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Heterogenous Carrier Transport Across Sublattice Melting in a Minimal Model Superionic Conductor

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(*submitted*)

by

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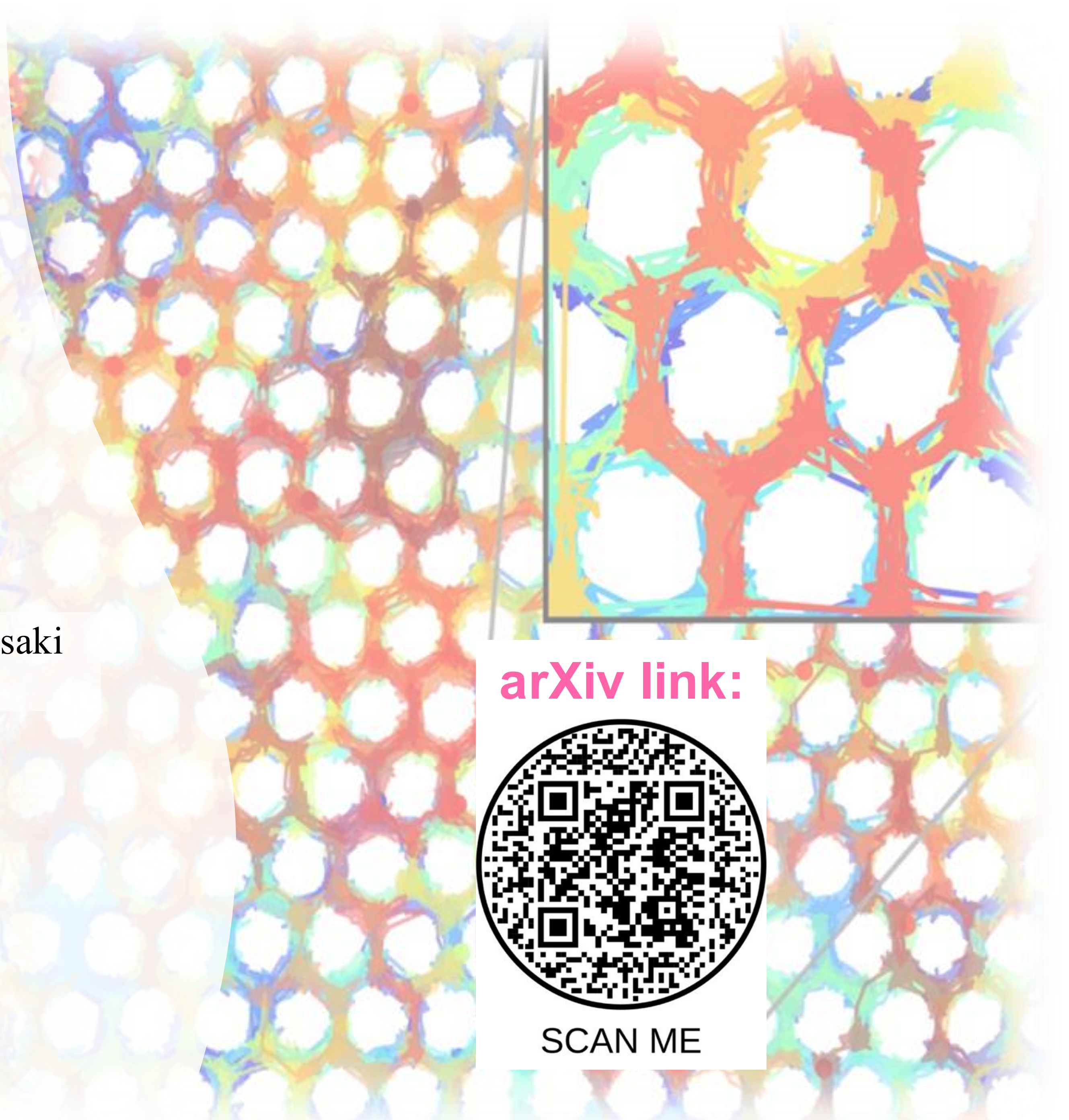

arXiv link:

SCAN ME

Mini-Workshop: Rheology of Dense Materials, YITP — March 18, 14:15

Collaborators

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Prof. Takeshi Kawasaki
(U. Osaka)

Background: Why Superionic Conductors Matter?

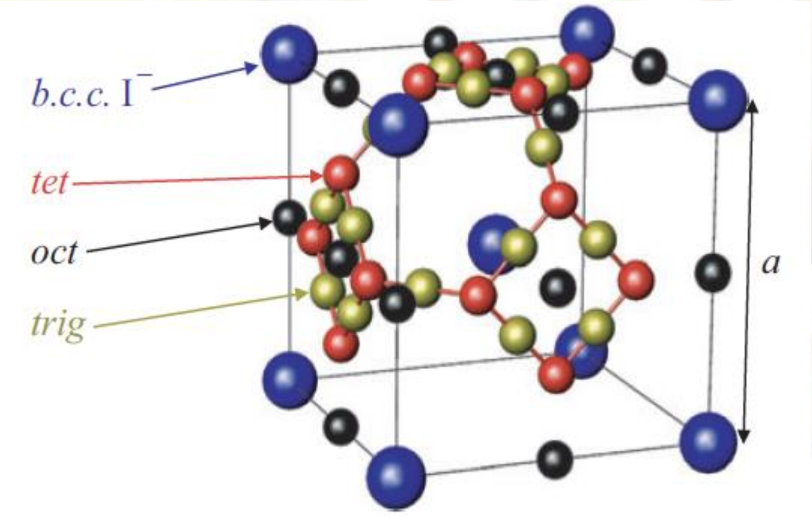
❑Fast Ion Transport in Solid Electrolytes

- **Superionic conductors**
  - Solid materials with *ionic conductivities comparable to liquid electrolytes*
  - Occurring at *temperatures far below the melting point*

- **Key feature:** *Crystalline host framework + Mobile ion sublattice*

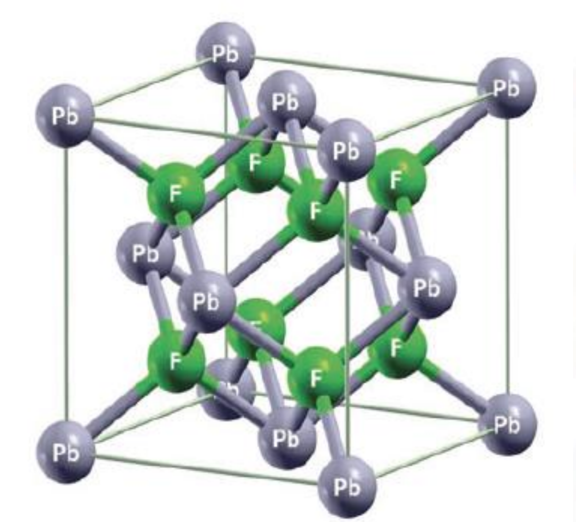
- **Examples:** AgI, PbF_2,
  LGPS ($Li_{10}GeP_2S_{12}$)

- **Applications:**
  - Solid-state batteries



α- AgI : Carrier: Ag^+

S. Hull, Rep. Prog. Phys. **67**, 1233 (2004).



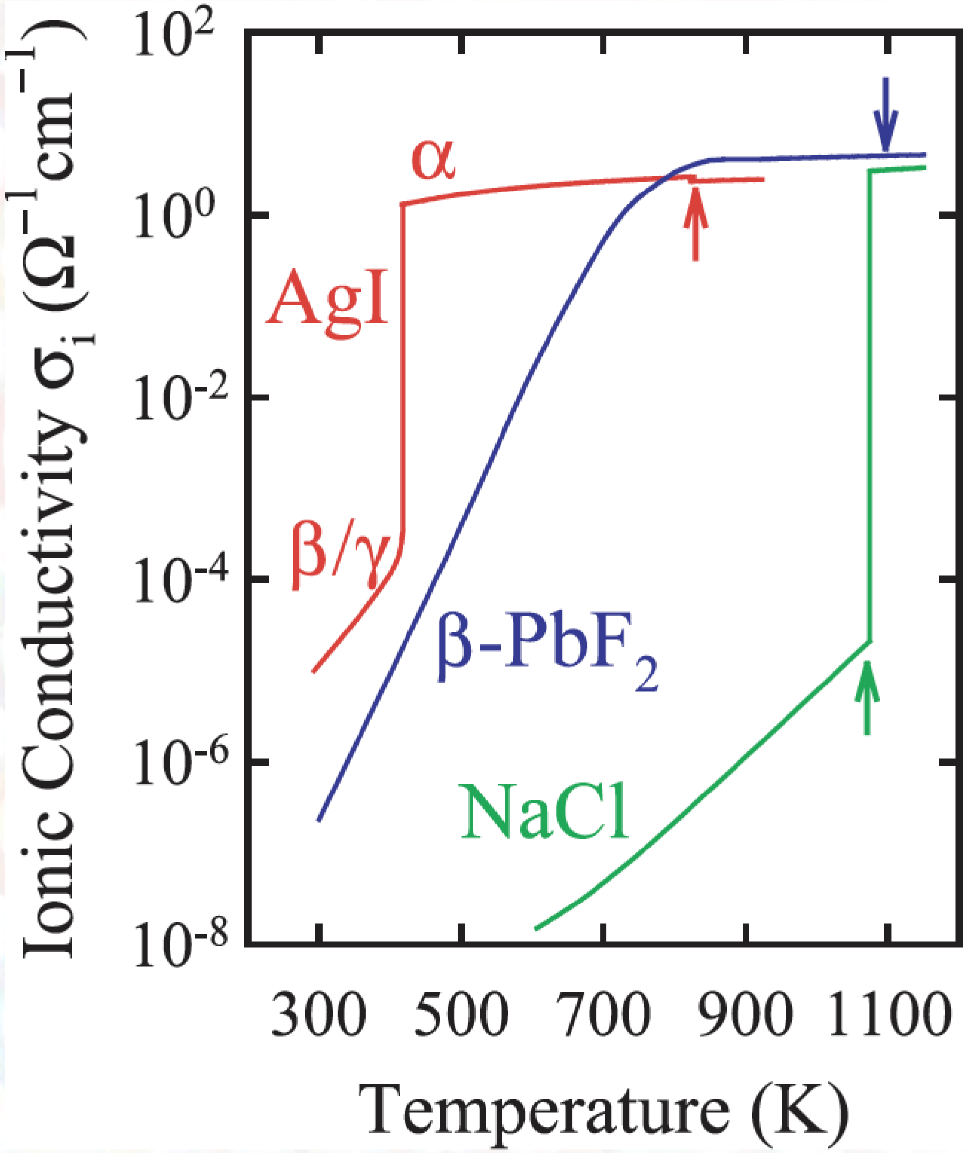
β - PbF_2: Carrier: F^-

C. Erk et al., Phys. Chem. Chem. Phys. **13**, 6029 (2011).

Background: "Phase" Transitions on Ionic Conductivity

- **"Phase" Transitions on Ionic Conductivity**
  - Melting transition (e.g., NaCl)
  - Transitions to superionic "phases" (e.g., AgI, PbF_2)
    - ❖ **Type I:** AgI — first order transition
    - ❖ **Type II:** PbF_2 — continuous transition (Faraday transition)

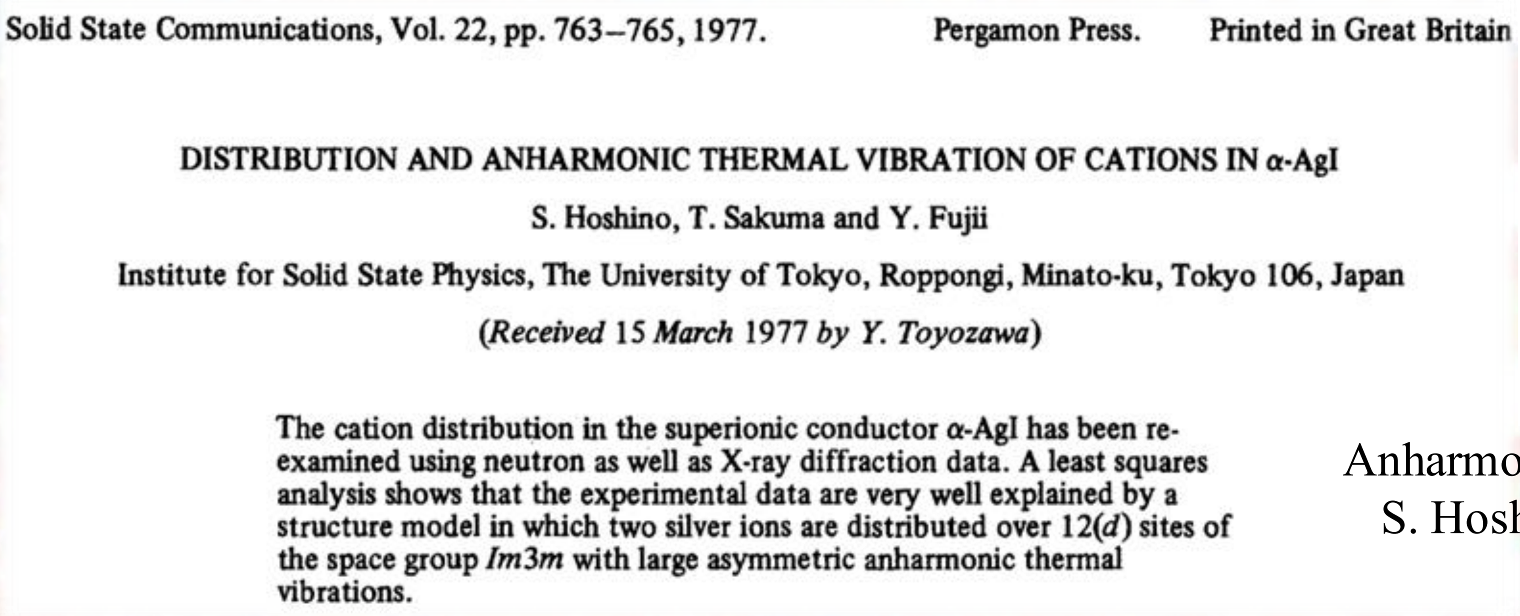
- The physical mechanism of the superionic state has not yet been fully elucidated.
- Several scenarios exist.



S. Hull, Rep. Prog. Phys. **67**, 1233 (2004).

Background: Carrier Dynamics in the Superionic Conducting Phase

■ Anharmonic Thermal Vibrations of Carrier Ions



Solid State Communications, Vol. 22, pp. 763–765, 1977. Pergamon Press. Printed in Great Britain

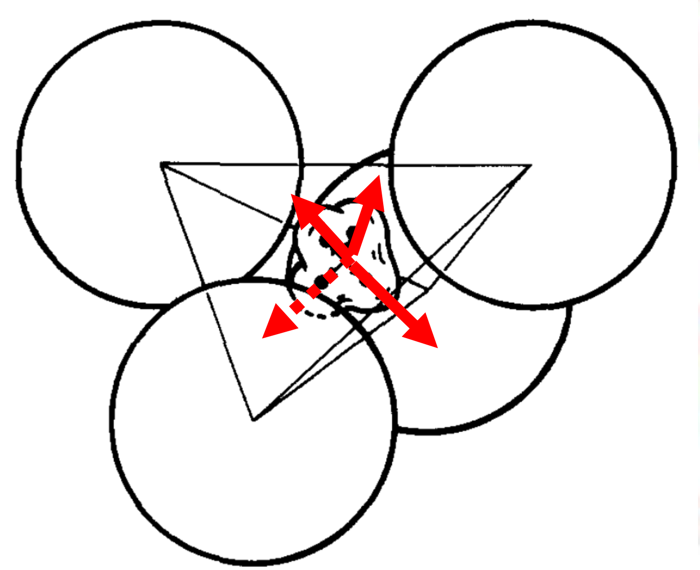
DISTRIBUTION AND ANHARMONIC THERMAL VIBRATION OF CATIONS IN α-AgI

S. Hoshino, T. Sakuma and Y. Fujii

Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

(*Received* 15 *March* 1977 *by Y. Toyozawa*)

The cation distribution in the superionic conductor α-AgI has been re-examined using neutron as well as X-ray diffraction data. A least squares analysis shows that the experimental data are very well explained by a structure model in which two silver ions are distributed over 12(*d*) sites of the space group *Im*3*m* with large asymmetric anharmonic thermal vibrations.



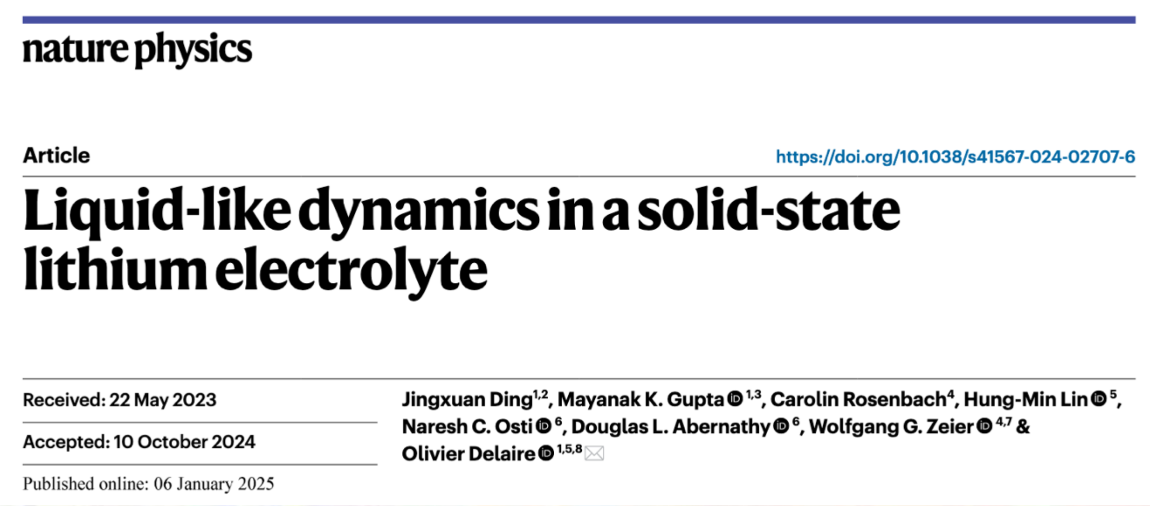
Anharmonic Thermal Vibrations of Silver Ions (Ag^+)
S. Hoshino et al. Solid State Com. **22**, 763(1977)

- ➢ Semi-liquid-like behaviour.
- ➢ Anharmonicity → lattice softening → Leading to high ionic conductivity.

Background: Sublattice melting

- **Sublattice Melting (Incorporating Anharmonicity)**
  Original work identified by NMR:
  J. B. Boyce and B. A. Huberman, *Solid State Communications* **21**, 31 (1977).

- **Recent progress**



nature physics

Article

https://doi.org/10.1038/s41567-024-02707-6

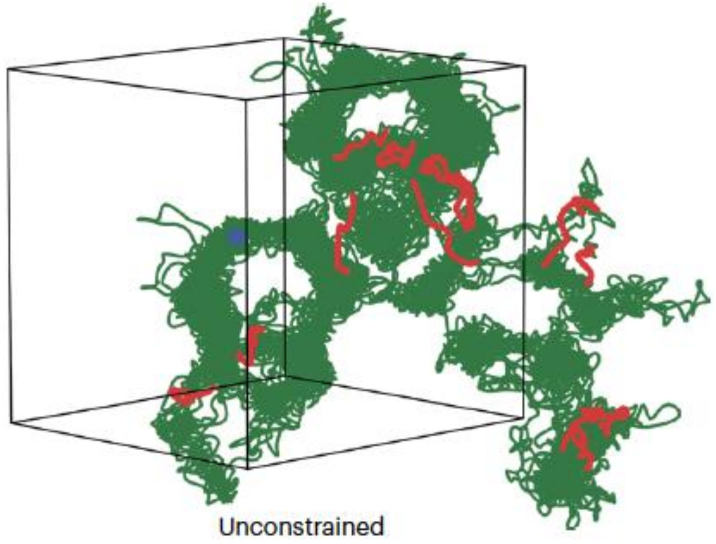
Liquid-like dynamics in a solid-state lithium electrolyte

Received: 22 May 2023

Accepted: 10 October 2024

Published online: 06 January 2025

Jingxuan Ding[1,2], Mayanak K. Gupta[1,3], Carolin Rosenbach[4], Hung-Min Lin[5], Naresh C. Osti[6], Douglas L. Abernathy[6], Wolfgang G. Zeier[4,7] & Olivier Delaire[1,5,8]

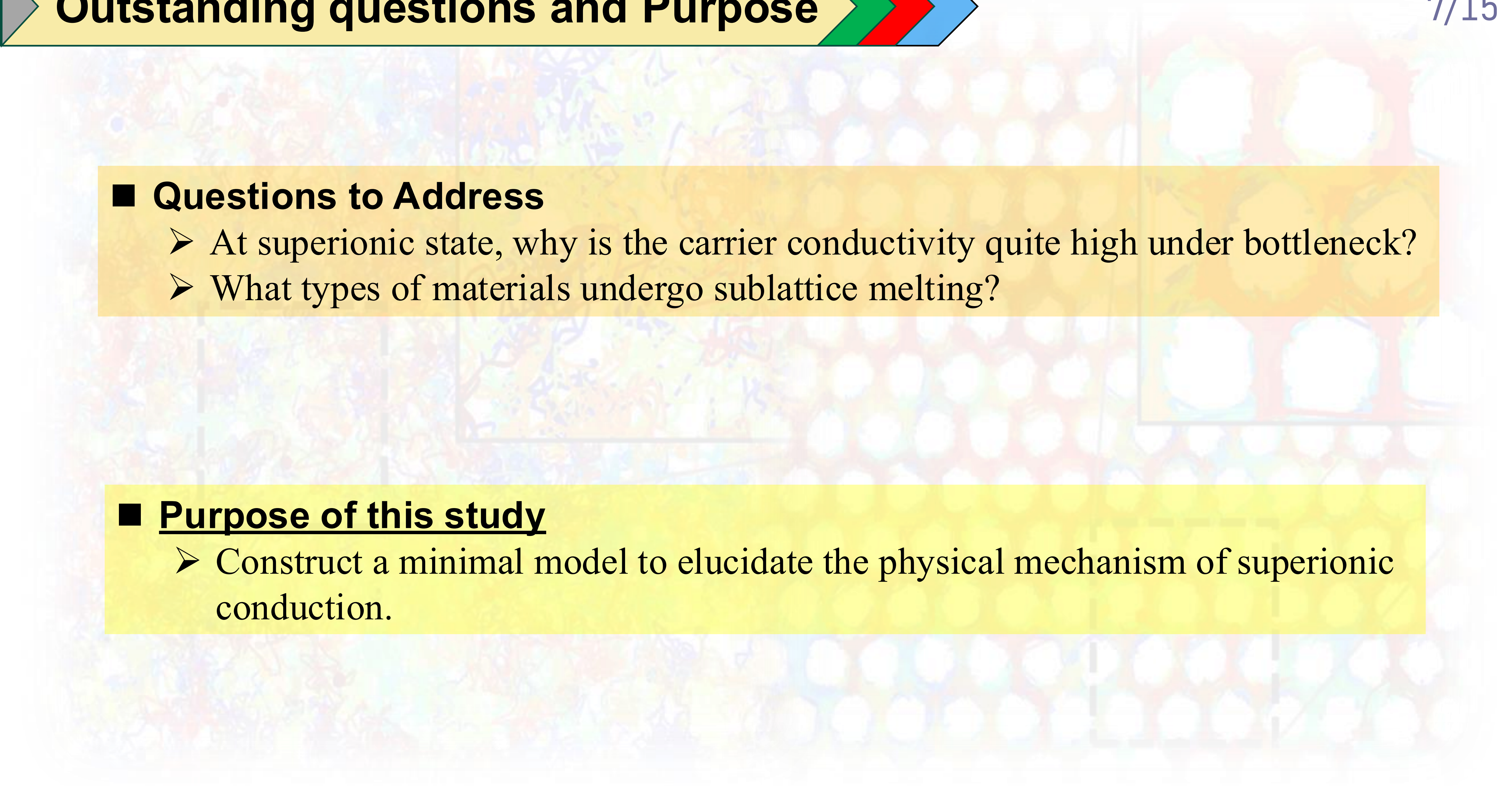


Neutron scattering + MLMD simulations

J. Ding, et al., Nat. Phys. **21**, 118 (2025).

- **Sublattice Melting:** Enables anharmonic, liquid-like ionic transport within a solid.
- **Bottleneck from host atoms:** restricts the free diffusion of the carrier.

Outstanding questions and Purpose



Questions to Address

- At superionic state, why is the carrier conductivity quite high under bottleneck?
- What types of materials undergo sublattice melting?

Purpose of this study

- Construct a minimal model to elucidate the physical mechanism of superionic conduction.

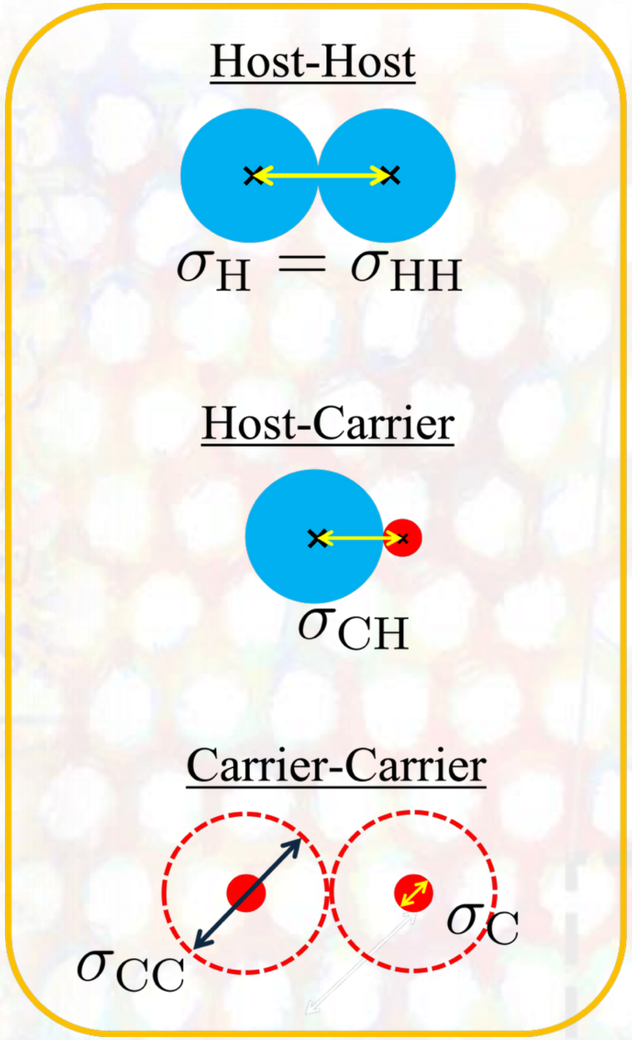
Model

- **Classical Molecular Dynamics Simulations** (2D & 3D); Total particle no. $N = 512$

- **Interparticle Interactions**
  - Weeks-Chandler-Andersen (WCA) potential

$$U_{ij}(r_{ij}) = \begin{cases} 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \epsilon_{ij}, & r_{ij} \leq r_c, \\ 0, & r_{ij} > r_c. \end{cases}$$

  - By introducing **non-additiveness** that mimics the long-range Coulomb interaction of carriers [Cf: With coulomb interaction: A. Fukumoto, A. Ueda, and Y. Hiwatari, J. Phys. Soc. Jpn. **51**, 3966 (1982)].



$\sigma_{\mathrm{CC}} \sim \sigma_{\mathrm{HH}}$

Stable Configuration at Low T

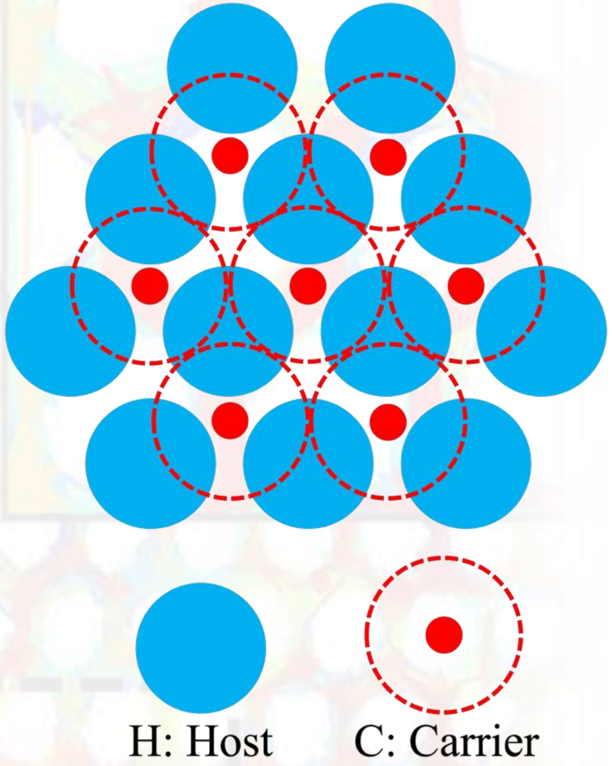


Table 1: Model parameters used in the simulations.

$N_{\mathrm{CC}} : N_{\mathrm{HH}}$	m_{CC}	m_{HH}	ϵ_{CC}	ϵ_{HH}	ϵ_{CH}	σ_{C}	σ_{H}	σ_{CC}	σ_{CH}	$a_{\mathrm{L-space}}$	t^*
1 : 1	1.0	1.0	0.001	1.0	1.0	0.154	1.0	1.044	0.577	1.044	$\sqrt{m\sigma^2/\epsilon}$

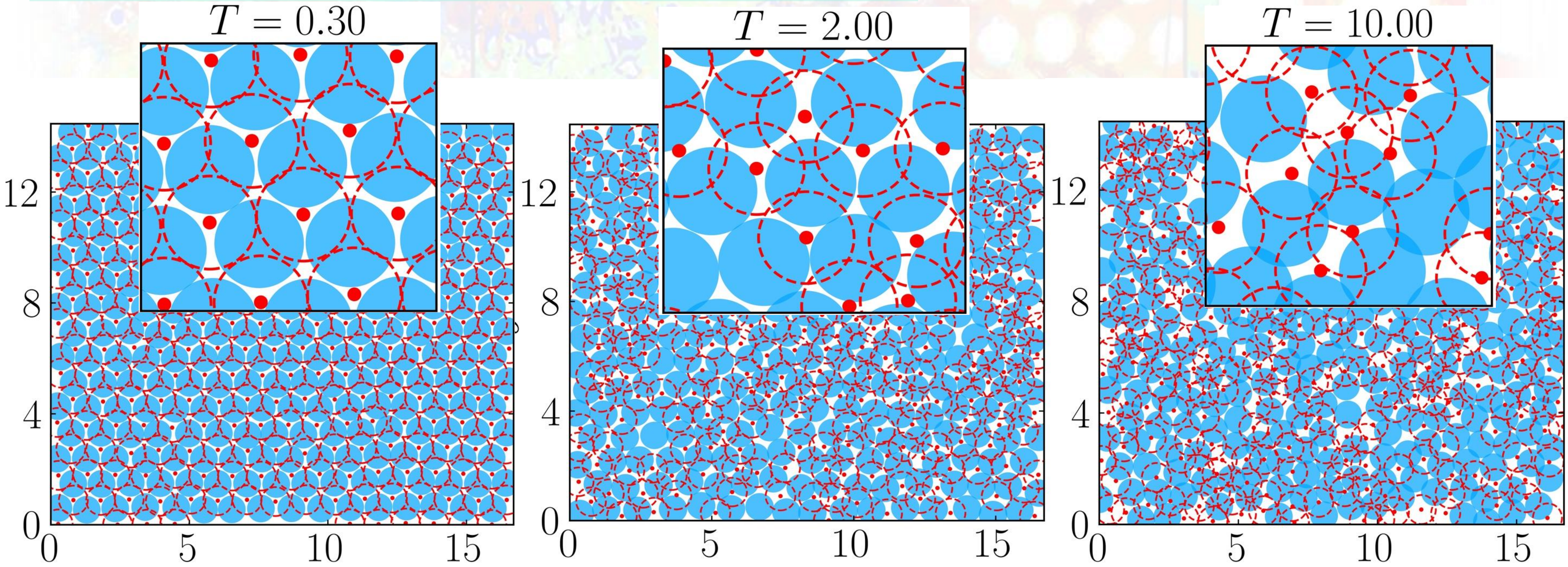
Area packing fraction,

$$\phi = \frac{A_{\mathrm{tot}}}{L_x L_y} \simeq 0.85$$

$a_{\mathrm{L-space}}$: Lattice spacing.

Results: Static Particle Structure — Snapshot

- **Temperature dependence of configurations**

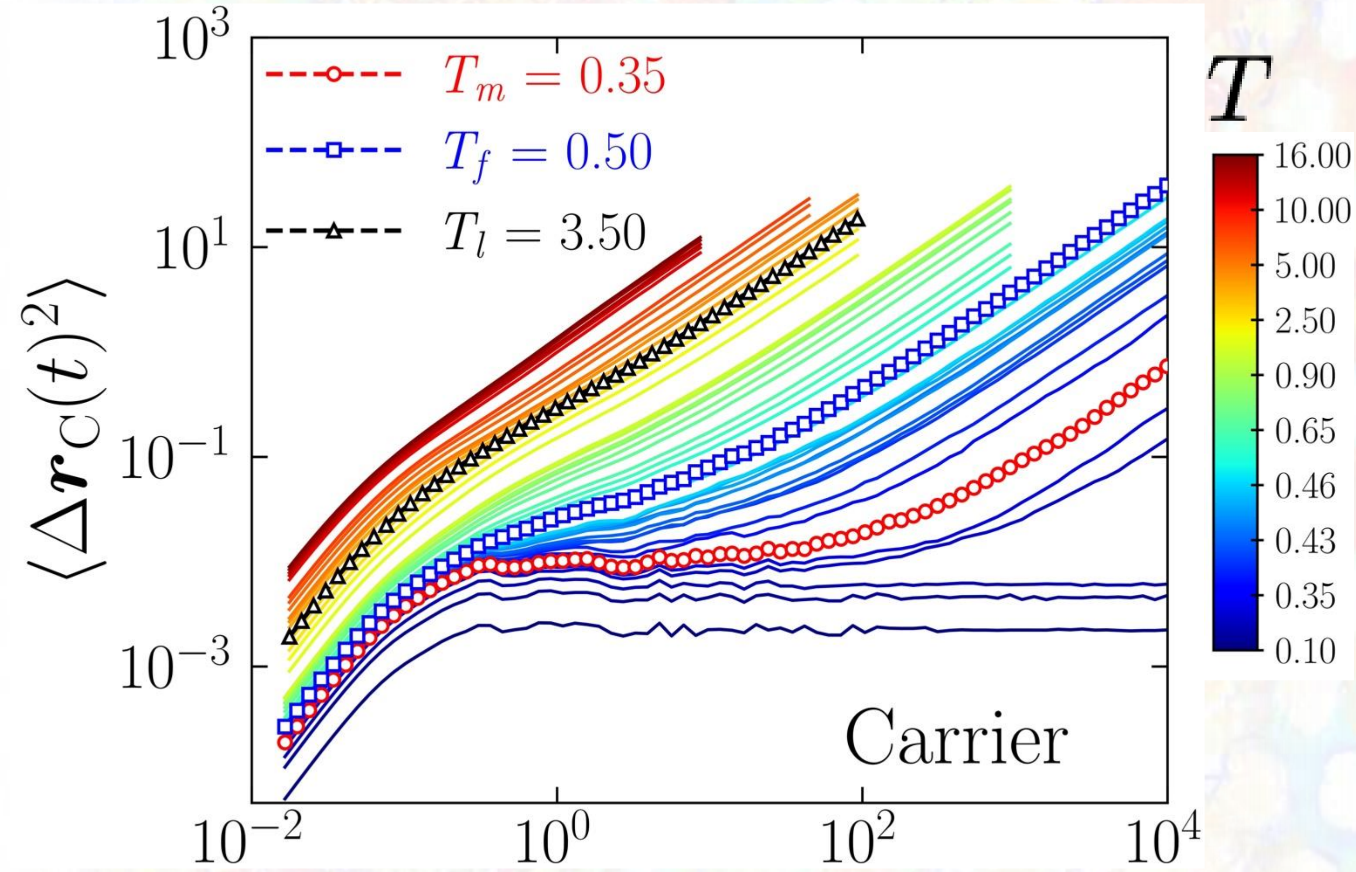


Equilibrium states at each temperature

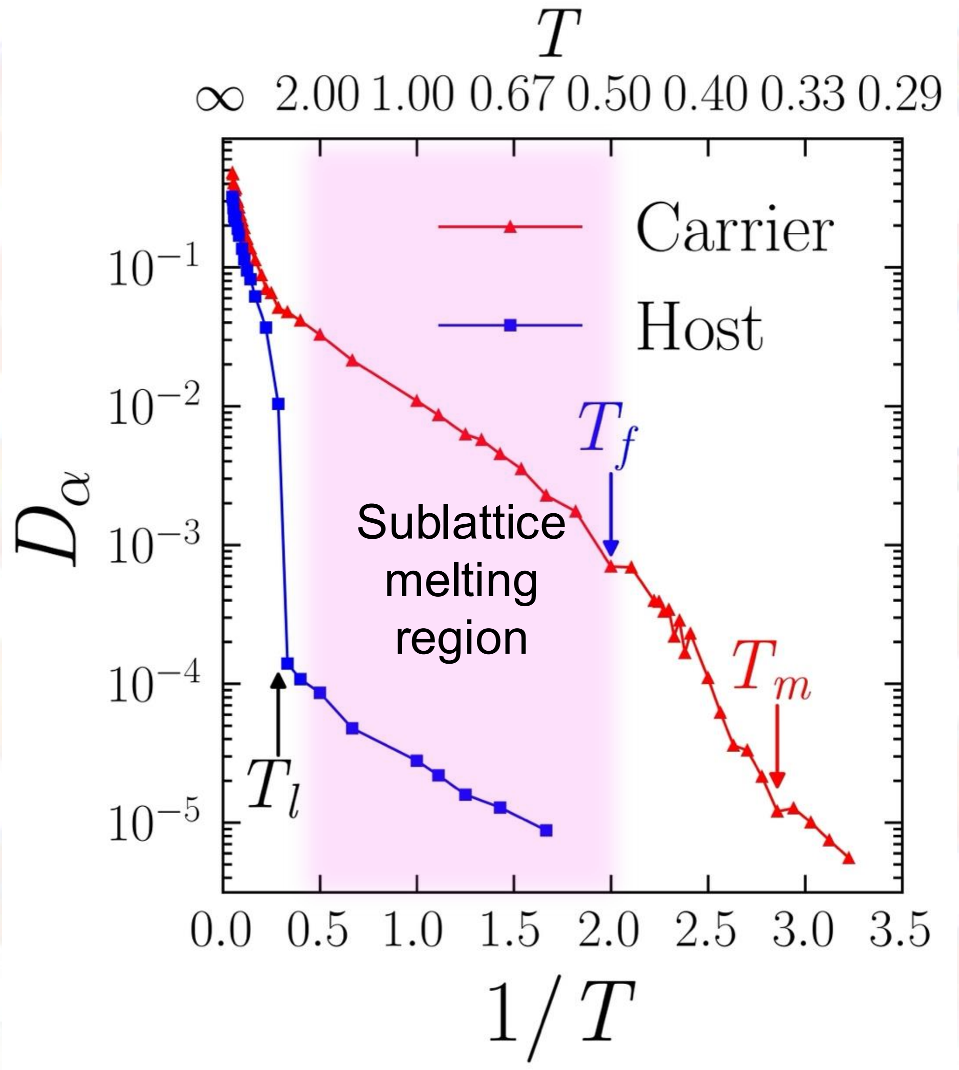
Each configuration is thermally selected

Results: Mean squared displacement (MSD) and diffusion constant

■ MSD of the carriers

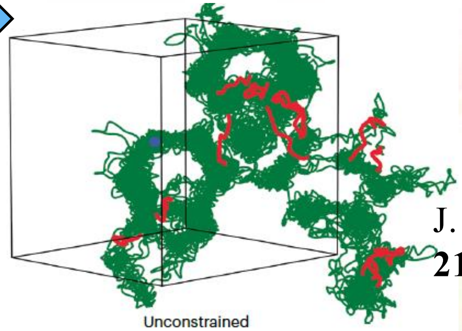


■ Diffusion constant of the carriers

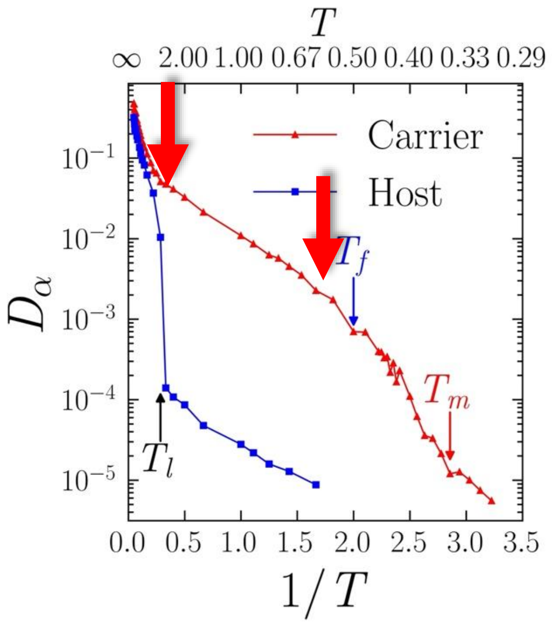


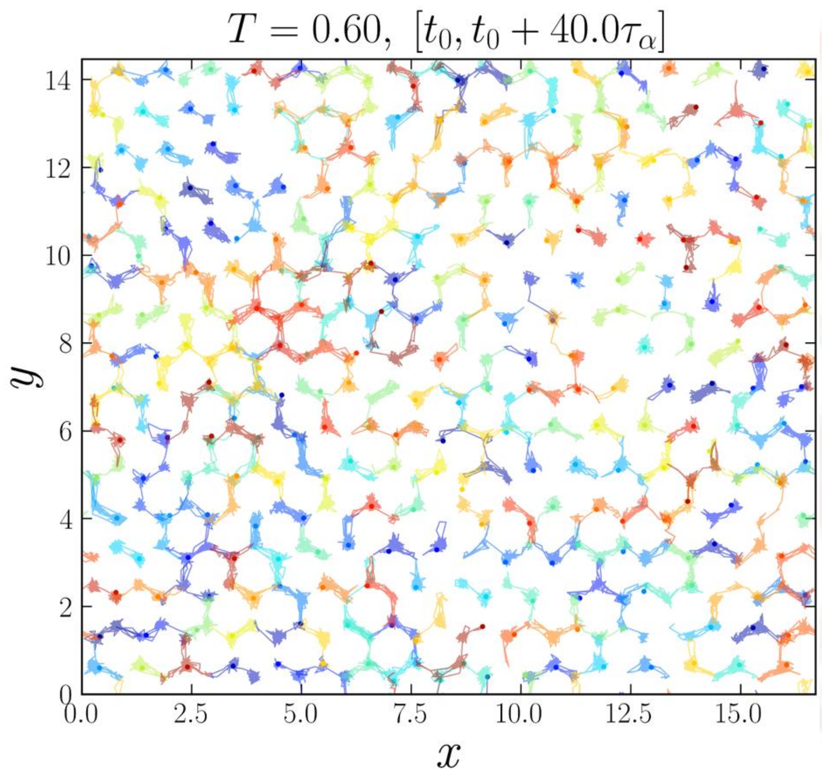
Results: Dynamics of carriers: trajectories

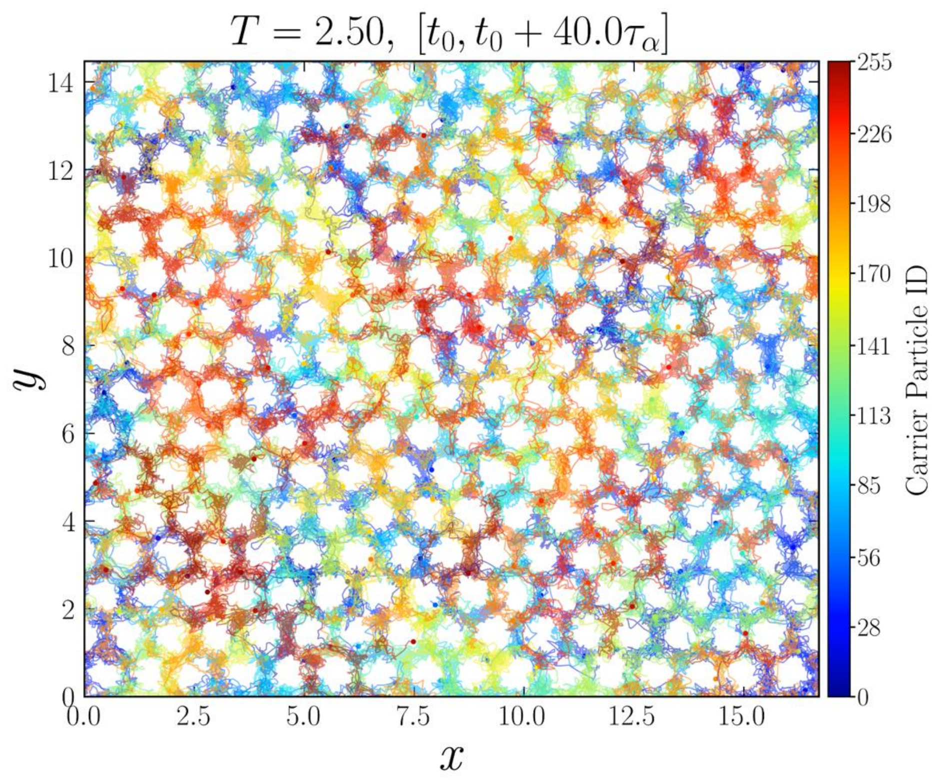
■ Trajectories of the carriers in sublattice-melts



J. Ding, et al., Nat. Phys. **21**, 118 (2025).



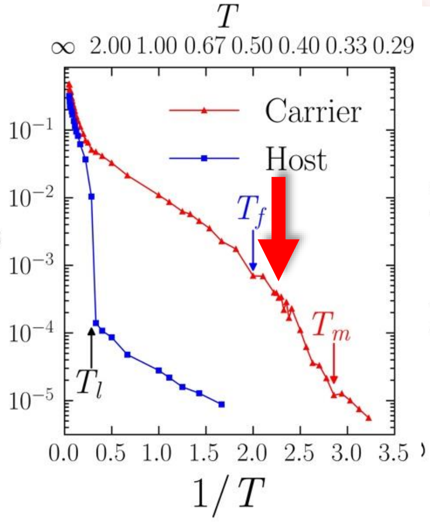


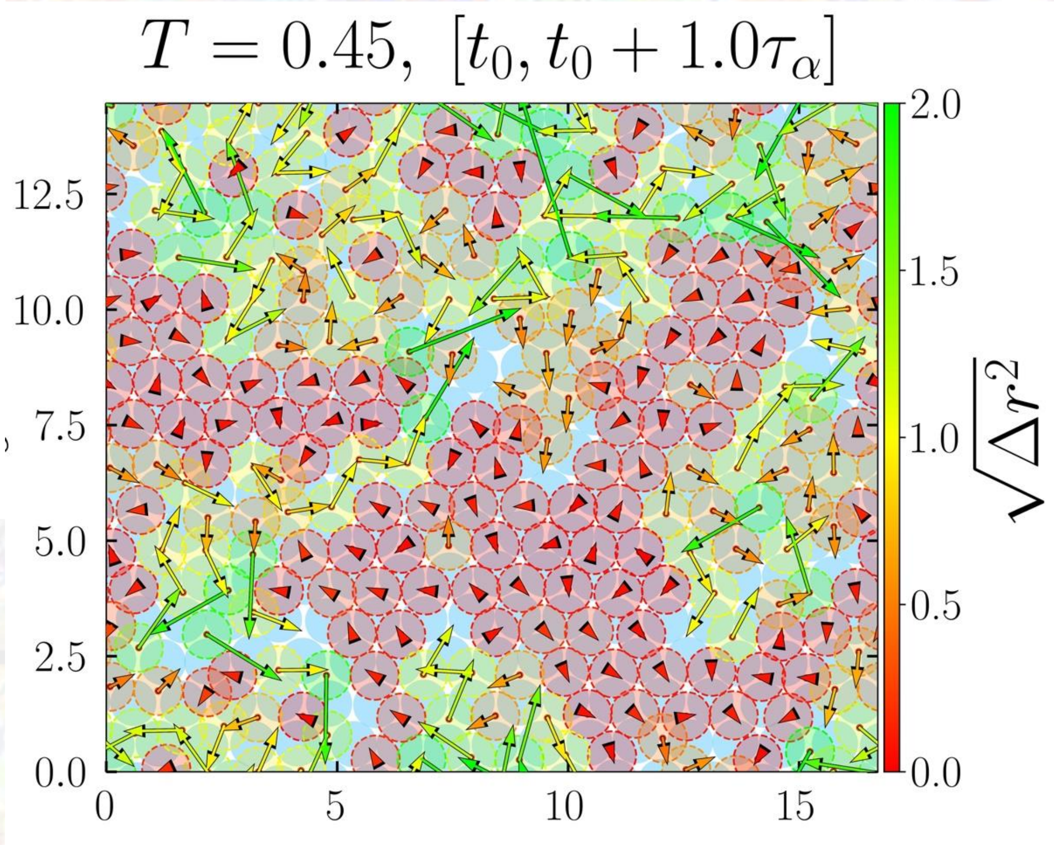


- ➢ The host forms a crystalline framework, while the carriers are molten and diffuse through the interstitial spaces.

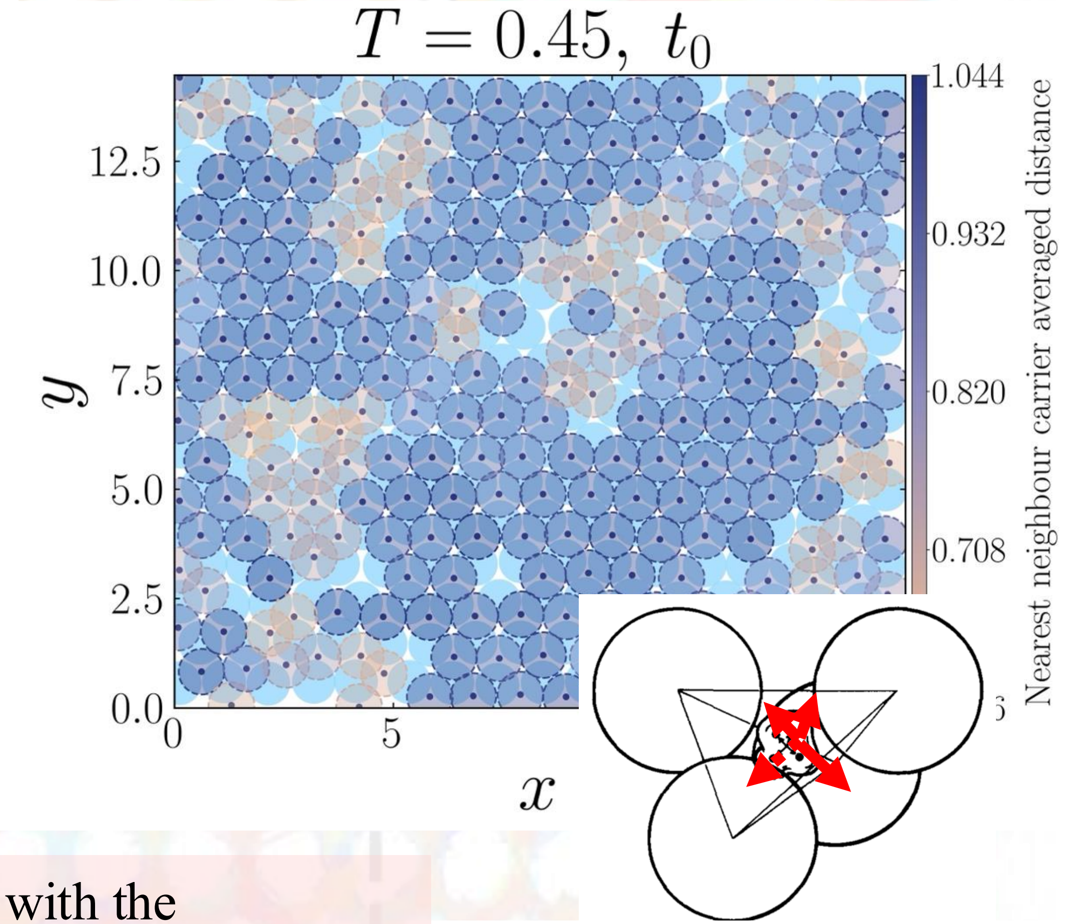
Results: Heterogeneous dynamics and structure of the carriers

■ Dynamical heterogeneity of carriers




$T = 0.45,\ [t_0, t_0 + 1.0\tau_\alpha]$

■ Carrier to carrier distance


$T = 0.45,\ t_0$

Anharmonic Thermal Vibrations of Silver Ions (Ag^+)
S. Hoshino et al. Solid State Com. **22**, 763(1977)

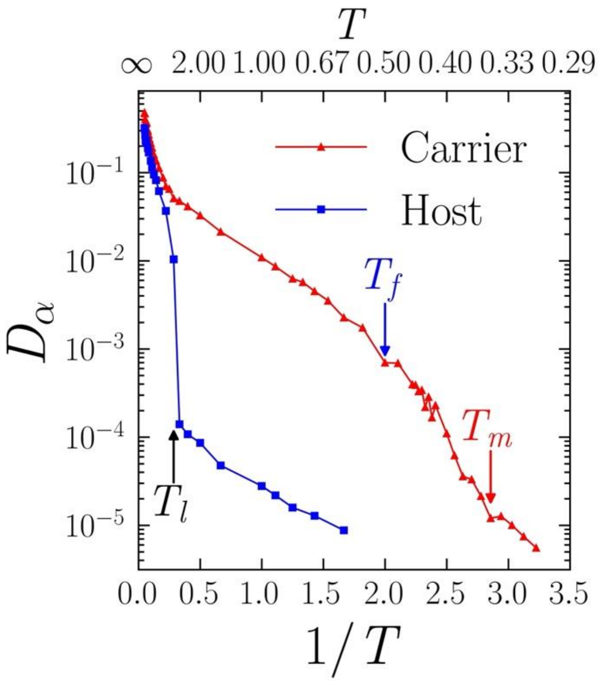
- Near the sublattice melting point, the dynamics correlated with the heterogenous structure: mobile carriers are in interstitial sites.
- Expect anharmonic vibration.

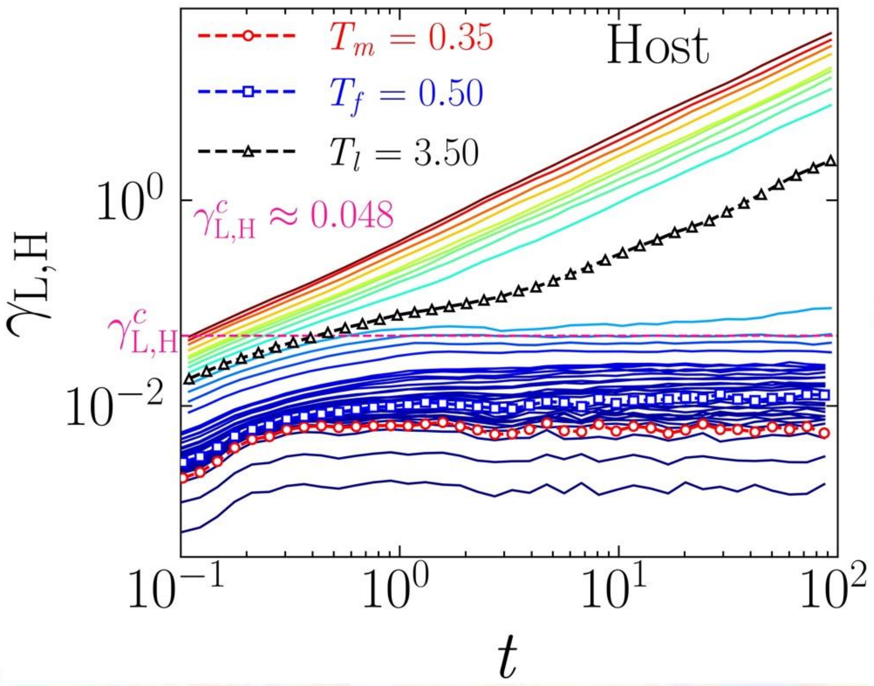
Results: Anharmonicity – Lindemann Index

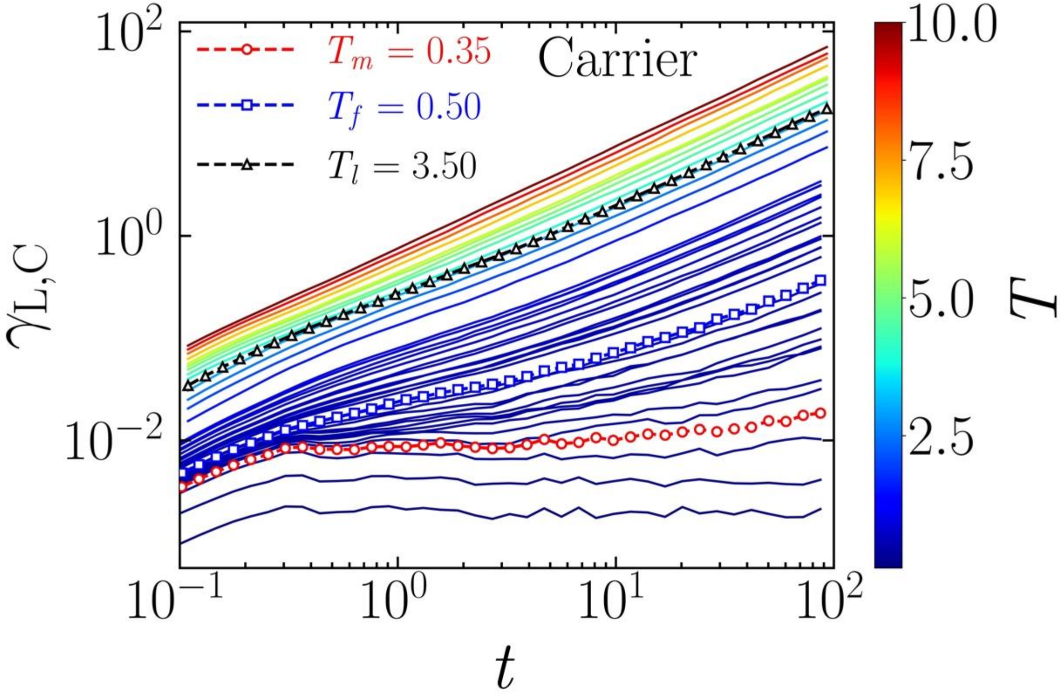
- **Lindemann Index**
  (mean-squared relative displacement between particles)

$$\gamma_{\mathrm{L},\alpha}(t) = \frac{1}{N_\alpha}\sum_{j\in\alpha}\frac{1}{n_j}\sum_{k\in\alpha,\ \mathrm{n.n.}(j)}\frac{\langle|\mathbf{u}_{jk}(t)|^2\rangle}{a^2_{\mathrm{L-space}}}.$$

$$\mathbf{u}_{jk}(t) = [\mathbf{r}_j(t) - \mathbf{r}_k(t)] - [\mathbf{r}_j(0) - \mathbf{r}_k(0)]$$







Lindemann Criterion (2D Colloidal Crystals): ~0.035
K. Zahn and G. Maret, *Phys. Rev. Lett.* **85**, 3656 (2000)

✓ Carrier motion: anharmonic, not structurally driven.

Results: Anharmonicity – Lindemann Index

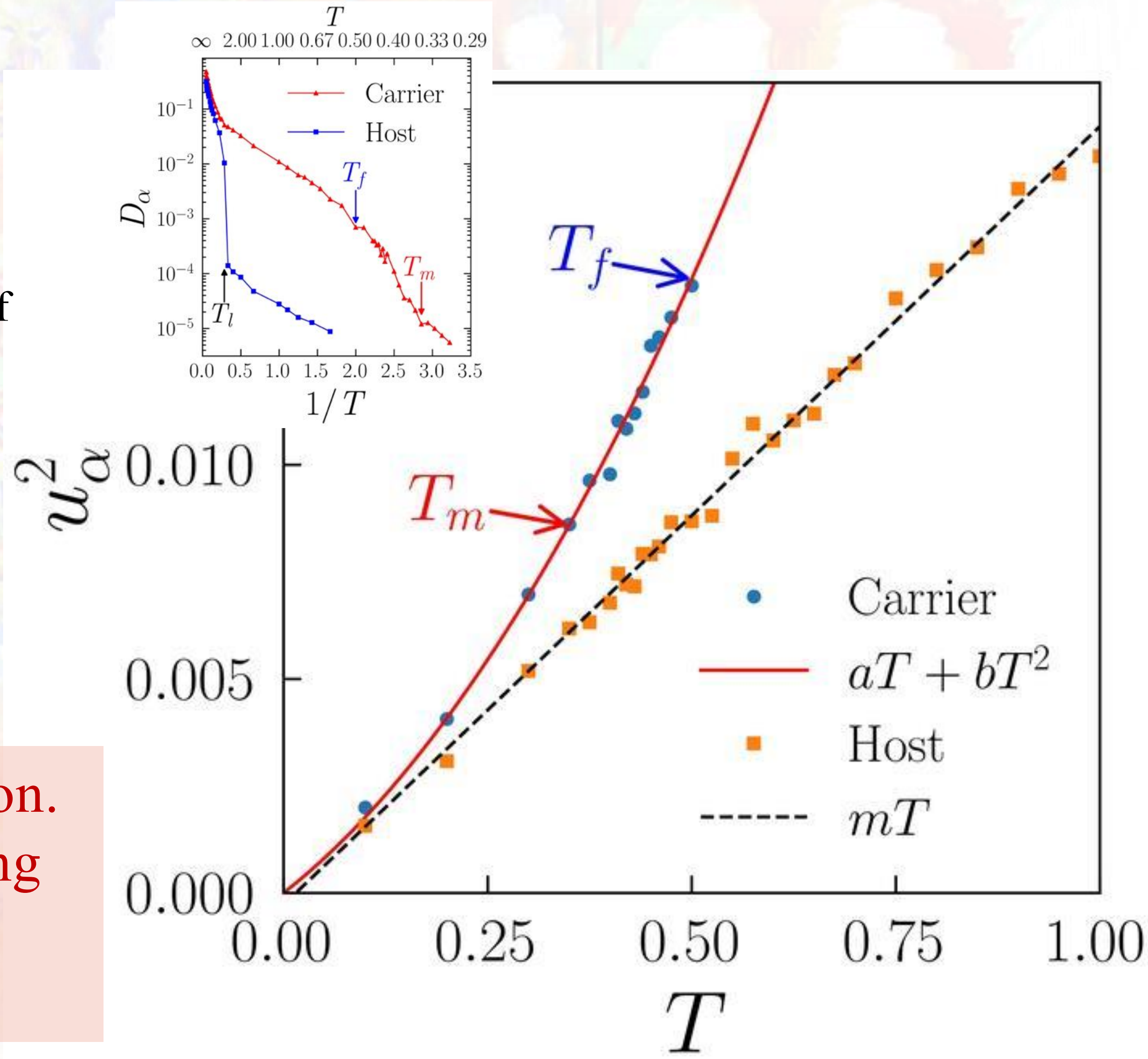
- **Debye–Waller Factor**
  (plateau height)

$$u_\alpha^2 = \gamma_{L,\alpha}(t_p) \quad t_p :$$ inflection point of the plateau

- **Harmonic Vibrational Amplitude**

$$u_\alpha^2 = \int_{2\pi/c}^{\omega_\mathrm{D}} \mathrm{d}\omega g(\omega) \frac{k_B T}{m\omega^2} \propto T$$

- Our model reproduces anharmonic vibration.
- Carrier anharmonicity drives local softening and sublattice melting
- This may result in high diffusivities.

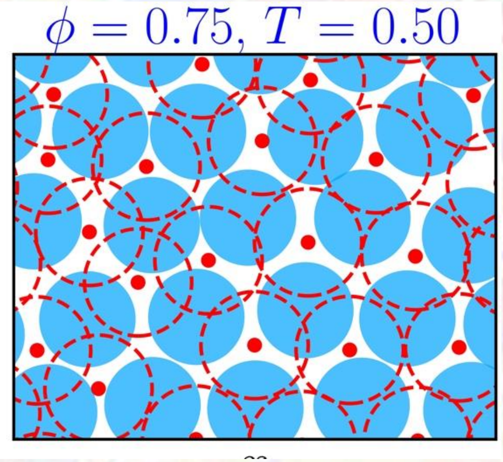


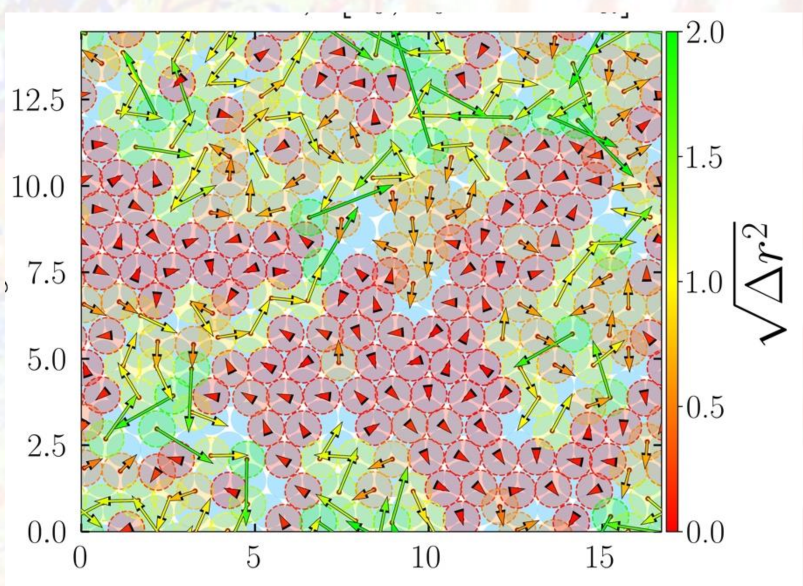
Summary and Perspective

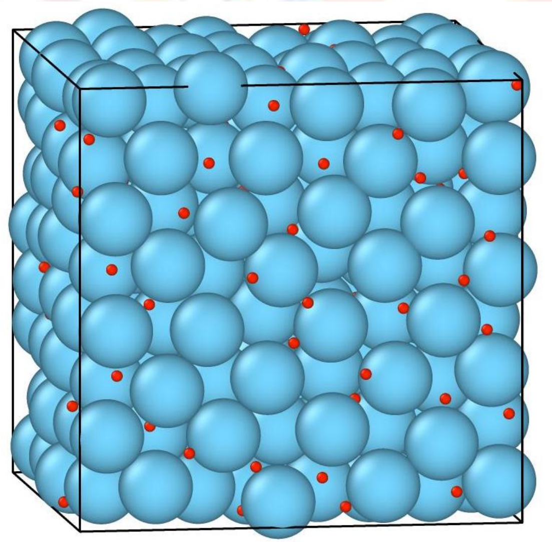
Summary

*S. Niyogi, T. Nakamura, G. Kobayashi, Y. Ando, T. Kawasaki (*submitted*)
https://arxiv.org/abs/2602.05545 (2026)

- Construction of a **minimal model exhibiting sublattice melting**.
- Heterogeneous carrier **dynamics and structure** near the sublattice-melting point.
- **Anharmonic carrier dynamics** is reproduced which may result in high diffusivities.

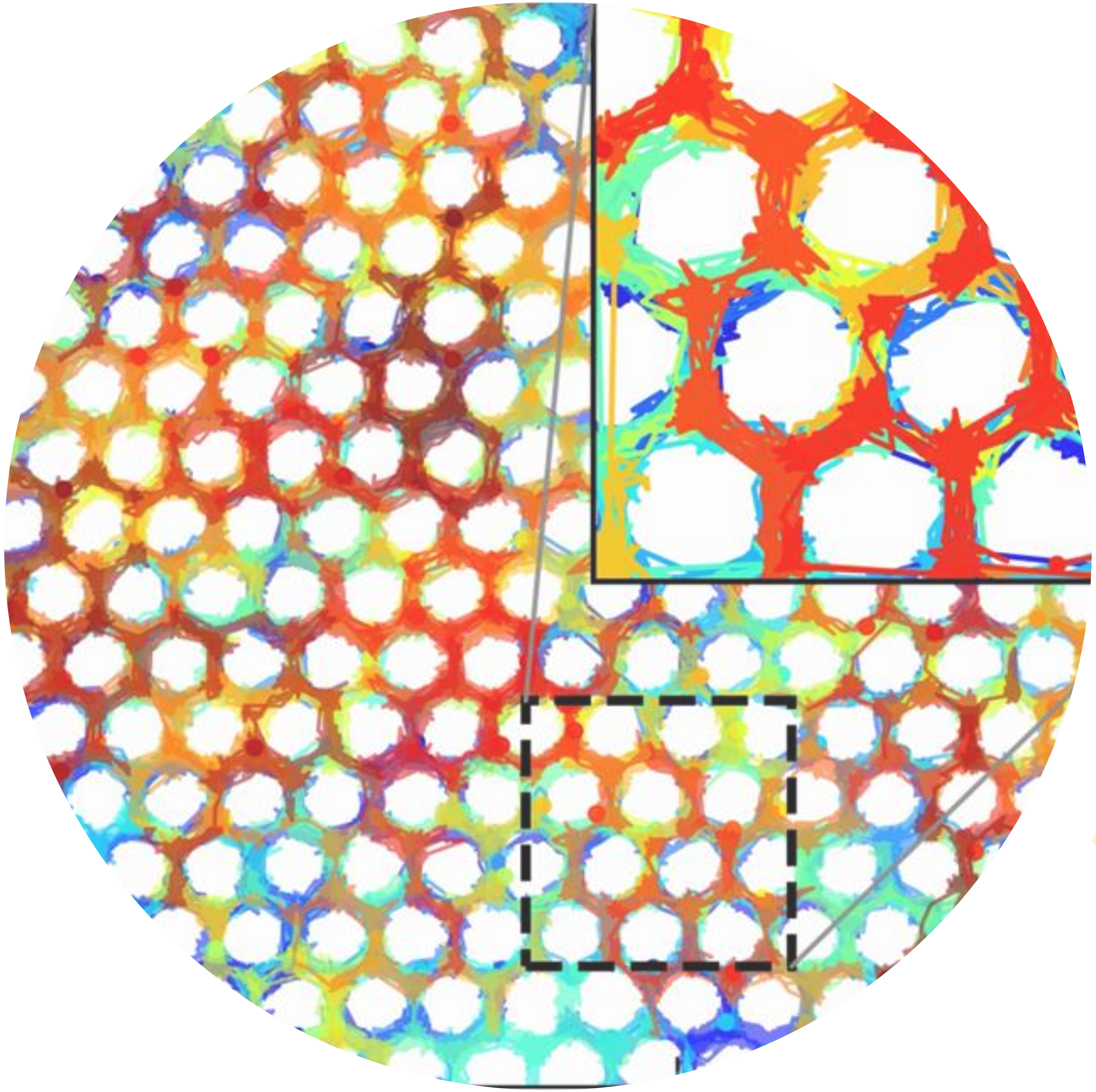






Perspective

- **Introduce structural disorder in the host lattice (polycrystalline and amorphous)**
  - Quantify the enhancement of carrier mobility in interfacial regions.
- **Bridge the simulations with experiments**
  - Provide quantitative guidelines for material design.



Thank You