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Nucleation of crystals that are mixed composites of all three polymorphs in the Gaussian core model

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We present results of computer simulations of homogeneous crystal nucleation in the Gaussian core model. In our simulations, we study the competition between the body-centered-cubic (bcc), face-centered-cubic (fcc), and hexagonal-close-packed crystal phases. We find that the crystal nuclei that form from the metastable fluid phase are typically “mixed”; they do not consist of a single crystal polymorph. Furthermore, when the fcc phase is stable or fcc and bcc phases are equally stable, this mixed nature is found to persist far beyond the size at the top of the nucleation barrier, that is, far into what would be considered the growth (rather than nucleation) regime. In this region, the polymorph that forms is therefore selected long after nucleation. This has implications. When nucleation is slow, it will be the rate-limiting step for crystallization. Then, the step that determines the time scale for crystallisation is different from the step that controls which polymorph forms. This means that they can be independently controlled. Also between nucleation and polymorph selection, there is a growing phase that is clearly crystalline not fluid, but this phase cannot be assigned to any one polymorph. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922321>]

I. INTRODUCTION

Most crystalline substances—including many of great industrial importance—exhibit multiple crystal forms, a phenomenon known as polymorphism.¹ For example, the simple amino acid glycine has three crystal polymorphs:² α , β , and γ . From aqueous solution, glycine typically crystallises into the metastable α form, not into the equilibrium γ polymorph.² Controlling which polymorph forms is often of crucial importance, especially in the pharmaceutical industry.³ Failure to control the polymorph that forms can be disastrous, as illustrated by the problems experienced in the late 1990s with the anti-HIV (human immunodeficiency virus) drug ritonavir. While already in production, an additional and highly stable second polymorph appeared and the carefully formulated drug started to recrystallize in this new form. This required an extremely expensive ($\approx$ \$250 million⁴) reformulation. Despite its importance, the mechanism by which one polymorph is selected preferentially during crystallization is currently poorly understood, and the subject of active research.^{1,5–9,12}

Here, our focus is on nucleation, the first stage of crystallization, during which a microscopically small nucleus of the crystal phase is formed in the metastable fluid phase. It is well known that what happens at nucleation can determine important physical properties of much larger crystals.¹³ Therefore, one would expect that nucleation plays an important role in determining which crystal polymorph forms.

We use computer simulations to study the crystallization of a simple model system that exhibits polymorphism, namely, the Gaussian core model (GCM), originally proposed by Stillinger.¹⁴ We have chosen to study the GCM since its phase dia-

gram has regions where the body-centered-cubic (bcc) crystal phase is stable, and others where the face-centered-cubic (fcc) crystal phase is stable.^{15,16} This contrasts with two alternative model systems whose nucleation has been well-studied, hard-spheres and Lennard-Jones, for which only close-packed crystals are thermodynamically stable.¹⁷

We perform Monte Carlo (MC) simulations of the GCM at a number of temperatures and pressures, some where the fcc phase is stable and others where the bcc phase is stable. In order to access regions of the phase diagram where the nucleation barrier is of the order of $10k_B T$ and above, we use specialist rare event methods, namely, Forward Flux Sampling (FFS)^{22,23} and Umbrella Sampling (US).²⁴

It is frequently imagined that polymorphs compete to nucleate first. In such a picture of competing polymorphs, the nucleus is typically envisaged as a small crystallite of one particular crystalline polymorph. For the GCM, the nucleus would thus be expected to be either fcc-like or bcc-like. Furthermore, Ostwald’s famous “step rule”¹⁸ says that the crystal phase that nucleates first should be the one that is closest in free energy to the metastable fluid phase rather than the phase that is thermodynamically stable. This would suggest that for the GCM, a bcc nucleus will form when the fcc phase is stable and vice versa.

However, our results show that the nucleus does not typically consist of only a single polymorph; it is usually a mixture of polymorphs. This observation is consistent with a previous study of the GCM by Russo and Tanaka.⁹ Mixed nuclei were also found in previous investigations by Lechner and co-workers.^{10,11} Lechner *et al.*^{10,11} find significantly more hexagonal-close-packed (hcp) ordering (and so less bcc and fcc) than we do for similar state points and using similar but not identical order parameters. We do not know the reason why we see less hcp ordering than they do. Therefore, the

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simple aforementioned picture of competing polymorphs is not correct for this system: it is not normally possible to say that the nucleus is one polymorph or the other. Additionally, because of the mixed nature of the crystal nuclei, no evidence of Ostwald's step rule is found for this system.

By extending our study to large system sizes, we find that when the fcc phase is stable, the polymorph disorder at small sizes persists as the nuclei grow far beyond the size at the top of the nucleation barrier (the "critical" size), where the nucleation rate is determined. Thus, polymorph selection for the GCM occurs long after nucleation.

Finally, since we have performed some simulations where the bcc phase is stable and others where the fcc phase is stable, we use our simulation results to compare if and how the nucleation behaviour differs in these two regions. We find that the bcc phase is "kinetically favoured," as similarly observed by Desgranges and Delhommelle for systems with Yukawa¹² and Inverse Power Law¹⁹ potentials (IPL).

The remainder of this paper is structured as follows: in Sec. II, we discuss the details of our computer simulations. In Sec. III, we discuss our simulation results. Finally, we give our conclusions in Sec. IV.

II. SIMULATION DETAILS

The GCM consists of a system of particles interacting via a purely repulsive, Gaussian pair potential

$$v(r) = \varepsilon \exp(-r^2/\sigma^2), \quad (1)$$

where r is the separation between two particles and the constants ε and σ have dimensions of energy and length, respectively. In all of our simulations, we truncate the potential at $r_c = 3.7\sigma$ and shift the potential (downwards) so that $v(r_c) = 0$. As is conventional, from hereon in, we express physical quantities in reduced units, that is, in terms of ε and σ . Therefore, pressure P is expressed in units of ε/σ^3 and temperature T is expressed in units of ε/k_B .

In order to study nucleation at relatively low supersaturations, we use specialist rare event simulation methods, namely, FFS^{22,23,25} and US.²⁴ In addition, we have performed some direct or "brute force" simulations where possible. We briefly describe each of these three simulation methods (FFS, US, direct simulation) below in Secs. II A–II C, with further details given in the Appendix.

For each simulation method, we require some way to determine the crystallinity of a particular spatial configuration of particles. Additionally, to study polymorphism, we must be able to distinguish between regions of different crystal structures. To achieve this, we use the orientational order parameters and method originally proposed by Lechner and Dellago²⁶ (LD). In principle, the LD method allows us to classify each individual particle as being in either the fluid, hcp, fcc, or bcc phase. Of particular relevance is the size of the largest crystalline cluster n . This is the number of particles that are all identified as either hcp, fcc, or bcc and are in the same cluster, where a particle is in the same cluster as another particle if at least one of its 12 nearest neighbours is in that crystalline cluster. We denote the number of particles of each polymorph in the largest crystalline cluster as n_{bcc} , n_{fcc} , and n_{hcp}

(hence, $n = n_{bcc} + n_{fcc} + n_{hcp}$). Further details of how the order parameters were implemented are given in the Appendix.

A. Forward flux sampling

Using the FFS method, we compute the rate k of nucleation of crystals from the metastable fluid phase. For the stochastic evolution of the system, we use NPT MC. Hence, the basic unit of time τ in our FFS simulations is a MC "cycle." Each cycle consists of a single attempted displacement move per particle and a single attempted volume move in which the (cubic) simulation box is either expanded or contracted isotropically.²⁰ The nucleation rate k is the number of crystals that form per unit time, per unit volume, and hence, it has units of $\tau^{-1}\sigma^{-3}$.

The pressures and temperatures for which we have performed FFS simulations are given in Table I. These points were chosen such that some lie in the region of the phase diagram where the fcc phase is stable, some where the bcc phase is stable, and others where both of these crystal phases are equally stable to a close approximation.^{15,16} For the order parameter in our FFS simulations, we use the size of the largest crystalline cluster n .

Although usually the primary aim of using FFS is to estimate the nucleation rate, here we are more interested in using the method in order to harvest a large number of crystal nuclei, whose polymorphic content can then be analysed statistically. The polymorphic content is studied as a "post-processing" step, that is, after the FFS simulations are complete.

B. Umbrella sampling

To supplement the FFS simulations, we also performed US simulations at some of the pressures and temperatures given in Table I.

In the US simulations, we measure the equilibrium probability (in the NPT ensemble) $P(n)$ of the system occupying a region of phase space in which the size of the largest crystalline cluster is n . This probability is measured by biasing the system in the normal way.²¹ From $P(n)$, a free energy barrier $\Delta G(n)$ can be computed as

$$\beta\Delta G(n) = -\ln[P(n)], \quad (2)$$

where $\beta = 1/k_B T$.

TABLE I. Temperature and pressure points at which we have performed FFS simulations, showing the stable phase at each of these points. At $T = 0.0037$, the fcc and bcc crystal phases are equally stable to a close approximation.^{15,16}

T	P	Stable phase
0.002	0.0055	fcc
0.002	0.0060	fcc
0.002	0.0065	fcc
0.002	0.85	bcc
0.002	0.90	bcc
0.002	1.00	bcc
0.0037	0.015	≈
0.0037	0.017	≈
0.0037	0.020	≈

In addition to computing a one-dimensional free energy barrier as a function of the size of the largest crystalline cluster as given in Eq. (2), we also computed a two-dimensional free energy surface

$$\beta\Delta G(n_{bcc}, n_{cp}) = -\ln[P(n_{bcc}, n_{cp})], \quad (3)$$

where $n_{cp} = n_{hcp} + n_{fcc}$ is the number of particles in the largest crystalline cluster that are in a close-packed crystal environment.

From the free energy barrier $\Delta G(n)$, the nucleation rate k can be approximated and hence compared with the results from FFS. For this, only the barrier height $\Delta G(n^*)$ is required, where n^* is the size of the largest crystalline cluster at the top of the barrier. The nucleation rate k can be written as²⁷

$$k = A \exp[-\beta\Delta G(n^*)]. \quad (4)$$

Here, A is the kinetic pre-factor given by²⁷

$$A \approx \rho f_{n^*} \sqrt{\frac{|\beta\Delta G''(n^*)|}{2\pi}}, \quad (5)$$

where ρ is the (reduced) number density of the fluid phase, $\Delta G''$ is the second derivative of the free energy barrier, and f_{n^*} is the rate at which particles are attached to the critical cluster, which is given by²¹

$$f_{n^*} = \frac{1}{2} \frac{\langle \Delta n^2(t) \rangle}{t}, \quad (6)$$

where $\langle n^2(t) \rangle = \langle (n(t) - n^*)^2 \rangle$ is the mean square deviation of the cluster size at the top of the barrier as a function of time. Equations (4)–(6) allow the results of US to be compared quantitatively with nucleation rates obtained from FFS.

As is the case for FFS, US allows us to harvest a large number of crystal nuclei that are representative of those formed during nucleation.

C. Direct simulation

If the chemical potential difference between the metastable fluid and the stable crystal phase is sufficiently large (i.e., the supersaturation is sufficiently high), crystallisation proceeds rapidly and can therefore be studied using direct or “brute force” simulations. In this case, we start from the metastable fluid phase and simply evolve the system in time using the same dynamical evolution as for FFS (*NPT* MC). During the simulation, we observe nucleation and subsequent growth.

Direct simulations were used to study crystallisation in large systems. Any results obtained from direct simulations are accompanied by the relevant simulation conditions (pressure and temperature) when they arise in the text.

D. Comparison to previous simulations

Our simulations extend those of Russo and Tanaka⁹ in two important ways. First, our simulations are for larger system sizes up to 100 000 particles, as opposed to 4000. This allows us to study large nuclei without worrying about the effects of periodic boundary conditions. Typically, we find that nuclei can only contain at most around 1/4 of the particles in the simulation box before the periodic boundary conditions come

into play. Therefore, these large system sizes are required for studying nuclei with many thousands of particles. Second, since we are using specialist rare event methods (FFS and US), we can perform simulations in the region in which the thermodynamic driving force for crystallization is too small to allow investigation by direct simulation. This is important since it is normally expected that the microscopic mechanisms by which nucleation proceeds can be quite different at high supersaturation (where direct or “brute force” simulation is possible) versus at low supersaturation (at which specialist rare event methods like FFS and US must be used).

III. SIMULATION RESULTS AND DISCUSSION

A. Comparison between FFS and US

Fig. 1 shows the nucleation barrier computed at $T = 0.002$, $P = 0.0055$, where the fcc crystal phase is stable. The barrier was produced by averaging 10 independent US simulations. The height of the barrier is $22.4 \pm 2.7 k_B T$, with the critical nucleus size 320 ± 10 . For these conditions, the kinetic prefactor was approximated by first computing f_{n^*} by performing a dynamical simulation starting from an approximately critical nucleus and using Eq. (6). The prefactor A was then computed using Eq. (5), giving $A = 0.025 \pm 0.007$. Using Eq. (4) then gives $k = 4.91 \times 10^{-12}$, with upper and lower estimates of 9.08×10^{-11} and 2.45×10^{-13} , respectively. The FFS result is $k = 1.86 \times 10^{-13}$, within the error bounds of the rate computed from US using Eq. (4). The FFS result itself is accurate to within approximately an order of magnitude.

We also compared the nuclei formed in the FFS simulations with those formed in the US simulations. The nuclei were found to be of similar polymorph composition. The nuclei fluctuate in shape, as would be expected for small objects in systems where the interfacial tension is not very large.²⁸

B. Mixed nature of nuclei

The main result of our study is that crystal nuclei that form in our simulations are typically of “mixed” polymorphic content. That is to say, the nuclei cannot be considered to be of one particular polymorph or another. An example of this is shown in Fig. 2, which is a typical example of a “critical”

FIG. 1. Free energy barrier computed from US simulations at $T = 0.002$, $P = 0.0055$, where the fcc phase is stable.

FIG. 2. Typical example of a critical sized nucleus in our system, consisting of 280 particles, produced in a FFS run at $P = 0.006$, $T = 0.002$. The yellow, orange, and green particles are in fcc-like, hcp-like, and bcc-like environments, respectively. The nucleus appears to be a “mixture” of these polymorphs.

nucleus seen in our simulations, in this case for $P = 0.006$, $T = 0.002$, where the fcc phase is stable. Here, we are defining a critical nucleus as a nucleus at the FFS critical interface, which is the first interface at which the probability of the nucleus reaching the final phase exceeds 0.5, as is conventional.^{29,30} We denote the size of the critical nucleus as n_{crit} and the fraction of particles of each crystal phase in the nucleus as $f_{fcc} = n_{fcc}/n$, $f_{hcp} = n_{hcp}/n$, and $f_{bcc} = n_{bcc}/n$. The nucleus in Fig. 2 has $f_{fcc} = 0.34$, $f_{hcp} = 0.19$, and $f_{bcc} = 0.47$.

In order to assess the polymorphic content of the nuclei quantitatively, we define the “mixedness” M of a crystal nucleus as

$$M = 1 - |2f_{bcc} - 1|^2. \quad (7)$$

By choosing this metric for measuring how mixed a nucleus is, we are implicitly not differentiating between fcc-like particles and hcp-like particles. This is sensible because of the similarity between the hcp and fcc crystal phases, and also because our main concern here is the competition between the bcc and fcc polymorphs, since these are the two stable polymorphs in the GCM phase diagram. The metric in Eq. (7) has a minimum value of 0 for a “pure” nucleus (when $f_{bcc} = 0$ or $f_{bcc} = 1$) and a maximum value of 1 (when $f_{bcc} = 0.5$).

We found that there was significant variability from one nucleus to the next in how mixed they were. In Figs. 3–5,

FIG. 3. Histogram of nucleus mixedness as a function of size for $T = 0.002$, $P = 0.0060$, where the fcc phase is stable. The histogram was produced using all of the ≈ 5000 nuclei generated by FFS. The vertical yellow line indicates the size of the critical nucleus $n = n_{crit}$.

FIG. 4. Same as Fig. 3, but for $T = 0.002$, $P = 0.90$, where the bcc phase is stable.

we show histograms of how the mixedness M of the nuclei evolves as the nucleus grows, for three different temperatures and pressures, one for which the fcc phase is stable ($T = 0.002$, $P = 0.006$, $\rho_{fcc} = 0.094$, Fig. 3), one for which the bcc phase is stable ($T = 0.002$, $P = 0.90$, $\rho_{bcc} = 0.57$, Fig. 4) and one for which both crystal phases are equally stable to a good approximation ($T = 0.0037$, $P = 0.017$, $\rho_{fcc} = \rho_{bcc} = 0.12$, Fig. 5). These figures are simply a visualisation of the polymorphic content of all of the nuclei that form in our FFS simulations (between 4500 and 6000, nuclei are produced, depending on the FFS simulation in question). To produce these figures, we have sorted the nuclei into bins of width 10. Each column is then normalised independently such that a vertical slice of Figs. 3–5 sums to unity.

Looking at Fig. 3, we see that when the fcc phase is stable, the nuclei are mixed at small sizes and remain mixed beyond the critical size. On average, M remains constant at a value of approximately 0.85. When the bcc phase is stable (Fig. 4), nuclei become less mixed as they become larger. In this case, M settles to a value of approximately 0.4 on average. Thus, the nuclei in the region where bcc is stable tend to be more pure than the nuclei in the region where fcc is stable. As shown in Fig. 5, when both crystal phases are of roughly equal stability, the situation is intermediate, with M decreasing from a high value as in the bcc case, but settling at a higher value of approximately 0.5.

C. Kinetic preference for bcc

In order to investigate how M depends on which crystal-line phase is stable, we can look at the number of particles of each polymorph in the nucleus, n_{bcc} , n_{fcc} , and n_{hcp} . Fig. 6 shows the number of particles of each polymorph for each of the 9 conditions at which we conducted FFS simulations. From Fig. 6, we see that for all conditions, the nucleus has on

FIG. 5. Same as Fig. 3, but for $T = 0.0037$, $P = 0.017$, where both bcc and fcc phases are equally stable to a good approximation (see Table I).

FIG. 6. Number of crystalline particles in each phase against nucleus size n for all of the temperatures and pressures at which we have performed FFS simulations. The points show averages over all clusters of size n produced in the FFS simulations, with the error bars showing the standard deviation. Each plot represents the ≈ 5000 nuclei produced using FFS at that pressure and temperature.

average a greater number of bcc-like particles than either fcc-like or hcp-like particles. Note that this is even true when the fcc phase is stable (Fig. 6, left column). This perhaps surprising observation is consistent with the previous simulations of the GCM done by Russo and Tanaka.⁹ The approximately linear variation of the number of particles of each polymorph with the cluster size shown in Fig. 6 suggests that for all of the simulation conditions we have investigated, we can define roughly constant growth rates. For the three polymorphs, these rates k_{bcc} , k_{fcc} , and k_{hcp} are the slopes of bcc, fcc, and hcp lines in Fig. 6. These rates are in the order $k_{bcc} > k_{fcc} > k_{hcp}$. Note that when these rates are all constant, the relative amounts of the polymorphs do not change. For example, the ratio of the number of bcc to fcc particles stays at k_{bcc}/k_{fcc} . So, the drift downward in most probable M values in Figs. 4 and 5 is due to variations in growth rates. From Fig. 6, the difference $k_{bcc} - k_{fcc}$ is seen to be greatest when the bcc phase is stable and smallest when the fcc phase is stable. That is to say, for all conditions, the bcc phase is “kinetically” favoured in nucleation; the extent to which it is favoured depends on the relative stabilities of the bcc and fcc phases.

Such a kinetic preference for the bcc phase was also observed and discussed by Desgranges and Delhommelle (henceforth D&D) for the Yukawa¹² and inverse power law¹⁹ potentials. In addition to pointing out this kinetic preference, D&D made an assessment of whether the polymorph that eventually crystallizes is selected at the nucleation stage or during the later stage of growth. For the Yukawa potential, D&D concluded that this depends on which polymorph is thermodynamically stable: when the bcc phase is stable, polymorph selection takes place at the nucleation step, but when the fcc phase is stable, polymorph selection occurs later during

growth via a more complicated mechanism.¹² But for the IPL potential, D&D concluded that polymorph selection never occurs at the nucleation step, it always occurs during growth.¹² These conclusions were made on the basis of the composition of the critical nuclei for these systems.

For the GCM, it is clear from Figs. 3 and 6 (left column) that when the fcc phase is stable, polymorph selection does not occur at the nucleation step. For this case in particular, the nuclei are mixed and remain mixed as they grow. The stable phase is the fcc phase, but the critical nucleus is typically predominantly bcc. Therefore, the fcc phase must be “selected” during growth. This selection could well be a slow process given the long lifetimes often associated with metastable phases. For the bcc phase, following D&D, we can decide whether or not the bcc polymorph has been selected at nucleation based on the fraction of particles in the nucleus that are identified as being bcc-like. In Fig. 7, the black squares compare the fraction of the stable polymorph in the critical nucleus when the fcc phase is stable with the fraction when the bcc phase is stable. Clearly, there is a marked difference between the two regions, with only typically 30%–40% of fcc-like particles in the fcc region but typically 70%–80% of bcc-like particles in the bcc region. The blue squares in Fig. 7 compare the largest cluster in the critical nuclei that consists of only the stable phase in the fcc and bcc regions. The fact that this value is lower for the fcc region than for the bcc region shows that in the fcc region, the fcc-like particles are spatially dispersed, whereas in the bcc region, the bcc-like particles tend to form a single connected cluster. While D&D did not suggest a particular cutoff for considering polymorph selection to have occurred, if we take a 2/3 ratio to be our cutoff, we would say that polymorph selection has occurred at nucleation when

FIG. 7. The black markers show the fraction of the stable phase in the critical nucleus for the three regions, averaged over all nuclei from the FFS simulations. For example, the black square in the region marked “fcc stable” shows the fraction of fcc-like particles in the critical nucleus when fcc is the stable phase. For the middle region where polymorphs are equally stable, we plot the fraction of bcc-like particles in the critical nucleus. The blue markers show the fraction of the critical nucleus that is all a single connected cluster of the stable phase. For both marker colors, the squares are the mean fraction of the stable phase, with the error bars showing the standard deviation.

the bcc phase is stable, but not when the fcc phase is stable. Therefore, the behaviour of the GCM is more akin to that of the Yukawa potential rather than the IPL potential.

In addition to using this arbitrary cutoff, we have looked at the distribution of the stable phase in the critical nuclei. We find that in the bcc region, nearly all (>90%) of the bcc particles in the nuclei themselves form a single compact cluster. This contrasts with fcc region, in which there are typically multiple small fcc clusters. Combined with the typically 70%–80% of bcc-like particles, the existence of a single dominant bcc cluster in the bcc region confirms that polymorph selection has already occurred at nucleation. Similarly, the fact that there are multiple small clusters of fcc particles in the fcc region, along with the fact that the nuclei typically consist of only 30%–40% fcc particles, confirms that polymorph selection has not occurred at nucleation in the fcc region.

D. 2d US plots

Figs. 8–10 show 2d US plots for the three different regions. When fcc is stable (Fig. 8), the free energy surface is relatively

FIG. 8. Free energy plot $\beta G(n_{bcc}, n_{fcc})$ for $T = 0.002$, $P = 0.0060$, where the fcc phase is stable. Only free energy values greater than $-5k_B T$ are shown on the plot. The white regions are where the free energy is $< -5k_B T$. Free energy values are only shown where they were measured in the US simulations; hence there are a few additional white regions in the main part of the plot where the particular values of n_{bcc} and n_{fcc} were not visited.

FIG. 9. Same as Fig. 8, but for $T = 0.0037$, $P = 0.017$, where bcc and fcc phases are equally stable.

flat, suggesting that mixed nuclei would be expected to form. When fcc and bcc are equally stable, beyond the barrier in the bottom left corner of Fig. 9, the free energy surface is again relatively flat. When bcc is stable (Fig. 10), the shape of the barrier suggests that a trajectory for which the nuclei remain mixed at small sizes is preferable in terms of free energy. The critical nucleus from 1d simulations at this pressure and temperature is 160. For all three regions, it is worth noting the fact that the bcc phase appears to have a higher growth rate than the fcc and hcp phases. This dynamic preference for bcc means that the features of the free energy landscapes in Figs. 8–10 may not accurately reflect the typical nucleation trajectories. That is to say, since the dynamics are biased towards bcc, typical nucleation trajectories would be expected to be pushed closer to the x-axis on plots of Figs. 8–10 than a minimum free energy pathway would suggest. In any case, the 2d US plots shown in Figs. 8–10 indicate that the mixed nuclei seen in our FFS simulations are to be expected.

E. Direct simulations of larger nuclei

In order to determine the size at which polymorph selection occurs when the fcc phase is stable, we studied the growth of nuclei far beyond the critical size that characterises nucleation. For this, simulations of larger systems of up to 100 000 particles were required. Since FFS simulations of large systems are computationally expensive, we instead ran direct “brute force” MC simulations (see Sec. II C). To make these direct simulations feasible, we adjusted the temperature and

FIG. 10. Same as Fig. 8, but for $T = 0.002$, $P = 0.90$, where the bcc phase is stable.

FIG. 11. Example of a crystallite far beyond the nucleation barrier, consisting of 12 637 particles, produced via direct simulation in the region where fcc is stable. The yellow, orange, and green particles are in fcc-like, hcp-like, and bcc-like environments, respectively.

pressure from the conditions given in Table I to provide a larger driving force for crystallisation.

In direct simulations, the nuclei grow with polymorph fractions qualitatively similar to those shown in Fig. 6. Fig. 11 shows a nucleus consisting of 12 637 particles formed at $T = 0.002\,62$, $P = 0.01$. For these conditions, the fcc phase is stable. The critical nucleus consists of approximately 100 particles, hence this nucleus is more than 100 times as large as a typical critical nucleus. However, as can be seen from Fig. 11, despite being far over the nucleation barrier, the system has not yet selected the fcc polymorph. Despite performing multiple such direct simulations, we did not observe a single crystallite resembling a “pure” fcc crystal at this pressure and temperature. Thus, polymorph selection when the fcc phase is stable occurs at length scales much greater than those associated with nucleation.

The mixed nature of even very large nuclei when the fcc phase is stable indicates that the growth rate of each polymorph is dominant over the rate of polymorph conversion (in this case from bcc to fcc). In our simulations, we find all of the particles in the box crystallize before this conversion takes place.

We might expect that closer to co-existence, the lower crystal growth rate would mean that polymorph selection occurs at smaller length scales (relative to the critical nucleus size). Unfortunately, it is difficult to test this hypothesis in our simulations, since at smaller chemical potential differences between the fluid and crystal phases, the rapid drop in the nucleation rate and accompanying large size of the critical nucleus make simulation unfeasible. However—when fcc is stable—even if the nucleus near the top of the barrier has a higher fraction of fcc-like particles at these smaller chemical potential differences, the bias in growth towards bcc may mean that subsequent growth produces a mixed nucleus.

IV. CONCLUSION

In conclusion, we studied the crystallization of the GCM, a simple model system that exhibits polymorphism. The main finding was that the nuclei that form are typically “mixed”; they cannot be thought of as being nuclei of a single polymorph.

Because of this, as also observed by Russo and Tanaka,⁹ we were unable to identify behaviour akin to Ostwald’s step rule; it is not the case that the nuclei that form consist of the metastable polymorph, which later transforms to the stable polymorph. Instead, small nuclei are polymorph disordered crystallites. This can be seen by examining the nuclei by eye or by defining a quantitative measure of the polymorph disorder.

Between the different regions of the phase diagram, there are differences in the polymorph composition of the nuclei. Where the bcc phase is stable, nuclei are less mixed on average than in the region where the fcc is stable. Here in particular, the bcc phase outgrew the other polymorphs, see Figs. 4 and 6. The bcc polymorph appears to be kinetically favoured. Why exactly this is the case is difficult to assess, though it was also found to be the case for similar systems in the previous studies of Desgranges and Delhommelle.^{12,19} In contrast, when fcc is the stable polymorph, the nuclei are mixtures of small domains of the polymorphs at all sizes, see Fig. 4. Then, growth of bcc and fcc domains are in balance, and so apparently, their growth is in some sense cooperative.

By simulating large systems, we found that when the fcc phase is stable, the mixed nature of the nuclei persists to sizes much greater than the critical nucleus, the size at which the nucleation rate is determined. The fact that not only nucleation but also growth proceeds in a polymorph disordered manner suggests that attempting to control nucleation may not always be an effective way to control the final crystal polymorph that forms.

V. DATA AVAILABILITY

The authors confirm that data underlying the findings are available without restriction. Details of the data and how to request access are available from the University of Surrey publications repository: [<http://epubs.surrey.ac.uk/807653>].

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APPENDIX: SIMULATION DETAILS

1. Details of FFS simulations

As stated in Sec. II, the time evolution in our FFS simulations is studied using *NPT* MC. For this, we use the normal Metropolis scheme with a maximum trial displacement and maximum volume change that ensures approximately 40% move acceptance (the exact values used depend on P and T). Although this scheme is usually used for computing static equilibrium properties (e.g., as we use it here for US simulations), it is also frequently used for dynamical evolution, especially in nucleation studies.^{29,30} Time in our FFS simulations is measured in “cycles,” with one MC cycle corresponding to (on average) a single attempted displacement move per particle and a single attempted volume change, accepted or rejected in the normal way.²⁰

At the beginning of the simulation, we initialize the positions of the particles in a random liquid-like configuration.

Since this configuration is likely to be rather unphysical, we then allow the system to relax by evolving for 2×10^5 MC cycles. During this relaxation phase, we do not observe complete crystallization of the fluid, which indicates that a barrier to nucleation exists. The resulting configuration is then used as the initial state for FFS.

The rate given by FFS is written as

$$k = \Phi \prod_{i=0}^{N-1} P(\lambda_{i+1}|\lambda_i), \quad (\text{A1})$$

where Φ is the “flux” through the first interface λ_0 , and $P(\lambda_{i+1}|\lambda_i)$ is the probability of the system reaching interface λ_{i+1} coming from the previous interface λ_i . As the order parameter λ , we used the size of the largest crystalline cluster, n , computed as explained below. For all of the simulations, we placed the first interface at $\lambda_0 = 12$ and consecutive interfaces at $\lambda_i = 10(i + 1)$. The number of interfaces was chosen differently for different pressures and temperatures to ensure that the conditional probability $P(\lambda_{i+1}|\lambda_i)$ was at least 0.98 for at the final interface. We took a minimum of 200 “shots” at each interface, with more taken where necessary to ensure a minimum of 50 successful shots at each interface.

2. Details of US simulations

In our US simulations, we apply a bias to the system of the form

$$W(\mathbf{r}^N) = \exp[-\beta\omega(\mathbf{r}^N)], \quad (\text{A2})$$

with a biasing potential ω given by

$$\omega(n(\mathbf{r}^N)) = \frac{1}{2}\kappa[n(\mathbf{r}^N) - n_0]^2, \quad (\text{A3})$$

where n is the size of the largest crystalline cluster, whose dependence on the co-ordinates $\mathbf{r}^N$ of all N particles has been written explicitly. We then compute the probability of the system having a largest cluster of size n in the biased ensemble using the normal Metropolis method, before debiasing the simulation to compute this probability in the unbiased (*NPT*) ensemble,²⁰ which we denote as $P(n)$.

As is normal,^{21,20} we divide the computation of $P(n)$ into windows, each with a different centre n_0 . All of our results were obtained with windows spaced by 50, i.e., $n_0 = 0, 50, 100, \dots$, and with the constant $\kappa = 0.1$ for every window. For each pressure and temperature at which we computed $\Delta G(n)$, we performed 10 US simulations, 5 in which each window was initialised with a perfect fcc nucleus and 5 in which each window was initialised with a perfect bcc nucleus. In each case, the initial nucleus was chosen to have approximately n_0 particles, with the surrounding fluid making up the remainder of the $N = 5000$ total particles. Before collecting data for determining $P(n)$, we relaxed the system for 2×10^5 MC cycles (with the bias potential). During this relaxation period, the initial nuclei in each window undergo significant reorganisation, indicating that the slightly artificial nature of the initial configurations should not impact the results. Data were then collected for 1×10^6 cycles. For efficiency—as is typical²¹—we ran 5 cycles without bias between every computation of W .

To compute $\Delta G(n)$, we first computed the relative probability in each window by averaging over all 10 simulations. Taking the negative of the logarithm of this relative probability gives the free energy in this window, up to a constant term. To “stitch” these windows together and hence compute a complete profile for $\Delta G(n)$, we simultaneously fitted the results in all windows to a single polynomial, as described in Ref. 19.

The two dimensional free energy surface $\Delta G(n_{cp}, n_{bcc})$ was computed in the same way as in the 1-d case, the main difference being the additional number of windows.

3. Computing n and the polymorph composition

To identify crystalline particles, we use the now standard method of Lechner and Dellago (henceforth, LD).²⁶ In contrast to other approaches, this method is designed specifically to discriminate between hcp, bcc, and fcc crystal structures and is therefore ideal for our study of polymorphism.

In the LD approach, we first compute for every particle i in the simulation the complex vector

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij}). \quad (\text{A4})$$

Here, the functions Y_{lm} are spherical harmonics, $-l \leq m \leq l$, $N_b(i)$ is the number of neighbors of particle i , and $\hat{\mathbf{r}}_{ij}$ is a unit vector connecting particles i and j . The summation is over all particles that are neighbours to particle i . The vector is computed for both $l = 4$ and $l = 6$. In our implementation, rather than using a distance cutoff, we define the neighbours of particle i to be the 12 nearest particles. Thus, $N_b(i) = 12$ for every particle. The advantages of this neighbourhood definition are discussed in detail in Ref. 31.

Next, for each particle i , we take the “average” of $q_{lm}(i)$ over its neighbourhood by computing the complex vector

$$\bar{q}_{lm}(i) = \frac{1}{N_b(i) + 1} \sum_{j=0}^{N_b(i)} q_{lm}(k). \quad (\text{A5})$$

Here, the sum starting at $j = 0$ runs over all neighbours of particle i plus the particle itself. This averaging procedure—which effectively means that the second shell of a particles’ neighbour is taken into account—is the key step that allows the LD method to distinguish effectively between crystalline polymorphs, see Ref. 26 for further discussion. Using the $\bar{q}_{lm}(i)$ vectors, we can compute for every particle i the local bond order parameters

$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2} \quad (\text{A6})$$

and

$$\bar{w}_l(i) = \frac{\sum_{m_1+m_2+m_3=0} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \bar{q}_{lm_1}(i) \bar{q}_{lm_2}(i) \bar{q}_{lm_3}(i)}{\left(\sum_{m=-l}^l |\bar{q}_{lm}(i)|^2 \right)^{3/2}}. \quad (\text{A7})$$

FIG. 12. Probability density functions (pdfs) for the local bond order parameters $\bar{q}_6(i)$, $\bar{w}_6(i)$, and $\bar{w}_4(i)$ for the liquid (fluid) and crystal phases of the GCM. Here, we show only the pdfs that are needed for the particle classification, see text for details. The pdfs shown were computed for $T = 0.002$, $P = 0.055$, although they are essentially unchanged at the other temperatures and pressures at which we have performed simulations.

Again, we compute the above quantities for $l = 4$ and $l = 6$ (though the $\bar{q}_4$ values are not needed in the classification procedure that follows). The term in parenthesis on the top line of Eq. (A7) is the Wigner $3 - j$ symbol.³²

As shown in Fig. 12, the values of $\bar{q}_6(i)$, $\bar{w}_6(i)$, and $\bar{w}_4(i)$ allow us to classify particle i as either liquid-like, fcc-like, hcp-like, or bcc-like. With reference to Fig. 12, we achieve this as follows. First, if $\bar{q}_6(i) < 0.3$ (top subplot), particle i is classified as liquid-like. Otherwise, if $\bar{w}_6(i) > 0$, it is classified as bcc-like (middle subplot). Finally, if the particle is neither liquid-like nor bcc-like, we look at $\bar{w}_4$ (bottom subplot). If $\bar{w}_4 > 0$, the particle is hcp-like, otherwise it is fcc-like.

Once each particle has been classified, we next consider only those particles identified as being in a crystalline environment (fcc, hcp, or bcc). We then compute all clusters of crystalline particles in the system. A particle is considered part of a cluster if it is within a cutoff distance r_{cl} of any other particle in the cluster. We set r_{cl} to be the average of the first and second neighbour distances for a perfect fcc crystal, which has a known density as determined from *NPT* simulations. We denote by n the size of the largest of these clusters. This largest

cluster is referred to as the “nucleus.” Finally, by using the classifications already computed, we can evaluate the number of particles in the nucleus in each of the three crystalline polymorphs, that is, n_{fcc} , n_{bcc} , and n_{hcp} .

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