Computer simulation of epitaxial nucleation of a crystal on a crystalline surface

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We present results of computer simulations of crystal nucleation on a crystalline surface, in the Lennard-Jones model. Motivated by the pioneering work of Turnbull and Vonnegut [Ind. Eng. Chem. 44, 1292 (1952)], we investigate the effects of a mismatch between the surface lattice constant and that of the bulk nucleating crystal. We find that the nucleation rate is maximum close to, but not exactly at, zero mismatch. The offset is due to the finite size of the nucleus. In agreement with a number of experiments, we find that even for large mismatches of 10% or more, the formation of the crystal can be epitaxial, meaning that the crystals that nucleate have a fixed orientation with respect to the surface lattice. However, nucleation is not always epitaxial, and loss of epitaxy does affect how the rate varies with mismatch. The surface lattice strongly influences the nucleation rate. We show that the epitaxy observed in our simulations can be predicted using calculations of the potential energy between the surface and the first layer of the nucleating crystal, in the spirit of simple approaches such as that of Hillier and Ward [Phys. Rev. B 54, 14037 (1996)]. © 2014 AIP Publishing LLC.

I. INTRODUCTION

Understanding crystallization is important for a wide variety of applications, in areas as diverse as pharmaceuticals, the food industry, atmospheric science, and protein crystallization. The first stage of crystallization is nucleation, the formation of a microscopic crystal nucleus. Because of the small size of the crystal nucleus, nucleation is difficult to study experimentally. Therefore, most investigations of nucleation have been computer simulation studies.

The vast majority of the simulation work performed to date has focused on homogeneous nucleation. However, in most cases of experimental interest nucleation is not homogeneous, instead it occurs on heterogeneities such as container walls or impurity particles. The reason for this is that on these surfaces part of the free energy cost of creating an interface surrounding the nucleating phase has already been paid. Heterogeneous nucleation is therefore typically many orders of magnitude faster than homogeneous nucleation, and the dominant mechanism.

Usually the heterogeneities on which crystal nuclei form present surfaces with some type of ordering. One expects that when these surfaces are crystalline, their structure and geometry will influence both the rate at which crystal nuclei form, and their orientation. This leads to the concept of epitaxy. The term epitaxy is used in a number of subtly different ways in the literature. Here, we define nucleation to be epitaxial when the nucleating crystal always forms with a particular fixed orientation to the surface lattice. This includes when the nucleus always forms with one of a number of orientations that are equivalent due to the symmetry of the surface. While this is common usage, sometimes this is instead called “oriented overgrowth,” and epitaxy is defined instead as simply crystal growth on a substrate (i.e., without necessarily having a fixed orientation). We want to avoid this ambiguity here.

Experiments have frequently observed that crystals can form epitaxially on substrates. These date back to Royer, who studied the epitaxial growth of alkali halides on mica from aqueous solutions. More recently, Stephens et al. observed that under certain conditions, calcite crystals form with a consistent alignment to a mica substrate. To what extent epitaxial growth is due to the degree of matching between the substrate lattice and that of the nucleating crystal has been discussed in the literature. It appears that for many systems, surface chemistry is more important than surface geometry, and that therefore epitaxy is highly system specific.

This paper expands on a previous publication that briefly presented some of the key results shown here. We present computer simulations of heterogeneous crystal nucleation for what is perhaps the simplest case of heterogeneous nucleation, nucleation on a flat crystalline surface. By focusing on a perfect crystalline plane we are able to study epitaxial nucleation in the simplest possible system. Even the most expertly cleaved surfaces studied in experiments provide topographical features such as ledges and wedges. Wedges are known to influence nucleation, and so in experiments it is difficult to discount the possibility that alignment is due to the presence of wedges. Furthermore, in experiments nucleation cannot be directly observed due to the small size of the nucleus. Only relatively large crystals can be observed, and it is difficult to determine whether the properties of these crystals should be attributed to nucleation or to the later stage of growth. Here we can study effects due to nucleation alone.

Our aim here is to investigate generic properties of heterogeneous nucleation, and thus we study a simple model system, namely, the Lennard-Jones (LJ) system. We have

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chosen this system since its phase diagram is readily available,\textsuperscript{22,23} and homogeneous crystal nucleation has been previously studied extensively.\textsuperscript{5–9,24}

We present results of Monte Carlo simulations of the LJ system at temperatures below the triple point, where the crystal phase is the thermodynamically stable phase. In this regime, the pressure is essentially zero.\textsuperscript{9} We start the system from the liquid phase, which has a higher free energy than the crystal phase. In order to compute nucleation rates we use Forward Flux Sampling (FFS), a rare-event method developed by Allen \textit{et al.}.\textsuperscript{25,26}

The main purpose of our study is to investigate how the properties of the crystalline surface influence both the nucleation rate and the structural properties of the crystal nuclei that form. We study two surfaces: a hcp lattice with an exposed (0001) plane, and a fcc lattice with an exposed (100) plane, which we henceforth refer to as the “cp surface” and “100 surface,” respectively. For both surfaces, we vary the disregistry or “lattice mismatch” between the surface and nucleating crystal, defined as\textsuperscript{27}

\[
\delta = 100 \frac{a_S - a_B}{a_B},
\]

where \(a_S\) is the lattice parameter of the surface, and \(a_B\) is the lattice parameter of the bulk LJ crystal.

The role of the lattice mismatch \(\delta\) in heterogeneous nucleation was considered long ago by Turnbull and Vonnegut.\textsuperscript{28} In contrast to the theoretical predictions of Turnbull and Vonnegut, we find that the nucleation rate is not maximum at exactly \(\delta = 0\), i.e., where the lattice parameter of the surface is equal to that of the bulk LJ solid. We attribute this to finite size effects that are inherent in nucleation. The nucleus is always a finite size crystal, and therefore does not have the same lattice parameter as the bulk solid. Furthermore, we find that these finite size effects mean that the notion of coherent nucleation, as suggested by Turnbull and Vonnegut,\textsuperscript{28} needs to be extended.

We use our simulation results to investigate when and why nucleation is epitaxial. We show that epitaxy can be predicted by examining the potential energy between the surface and first layer of the nucleating crystal, as a function of the angle of orientation. This is in the spirit of the simple approach used by Ward and co-workers.\textsuperscript{29} Thus, to some extent, our study validates the utility of this simple approach to predicting epitaxy.

The remainder of this paper is structured as follows. In Sec. II, we describe our numerical simulations in detail. In Sec. III, we present the results of the simulations. We analyze the results in the context of Classical Nucleation Theory (CNT)—in particular the theory of Turnbull and Vonnegut—in Sec. IV. In Sec. V, we discuss the role of epitaxy and how to predict whether or not nucleation should be epitaxial. Finally, we give our conclusions in Sec. VI.

II. DETAILS OF SIMULATIONS

A. Simulation setup and interaction potentials

Our simulation setup is shown in Fig. 1. The particles in our simulation can be divided into surface particles (colored red in Fig. 1), which are held in fixed positions throughout the simulation, and moving particles (both yellow and blue in Fig. 1). In all of the results reported in this paper we use 3520 moving particles. The complete surface consists of 3 layers of \(20 \times 22\) particles, so that the system has 4840 particles in total. We note that 3 layers is sufficient for the surface to appear to the moving particles as a bulk crystal of number density \(\rho_S\). We define the lattice parameter of the surface \(a_S\) that appears in Eq. (1) as the nearest neighbor distance between surface particles. This means that, for a given \(\rho_s\), the mismatch \(\delta\) is the same for both the cp and 100 surfaces (since \(\delta = 2^{1/6}/\rho_S^{1/3}\)).

Since there are two species of particle, surface (S) and moving (M), our system is a binary mixture (albeit a slightly artificial one due to the rigidity of the surface particles). All of the particle interactions are governed by a standard pairwise truncated and shifted LJ interaction potential given by

\[
U_{AB}(r) = \begin{cases} 
U^{LJ}_{AB}(r) - U^{LJ}_{AB}\left(r_c\right), & r \leq r_c, \\
0, & r > r_c,
\end{cases}
\]

where

\[
U^{LJ}_{AB}(r) = 4\epsilon_{AB} \left( \frac{\sigma_{AB}}{r} \right)^{12} - \left( \frac{\sigma_{AB}}{r} \right)^6
\]

is the normal LJ potential and \(A, B = M, S\). Thus four parameters, \(\epsilon_{MM}, \epsilon_{MS}, \sigma_{MM}, \) and \(\sigma_{MS}\) are needed in order to fully specify the interactions (\(\epsilon_{SS}\) and \(\sigma_{SS}\) are irrelevant since the positions of the surface particles are fixed). For all of our simulations, we take the cutoff radius to be \(r_c = 2.5\sigma_{MM}\).

A natural choice for the well depths is to make them equal in size, \(\epsilon_{MS} = \epsilon_{MM}\). However, we found that this choice leads to rapid freezing of the system at the temperatures accessible to our study. That is, the metastable liquid rapidly forms a crystalline layer on the surface which percolates across the simulation box, i.e., “wets” the surface, before growing vertically layer by layer. This is undesirable behavior since our aim is to study nucleation in a 3d system rather than any 2d aspects of crystallization.\textsuperscript{30}

To inhibit a complete crystalline layer forming, it was necessary to reduce the strength of the attractions between...
the moving and surface particles. We achieved this by setting $\epsilon_{MS} = 0.3\epsilon_{MM}$, i.e., by setting the well depth between a surface and a moving particle to 30% of the well depth between two moving particles. By varying this, we found that crystallization is very sensitive to the value of $\epsilon_{MM}$. For example, on increasing $\epsilon_{MM}$ from 0.3 to 0.38, the nucleation rate increases by approximately four orders of magnitude. The experimental analogue of this observation is that the chemical functionality of the surface is important, and likely more important in determining the nucleation efficiency than the geometrical properties of the surface. This fact has been discussed previously in the literature.$^{14}$ Here our focus is on the effects of the geometry of the surface, but we should bear in mind that the form of the interactions between the surface and fluid is also important for a real system.

For $\sigma_{MS}$ and $\sigma_{MM}$, in the first instance we made the natural choice $\sigma_{MS} = \sigma_{MM} = 1$. However, the problem with this approach is that the minimum in the cross potential $U_{MS}^{LJ}$ is always located at $r_{min} = 2^{1/6}$, even as we increase $\rho_S$ (which we do to tune the value of the mismatch $\delta$) to make the nearest neighbor spacing $a_S$ much smaller than $r_{min}$. Thus, this simple scheme effectively results in two different length scales, $\sigma_{MS}$ and $a_S$, in the surface-liquid interaction. In order to avoid this, we also studied a second potential with $\sigma_{MS}$ defined by $a_S = 2^{1/6}\sigma_{MS}$, i.e., so that the minimum in the potential between moving and surface particles is equal to the lattice parameter of the surface.

To summarize, we performed simulations for two distinct interaction potentials between surface (S) and moving (M) particles, both based on the LJ interaction potential of Eq. (3), and with both $\epsilon_{MS} = 0.3\epsilon_{MM}$.

1. $\sigma_{MM} = \sigma_{MS} = 1$,
2. $\sigma_{MM} = 1, \sigma_{MS} = 2^{-1/6}a_S$.

In Secs. III–V, we refer to these as simply potential 1 and potential 2, respectively. We note that some results, for potential 2 only, have been given in a previous publication.$^{20}$ We define $\epsilon = \epsilon_{MM}$ and $\sigma = \sigma_{MM}$, and work with the parameters $\epsilon$ and $\sigma$ henceforth.

Our simulation box has periodic boundary conditions in the two horizontal directions, and is a hard wall in the vertical direction (at the top, cf. Fig. 1). The dimensions of the simulation box in the horizontal directions are dependent on $\rho_S$, since each layer of the surface is taken to have exactly 20 $\times$ 22 particles. For all of the simulation conditions, the vertical dimension is chosen such that, for every choice of $\rho_S$, the volume of the simulation box is 6820$\sigma^3$. The vertical dimension is considerably larger than the position of the interface between the metastable liquid and vapor phases.

### B. FFS simulations and order parameter

We computed nucleation rates for two different temperatures, $k_B T = 0.47\epsilon$ and $k_B T = 0.5\epsilon$. Both temperatures are below the triple point, located at$^{9} k_B T_{TP} \approx 0.65\epsilon$. They correspond to an undercooling of 28% and 23%, respectively.

To compute nucleation rates, we used the FFS scheme, a rare-event technique developed by Allen et al.$^{31}$ The dynamics in our FFS simulations are given by the normal Metropolis Monte-Carlo (MC) scheme with maximum trial displacement $\Delta x = \pm 0.1\sigma$. As the unit of time $\tau$, we use a MC cycle, which corresponds to one attempted displacement move per (moving) particle. Therefore, nucleation rates are expressed in units of $\tau^{-1}\sigma^{-2}$. Further details of our simulations can be found in the Appendix.

For the order parameter in our FFS simulations we used the size of the largest crystalline cluster, $N_{cl}$, as identified by the local $q_6$ bond-order parameter introduced by ten Wolde and co-workers$^{6}$ and used in a number of previous studies of homogeneous LJ crystal nucleation.$^{8,9,31,32}$ We note, however, that there are some subtleties to computing $N_{cl}$ in our system because of the presence of the surface particles. Therefore, we have detailed the entire procedure in the Appendix.

### III. SIMULATION RESULTS

In our simulations, we vary the mismatch $\delta$ by varying the lattice parameter of the surface $a_S$ and study the nucleation rate as a function of $\delta$. In order to obtain an accurate value for $a_S$ and hence $\delta$ at a given $a_S$, we performed NPT simulations at zero pressure$^{34}$ to compute the bulk lattice constant $a_B$ of the stable fcc crystal. This was done for temperatures $k_B T = 0.47\epsilon$ and $k_B T = 0.5\epsilon$. At these temperatures, we found $a_B = 1.128(2)\sigma$ and $1.131(2)\sigma$, respectively, where the number in brackets is the approximate error in the final digit.

Figs. 2 and 3 show nucleation rates as a function of mismatch $\delta$ for the cp surface and the 100 surface, respectively. The rates are expressed in units of $\tau^{-1}\sigma^{-2}$. Clearly, for both surfaces and both potentials, the nucleation rate is at a maximum close to, but not exactly at, $\delta = 0$. The maximum in the rate occurs at $\delta \approx 3$ for the cp surface and $\delta \approx 1$ for the 100 surface.

Another feature evident from Figs. 2 and 3 is that the nucleation rate is not symmetric around the maximum for either surface; it falls off more rapidly at positive mismatch (when the surface lattice parameter is “too big” for the crystal that wants to form) than at negative mismatch (when the surface lattice parameter is “too small”). This is particularly evident when comparing the effects of increasing $\rho_S$ and $\delta$ on the nucleation rate.
for potential 1 at large negative mismatches, for which the rate rises roughly linearly with mismatch (for both surfaces). The reason for this linear dependence is that $\sigma_{MS}$ is constant for potential 1 (see Sec. II), it does not vary with $\delta$. This means the energy per unit surface area increases linearly as $\delta$ becomes more negative (that is, as the surface is compressed). This fact motivated the use of potential 2.

For the cp surface, as shown in Fig. 2, the nucleation rate has a minimum at $\delta \approx -8$ for potential 1. This minimum is likely to be the point at which the mismatch is no longer the dominant factor determining the rate, instead the rate is simply determined by the overall attractiveness of the surface, which varies linearly with $\delta$ (see Sec. II A). This argument suggests that the rate should plateau for potential 2, which is consistent with Fig. 2. For the 100 surface, there is a minimum in the nucleation rate at $\delta \approx -6$ for potential 1. This mismatch is roughly in the middle of the “transition region” (discussed in Sec. V). Therefore, a minimum in the rate makes sense intuitively since the surface is not a good match for either cp or 100 planes of the nucleus. This argument suggests that, since the minimum in the rate for the 100 surface is due to its geometry, it should also be present for potential 2, which is consistent with the results in Fig. 3.

Figs. 4 and 5 show the variation of $N_{cl}^*$, the value of the order parameter $N_{cl}$ at the critical interface, which is the interface at which the nuclei have on average a probability of 0.5 of crystallizing. As in previous studies using FFS,9 $N_{cl}^*$ can be used as an estimate of the size of the critical nucleus that appears in the CNT description. It should be noted, however, that this is by no means guaranteed to be a good estimate; the quality of the estimate is essentially a measure of how good the order parameter is as a reaction co-ordinate. For homogeneous nucleation in the LJ system, it was previously found that $N_{cl}^*$, which can be thought of as the “size” of the nucleus, does not on its own constitute a good reaction co-ordinate.8, 32 In any case, the trend shown in Fig. 4 is as expected: as the rate increases, $N_{cl}^*$ decreases. Also, for both surfaces the minimum value of $N_{cl}^*$ is located at the mismatch for which the nucleation rate is a maximum.

Examples of nuclei at the critical interface are shown for the cp surface in Fig. 6. We find that on the cp surface, for all mismatches $\delta$, the nucleus always forms with a close packed layer in contact with the surface. For the 100 surface, the nucleus has a 100 layer in contact with the surface for mismatches $\delta \gtrsim -3$. But for large negative mismatches, $\delta \lesssim -8$ (when the surface is much “too small” for the bulk crystal that is nucleating), the nucleus instead forms with a close packed layer in contact with the surface. This rotation of the nucleus to present a different lattice plane to the surface is marked by a jump in the “critical nucleus” size $N_{cl}^*$, as can be seen in Fig. 5. In the intermediate region $-8 \lesssim \delta \lesssim -3$, we find that the first layer of the nucleus exhibits regions of four-fold and regions of six-fold symmetry.

FIG. 3. Same as Fig. 2, but for 100 surface.

FIG. 4. $N_{cl}$ at critical interface for cp surface. Error bars are standard deviations from the 5 FFS simulations.

FIG. 5. Same as Fig. 4, but for 100 surface. In the cross hatched region, the nucleus forms with a close packed layer in contact with the surface. Outside this region, the first layer has the same (100) symmetry as the top layer of the surface.

FIG. 6. Examples of crystal nuclei at the FFS critical interface for three different mismatches. The surface is close packed, with surface potential 1 (see Sec. II A). From left to right, the clusters have $N_{cl} = 230, 210,$ and $430$ particles. The nucleus on the left can be seen to be rotated by $\approx 30^\circ$ with respect to the surface.
Comparing the nucleation rates on the two surfaces (Fig. 7), we find that in the region of the maximum, the rates for the two surfaces are comparable. At the largest positive mismatch at which we have computed nucleation rates for both surfaces, the rate is larger for the cp surface. A likely explanation for this is that it is due to the higher density per unit area of the cp surface; there are a greater number of potential “wells” per unit area above the cp surface. At the largest negative mismatches, the rate is larger for the 100 surface. This is the region in which the nucleus forms with a close-packed layer on the 100 surface (cf. Fig. 12). We revisit the subject of the orientation of the nuclei in Sec. V.

IV. CLASSICAL NUCLEATION THEORY AND THE ROLE OF LATTICE MISMATCH

A. Nucleation on a flat surface

According to CNT, heterogeneous nucleation on a flat surface can be described using the same parameters as for homogeneous nucleation, along with a single additional parameter, the contact angle \( \theta \). The CNT nucleation rate can be written as

\[
k_{\text{CNT}} = K_s \exp(-\Delta F^*/k_B T),
\]

where

\[
\Delta F^* = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta f_c)^2} f(\theta).
\]

Here \( K_s \) is known as the kinetic prefactor, \( \gamma \) is the liquid-crystal surface tension, \( \Delta f_v \equiv \rho_c \mu_c - \rho_l \mu_l \) is the free energy difference per unit volume between bulk liquid and crystal phases, with \( \rho_c \) and \( \rho_l \) the bulk densities, and \( \mu_c \) and \( \mu_l \) the chemical potentials (of crystal and liquid, respectively). The surface tension \( \gamma \) is assumed to be isotropic. Although this is not the case for a crystal phase, for the LJ solid calculations indicate that the orientation dependence of \( \gamma \) is relatively small.

Equations (4) and (5) differ from the corresponding CNT expressions for homogeneous nucleation in two ways: (i) the kinetic prefactor \( K_s \) in Eq. (4) is smaller than that for homogeneous nucleation and (ii) the free energy barrier given by CNT is reduced in the case of heterogeneous nucleation by the factor \( f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4 \), where \( \theta \) is the contact angle. The reduction of the free energy barrier is dominant, and therefore heterogeneous nucleation is typically much faster than homogeneous nucleation.

CNT can be used to predict how the nucleation rate scales with supersaturation, which in our case is set by the temperature of the undercooled liquid. First, we can write

\[
\frac{d}{dT} \Delta f_v \approx \frac{1}{\sigma^3} \frac{d}{dT} \Delta \mu,
\]

where we have made the approximation \( \rho_c = \rho_l \) (for the LJ system \( \rho_c \approx \rho_l \approx 1/\sigma^3 \)). Next, we assume that \( \Delta \mu \) varies linearly with temperature over the relatively small temperature range accessible to our simulations (a reasonable assumption),

\[
\Delta \mu = b \Delta T,
\]

where \( b \) is a constant, and \( \Delta T = T_{tr} - T \), with \( T_{tr} \) the triple point temperature.

Using Eqs. (4)–(7), the logarithm of the CNT rate can be written as

\[
\ln(k_{\text{CNT}}) = \ln K_s - \frac{16\pi}{3} \frac{\gamma^3}{(\Delta f_c)^2} \frac{1}{k_B b^2} \frac{1}{\Delta T^2 T},
\]

where \( \Delta T = T_{tr} - T \).

In order to test the applicability of Eq. (8), we performed additional FFS simulations in the temperature range \( k_B T = 0.47 - 0.5 \). As shown in Fig. 8, the CNT scaling of the nucleation rate with \( 1/\Delta T^2 T \) is consistent with our simulation results.

As a more quantitative test of CNT, we can estimate the coefficient of \( 1/\Delta T^2 T \) in the second term of Eq. (8), using data for the LJ system available in the literature. Taking \( \Delta \mu = 0.29 \epsilon \) at \( k_B T = 0.45 \), as given by van Meel et al., Table I of Ref. 9 and extrapolating up to \( \Delta \mu = 0 \) at the triple point at \( k_B T_{tr} = 0.65 \epsilon \), we obtain \( b \approx \Delta \mu/k_B T = 1.45 \). As an estimate for the liquid-crystal surface tension we take \( \gamma = 0.347 \epsilon/\sigma^2 \), which is the planar surface tension for the liquid-crystal surface tension.
The contact angle \( \theta \) is difficult to estimate. Although in principle it could be calculated from Young’s equation,\(^36\) this involves an accurate knowledge of all three of the liquid-crystal, surface-crystal, and surface-liquid interfacial tensions. However, we only know the first of these interfacial tensions with any reasonable accuracy. Another option is trying to compute the contact angle from the nuclei that are observed to form in our FFS simulations. But this is also problematic since, in addition to being small (\( \sim 300 \) particles) and diffuse objects (cf. Fig. 6), the size and shape of the nuclei depend on the details of the order parameter. Therefore, for this rough estimate, we take the contact angle to be \( \theta = 90^\circ \) \((f(\theta) = 1/2)\), which appears reasonable given the shape of the crystal nuclei observed in our simulations. Using these numbers, we obtain for the coefficient appearing in front of the \( 1/\Delta T^2T \) term in (8) the value \(-0.17\), which is roughly a factor of 2 smaller than the fit to our FFS results shown in Fig. 8. Given the inaccuracies inherent in this estimation, this is reasonable agreement. We note that the fit to out FFS results also gives a value for the logarithm of the kinetic coefficient, 7.08 (in units of \( \text{r}^{-1}\sigma^{-2} \)), but again this should only be taken as a rough estimate.

\[ \begin{align*}
\text{B. Nucleation with lattice mismatch}
\end{align*} \]

Turnbull and Vonnegut\(^28\) (henceforth T&V) considered the fact that in heterogeneous nucleation, the lattice parameter of the surface can be different to that of the bulk crystal phase that is nucleating. They developed a theory that accounts for the lattice mismatch \( \delta \), as defined in Eq. (1), and therefore extends the conventional CNT expressions given in Eqs. (4) and (5).

T&V’s theory makes a number of predictions. The first is that the nucleation rate should be maximized for \( \delta = 0 \). Another is that, for a sufficiently small mismatch \( \delta \), the crystal nucleus will form “coherently,” meaning that the lattice of the nucleus will strain to perfectly fit the surface lattice. To consider coherent nucleation, we define the strain in the crystal nucleus,

\[ \xi = 100 \frac{x - a_B}{a_B}, \tag{9} \]

where \( x \) is lattice parameter of the nuclei that form, and, as previously, \( a_B \) is the lattice parameter of the bulk crystal. In the language of T&V, coherent nucleation corresponds to \( x = a_B \), and therefore \( \xi = \delta \) (cf. Eq. (1)).

At sufficiently large \( \delta \) values, T&V predicted that the strain free energy for coherent nucleation is too great and that therefore nuclei will form incoherently \( (\xi \neq \delta) \). This results in a threshold value \( \delta_c \), the maximum mismatch at which nuclei will form coherently: nucleation is coherent for \( |\delta| \leq \delta_c \), and incoherent for \( |\delta| \geq \delta_c \). The threshold mismatch is given by T&V as\(^28\)

\[ \delta_c = 100(4\pi \gamma / 60 k_B T)^{1/2} (\alpha / c), \tag{10} \]

where \( \alpha \) is a parameter that quantifies how much the surface-crystal interfacial tension increases with \( \delta \), and \( c \) is an effective elastic modulus of the crystal, with the strain energy per unit volume of the nucleus defined as \( c \epsilon^2 \). The factor of 60 \( k_B T \) is the free energy barrier to nucleation assumed by T&V.

As discussed in Sec. III (cf. Figs. 2 and 3), our simulation results show that the first prediction of T&V—that the nucleation rate is maximized at \( \delta = 0 \)—is not quite correct. To understand why this is the case, we computed the strain \( \xi \), as defined in Eq. (9), in the nuclei produced from our FFS simulations. This also allowed us to examine the T&V idea of coherent nucleation.

We computed the strain \( \xi \) at a given nucleus size of \( N_{cl} = 300 \), which is close to the top of the nucleation barrier. For every mismatch \( \delta \) we have around 600 nuclei of this size. We obtained a value for the lattice parameter of the nucleus, \( x \), and hence \( \xi \), for each of the first five layers of each nucleus by averaging the nearest neighbor separation for all pairs of neighbors in that layer (see Fig. 9). For this calculation, we defined neighbors as particles within 1.35\( \sigma \). We then averaged over the 600 or so nuclei.

Results for strain are shown in Fig. 10. We see that at all mismatches, the strain is non-zero even for layers far from the surface (i.e. layers 3, 4, and 5). In other words, the spacing between the particles in the nucleus is never that in the bulk crystal. The reason for this is that our nuclei are small and so do not have the same lattice constant as a bulk crystal. The strain of \( \approx 1\% \) from the bulk lattice parameter as seen in Fig. 10 is consistent with that of isolated LJ clusters of comparable size.\(^37\) That is, when computed by averaging the nearest neighbor distances, the “lattice constant” of these clusters is also larger than the bulk LJ crystal by \( \approx 1\% \).

The lattice constant in the finite nucleus perfectly matches the surface lattice when \( \xi = \delta \), so we plot the line \( \xi = \delta \) in Fig. 10. For the cp surface, the \( \xi = \delta \) line crosses the calculated strain at \( \delta = 3 \), and this corresponds to the maximum in the nucleation rate. Therefore, the maximum in the rate occurs when the average lattice parameter of the first layer of the nucleus equals that of the surface. It is just that this does not occur when either lattice constant equals the bulk lattice constant, at \( \delta = 0 \). Based on this analysis, we would expect that increasing the temperature towards the triple point at \( k_B T = 0.65 \) (i.e., lowering the supersaturation) would cause the maximum in the nucleation rate to move closer to \( \delta = 0 \). The reason for this is that as the supersaturation is lowered, the critical nucleus becomes larger, and it therefore
has a lattice parameter more similar to the bulk crystal. Unfortunately, the low nucleation rate at temperatures closer to $k_B T = 0.65$, we are unable to test this hypothesis (even using FFS).

To test for coherence at varying $\delta$, we look at the strain $\xi$ in the first layer of the nuclei. As shown in Fig. 10, for both surfaces there is a region of $\delta$ values for which the strain $\xi$ varies approximately linearly with $\delta$ (the region marked “coherent”). The region is asymmetric with respect to $\delta = 0$, but roughly symmetric about the mismatch for which the nucleation rate is a maximum. However, the slope is less than one. This means that on average the spacing between the particles on the first layer of the nucleus does not expand or contract sufficiently to perfectly match the surface lattice spacing. Despite the fact that we do not have $\xi = \delta$, we can identify this region as “coherent” nucleation in the sense intended by T&V. Specifically, we can attribute the slope of less than one to finite size effects that are inherent in nucleation.

![FIG. 10. Strain $\xi$ as a function of mismatch between surface and the bulk crystal, $\delta$. Results are for potential 2. Top and bottom panels are for cp and 100 surfaces, respectively. The solid lines are $\xi = \delta$. For the cp surface three regions are indicated. From left to right they are: the region where nucleation is not epitaxial, the region where it is coherent, and the region where it is epitaxial but not coherent. For the 100 surface the regions are, from left to right: where the nucleus forms with a cp plane in contact with the substrate, a transition region, a region where nucleation is with a coherent 100 plane in contact with the substrate, and another transition region.](image)

V. THE ROLE OF EPITAXY

A. Epitaxial nucleation observed in simulations

In our simulations, we frequently observe that, at a given lattice mismatch, the crystal nuclei that form always have the same orientation with respect to the lattice of the surface. As discussed previously, this is known as epitaxial nucleation.

Coherent nucleation, as discussed in Sec. IV B, is by definition epitaxial. The unit cell of the nucleus is oriented at an angle of $0^\circ$ to that of the surface. Outside this region (marked “coherent” in Fig. 10), we find that the two surfaces show different behavior, and hence we discuss each surface in turn.

For the cp surface, to the right of the coherent region marked in Fig. 10 (when the surface lattice is “too big” for the nucleating crystal), we find that nucleation remains epitaxial, with the same orientation angle of $0^\circ$. But when the surface lattice is “too small,” we find that epitaxy is gradually lost. We reached this conclusion by computing the orientation of the nuclei with respect to the surface for different mismatches $\delta$. For this, we define the orientation angle as the angle between the unit cell of the surface and the first layer of the nucleus. We calculate this for a given nucleus as follows. First, we compute every vector $r_{ij}$ between two nearest neighbor particles $i$ and $j$ in the first layer of the nucleus. Typically, the first layer has around 50–80 particles. We compute the angle between each neighbor vector $r_{ij}$ and each of the six neighbor vectors of the cp surface. This gives six angles $\theta_{ij}(k)$: $k = 1, \ldots, 6$. We then define the orientation angle for the neighbor pair as the smallest of these angles, $\psi_{ij} = \min(\theta_{ij}(k))$. The angle $\xi$ is thus between $0^\circ$ and $30^\circ$. Finally, we define the orientation angle of the nucleus by averaging $\psi_{ij}$ for all neighbor pairs $ij$. 

chack and Laird at the triple point, $\gamma = 0.347 e\alpha^2$. For the second parameter, $c$ is simply half the value of the Young’s modulus $E$, which has been calculated for the LJ solid at $k_B T = 0.5e \approx 30 e/\sigma^2$. A value for $\alpha$ is more difficult to estimate. However, we can assume that it is at most of the same order of magnitude as $\gamma$. Approximating $\alpha$ by $\gamma$ gives a numerical value of $100 \alpha/\sigma c \approx 2.3$. Therefore, we find that the threshold for coherent nucleation is $\delta \approx 1$, i.e., one would only expect coherent nucleation when the mismatch between the surface lattice and bulk crystal is approximately 1% or less. Given the large uncertainties in the numerical values used to arrive at this estimate, it is encouraging that it is of the same order of magnitude as the width of the coherence region observed in our simulations, which is around 5%. We note that a better agreement would be obtained by assuming that the nucleation barrier is less than $60 k_B T$, the value used by T&V.
in the layer. We find that this procedure is reliable in that the orientation angle determined for a given nucleus corresponds to the orientation that is evident from visual inspection of the nucleus.

Fig. 11 shows the distribution of nuclei orientations on the cp surface for three different mismatches. At $\delta = -1$ and $\delta = 12$, as shown in Figs. 11(b) and 11(c), there is a very narrow distribution of orientation angles; nucleation is epitaxial. Contrast this with the very broad distribution of angles for $\delta = -13$ in Fig. 11(a). For these large and negative mismatches, nucleation is no longer epitaxial.

For the 100 surface, we find that on either side of the coherent region marked on Fig. 10 there is a “transition region” in which the first layer of the nucleus shows regions of four-fold and regions of six-fold symmetry, see Figs. 12(b) and 12(d). Nucleation is therefore not epitaxial in this transition region. It seems possible the behaviour here is analogous to that seen previously in experiments with alkali halides, which in some cases appear to form as disordered (100) layers when crystallizing on a mica substrate (see specifically Fig. 2 of Ref. 18 and accompanying discussion). Beyond this transition region, at large negative mismatches, we find that the first layer is a well ordered close packed layer (Fig. 12(a)). For all nuclei the close packed layer that forms on the surface has a fixed orientation with a row of particles aligned with the surface rows, as illustrated in Fig. 12(a); therefore, nucleation is epitaxial. We expect that this epitaxial nucleation is likely to also occur at large positive mismatches, although due to the low nucleation rate (cf. Fig. 3) we were unable to grow nuclei large enough to see this directly.

Our findings thus support experimental results which show that epitaxy can be observed even when the mismatch between the surface lattice and that of the nucleating crystal is large (>10%). By growing the nuclei beyond the critical size, we were unable to detect a change in orientation of the nuclei, and therefore our results suggest that the orientation of crystals is set at the time of nucleation.

B. Predicting epitaxy

Ideally, one would like to be able to predict in advance if nucleation on a given surface will be epitaxial, and, if so, the orientation between the unit cell of the surface and that of the nucleating crystal.

One approach that has been used to predict epitaxy in this sense has been developed by Hillier and Ward (henceforth HW). The approach of HW is based on the fact that the potential energy between a surface and an infinite crystalline overlayer is translationally invariant, and hence only depends on the orientation angle between the unit cell of the surface and that of the overlayer. HW calculate a normalized interaction between the two crystal lattices, as a function of angle, and for different lattice planes, to determine both the favored lattice plane of the crystal that forms in contact with the surface, and the favored angle. This approach is frequently used in experiments to assess the possibility of epitaxy for a particular substrate.

In the spirit of HW, we decided to investigate whether the occurrences of epitaxy observed in our simulations (as detailed in Sec. VA) can be explained by considering the energetics of a single crystal overlayer on our cp/100 surface. To assess this, we performed calculations of the potential energy between the surface and an overlayer with dimensions that are typical of a nucleus of size $N_\text{cl}^*$. It should be noted that these potential energy calculations are in fact a level of detail beyond the approach developed by HW, which considers only the interplay between the geometry of the surface and that of the overlayer. In fact, an agreement with potential energy calculations of the type we perform—in the limit of a sufficiently large overlayer—is used by HW to justify their approach.
In all cases, we fix the lattice constant of the overlayer at the bulk value $a_B$, although varying this does not affect our conclusions.

For the cp surface, we consider a close packed overlayer with two different geometries, as shown in Figs. 13(a) and 13(b), one with orthogonal boundaries and one with non-orthogonal boundaries. For the 100 surface, we also consider an overlayer with the same geometry as the surface itself (a fcc (100) plane, with orthogonal boundaries, see Fig. 13(c)). We place the lower left corner particle, shown in gray in Fig. 13, in a local minimum of the surface potential; this sets the vertical distance between the top layer of the surface and the overlayer. We then rotate the overlayer about the lower left corner particle shown in Fig. 13, and compute the potential energy per particle between the surface and overlayer as a function of the orientation angle, $u(\phi)$. If $u(\phi)$ displays a distinct minimum (in fact multiple minima at angles that reflect the symmetry of the surface) at a particular orientation angle, this means there is an energy penalty to rotating the overlayer. Thus nucleation is predicted to be epitaxial, with preferred orientation angles between the surface and nucleus which correspond to the positions of the minima.

In short, we find that the predictions of this simple approach agree with our simulation results. That is, the potential energy calculations predict relative orientations between the surface and crystal nuclei that match those seen in our simulations. In Figs. 14 and 15, we show this in the most illustrative cases for cp and 100 surfaces, respectively.

On the cp surface (see Fig. 14), when the mismatch $\delta$ is small, $u(\phi)$ displays distinct minima at $0^\circ$, $60^\circ$, $120^\circ$, etc. The minima are slightly distorted due to the finite size of the overlayer; $u(\phi)$ has a periodicity of $120^\circ$ rather than the $60^\circ$ periodicity of an infinite overlayer. In any case, the distinct minima predict that nucleation should be epitaxial, with the same orientation angle we see in our simulations (Figs. 11(b) and 11(c)).

For large negative mismatches (e.g., $\delta = -13$ as shown on Fig. 14), $u(\phi)$ is essentially flat, with variations on the order of $0.01e \ll k_BT$. The fact that the potential energy is essentially independent of orientation angle in this regime suggests that nucleation should not be epitaxial. This is in agreement with our simulation results that show nuclei form with a wide range of orientations (Fig. 11(a)).

On the 100 surface (see Fig. 15), as discussed in Sec. VA, for a large negative mismatch ($\delta \lesssim -10$) the nuclei that form in our FFS simulations have an overlayer that is close packed rather than 100. Again, this is predicted by our potential energy calculations: as shown in Fig. 15, a close packed overlayer is energetically preferable at such a large (negative) mismatch, with the preferred orientation angle of $30^\circ$ (or equivalently $0^\circ$, $60^\circ$, $90^\circ$) matching the orientation seen in our simulations (Fig. 12(a)).

As a final comment on predicting epitaxy, we should point out the potential energy approach we take here is in a sense quite distinct from the HW approach. The HW approach takes into account the geometry of the surface only, whereas the potential energy contains details of both the geometry and of the specific surface-fluid interactions.

VI. CONCLUSION

In this paper, we have presented a detailed study of crystal nucleation of a Lennard-Jones liquid on a flat crystalline surface. To compute nucleation rates we used the FFS method of Allen et al.25,26

As expected, the nucleation rate goes through a maximum when the surface lattice parameter is closely matched to that of the nucleating crystal phase. However, the maximum does not correspond to an exact match between these lattice parameters. This can be explained by finite size effects that are inherent in nucleation. The crystal nucleus that forms is a small object of a few hundred particles and has an effective lattice spacing that deviates from the bulk equilibrium value.

The theory of Turnbull and Vonnegut,28 although ignoring these finite size effects, correctly predicts that nucleation at small mismatches is coherent, in the sense that the
crystal nucleus expands or contracts to maintain registry with the surface lattice. However—once again because of finite size effects—we found that Turnbull and Vonnegut’s concept of coherence needs to be altered to take into account the fact that the small nuclei can relax structurally, and therefore need not be in perfect registry with the surface, as would be the case for an infinite crystal plane.

In many cases the nuclei were found to form epitaxially, that is, all nuclei that formed had the same relative orientation to the surface. It was shown that potential energy calculations that consider only the energetics between the surface and the first layer of the nucleating crystal can be used to effectively predict this epitaxy. The calculations successfully predict both whether or not nucleation is epitaxial, and, if it is epitaxial, the orientation of the nuclei that form relative to the surface. The success of this approach, assuming it can be generalized to other systems, suggests that these types of calculations—which are vastly less computationally intensive than simulations of nucleation, such as the FFS simulations reported here—are a useful tool for diagnosing heterogeneous nucleation.

Finally, we found a number of features that agree qualitatively with experimental results. We found that crystallization is highly sensitive to the surface geometry, and to the strength of the attractions between the molecules of the surface and those of the nucleus. In experiment, these two effects are difficult to isolate as they cannot be varied independently. However, it seems likely that both effects are important in explaining the variability in experiment. Steps and other defects may also be important in many systems. We also agree with experimental findings, e.g., Sarma et al.,14 in finding that epitaxy is possible even when the mismatch between the surface lattice and nucleating crystal is large (>10%). To bring experiment and simulation together, future work will need to include both simulations on surfaces with steps and other defects, and experiments on surfaces as well characterized as possible.

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APPENDIX: SIMULATION DETAILS

1. Monte Carlo dynamics

The dynamics in our FFS simulations are given by the normal Metropolis Monte Carlo (MC) scheme with maximum trial displacement $\Delta x = \pm 0.1 \sigma$.34 Although this scheme is usually used for computing static equilibrium properties, it is also often used as an approximate form of the dynamics. We measure time in “cycles.” One MC cycle corresponds to 4840 (the number of moving particles in the system) attempted displacement moves. On each attempted displacement move, we pick a (moving) particle randomly and displace it, accepting the move with probability related to the difference in energies in the normal way. Thus in a single cycle, we might have attempted to move one particle three times, and some others zero times. But on average, we make one displacement attempt for each moving particle. This is a standard scheme when performing NVT MC, since it preserves detailed-balance.34

2. Equilibration

At the beginning of the simulation, we initialize the positions of the moving particles in a random liquid-like configuration above the surface. However, this is not a good starting point for the FFS simulations, since this “random” configuration is likely to be rather unphysical. Therefore, before beginning the FFS simulations we “equilibrate” the system. It should be noted that this equilibration is simply a way to generate the initial state for the FFS simulations, that is, a particle configuration that corresponds physically to a homogeneous undercooled liquid (on a surface). For the purposes of the FFS simulations, we also require that this configuration has a largest cluster size $N_{cl} < 12$.

To equilibrate the system we evolve the system for $2 \times 10^5$ MC cycles. During this phase, we do not observe complete crystallization of the liquid, which indicates that a barrier to nucleation exists. Although the system will have experienced some (possibly large) fluctuations in the size of the largest cluster $N_{cl}$, these are not of interest at this point. If after $2 \times 10^5$ cycles, the maximum cluster size in the system $N_{cl}$ happens to be greater than 12 (which is not typical), we run additional cycles until it is less than 12. Thus, after equilibration we have a particle configuration that corresponds to a homogeneous undercooled fluid on a surface, with $N_{cl} < 12$. This configuration is used as the input to FFS.

3. FFS and interface positioning

After equilibration is complete, we use FFS to compute the nucleation rate. The rate given by FFS is written as

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

where $\Phi$ is the “flux” through the first interface $\lambda_0$, and $P(\lambda_{i+1} | \lambda_i)$ is the probability of the system reaching interface $\lambda_{i+1}$ coming from the previous interface $\lambda_i$. The interfaces are defined as isosurfaces of an order parameter that characterizes the transition from liquid to crystal. The order parameter we choose here is $N_{cl}$, the size of the largest crystalline cluster in the system. Therefore, different values of $\lambda$ correspond to different values of $N_{cl}$. It should be noted that the chosen order parameter is only required to characterize the initial and final states in the transition (in this case the liquid and the crystal), that is, the order parameter need not be a reaction co-ordinate.26

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 mismatches $\delta$ in order to ensure that the conditional probability $P(\lambda_{i+1} | \lambda_i)$ was at least 0.98 for at the final interface. The position of the final interface varied from 300 for small $\delta$ (29 interfaces in total) up to 500 (49 interfaces in total) for the larger values of $\delta$. 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. The flux \( \Phi \) was determined from 200 crossings of the first interface. To arrive at a final value for the nucleation rate, we took the average of 5 independent FFS runs.

4. Computing order parameter \( N_{cl} \)

To compute the order parameter used in our FFS simulations, \( N_{cl} \), one first assigns to every particle in the system, that is, to every moving particle and every surface particle, a 13-dimensional vector \( \mathbf{q}_6(i) = (q_6(i)_1, q_6(i)_2, \ldots, q_6(i)_6) \) that characterizes its local environment. The elements of \( \mathbf{q}_6(i) \) are

\[
q_6(i)_m = \frac{1}{N_6(i)} \sum_j Y_{6m}(\hat{r}_{ij}) ,
\]

where \( Y_{6m} \) is a sixth order spherical harmonic, and \(-6 \leq m \leq 6\). Here \( N_6(i) \) is the number of neighbors of particle \( i \), and \( \hat{r}_{ij} \) is a unit vector connecting particles \( i \) and \( j \). Two particles are defined to be neighbors if their separation \( r_{ij} < 1.5\sigma \), and the sum in Eq. (A2) is over all neighboring particles \( j \). Next, the \( \mathbf{q}_6(i) \) vectors are normalized and, for each particle \( i \), the dot product between the normalized vector \( \hat{\mathbf{q}}_6(i) \) with that of each of its neighbors \( j \) is computed. particles \( i \) and \( j \) are said to form a “link” if \( \hat{\mathbf{q}}_6(i) \cdot \hat{\mathbf{q}}_6(j) \) exceeds a threshold of 0.65. We note that a link can be made between a moving particle and a surface particle—usually one that is on the top layer of the surface—as well as between two moving particles (and a link is always made between two neighboring surface particles, in this case \( \hat{\mathbf{q}}_6(i) \cdot \hat{\mathbf{q}}_6(j) = 1 \)). If a particle has at least six links then it is identified as being in a crystalline environment.

Next, we consider only those particles identified as being in a crystalline environment that are also moving particles (that is, we discard the surface particles). We perform a cluster analysis on these particles. The cluster analysis involves computing the largest connected component of an undirected graph40 with particles as vertices and edges between any two neighboring particles (again, although we could use a different criterion from that used previously, we take two particles to be neighbors if \( r_{ij} < 1.5\sigma \)). The order parameter used for our FFS simulations, \( N_{cl} \), is the number of particles in the largest cluster. We refer to this group of particles as the “nucleus,” in reference to classical nucleation theory, and we refer to a nucleus of “size” \( N_{cl} \).

16J. H. van der Merwe, Faraday Discuss. 5, 201 (1949).
27Our definition of \( \delta \) differs by a factor of 100 from that given in Ref. 28, i.e., we express the mismatch in percentage terms.