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Imaging Field-Driven Melting of a Molecular Solid at the Atomic Scale

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Supplementary Materials for

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Materials and Methods

(1) Resolving solid and liquid phase structures with STM



Fig. S1: Self-assembled F4TCNQ structures on graphene in the solid and liquid phases. (a)

An STM image of molecular chains (the "solid" phase) reveals two coexisting tiling geometries, linear and zig-zag, both with an intermolecular distance of 8.5 Å (I = 1 pA, V = 2V). This image was obtained after allowing the sample to reach equilibrium under diffusive conditions with I_{SD} = 1.9 mA and V_G = -12V. (b) Molecules in the ionic liquid phase show an evenly spaced distribution (I = 1 pA, V = 2V). This image was obtained after allowing the sample to reach equilibrium under diffusive conditions with I_{SD} = 1.15 mA and V_G = 60V. The structure factor S(q) and radial distribution function g(r) plotted in Fig. 1(k) of the main text are both extracted from the molecular positions shown in this image.

(2) Device capacitance measurement

The capacitance of our graphene device was determined by fitting the Dirac point energy as a function of gate voltage obtained from dI/dV spectra taken on pristine graphene. The method we used for fitting the Dirac point energy for each dI/dV curve is described in ref. [¹]. We then used the following well-known expression to fit the energy position of the Dirac point as a function of applied gate voltage for a graphene FET:

$$E_D(V_G) = -sgn(V_G)\hbar v_F \sqrt{\pi C |V_G - V'|}, \qquad (S1)$$

where V' is a shift arising from impurity doping (which can vary with location). The extracted value of capacitance per area is $(6.9 \pm 0.1) \times 10^{10} |e| V^{-1} cm^{-2}$.



Fig.S2: Extracting device capacitance: The device capacitance of 6.9 $\times 10^{10} |e| V^{-1} cm^{-2}$ was extracted by fitting Eq.(S1) (solid curve) to our FET data (circles).

(3) Determining E_F from V_G and N_l (analytical model)

To find E_F (the graphene FET Fermi energy) in terms of N_l (the total number of liquid phase molecules) and V_G (the backgate voltage) we make use of total charge conservation for

electrons in the molecular LUMO and graphene band states. Assuming no intrinsic charge doping on the pristine graphene device, the total charge density introduced by electrostatic gating the molecule-decorated device is $-CV_G$ (in units of $|e| \ cm^{-2}$). Electrons introduced by gating can either occupy molecular LUMO states or graphene band states. Since each molecular LUMO can carry one electron of charge, the charge density carried by N_l isolated molecules over an area A is $\frac{-N_l}{A} |e| \ cm^{-2}$. The charge density held in the graphene band states is given by the difference between the Fermi level E_F and the Dirac point energy E_D : $\frac{|E_D - E_F|^2}{\pi \hbar^2 v_F^2}$ ($E_F < E_D$ for the regime relevant this work). Combining these charge densities yields:

$$-CV_G = -\frac{N_l}{A} + \frac{|E_D - E_F|^2}{\pi \hbar^2 v_F^2}.$$
 (S2)

This expression allows us to express E_F as a function of N_l and V_G :

$$E_F = E_D - \sqrt{\pi \hbar^2 v_F^2 (\frac{N_l}{A} - CV_G)}.$$
(S3)

(4) Determining N_l^{eq} from minimization of $U(N_l, E_F)$:

Starting from the expression for total energy U in Eq. (4) of the main text, we find that for N total molecules on the surface (with the number of liquid phase molecules = N_l), U can be expressed as

$$U = E_L N_l - \alpha (N - N_l - 1) + \frac{2A}{3\pi\hbar^2 v_F^2} [E_L^3 - E_F^3 + \frac{3}{2} E_D E_F^2 - \frac{3}{2} E_D E_L^2].$$
(S4)

Minimizing U with respect to N_l ,

$$\frac{\partial U}{\partial N_l}\Big|_{N_l = N_l^{eq}} = (E_L + \alpha) + \frac{2A(E_D - E_F)E_F}{\pi\hbar^2 v_F^2} \frac{\partial E_F}{\partial N_l}\Big|_{N_l = N_l^{eq}} = 0$$
(S5)

yields the equilibrium density of molecules N_l^{eq}/A expressed in Eq. (5) of the main text:

$$\frac{N_l^{eq}}{A} = CV_G + \frac{|E_D - (E_L + \alpha)|^2}{\pi \hbar^2 v_F^2} .$$

(5) DFT calculations

We performed *ab initio* DFT simulations of molecular chains in vacuum and also for a pair of molecules on graphene using the FHI-aims code^{2,3} with the PBE functional⁴ and a Hirshfeld van der Waals correction,⁵ as well as a tier 2 basis set for all atoms. These results show that DFT-calculated electronic structure of the molecular chains is consistent with the experimental results shown in the main manuscript, as follows:

(a) LUMO energies of chains:

In order to understand the chain electronic structure as a function of chain length, the molecules were arranged in zig-zag and linear chains and the atomic positions of molecular chains were allowed to relax until the forces on each atom became smaller than 0.005 eV/Ångstrom, while constraining the *z*-coordinates of all atoms to lie in a plane.

Fig. S3 shows the Kohn-Sham LUMO energies $E_L^{(N)}$ of chains with N molecules (up to N = 8) relative to the LUMO energy of an isolated molecule $E_L^{(1)}$, $\Delta E = E_L^{(N)} - E_L^{(1)}$. The LUMO energies of the chains are always higher than the LUMO energy of the isolated molecule and ΔE approaches approximately 40 meV as N increases. Plotting the wavefunctions of the chain end LUMO states (see Fig. S4) reveals that they are localized on the outermost molecules of the chain. The higher-lying unoccupied states of the chains are formed from the LUMOs of molecules in the middle of the chain. These levels lie approximately 80 meV higher than the single molecule LUMO for long chains. These results are in good agreement with the experimental findings.



Fig. S3: F4TCNQ LUMO energies, relative to that of the isolated molecule, obtained from **DFT as a function of number of molecules in a molecular chain.** An isolated molecule has the lowest LUMO energy, while molecules within a chain have higher LUMO energies, with the end molecules on the chain having a LUMO which is lower in energy than the rest of the molecules in the chain.



Fig. S4: dI/dV maps of F₄TCNQ near LUMO energies of different molecular

configurations. (a)-(c) Experimental dI/dV maps of a chain and single molecules taken under an external gate voltage $V_G = -60V$ at different energies (for the same region of surface) (a) $V_s = 220 \text{ mV}$, (b) $V_s = 300 \text{ mV}$, (c) $V_s = 350 \text{ mV}$. The dI/dV maps confirm that the single molecule LUMO is the lowest in energy, followed by molecules at the chain end, and then molecules at the center of the chain. (d)-(f) Theoretical electron density contour at energies corresponding to LUMOs of the single molecule, chain end, and chain center.

(b) Inter-molecule bonding energy (α):

To calculate the bonding energy between F4TCNQ molecules in a chain we prepared a graphene flake consisting of 8x8 graphene unit cells and hydrogen-passivated edges. The structure was relaxed while constraining the z-positions of the atoms to reside in a plane. We then performed constrained DFT calculations for a pair of adsorbed F4TCNQ molecules to ensure that the molecules remain uncharged (reflecting the uncharged character of molecules in chains), see Fig. S5. The binding energy was calculated from

$$-\alpha = E_{pair} - (E_{single,1} + E_{single,2} - E_{gra}), \qquad (S6)$$

where E_{pair} is the total energy of both molecules on the graphene flake, E_{gra} is the energy of the graphene flake without any molecules, and $E_{single,1/2}$ denotes the energy when one or the other molecule is removed from the flake. Note E_{gra} is needed to cancel the double counting of the energy of the flake from $E_{single,1} + E_{single,2}$. We find that the bonding energy is $\alpha \sim 45$ meV from these calculations. This is similar to the experimental upper bound on α that was determined from our STM spectroscopy ($\alpha_{exp} \leq 40$ meV).



Fig. S5: Graphene flake with two adsorbed F4TCNQ molecules.

(6) Monte Carlo simulations

We employed a standard Metropolis Monte Carlo algorithm to simulate the dynamical collective behavior of uncharged molecules in chains together with isolated molecules (both charged and uncharged), and electrons residing in either the LUMO of isolated molecules or in graphene Dirac band states. The thermal energy in the simulations was taken to be $k_BT = 1$ meV.

For our simulations the molecules occupy sites on a coarse-grained triangular lattice with an area per site corresponding to 12 graphene unit cells and a lattice spacing of approximately 1 nm, see Fig. S6. A molecule can have one of three possible orientations which point along the vectors connecting a graphene carbon atom to nearest neighbor sites. This lattice is constructed as follows: if a molecule occupies a given site, the neighboring sites (shown in green in the top left panel of Fig. S6) are the ones that the nearest-neighbor molecules would occupy if the molecules were part of the same chain (either zigzag or linear). The red sites in the top left panel of Fig. S6 are nearest-neighbor sites that cannot be occupied because we only consider side-byside bonding and not end-to-end bonding of molecules (since the latter is not observed experimentally). If a second molecule occupies one of the two neighboring sites on one "side" of the first molecule, then the other site becomes inaccessible (see top right panel of Fig. S6). As a consequence, each molecule can only form up to two bonds with its neighbors. A third molecule can occupy one of two sites on the other "side" of the first molecule which gives rise to either a zigzag arrangement (bottom left panel) or a linear configuration (bottom right panel). The energy per bond is taken to be -10 meV.

Electrons can either occupy graphene states or the LUMO of isolated molecules (we ignore the possibility of charged chains, but allow for uncharged isolated molecules). If a molecule becomes charged, it induces an electrostatic Hartree potential which is experienced by the other charged molecules. The corresponding contribution to the total energy is given by

$$E_H = \frac{1}{2} \sum_{i \neq j} W_{ij} n_i n_j , \qquad (S7)$$

where $n_{i/j}$ are the charges of the molecules (-|e| or 0), *i* and *j* label the isolated molecules located at positions $\tau_{i/j}$, and W_{ij} is the screened Coulomb interaction between these charges. In our simulations, we use the Thomas-Fermi theory result for doped graphene, i.e. $W_{ij} =$

 $e^2/(4\pi\epsilon_0\epsilon\kappa^2|\boldsymbol{\tau}_j-\boldsymbol{\tau}_i|^3)$ with κ denoting the inverse screening length and ϵ the background dielectric constant. We use $1/(\epsilon\kappa^2) = 25$. In this context the molecules are treated as point charges located on the sites of the effective triangular lattice.

At the beginning of the simulation 300 molecules are distributed randomly on a 50x50 supercell of the effective triangular lattice. The molecular orientations are also initially random. Next, we generate a trial move which is either accepted or rejected by the Monte Carlo algorithm and one iteration of the algorithm is completed when each of the 300 molecules has carried out a trial move. In each move, the molecules can hop from their current site to nearest neighbor sites

and also change orientation. We consider three cases: (i) if an isolated molecules hops onto the nearest neighbor site of another molecule, its orientation aligns with that of its neighbor and a bond is formed; (ii) if an isolated molecule hops onto a site without nearest neighbors, its orientation changes randomly; (iii) if a molecule dissociates from a chain, its orientation does not change.

To generate a more realistic initial configuration corresponding to the experimental setup, we performed 160 iterations in the presence of a linear potential in the x-direction with a gradient of -10 meV/nm to mimic the electromigration force of the flowing current used experimentally to create initial molecular configurations. Then 150 electrons were added into graphene states (assuming that all graphene states up to the molecular LUMO level are always filled) and turned off the electromigration potential. In the presence of the electrons, the procedure for a single move in the Monte Carlo simulation was extended according to the following rules: (i) if a molecule is uncharged and not bound to another molecule after it has hopped to a nearestneighbor site, an electron can be transferred from the highest occupied graphene state to the LUMO; (ii) if an isolated molecule is initially charged and does not form a bond to another molecule in the move, its charge can be transferred to the graphene; (iii) if a molecule is converted from an isolated, uncharged state to a bonded configuration, it cannot become charged in that move; (iv) if a molecule is initially charged and forms a bond to another molecule, its charge must be transferred to the graphene; (v) if a molecule dissociates from a chain, it can become charged.

After each extended move involving a molecular displacement, re-orientation, electron transfer, or bond formation, the change in the total energy of the system (now consisting of a term describing the electrons in the graphene, a term describing the bonding between molecules,

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a term describing the charging of molecules, and the Hartree interaction between charged molecules) is calculated and the Monte Carlo algorithm decides whether to reject or accept the move. We ran the simulation for 400 iterations.



Fig. S6: Allowed adsorption sites defined in the Monte Carlo simulation: The allowed adsorption sites form a triangular lattice. Adsorbed molecules can either form a zigzag chain (bottom left) or a linear chain (bottom right).

(7) Radial distribution function calculation

After obtaining the molecular centroid positions r_i using the trackpy software suite,⁶ the radial distribution function g(r) shown in Fig. 1(k) of the main text was calculated using this standard definition:⁷

$$g(r) = \frac{1}{\rho_{avg}} \left\langle \frac{dN_i(r)}{2\pi r dr} \right\rangle$$
(S8)

where $N_i(r)$ is the number of molecules within a concentric ring of radius r and thickness drcentered around molecule i, and ρ_{avg} is the average density of molecules on the surface. Molecules within the radial bin (r, r + dr) contribute to the count of $N_i(r)$. The ensemble average $\langle \cdot \rangle$ is then taken over all molecules i within a radius of $r \leq d/4$ of the center of the scan frame, where d is the width of the square scan frame (this is to ensure exclusion of edge molecules so that the average is not skewed by edge effects).

(8) Structural characterization of molecular chains

The structure factor, $S(\mathbf{q})$, of the solid chain phase was determined by first recording the center positions of molecules within linear and zigzag chains using STM topography (Figs. S7(a), (c)). $S(\mathbf{q})$ was then obtained from the molecular positions using the freud-analysis numerical analysis software.⁸ (Figs. S7(b), (d)). The structure factor $S(\mathbf{q})$ is defined as

$$S(\mathbf{q}) = \frac{1}{N} \sum_{j=1}^{N} \sum_{k=1}^{N} e^{-i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)}$$
(S9)

where R_j , R_k are the centroid positions of pairs of molecules, and the sum is taken over all N particles. The molecular quasi-1D solid chain geometries exhibit an $S(\mathbf{q})$ with a clear periodicity of ~ (8.5Å)⁻¹ along the chain growth direction (Fig. S7 (a), (b)). In the direction perpendicular to the chain growth, the periodicity is less well-defined due to variability in inter-chain separation, thus corroborating that the molecules are in a quasi-1D solid. Molecules self-assembled into a mixture of zigzag and linear chain geometries (Fig. S7(c)) exhibit an $S(\mathbf{q})$ that shows an array of diffraction spots separated by ~ (8.5Å)⁻¹ (Fig. S7(d)). In the direction perpendicular to the chain

growth, however, the periodicity is again less well-defined due to the variability in inter-chain distance, corroborating the quasi-1D structure. We found that the inter-molecular distance within a molecular chain is partially constrained by the underlying graphene lattice. In Fig. S8 we show STM topography data indicating that molecular chains are aligned with the underlying graphene lattice (the graphene lattice orientation was found from atomically-resolved STM topography data). The adsorption sites of molecules within chains are observed to lie on the "bridge" site of graphene (i.e., the center point of the molecule). The resulting inter-molecule separation within molecular chains is 8.52Å. In Fig. S9 dI/dV spectroscopy data is shown that was taken on different molecules within two molecular chains. Molecules 1 and 2 are part of a linear chain segment in the first chain and molecules 3, 4, 5 are part of a zigzag chain segment. The LUMO energies of the molecules within both the linear and zigzag segments are found to be nearly identical.



Fig. S7: Structural characterization of different molecular chain geometries: (a) STM topography of molecular chains in the linear geometry. Red dots indicate the center positions of the identified molecules. (b) The corresponding structure factor $S(\mathbf{q})$ calculated from the molecule center positions found in (a). (c) STM topography of molecular chains of mixed zigzag and linear geometries. (d) The corresponding structure factor $S(\mathbf{q})$ calculated from the molecule center positions found in (a). (c) STM topography of molecular chains of mixed zigzag and linear geometries. (d) The corresponding structure factor $S(\mathbf{q})$ calculated from the molecule center positions found in (c).



Fig. S8: Structure of molecular chains overlaid on the graphene lattice: STM topography of a molecular chain (including molecular model) overlaid on top of the measured graphene lattice. The graphene lattice orientation was found from atomically-resolved STM topography data. The inter-molecular distance of molecular chains was found to be 8.52Å.



Fig. S9: dI/dV spectra of molecules in different structural geometries within molecular chains: (a) STM topography of molecular chains. (b) dI/dV spectra taken on different molecules located at positions marked by an "x" in (a).

(9) Long-term monitoring of phase equilibrium:

In order to determine the sufficient current and pulse duration to reach equilibrium between solid and liquid phase molecules, we performed long-term monitoring of the solid-liquid phase boundary under different current pulse durations. This can be seen in Fig. S10 which shows an experiment where a source-drain current of 1mA was used to heat the device while the gate voltage V_G was held at -20V. The surface molecular configuration was initially prepared by heating the device with 1mA current at V_G=-60V for $\Delta t > 1$ sec. The resulting initial equilibrium surface molecular configuration is shown in Fig. S10 (a) and shows only solid-phase molecules as expected. The gate voltage was then switched to Vg=-20V and source-drain current pulses of 1mA with durations ranging from 1, 20, 60, 180, and 600s were applied to the device. The resulting surface molecular configurations after the current pulses are shown in Fig. S10 (b)-(f). We observe that the average concentration of molecules does not change significantly between 1s and 860s of current flow, thus demonstrating that equilibrium is reached within 1s of current pulse. We conclude that the pulse durations of 180s used in Fig. 1 (a)-(h) are sufficient to establish equilibrium between solid and liquid phases.



Fig. S10: Long-term stability of liquid- and solid-phase equilibrium: (a) STM topograph of the surface molecular configuration prepared by heating the graphene device with a 1mA source-drain current pulse for for $\Delta t > 1$ sec while holding V_G=-60V. Solid phase molecules aggregate in the top left corner of the image. (b)-(f) STM topographs of the surface after applying a 1mA current pulse while holding V_G=-20V for 1, 20, 60, 180, and 600s, respectively. The equilibrium densities of solid and liquid phase molecules is established within 1s of applying the current pulse while holding V_g=-20V.

(10) Thermodynamic theory of electrostatically-driven phase transitions in the grand potential framework

In an open system where particles are allowed to be exchanged with a reservoir, the thermodynamic potential that is minimized is the grand potential Φ . Since electrons can be moved between the silicon back gate (the reservoir) and the molecule-decorated graphene system by application of a gate voltage, the system is open for electrons. For all other particles, such as the solid phase molecules and liquid phase molecules, the system is closed, thus we define the grand potential to be

$$\Phi = U - TS - E_F N_e, \qquad (S6)$$

Where U is the internal energy of the system (graphene plus molecules), T is the overall temperature, S is the entropy of the system, E_F is the electrochemical potential of electrons (Fermi level) in the systems and N_e is the number of electrons in the system. Additionally, we can define a chemical potential μ_l and μ_s for the two other species of particles: liquid phase molecules and solid phase molecules, given N_l as the number of liquid phase molecules, and N_s as the number of solid phase molecules. The thermodynamic identity of this system then reads

$$d\Phi = -SdT - pdV - N_e dE_F + \mu_l dN_l + \mu_s dN_s.$$
(S7)

Here the parallel between the Fermi level E_F and temperature *T* becomes clear: they both act as the natural variable (differential) term in the grand potential. If a temperature-driven first-order phase transition occurs, then the entropy of the two phases is discontinuous, resulting in a jump in the entropy between the two phases $\Delta S = \frac{d\Phi_1}{dT}|_{V,E_F,N_l=N,N_S=0} - \frac{d\Phi_S}{dT}|_{V,E_F,N_l=0,N_S=N}$, where Φ_1 is the grand potential when all molecules are in the liquid phase, Φ_S is the grand potential when all molecules are in the solid phase, *N* is the total number of molecules, N_l is the number of liquid phase molecules, and N_s is the number of solid phase molecules. The latent heat $T\Delta S$ is needed to melt all the solid phase molecules into liquid phase molecules for this first order phase transition. In analogy to this, for the case of an electrostatically-driven phase transition, the number of electrons in the system is the discontinuous quantity where $\Delta N_e = \frac{d\Phi_1}{dE_F}|_{V,T,N_l=N,N_s=0} - \frac{d\Phi_s}{dE_F}|_{V,T,N_l=0,N_s=N}$. The latent energy $E_F\Delta N_e$ is then needed to melt all the solid phase molecules into liquid phase molecules for this first order phase transition.

Movie access: Three movies showing solid-liquid phase transitions for F₄TCNQ molecules on graphene FET devices (Movie S1, Movie S2, and Movie S3) can be found at this website: <u>https://crommie.berkeley.edu/f4tcnq_movies</u>

Movie Descriptions:

Movie S1: Molecules condensing into molecular chains: This movie shows sequential STM images of the surface configuration of F4TCNQ molecules on graphene transforming from a liquid phase to a solid phase (i.e., a freezing transition). At the start of the movie, an equilibrium molecular configuration is shown that was prepared by simultaneously applying I_{SD}=1.3mA and $V_G = 60V$ to the graphene device for 180s. Each subsequent frame shows the sample after lowering V_G to $V_G = -5$ V and sending a current pulse through the device for $\Delta t = 100$ ms (i.e., each frame shows a forward step in time of $\Delta t = 100$ ms while keeping $V_G = -5$ V constant). Molecular chains are observed to continually condense throughout the movie.

Movie S2: Molecular chains dissociating into single molecules: This movie shows sequential STM images of the F4TCNQ molecular configuration on graphene transforming from a solid

phase back to a liquid phase (i.e., a melting transition). This movie begins where Movie S1 ends, with the surface in a solid molecular configuration (i.e., "frozen") that is obtained after holding the gate voltage at $V_G = -5$ V under diffusive conditions for $\Delta t = 500$ ms. In this movie V_G is set to $V_G = 60$ V and each frame shows the surface evolution after an amount of time $\Delta t = 500 \ \mu s$ while keeping the source-drain current at $I_{SD} = 1.1$ mA. Molecules are observed to dissociate from the chains (i.e., to melt) throughout the movie. By the end of this movie the surface molecular configuration has returned to the equilibrium configuration at $V_G = 60$ V seen at the beginning of Movie S1.

Movie S3: Wave of single molecules emerging from molecular chains: This movie shows sequential STM images of a highly nonequilibrium "wave" of liquid phase F₄TCNQ molecules on graphene emerging from a molecular solid. At the start of the movie an equilibrium molecular configuration is shown that was prepared by simultaneously applying $I_{SD}=1mA$ and $V_G=-20V$ to the graphene device for 180s. During the movie V_G is set to 60V and each frame shows the time evolution of the surface after subjecting it to a source drain current of $I_{SD} = 1.3$ mA for $\Delta t =$ 100 µs. This is a nonequilibrium melting process.

References:

- Liou, F. *et al.* Imaging Reconfigurable Molecular Concentration on a Graphene Field-Effect Transistor. *Nano Letters* 21, 8770–8776 (2021).
- Blum, V. *et al.* Ab initio molecular simulations with numeric atom-centered orbitals. *Computer Physics Communications* 180, 2175–2196 (2009).

- 3. V. Blum *et al.* FHI-aims. All-electron electronic structure theory with numeric atom-centered orbitals. (2009).
- Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* 77, 3865–3868 (1996).
- Tkatchenko, A. & Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Physical Review Letters* 102, 73005 (2009).
- Allan, D. B., Caswell, T., Keim, N. C., van der Wel, C. M. & Verweij, R. W. softmatter/trackpy: Trackpy v0.5.0. (2021) doi:10.5281/ZENODO.4682814.
- Hansen, J.-P. & McDonald, I. R. Statistical Mechanics and Molecular Distribution Functions. in *Theory of Simple Liquids (Second Edition)* (eds. HANSEN, J. P. & McDONALD, I. A. N. R.) 13–44 (Academic Press, 1986). doi:https://doi.org/10.1016/B978-0-08-057101-0.50006-8.
- Ramasubramani, V. *et al.* freud: A Software Suite for High Throughput Analysis of Particle Simulation Data. *Computer Physics Communications* 254, 107275 (2020).