Supplemental information for

"Surface roughening, premelting, and melting of monolayer and bilayer crystals"

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I. SIMULATION DETAILS

We perform a molecular dynamics (MD) simulation by employing two methods, namely the Nose-Hoover thermostat [1] in LAMMPS and deterministic thermostat [2], which produce the same result. The time step $\Delta t = 10^{-3}$. The whole simulation box is displayed in Fig. S1. For a bilayer and trilayer confined between two walls, the interaction between a particle and a wall is $U(r) = 12000 \times (r - 0.5)^2$ at separation r < 0.5; otherwise U(r) = 0.



FIG. S1: A monolayer triangular lattice (blue region) is composed of 60×160 particles in the simulation box with the periodic boundary condition. The red rectangle is the area shown in Figs. 1(a-d, h-k).

We found that roughening or premelting behaviors are sensitive to the degree of equilibration and that solid interfaces require an extremely long equilibration time. It is probably because the premelting occurs near the crystal-liquid-vapor triple point where chemical potential difference between crystal and liquid is small, i.e. the driving force of surface melts is weak. For example, a monolayer crystal does not become fully rough at T = 0.34 until the simulation has exceeded 1.5×10^8 simulation steps (i.e., $t = 1.5 \times 10^5$), as shown in Figs. S2(a, b), and does not fully melt at $T = 0.396 > T_{\rm m} = 0.3958$ until the simulation has exceeded 10^8 simulation steps, as indicated in Figs. S2(c, d). Therefore, the thickness of the premelted surface liquid layer cannot be accurately measured if the equilibration time is not sufficiently long. In fact, previous simulation studies on the premelting of 3D crystals were conducted with merely several thousands of steps of equilibration time; thus, they produced different $T_{\rm m}$ and mixed the roughening and premelting regimes [3-5]. In the only study on the premelting of 2D crystals, the particles also did not have a sufficiently long equilibration time, so their measured melting temperature $T'_{\rm m}$ was much higher than the real $T_{\rm m}$ [6]. This may have caused the measured thickness of the surface liquid to be very large at $T_{\rm m} < T < T_{\rm m}$ and led to incomplete premelting being mistaken for complete premelting. We slowly increase the temperature at $\Delta T = 0.02$ /step from T = 0 and equilibrate for 10^6 simulation steps at each temperature. ΔT is smaller (e.g., 0.0001) in the roughening regime

(monolayer: $0.25 \leq T \leq 0.38$, bilayer: $0.3 \leq T \leq 0.48$, trilayer: $0.34 \leq T \leq 0.5$) and premelting regime (monolayer: $0.39 \leq T \leq 0.396$, bilayer: $0.5 \leq T \leq 0.5115$, trilayer: $0.52 \leq T \leq 0.5218$), with 1.5×10^8 steps required to reach full equilibrium at each temperature.



FIG. S2: Evolution of the surface of a monolayer crystal. Surface roughening occurred at T = 0.34 after (a) 5×10^7 and (b) 1.5×10^8 simulation steps and at $T = 0.396 > T_{\rm m} = 0.3958$ after (c) 3×10^7 and (d) 7×10^7 steps. The red boxes denote the liquid regions. The crystal is completely melted after 10^8 steps at T = 0.396.

II. DYNAMICAL STRUCTURE FACTOR AND MODULI OF CRYSTALS



FIG. S3: (a, b) Longitudinal (L) and transverse (T) dynamical structure factors $S_{L,T}$ of the monolayer crystal at temperature T = 0.39. (c, d) Dispersion relations derived from (a, b), respectively, and similarly derived from $S(k,\omega)$ at other temperatures.



FIG. S4: (a, b) Longitudinal (L) and transverse (T) dynamical structure factor $S_{L,T}$ of the bilayer crystal at temperature T = 0.46. (c, d) Dispersion relations derived from (a, b), respectively, and similarly derived from $S(k, \omega)$ at other temperatures.

The dynamical structure factor [7]:

$$S_{\rm L,T}(k,\omega) = \frac{k^2}{2\pi N\omega^2} \int_0^\infty dt \langle \vec{J}_{\rm L,T}(k,t) \cdot \vec{J}_{L,T}(-k,t) \rangle, \qquad (1)$$

where the longitudinal (L) current is

$$\vec{J}_{\rm L} = \sum_{j} [(\vec{v}_j(t) \cdot \hat{k})\hat{k}] \exp[\mathrm{i}\vec{k} \cdot \vec{r}_j], \qquad (2)$$

and the transverse (T) current is

$$\vec{J}_{\mathrm{T}} = \sum_{j} [\vec{v}_{j}(t) - (\vec{v}_{j}(t) \cdot \hat{k})\hat{k}] \exp[\mathrm{i}\vec{k} \cdot \vec{r}_{j}].$$
(3)

The sums include all N particles. ω is the vibration frequency, and k is the wave number. $S(k, \omega)$ reflects the density correlations in both space and time, which is a generalization of the static structure factor [7]. It can be experimentally measured through inelastic neutron scattering or X-ray Raman scattering [8]. Here, we calculate $S(k, \omega)$ from the particles' positions and velocities by using Eqs. 1-3. Figs. S3(a, b) show the longitudinal and transverse dynamical structure factor at T = 0.39 for the bulk crystal of the monolayer. The peak positions yield the dispersion relation $\omega(k)$ [7], the slope of which represents the sound velocities $c_{\rm L,T}$ shown in Figs. S3(c, d). The shear modulus G in Fig. 3(d) and bulk modulus B can be derived from $c_L = \sqrt{(4G/3 + B)/\rho}$ and $c_T = \sqrt{G/\rho}$, where ρ is the number density. The Young's modulus in Fig. 4(b) is Y = 9GB/(3B + G). The results for the bilayer are displayed in Fig. S4.

III. LOCAL STRUCTURE OF THE SURFACE LIQUID



FIG. S5: Local structure factor of liquids in different y regimes for the (a) monolayer and (b) bilayer. y = 0 is defined as the center of the bulk crystal (i.e., the middle of two free surfaces presented in Fig. S1).



FIG. S6: Peak position k^* for S(k) at different surface depths y for the (a) monolayer and (b) bilayer.

The local structure around particle i can be characterized by the local structure factor [7]:

$$S_i = 2\pi \int_0^\infty r dr g(r) J_0(kr) = \sum_{n=1}^{N-1} J_0(kr_{in}) / \rho$$
(4)

where r_{in} is the distance between particles *i* and *n* in the *xy* plane, ρ is the number density, and J_0 is the 0th order of the Bessel function of the first kind. How the local structure changes at different depths across the liquid-crystal interface as the premelted liquid expands with increasing temperature is a matter of research interest. Thus, we computed the average local structure factor at different *y*: $S_{y^*}(k) \equiv \langle S_i(k) \rangle_{y^* < y_i < y^* + 1}$; see Fig. S5 for examples.

The location of the main peak in $S_{y^*}(k)$, k^* , characterizes the local structure of particles whose y coordinates are between y^* and $y^* + 1$. $k^*(y^*)$ describes the local structural change across the liquid-crystal interface during premelting. As illustrated in Fig. S6(a), $k^*(y^*)$ is almost a constant near the premelting temperature of the monolayer, indicating that the local structure of the surface liquid is similar to that of the crystal for the monolayer system. By contrast, the bilayer near its premelting transition exhibits a notable difference between k^* at a large y^* (surface liquid) and at a small y^* (crystal) (Fig. S6(b)), indicating that the premelted liquid and the bilayer crystal have different structures.

IV. MEAN SQUARE DISPLACEMENT OF THE SURFACE LIQUID PARTICLES



FIG. S7: MSDs of the particles at $\Delta y \in [1.5, 2.5], [2.5, 3.5], \text{ and } [3.5, 4.5]$ along the x (dashed lines) and y (solid lines) directions for (a) monolayer and (b) bilayer surface liquids.

The mean square displacement of particle *i* is defined as $MSD_i(t) = \langle (r_i(t) - r_i(0))^2 \rangle$, where $r_i(t)$ is the position of particle *i* at time *t*. We measured the MSDs of the surface liquid particles along the *x* and *y* directions at different distances to the solid-liquid interface, as shown in Fig. S7. The slope of the log-log plot of the MSD in Fig. S7 gives five layers of liquid particles near the solid surface exhibited subdiffusions (i.e., $\alpha < 1$), whereas other liquid particles were the same as a normal bulk liquid with diffusive behavior ($\alpha = 1$) as shown in Fig. 3a of the main text.

V. SURFACE ROUGHENING AND PREMELTING OF THE TRILAYER



FIG. S8: Free surface of a trilayer crystal at different temperatures under thermal equilibrium. Particles are colored by their MSD(t = 5). Particles with MSDs lower than 0.05 and higher than 0.15 are colored as 0.05 and 0.15, respectively.

We simulated a trilayer by using the Noose-Hoover thermostat in LAMMPS with 30×160 particles per layer in an $L_x \times L_y = 30 \times 160\sqrt{3}$ box confined between two parallel plates with a separation of 2.66 in the z direction and under period boundary conditions in the xy direction, as shown in Fig. S8. Their surface roughening (Fig. S9), premelting (Fig. S10), and melting behaviors were similar to those of bilayers.



FIG. S9: Surface roughness of the trilayer crystal. (a) Normalized spatial correlation $g_{\rm h}(x)/g_{\rm h}(0)$ (symbols) of the height function of the vapor surface fitted with $\exp(-x/\xi)$ (dashed curves). (b) Fitted ξ from (a). Dashed line marks the onset of premelting.



FIG. S10: Thickness l of the premelted liquid layer for trilayer crystal. $l \sim (T_{\rm m} - T)^{\beta}$ with fitted $T_{\rm m} = 0.5216 \pm 0.0001$ and $\beta = 0.65 \pm 0.02$ (line).

In the case of complete premelting, l usually exhibits a logarithm or power-law divergence. Mean-field theory predicts that the power-law exponent would be 1/3 for 3D crystals composed of particles with long-range attractions [9], whereas we observed it to be 0.5 ± 0.02 for the bilayer and 0.65 ± 0.02 for the trilayer. This difference was attributable to the different dimensionalities and the fact that mean-field theory ignores thermally excited capillary waves on a free surface.



VI. EVOLUTION OF A CRYSTAL FULLY EMBEDDED IN VAPOR

FIG. S11: (a) A square-shaped bilayer crystal with a triangular lattice initially at T = 0.01. (b) The crystal become circular without facets at T = 0.49.

When a bilayer crystal with a triangular lattice is set to have (10) and (11) facets on the free surface, it will premelt into a circular shape (Fig. S11), suggesting that the surface tension is insensitive to lattice anisotropy.

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