Solute-Interface Interactions: Experimental and Atomistic Simulation Results

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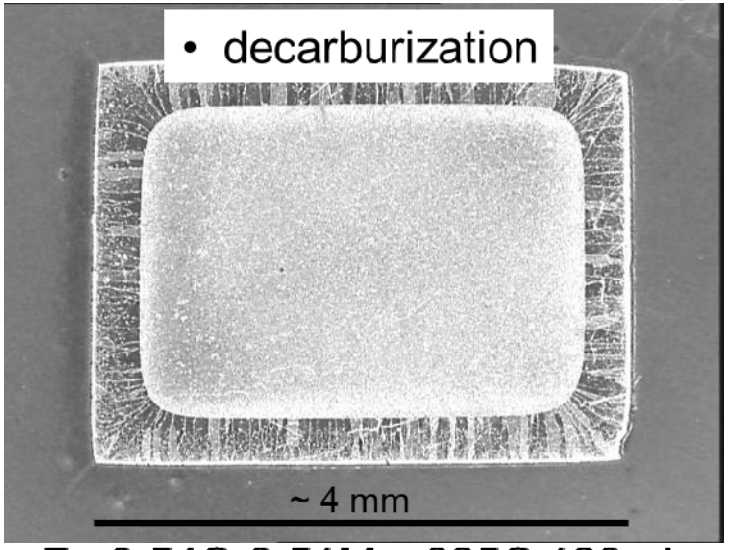
NSERC CRSNG

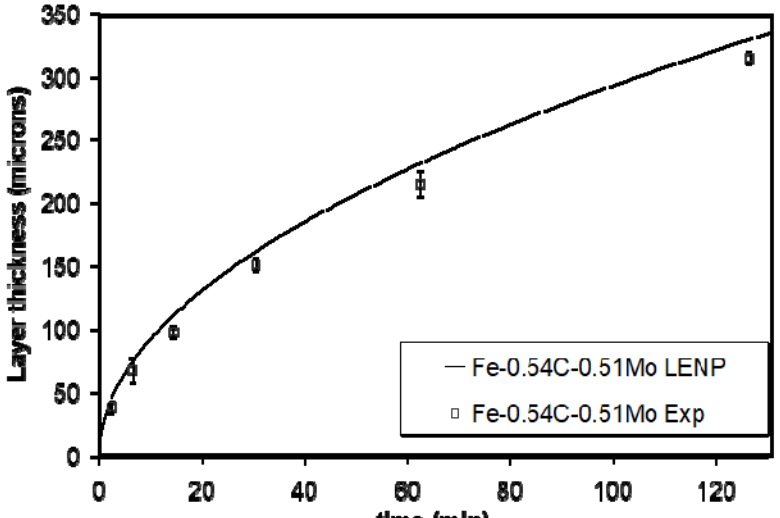
Review of Experimental Results

McMaster University

- We have examined a number of ternary and quaternary systems:
  - Fe-Mo-C
  - Fe-Cr-C
  - Fe-Mn-C
  - Fe-Si-C
  - Fe-Ni-C
  - Fe-Mn-Si-C
  - Fe-Mn-Mo-C



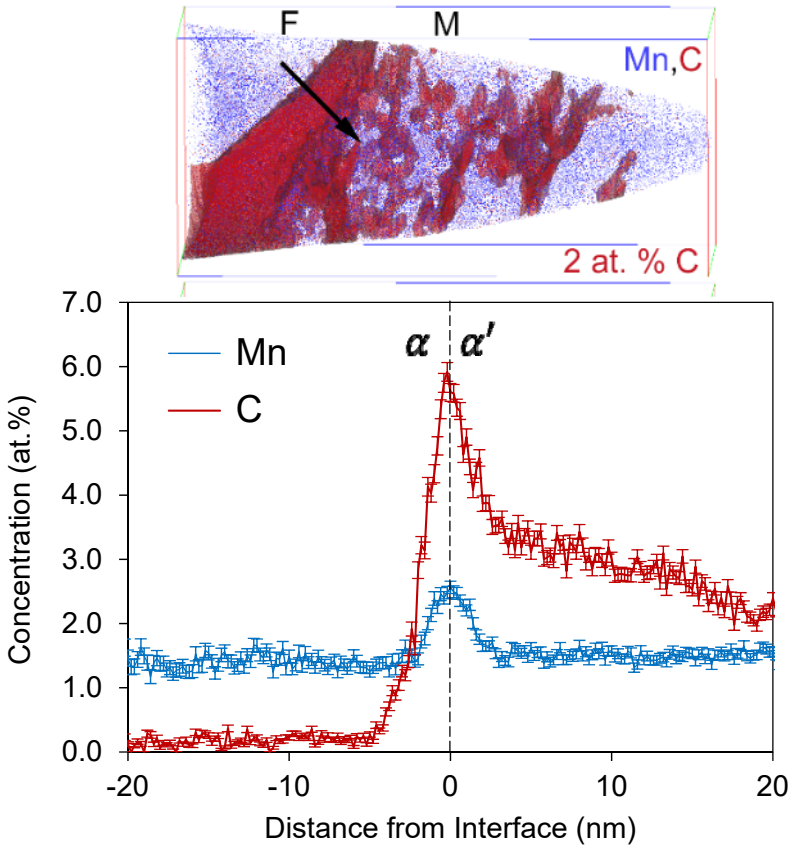
Fe-0.54C-0.51Mo; 825C 128min



C. R. Hutchinson et al, Met. Trans A37, 1711.

Review of Experimental Results

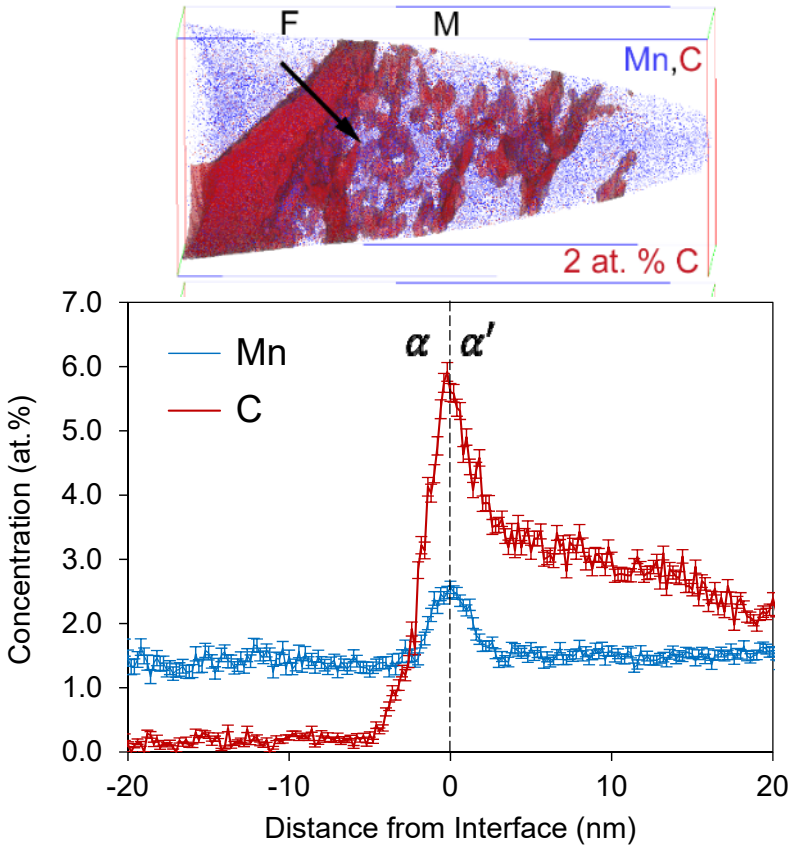
- Atom probe shows segregation to the interface.
- We measure the enrichment and use it to calculate a binding energy.



Langelier et al., Microsc. Microanal. 23, 385.

Review of Experimental Results

- There are several key points to remember about the experimental results:
  - The atom probe data shows segregation over a wide region.
  - We don't know the velocity of the interface.
  - We can only calculate an effective binding energy.



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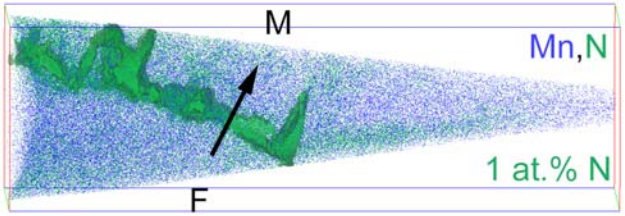
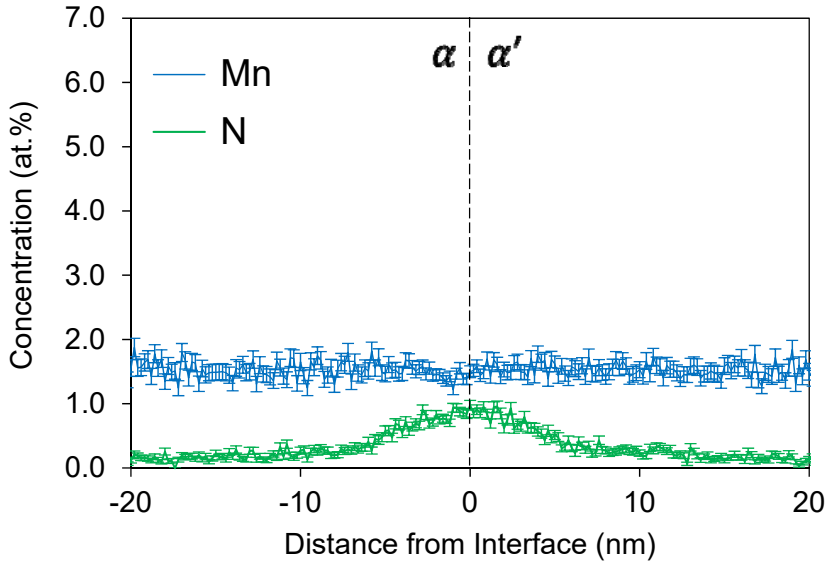
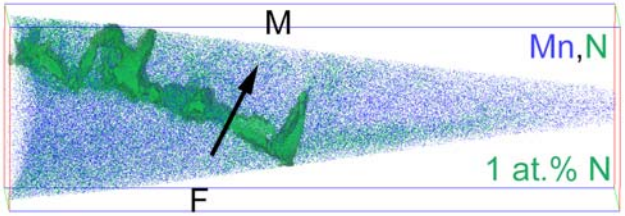


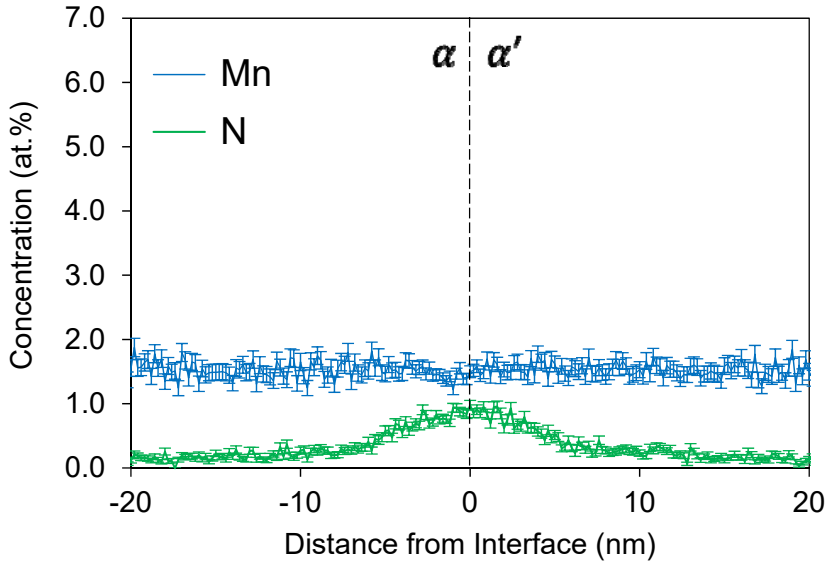


Langelier et al., Microsc. Microanal. 23, 385.

Review of Experimental Results

- There are several key points to remember about the experimental results:
  - The atom probe data shows segregation over a wide region.
  - We don't know the velocity of the interface.
  - We can only calculate an effective binding energy.
  - In some systems, we see large variations in the measured enrichment.





Langelier et al., Microsc. Microanal. 23, 385.

Review of Experimental Results

McMaster University

kJ/mole	**Austenite G.B.**	**Ferrite G.B.**	**Ferrite/Aust.**
Mo	-15+/- 3 (Enomoto et al.)	-28 +/- 2 (Murayama & Smith)	-19 +/- 2 **-25 +/- 3**
Cr		-8 [Lejček & Hofmann]	-9 +/- 2 **-18 +/- 3**
Ni	Too small to measure (Enomoto et al.)		0 **0 to -5**
Mn	-8+/-3 (Enomoto et al.)	-8+/-4 (Kaufman)	-6 to -8 in Fe-Mn-C **Less than 5 for Fe-Mn-N** **-10 to -15 for Fe-Mn-C**
Si	-23+/-6 (Enomoto et al.)	-7 [Lejček]	**Difficulty to determine, but appears to be repulsive in Fe-C-Si**

Quaternary Systems

- Fe-Mn-Si-C:
  - Example of a system in which we expect strong interactions between substitutional elements.
  - Is also interesting because of the X-C interactions; Si-C repulsive, Mn-C attractive.

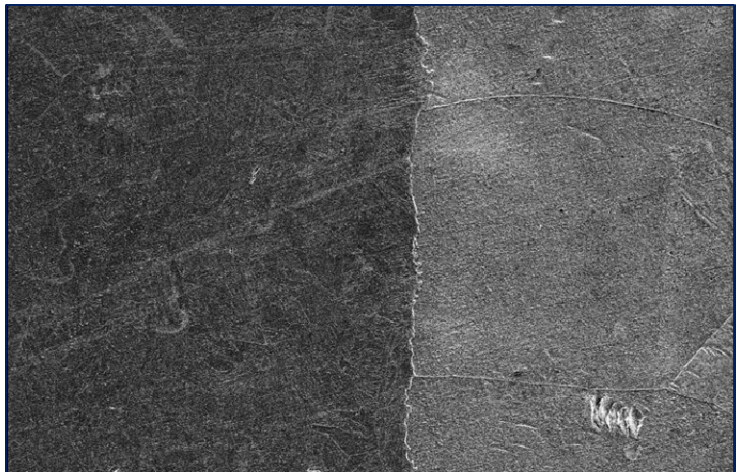
- Fe-Mn-Mo-C:
  - Example of a system in which we don't expect strong interaction between substitutional elements.

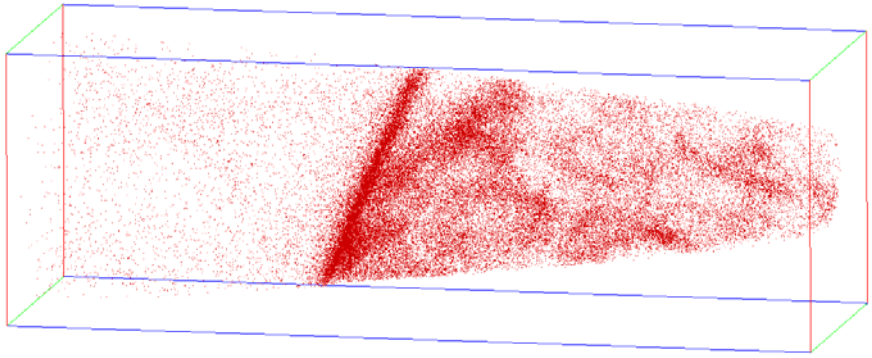
ε	Ferrite
C-C	6.5
Mn-Mn	−4.5
Si-Si	21.2
C-Mn	−7.5
C-Si	8.0
Mn-Si	−11.0

Interaction parameters @ 650C Guo et al., Met. Trans A, 37, 1721

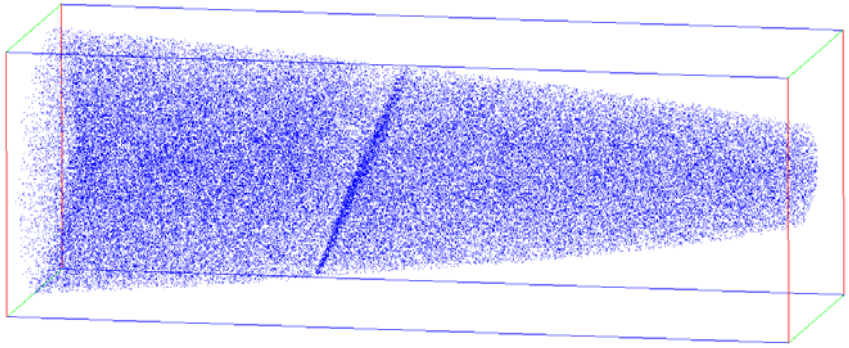
Fe-1.5wt%Mn-1.3wt%Si-0.7wt%C

755°C for 16 minutes

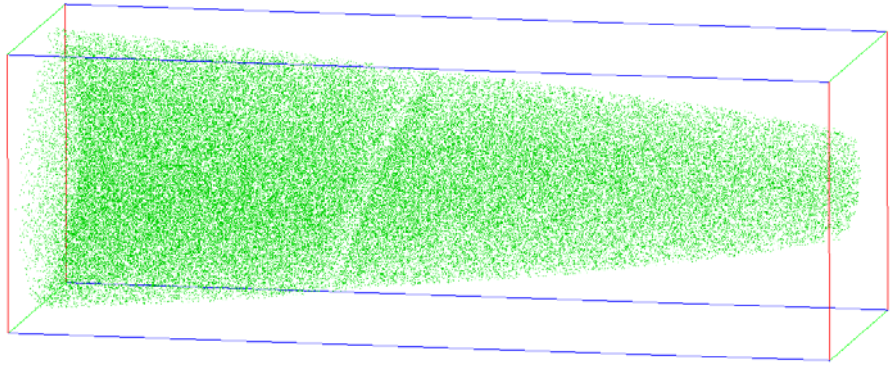




C



Mn

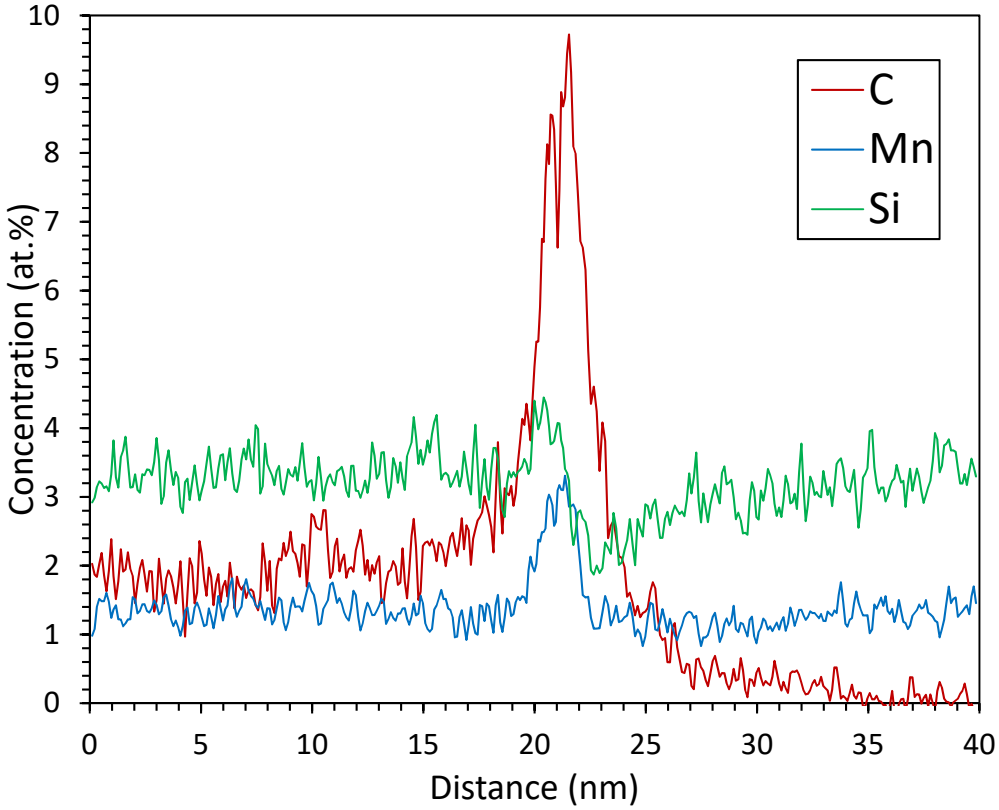


Si

Fe-1.5wt%Mn-1.3wt%Si-0.7wt%C

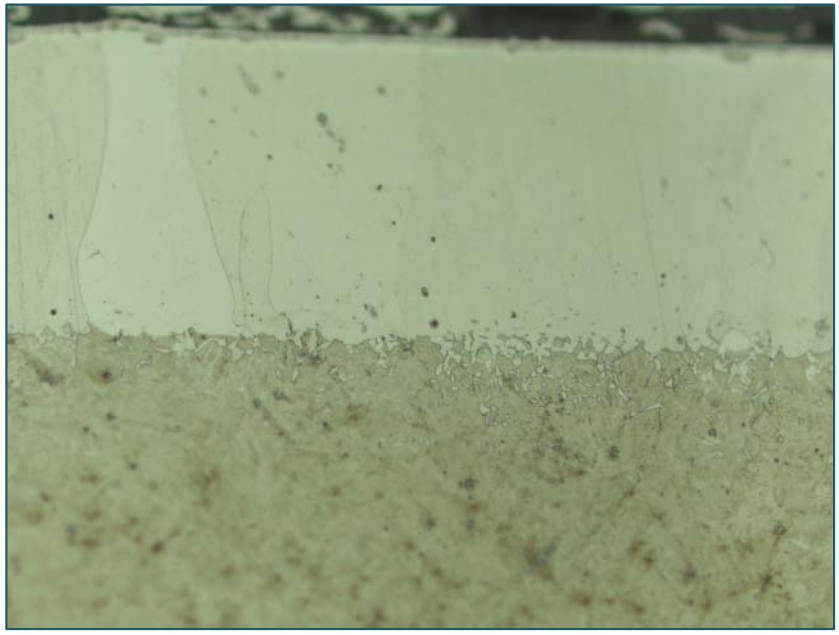
755°C for 16 min

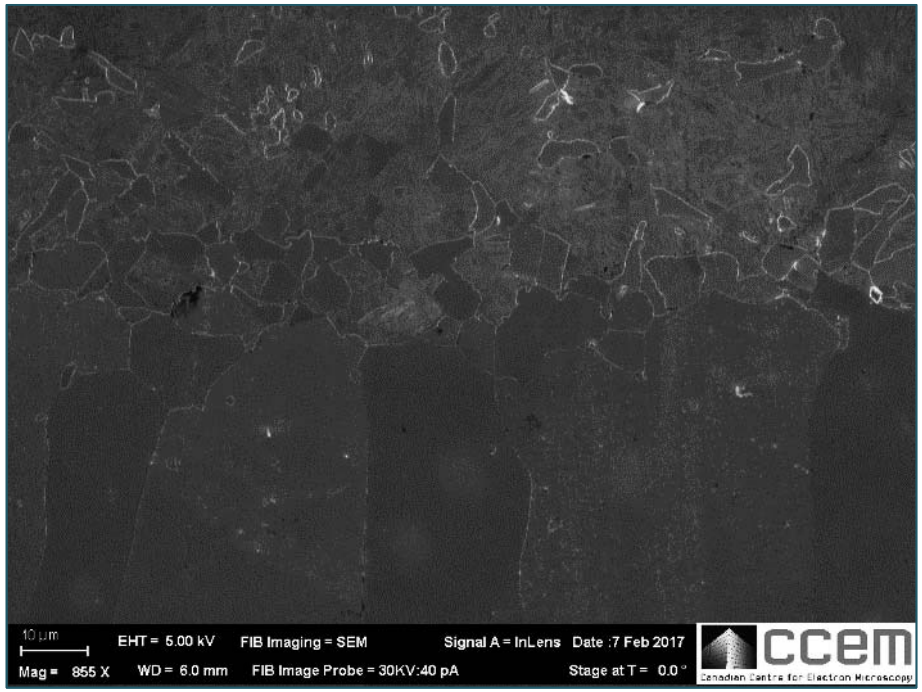
- Si shows a complicated profile with possible desegregation on one side of the interface.
- Mn segregates to levels comparable to the ternary system.
- No evidence of Mn/Si co-segregation.



Fe-1.5wt%Mn-1.3wt%Si-0.7wt%C

755°C for 4 hours



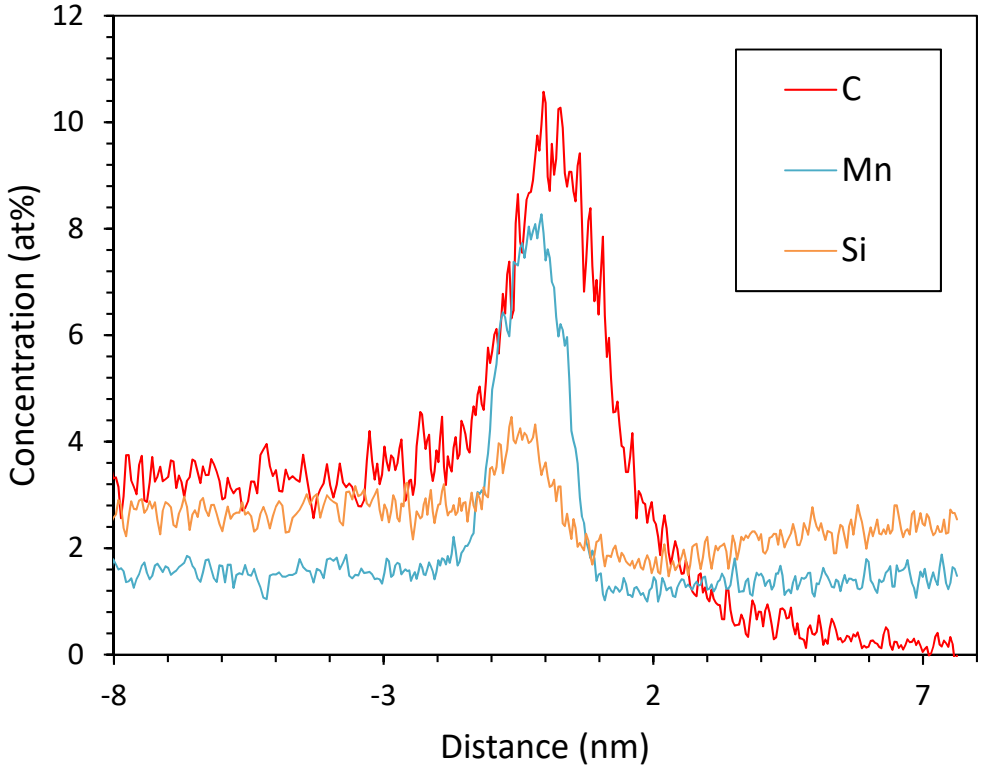


Many areas of the interface were not suitable for a liftout due to the roughness of the interface

Fe-1.5wt%Mn-1.3wt%Si-0.7wt%C

755°C for 4 hrs

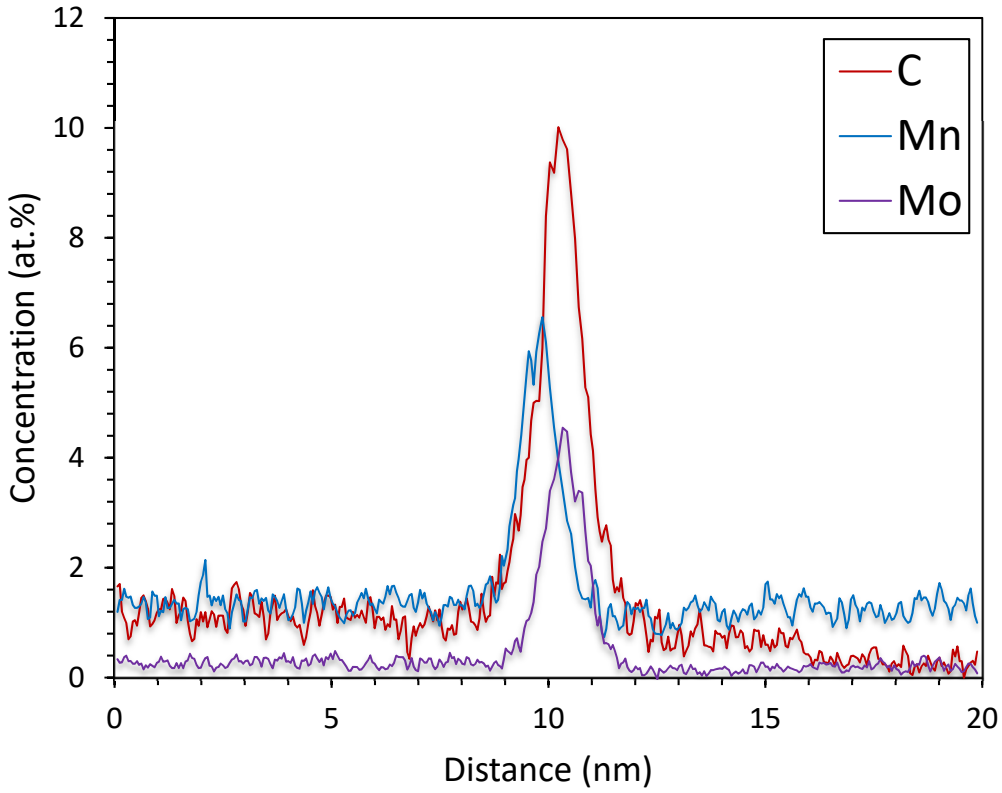
- Complex Si profile.
- Mn segregates stronger than previous sample.
- Could this unusually high value be due to Mn/Si interaction?



Fe-1.3%Mn-0.5%Mo-0.5%C

23.5 min at 755°C

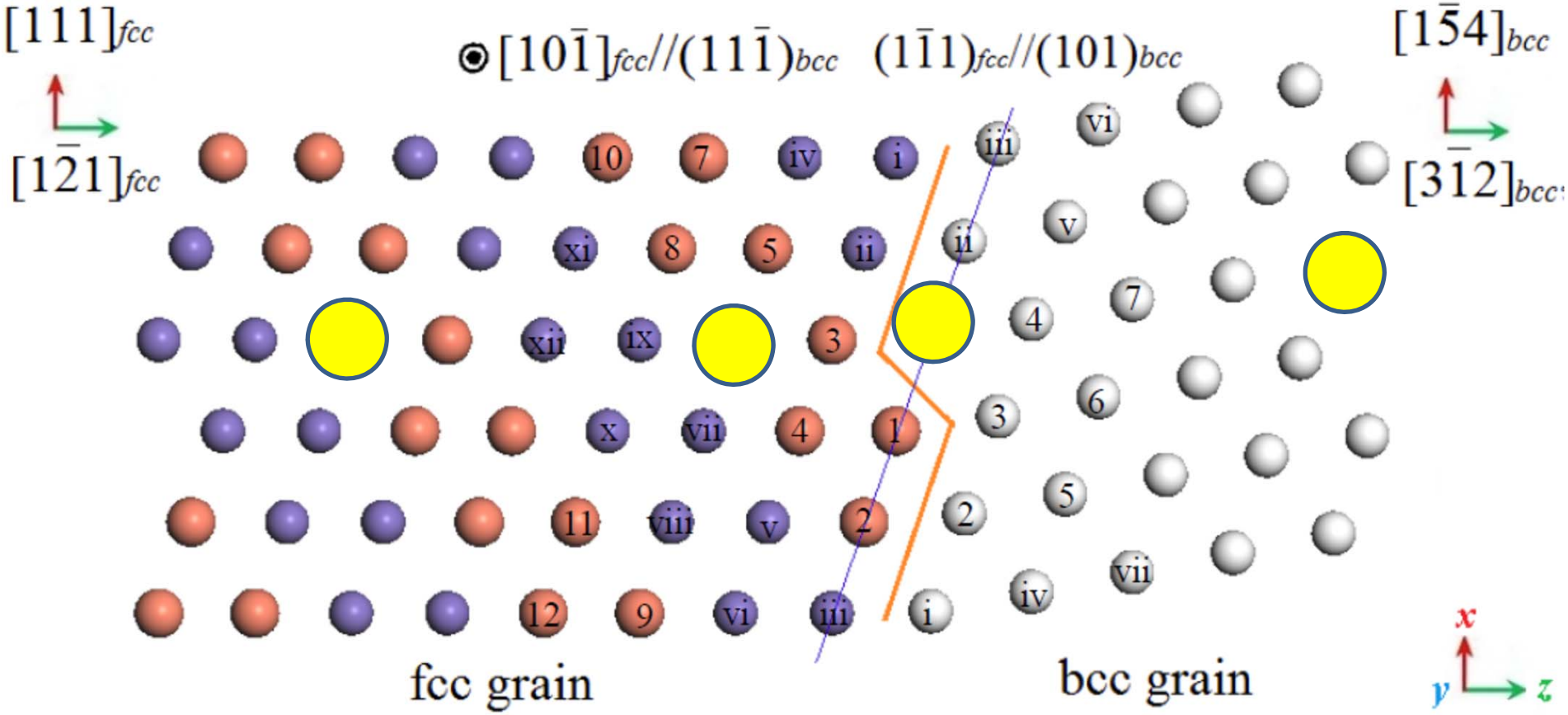
- Mn segregation is similar to the ternary.
- Mo segregates more strongly than observed for the ternary.
- At longer times, both elements showed less segregation. We are repeating the measurements.



Density functional theory (DFT)
α–γ (bcc-fcc) interface in Fe

Ground state theory: T = 0K

K-S orientation relationship: $(111)_{fcc} \parallel (101)_{bcc}, [10\bar{1}]_{fcc} \parallel [1\,1\bar{1}]_{bcc}$

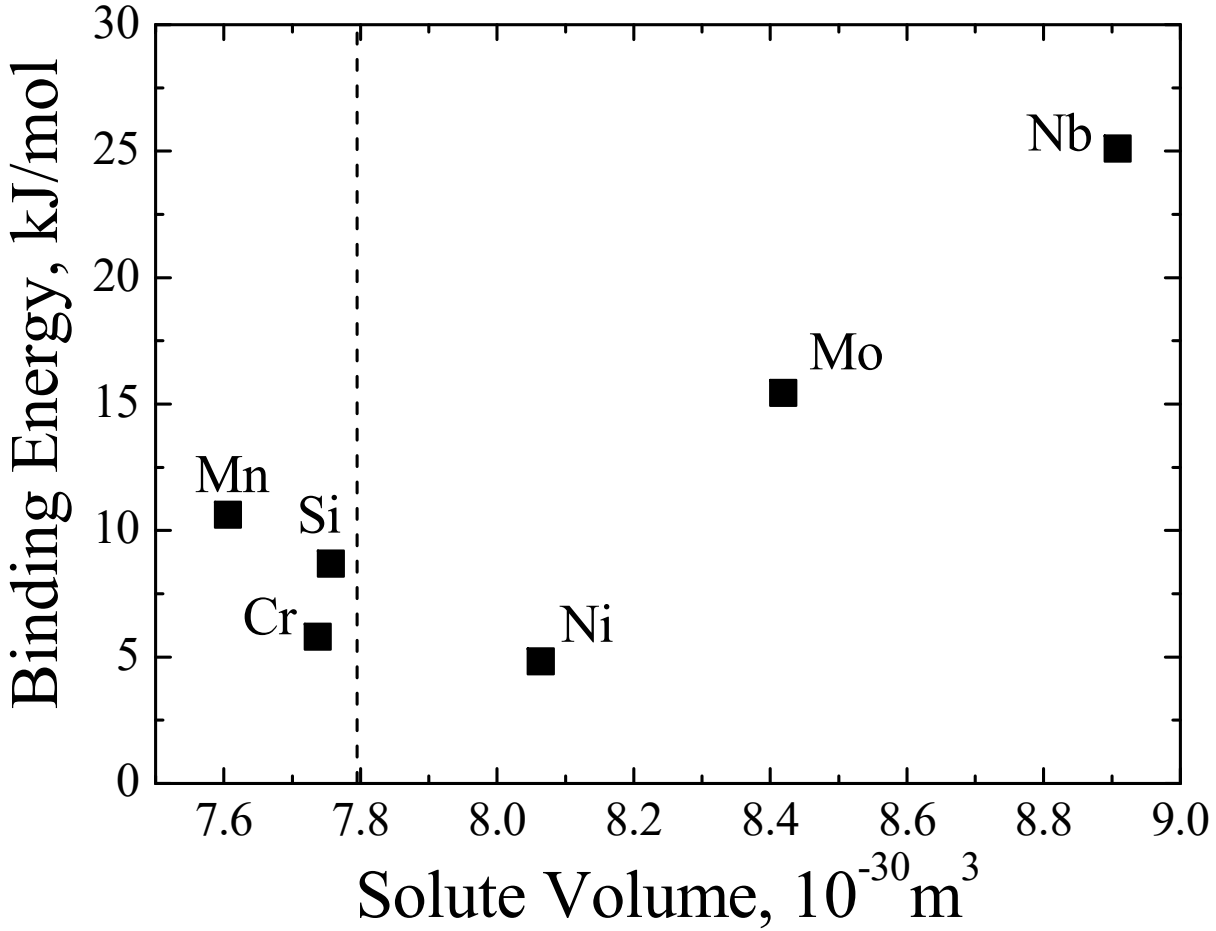


Double-layer antiferromagnetic

Binding energies with α– γ interface in Fe

Enrichment factor for 500 – 800 °C

$$\frac{C_{interface}}{C_{bulk}} = \exp(-\frac{E}{kT})$$



H. Jin (2018)

***E*…Representative binding energy that can be used for comparison with experiments where concentrations (i.e. enrichment factors) are measured**

Comparison of APT and DFT results

Width of interface

DFT: approximately 1 nm APT: approximately 2 – 5 nm

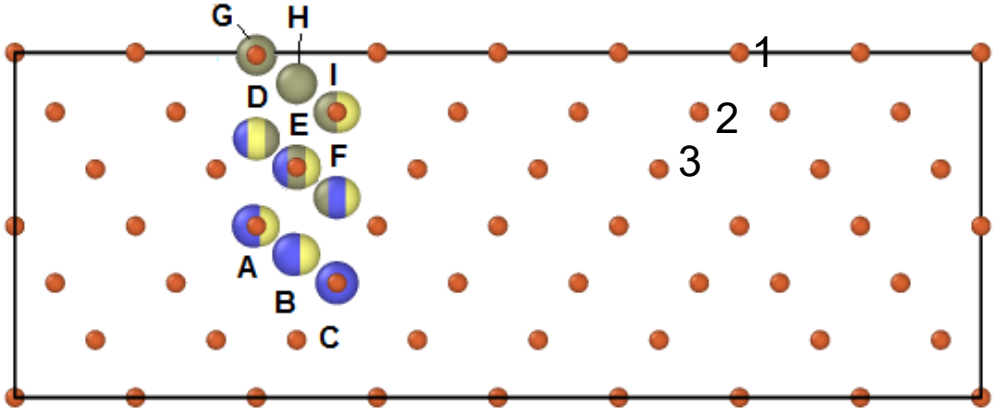
"chemical" width of interface due to co-segregation with C?

broadening of APT width due to interface structure (steps etc.)?

Binding energies (kJ/mol)

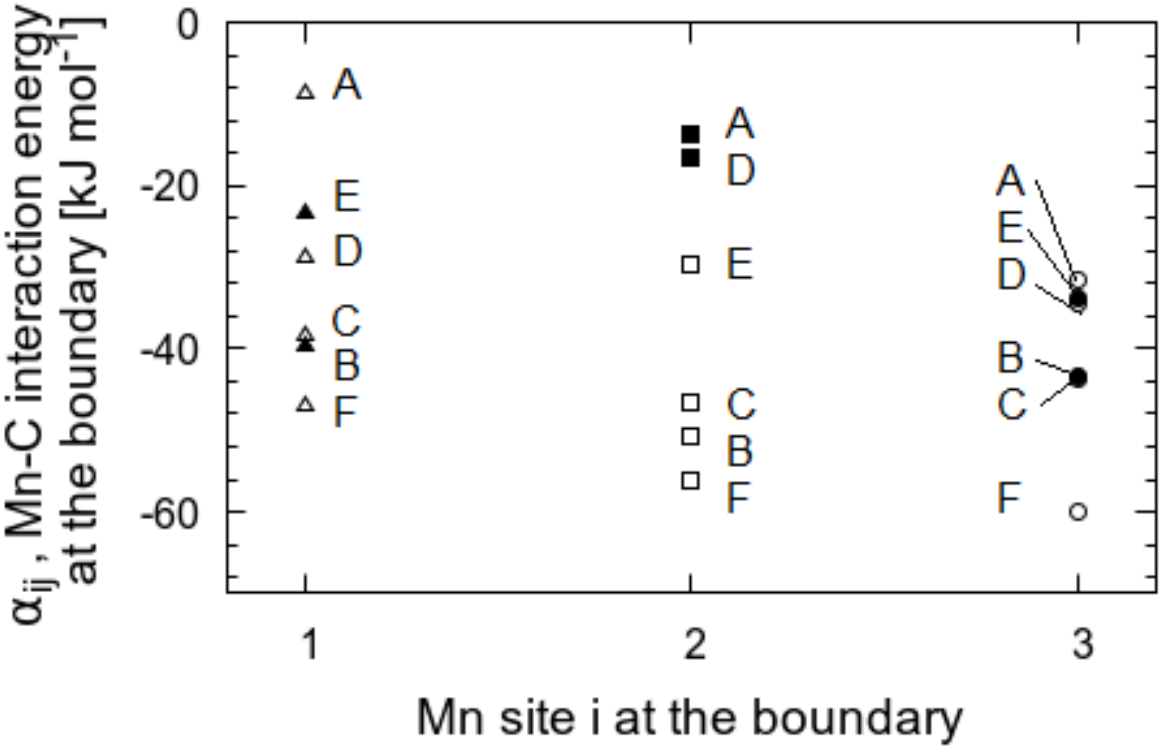
Element	DFT	APT
Mo	15	19 – 25
Mn	10 – 13	5 – 15
Cr	3	9 – 18
Ni	5	0 – 5

Σ3 grain boundary as model case for Fe-C-Mn



Each substitutional site (1, 2, 3) is associated with 6 octahedral sites

Need to consider 18 C-Mn pairs



Mn – C co-segregation

$$E^{ij}_{Mn-C} = E^{i}_{Mn} + E^{j}_{C} + \alpha_{ij}$$

Effective binding energy of Mn

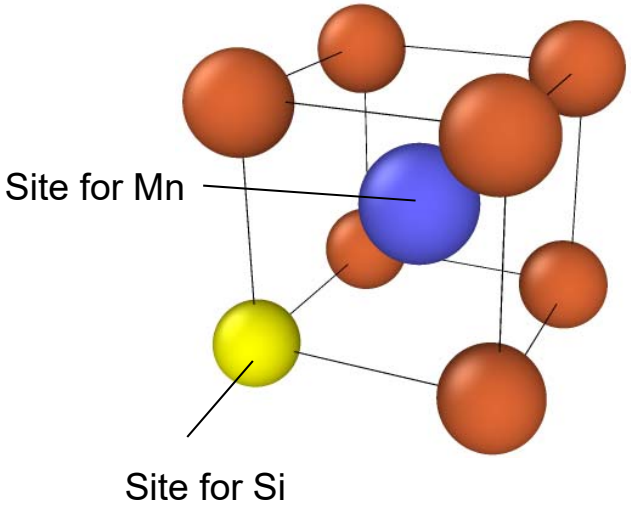
$$E^{eff}_{Mn} = E^{i}_{Mn} + \alpha_{ij} X^{j}_{C}$$

$$X^{j}_{C} \sim 0.1:$$

$$E^{eff}_{Mn} = E^{i}_{Mn} + (3-5)kJ/mol$$

T. Wicaksono (2017)

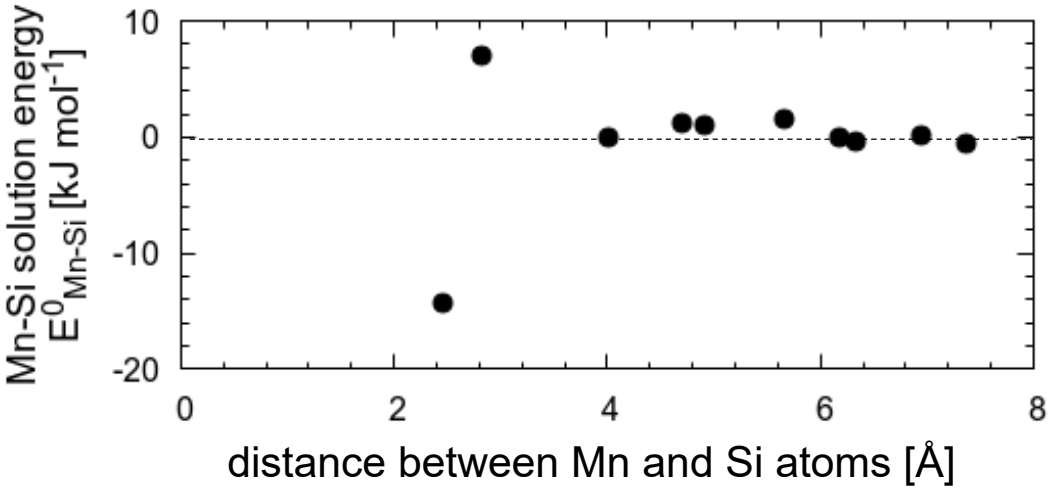
Mn-Si Interaction in bcc-Fe



$$E^0_{Mn-Si}(d_{Mn-Si}) = \left(E^0_{Mn-Si,total} + E^0_{pure}\right) - \left(E^0_{Mn,total} + E^0_{Si,total}\right)$$

$E^0_{X,\ total}$ = total energy of bulk cell with containing 1 X species

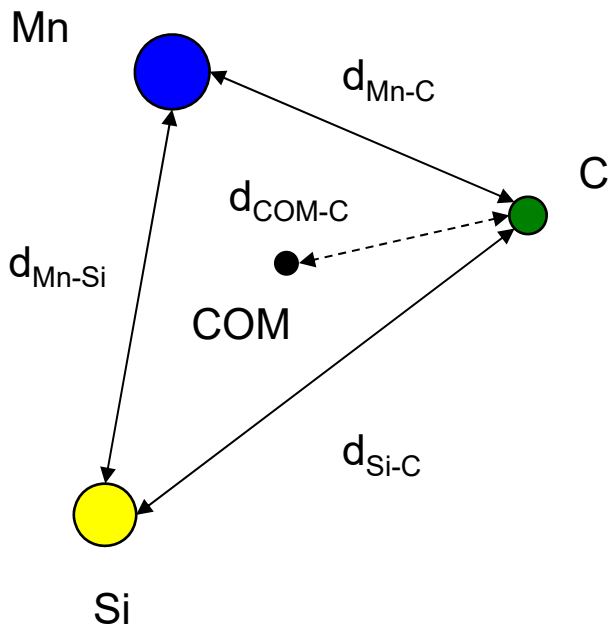
$d_{Mn\text{-}Si}$ = distance between Mn and Si



Interactions in Fe-C-Mn-Si

C-Mn attractive, C-Si repulsive in ternary system

$\Delta E_{MnSi \leftarrow \infty C} =$ Change in energy due to bringing a C atom from far away in the bulk bcc to the vicinity of Mn-Si pair



COM: center of mass

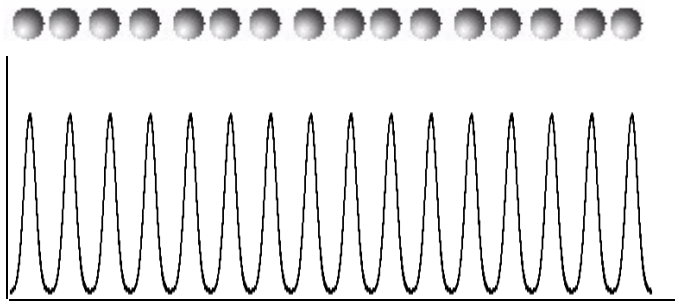
d_{Mn-Si} [Å]	d_{Mn-C} [Å]	d_{Si-C} [Å]	d_{COM-C} [Å]	$\Delta E_{(MnSi \leftarrow \infty C)}$ [kJ/mol]
2.45	1.42	2.00	0.82	+11
	1.42	3.47	1.57	-39
	2.00	1.42	0.82	+14
	2.00	3.17	1.57	-29
	2.00	4.25	2.06	-27
	3.17	2.00	1.57	+10
	3.17	3.47	2.06	-9
	3.47	1.42	1.57	+15
	3.47	3.17	2.06	+4
	4.25	2.00	2.06	+9

What about atomistic simulations of segregation kinetics and interface migration with appropriate diffusional timescales?

Alloy Diffusional Molecular Dynamics

Integrate over atomic vibrations

Instantaneous atom positions



Gaussian Distributions

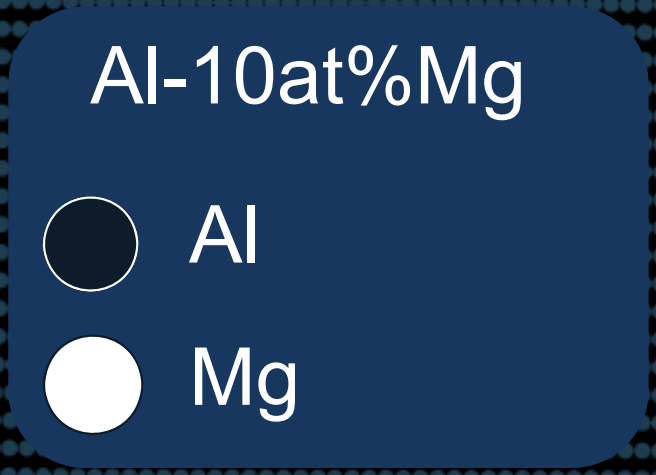
Use EAM potentials to obtain free energy density

Application to Mg segregation in Al-Mg system

Evgeniya Dontsova

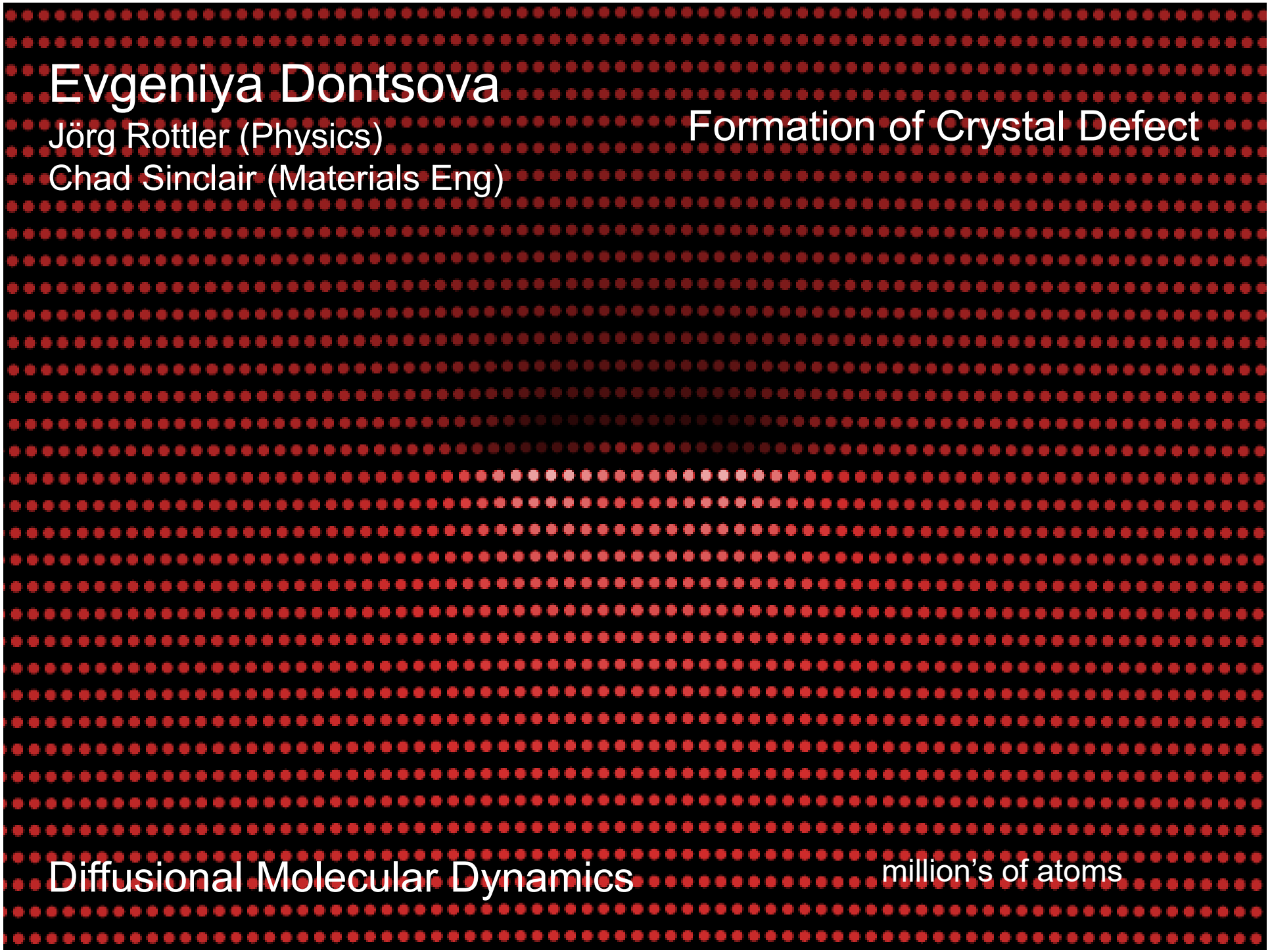
Jörg Rottler (Physics)

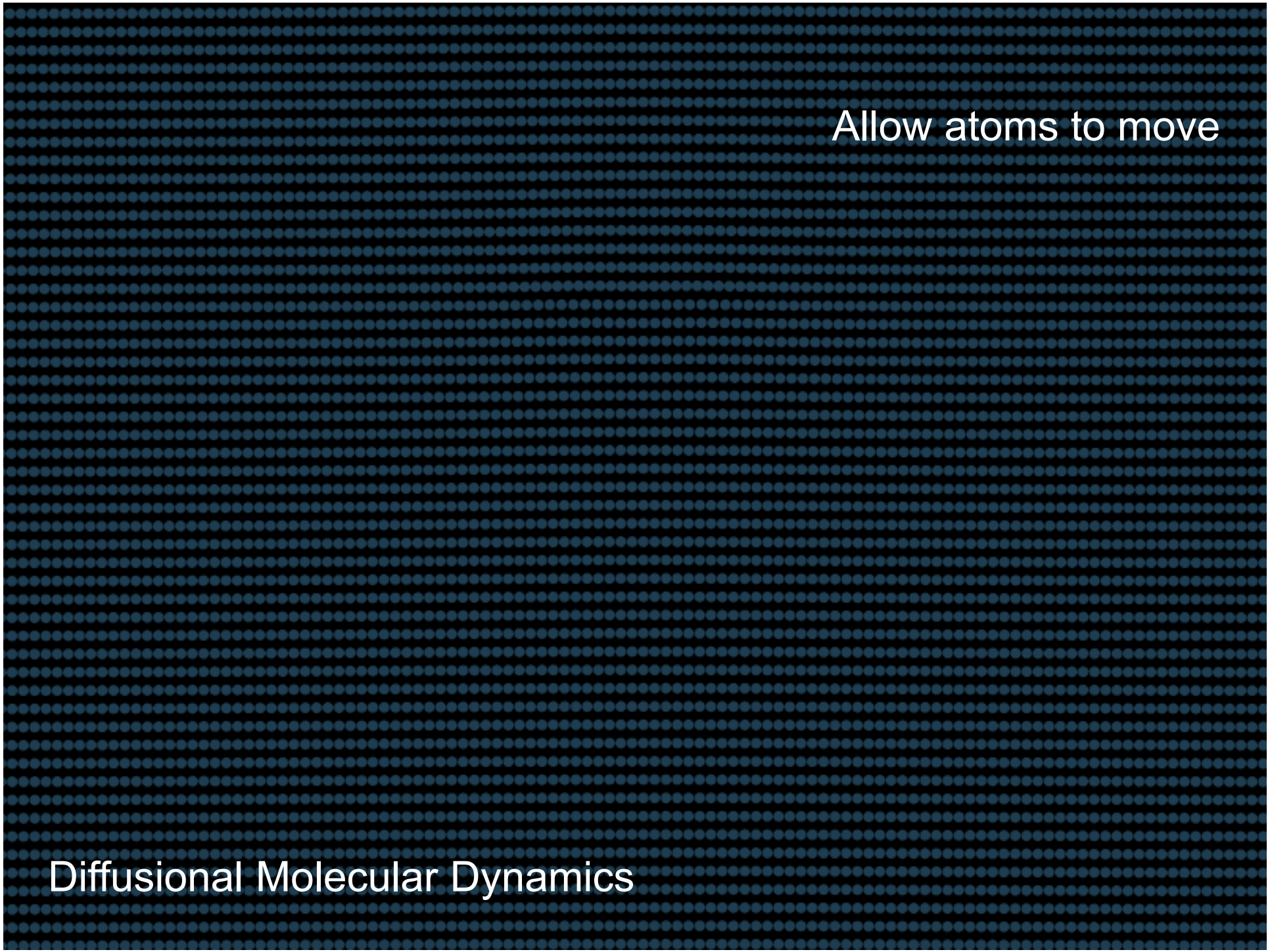
Chad Sinclair (Materials Eng.)



Diffusional Molecular Dynamics

million’s of atoms


Evgeniya Dontsova
Jörg Rottler (Physics)
Chad Sinclair (Materials Eng)
Formation of Crystal Defect
Diffusional Molecular Dynamics
million's of atoms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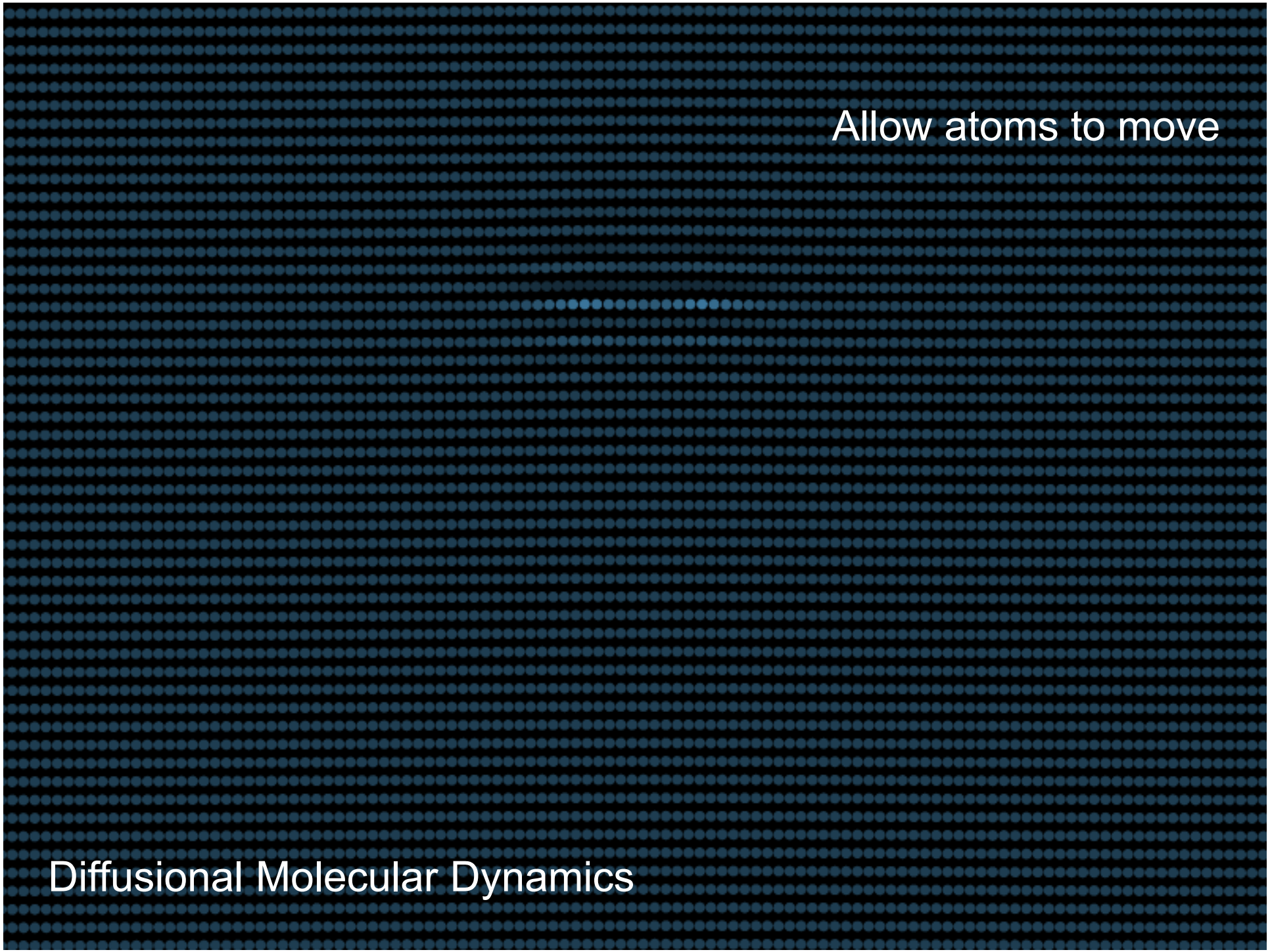
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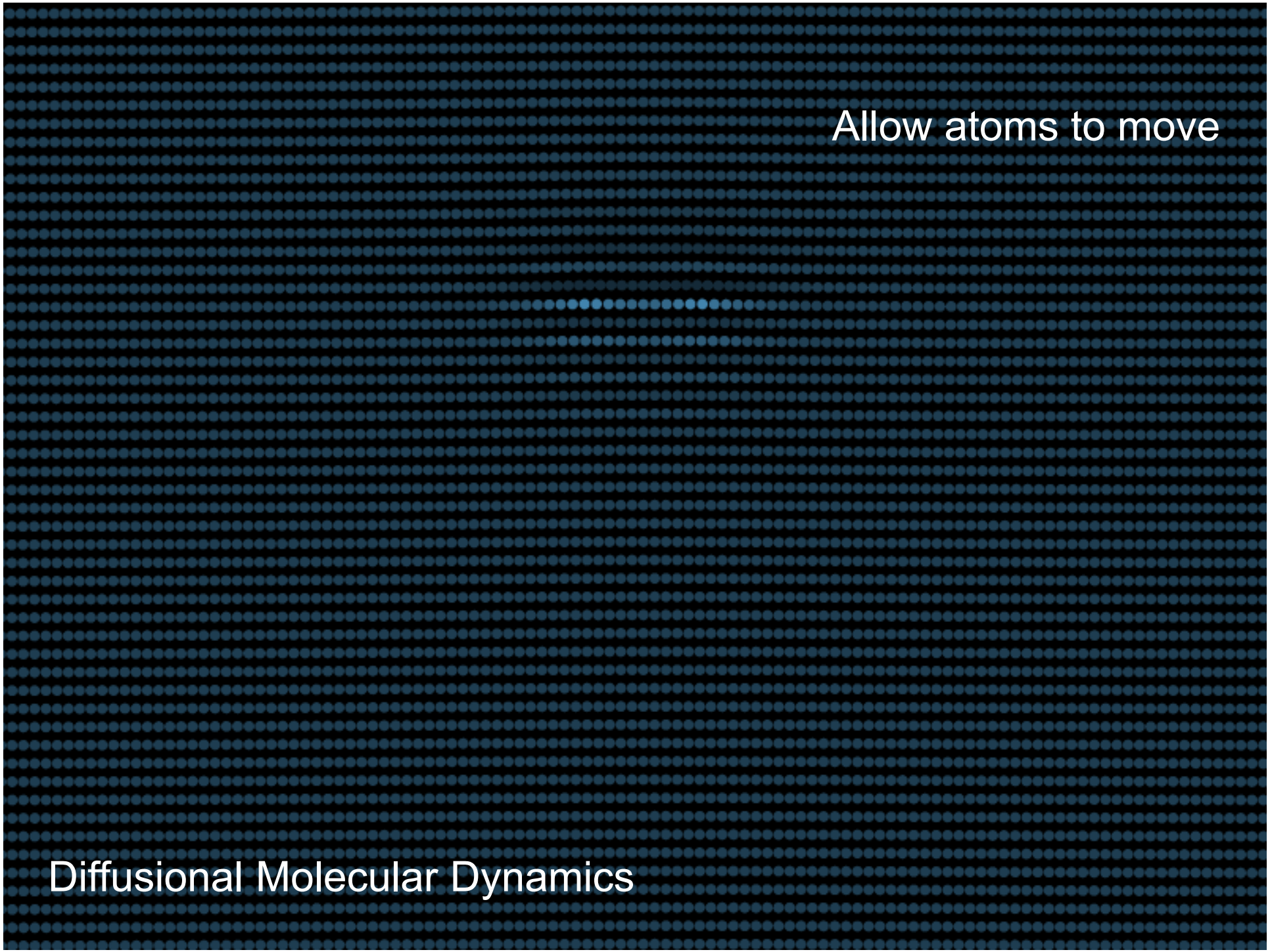
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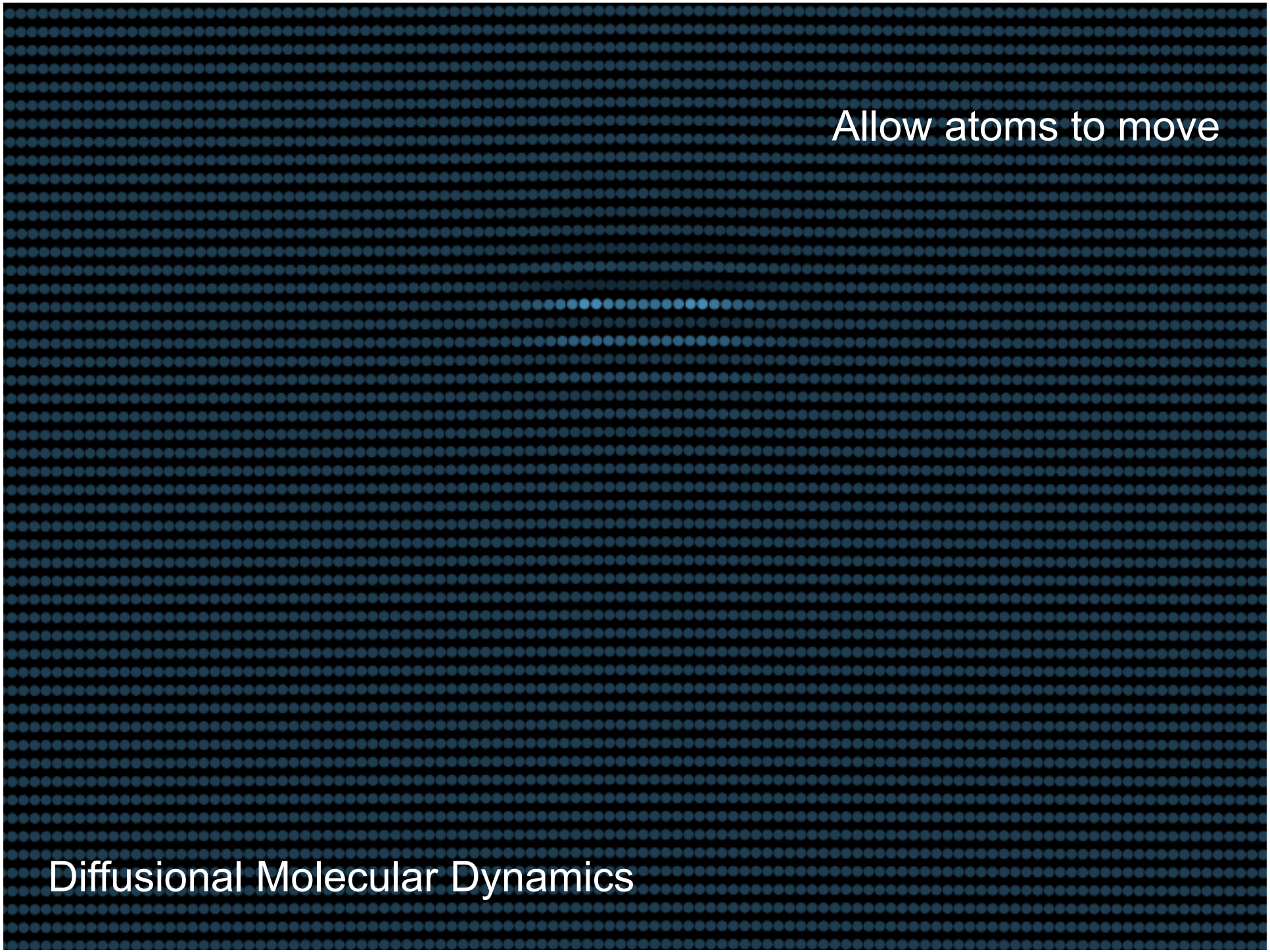
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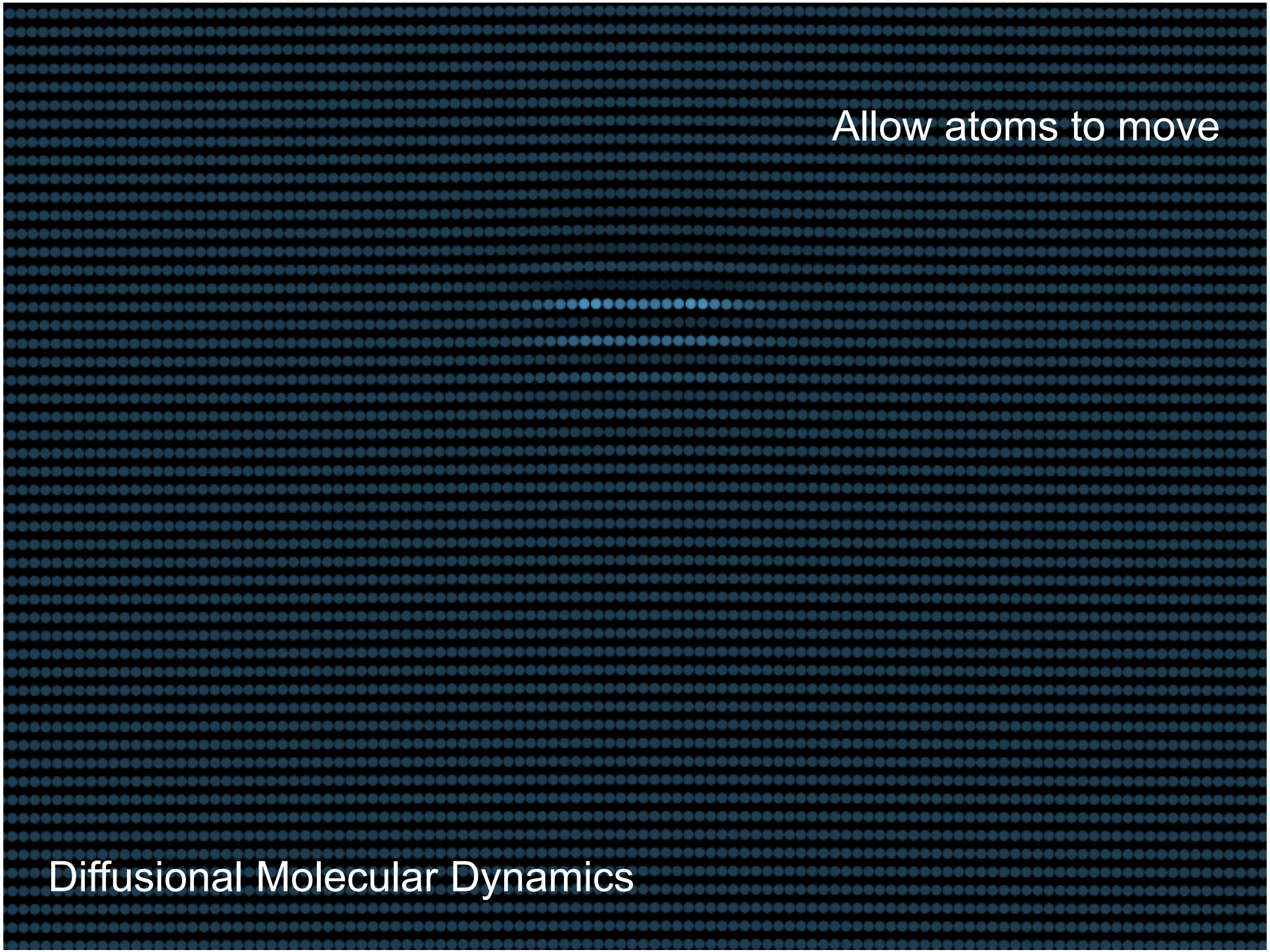
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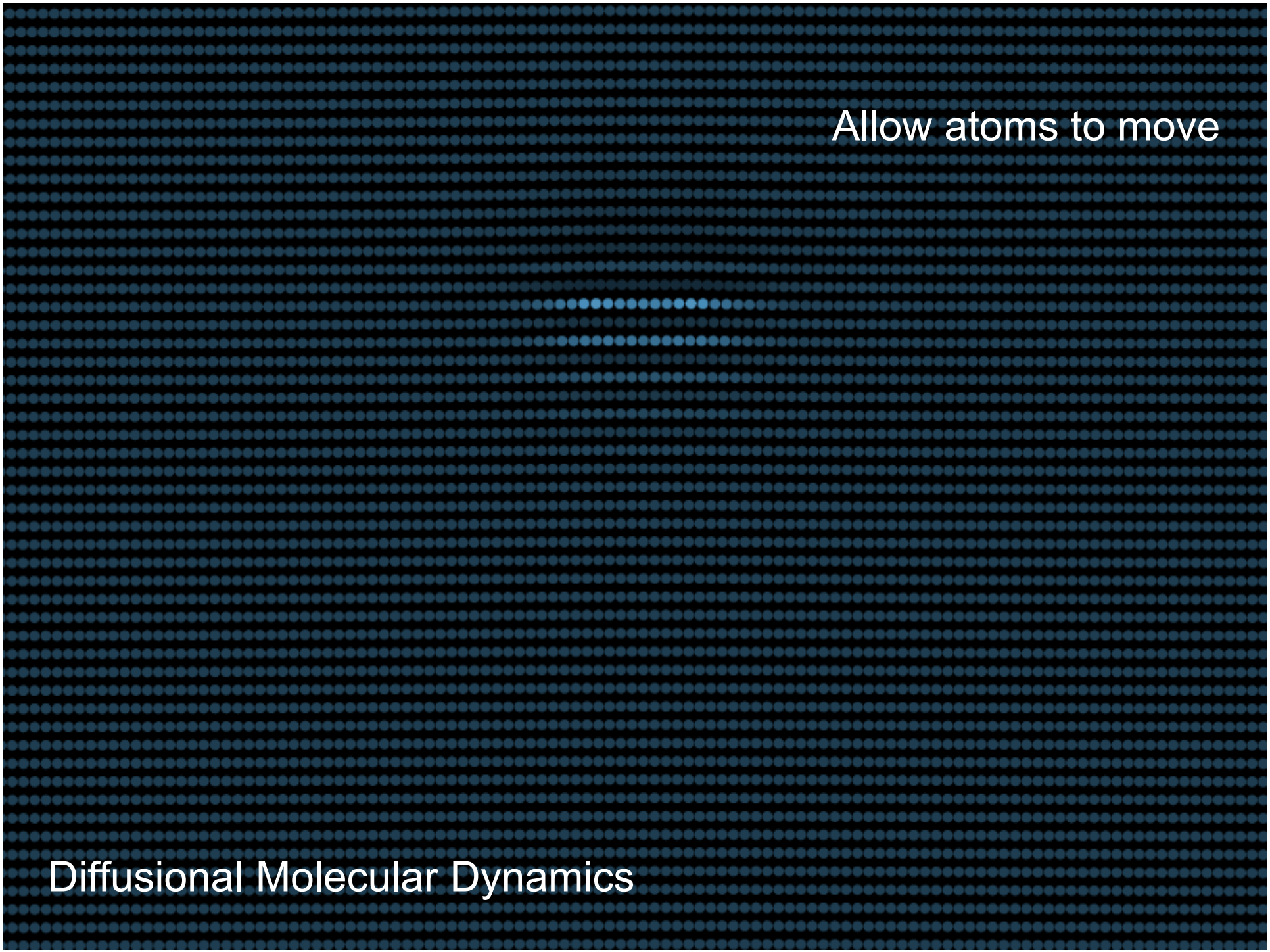
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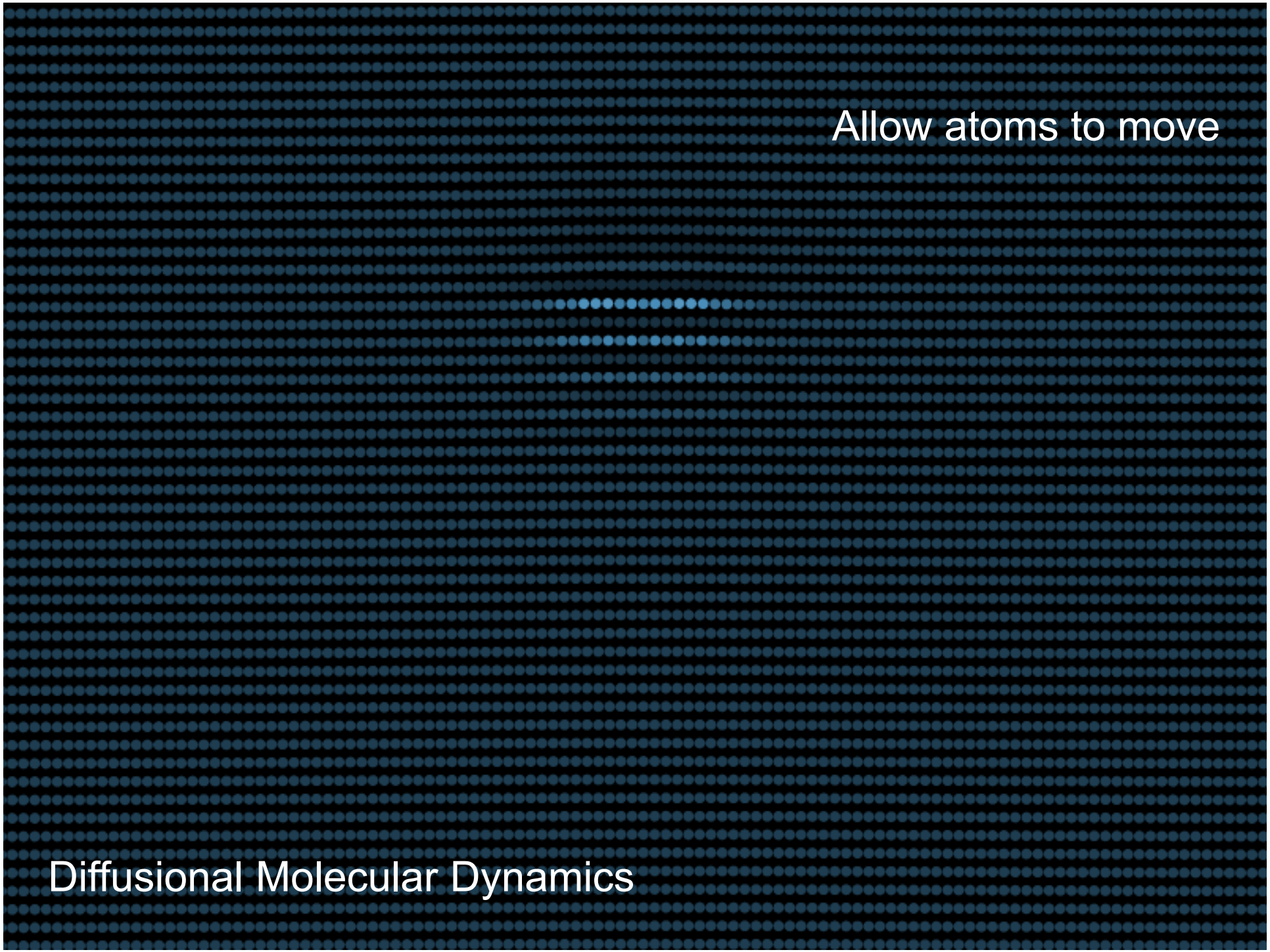
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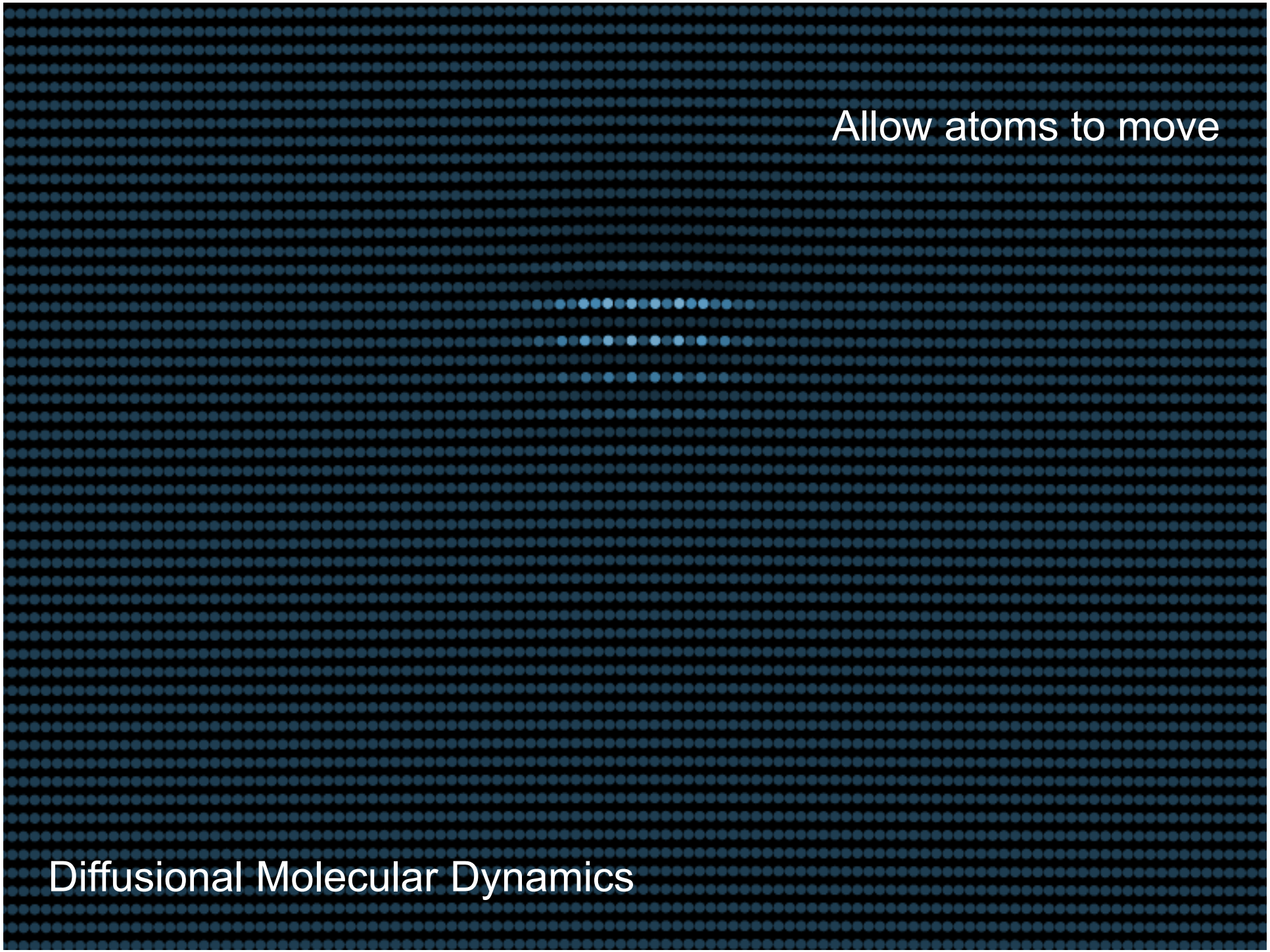
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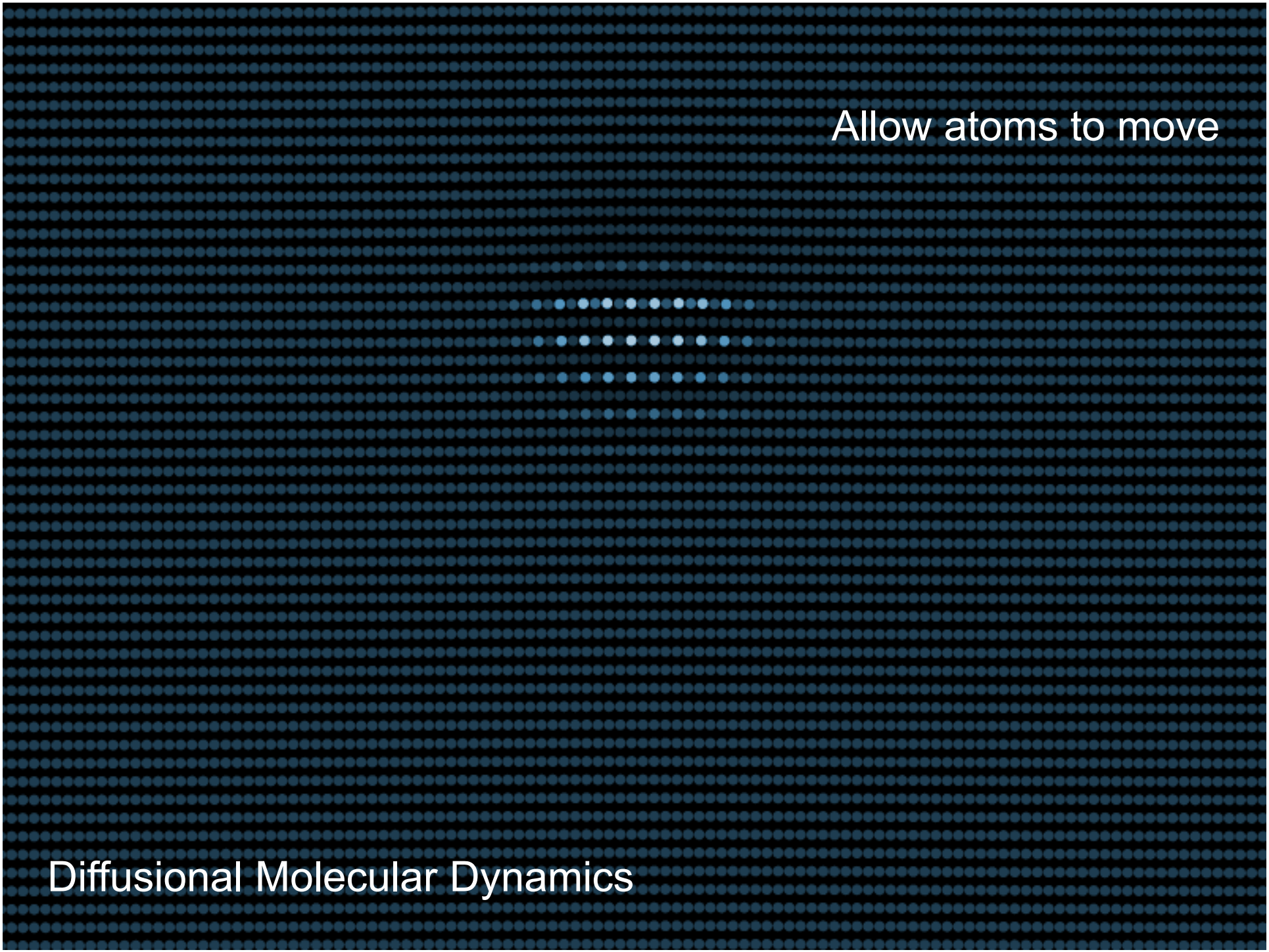
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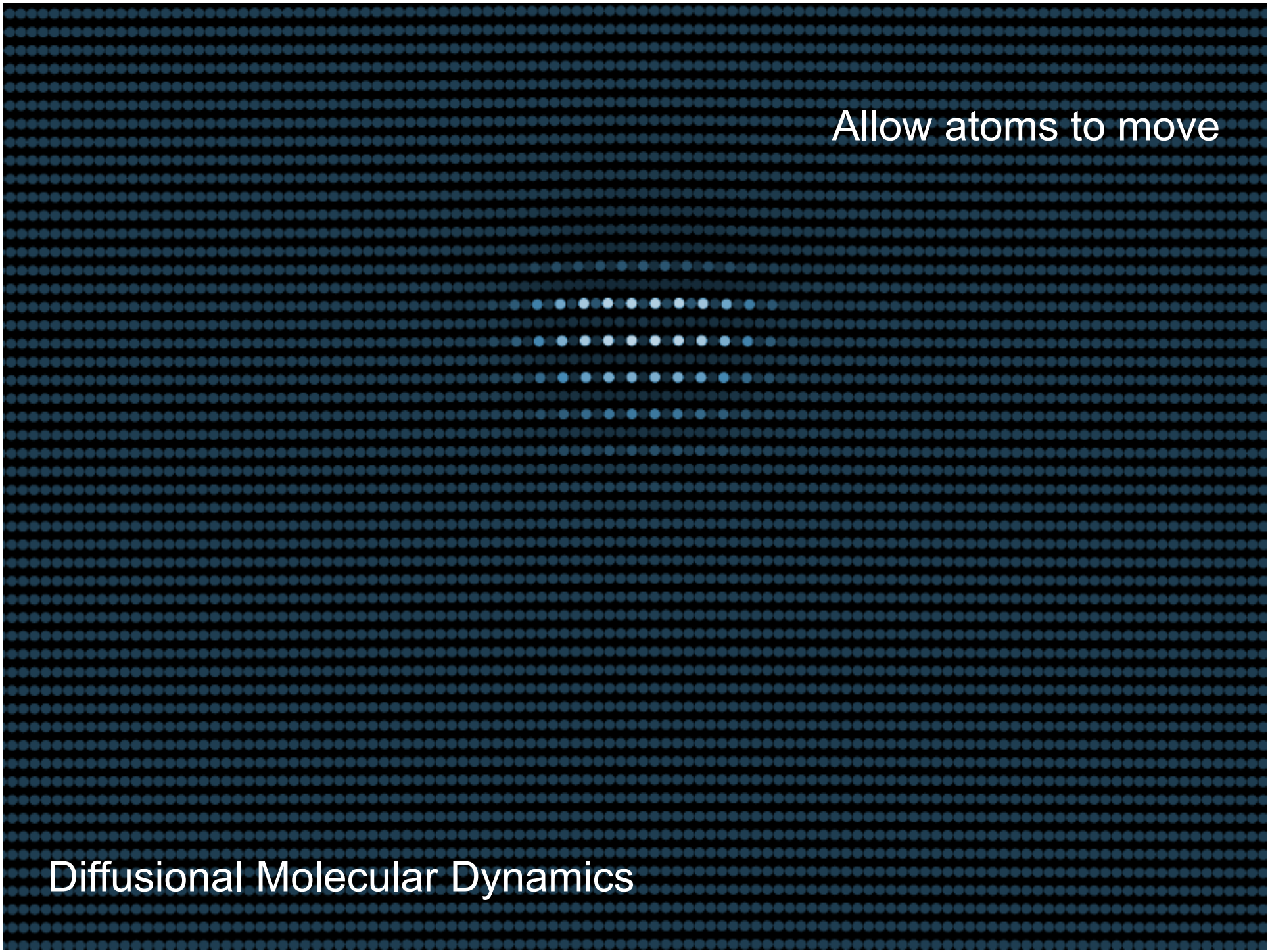
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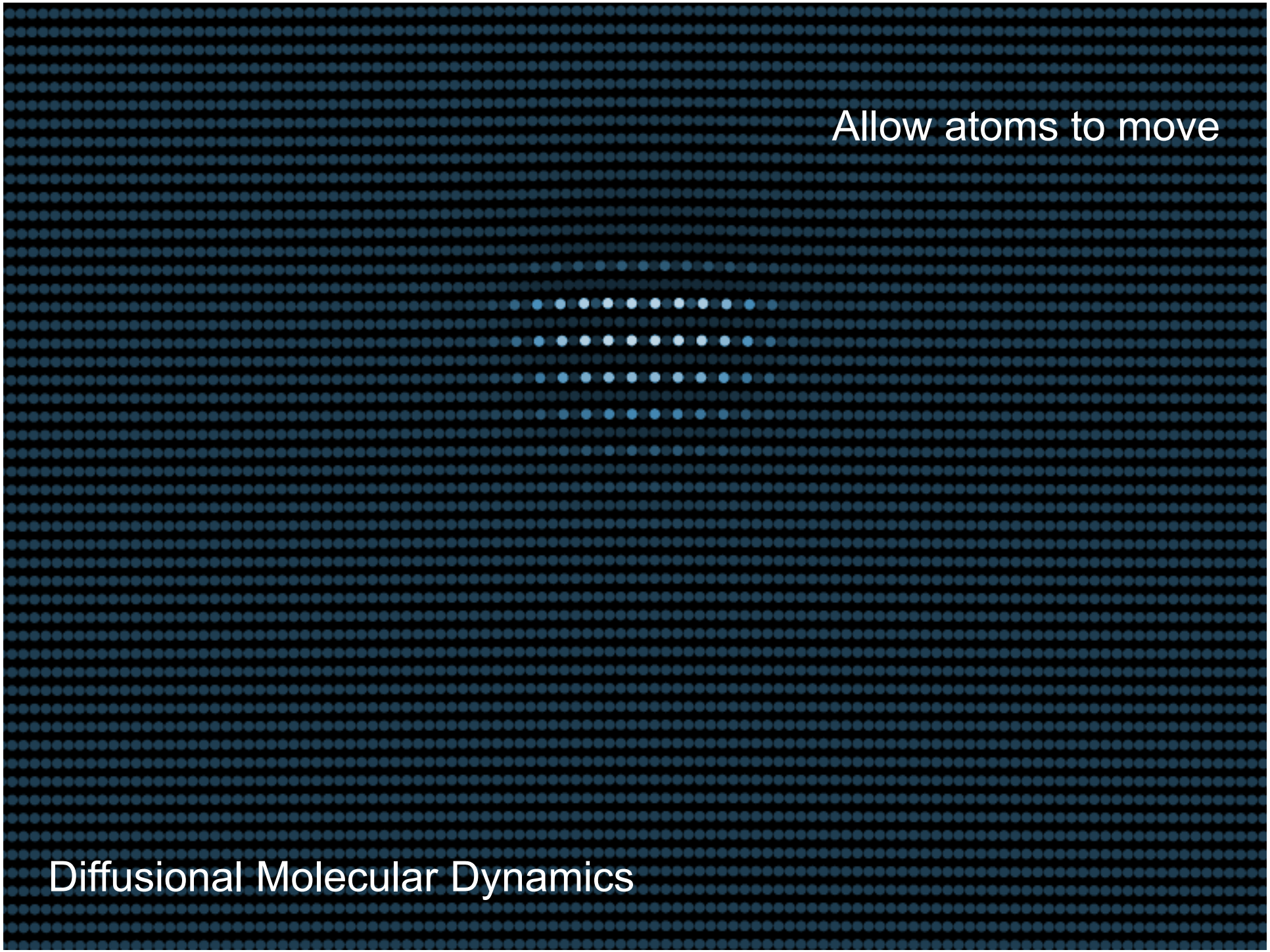
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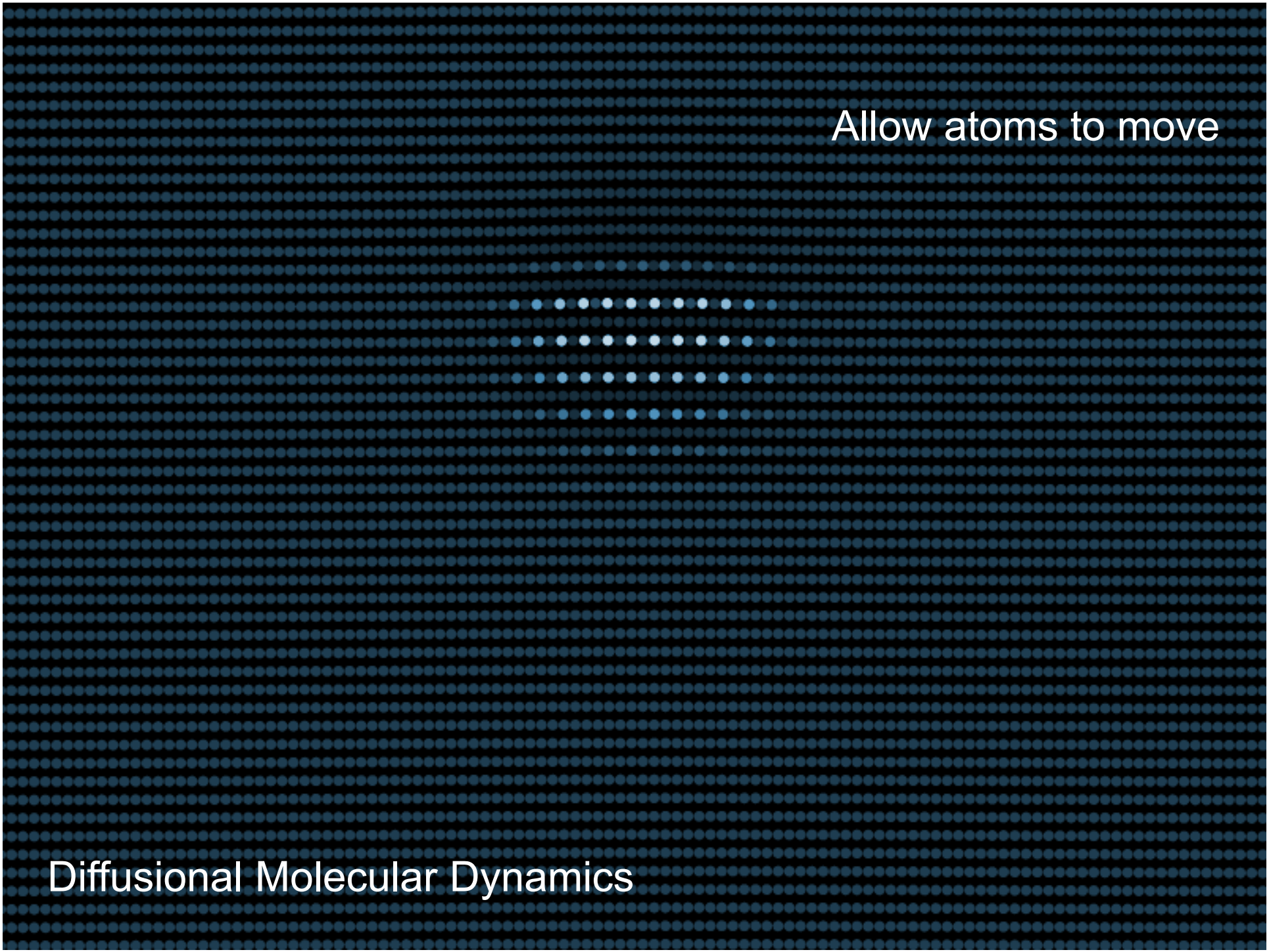
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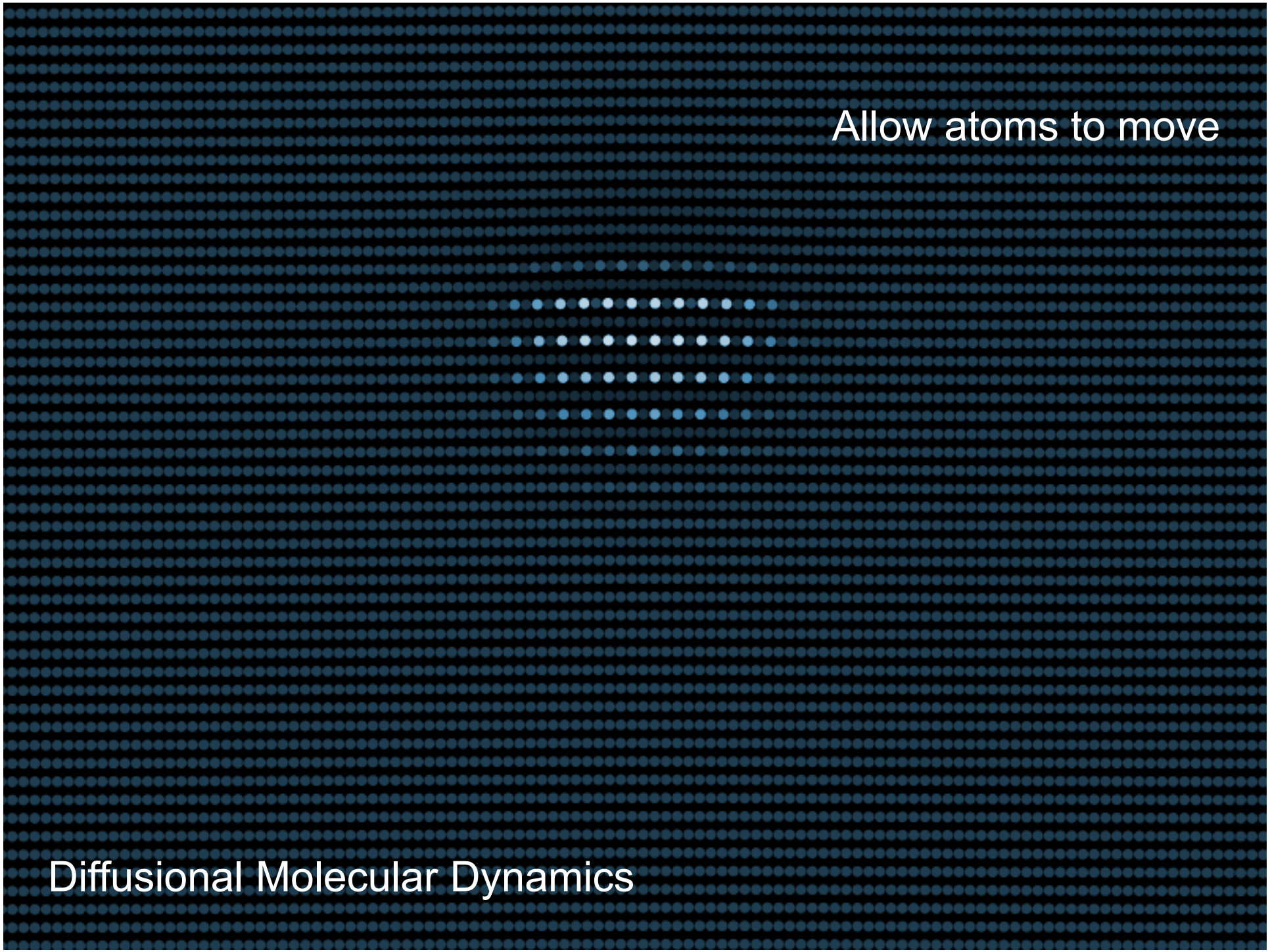
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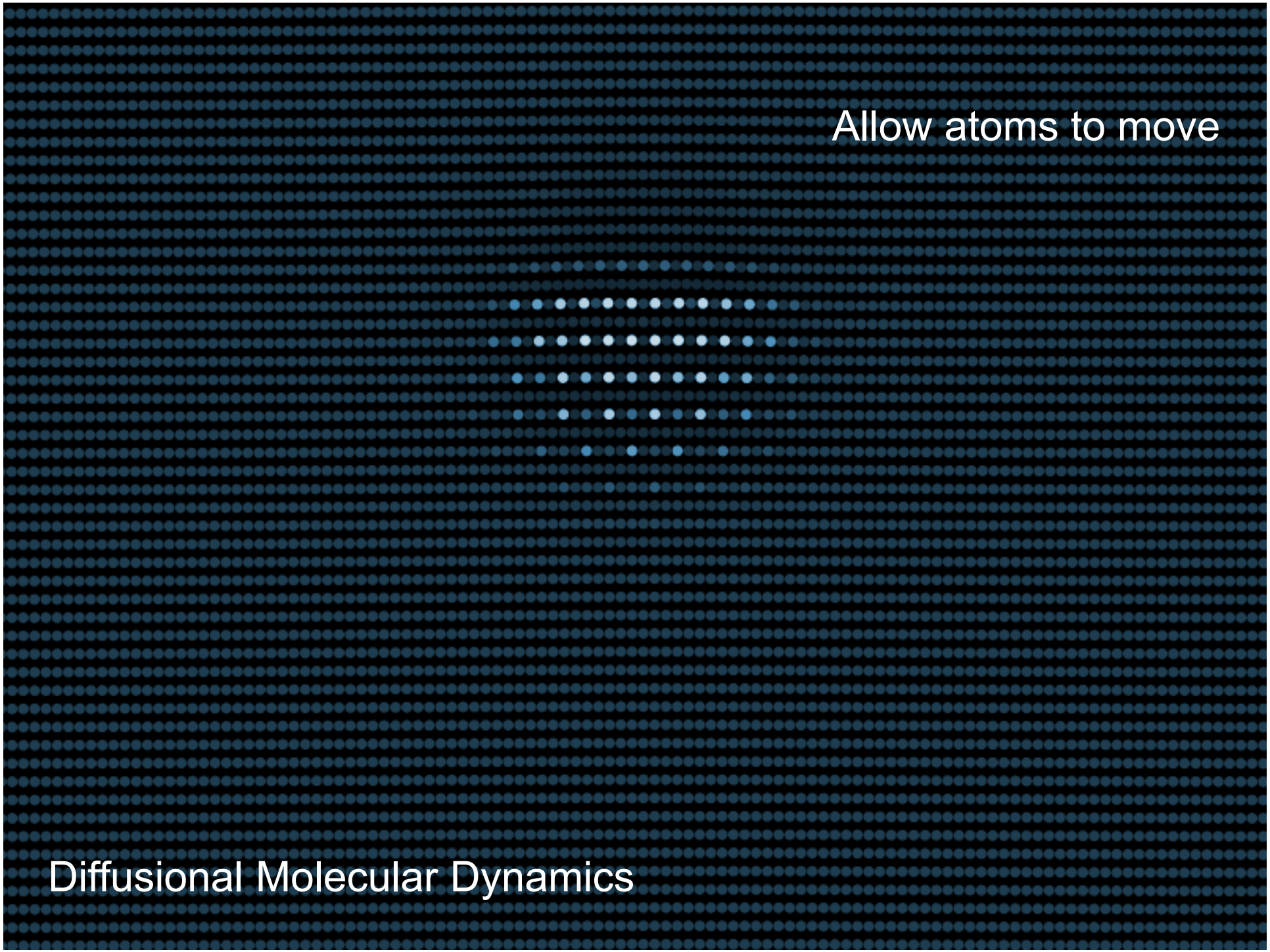
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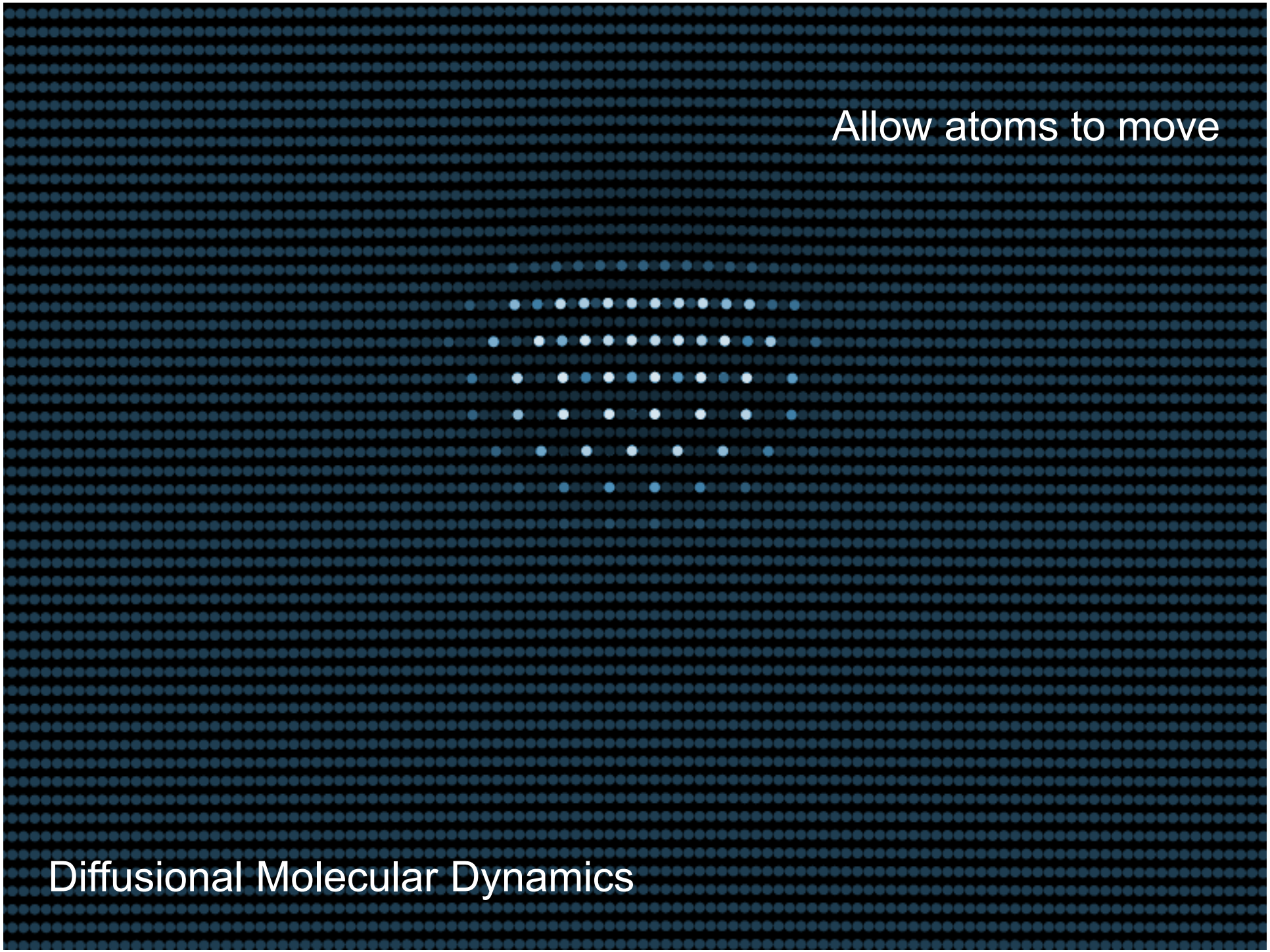
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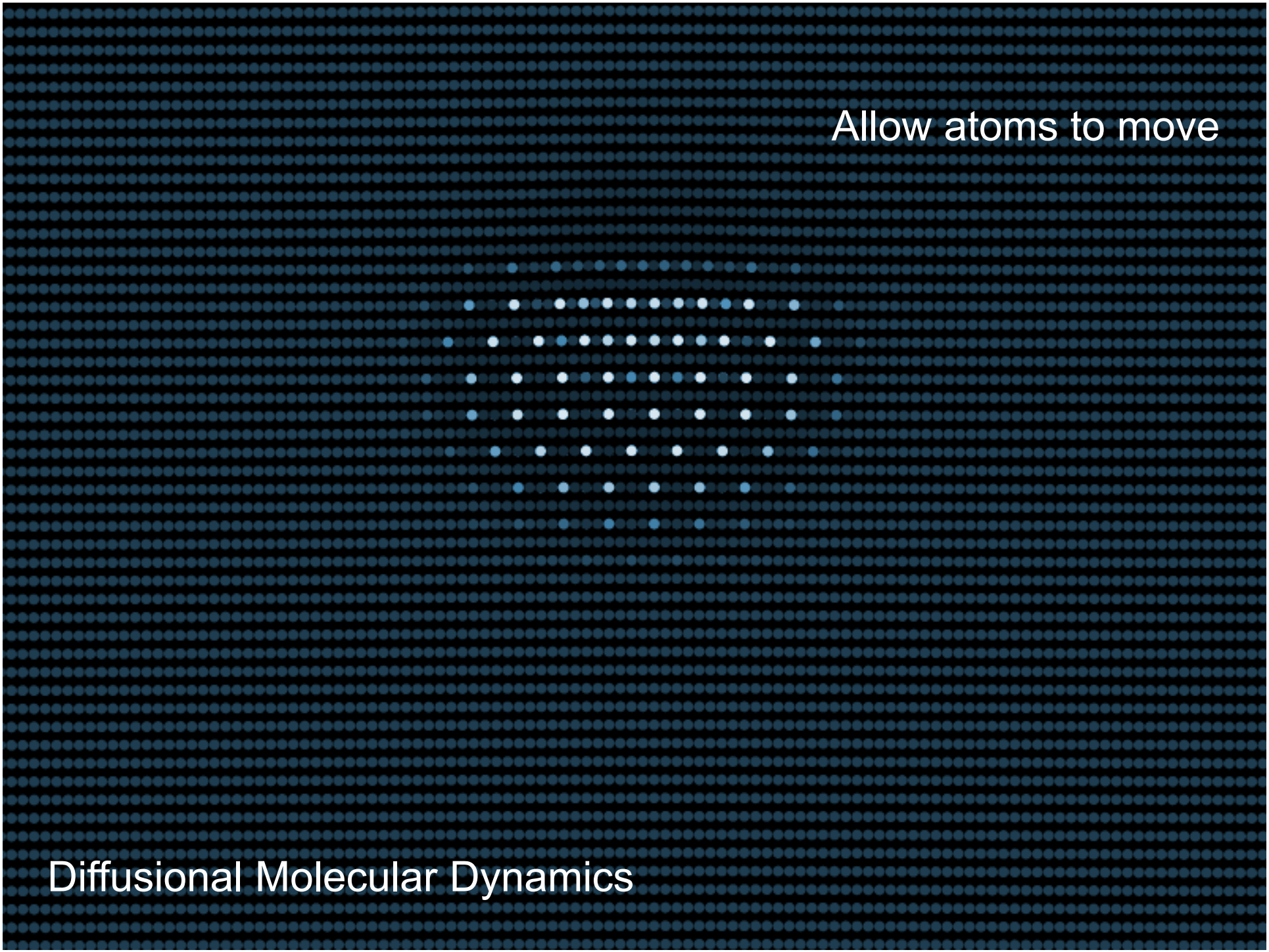
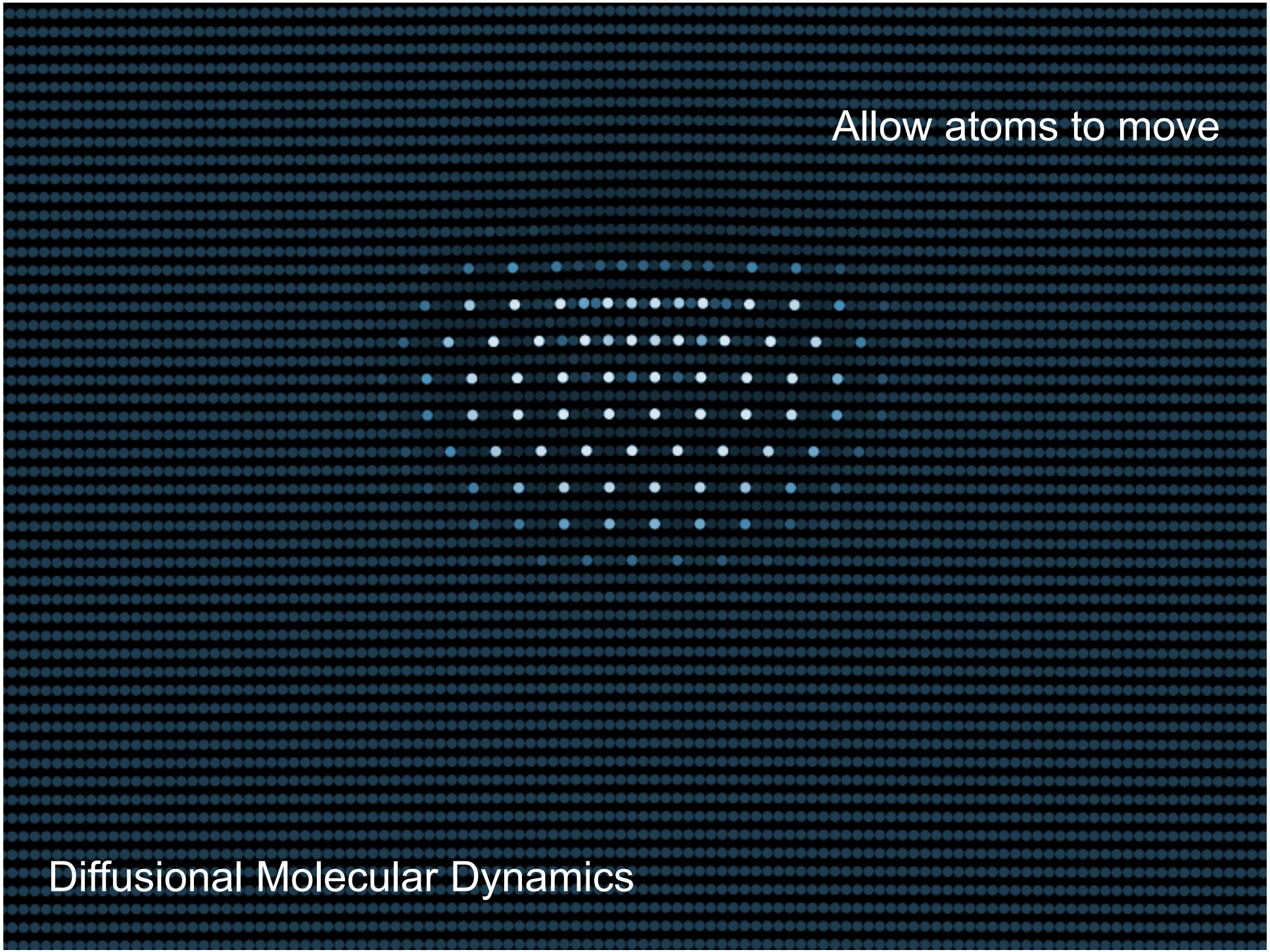

Allow atoms to move
Diffusional Molecular Dynamics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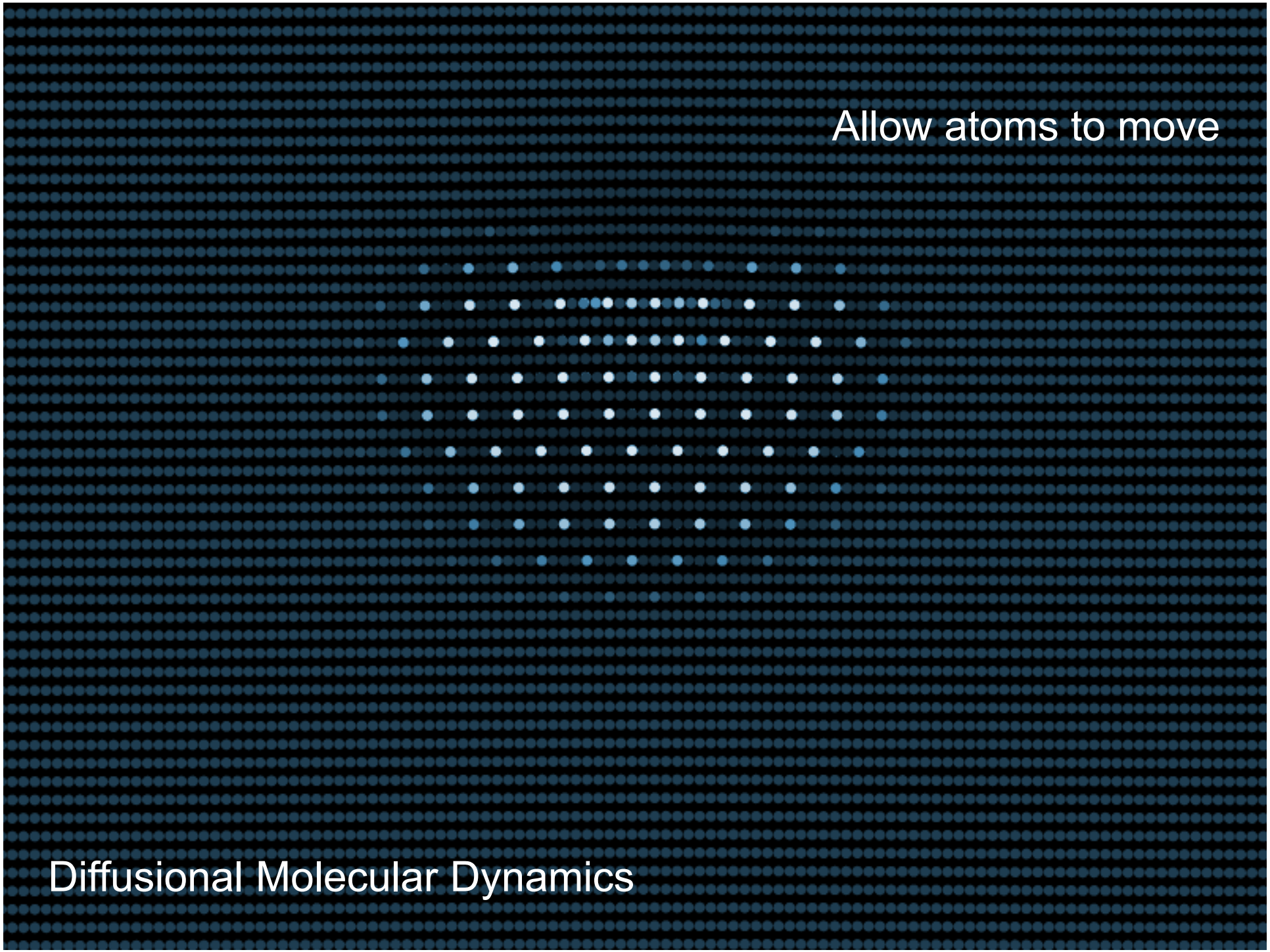
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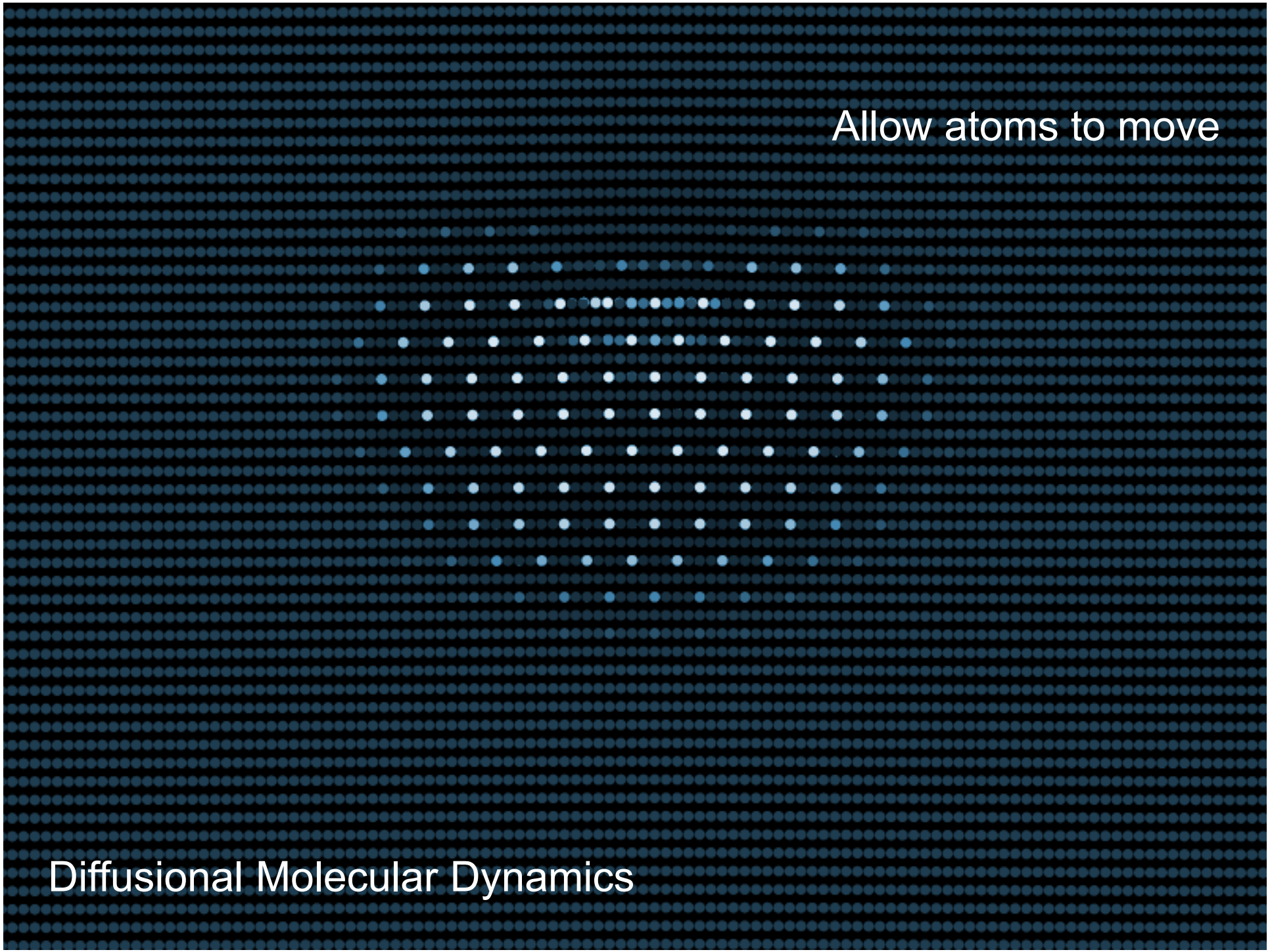
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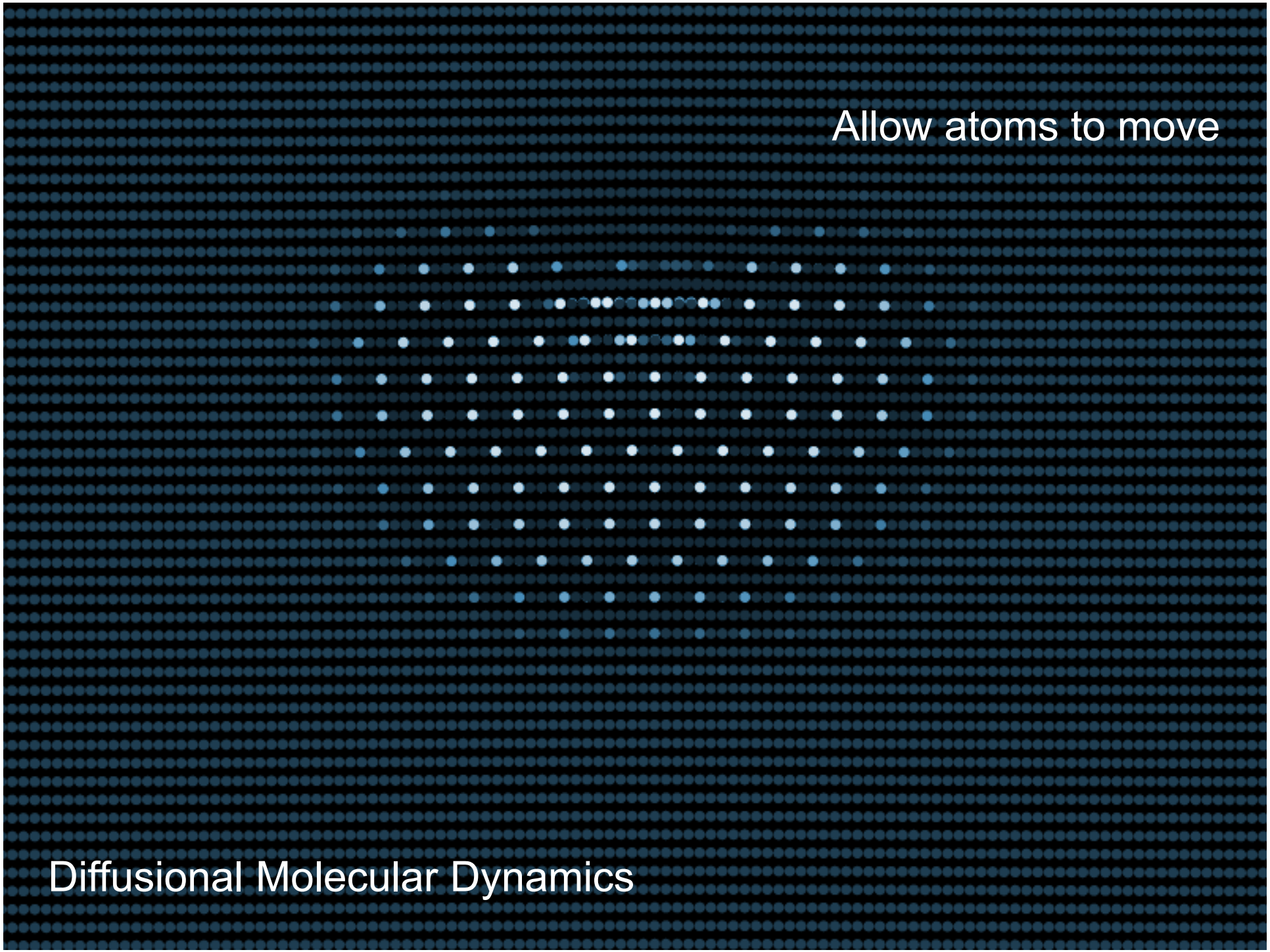
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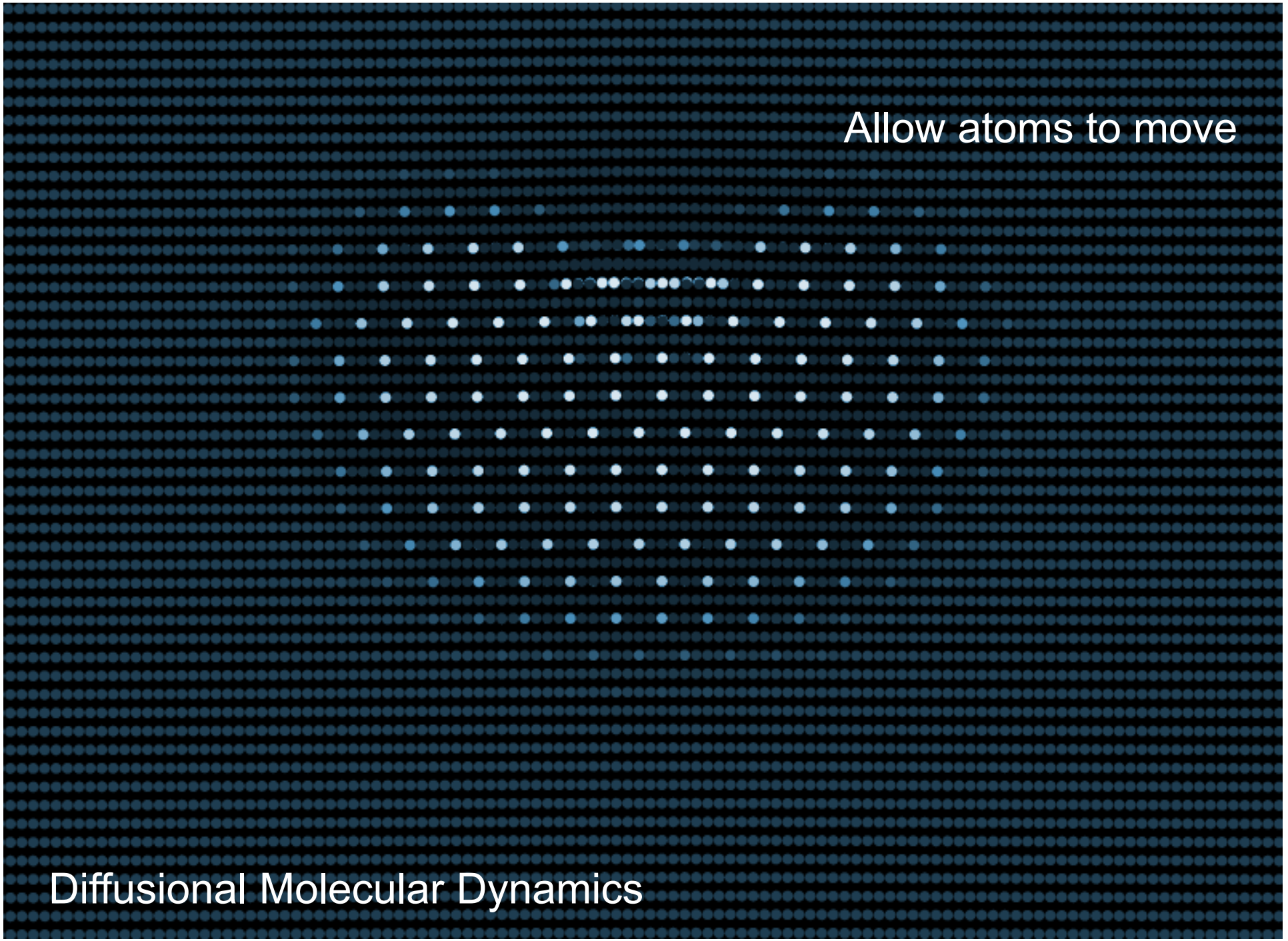
Diffusional Molecular Dynamics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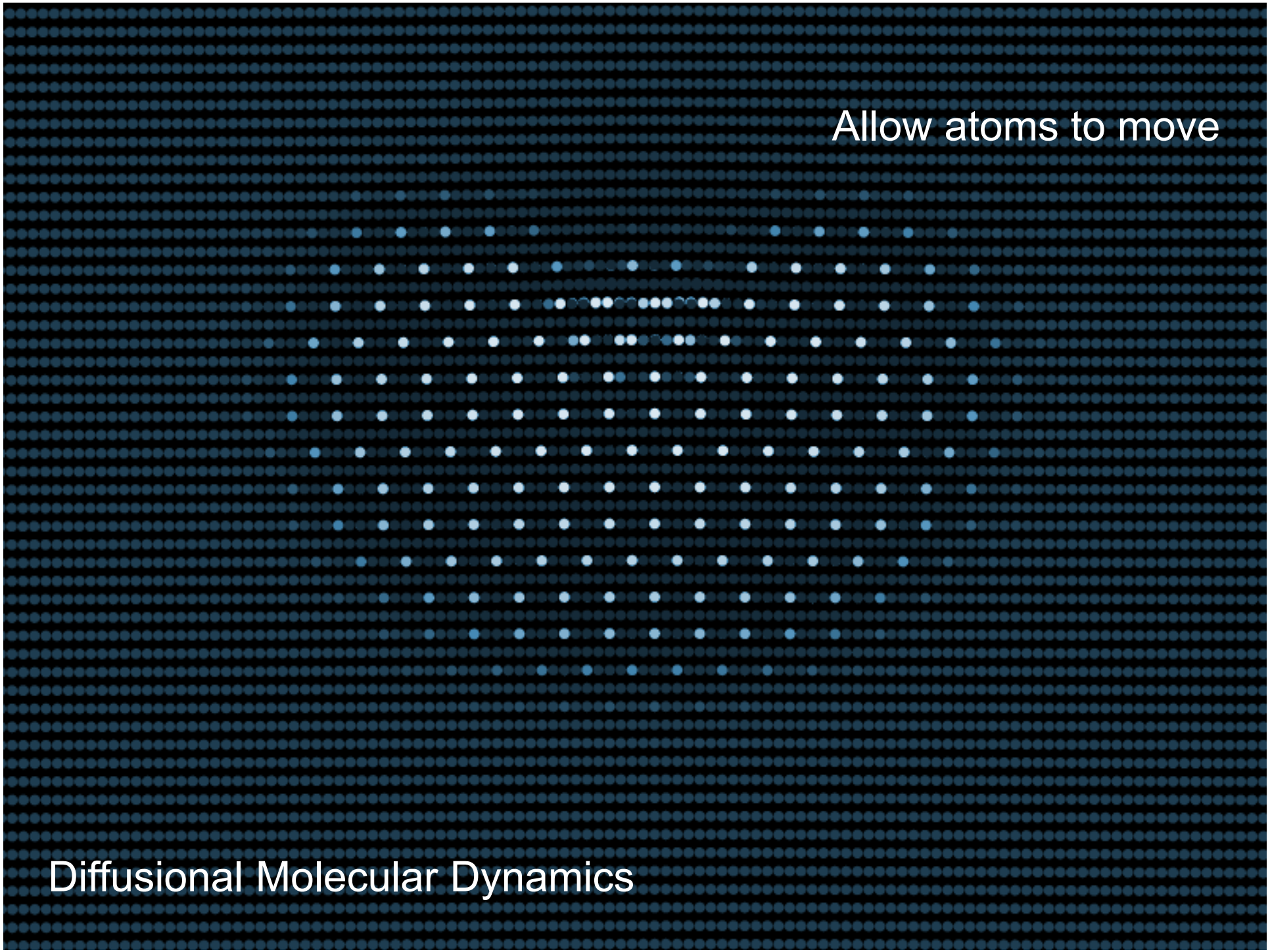
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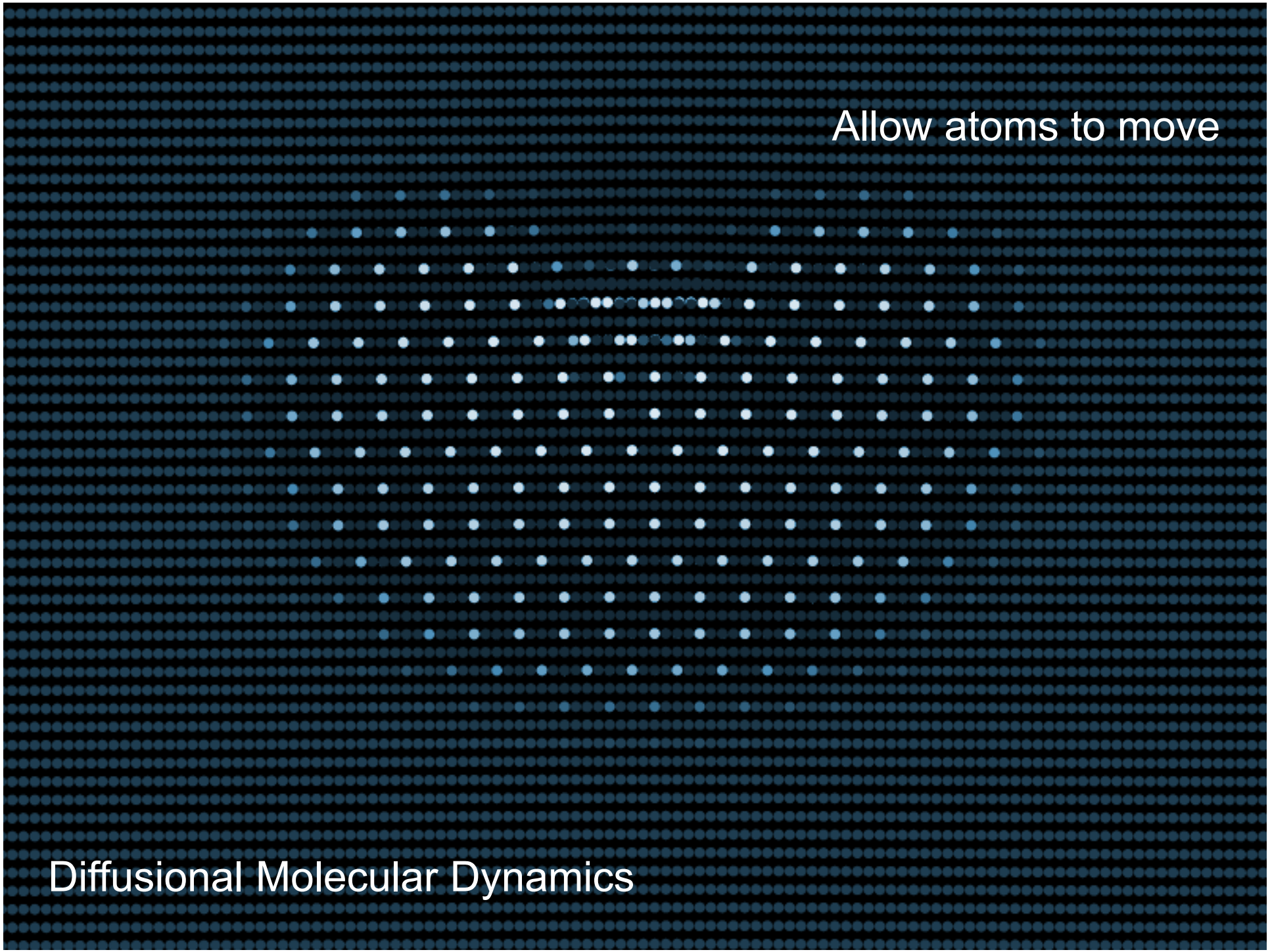
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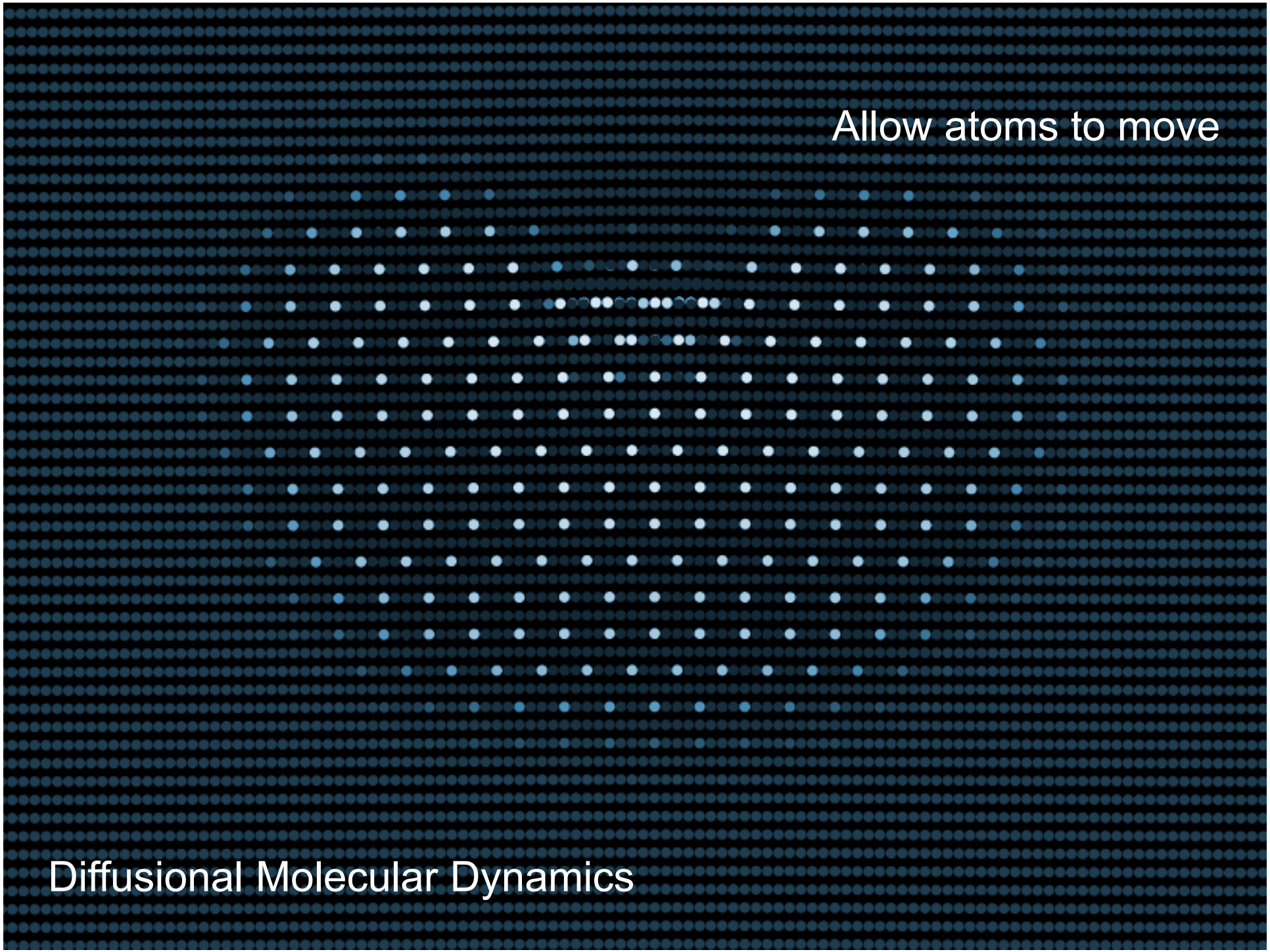
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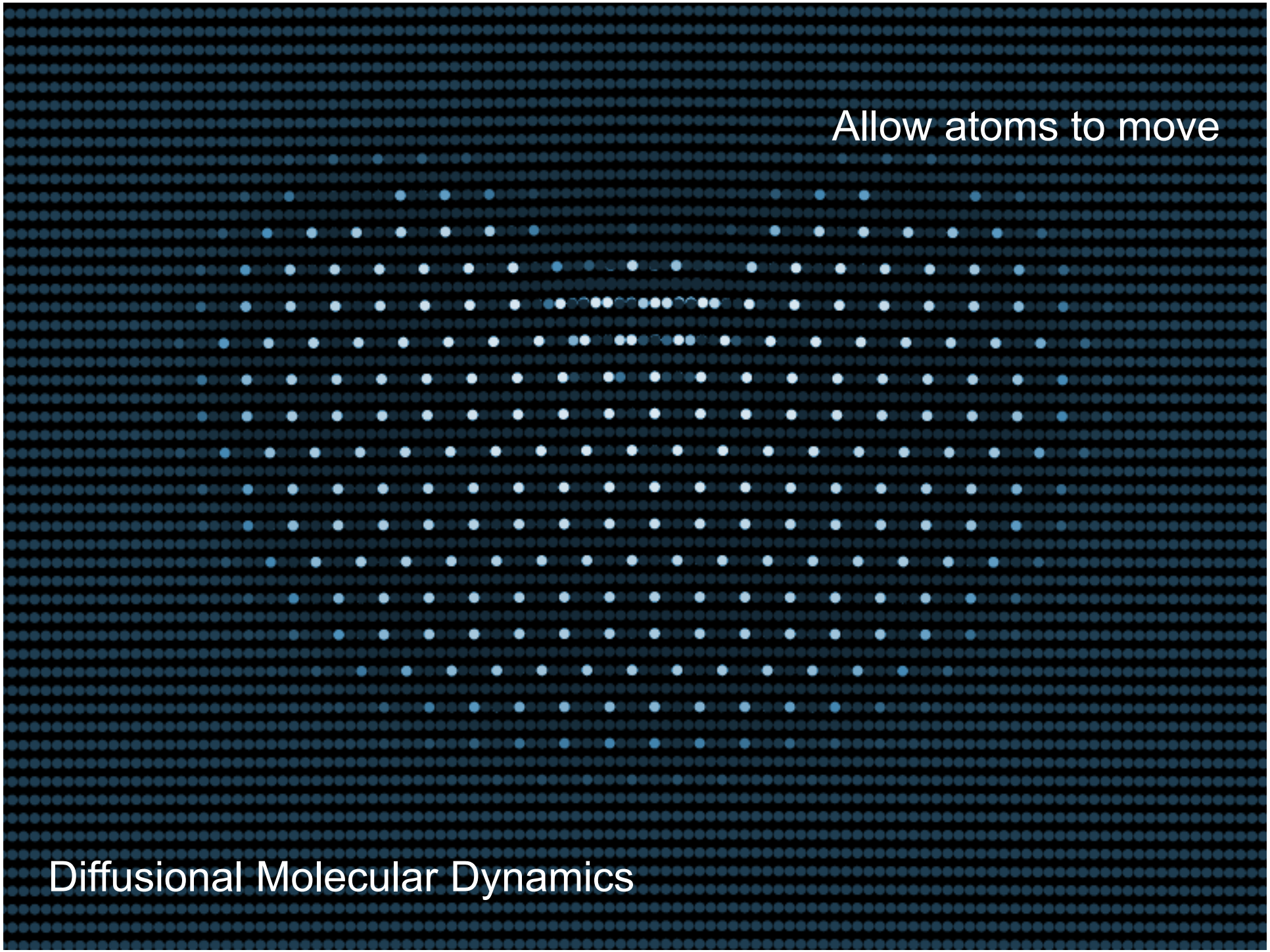
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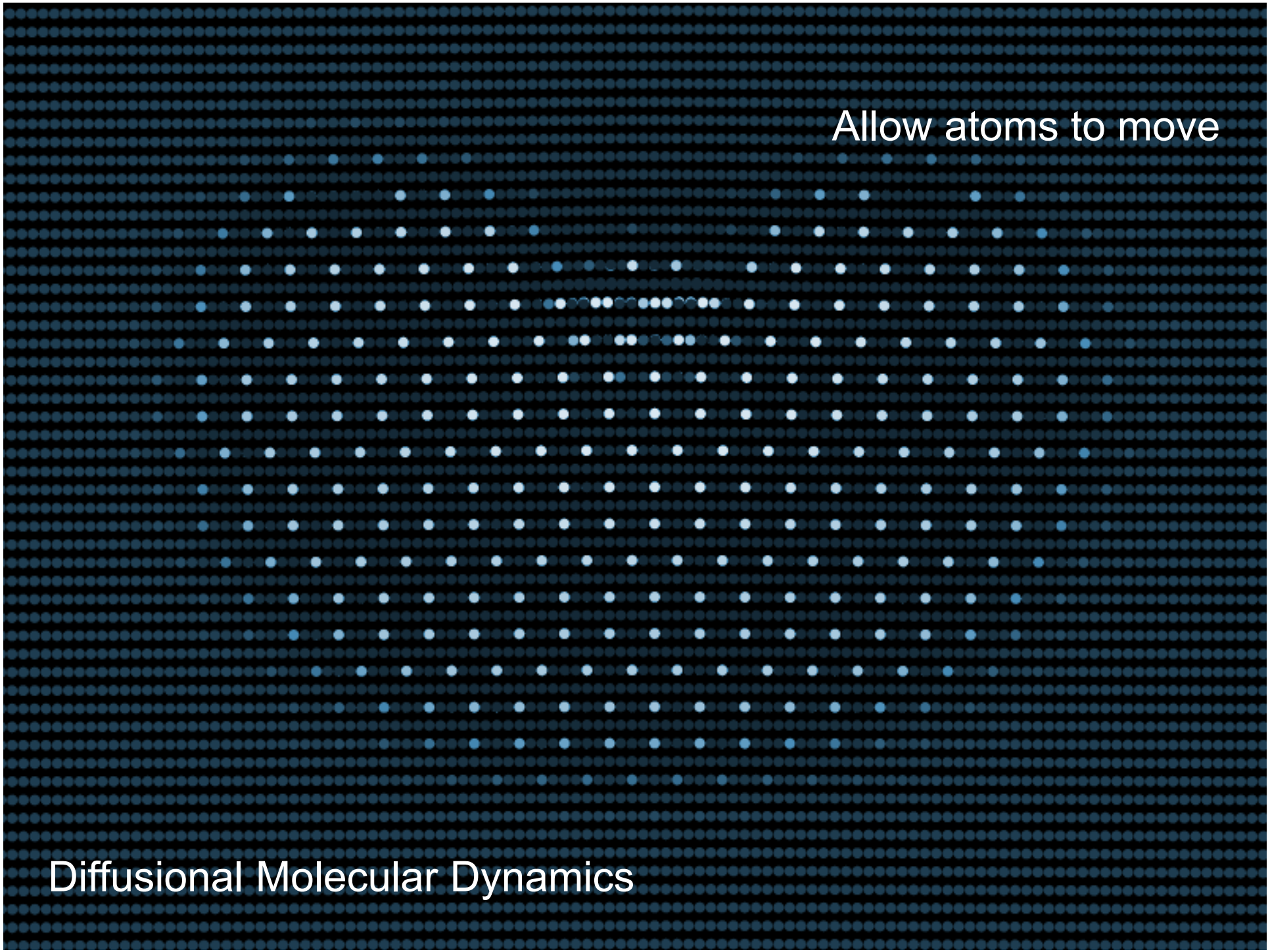
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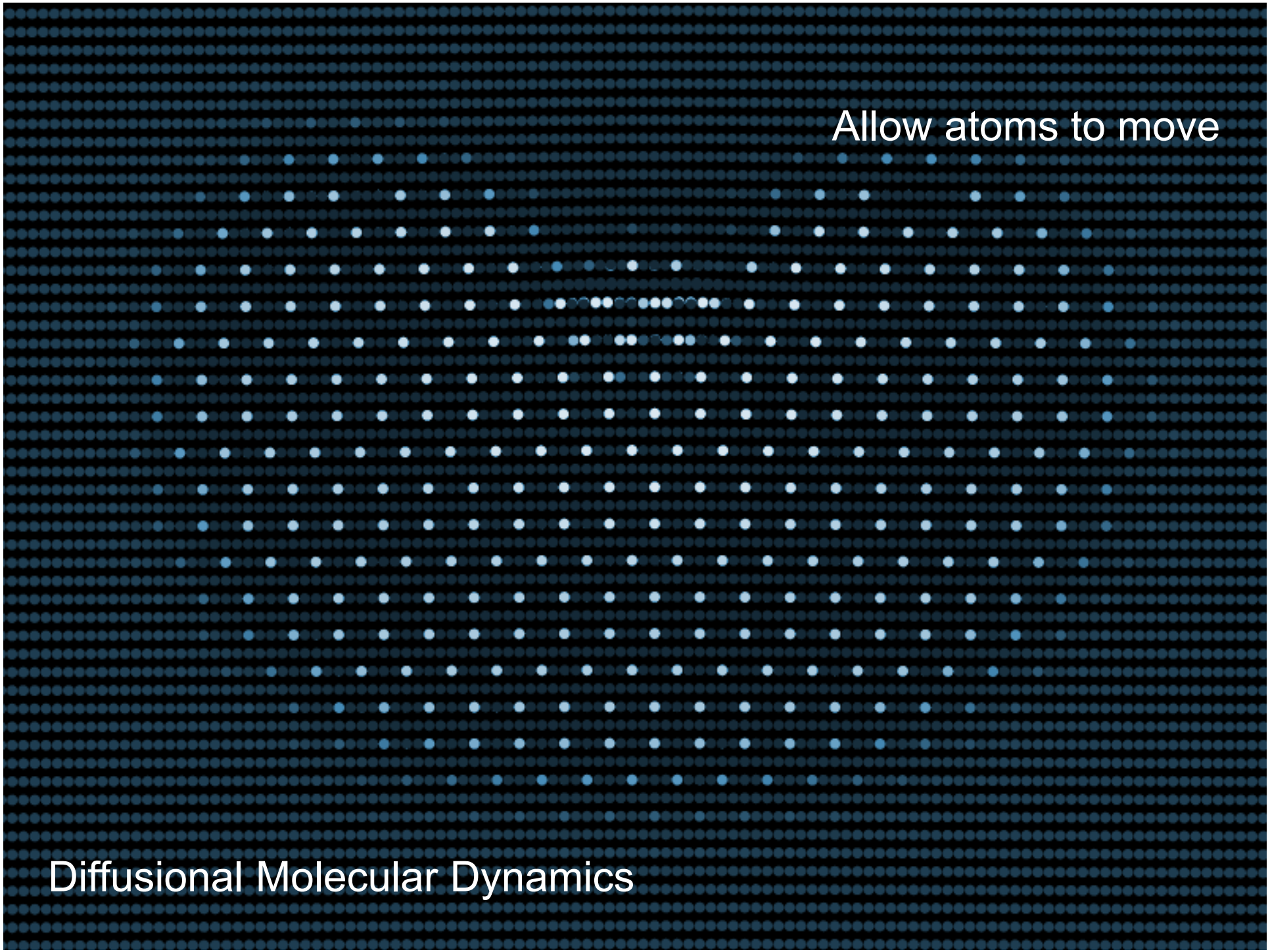
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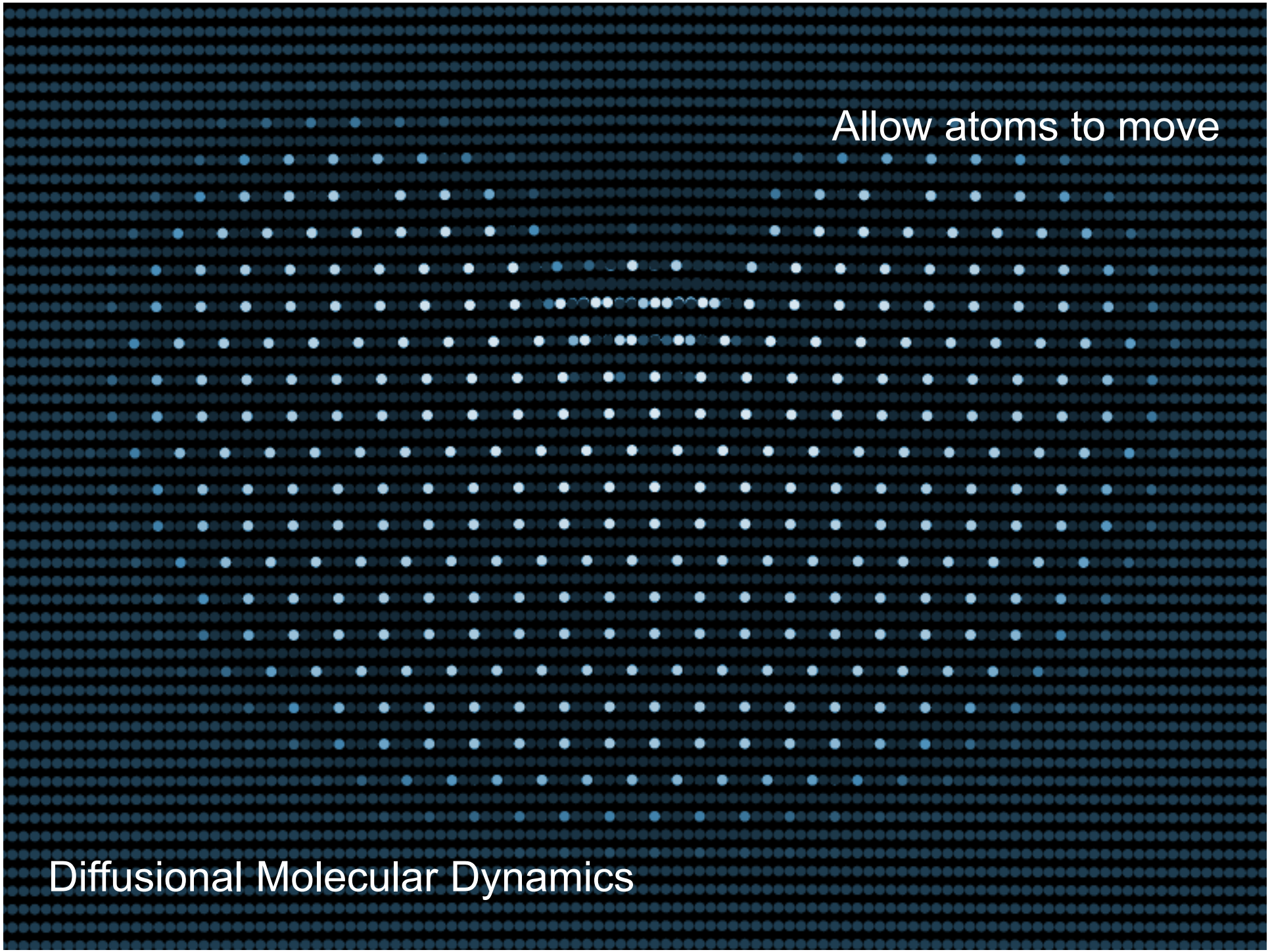
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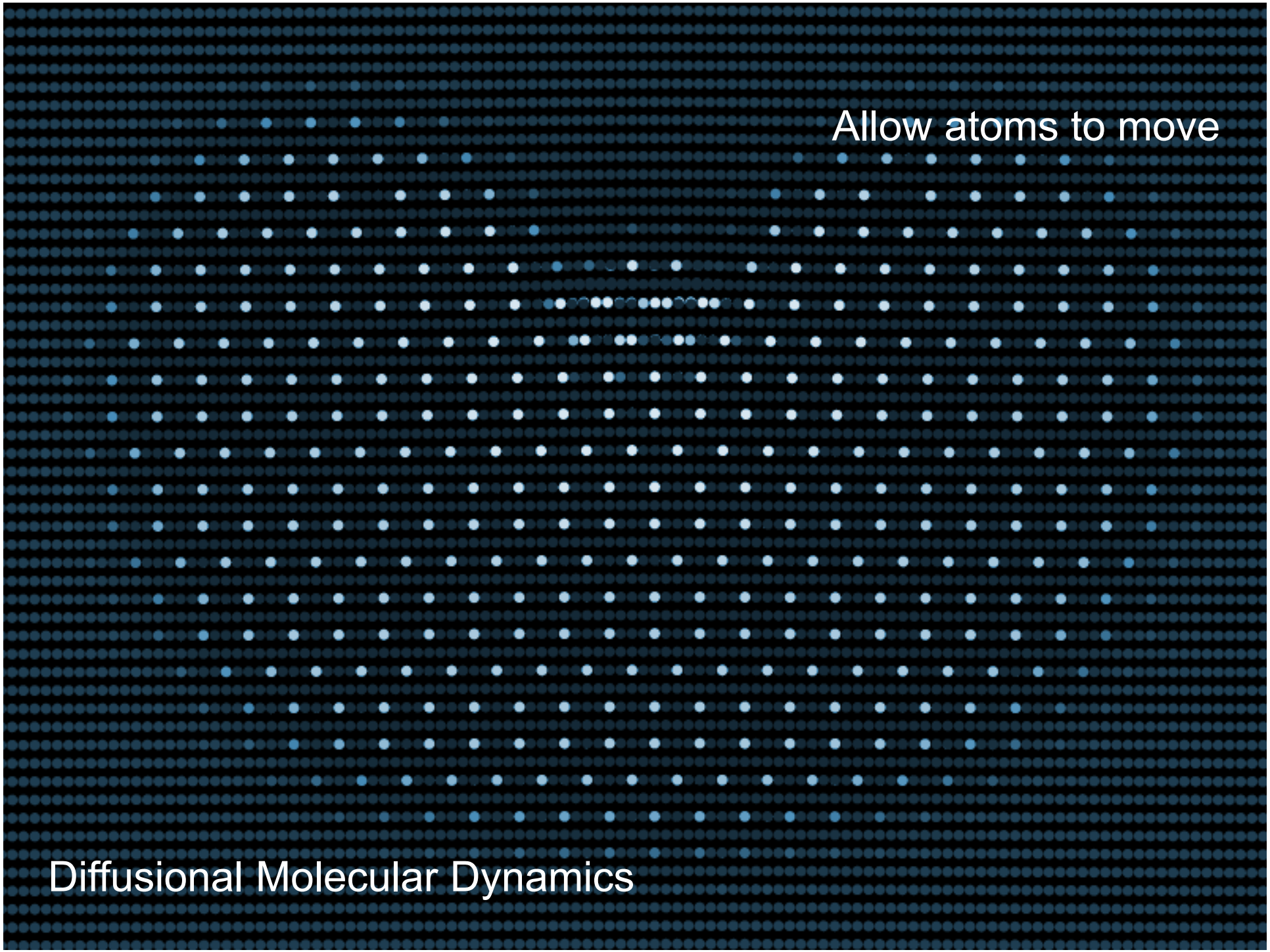
Diffusional Molecular Dynamics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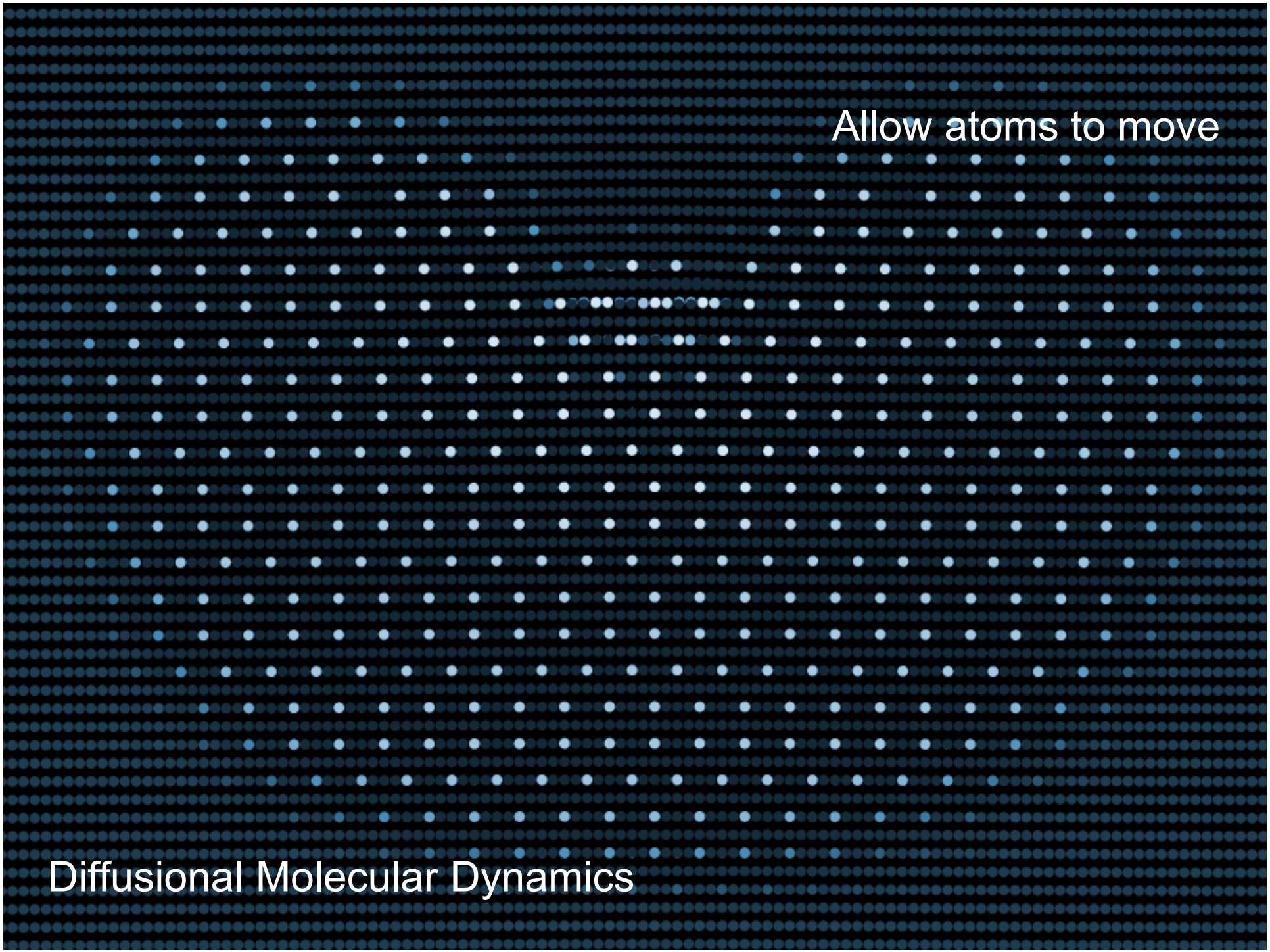
Diffusional Molecular Dynamics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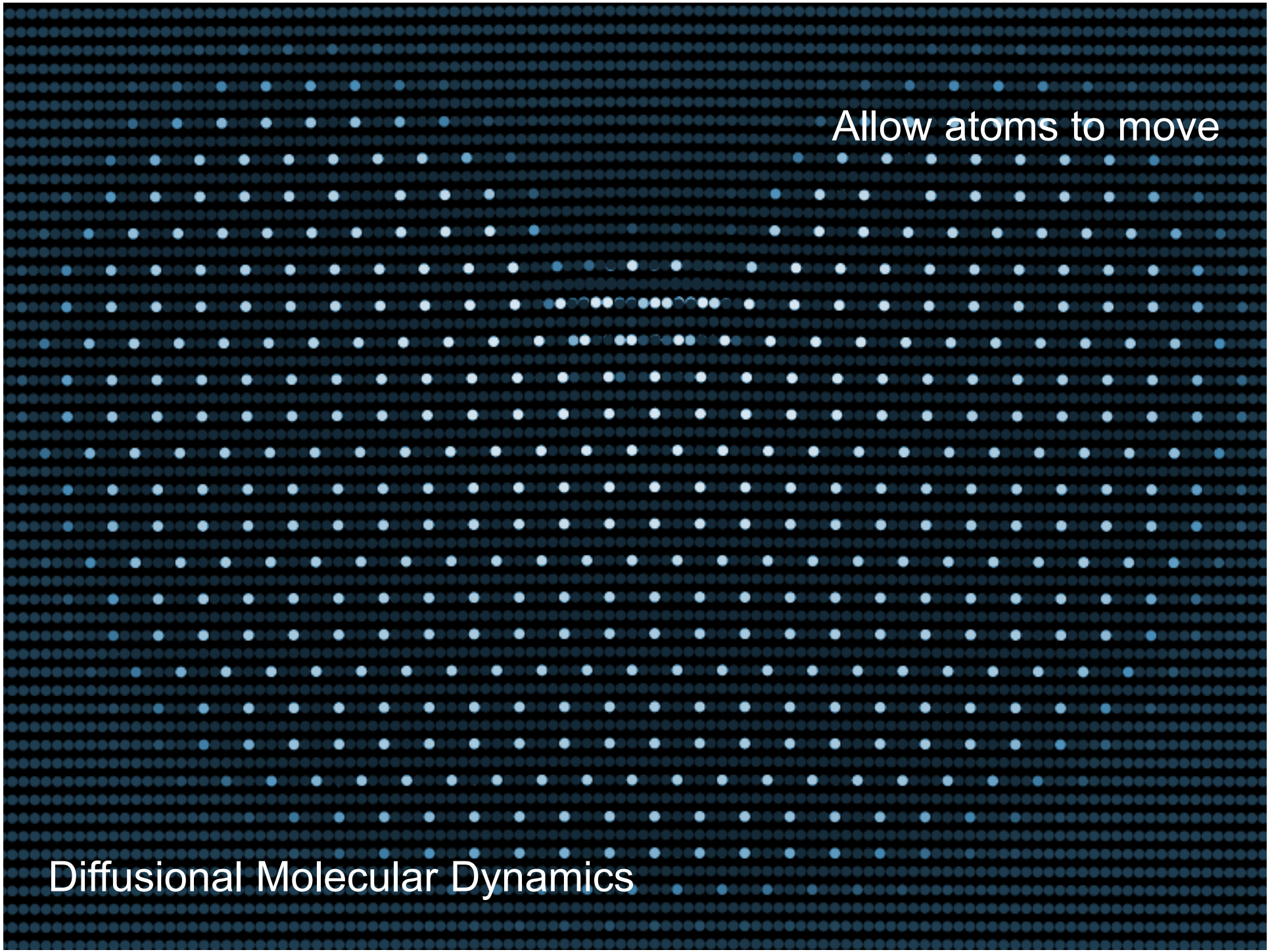
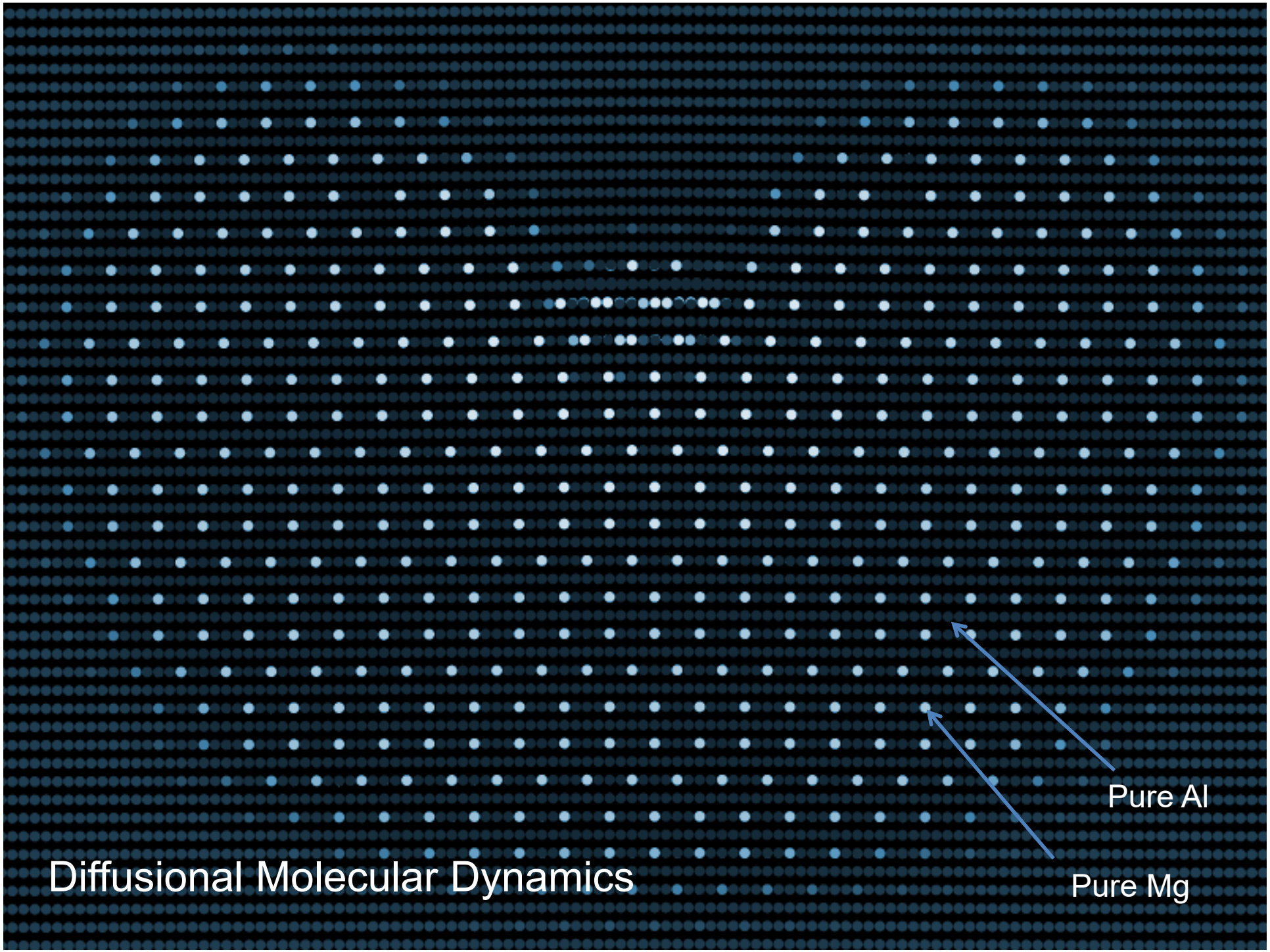
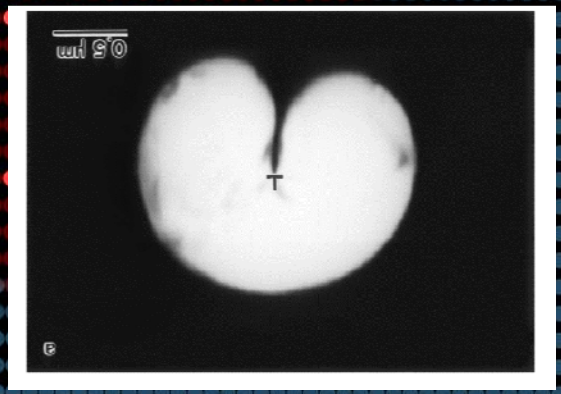
Diffusional Molecular Dynamics


Allow atoms to move
Diffusional Molecular Dynamics


Pure Al
Pure Mg
Diffusional Molecular Dynamics



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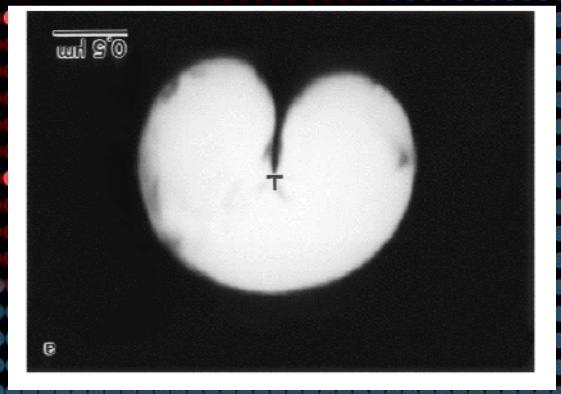
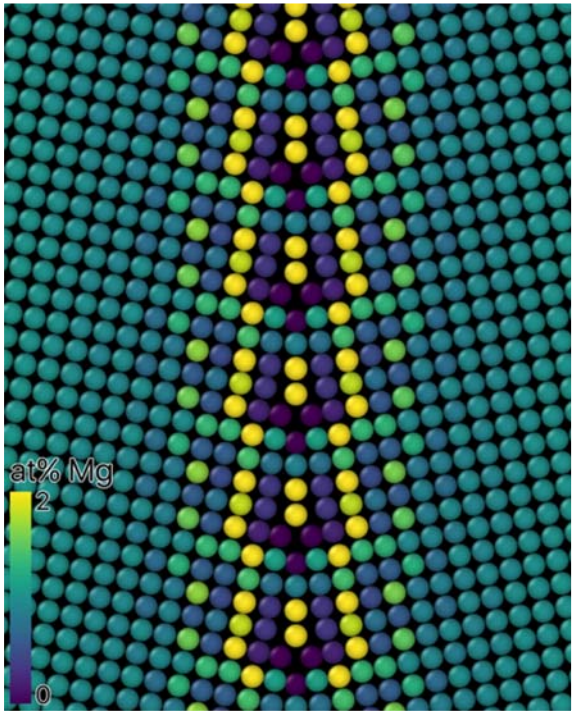
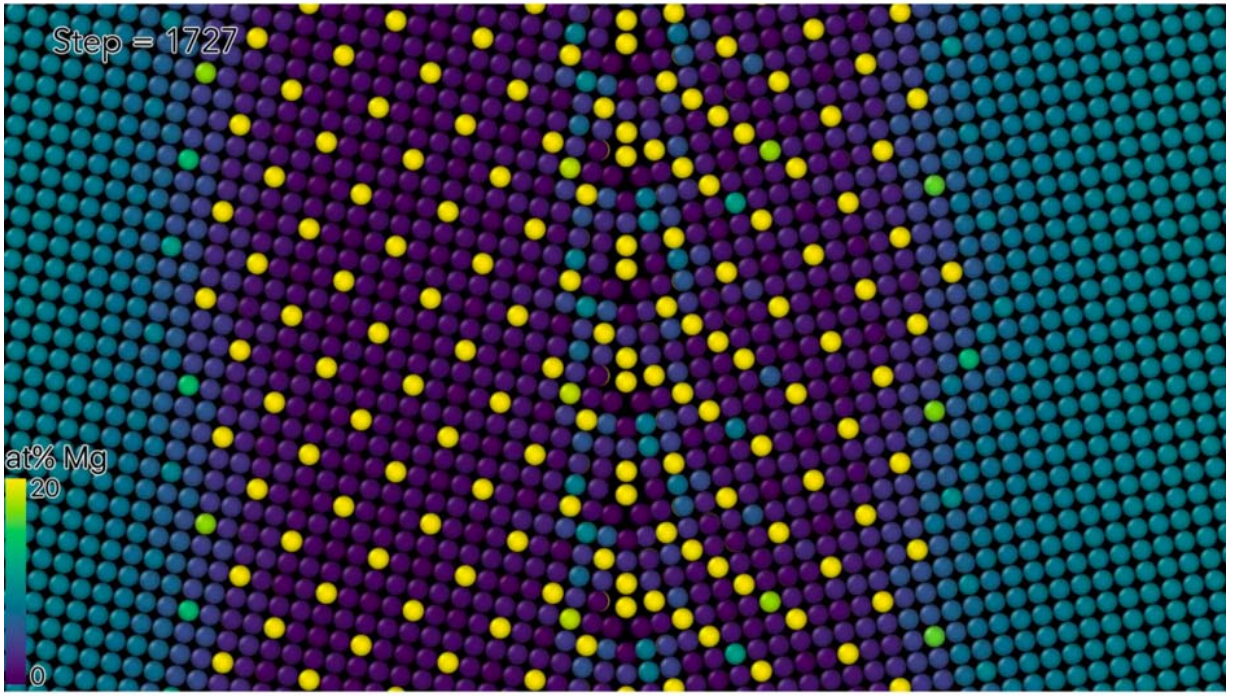


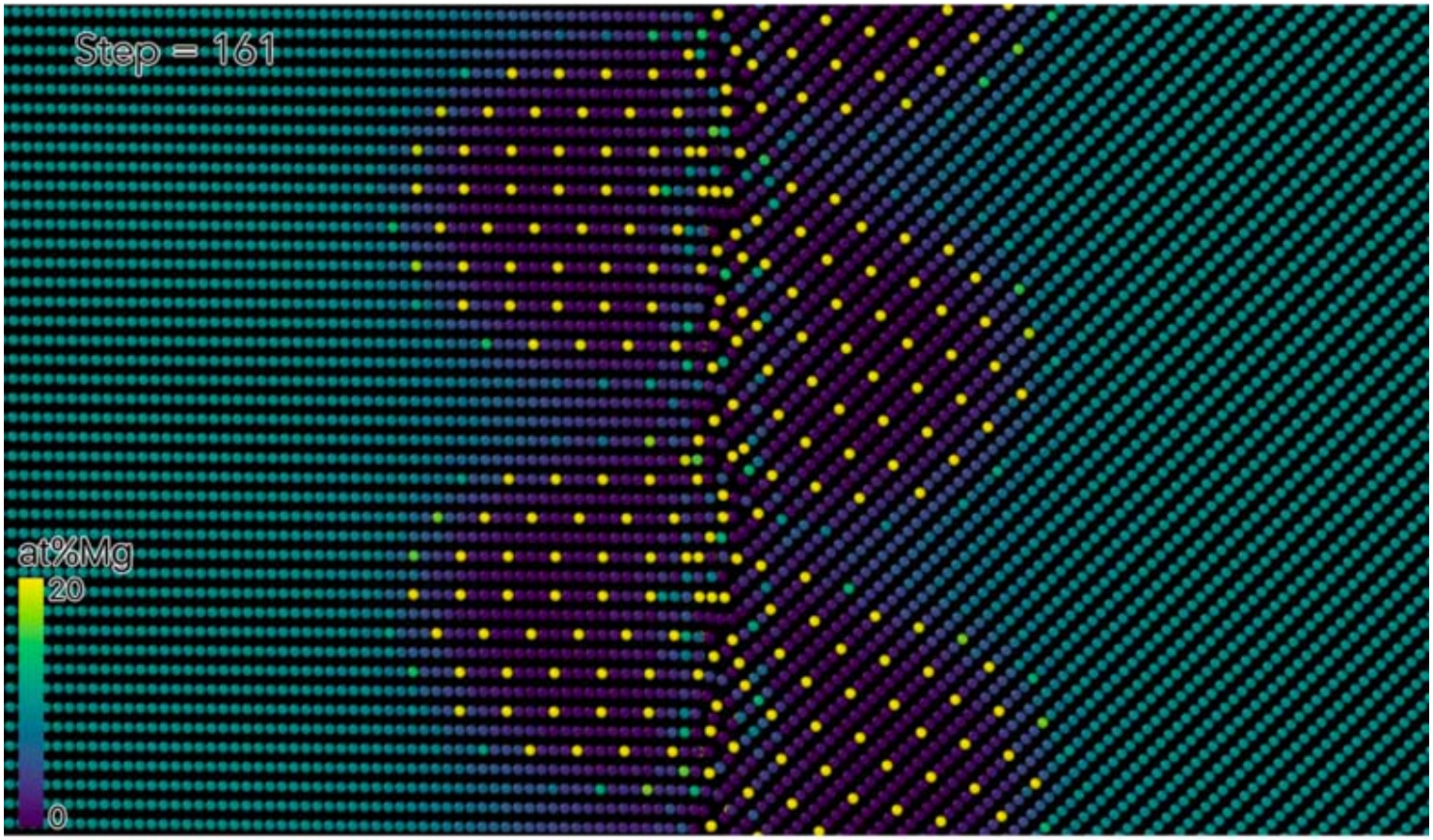
Diffusional Molecular Dynamics

Mg segregation to symmetric tilt boundary





Mg segregation to asymmetric tilt boundary



Conclusions

- Trends of DFT simulations (T=0K!) consistent with experimental results (APT) for binding energies of alloying elements to the bcc-fcc interface in iron
- Extension of APT studies and DFT simulations to multi-component Fe systems in progress – initial results available for Fe-C-Mn-Mo, Fe-C-Mn-Si, Fe-C-Mn-Al
- Extension of atomistic simulations for segregation kinetics and interface migration at diffusional timescales using aDMD in addition to PFC