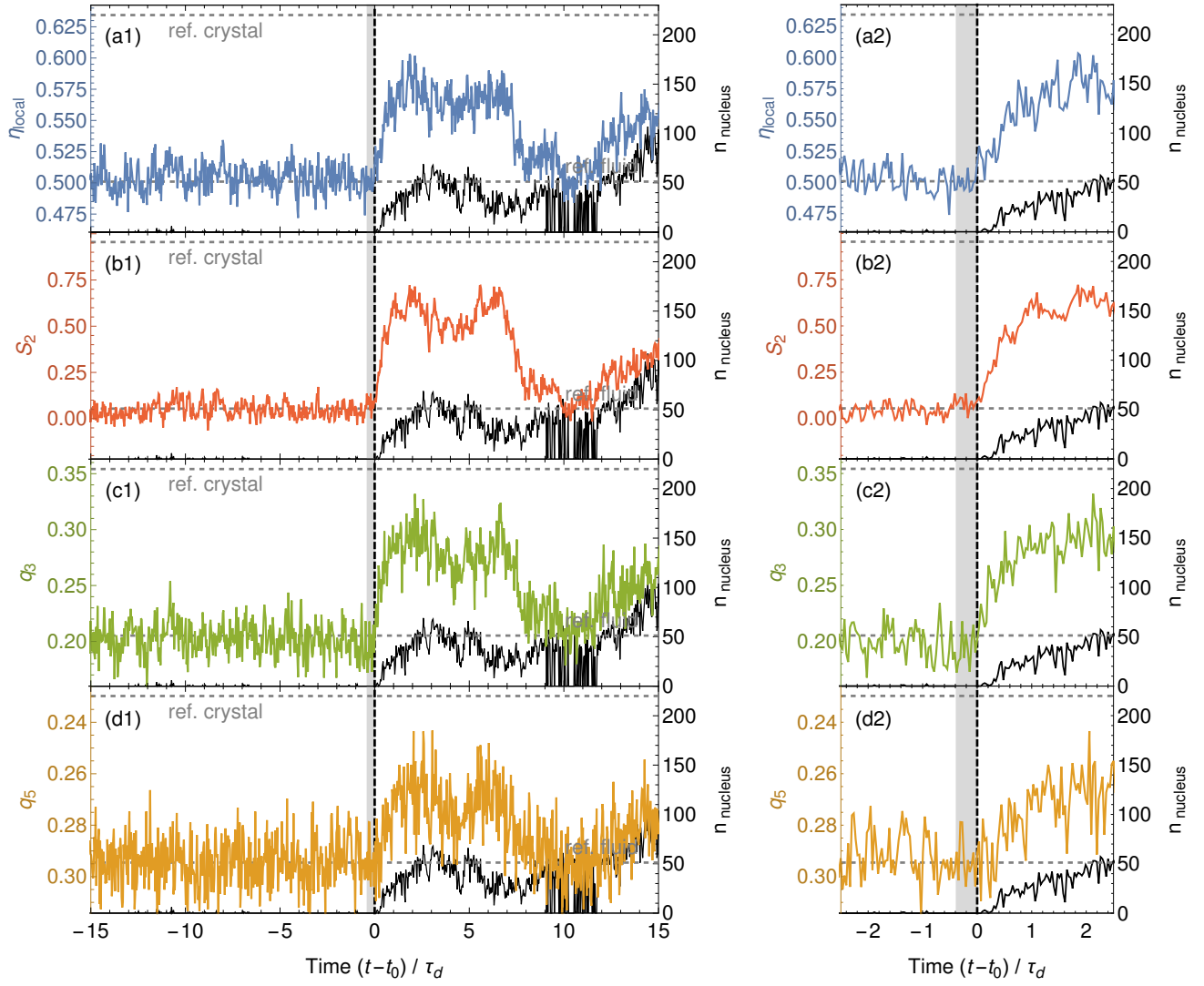


FIG. S6. Time evolution of the average local order parameters at the birthplace of the crystal nucleus for another typical nucleation event at packing fraction $\eta = 0.501$. See caption of Fig. S5 for an explanation of the figures. The initial nucleus melts at $(t - t_0)/\tau_d \sim 10$, after which it resumes its growth in a slightly shifted location.

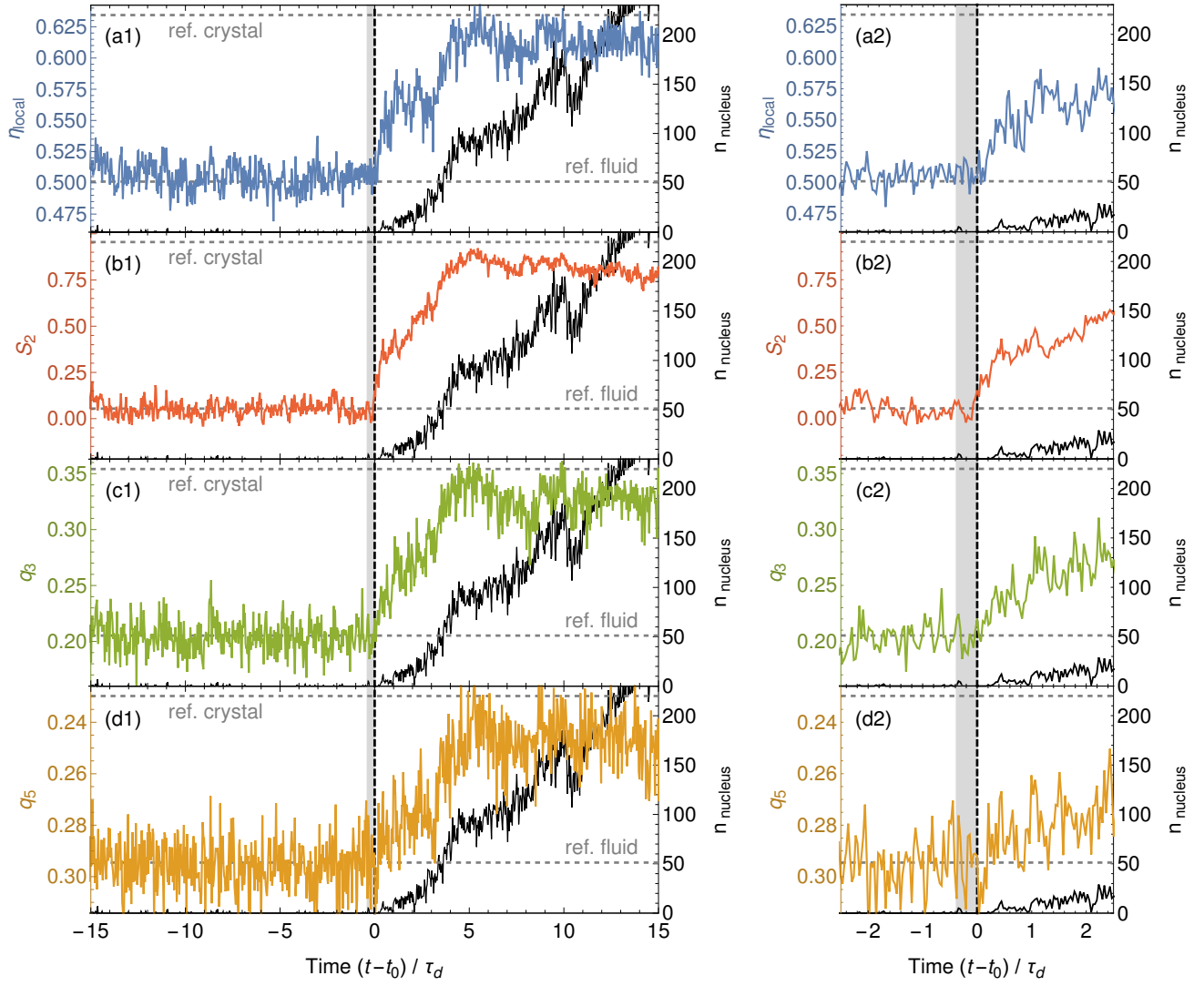


FIG. S7. Time evolution of the average local order parameters at the birthplace of the crystal nucleus for another typical nucleation event at packing fraction $\eta = 0.501$. See caption of Fig. S5 for an explanation of the figures.