Solid-Liquid Interfacial Premelting

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We report the observation of a pre-melting transition at chemically sharp solid-liquid interfaces using molecular-dynamics simulations. The transition is observed in the solid-Al—liquid-Pb system and involves the formation of a liquid interfacial film of Al with a width that grows logarithmically as the bulk melting temperature is approached from below, consistent with current theories of premelting. The pre-melting behavior leads to a sharp change in the temperature dependence of the diffusion coefficient in the interfacial region and could have important consequences for phenomena such as particle coalescence and shape equilibration, which are governed by interfacial kinetic processes.

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The term pre-melting refers to the formation of thermodynamically stable liquid films at solid interfaces subjected to temperatures below but near the bulk melting temperature ($T_m$) [1,2]. Surface pre-melting (SP), the formation of a pre-melting layer at a solid-vapor interface, was first observed experimentally by Frenken and van der Veen [3] using proton scattering. Since then, advances in experimental techniques have provided powerful tools for direct atomic-resolution observations of this surface phase transition [4–10]. These experimental studies have been complemented by a number of detailed atomistic simulations probing the existence and atomic-level mechanisms of SP (Refs. [11–18] and references therein). Premelting at solid-solid interfaces has also been reported in the literature and can take two basic forms: pre-melting at solid-solid heterophase boundaries and grain-boundary pre-melting. Examples of the former are found at interfaces between Pb and Al [19], SiO and Al$_2$O$_3$ [20], as well as in ice at solid substrates, which plays a role in frost heave [11,21–23]. Premelting at grain boundaries has been the subject of numerous continuum modeling studies [24–30], atomistic simulations (Ref. [18] and references therein), and experimental [31] studies.

In this work, we report molecular-dynamics (MD) simulation results on Al-Pb solid-liquid interfaces that predict the existence of a third class of pre-melting transition, namely, solid-liquid pre-melting (SLP). In this process, a pre-melting liquid layer forms at a solid-liquid interface, below $T_m$ of the solid. Such a transition should, in principle, be possible at chemically heterogeneous solid-liquid interfaces in which the melt phase of the solid and the liquid phase are mutually immiscible, as is the case with Al and Pb near $T_m$ for Al. To the best of our knowledge, solid-liquid pre-melting has not been previously reported under ambient pressures, either experimentally or by simulation, although some evidence of SLP has been reported in simulations of solid-liquid interfaces under extremely high pressures (diamond anvil) [32,33]. As we will demonstrate, the process of SLP leads to a sharp change in the temperature dependence of the diffusion coefficient in the interfacial region, which is expected to have important consequences for the kinetics of interface-controlled processes such as particle shape equilibration or coalescence of liquid nanoparticles in solids governed by interface-mediated Brownian motion [34,35].

Thermodynamically, pre-melting occurs near $T_m$ when the interfacial free energy $\gamma_{sa}$ between the solid and another phase $\alpha$ ($\alpha = \text{solid, liquid, or gas}$) is larger than the sum of that for the solid-melt ($\gamma_{sl}$) and melt-$\alpha$ ($\gamma_{la}$) interfaces,

$$\Delta \gamma = \gamma_{sa} - [\gamma_{sl} + \gamma_{la}] > 0.$$  

(1)

Thus, if the undercooling ($\Delta T = T_m - T$) is not too great, it is thermodynamically favorable to form a thin film of metastable liquid because the increase in bulk free energy is more than compensated for by a lowering of the total interfacial free energy. The width of the interface as a function of undercooling depends on $\Delta \gamma$ and $\Delta T$ as well as the nature of the potential of interaction between the two interfaces, the so-called “disjoining potential.” The pioneering theoretical studies by Kikuchi and Cahn [36] on grain-boundary pre-melting and Lipowsky [37] on SP both predict a logarithmic dependence [38] of the width of the pre-melting layer with respect to the undercooling [39],

$$w(\Delta T) = -w_0 \ln[\Delta T/T_0],$$

(2)

where $w_0$ and $T_0$ are constants specific to the given interface.

The system.—The Al-Pb system is an ideal model alloy for the study of chemically heterogenous solid-liquid interfaces. The phase diagram is a simple monotectic that has a broad liquid-liquid miscibility gap, negligible solubility of Pb in the Al solid phase, and a large melting point separation (600 K for Pb and 933 K for Al). We have previously reported results from MD simulations on this system at 625 K, a temperature just above the melting point of Pb [40]. The simulation results are consistent with an in situ transmission-electron-microscopy (TEM) study of liquid...
Pb inclusions embedded in a crystalline Al matrix [41] in that the (111) interface is shown to be faceted, while (110) and (100) are rough at this temperature. The experiments also show that the (111) interface undergoes a roughening transition about 100 K below the melting point of Al.

Simulation details.—In our simulations of the Al-Pb solid-liquid interface, we employ a classical many-body potential developed by Landa et al. [42] to model the interatomic interactions. This potential predicts mutual immiscibility of Pb and Al in the solid state and a large-liquid state miscibility gap consistent with the experimental phase diagram up to 1200 K. The melting points of this potential [40] are 615.2(2) K and 922.4(2) K for Pb and Al, respectively. The MD simulations are performed using LAMMPS [43]. Equilibrated solid-liquid interfaces are set up at varying temperatures $T$ ranging from 625 to 900 K, separated by 25 K up to 900 K with additional simulations at 912, 920, 921, and 922 K. Three crystallographic orientations for the Al-Pb interfaces are examined: (100), (110), and (111).

To produce the equilibrated interfaces, constant-area, constant-normal-pressure MD ($N_{PZ}AT$) simulations up to 50 ns in length are used to yield the appropriate equilibrium number density, $\rho$, pressure (1 bar), and composition. These are followed by constant NVT simulations to collect production data. Five replica systems (each containing two independent interfaces) are used at each temperature and orientation to improve statistics. For additional details as to the methods of interface setup, equilibration, and analysis, see the Supplemental Material [44] and Ref. [40].

Characterization.—The solid-liquid interfaces are characterized through the determination of interfacial profiles, which show the change in specific properties (e.g., density, local structural order, composition, and diffusion constant) as functions of the distance normal to the interfacial plane, defined as the $z$ direction. The $z$ coordinate is measured relative to a Gibbs dividing surface, defined here such that the excess number of Al atoms $\Gamma_{a1}$ is zero (Supplemental Material [44]). To determine the extent of the premelting layer, we utilize two different order-parameter (OP) profiles. The first profile uses a local structure OP that distinguishes solid from liquid phases [45] and is normalized to 1 in the solid phase and 0 in the liquid phase. The second is a compositional order parameter equal to 1 in a pure Al system and 0 for pure Pb. For an Al-Pb solid-liquid interface without a premelting layer, these two order-parameter profiles will be approximately coincident; however, in the presence of a premelting layer (a liquid Al layer separating solid Al from liquid Pb), the interfacial position indicated by these two OP profiles will be separated by the width of the premelting layer $w$.

Figure 1 shows NVT snapshots of equilibrated (111) Al-Pb interfaces at increasing temperature for three different temperatures (625, 850, and 922 K), together with the corresponding time-averaged structural and composition OP profiles. For low $T$ (top panel) just above $T_m^{Al}$, the (111) interface is faceted [40] and two profiles are nearly coincident. For high $T$ (bottom panel) just below $T_m^{Al}$, the two profiles are separated by nearly 10 Å, indicating the presence of a premelting layer of liquid Al sandwiched between solid Al and liquid Pb. In the central panel at 850 K, only the first complete layer of Al at the interface is structurally disordered.

Results.—Contour plots of the fine-scale density profiles, $\rho(z, T)$, are shown in Fig. 2 for the (100), (110), and (111) Al-Pb solid-liquid interfaces as functions of temperature and distance ($z$) normal to the interface. Also plotted in Fig. 2 are the temperature-dependent interfacial positions defined by the midpoints of the structural and compositional order parameters. The distance between these two interfacial positions diverges as the Al melting point [46] is approached, due to the formation of the premelting layer. The peaks of the density profiles are seen as vertical striations in the plot, which are stronger and more highly localized in the solid phase, to the left of the structural order parameter curve. To the right of the structural order parameter curve, the density peaks are smaller in magnitude and more diffuse, consistent with the usual structural ordering of a liquid near a surface. The much smaller magnitude of the liquid structural

FIG. 1 (color online). Snapshots of Al-Pb (111) solid-liquid interfaces at three different temperatures. Top panel: 625 K, interface is faceted [40]; middle panel: 850 K, interface is rough; bottom panel: 922 K, interface is premelted. In the image, the crystalline Al atoms (as determined from the structural OP) are black (dark blue online), the liquid Al atoms (premelted layer) are light gray (green online), and the liquid Pb atoms are shown in dark gray (red online). In each image, the average structural OP and chemical OP are plotted as dotted and solid lines, respectively. The premelting width $w$ is defined as the distance between the two OPs (at half value).
ordering in (110), relative to (100) and (111), was previously noted and discussed in Ref. [40]. Note that the position of the interface as defined by the composition OP is roughly independent of temperature, due to the mutual immiscibility of liquid Pb in both solid and premelted Al. The slight shift of this position towards higher \( z \) near \( T_m \) for Al is due to the lower density (relative to the solid) of the growing premelted Al layer.

Figure 2 shows that solid-liquid premelting occurs in this system for all orientations studied, with nearly identical behavior. This is in contrast to surface premelting in many fcc metal surfaces, in which (110) surfaces are prone to premelting, while premelting is not seen in the other orientations [7,14]. Note that we have examined the local structure of the Al liquid within the premelting layer and found it to be consistent with that of bulk liquid, showing little influence of either confinement or the nearby presence of the liquid Pb phase (Supplemental Material [44]).

Our previous simulations at 625 K [40] suggested that the (100) and (110) interfaces are rough at that temperature, whereas the (111) interface is faceted. However, visual inspection (together with orientational order parameter analysis) indicates that the (111) interface undergoes a roughening transition at higher temperatures (for example, see the middle panel of Fig. 1). To probe this behavior in further detail, we examine the transport of Al atoms within the first layer of Al, which is characterized through the calculation of diffusion-constant profiles \( D(z) \) determined from the mean-squared displacement of Al atoms versus time; see Refs. [40,47] for details. The full diffusion constant analysis is presented in the Supplemental Material [44], but here we focus on the diffusion constant measured within the first Al layer (that is, the particles making up the density peak closest to \( z = 0 \) on the negative side in Fig. 2). Figure 3 shows a log-linear plot of diffusion constant versus \( 1/k_B T \) for the particles in the first Al layer for the three interfacial orientations studied. The magnitude of the slope of this Arrhenius plot of \( D \) can be interpreted as an activation energy for diffusion. Except very close to \( T_m^{Al} \), the slope for the rough (100) and (110) interfaces is constant. For (111), however, the slope undergoes a discontinuous change at a temperature of about 826(4) K, indicating a sudden decrease in the activation energy for diffusion in this layer to a value that is comparable to that of the rough (100) and (110) interfaces. This temperature at which the activation energy changes coincides roughly with the temperature at which the interfacial width begins to show a logarithmic dependence on undercooling (see below). The temperature is also very near the roughening temperature of 823 K previously reported for the (111) interface based on in situ TEM experiments of Pb inclusions in an Al matrix [41]. The close correspondence between these temperatures suggests that roughening and the onset of premelting approximately coincide for this interface.

As discussed earlier, theoretical considerations [36,39] predict a logarithmic dependence of the premelting width on undercooling [Eq. (2)]. To examine the validity of Eq. (2) for the solid-liquid premelting transition in Al-Pb, we plot the calculated width of the premelting layer \( w \) as a function of the undercooling, \( \Delta T = T_m - T \) on a linear-log plot in Fig. 4. The data are well described by Eq. (2) for all
three interfacial orientations for undercoolings up to 100 K—deviations are seen at lower temperatures when the width approaches atomic dimensions, as expected. Using a weighted least-squares linear regression over the temperature range 875 to 921 K, we obtain estimates for \( w_0 \) and \( T_0 \). Central to the derivation of Eq. (2) is the assumption that the interaction between the two interfaces bounding the premelted layer (the so-called “disjoining potential”) is exponential and repulsive [48]  

\[
\phi_d(w) = \Delta \gamma e^{-w/w_0},
\]

where \( w_0 \) is the length scale of the interaction and \( \Delta \gamma \) is given in Eq. (1). The quantity \( T_0 \) in Eq. (2) is given by \( T_0 = \Delta \gamma T_m/w_0 \rho L \), where \( \rho \) is the number density and \( L \) is the latent heat. The fitted values of \( w_0, T_0, \) and \( \Delta \gamma \) are given in Table I. This fitting gives an estimate of about 1.4–1.5 Å for the range of the disjoining potential, which is relatively independent of orientation.

**Discussion and summary.**—Using MD simulation we predict the existence of a solid-liquid interface premelting transition at the interface between solid Al and liquid Pb. That is, as the melting point of Al is approached from below, the surface of the crystalline Al melts to form a premelting layer of liquid Al separating the solid Al and liquid Pb bulk phases. This transition was seen in the simulations for all interfacial orientations studied: (100), (110), and (111). Although solid-vapor and grain-boundary premelting transitions are well established in the literature, premelting of a solid-liquid interface has not, to our knowledge, been previously reported at ambient pressures. Such a transition requires that the melt phase of the solid and the bulk liquid be mutually immiscible, which is true for the Al-Pb system studied here. The width of the premelting layer is shown to depend logarithmically on the undercooling \( \Delta T \), as predicted by theoretical considerations [36,39,48].

At lower temperatures, near the melting point of Pb, we have previously shown that the (100) and (110) interfaces are rough, whereas the (111) interface is faceted—in agreement with experimental observations on liquid Pb inclusions in a solid Al matrix [41]. In the current simulations, we observe a change in the activation energy of Al surface diffusion at the (111) interface at 826(4) K, which correlates well with both the experimental observations of a roughening transition at 825 K for this orientation [41] and the observed onset of premelting in the present simulations (as evidenced by the logarithmic dependence of the premelting width on \( T \)). There are a number of other solid-liquid interfacial systems in which the melt phase of the solid is immiscible in the bulk liquid, such as, for example, the interface between ice and liquid hydrocarbons, so further study of possible premelting in such systems is warranted.

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**TABLE I.** Values of \( w_0, T_0, \) and \( \Delta \gamma \) [defined in Eqs. (1) and (2)] from a weighted linear least-squares regression of the data for \( w \) versus \( \ln(T_m - T) \). Values in parentheses represent 95% confidence level error estimates in the last digits shown.

<table>
<thead>
<tr>
<th></th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
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<tbody>
<tr>
<td>( w_0 ) (Å)</td>
<td>1.47(3)</td>
<td>1.46(3)</td>
<td>1.36(4)</td>
</tr>
<tr>
<td>( T_0 ) (K)</td>
<td>1.28(12) \times 10^3</td>
<td>1.09(9) \times 10^3</td>
<td>1.45(14) \times 10^3</td>
</tr>
<tr>
<td>( \Delta \gamma ) (mJ m(^{-2}))</td>
<td>174(16)</td>
<td>148(13)</td>
<td>183(18)</td>
</tr>
</tbody>
</table>

[37] For real systems with long-range forces (e.g., dispersion), the logarithmic divergence of the width does not strictly hold in the limit that $T \rightarrow T_m$ but must give way very close to $T_m$ to either a power-law divergence or a finite threshold (incomplete premelting) [11]. Such long-range forces are absent from the EAM model used here; however, the observed premelting widths do not exceed a few lattice constants and short-ranged structural forces are expected to be dominant over long-range dispersion for the conditions studied.
[45] Strictly speaking, the divergence occurs at the monotectic temperature of the Al-Pb system, but given the negligible solubility of Pb in solid Al, the Al melting temperature and the monotectic temperature are identical to the resolution of the current study.
Supplemental Information for “Solid-liquid interfacial premelting”
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SECTION S1. ADDITIONAL SIMULATION DETAILS

Periodic boundary conditions in all three Cartesian directions were applied for all simulations using a time step of 1.0 fs. The temperature in all MD simulations was controlled using a Nosé-Hoover thermostat \cite{1} with a thermostat relaxation time of 0.1 ps, while in the \textit{NPT} and \textit{NP}_{z\text{AT}} simulations, pressure was controlled using an Anderson barostat,\cite{1} with a relaxation time of 1.0 ps. Temperature and pressure (including \textit{xx}, \textit{yy} and \textit{zz} tensor components) profiles, which show the variation of temperature and pressure along the \textit{z}-axis, were examined for all simulations to confirm the absence of temperature gradients and bulk stress.

The construction of the equilibrium solid-liquid interfaces at all temperatures follows the procedures described in Ref. \cite{2} for the Al-Pb solid-liquid interface at 625K. The starting configurations for the interface simulations were constructed by first creating separate Al (solid) and Pb (liquid) samples. Samples of bulk Al crystals were prepared in a face-centered cubic (fcc) lattice with the correct temperature-dependent equilibrium lattice constant \(a_{\text{Al}}(T)\) for the model of Al for \(T\) in the range 625K to 922K and 1 bar pressure. The dimensions of the cross-section (\(L_x\) and \(L_y\)) were chosen to be square or nearly square. Separate samples of liquid Pb containing approximately...
17,000 atoms with atomic density $\rho_l^{\text{Pb}}(T)$ were created with cross-sectional dimensions matching the corresponding crystal samples with the z-axis dimensions $L_z(T)$ allowed to fluctuate using $NP_zAT$ MD simulations to yield the appropriate liquid Pb equilibrium number density at 1 bar and $T$. The fcc Al and liquid Pb atomic densities, $\rho_s^{\text{Al}}(T)$ and $\rho_l^{\text{Pb}}(T)$, were carefully measured in a series of bulk $NPT$ MD simulations (4000 particle simulation cell, 500,000 MD steps for collecting averages at each temperature) and the data so obtained were used to construct the following interpolation formulas:

\begin{align}
\rho_s^{\text{Al}}(T) & = 6.17718 \times 10^{-2} - 5.54351 \times 10^{-6}T + 3.65119 \times 10^{-9}T^2 - 2.39905 \times 10^{-12}T^3 \quad (\text{S.1}) \\
\rho_l^{\text{Pb}}(T) & = 3.44053 \times 10^{-2} - 8.72169 \times 10^{-6}T + 7.60147 \times 10^{-9}T^2 - 2.77073 \times 10^{-12}T^3 \quad (\text{S.2})
\end{align}

where the densities are in units of $\text{Å}^{-3}$. The fcc Al lattice constant $a^{\text{Al}}(T) (\text{Å})$ is obtained from the formula $a^{\text{Al}} = \frac{3}{4}/\rho_s^{\text{Al}}$.

The initial interface configurations were assembled by conjoining the solid Al and liquid Pb samples at their common cross-sections and applying periodic boundary conditions to the conglomerate [2]. The solid-liquid systems were then equilibrated using $NP_zAT$ MD simulations up to 50 ns, to ensure the total energy, volume and composition in the liquid phase relaxed to their equilibrium values. We found the equilibrium concentration of Al in bulk liquid Pb to be approximately 0.03% at 625K and 0.7% at 921K; these values demonstrate negligible miscibility of Pb and Al in the liquid phase - consistent with the experimental phase diagram. To calculate the equilibrium interfacial properties, we followed the initial $NP_zAT$ runs with fixed volume $NVT$ MD simulations. To ensure that we use the proper value of $L_z$ in starting these $NVT$ simulations, we calculate the average $L_z$ from the final 5 ns of the $NP_zAT$ simulation runs and start the $NVT$ simulations from configurations from the $NP_zAT$ simulations with an $L_z$ that matches the average. In addition, to avoid the Brownian motion of the Al crystal slab, which can artificially broaden the calculated interfacial profiles, we subtract the linear momentum for the innermost layers [3] of the Al crystals during the $NVT$ production simulations. To improve the statistics, we performed five replica $NVT$ simulations for each system [2], each of which is run for 1ns to generate 1000 configurations for analysis. There are two independent interfaces in each simulation box, therefore, we have ten independent interfaces for each orientation from which to calculate the interfacial properties.

Snapshots of equilibrium premelted ($T = 922$K) Al-Pb solid-liquid interfaces for (100), (110) and (111) orientations are shown in Fig. S1. All three interfaces undergo solid-liquid interface
premelting transitions as discussed in the main text. The snapshots of the low temperature non-premelted interfaces ($T = 625\text{K}$) can be found in Ref. [2].

**Fig. S1** Equilibrium MD snapshots of the premelted Al-Pb (100), (110) and (111) solid-liquid interfaces at 922K. The atom coordinates are projected onto the plane of the page. From top to bottom, the directions perpendicular to the page are [010], [001] and [011], respectively. The Pb and Al atoms are colored red and blue, respectively.

**SECTION S2: GIBBS DIVIDING SURFACE (GDS)**

To determine the Gibbs Dividing Surface (GDS) we define $L_l$ and $L_s$ to be the $z$-direction widths of the liquid Pb and solid Al phases, respectively, so that the total length of the box is $L_z = L_l + L_s$. We chose a GDS in which the excess number of Al atoms ($\Gamma_{Al}$) is equal to zero,

$$\Gamma_{Al} = \frac{N_{Al}}{A_{xy}} - \rho_{Al}^l L_z - (\rho_{Al}^s - \rho_{Al}^l) L_s = 0 $$

(S.3)

where $N_{Al}$ is the total number of particles of Al, $A_{xy}$ is the interface cross-section area and $\rho_{Al}^s$ and $\rho_{Al}^l$ are the densities of Al in the solid and liquid phases, respectively. In our previous study [2],

3
the solubility of Al in liquid Pb at 625K, \( \rho_{Al}^f \), was neglected and Eq. S.3 was solved as \( L_s = N_{Al}/(A_{xy} \rho_{Al}^s) \). However, due to the small, but nonneglegble, value of \( \rho_{Al}^f \) at the higher temperatures, the solution to Eq. S.3 becomes

\[
L_s = \frac{N_{Al} - \rho_{Al}^f A_{xy} L_s}{A_{xy} (\rho_{Al}^s - \rho_{Al}^f)}
\] (S.4)

to give the position of the GDS. Once the GDS was determined at a given \( T \), interfacial excess quantities can be calculated for each \( T \) and orientation, including excess stress \( [\tau(T)] \), excess energy \( [e^{Al}(T)] \) and the excess number of Pb atoms \( [\Gamma_{Pb}(T)] \). These values will be reported in future work.

SECTION S3. CALCULATION OF INTERFACIAL PROFILES

For the densities (\( \rho \) and \( \rho_{Al} \)) and local structural order parameter (\( \psi \) defined in equation (9) in Ref. [4]), we determine fine-grained profiles by binning the simulation box in the \( z \) direction and averaging the quantity of interest within each bin over the \( xy \) plane. The bin size for these profiles was chosen to be 1/40th of the inter-plane spacing in the Al crystal at the corresponding \( T \). The density and local structural order parameter (OP) profiles across the interface, \( \rho(z) \), \( \rho_{Al}(z) \), \( \rho_{Pb}(z) \) and \( \psi(z) \), are computed as the average number of total atoms, Al atoms, Pb atoms and OP in each discrete bin of spacing \( \Delta z \) divided by the volume of the bin, \( V_z \), in which, \( V_z = A_{xy} \Delta z = L_x L_y \Delta z \).

\[
\rho(z) = \frac{\langle N_z \rangle}{V_z}; \quad \rho_{Al}(z) = \frac{\langle N_{Al}^z \rangle}{V_z}; \quad \rho_{Pb}(z) = \frac{\langle N_{Pb}^z \rangle}{V_z}; \quad \psi(z) = \frac{\langle \psi_z \rangle}{V_z}
\] (S.5)

where \( \langle N_z \rangle \), \( \langle N_{Al}^z \rangle \), \( \langle N_{Pb}^z \rangle \) and \( \langle \psi_z \rangle \) are the average number of total atoms, Al atoms, Pb atoms and OP in the discrete bin, respectively.

Fig. S2 shows the (100), (110) and (111) fine-grained total density profiles at three different temperatures. In all interfacial profiles, the GDS, as defined above, is placed at \( z = 0 \). In the current study, we have calculated 16 density profiles from 625K to 922K. In order to better present results, all 16 profiles were aligned by the GDS and spaced in the temperature dimension (or axis). If we focus on a certain point on \( z \), 16 density profiles offer 16 points along \( T \) axis. We employed a Gaussian function to smooth such coarse-grained variation by calculating weighted averages [5] between the neighboring grid points. Finally, smoothed density contour maps with fine grid mesh are obtained (see in Fig. 2 in the main text).

The oscillations in fine-grained \( \rho(z) \), \( \rho_{Al}(z) \), \( \rho_{Pb}(z) \) and \( \psi(z) \) profiles can be smoothed by a weighted average over neighboring values, which is known as finite impulse response filter (FIR) smoothing algorithm [3, 6], to generate the coarse-scale smoothed profiles, e.g., smoothed \( \psi(z) \)
Fig. S2 Equilibrium fine-grained total density profiles for (100) (top panel), (110) (middle panel) and (111) (bottom panel) Al-Pb interfaces at three different temperatures. Solid lines for 625K, dashed lines for 850K, dotted lines for 922K. The position of the GDS is \( z = 0 \), \( z < 0 \) for the Al side and \( z > 0 \) for the Pb side.

Profiles are shown in Fig. 1 in the main text. The details of the FIR smoothing can be found in Refs. 2 and 3. The coarse-scale smoothed Al concentration profiles (also shown in Fig. 1 in the main text) are obtained from the ratio between the coarse-scale smoothed Al density profiles and the coarse-scale smoothed total density profiles,

\[ X_{\text{Al}}(z) = \frac{\rho_{\text{Al}}(z)}{\rho(z)}, \]  

(SE.6)

SECTION S4: LATERAL STRUCTURAL ANALYSIS OF INTERFACIAL AL AND PB LAYERS

In order to verify that our premelting Al layer has a structure that is consistent with bulk liquid Al, we have examined the local structure of the premelted Al for all three interfaces by analyzing the two-dimensional (in-plane) radial distribution function (RDF), \( g_{2d}(r) \), for the both the first
Fig. S3 Two-dimensional (in-plane) RDF of the first liquid Pb layer (Pb$_1$) and the adjacent liquid premelting layer of Al (Al$_1$) at 922K for (100) (top panel), (110) (middle panel) and (111) (bottom panel) Al-Pb interfaces. These are compared with the two-dimensional RDF calculated for bulk liquid Al (Al$_b$) and bulk liquid Pb (Pb$_b$) at the same temperature.

The positions (relative to the GDS) and the layer width ($w_l$) between the two density minima ($z_1$, $z_2$) employed in the two-dimensional RDF calculation are listed in Table S1. For comparison, we have also carried out a two-dimensional RDF analysis for the bulk liquid Al and bulk liquid Pb at 922K, using the same layer width listed in Table S1.

Fig. S3 shows the calculated two-dimensional RDF for the interfacial Al and Pb layers at 922K. For all orientations, the $g_{2d}(r)$ peaks in Al$_1$ and Pb$_1$ are commensurate with those of their respective bulk liquid phases, with only minor differences in amplitude. Overall, the Al in the premelting layer is consistent in structure to the bulk liquid phase with only minor deviations due to the influence of the neighboring liquid Pb phase and to confinement.
Table S1 The position and width of the interfacial layer employed in the two dimensional radial distribution function calculation.

<table>
<thead>
<tr>
<th></th>
<th>$z_1$ (Å)</th>
<th>$z_2$ (Å)</th>
<th>$w_1$ (Å)</th>
<th>$z_1$ (Å)</th>
<th>$z_2$ (Å)</th>
<th>$w_2$ (Å)</th>
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<tbody>
<tr>
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<td>0.03</td>
<td>2.19</td>
<td>0.70</td>
<td>3.20</td>
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<td>(110)</td>
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</tr>
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<td>(111)</td>
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<td>0.50</td>
<td>3.22</td>
<td>2.72</td>
</tr>
</tbody>
</table>

SECTION S5: CONSTRUCTION AND ANALYSIS OF INTERFACIAL DIFFUSION-CONSTANT PROFILES

**Fig. S4** Equilibrium coarse-grained diffusion constant profiles for (100), (110) and (111) Al-Pb interfaces at three different temperatures. Bottom panel: 625K, middle panel: 850K, top panel: 922K. Cubic-spline interpolations are employed to smooth the coarse-grained profiles, and plotted with solid lines. The position of the GDS is $z = 0$, $z < 0$ for the Al side and $z > 0$ for the Pb side.

The diffusion constant profile is a coarse-grained profile that measures the spatial dependence...
(z-direction) of the diffusion constant using a much larger bin size compared with fine-grained profiles\cite{3}. In the current study, bins in \( z \) are defined as the regions between the minima of the fine-grained density profiles on the solid phase side of the interface. On the liquid phase side of the interface and the premelted region, we chose a smaller bin size (about 1 to 2 Å) in order to capture more accurately the shape of the profile in the interfacial region, as high temperature interfaces have a more complicated structure compared with the low temperature interfaces. The diffusion constant in each bin is determined from the slope of the diffusive regime of the mean-square displacement (MSD) as a function of time for the particles starting out in the bin,

\[
D(z) = \lim_{t \to t_D} \frac{d}{dt} \left\langle \left[ r_j(t) - r_j(t_0) \right]^2 \right\rangle_z;
\]  

(S.7)

\[
D_{xy}(z) = \lim_{t \to t_D} \frac{1}{4} \frac{d}{dt} \left\langle \left[ x_j(t) - x_j(t_0) \right]^2 + \left[ y_j(t) - y_j(t_0) \right]^2 \right\rangle_z;
\]  

(S.8)

\[
D_z(z) = \lim_{t \to t_D} \frac{1}{2} \frac{d}{dt} \left\langle \left[ z_j(t) - z_j(t_0) \right]^2 \right\rangle_z
\]  

(S.9)

For an isotropic bulk system, \( D = D_{xy} = D_z \) is expected. More details of the diffusion calculation be found in Refs. \cite{3} and \cite{2}. The MSDs used in this analysis are calculated out to 30 ps, which is sufficient time for the dynamics to become diffusive (i.e. the MSD is linear in time), but short enough that the vast majority of atoms diffuse less than one bin spacing in the \( z \) direction. The small fraction of the atoms that cross bin boundaries does produce a small amount of additional smoothing of the profile, but the effect is generally minimal, as contributions from either side of a given bin tend to approximately cancel.\cite{3} We also note that the bulk diffusion constants determined for the model potentials considered here somewhat underestimate the diffusion in the actual system as measured experimentally. At 922K, we find a diffusion constant for Al of \( 3.1 \times 10^{-5} \) cm\(^2\) s\(^{-1}\), whereas the result from experiment\cite{7} (extrapolated to 922 K using an Ahrenius law) is \( 5.68 \times 10^{-5} \) cm\(^2\) s\(^{-1}\). For Pb at 922K, we find for our model \( D_{\text{Pb}} = 3.4 \times 10^{-5} \) cm\(^2\) s\(^{-1}\) in contrast to \( 4.8 \times 10^{-5} \) cm\(^2\) s\(^{-1}\) from experiment\cite{8} (also extrapolated to 922 K). However, the underestimation of \( D \) in both Al and Pb is similar and we do not expect this underestimation to alter the qualitative conclusions of the analysis presented here.

Symbol points in Fig. S4 are calculated coarse-grained profiles. Note that, the diffusion constants in Fig. S4 include particles of both types (Al and Pb). A cubic-spline interpolation is employed to smooth each coarse-grained \( D(z) \) profile, that is, the solid lines in Fig. S4. All smoothed profiles were aligned by the GDS and spaced along the temperature axis to generate
a fine grid mesh as described in Fig. S3. Fig. S5 plots the contour map of the (100) interfacial diffusion constant, to note that (110) and (111) contour map has similar character as (100) and will be reported elsewhere. For all panels in Fig. S5, $D$, $D_{xy}$ and $D_z$, are smaller than can be measured on MD time scales in the bulk solid ($z < -15\,\text{Å}$). While in bulk liquid Pb ($z > 10\,\text{Å}$), the $T$ dependence of $D$, $D_{xy}$ and $D_z$ follows an Arrhenius law. At low temperatures, $D$, $D_{xy}$ and $D_z$ increase monotonically across the interface from solid to liquid [2]. Similar to the density contour map, the interfacial diffusion-constant contour maps also show a clear $T$-dependent interfacial broadening, in which a growing region of interfacial Al exhibits liquid-like diffusivity, consistent with a premelting transition.

The contours for $D$ and $D_{xy}$ exhibit a positive peak at about $z = 1\,\text{Å}$ at high temperatures where premelting is significant. This peak occurs at the boundary between premelted Al(l) and Pb(l). Note that, a similar positive peak is not found $D_z$, indicating that there is considerable anisotropy between in plane diffusivity and normal diffusivity at the high $T$ Al-Pb solid-liquid interface. Fig. S6 plots the $D(z)$, $D_{xy}(z)$, and $D_z(z)$ profiles for all three orientations at 922K, in order to show the aforementioned peaks more clearly. We have measured the magnitude of these
Fig. S6 Equilibrium coarse-grained diffusion constant profiles for (100), (110) and (111) Al-Pb interfaces at 922K. Top panel: total diffusion $D$, middle panel: $xy$ diffusion, bottom panel: $z$ diffusion. Cubic splines interpolations are employed to smooth the coarse-grained profiles, and plotted with solid lines. The position of the GDS is $z = 0$, $z < 0$ for the Al side and $z > 0$ for the Pb side.

peaks in the 922 K diffusion-constant profile and find that the magnitude of the peak is about 20% larger than the bulk values for both Al and Pb.

An independent calculation of the diffusion constant profile of an equilibrium liquid-liquid Al-Pb interface at 922K was carried out to further investigate the structure of the diffusion profiles. The open circles in Fig. S7 show the total, $xy$ and $z$ diffusion-constant profiles for the Al-Pb liquid-liquid interface at 922 K. The corresponding diffusion-constant profiles for the Al-Pb (100) solid-liquid interface at 922 K are also plotted with open square symbol. So that Fig. S7 can be compared easily with Fig. S5 and Fig. S6, we use a $z$-coordinate defined such that the position of the Al(l)/Pb(l) interface (defined as the midpoint of the Al/Pb concentration profile) has the same position (in $z$) in all three figures. From Fig. S7 we see that the diffusion constants reach the bulk liquid values about 10 Å away from the interface on both the Al and Pb sides. The diffusion profile
Fig. S7 Total (top panel), $xy$ (middle panel) and $z$ (bottom panel) diffusion constant profiles of 922K (100) Al-Pb solid-liquid interface (open squares) and Al-Pb liquid-liquid interface (open circles), compare with Al and Pb self diffusion constant profiles (filled circles), blue for Al and red for Pb.

in the Al(s)/Al(l)/Pb(l) system is seen in Fig. S7 to be nearly identical to that for the equilibrium liquid-liquid system in the Pb(l) region ($z > 1$ Å) and the peaks in the total $D$ are the same for the two systems - indicating that the peak in total $D$ is a consequence of the fact that we have a liquid-liquid interface and not anything specific to the finite width of the Al premelting layer.