Supporting Information for "Microscopic Mechanisms, Morphology and Defects Formation in the Thermally Activated Crystallization of Methylammonium Lead Iodide"

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Structures and Control Files for Molecular Dynamics Simulations

In the gzip archive *supporting.tgz*, for each figure of the main manuscript, we provide a corresponding directory containing a file FIGURE.xyz with the atomistic structures in xyz format, a README file with additional information, a file *rep.vmd* with the graphical settings for VMD[1] of the corresponding figure. For each panel we also report the files for running MD by LAMMPS software:[2] the control file, the data file and the parameters of the MYP2 model, named *input.**, *dlpoly2lammps.data*, *parameters.manybody.myp2* and *dlpoly2lammps.nonbonding.myp2*.

Analysis of crystallization velocity

The study of the kinetics of crystallization as a function of temperature (see main text), was performed on a system of 1536 atoms stoichiometrically neutral, composed of 96 formula units ($MAPbI_3$), for a total of 8 layer, so each layer has 16 formula units (4x4 cubic unit cells). The duration of the molecular dynamics (MD) simulation is variable depending on the crystallization velocity (shorter simulations at higher temperatures), ranging between 0.060-1 μs.

The instantaneous crystalline fraction was obtained by calculating the structure factor $S_{\vec{k}}(t)$ from MD trajectories. We chose $\vec{k} = (1.96, 0, 0)$ Å^{-1} that is close to a reciprocal vector of the MAPI crystal. In Fig.1 it is reported an example of the structure factor as a function of time at 700 K. $S_{\vec{k}}(t)$ evolves almost linearly during the initial 10 ns of the annealing and then tends to decelerate as the crystallization saturates.

For the planar geometry considered for the kinetic analysis, the crystallization velocity corresponds to the time-displacement of the (001) crystalline boundary. This can be obtained by multiplying the derivative $dS_k(t)/dt$ *i.e.* the rate of the crystalline fraction) to the constant factor $\frac{V}{S}$, *i.e.* the volume V of the simulation box divided by its in-plane surface area S. The velocity is obtained by fitting the slope of the $S_{\vec{k}}$(t) curve in the initial linear region. We fitted the data with a piecewise linear function, with the extremes of the intervals such that a new disordered layer is fully crystallized.

An example of the fitting script in GNUplot[3] language is reported below:

```
#sf__ : file data with the values of the structure factor

f(x) = m*x + q
fit [0:1000] f(x) ’sf__’ u 1:2 via m, q
set table "fit.dat"
unset table

f1(x) = a*x  + b
fit [1000:8000] f1(x) ’sf__’ u 1:2 via a, b
set table "fit1.dat"
unset table

a2=m
b2=q
m2=a
x1=1000
x2=8000

f2(x) = (x < x1) ?  a2 * x + b2 : (x<x2) ? m2*x + (a2-m2)*x1 + b2 : m3*
   x + m2*x2 + (a2-m2)*x1 + b2
```

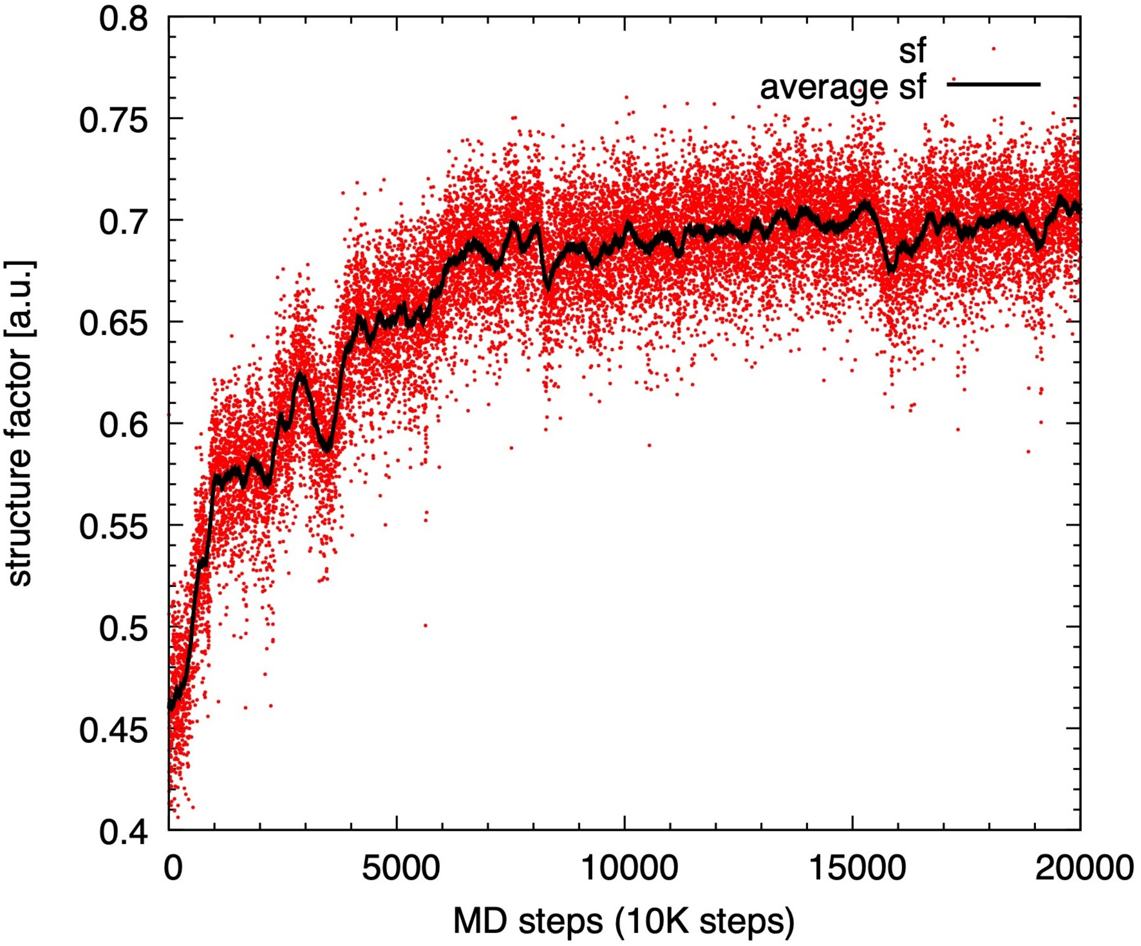

Figure 1: Structure factor calculated as a function of molecular dynamics steps at 700 K. Red dot represents the instantaneous value calculated every 10 ps; black line is obtained by averaging over a running interval of 100 points.

```
fit f2(x)  ’sf__’ u 1:2 via a2,m2,b2,x1,x2,m3

set table "fit2.dat"
```

In Fig.2 we show the structure factors with their respective fits of three annealing temperatures as example.

The calculated crystallization velocities in Å/10ps (column 2) and corresponding error intervals (column 3-4 are the lowest and highest values respectively) are reported below for different temperatures.

```
300  0.00000015   1e-8          0.0000091
340  0.00000070   1e-7          0.00001238
390  0.00000082   5.07147e-07   6.6e-06
400  0.00000516   1e-7          0.00001205
425  0.00000303   1e-7          2e-05
450  0.00000432   0.00000170    1.269e-05
475  0.00000724   0.00000244    1.88e-05
```

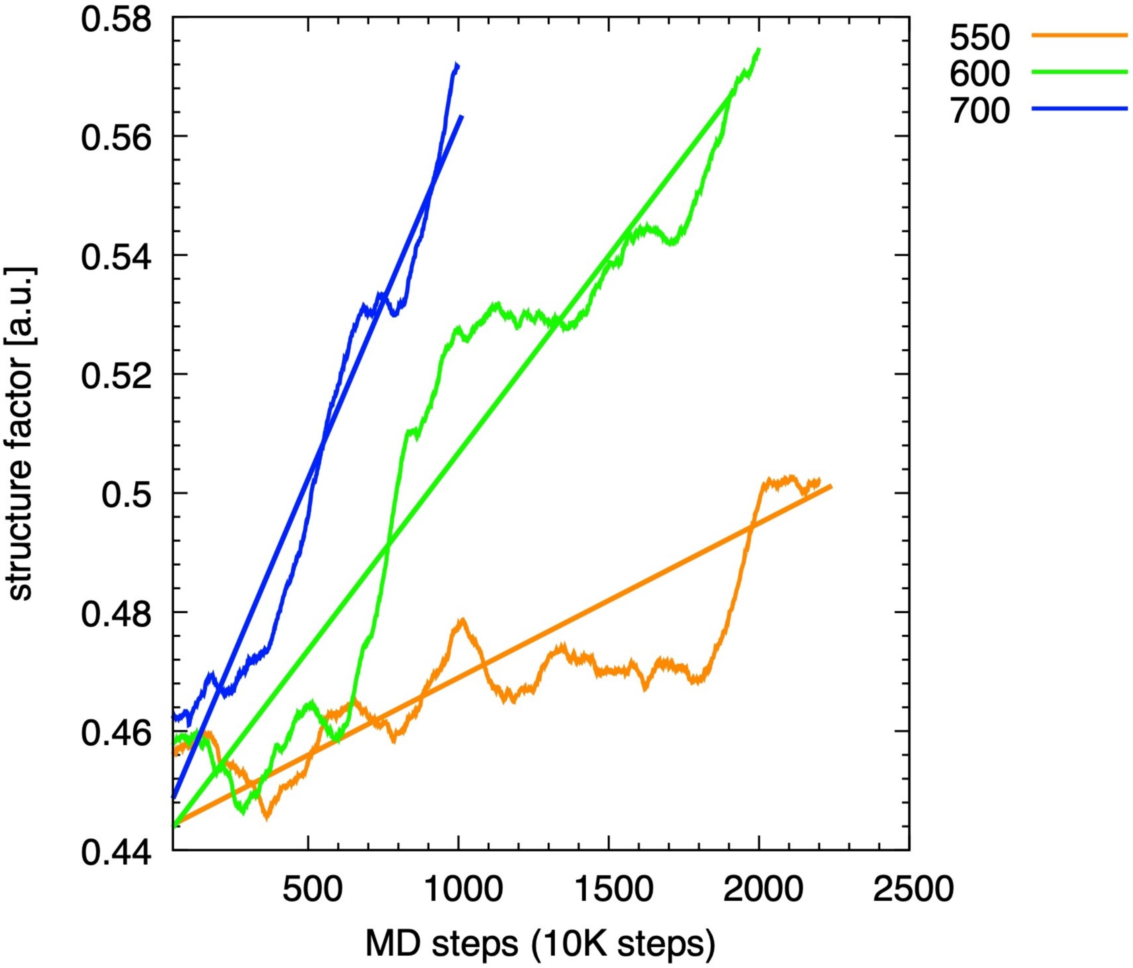

Figure 2: Structure factors and respective fits as a function of molecular dynamics steps for three annealing temperatures. Linear fitting calculated in the interval of MD steps corresponding to the crystallization of the first layer.

```
500   0.00000629    0.00000185     1.673e-05
550   0.00002597    0.00001117     0.00004077
600   0.00006624    0.00004866     0.00008382
650   0.00008195    6.318e-05      0.00010072
700   0.00011935    0.00010234     0.00013636
750   9.78897e-05   7.318e-05      0.00014072
```

Kinetic model and fitting of the crystallization velocity data

The model of velocity as a function of temperature described in the main text relies on the transition state theory. It states that the transformation probability ν_{12} from state 1 to state 2 is $\nu_{12} \sim e^{-\frac{E_{12}}{kT}}$, where E_{12} is the associated energy barrier. The probability of the reverse transformation is $\nu_{21} \sim e^{-\frac{E_{21}}{kT}}$. The net probability ν of transformation from state 1 to state 2 is accordingly

$$\nu = \nu_{12} - \nu_{21} \sim e^{-\frac{E_{12}}{kT}} - e^{-\frac{E_{21}}{kT}} = e^{-\frac{E_{12}}{kT}}(1 - e^{-\frac{E_{21}-E_{12}}{kT}}) = e^{-\frac{E_{12}}{kT}}(1 - e^{-\frac{\Delta H}{kT}})$$

$\Delta H = E_{21} - E_{12}$ is the energy difference between the two transforming phases with equilibrium temperature T_0. The velocity of the crystalline front is proportional to the rate ν and is obtained by multiplying ν by the spatial advancement associated to each event (*i.e.* $v = V_0/S \cdot \nu$, where V_0 is the unit volume and S is the interface area of the simulation box).

If the barrier E$_{12}$ (corresponding to E$_a$ in the main text) is larger than ΔH we can consider the barrier independent on temperature. On the contrary, the temperature dependence of $\Delta H = E_{21} - E_{12}$ must be taken into account in most cases, particularly at temperatures close to T_0 at which the ΔH changes sign. To this aim we choose a power-law dependence of ΔH on T, *i.e.* $\Delta H \approx (1 - \frac{T}{T_0})^m$, in the spirit of critical exponents of phase transitions.

The fitting of the atomistic data by the kinetic model (see main text) was done by GNUplot[3] (see below)

```
# Arrheniums
k = 8.6e-05
v=1e-5; E=0.2

f(T)=v*exp(-1.0*E/k/T);
fit [400:780][1e-6:] f(T) 'VELOCITY' u 1:2 via v,E

# Arrheniums + enthalpy

v(T)=(x<x0) ? v0*exp(-Ea/k/T)*(1 - exp(-1* DH0 *((1 -(T/T0))**m))) :
   0/0 ;
Ea=E*1.9; v0=v*2600;  DH0=0.03 ; T0=780 ; m=0.45;
fit [400:780][1e-6:] v(T) 'VELOCITY' u 1:2 via v0,Ea,DH0
```

The optimal parameters are reported below and provides, in addition to the activation energy that is discussed in the main text, an energy difference between the ordered and the disordered phases close to 21 meV, with a critical exponent close to 0.5.

```
v0   = 7.20329   [Angstrom/10ps]
Ea   = 0.373644  [eV]
DH0  = 0.0211519 [eV]
```

```
T0   = 780       [K]
m    = 0.45
```

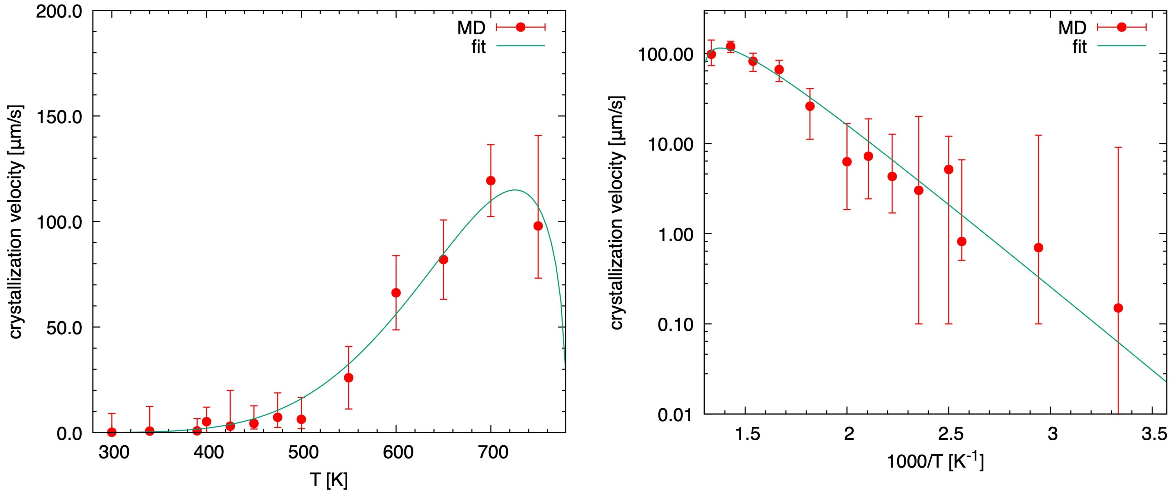

Figure 3: Crystallization velocity as a function of temperature. (left) linear scale; (right) Arrenius plot; error bars are reported.

Static energy barrier

In Fig.4 it is reported the energy profile calculated while applying a linearly increasing moment force during 10 K dynamics. The moment is obtained by applying two opposite forces on the uppermost Pb and on one Pb atom of the bulk. The snapshots represents the corresponding atomistic configuration at different simulation times. The first barrier (indicated by the black horizontal line) is necessary to break the Pb-I bond and align the Pb atom vertically at the edge a cube. By continuing the simulation, the external force is able to separate the $MAPbI_3$ unit from the surface.

The lammps input file of this calculation is reported below.

```
######  control_lammps_header
units       real
boundary p p p
atom_style  full
pair_style   hybrid/overlay tersoff lj/charmm/coul/long 9.9 10. buck/
   coul/long 9.9 10.
bond_style      harmonic
angle_style     harmonic
special_bonds   amber
dihedral_style  charmm
kspace_style pppm 1.0e-4
kspace_modify diff ad
read_data    dlpoly2lammps.data
```

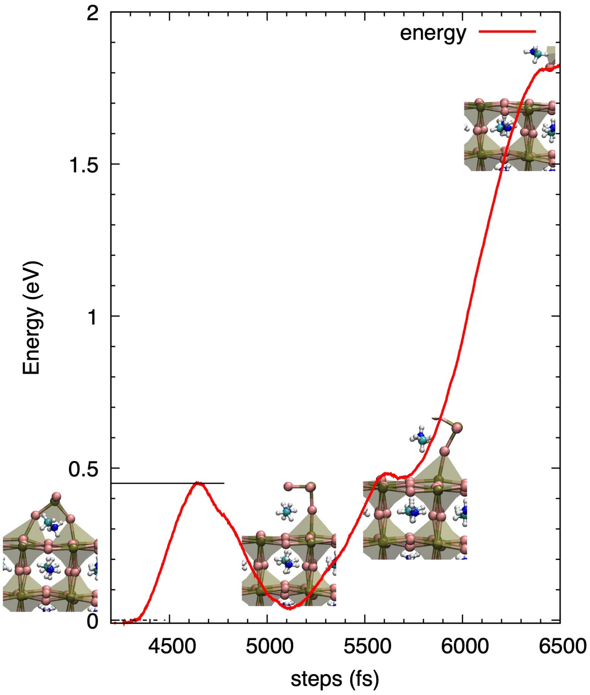

Figure 4: Energy profile as a function of simulation steps during MD dynamics at 10 K in which a constant force is applied to the lead atom until.

```
include dlpoly2lammps.nonbonding.myp2
timestep    1.0
restart 1000 restart.a restart.b
thermo 100
group frozen id 1 #blocks the first atom otherwise modify it
group free   subtract all frozen
group Lead id 49

variable ts   equal "step"
variable fz   equal "v_ts * 0.003"
variable fy   equal "v_ts * 0.003"
variable ffz   equal "-1.0 * v_ts * 0.003"
variable ffy   equal "-1.0 * v_ts * 0.003"
thermo_style custom step temp etotal cella cellb cellc  spcpu cpuremain
    v_fz
thermo      1

velocity frozen set 0. 0. 0.
fix 0 frozen setforce 0. 0. 0.
 fix 00 all momentum 1 linear 1 1 1 angular
  dump 1 all dcd 100 trajcg.dcd
  dump_modify 1 unwrap yes

  fix pull1 Lead addforce 0 v_fy v_fz
   fix pull2 frozen addforce 0 v_ffy v_ffz
    fix 000 free nvt temp 10.0 10.0 100 #aniso 1 1 500 #x 1.0 1.0 500 y
    1 1 500
        run 8500
    unfix 000
   unfix pull2
  unfix pull1

  undump 1
 unfix 00
```

```
unfix 0
```

Crystallization at different temperatures

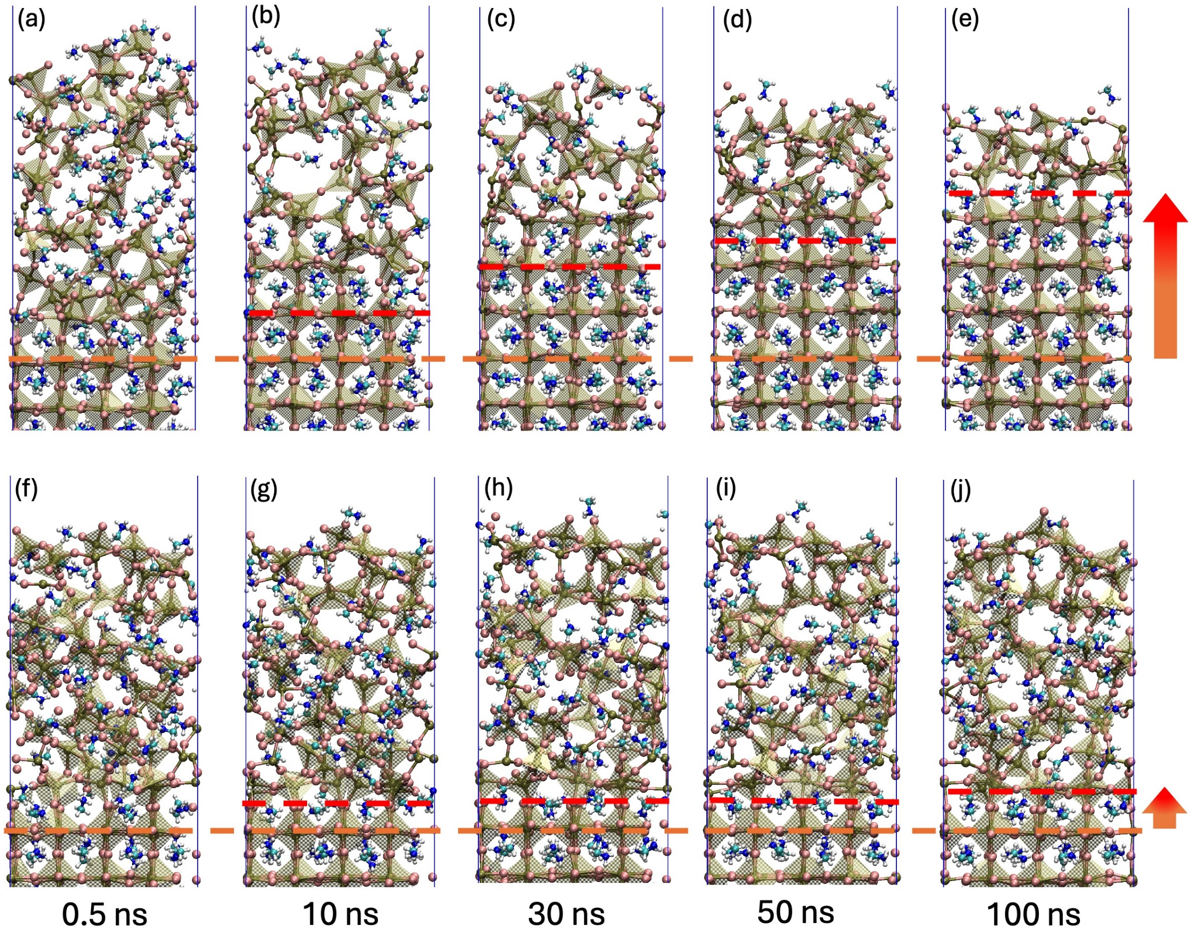

Figure 5: Snapshots extracted from NPT trajectories showing the crystallization of the deposited precursors along the (001) MAPI crystallographic direction for two annealing temperatures: 700 K (panels a-e), 390 K (panels f-j).

In Fig.5(panels f-j) it is reported a comparison between the microstructure evolution of the same system during annealing at 390 K (bottom) and 700 K (top) showing a faster kinetics at higher temperature.

Stranski-Krastanov mechanism

The growth characteristics observed during MD (see bottom panel of Fig.6) are located between the layer-by-layer and the three-dimensional growth models, and are consistent

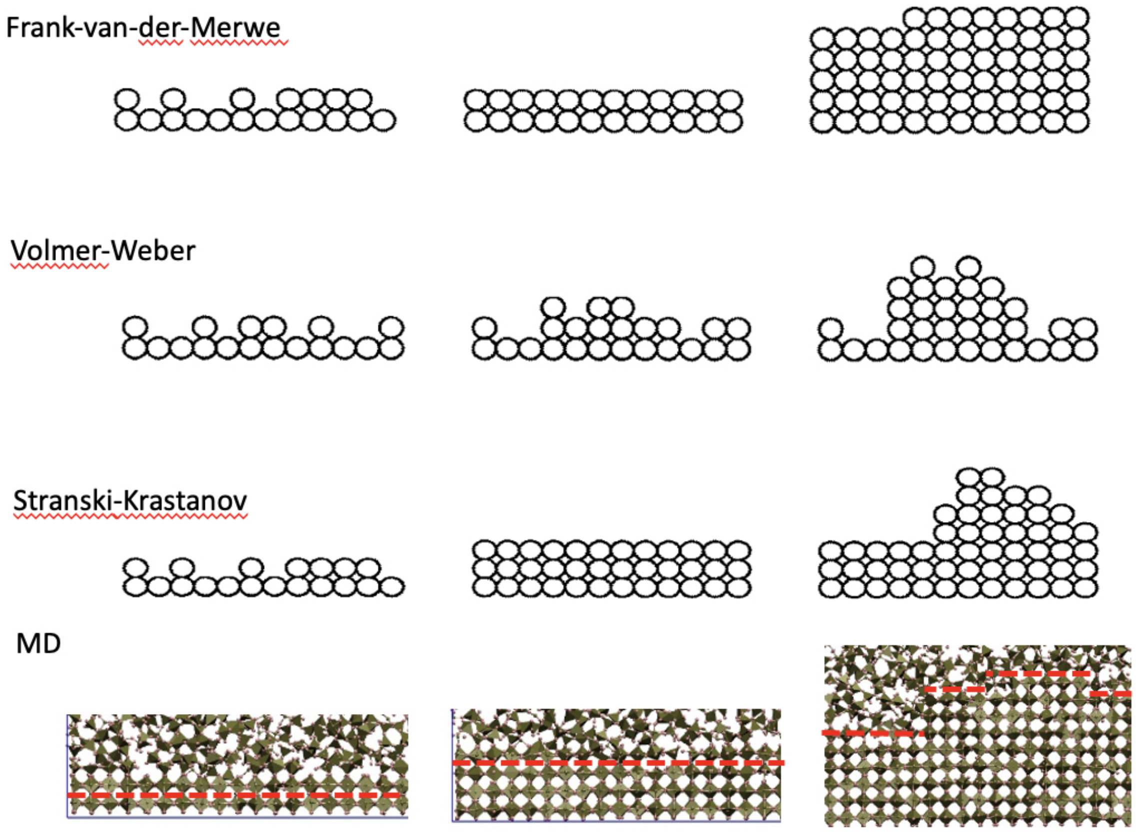

Figure 6: Comparison between possible mechanisms of growth[4] and MYP2 molecular dynamics indicating the Stranski-Krastanov regime MAPI.

with the Stranski–Krastanov evolution.[4]

Additional material can be found at the link `https://www.dsf.unica.it/~mattoni/` or requested by email `mattoni@iom.cnr.it`

References

(1) Humphrey, W.; Dalke, A.; Schulten, K. VMD – Visual Molecular Dynamics. *Journal of Molecular Graphics* **1996**, *14*, 33–38.

(2) Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; in 't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; Shan, R.;

Stevens, M. J.; Tranchida, J.; Trott, C.; Plimpton, S. J. LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comp. Phys. Comm.* **2022**, *271*, 108171.

(3) Williams, T.; Kelley, C.; many others Gnuplot 4.6: an interactive plotting program. `http://gnuplot.sourceforge.net/`, 2013.

(4) Levi, A. C.; Kotrla, M. Theory and simulation of crystal growth. *Journal of Physics: Condensed Matter* **1997**, *9*, 299.