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Kinetic coefficient of steps at the Si(111) crystal-melt interface from molecular dynamics simulations

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Nonequilibrium molecular dynamics simulations are applied to the investigation of step-flow kinetics at crystal-melt interfaces of silicon, modeled with the Stillinger-Weber potential [Phys. Rev. B **31**, 5262 (1985)]. Step kinetic coefficients are calculated from crystallization rates of interfaces that are vicinals of the faceted (111) orientation. These vicinal interfaces contain periodic arrays of bilayer steps, and they are observed to crystallize in a step-flow growth mode at undercoolings lower than 40 K. Kinetic coefficients for both [110] and [121] oriented steps are determined for several values of the average step separation, in the range of 7.7–62.4 Å. The values of the step kinetic coefficients are shown to be highly isotropic, and are found to increase with increasing step separation until they saturate at step separations larger than ~ 50 Å. The largest step kinetic coefficients are found to be in the range of 0.7–0.8 m/(sK), values that are more than five times larger than the kinetic coefficient for the rough (100) crystal-melt interface in the same system. The dependence of step mobility on step separation and the relatively large value of the step kinetic coefficient are discussed in terms of available theoretical models for crystal growth kinetics from the melt. © 2007 American Institute of Physics. [DOI: [10.1063/1.2754682](https://doi.org/10.1063/1.2754682)]

I. INTRODUCTION

In the growth of crystals from the melt or solution the properties of solid-liquid interfaces often play a critical role controlling morphology and defect densities. In the case of inorganic materials grown from their melt phase, quantitative modeling of solidification is often hindered by a lack of detailed experimental data concerning the intrinsic properties of crystal-melt interfaces. Specifically, modeling of nucleation and solidification growth morphologies requires knowledge of the magnitudes and associated crystalline anisotropies of the crystal-melt interfacial free energies and mobilities. Due to the inherent difficulty associated with direct experimental studies of solid-liquid interfaces at high temperatures, measured data for the properties of crystal-melt interfaces are presently available for very few systems. Since the pioneering work of Broughton *et al.*¹ much of the most detailed information concerning the intrinsic properties of crystal-melt interfaces has been derived from atomic-scale molecular dynamics (MD) and Monte Carlo simulations. Such simulations have determined the magnitudes and anisotropies of crystal-melt interfacial free energies^{2–10} and kinetic coefficients^{7,11–17} for numerous elemental systems, modeled with Lennard-Jones, hard-sphere, and repulsive power-law potentials, as well as embedded atom method models for metals. For these systems, which crystallize in simple fcc, bcc, and hcp crystal structures, crystal-melt inter-

faces are atomically rough, with properties that are relatively weakly anisotropic. Far less attention has been devoted to the properties of faceted crystal-melt interfaces, and the theoretical understanding of these interfaces remains less developed.

The growth of a faceted crystal from its melt is typically governed by the formation and lateral motion of steps. While the structure, and thermodynamic and kinetic properties of steps at crystal-vapor interfaces have been studied extensively (see, e.g., Ref. 18 and references therein), both theoretically and experimentally, relatively few fundamental studies have been undertaken related to steps at crystal-melt interfaces.¹⁹ The current work is devoted to the study of the structure and kinetic properties of steps in a model elemental system displaying faceted crystal-melt interfaces, namely, the Stillinger-Weber (SW) model of elemental Si. A primary focus of this work is to characterize the magnitude and anisotropy of the step kinetic coefficient, β_{step} , defined as the proportionality constant between step velocity and undercooling, $\Delta T = T_M - T$, at low undercoolings. The magnitude of the step kinetic coefficient and its relationship to facet orientation and step separation is information of fundamental importance for theories of the solidification of faceted crystals.

The work presented here is an extension of earlier molecular dynamics studies of crystal-melt interfaces in SW Si. Early work from Landman *et al.*²⁰ revealed the formation of {111} oriented facets in MD simulations of a SW Si crystal-melt interface with an average orientation normal to (100); the study also showed crystalline ordering in the melt region

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close to the interface. Subsequent work by Luedtke *et al.*²¹ to investigate crystal growth from the melt at the (111) interface of SW Si showed clearly the qualitative nature of the “layer-by-layer” growth mode for this faceted interface. In a study that was more focused on a quantitative understanding of crystal growth rates, Grabow *et al.*²² concluded that a Wilson-Frenkel-type theory²³ describes the dependence of the rate of growth on undercooling at both (100) and (111) crystal-melt interfaces in SW Si. In a related area of research, molecular dynamics simulations with empirical potentials for Si have also been used to investigate the growth of Si crystals from the amorphous phase.^{24–26} The current work involves the application of nonequilibrium molecular dynamics simulations to the study of step kinetics, from simulations of the growth of SW Si crystals with interfaces vicinal to the faceted (111) orientation. It is demonstrated that the study of step-flow growth kinetics requires system sizes and simulation times considerably larger than those used in previous studies of crystal-melt interfaces in SW Si, and the current work is thus made possible by recent advances in computing power and simulation algorithms.

In the remainder of this paper we discuss in detail the methods for setting up and equilibrating the simulation systems, for analyzing the results to extract step kinetic coefficients, and the effects of the MD algorithm parameters on the results. We confirm that steps have a bilayer structure and we find that the step-flow mode is stable up to undercoolings of 40 K. Computed step kinetic coefficients have values that increase with step separation at nanometer step spacings, saturating to values that are more than five times larger than the kinetic coefficient of the rough (100) interface. The connection between these results and the atomistic structure of the steps is discussed, emphasizing the diffuse nature of the steps. The remaining presentation starts with an outline of the computational methods used and detailed information about the simulated systems. The computed kinetic coefficients and related results are presented in Sec. III, followed by a discussion and summary.

II. COMPUTATIONAL METHOD

The interactions between silicon atoms are approximated by the SW classical empirical potential.²⁷ A notable feature of the SW potential is its prescription for three-body interactions. The three-body forces enforce the tetrahedral structure of the diamond lattice through an angular term that seeks to set the angle θ between bonds in the solid phase to the equilibrium value of $\cos \theta = -1/3$. The equations of motion for most of the molecular dynamics simulations presented here are solved by the LAMMPS 2001 (Ref. 28) parallel code to which we added routines specific to the SW potential. LAMMPS provides a parallel implementation of a Nosé-Hoover-type algorithm²⁹ for simulations of systems in contact with a thermostat and/or a barostat. Some simulations are performed with a more recent version of LAMMPS which includes its own implementation of the SW potential. The consistency of the results obtained using two independent implementations of the same SW potential affords a high degree of confidence in the accuracy of the computations.

Coexisting liquid and crystal phases of silicon are prepared with a direct coexistence technique developed by Morris and co-workers.^{30–32} The procedure starts with the equilibration of a solid system employing *NPT* ensemble dynamics at the desired pressure, $P=0$ in our case, and temperature T , ideally just below the melting temperature $T_M \approx 1677$ K. The initial simulation box is a parallelepiped with the z axis along a vicinal interface normal $[hkl]$. The vicinal directions $[hkl]$ are obtained by rotating $[111]$ around the $[\bar{1}2\bar{1}]$ or $[10\bar{1}]$ directions, leading to steps along $[\bar{1}2\bar{1}]$ and $[10\bar{1}]$, respectively. Constraints are placed on the vicinal orientations by the requirement of periodic boundary conditions. Our choices for the vicinal orientations are listed in Table I. The final configuration from the *NPT* ensemble equilibration of the crystal, ω_{crystal} , is used as initial configuration in an $N A_{xy} P_z T$ run that melts the solid to produce a liquid silicon phase. The boundaries in the x and y directions, and implicitly the side area A_{xy} of the simulation box, are held fixed and only the pressure component along the perpendicular direction, P_z , is controlled with the Nosé-Hoover algorithm. The temperature of the thermostat is gradually increased to $T_f=3000$ K to completely melt the crystal. After a short run (50–100 ps) with the thermostat set to T_f , the thermostat temperature is quickly restored to the initial value T followed by a 100–200 ps long equilibration of the melt at temperature T . The final configuration of the supercooled liquid, ω_{melt} , and the initial solid configuration, ω_{crystal} , are joined along the z direction to form a new simulation cell with two solid-liquid interfaces of area A_{xy} in the xy plane. In order to avoid the overlapping of atoms at the interface, a small region of vacuum of length 0.5 Å and area A_{xy} is inserted between the solid and liquid configurations. The stress built at the interfaces is further relieved by a short $N A_{xy} P_z T$ run (200–300 ps) of the combined crystal-melt system with the thermostat at temperature T and the volume of the simulation box allowed to relax in the z direction perpendicular to the interface. Finally, the solid-liquid system is allowed to reach coexistence equilibrium in an *NVE* ensemble run. The temperature in the system adjusts naturally to the coexistence value $T_M \approx 1677$ K. In some cases we used an alternative approach: the atoms of a portion of the initial crystal configuration are held fixed while the rest of the crystal is melted and then cooled back to a temperature close to the melting point. The combined crystal-melt system is then equilibrated in the same manner as for the procedure described above. We find no difference in calculated growth rates in the systems built with the two slightly different procedures.

The growth of the crystal phase is investigated in nonequilibrium simulations. An undercooling ΔT is imposed on the system and the pressure in the z direction is held constant with the Nosé-Hoover thermostat and barostat. The appropriate ensemble is the $N A_{xy} P_z T$ ensemble mentioned above. The starting configuration for the nonequilibrium run is one of the configurations from the preliminary *NVE* coexistence run. In most cases the initial velocities are rescaled so that the temperature corresponds to the imposed undercooling ΔT but for small undercoolings the time required to reequilibrate the system at the lower temperature is short enough not to

TABLE I. Orientation and dimensions of the simulated systems. When two systems have the same crystal-melt interface orientation a subscript is attached to the direction of the normal or to the interface plane specification for ease of reference. l is the average separation between steps, L_y is the length of the simulation cell in the direction of the steps, and L_z^{initial} is the initial length of the cell in the direction perpendicular to the interface (L_z is a variable quantity in the crystal growth simulations).

Interface orientation	Step direction (y)	l (Å)	L_y (Å)	L_z^{initial} (Å)	N_{atoms}
(321) _a	$[\bar{1}2\bar{1}]$	7.7	53.5	117.9	16 128
(321) _b			107	117.9	32 256
(543) _a	$[\bar{1}2\bar{1}]$	15.4	53.5	148.9	19 200
(543) _b			106.9	148.9	38 400
(765) _a	$[\bar{1}2\bar{1}]$	23.1	40.1	110.7	15 840
(765) _b			80.2	109.8	31 680
(987) _a	$[\bar{1}2\bar{1}]$	30.9	93.6	146.5	65 184
(987) _b				292.9	130 368
(11, 10, 9)	$[\bar{1}2\bar{1}]$	38.6	120.4	182.7	130 464
(13, 12, 11)	$[\bar{1}2\bar{1}]$	46.3	133.7	219	208 320
(7, 10, 7)	$[10\bar{1}]$	17.83	108.1	148.3	44 352
(343) _a	$[10\bar{1}]$	22.3	54.0	182.6	34 272
(343) _b			115.8	182.6	73 440
(343) _c			231.6	182.5	146 880
(787)	$[10\bar{1}]$	49.0	115.8	198.9	58 320
(9,10,9) _a	$[10\bar{1}]$	62.4	115.8	252.8	94 320
(9,10,9) _b			231.6	253.0	188 640

affect the analysis. Nonequilibrium molecular dynamics simulations have been used before to determine the kinetic coefficient of rough solid-liquid interfaces in Lennard-Jones systems (e.g., Refs. 33 and 34) and metals (e.g., Refs. 7 and 16). Briels and Tepper have found that the value of the kinetic coefficient obtained from nonequilibrium simulations agrees with the result derived from an analysis of the fluctuations in the number of atoms in the solid phase at solid-liquid equilibrium.³³

Due to the different atomic densities in the crystal and liquid phases, the growth of the crystal at constant P_z is accompanied by a change in system volume, manifested in an $N A_{xy} P_z T$ simulation by a change in periodic length in the z direction. The average velocity R_z of the solid-liquid interface can be determined directly from the rate of change of the system's volume V (or length in the z direction L_z since $V = A_{xy} L_z$ and A_{xy} is fixed),

$$R_z = \frac{1}{2A_{xy}} \frac{v_s}{v_s - v_l} \frac{dV}{dt}, \quad (1)$$

where v_s and v_l are the volumes per atom in the solid and liquid phases, respectively. There are two interfaces in the periodic cell, hence a factor of 2 in the denominator. The growth at a vicinal interface is commonly expressed in terms of the growth velocity along the high symmetry direction, here $[111]$, R_{111} . Simple geometry yields

$$R_{111} = \frac{R_z}{\cos \theta}, \quad (2)$$

with θ the small angle between the vicinal direction $[hkl]$ and $[111]$. For the case of solidification or melting by step flow, it is natural to identify an average velocity of the steps v_{step} ,

$$v_{\text{step}} = R_{111} \frac{l}{h} = \frac{R_{111}}{\tan \theta}, \quad (3)$$

where h is the step height and l is the average step separation. It is important to stress that Eq. (3) assumes step-flow growth only and does not take into account a change in growth mechanism, such as two-dimensional island nucleation, that may occur as θ approaches zero. Analogous relations hold for the kinetic coefficients, so the step kinetic coefficient $\beta_{\text{step}} = v_{\text{step}} / \Delta T$ is obtained from the kinetic coefficient of the interface $\beta_z (= R_z / \Delta T)$ as

$$\beta_{\text{step}} = \frac{\beta_{111}}{\tan \theta} = \frac{\beta_z}{\sin \theta}. \quad (4)$$

In the following sections it will be useful to discuss the structural features of the steps as they relate to the calculated mobilities. For this purpose it is useful to analyze the local structure surrounding each atom as a basis for distinguishing between crystalline and liquid environments, and in order to identify interface and step boundary locations. We use a slightly modified version of the discriminator function proposed by Morris and Song⁶ for fcc crystals in our analysis of the local structure surrounding each atom. For completeness, we provide the equation for the discriminator function $\psi(i)$ of atom i , adapted to the geometry of a diamond-cubic crystal,

$$\psi(i) = \left| \frac{1}{ZN_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{j=1}^Z \exp(-i\mathbf{q}r_j) \right|^2, \quad (5)$$

where Z is the number of atoms j found in a sphere of radius 3 Å surrounding atom i and $N_{\mathbf{q}} = 12$ is the number of reciprocal lattice vectors corresponding to the 12 next nearest neighbor directions in a diamond lattice. By design, $\psi(i) = 1$

FIG. 1. The bilayer nature of the steps is shown in a projected view of a portion of a crystal-melt system. The arrow indicates the $[111]$ direction and the direction of the steps $[1\bar{2}1]$ is perpendicular to the plane of the page. The melt and crystal regions are distinguished by the shade used to plot the atoms, with the darker shades corresponding to the ordered region.

if the atom i has four other atoms positioned at the exact locations of the four nearest neighbors of an atom in a perfect diamond-cubic crystal and $\psi(i) \approx 0$ for an atom in the melt phase. It is sometimes useful to smooth the discriminator function by averaging its value with the discriminator values of the Z neighbors mentioned above,

$$\psi'(i) = \frac{1}{Z+1} \left(\psi(i) + \sum_{j=1}^Z \psi(j) \right). \quad (6)$$

Once the discriminator values are computed for each atom, determining the positions and contours of the steps is a matter of coarse-graining the bilayers that are divided into crystal and melt regions by the steps, and fitting the discriminator profile across the steps to find the best estimates for the location of the discretized steps. Such a tracking algorithm is an extension of previous work on crystal-melt interface location employed primarily in the context of the capillary fluctuation method.^{3,35} Further details of this procedure applied to steps will be provided in a future publication.

III. RESULTS

The growth at several interfaces covering average step separations l from 7.7 to 62.4 Å is simulated over a wide range of undercoolings. Details related to the orientation of the interfaces and system sizes are summarized in Table I. An immediate observation on the geometry of the stepped interfaces is the bilayer structure of the steps over the whole range of step separations analyzed, as illustrated in the cross-sectional view of the interface shown in Fig. 1. Unlike their crystal-vapor counterparts, the steps formed at the crystal-melt interface are very rough and diffuse. Figure 2 highlights the structure of the step in a plan view, showing a layer of atoms with a step separating crystalline (on the right) and liquid (on the left) regions. The roughness of the step manifests itself in the meandering nature of the step boundary, indicated by the solid black line, as calculated from the discriminator profile algorithm described in the previous section. In addition to their pronounced roughness, the boundaries are not structurally sharp, and are instead diffuse in character. The diffuse nature of the steps is apparent from the observed fluctuations in the degree of order/disorder that can be readily observed on both sides of the step boundary.

Before undertaking a quantitative analysis of the growth simulations, it is important to verify that the step-flow growth mode is operative. As a function of undercooling the

FIG. 2. Top part identifies a bilayer with two horizontal lines (same view-point as in Fig. 1) which is then plotted using a plan view in the bottom part of the figure. The size of the disks representing the atoms in the bottom part is proportional to the position of the atoms along the $[111]$ direction, perpendicular to the page. The arrow points in the $[1\bar{2}1]$ direction of the step. The line is a coarse-grained fit of the edge of the step. The degree of local order is represented by changes in the coloring of the disks, with a darker shade for the larger degree of local order.

mechanism for growth of a faceted interface can change from that of island nucleation and growth to rough growth,³⁶ and similarly, as one increases the undercooling for a vicinal interface, the nucleation of islands on the terraces can lead to roughening and the breakdown of the step-flow growth. To verify the step flow in our simulations, we employed analyses consisting of either simply visualizing the trajectory with the aid of visualization software or, in a few cases, tracking the moving steps with the aid of the discriminator analysis described above. Figure 3 shows the results of such a test, plotting the position of three steps at the top and bottom interfaces as a function of simulation time. The steps at each interface move approximately in parallel, confirming the as-

FIG. 3. Average position of steps as a function of time during a crystal growth simulation for the system $(543)_p$. The undercooling is 25 K. There are three steps for each of the two interface in the periodic system. The average positions of the top three steps are inverted and shifted relative to the time axis for easier comparison with the three steps at the bottom.

FIG. 4. Example of interface roughening occurring during crystal growth at the (13,12,11) interface for an undercooling of 40 K.

sumption of uniform step flow. Interestingly, the three steps at the top move at a slower pace initially but the velocities of the steps at the two interfaces get closer over the last 200 ps of the simulation. This feature of the results demonstrates the relatively long time scales associated with the intrinsic fluctuations in step velocities, and the need for sampling over sufficiently long simulation times to acquire adequate statistics. While the step-flow growth mode is observed in all of the simulations at low undercoolings, a breakdown of this growth mode can be noticed for undercoolings larger than or equal to 35–40 K. An example is given in Fig. 4 showing an interface that has been roughened due to the breakdown of the step-flow growth mode. The breakdown of step-flow growth is expected at undercoolings that are large enough to allow the nucleation and growth from the melt of crystal islands on the terraces. The results reported in the remainder of this section include only simulations featuring stable step-flow growth.

As is usually the case with computer simulations, it is necessary to show that the physical quantities determined in the course of the simulations are independent of the algorithms employed and the finite size of the simulated systems. The key component of the computational method employed here is the nonequilibrium Nosé-Hoover simulation of the crystal-melt system in contact with a thermostat and a barostat. The coupling of the system with the thermostat and the barostat is controlled by two parameters with dimensions of time, τ_T and τ_P , which effectively set the relaxation times of temperature and pressure fluctuations in the system. While equilibrium Nosé-Hoover simulations are known to be robust for a range of coupling parameters, nonequilibrium simulations introduce a time scale related to the rate of change of the system's properties. For the case of crystal growth simulations one must ensure that temperature and pressure fluctuations decay on a time scale smaller or comparable to the time it takes to grow at most a few layers of crystal. The choice of barostat and thermostat parameters has been discussed by Tepper and Briels in the context of crystallization simulations in a Lennard-Jones system.³⁴ These authors chose the lowest thermostat and barostat relaxation times that lead to Gaussian temperature and pressure distributions at equilibrium. We supplement the equilibrium analysis with tests of the dependence of crystal growth rates on barostat and thermostat relaxation times. As shown in Fig. 5, we find that the rates of growth (the slopes of the volume increase with time) obtained with different thermostat and barostat parameters are scattered by no more than 7% around an average value, consistent with expected statistical uncertainties.

FIG. 5. Volume per atom during crystal growth simulations for the (765) system at 30 K undercooling with various parameters for the Nosé-Hoover thermostat and the barostat. The six sets of volume data have been shifted by 0.1 Å^3 relative to each other from bottom to top (bottom data not shifted) for comparison. The corresponding thermostat and barostat relaxation time parameters τ_T and τ_P are, from bottom to top; $\tau_T=10 \text{ fs}$ and $\tau_P=1000 \text{ fs}$, $\tau_T=10 \text{ fs}$ and $\tau_P=10\,000 \text{ fs}$, $\tau_T=10 \text{ fs}$ and $\tau_P=100\,000 \text{ fs}$, $\tau_T=100 \text{ fs}$ and $\tau_P=1000 \text{ fs}$, $\tau_T=10\,000 \text{ fs}$ and $\tau_P=1000 \text{ fs}$, and $\tau_T=10\,000 \text{ fs}$ and $\tau_P=1000 \text{ fs}$.

The average growth rates are thus independent of the value of the adjustable barostat and thermostat parameters over an interval spanning several orders of magnitude, and only the frequency of volume fluctuations is affected by the choice of these relaxation times. The quality of the thermostating algorithm is conveniently verified by comparing the temperature distribution sampled in the course of the nonequilibrium run with the expected Gaussian distribution of mean temperature $\langle T \rangle$ and variance $2\langle T \rangle^2/(3N)$, where N is the number of atoms in the system. A test of this kind is exemplified in Fig. 6. The sampling of the P_{zz} component of the pressure can be similarly tested. Figure 7 shows again the desired Gaussian character of the distribution.

Possible finite size effects are investigated for a few systems by varying the size of the simulation cell in the direction of the steps (L_y) and in the direction perpendicular to the vicinal interface (L_z). The step length L_y could potentially have a significant role in the dynamics of the steps due to its effect on step roughness. We assess the role of the step length in the crystal growth process by computing growth rates for systems with step lengths in the range of 40.1 to 231.6 Å. The results in Fig. 8 give rise to interface mobilities varying by less than 4% for [121]-oriented steps and 5% for the [101]-oriented steps; these results are within statistical uncertainties in both cases and therefore show no statistically significant variation in step mobilities with step length over the range of lengths investigated. Furthermore, Fig. 8 also serves

FIG. 6. Probability distributions for the temperature T of systems undergoing simulated crystal growth at a temperature T_{target} 30 K below the melting temperature. Three sets of data are shown, all for the same system with (765) interfaces but for three different thermostat relaxation times: diamonds for $\tau_T=10$ fs, stars for $\tau_T=100$ fs, and triangles for $\tau_T=10\,000$ fs. The solid line is the expected Gaussian probability distribution of temperatures in the canonical ensemble for the imposed target temperature. The variance of the Gaussian curve is $2T_{\text{target}}^2/(3N)$ with $N=31\,680$ the number of atoms.

as evidence of the isotropic nature of step kinetics. The growth rates for steps along [110]- and [121]-type directions, at virtually identical step separations, are within statistical uncertainties. The finite size of the systems in the z direction has to be large enough to avoid unwanted interactions between the two crystal-melt interfaces of the simulation cell. As can be seen in Table I the distance between the two interfaces, $L_z/2$, is several times larger than the step separation. We also test the sensitivity of the results to a doubling

FIG. 7. Typical probability distribution for the p_{zz} component of the pressure tensor in a system undergoing simulated crystal growth in the $NA_{xy}P_zT$ ensemble. The barostat relaxation time is set to $\tau_p=1000$ fs. The line is a Gaussian centered on the imposed pressure p_{zz}^{target} and the width given by the variance of the data.

FIG. 8. Growth rates for several undercoolings in systems with different step lengths and step orientations but equal or almost equal average step separation. Rates for the (765)_b system, with $L_y=80.2$ Å and step orientation $[\bar{1}2\bar{1}]$, are represented by filled diamonds. Empty diamonds are used for the (765)_a system, where the step length L_y is half the value of (765)_b. Filled stars, empty stars, and smaller empty stars represent the growth rates for the (343)_c, (343)_b, and (343)_a systems, respectively, with step orientation $[10\bar{1}]$ and step lengths L_y of 231.6, 115.8, and 54 Å, respectively.

in the value of L_z for the (987) system. As shown in Fig. 9 there are no statistically relevant finite size effects in the range of L_z investigated. The kinetic coefficients for the two systems do not differ by more than 5%, within the expected statistical uncertainties.

Figure 10 shows a clear linear dependence of the rate of growth on undercooling for low undercoolings. A point that has been discussed at some length in the literature is the symmetry of crystal growth/melting rates derived in computer simulations.³⁴ We verify the equality of the rates of growth and melting for one of the systems, (13,12,11), in Fig. 11. The kinetic coefficient of the steps, as defined in Eq. (4), is derived from the slopes of the linear fits between growth velocity and undercooling. The results are summarized in Fig. 12 as a function of average step separation and in Table II. The few kinetic coefficients computed for steps along [101]-type directions suggest an isotropic step kinetic coefficient for this system. While the rate of growth of the crystal decreases with decreasing step density (increasing

FIG. 9. Two sets of growth rates corresponding to the (987)_a and (987)_b systems described in Table I. The filled symbols represent rates for (987)_a and empty symbols are used for the rates of growth in (987)_b, which has a value of $L_z=293$ Å twice as large as that of (987)_a.

FIG. 10. Crystal growth rates in the [111] direction, R_{111} , at several solid-melt interfaces and for various undercoolings ΔT . The symbols correspond to $(321)_a$ system (open triangles), $(321)_b$ system (filled triangles), $(543)_a$ system (open diamonds), $(543)_b$ system (filled diamonds), $(765)_a$ system (open squares), $(765)_b$ system (filled squares), $(987)_a$ system (open stars), $(987)_b$ system (filled stars), $(11,10,9)$ system ($\times$), $(13,12,11)$ system ($+$), and $(7,10,7)$ system (open hexagons).

step separation), the mobility of the steps increases as the separation between steps increases over the range of step separations smaller than approximately 50 Å. For the largest step separation studied, 62.4 Å, the step kinetic coefficient appears to have reached a plateau. The kinetic coefficient for steps at a (111) crystal-melt silicon interface has been estimated from experimentally measured growth morphologies to be 0.5 m/(sK); this estimate, shown by the dashed line in Fig. 12, is in very reasonable agreement with the computed values at larger step separations.

IV. DISCUSSION

Nonequilibrium molecular dynamics (MD) simulations have been employed to compute the kinetic coefficients β_{step}

FIG. 11. The symmetry of crystallization and melting rates in the [111] direction, R_{111} , for the $(13,12,11)$ interface.

FIG. 12. Kinetic coefficients for steps at several interfaces plotted vs the average step separation l . The dashed line marks an experimental value of the step kinetic coefficient at silicon crystal-melt interfaces as determined in Refs. 37 and 38. Empty symbols correspond to steps oriented along the [121] direction and filled symbols represent kinetic coefficients for steps along the [101] direction.

of [101] and [121] steps on the faceted (111) crystal-melt interface of Stillinger-Weber (SW) Si. The kinetic coefficients are found to be highly isotropic, with results for [101] and [121] steps showing no statistically significant differences for comparable values of the step separations. The magnitudes of β_{step} depend significantly on step spacing for nanometer-scale step separations; the kinetic coefficient decreases by approximately 50% with a reduction in step separation from ~ 50 to 7.7 Å. For large step separations the kinetic coefficients reach a limiting value in the range of 0.7–0.8 m/(sK). To place the current results in proper perspective it is interesting to compare the computed magnitudes for β_{step} , and the dependence on step separation, with the predictions of theoretical models for crystal growth kinetics.

In the theoretical framework of Wilson and Frenkel (see, e.g., Ref. 33) the solidification velocity is described in terms of the rates of atom attachment and detachment to and from the crystal-melt interface. The diffusion-limited growth model yields the step velocity

$$v(T) = fd \frac{6D(T)}{\lambda^2} \exp\left(-\frac{\Delta H}{k_B T_M}\right) \times \left[1 - \exp\left(-\frac{\Delta H(T - T_M)}{k_B T T_M}\right)\right], \quad (7)$$

where ΔH is the enthalpy difference (per atom) between the

TABLE II. Values of the step kinetic coefficients β_{step} plotted in Fig. 12.

l (Å)	β_{step} [m/(sK)]
7.7	0.29
15.4	0.40
17.8	0.46
22.3	0.48
23.1	0.51
30.9	0.61
38.6	0.64
46.3	0.74
49.0	0.79
62.4	0.68

liquid and the solid phases, $D(T)$ is the temperature dependent diffusion coefficient of atoms in the liquid phase, λ is the diffusional mean free path in the liquid, d represents the distance the step moves with the attachment of a row of solid atoms, and f can be thought of as a kink density, representing the fraction of step sites available for atom attachment from the melt. In the limit of small driving forces, the theory yields an expression for the kinetic coefficient β_{step}

$$\beta_{\text{step}} = fd \frac{6D(T_M)}{\lambda^2} \frac{\Delta H}{k_B T_M^2} \exp\left(-\frac{\Delta H}{k_B T_M}\right). \quad (8)$$

In applying Eq. (8) to Stillinger-Weber Si, we can use the computed values of $D=0.7 \text{ \AA}^2/\text{ps}$, $\Delta H=0.32 \text{ eV}$, and $T_M=1677 \text{ K}$; we further assume a value of λ equal to the nearest-neighbor bond length ($R_{\text{NN}}=2.36 \text{ \AA}$), a distance between atom rows $d \approx 1.64 \text{ \AA}$, and use as an upper bound $f=1$. With these parameter values, Eq. (8) predicts a value of $\beta_{\text{step}}=0.02 \text{ m}/(\text{sK})$, which is more than an order of magnitude smaller than the molecular dynamics results. The result of this comparison is consistent with a similar analysis by Chernov^{19,36} who noted that the Wilson-Frenkel theory leads to estimates for β_{step} much smaller than the experimental result of Voronkov^{37,38} mentioned in the previous section.

A further comparison between the Wilson-Frenkel theory and the MD data can be made on the basis of the *relative* values of the kinetic coefficients for Si steps and for a rough crystal melt interface in the same system. The (100) crystal-melt interface in SW Si is molecularly rough and grows in a “normal” manner, with a velocity that is linearly proportional to interface undercooling. If one makes the reasonable assumption that f and d in Eq. (8) take similar values for the rough (100) interface and for steps, the Wilson-Frenkel theory would predict comparable values for both kinetic coefficients. To test this prediction we have computed β_{100} for SW Si following the same MD approach described in Sec. II. We obtain the (100) interface kinetic coefficient $\beta_{100}=0.122 \pm 0.003 \text{ m}/(\text{sK})$ [in agreement with an earlier estimate of $0.1 \text{ m}/(\text{sK})$ from MD simulations of a much smaller SW Si system³⁹]. This value is more than five times smaller than β_{step} in the limit of large step separations. The comparison reinforces the point that in its simplest form the Wilson-Frenkel theory is unable to account for the relatively large values of the kinetic coefficients for steps at crystal-melt interfaces in elemental Si.

To gain insights into the origin of the unexpectedly large values for β_{step} , derived both from experimental measurements and from MD simulations in elemental Si, it is interesting to consider in further detail the nature of the step structure. We focus, in particular, on two important structural features: the ordered nature of the liquid layer adjacent to the step, and the diffuse nature of the transition region across the step.

Considering first the structure of the liquid layer adjacent to the step, it is useful to analyze again the plan view in Fig. 2. In this figure, the degree of structural order (as measured with the discriminator function described in Sec. II) is indicated by the shading of the atoms, with darker colors corresponding to a higher degree of local order. The short-range ordering of the liquid layer adjacent to the step is readily

FIG. 13. A graphical representation of the degree of local order in consecutive bilayers at the (11,10,9) interface during crystal growth (undercooling of 15 K). The shade of the disks representing the atoms is proportional to the value of the discriminator function that quantifies local order, with darker shades corresponding to the crystal structure. The bilayer depicted in the bottom part of the figure acts as a “substrate” for the bilayer in the top part. The diffuse contour of the steps is a consequence of ordering fluctuations induced by the crystalline “substrate.”

observed, and such ordering is not surprising when one considers that the atoms in this region sit atop a well-formed crystalline layer. The ordering in the liquid, induced by the proximity of the underlying crystalline plane, is illustrated further in Fig. 13, showing two consecutive layers parallel to the crystalline (111) planes, displaced relative to one another by one interplanar spacing into the liquid. In this figure, the step boundary for the top panel is to the right of that in the bottom panel. The increase in the degree of order in the liquid region (top panel) located atop the crystal terrace (bottom panel) is apparent. In light of these observations a plausible qualitative explanation for the large magnitude of β_{step} is that the enhanced order in the liquid layer adjacent to the step gives rise to a reduction in the barrier to crystallization, relative to the Wilson-Frenkel theory which implicitly assumes a sharp boundary between the crystal and a bulk liquid. The effects on crystallization velocities associated with smectic ordering of the liquid layer adjacent steps have been discussed by Chernov,¹⁹ who noted that such ordering should better prepare the liquid for crystallization during step motion, provided that the same ordering does not significantly reduce the atomic mobility in this layer.

We focus next on another important feature of the step structure, the diffuse nature of the transition from the crystal terrace to the liquid across the step boundary, as can be observed in Fig. 2. In their theory for the mobility of rough crystal-melt interfaces in elemental solids, Mikhnev and Chernov⁴⁰ derived a linear proportionality between the ki-

netic coefficient and the width of the diffuse density profile across the interface. Mikheev and Chernov briefly discussed the extension of their theory to steps, giving a formula that expresses the ratio of the kinetic coefficient for a step (β_{step}) to that for a rough solid-liquid interface (β) as $\beta_{\text{step}}/\beta \sim \xi_{\parallel}/d$, where $\xi_{\parallel}/d$ is a dimensionless measure of the correlation length for height fluctuations on the terrace. This relationship is interesting given that the MD results produce a kinetic coefficient for the steps that is roughly five times larger than that for the rough (100) interface. In the Mikheev-Chernov theory this MD result would be interpreted as implying that there is a large value for the lateral correlation length for ordering (“height”) fluctuations in the liquid layer. A direct test of this prediction lies beyond the scope of the present work, but should be possible from a detailed analysis of the ordering fluctuations in the liquid interfacial liquid layer at a large flat (111) interface.

We turn finally to a discussion of the dependence of step kinetic coefficient on step separation (shown in Fig. 12). From an analysis of step contours (see, e.g., Fig. 2) we find that wider-spaced steps are dramatically rougher than their counterparts with small step separations. This result is to be expected, as repulsive interactions between the steps should generally increase in strength as the interstep distance decreases, leading to a reduction in the meandering amplitude. The reduced magnitude of the step kinetic coefficient at small step separations may reflect that a straighter, weakly meandering step has fewer regions that are favorable for attachment of atoms from the melt, thus making the step less mobile. In this picture the roughness of the step plays a role similar to the parameter f in Eq. (8), and once the step separation exceeds a value that appears to lie in the range of 50–60 Å, the interactions may become weak enough to lead to a plateau for the step kinetic coefficient. An alternative explanation for the dependence of β_{step} on step separation relates to the Mikheev and Chernov theory described in the previous paragraph. Specifically, if the step kinetic coefficient is related to the correlation length for ordering fluctuations in the liquid interfacial layer, the value of β_{step} is expected to decrease as the step separations become smaller than this intrinsic length scale. In this picture, the results in Fig. 12, showing monotonically decreasing values of β_{step} for separations below ~ 50 Å, would suggest intrinsic correlation lengths that are several nanometers in magnitude. Again, validation of this prediction would require detailed analysis of the ordering fluctuations in the liquid interfacial layer.

V. SUMMARY AND CONCLUSIONS

We have performed an extensive computational investigation of the kinetic coefficient of steps, β_{step} , at crystal-melt interfaces in a Si model system. Nonequilibrium molecular dynamics simulations of crystal growth provide direct access to the interface kinetics and, implicitly, to the kinetics of the steps that constitute the vicinals of the high-symmetry Si(111) crystal-melt interface. The step-flow character of the growth kinetics has been verified for undercoolings lower than 40 K and step separations spanning the range from 7.7 to 62.4 Å. We have found no statistically relevant finite

size effects over a broad range of step lengths. The kinetic coefficients for steps oriented along [101] and [121], but separated by the same average interstep distance, have been shown to have the same magnitude, within statistical uncertainties, thus proving the isotropy of the step kinetic coefficient in the analyzed system. An important finding is the strong dependence of the step kinetic coefficient on step separation for step separations in the range of 7.7– ~ 50 Å. The magnitude of β_{step} more than doubles over this range of step separations but it appears to reach a plateau at a value of 0.7–0.8 m/(sK) for step separations larger than 50 Å. We have discussed the magnitudes of β_{step} in the context of the Wilson-Frenkel theory for crystal growth at rough interfaces and found the predictions of the theory to be an order of magnitude smaller than the molecular dynamics results. The large value of β_{step} relative to the kinetic coefficient of a rough crystal-melt interface in the same model system is qualitatively explained by the enhanced ordering of the liquid atoms adjacent to the step. Two possible explanations for the dependence of the step kinetic coefficient on step separation have been discussed. One is based on a picture of interacting steps whose meandering amplitude decreases as the interacting steps get closer to each other, thus shrinking the region near the step edge that is more favorable to attachment of atoms from the melt. An alternative discussion of the dependence of β_{step} on the average terrace width has been offered based on a result of Mikheev and Chernov.⁴⁰ The Mikheev-Chernov result introduces a length scale associated with the correlation length for ordering fluctuations in the liquid interfacial layer. For step separations smaller than this length scale it is expected to see a decrease in the magnitude of β_{step} , as observed in the molecular dynamics results. The fundamental questions raised by the results shown here point to the need for a quantitative investigation of the structure of the (111) and vicinal crystal-melt interfaces in this model Si system. It has become particularly clear that the structure of the melt region adjacent to the crystal plays a crucial role in determining the complex kinetic properties of steps.

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