Solid-liquid phase transitions in single crystal Cu under shock and release conditions

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Solid-liquid phase transitions in single crystal Cu during shock and subsequent release are studied with large-scale classical molecular dynamics simulations. During shock compression, although the equilibrium states far behind shock front converge to the same Hugoniot, the pathways from metastable states right behind the shock front to the final equilibrium states and the resulting microstructures are orientation-dependent. Premelting is followed by recrystallization of supercooled melt into a polycrystalline solid for the [110] and [111] shocks, and a superheated, more ordered, solid is observed prior to shock melting for the [100] shock. The differences in the microstructure in the behind-shock region in turn give rise to different release melting behaviors (including premelting and superheating) along different release paths for these loading orientations.

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I. INTRODUCTION

Understanding solid-liquid phase transitions of metals under shock wave loading is essential to shock physics and its applications, a subject of extensive experimental and theoretical investigations.1–8 With the rapid development of computing ability, molecular dynamics (MD) simulations provide a powerful tool to reveal atomistic processes and physics of solid-liquid transformations (melting and recrystallization) and significant insights have been gained.9–14 For face-centered-cubic (fcc) metallic single crystals, shock-induced melting transitions show strong anisotropy.15–17 For example, it is found that Cu crystals undergo 7–8% premelting for shocks along [110] and [111] but experience as much as 20% overheating along [100].18 In contrast, an orientation-independent Hugoniot in terms of shock velocity-particle velocity (u_s − u_p) is obtained in experiments on single crystal Cu at lower shock strengths.18 Using moving-window MD simulations, Budzевич et al. studied the shock-induced solid-liquid transition in Al and observed “cold melting” followed by recrystallization for shocks along [110] and [111] but overheating-melting along [100]. Nevertheless, the final equilibrium states converge to an orientation-independent Hugoniot at high pressures.19 Cu is an important model metal, and it is of great interest in understanding the exact nature of shock-induced solid-liquid transitions in single crystal Cu.

In experiments on phase transition dynamics in metals, one often measures a released rather than peak shock state owing to the lower impedance buffer windows. Interpretation of shock-recovered materials also requires knowledge on the release paths. Therefore, it is crucial to understand phase transformations upon release as well. Xie et al. explored melting of shock-loaded Cu during release and obtained basic features of release melting and critical shock strengths.13 However, given the small computation scales in their study, the release profiles may not have fully evolved; in addition, the orientation dependence of release melting, if any, remains unexplored. Here, we use large-scale MD simulations to examine systematically solid-liquid phase transitions in single Cu under both shock and release conditions. Three typical low-index crystallographic axes, [110], [111], and [100], are chosen as the shock direction. The long time evolutions of the metastable states right behind the shock front, as well as, the release wave profiles are monitored, which enable us to obtain the equilibrium shock states and microstructure far behind shock front and “stable” structure of release waves. Sec. II briefly describes the methodology for MD simulation and analysis, followed by the results and discussion on shock melting and its orientation-dependence in Sec. III, release melting in Sec. IV, and summary in Sec. V.

II. METHODOLOGY

The dynamics of solid-liquid phase transition in single crystal Cu under shock loading and release are investigated with large-scale non-equilibrium molecular dynamics simulations. The simulated specimens are about 360 nm × 20 nm along the Cartesian x-, y-, and z-axes. Three typical low-index crystallographic directions, [110], [111], and [100], are chosen as the shock direction (x-axis). The embedded atom method (EAM) potential developed by Mishin et al.20 is adopted to describe the interactions among Cu atoms. This potential yields a thermodynamic (equilibrium) melting curve that agrees very well with static experiments16,21 and has also been successfully used to study the dynamic responses of Cu including shock-induced plasticity, spallation, and melting over a very wide pressure range. Prior to shock loading, the initial structures are equilibrated with the constant-pressure-temperature (NPT) ensemble under ambient conditions, and three dimensional (3D) periodic boundary conditions are applied. After the specimen reaches thermal equilibrium, periodic boundary conditions...
are imposed only along the transverse directions (y and z directions) to mimic shock loading. Shock wave is generated using the momentum mirror method where the specimen impacts a piston of infinite mass at a velocity $-u_p$ along the x-axis, yielding a shock wave propagating away from the piston at $u_s - u_p$. Here $u_s$ denotes shock velocity. The equation of motion is integrated via the Velocity-Verlet algorithm with a time step of 1 fs in all simulations. System size effect is also checked but not systematically. A larger system with doubled transverse dimensions (360 nm x 40 nm x 40 nm) shocked along the [110] and [111] directions for $u_p = 2.25$ km/s is explored, and it is observed that system size has little influence on the general simulation results. The instant when the target impacts the momentum wall is set as the time origin ($t_0$) in the following discussions.

To quantify structural disordering of a specimen during shock and release, local order parameter $Q_6$ is utilized, which measures the symmetry correlation of an atom with its nearest neighbors. In practice, $Q_6$ is averaged over the atoms in a small cubic cell with a width of 5 Å to better represent local disordering. There are other parameters to measure structural disordering such as the Morris and Song order parameter which has also been successfully used to discern liquid or solid state. Here, we adopt $Q_6$ due to its convenient numerical implementation, since different sets of direction vectors should be chosen for different reference frames in computing the Morris and Song parameter. Because the properties of the material behind the shock vary along the shock direction, 2D in-plane radial distribution function (RDF) rather than 3D spherical RDF is also used as a characterization tool to help interpret the phases (solid vs. liquid).

III. SHOCK MELTING AND ORIENTATION-DEPENDENCE

The dynamic responses of fcc metals such as single metal Cu under shock wave loading, including plasticity and solid-liquid transition, have been explored extensively in previous works. Here, we examine the long time evolution of the metastable states near the shock front towards the equilibrium states far behind the shock front, and the effects of loading directions.

A. [110] and [111] directions

First, we present general characteristics of shock-induced plasticity at a lower pressure to compare with those of the solid-liquid transition at higher pressures. It is well known that for shock strengths above the Hugoniot elastic limit (HEL), shear stresses are relaxed via different dislocation activities. Figure 1 shows the atomic configuration of Cu shocked along the [110] orientation to a pressure of 81 GPa and the profiles of pressure ($P$), shear stress ($\sigma_{sh}$), temperature ($T$), and order parameter ($Q_6$) along the x-axis, where $\sigma_{sh} = \frac{1}{2} [\sigma_{xx} - \frac{1}{3} (\sigma_{yy} + \sigma_{zz})]$. The shear stress cumulates in the elastic region, which is later relaxed through the nucleation of a large number of dislocations, and this is accompanied by a rapid rise in $P$ and $T$ at the plastic front [Figs. 1(b) and 1(c)]. Among these newly nucleated dislocations, only those with supercritical dislocation core sizes survive and grow, and the others annihilate, resulting in a lower defect density and an enhancement of structure order in the region far behind the plastic front, as seen from the $Q_6$ profile in Fig. 1(c) and the in-plane RDFs in Fig. 2. Furthermore, the positions of the pronounced peaks displayed in the RDFs of planes 2 and 3, in particular at long interatomic distances, coincide with those of a compressed FCC structure to the same pressure indicating a crystalline state with long range order behind the shock front. When $P$ approaches the maximum value, $\sigma_{sh}$ decreases and $T$ increases slowly, suggesting ongoing dislocation activities that transform the shocked material towards hydrostatic state.

When shock is strong enough, a new shear relaxation mechanism named mechanical melting has been proposed and studied using MD simulations on single crystal Al and Cu. A typical picture of mechanical melting is illustrated in Fig. 3, showing the dynamic response of Cu shocked along [110] to a pressure of 166 GPa. The shear stress accumulated by the elastic precursor is relaxed via the ultrafast

![FIG. 1. (a) Atomic configuration of a thin (10 Å) slice of Cu shocked along [110] to a pressure of 81 GPa at 50 ps after impact. Atoms are color-coded according to the central symmetry parameter, where light colors indicate stacking faults and dislocations. Visualization uses AtomEye (Ref. 27). (b) Pressure and shear stress profiles along the shock direction. (c) Temperature and $Q_6$ profiles along the shock direction. Shock direction: left → right.](image1)

![FIG. 2. In-plane RDFs at three positions behind the shock front specified by the dashed lines in Fig. 1.](image2)
shear-induced mechanical melting which completes within a very thin (\(\approx 1 \text{ nm}\)) shock front. Because temperature of the melt is much lower than the equilibrium melting temperature \(T_{\text{m,eq}}\) at the corresponding pressure, it is a metastable, supercooled partial melting state as analyzed below. The thermodynamic melting temperature of the chosen potential under this shock pressure is about 4900 K, as seen from Fig.10, and temperature of the melt right behind shock front is about 2900 K, suggesting a premelting as much as 60%. Although it is attributed to “mechanical melting” in previous studies, the melting may have occurred locally and transiently via dislocation-induced hotspots, so the average temperature is still low; in addition, premelting may occur at defects such as grain boundaries,\(^\text{24}\) and this could be the case for shock-induced premelting. Since the origin of this kind of melting is still not completely understood, we refer to it as “cold melting” tentatively.

In order to verify that the material right behind the shock front is liquid or solid-liquid mixture, we compare the structure and diffusion property with a reference supercooled liquid. The reference liquid is obtained in two steps: a solid with the same density as the state at the shock front is heated incrementally into the liquid regime using constant-volume-temperature \((NVT)\) ensemble with 3D periodic boundary conditions; then the liquid is rapidly quenched to the temperature of the shocked-induced supercooled state. Temperature is controlled with a Nosé-Hoover thermostat in the \(NVT\) ensemble.\(^\text{28}\) Recrystallization of the reference liquid at the quench temperature is also monitored using microcanonical \((NVE)\) ensemble, and its diffusion property and temperature increase can be obtained during solidification process. Figure 4 shows the in-plane RDFs at various positions of the shocked material as well as that of the reference liquid. We can see that the structure of the specimen right behind the shock front is essentially the same as the reference liquid.

The supercooled melt behind the shock front recrystallizes gradually along with an increase in temperature [Fig. 3(c)] and transforms into a solid state within \(\approx 10\) ps, as seen from the change of RDFs and the time evolution of MSD [Figs. 4 and 5]. Though the supercooled melt behind the shock front is actually a local \(NVE\) system, the increase of temperature during recrystallization is about 850 K nearly identical to that of the reference liquid suggesting that the solidification process is rather faster than the thermal diffusion between the melt and surroundings. In addition, the resulting configuration is essentially a polycrystalline solid, and no well-defined defective structures, such as dislocations, twins, or shear bands, can be discerned. Since the solidification rate of the supercooled melt is dependent on coefficient \(D \approx 7 \times 10^{-10} \text{ m}^2/\text{s}\), close to that of the reference supercooled liquid \((D \approx 6.5 \times 10^{-10} \text{ m}^2/\text{s})\), confirming again that the shock-induced supercooled state is liquid-like. However, the supercooled melt is not purely liquid but contains a few solid crystallites which serve as recrystallization nuclei during solidification. Consequently, the recrystallization time is reduced as compared with that of the reference liquid.

FIG. 3. (a) 2D distribution of \(Q_6\) averaged over a thickness of 10 Å along [110] for the [110] shock to a pressure of 166 GPa at 40 ps. Blue (red) regions indicate the cold-melted (solid) phase. (b) Pressure and shear stress profiles along the shock direction. (c) Temperature and \(Q_6\) profiles along the shock direction. Shock direction: left \(\rightarrow\) right.

FIG. 4. In-plane RDFs at three positions behind the shock front specified by the dashed lines in Fig. 3 and that for the reference supercooled liquid.

FIG. 5. Time evolution of MSDs of particles in the region behind the shock (peak pressure of 166 GPa). The dashed line indicates the linear increase regime of the MSDs and diffusion coefficient is obtained as \(1/6\) of its slope.
$T_{\text{eq}}^m - T_H$ (subscript $H$ denotes Hugoniot), i.e., the degree of supercooling, recrystallization time increases sharply as the shock state approaches the equilibrium melting curve. As an example, the shocked Cu maintains a solid-liquid mixture state within the simulation time and does not achieve thermodynamic equilibrium state for shock pressure of 194 GPa (Fig. 6). In this case, the recrystallization process in the supercooled melt has distinct characteristics: initially, recrystallization nucleus emerge homogenously inside the supercooled melt; when some nucleus reach the critical size, they grow steadily accompanied with an adiabatic temperature rise which lowers the probability for further homogeneous nucleation correspondingly; finally, the recrystallization process which is mainly governed by these bigger clusters continues heterogeneously leading to a significant fluctuation in the temperature profile [Fig. 6(b)]. Moreover, it should be noticed that the unique recrystallization behavior could be related to the relatively small system size and extremely low recrystallization rate. For even stronger shock (223 GPa), the specimen retains metastable liquid phase ($\sim 15\%$ supercooling) without apparent recrystallization within the simulation time.

The picture of cold melting followed by recrystallization is similar to that observed in single Al shocked along [110] and [111]. Based on our systematic simulations, the pressure range, in which cold melting-recrystallization predominates, is determined as 121 GPa – 194 GPa for Cu shocked along [110] direction by comparing the RDFs, MSD, and temperature increase of the shocked material with these of the corresponding reference liquids. For shocks lower than the pressure range, the shear stress buildup at the shock front is largely released by the generation of point and extended defects as shown in Fig. 1. However, there is no strict distinction between these two shear relaxation mechanisms. Cold melting could be the result of an avalanche of defect generation.

Figure 7 displays the dynamics response of Cu shocked along [110] to 100 GPa. At first sight, the shear stress seems to be relaxed by production of well-defined defective structures, such as dislocations and stacking faults as seen in Fig. 7(a), and the atomic structure right behind the shock front also exhibits a more ordered state compared with the corresponding reference liquid (Fig. 8). However, a closer look at the evolution of microstructure behind the shock front reveals a more complex picture (Fig. 9). After the passage of the shock wave, liquid nuclei surrounded by the plastically deformed solid emerge (32 ps in Fig. 9). Then, the supercooled liquid nuclei recrystallize quickly inside the surrounding solid and the material as a whole converts into a deformed solid phase [Figs. 8 and 9]. At the same time, defective structures in the solid part preserve and grow, forming various kinds of extended defects far behind shock front [Fig. 7(a)]. Although both the recrystallization of the liquid nuclei and the activities of defective structures could contribute to the rise of temperature behind the shock front [Fig. 7(c)], it is impossible to separate their contributions. With increasing shock strengths, the proportion of liquid counterpart in the region right behind shock front increases.

FIG. 6. (a) 2D distribution of $Q_6$ averaged over a thickness of 10 Å along [110], for Cu shocked along [110] to a pressure of 194 GPa at 50 ps. Blue (red) regions indicate the cold-melted (solid) phase. (b) Temperature profiles along the shock direction. Shock direction: left – right.

FIG. 7. (a) Atomic configuration for Cu shocked along [110] to a pressure of 100 GPa at 50 ps. Atoms are color-coded according to the central symmetry parameter where light colors indicate stacking faults and dislocations. (b) Pressure and shear stress profiles along the shock direction. (c) Temperature and $Q_6$ profiles along the shock direction. Shock direction: left – right.

FIG. 8. In-plane RDFs at different positions behind the shock front specified by the dashed lines in Fig. 7 and for the reference supercooled liquid.
accordingly till nearly complete melting state at 166 GPa as shown in Fig. 3.

Given different shock states, the $T$–$P$ Hugoniot for Cu shocked along [110] direction is obtained. For moderate shock strengths, two $(P, T)$ points, one with the metastable supercooled melt right behind the shock front and the other equilibrium state far behind the shock front, are determined from the $T(x)$ and $P(x)$ profiles.

Despite distinct pathways from the metastable states right behind the shock front to the final equilibrium states, the final solid/liquid states for different loading directions converge to the same solid/liquid branch of the $T$–$P$ Hugoniot. Thus, the orientation–independent Hugoniot curves can be fitted using the combined sets of $(P, T)$ points of the [110], [111], and [100] directions. The fitted solid and liquid branches of the $T$–$P$ Hugoniot and their extrapolations are drawn as the blue and red curves, respectively, in Fig. 10. The simulated thermodynamic melting curve of Cu using the Mishin potential is also shown in Fig. 10 as the solid black curve. Note that the liquid Hugoniot branch also includes solid-liquid mixture or partial melting states, and a pure metastable liquid Hugoniot is not available from these simulations. Solid black vectors connecting open and filled squares, which lie on the extended liquid and the solid Hugoniot branches, indicate trajectories from the metastable supercooled melt right behind the shock front to the final equilibrium solid state as described in Fig. 3. Dashed vectors at 194 GPa and 223 GPa refer to the cases where the specimens maintain nonequilibrium supercooled solid-liquid mixture and supercooled pure liquid state in the simulation times. The open square with red vector at 100 GPa lies between the two Hugoniot branches corresponding to the special case of the solid-liquid mixing state with a large proportion of solid constituent at the shock front as shown in Fig. 9. Note that though the metastable supercooled states for pressures between 121 GPa and 166 GPa lie on the extended liquid branch of Hugoniot, they are also solid-liquid mixing states essentially but with larger portions of liquid constituent. For pressures above 250 GPa, the specimen melts immediately behind shock front and the shock Hugoniot transits into the liquid branch (filled red squares).

For Cu shocked along [111], the dynamic behaviors are similar to those along [110]: plastic deformation, shock-induced cold melting followed by recrystallization, and shock melting take place in sequence with increasing shock pressures. However, since shear stress at shock front for [111] is relatively smaller than for [110] under the same shock strength, e.g., $\sigma_{sh} \approx 20$ GPa and 25 GPa for [111] and [110] at $P = 167$ GPa, respectively, a higher pressure is required for the activation of cold melting. Hence, cold melting followed by recrystallization for [111] direction is within the pressure range of 143–194 GPa (Fig. 11).
B. [100] direction

The shear stresses for the [100] shocks are much smaller than those for [110] and [111] under the same shock strength, so a different shear release behavior is expected. Indeed, it has been pointed out in previous studies that although the α Cu single crystal shocked along [110] or [111] undergoes certain degree of premelting, it can be superheated by as much as ~20% along [100]. Supercooled melt-recrystallization is absent even for very strong shocks along [100]. In contrast, superheating is present, and the degree and duration of superheating are dependent closely on the difference between \( T_H \) and \( T_m \). Eq. As an example, the shocked specimen at (231 GPa, 6640 K) sustains a solid state in the simulation time (40 ps) with 14% overheating (the corresponding equilibrium melting temperature is 5810 K). With increasing shock intensity, the superheated material undergoes solid-liquid transition in a like manner of the [100] shocked Al (Fig. 12): a degree of 20% overheating predominates for about 15 nm from the shock front, and the superheated solid gradually transforms into an equilibrium liquid phase over next ~100 nm with a reduction in \( T \) from approximate 7100 K to 5900 K [Fig. 12(c)].

The solid-liquid transition from superheated state right behind the shock front to liquid is also manifested in the change of the in-plane RDFs from the one with pronounced peaks at long distance to the one identical to that of the reference liquid phase (Fig. 13). The (extended) solid and liquid branches of Cu shocked along [100] direction are drawn in Fig. 14. The open square with the dashed red arrow corresponds to the superheated solid state that persists in the simulation time. The path from the superheated solid right behind shock front to the equilibrium liquid shown in Fig. 12 is indicated by the solid black arrow. At higher pressures, the crystal melts rapidly within a very narrow region behind the shock front, and the Hugoniot enters the liquid regime.

IV. RELEASE MELTING

When a shock wave reaches a free surface, it is reflected as release fans, which unload the shocked material into partially or fully released states. A phase transition from a compressed solid state into liquid may take place during release, a process termed as release melting. Although the simulated solid branches of the Hugoniot converges for different loading directions, the resulting microstructures in the region behind shock are quite different: “Polycrystalline” solid for the [110] and [111] shocks and a more ordered solid for the [100] shock. Therefore, it is reasonable to expect different release melting behaviors for different directions.

For the [110] and [111] shock loading below ~140 GPa, the materials remain solid during the entire release process from the shocked to fully released state. For higher shock pressures, melting of polycrystalline Cu occurs in partially and fully released states; the polycrystalline structure forms upon shock as a result of “cold” partial melting and subsequent recrystallization. Figure 15 shows representative snapshots of release melting for the [110] shocks to 142 GPa (a) and 166 GPa (b). Release melting arises initially in some highly disordered regions of the partially released...
polycrystalline Cu, which grows into a solid-liquid mixture [the dashed red rectangle in Fig. 15(a)] or a completely melted phase [the dashed red rectangle in Fig. 15(b)] in the fully released state. However, a narrow region near the free surface maintains crystalline structure at all times, since it undergoes much less compression due to the interaction between the incident shock and immediately formed release fans. For shocks along [110], an elastic precursor is reflected at the free surface and the resulting release fan weakens the incoming plastic shock, and the region near the free surface remains elastic without phase transformations throughout the entire shock and release process. The thickness of this near-surface region decreases with increasing shock pressure as expected.

Figure 16 shows typical release wave profiles for the [110] and [111] shocks to 166 GPa. For [110], the release profiles vary continuously without clear indication of melting but split into an ambiguous “two-wave” structure just before entering the fully released state [black arrow in Fig. 16(a)], which might be a signature of phase transition. However, the “two-wave” structure is rather unclear, and, maybe, a much larger specimen should be tested which is out of our current computation ability to give a definitive conclusion in the future. By combining the distribution of $Q_6$ and release wave profiles, we determine the onsets of both partial and full release melting. The ($P$, $T$) states where release melting begins under various conditions are listed in Table I. For [110], partial release melting in the highly disordered region occurs at ~81 GPa and ~2850 K, while complete release melting happens at ~1 GPa and ~1360 K [dashed and solid arrows in Fig. 16(a)]. Since the equilibrium melting temperature at 81 GPa is 3500 K, partial release melting occurs with 14% premelting. Moreover, when it initiates, partial melting seems to progress continuously during further release, with no clear indication of phase transition in the release wave profiles. Right before full release, the material melts completely with an unclear phase transformation signature in the release profiles. The features of release melting for the [111] shocks are almost identical to those for [110], as seen from the release profiles in Fig. 16.

Conversely, despite of a great deal of defective structures, the behind-shock region remains essentially a monocrystalline structure for the [100] shocks, as opposed to the polycrystalline structure for the [110] and [111] shocks. Release melting for the [100] shocks occurs at shock

<table>
<thead>
<tr>
<th>Direction</th>
<th>$P_H$ (GPa)</th>
<th>$P_{Rm}$ (GPa)</th>
<th>$T_{Rm}$ (K)</th>
<th>$T_{Em}$ (K)</th>
<th>$h_{Rm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110]</td>
<td>142</td>
<td>22</td>
<td>1750</td>
<td>2120</td>
<td>0.825</td>
</tr>
<tr>
<td></td>
<td>166</td>
<td>81</td>
<td>2850</td>
<td>3500</td>
<td>0.864</td>
</tr>
<tr>
<td></td>
<td>143</td>
<td>21</td>
<td>1800</td>
<td>2090</td>
<td>0.861</td>
</tr>
<tr>
<td></td>
<td>167</td>
<td>59</td>
<td>2680</td>
<td>3060</td>
<td>0.876</td>
</tr>
<tr>
<td>[100]</td>
<td>165</td>
<td>2</td>
<td>1610</td>
<td>1415</td>
<td>1.138</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>14</td>
<td>2100</td>
<td>1860</td>
<td>1.129</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>78</td>
<td>3950</td>
<td>3450</td>
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<td>230</td>
<td>124</td>
<td>4920</td>
<td>4260</td>
<td>1.155</td>
</tr>
</tbody>
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$T_{Em}$ is the equilibrium melting temperature at the corresponding shock pressure. $h_{Rm} = T_{Rm}/T_{Em}$ provides a measurement of the degree of overheating ($>1$) or supercooling ($<1$) of release melting.
pressures greater than 142 GPa, which is the same as for the other two directions. Upon release from the [100] shock to 142 GPa, only a very thin (several nanometers) melted surface region appears in the fully released state due to the additional surface energy that lowers the energy barrier to melting [Fig. 17(a)]. While releasing from higher pressures, interior melting also occurs at partially released states. Different from the [110] and [111] cases where a very wide partial melting region develops and continuously broadens with the progression of release [Fig. 15(b)], the partial melting region is much narrower and the material reaches complete melting state rapidly for the [100] case [Fig. 17(b)]. Consequently, the release wave splits into a two-wave structure with a leading plastic release wave followed by a solid-liquid transition wave, which can be discerned in the release wave profiles [black and red lines in Fig. 18]. Furthermore, the velocity of the melting front can be calculated from the stable two-wave profiles at different times. The velocities of the melting front are about 3.8 km/s and 4.6 km/s for releasing from 165 GPa and 190 GPa, respectively, which are close to the experimental bulk sound velocities of Cu at corresponding pressures. For release from higher pressures, much longer simulation time is needed for the observation of a stable phase transition wave; however, the slope change in the release wave profile is also an indication of melting [blue lines in Fig. 18, in particular the temperature profile]. Table I indicates that release melting from various pressures occurs with ~15% superheating for the [100] shocks.
Given $P(x)$ and $T(x)$, the $T$–$P$ release paths can be plotted, and the characteristics of release melting for different shock directions, identified from the release paths. For equilibrium phase transitions, release melting should occur at the intersection of a release path and the equilibrium melting curve $\left[T_{\text{Eq}}^m(P)\right]$. Nonequilibrium melting is observed with maximum premelting (superheating) of about 15% (14%) in our simulations, so release melting should occur at the cross-point of the release path and $0.85T_{\text{Eq}}^m(P) \left(1.147T_{\text{Eq}}^m(P)\right)$ if we assume the same amount of premelting (overheating) during release.

Upon release from $\sim 140$ GPa [Fig. 19(a)], all of the three release curves vary smoothly and coincide with each other for pressures above $\sim 20$ GPa. Then the [110] and [111] curves deviate from the [100] curve at the intersection with $0.85T_{\text{Eq}}^m(P)$ due to release melting. Although the [100] curve intersects $T_{\text{Eq}}^m(P)$ at nearly fully released state, the material preserves a solid state except for the thin liquid surface layers, indicating a superheated solid state. Conversely, the [110] and [111] curves lie totally below $T_{\text{Eq}}^m(P)$ and intersect with $0.85T_{\text{Eq}}^m(P)$ with premelting, suggesting a supercooled state. For a higher shock pressure of about 165 GPa [Fig. 19(b)], release melting for the [110] and [111] shocks can also be identified through the deviation of their release curves from the [100] curve along with $0.85T_{\text{Eq}}^m(P)$. Release melting for the [100] shock does not take place at the cross-point of its release path with $T_{\text{Eq}}^m(P)$ as well but with $1.147T_{\text{Eq}}^m(P)$, indicating superheating-release melting; an abrupt drop in $T(P)$ at the intersection with $1.147T_{\text{Eq}}^m(P)$ (red arrow) owing to the latent heat of melting. The lack of sudden drop of $T$ in the [110] and [111] release curves is attributed to continuously progressing partial melting.

Figure 20 shows the release paths of the [100] shocks to higher pressures including the maximum superheating case in our simulations. The curves exhibit three distinct regimes: Solid, partial release melting, and complete release melting. The kinks (open symbols) on these curves demonstrate the regime of partial release melting, and release melting from different pressures all begins at the intersections of the release curves and $1.147T_{\text{Eq}}^m(P)$.

Finally, the critical states where release melting happens as deduced from the release path analyses, are essentially consistent with the values listed in Table I, which are determined with the help of $Q_{\text{R}}$ and release wave profiles.

V. SUMMARY

We have conducted large-scale MD simulations to study the solid–liquid phase transition behaviors of single crystal Cu under both shock and release conditions. Our results show that, although the equilibrium states converge to the same Hugoniot, the pathways from metastable states right behind the shock front to the final thermal equilibrium states far behind the shock front, and the resulting microstructures are strongly dependent on the loading directions. For weak shocks along [110] and [111], shear stress cumulating in the elastic compression region is relaxed by shock-induced plasticity. When shocks are strong enough, shear stress is released through cold melting followed by recrystallization, transforming specimen from a metastable supercooled melt right behind shock front to an equilibrated polycrystalline solid far behind the shock front. However, there is no clear division between these two mechanisms (plastic deformation and cold melting), sometimes they function simultaneously. Whether cold melting is of thermal origin is unclear and remains to be fully examined, though. Conversely, the specimen shocked along [100] orientation maintains a more ordered solid state with certain degree of superheating before melts gradually into an equilibrium liquid phase.

Due to different microstructures in the far-behind-shock region for various loading directions, the release melting dynamics also differ upon release. Release melting occurs when the material released from pressures above about 140 GPa for all three shock directions. For the [110] and [111] cases, partial release melting with supercooling arises in some highly disordered regions of the partially released specimens and the thickness of the region continuously broadens with the progression of release, causing no apparent indications of melting in the release wave profiles. However, for the [100] case, partial melting occurs with superheating. The partial melting region is much narrower compared with the other orientations, and the specimen quickly enters the complete melting phase accompanied with the split of the release wave into a two-wave structure upon release melting.

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FIG. 20. Simulated $T$–$P$ curves for release from the [100] shock to 190 GPa (magenta circle), 218 GPa (blue triangle), and 230 GPa (dark yellow square). Also shown are the extended solid branch of the $T$–$P$ Hugoniot (red solid line) and the thermodynamic melting curve $T_{\text{Eq}}^m$ (black solid line), and $1.147T_{\text{Eq}}^m$ (black dashed line). Open symbols refer to the partial release melting.