

Molecular dynamics of Li^+ transport in a model solid electrolyte interphase (SEI)

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Challenges

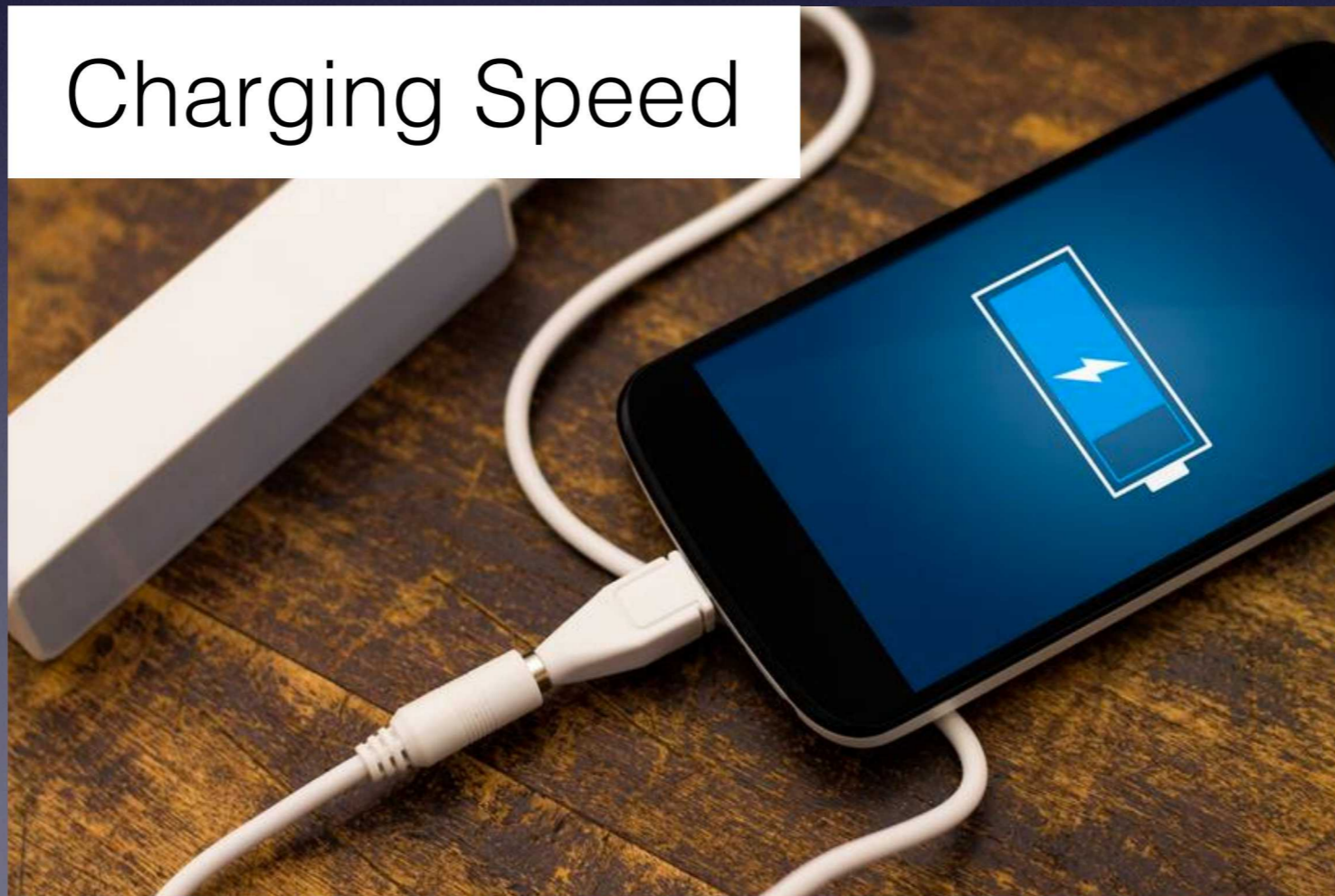
Capacity



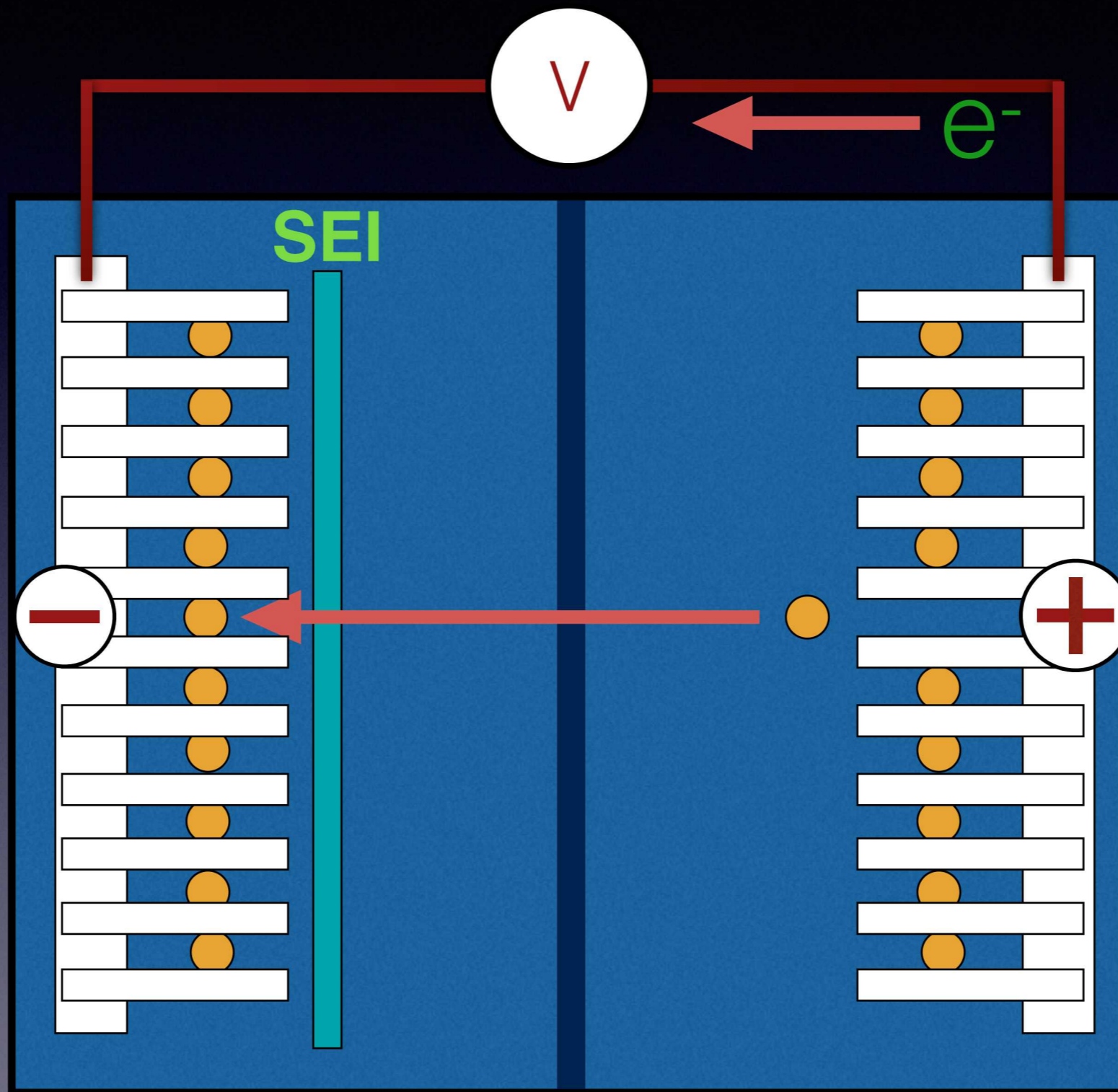
Safety



Charging Speed

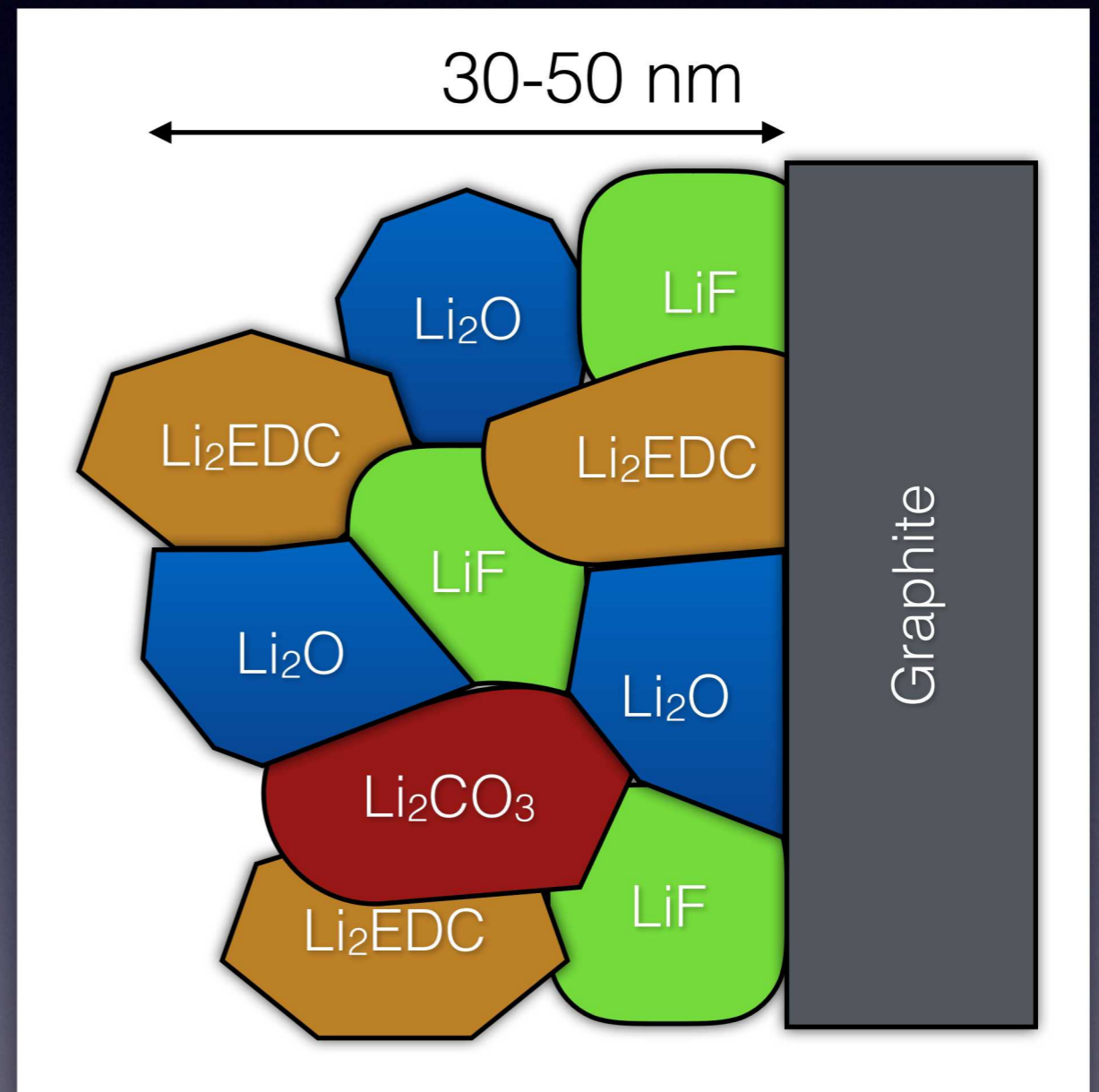


Solid Electrolyte Interphase(SEI)

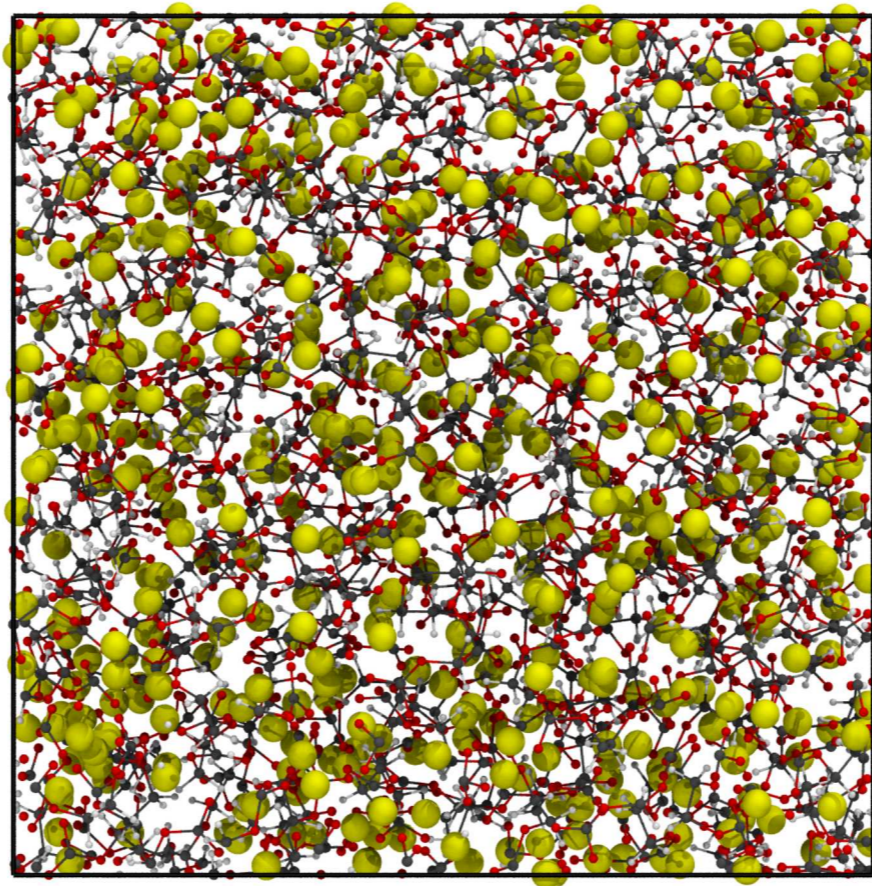
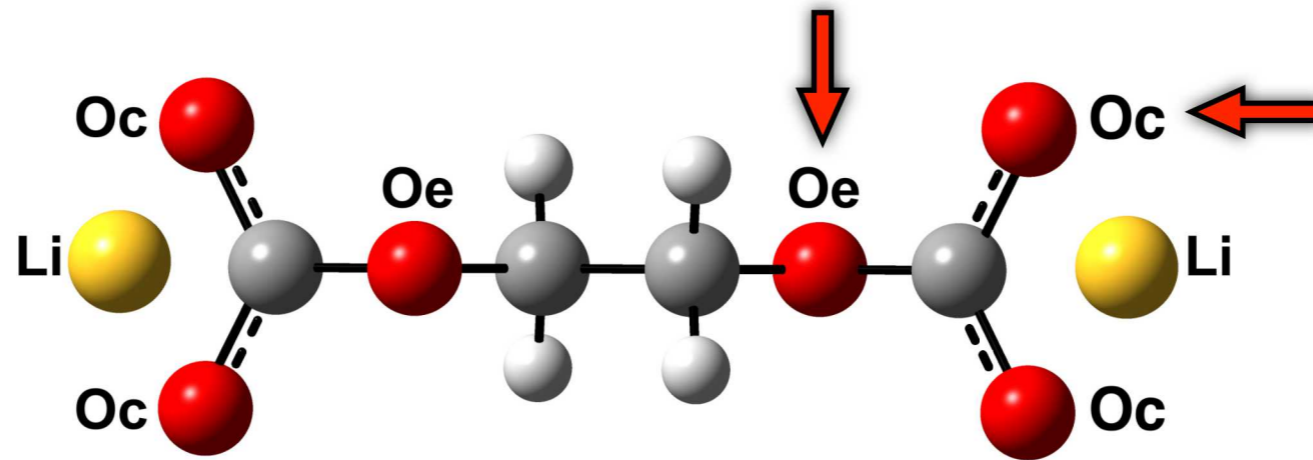


SEI Composition

- Exact composition is unknown.
- Major component :
(Li_2EDC) di-lithium ethylene di-carbonate.



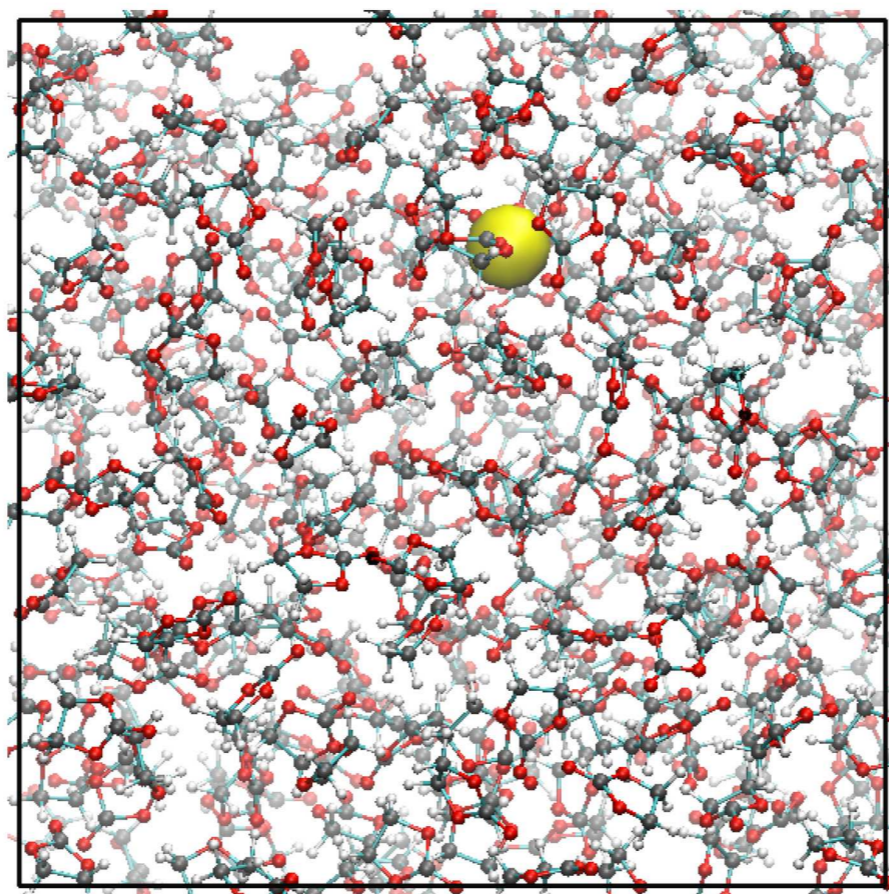
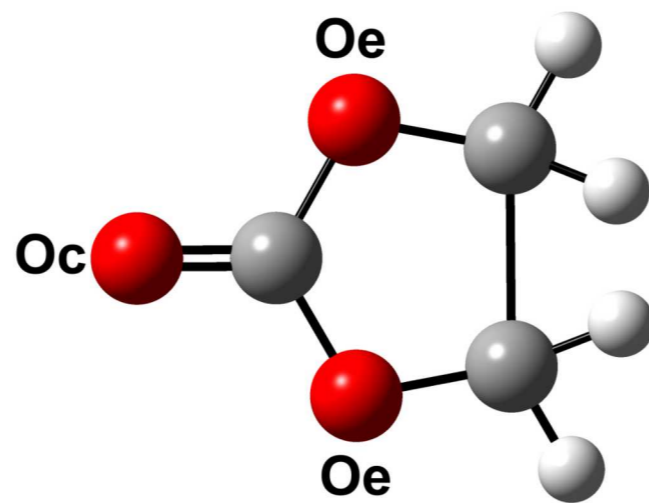
Model SEI = 256 Li₂EDC



512 Li⁺ and 256 **EDC**²⁻

T = **700** → **500** → **333** (K)

Comparison (Li⁺ in EC)



1 Li⁺ in 249 **EC**

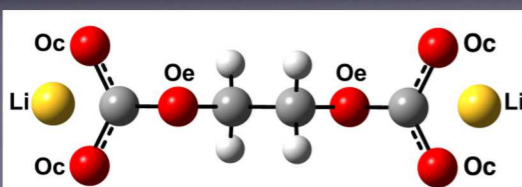
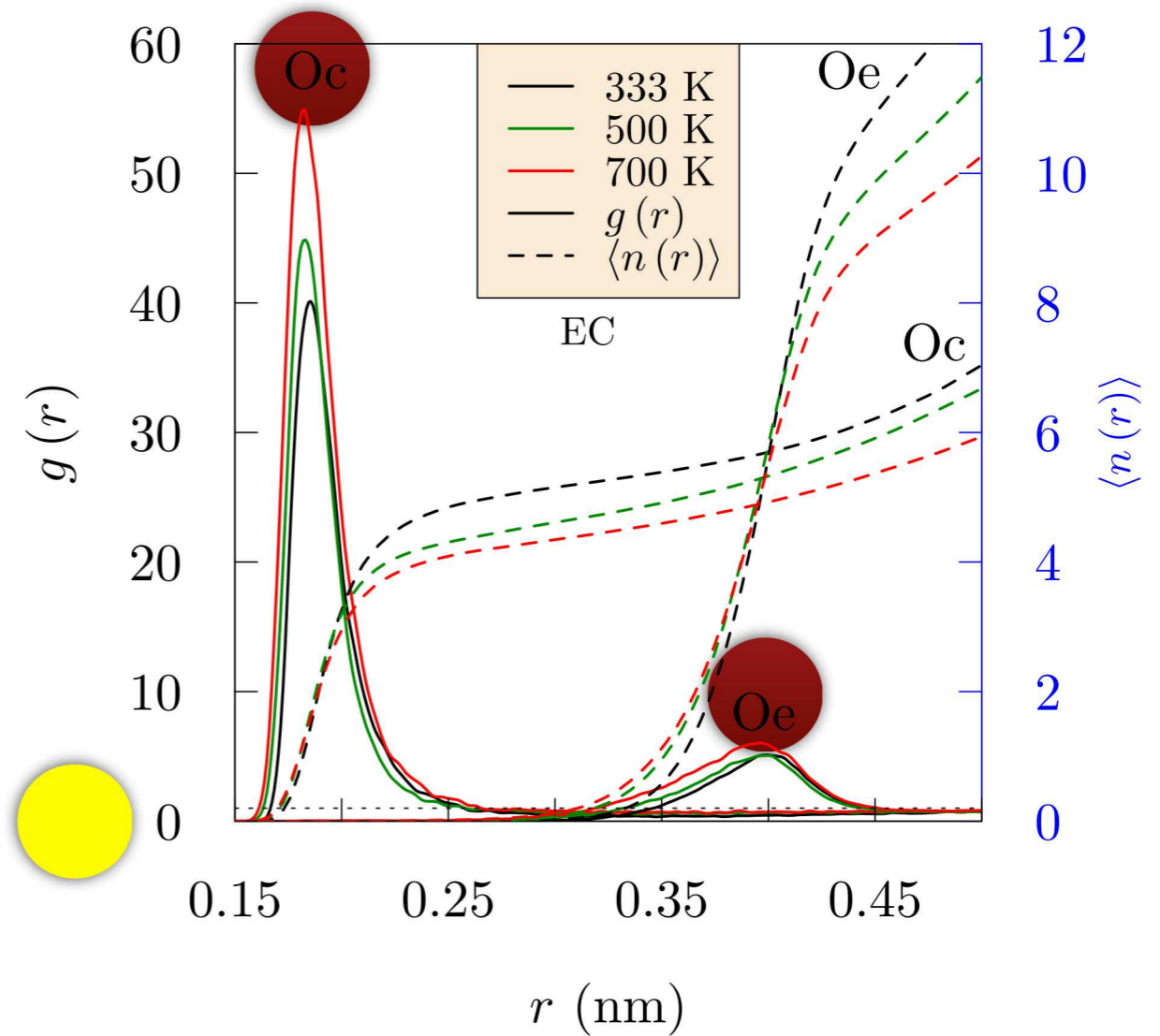
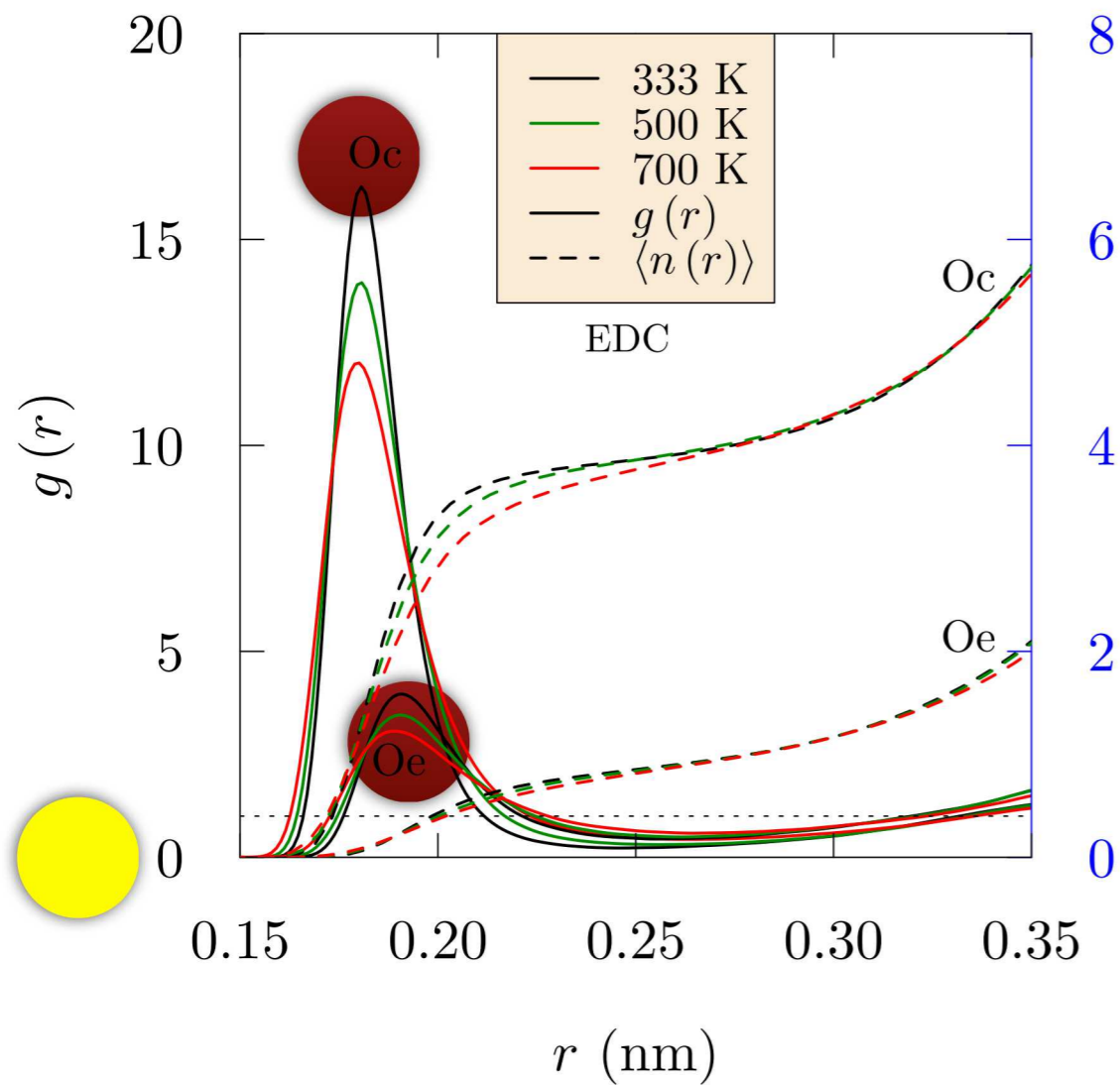
Results

Muralidharan, A; Chaudhari, MI; Pratt, LR; and SB Rempe, *Sci. Rep.* 8:10736 (2018).

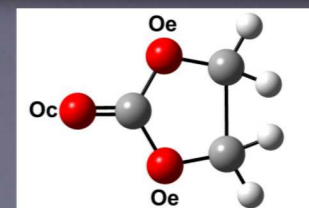
Chaudhari, MI; Muralidharan, A; Pratt, LR; and SB Rempe, *J. Chem. Phys.* 148:222821 (2018).

Chaudhari, MI; Nair, JR; Pratt, LR; Soto, FA; Balbuena, P; and SB Rempe, *J. Chem. Theory Comput.* 12:5709 (2016).

Radial distribution function $g(r)$

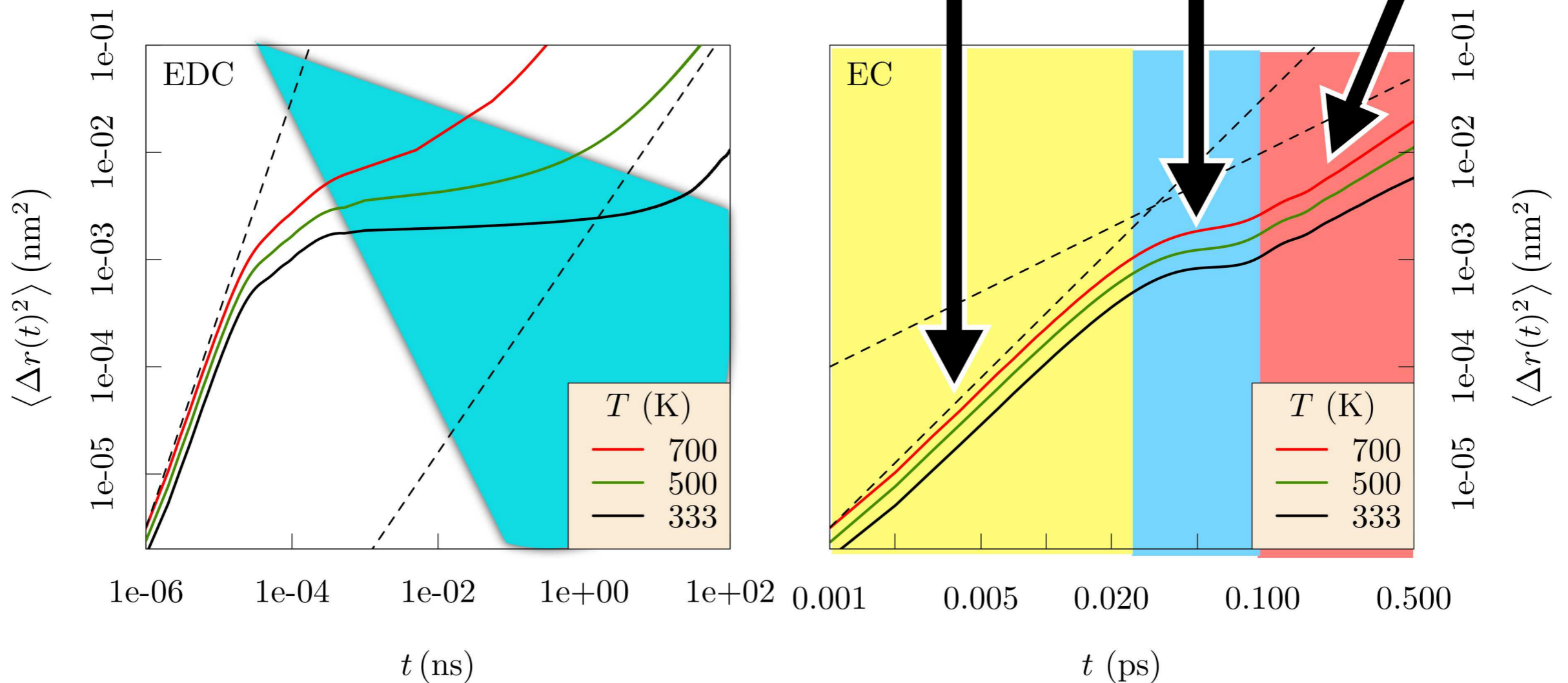


agree w/ polarizable ff results
Borodin et al *JPC C* (2013, 2014)



Mean-squared displacement of Li⁺ ion

ballistic trapping diffusive



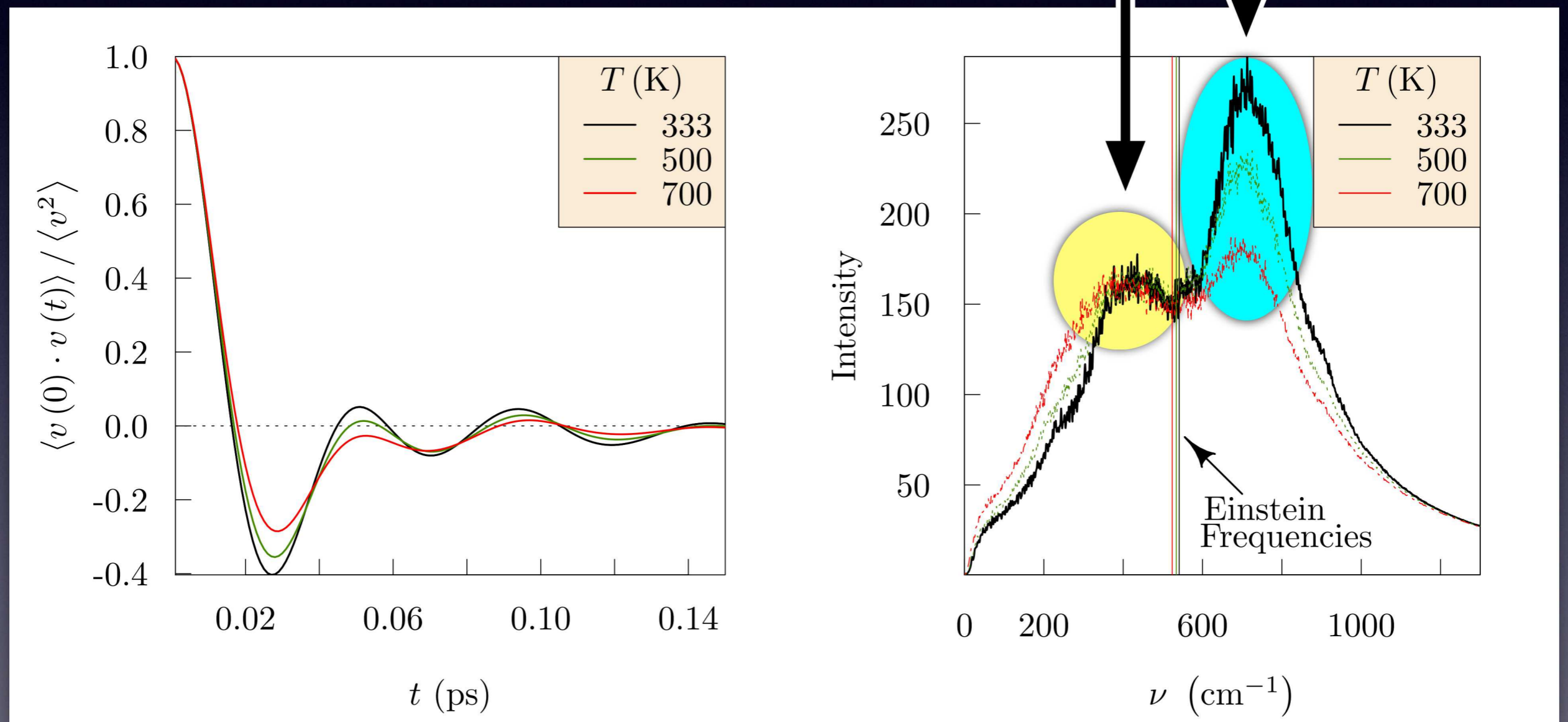
glassy ($D \sim 10^{-12}$ cm²/s, $C \sim 10^{-9}$ S/cm)

liquid ($D \sim 10^{-5}$ cm²/s, $C \sim 10^{-2}$ S/cm)

Vibrational spectra of Li⁺

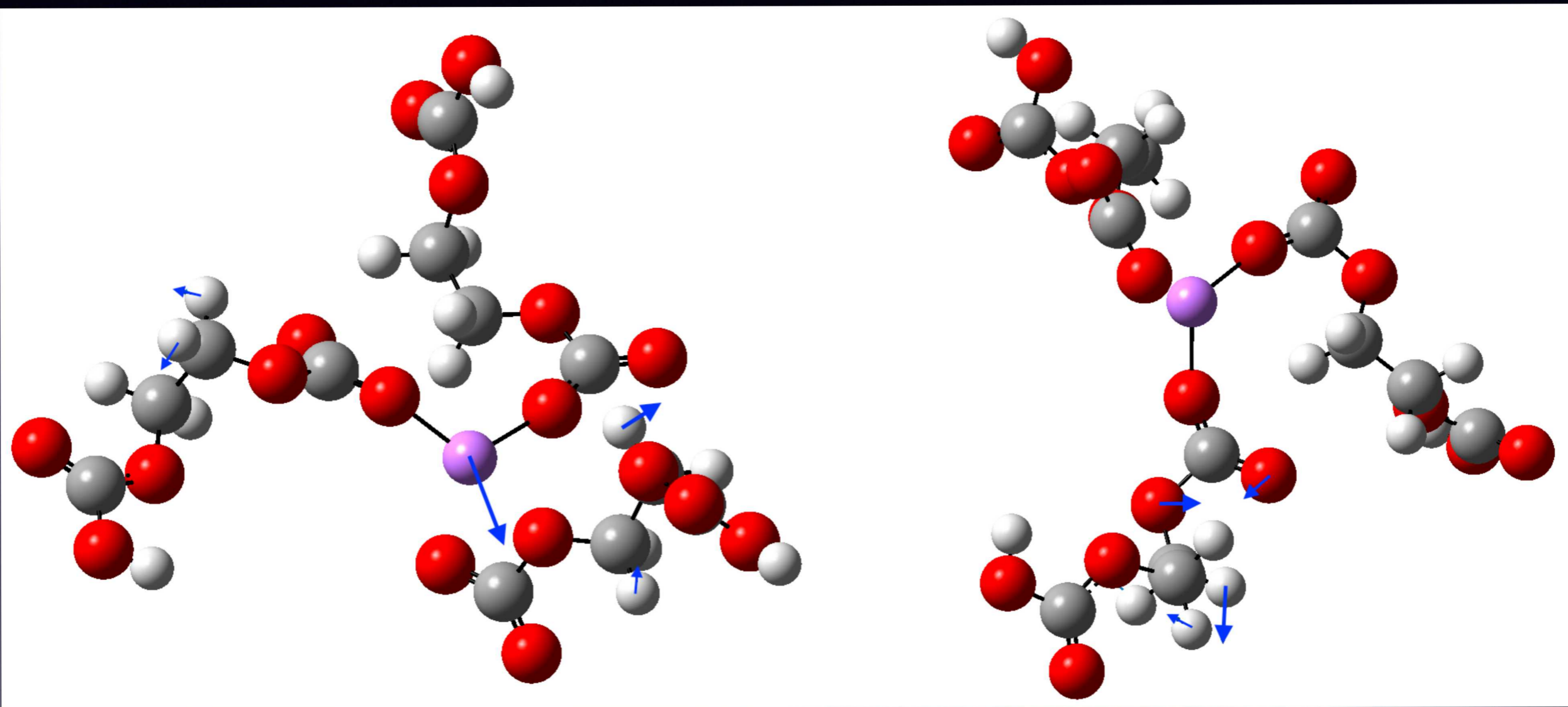
Velocity auto-correlation function

Two prominent modes in EDC



Li in EDC

Identification of Li modes



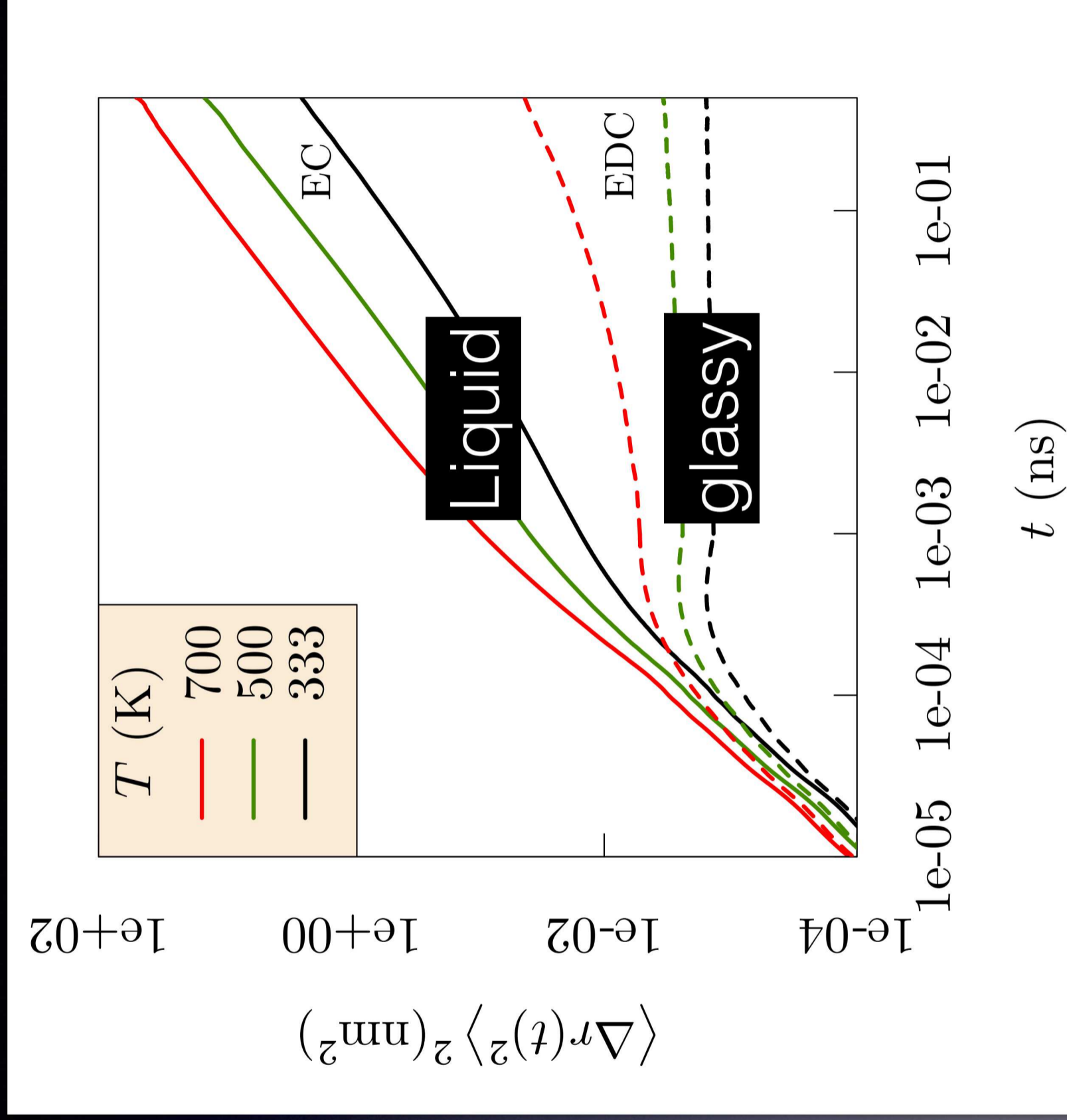
436 cm^{-1}

Li trapped in cage

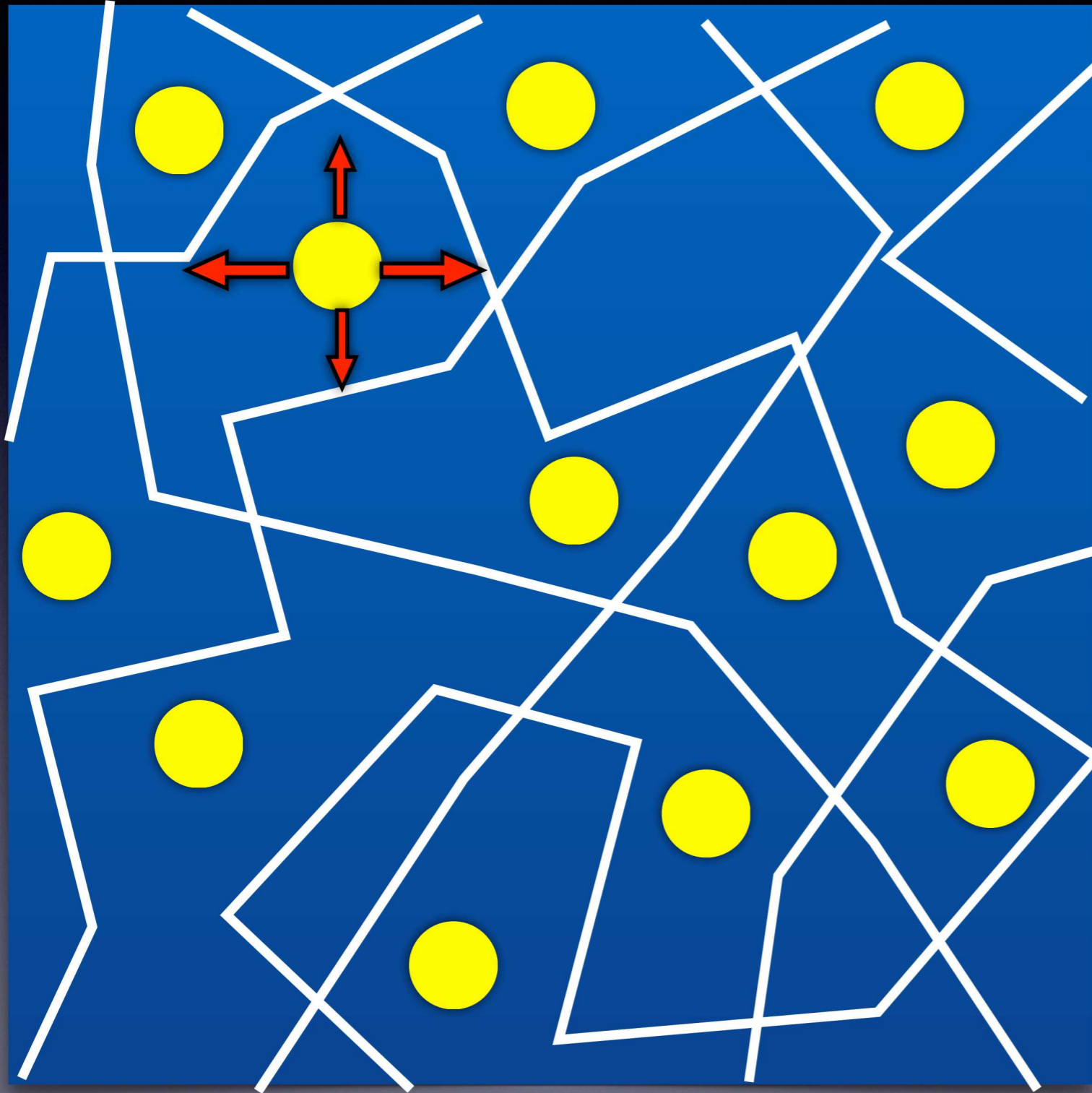
681 cm^{-1}

EDC moves

Mean-squared displacement of EDC and EC solvents (CO₃)



SEI story so far..



- Glassy EDC matrix
- Li⁺ trapped in cages
- 436 & 681 cm⁻¹
- Li⁺ jump Probabilities?
- Li⁺-Li⁺ correlations?

Van Hove time correlation function for Li⁺

$$G(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta(\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_i(t)) \right\rangle$$

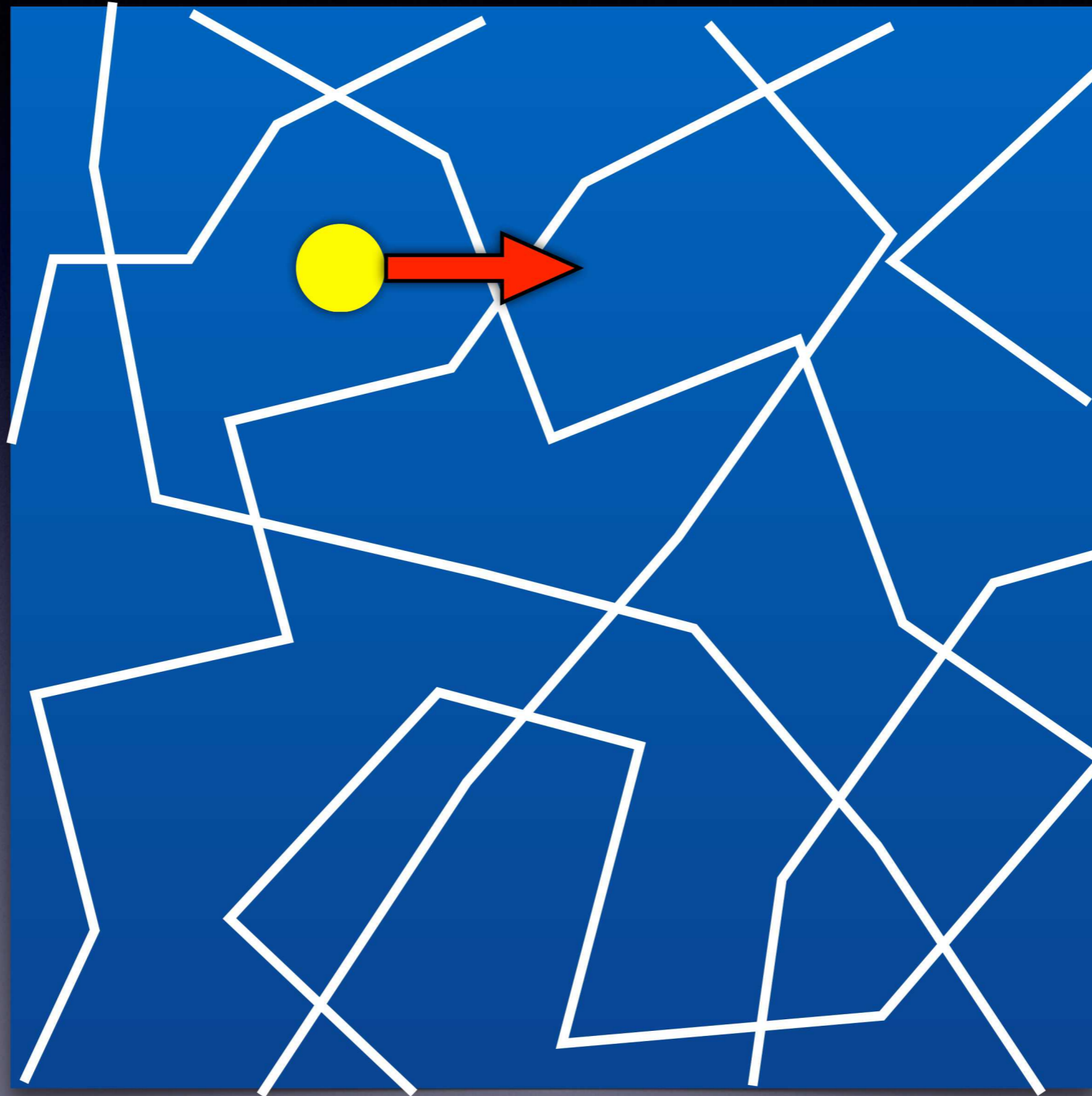
$$G(r, t) = G_s(r, t) + G_d(r, t)$$

$$i = j \quad i \neq j$$

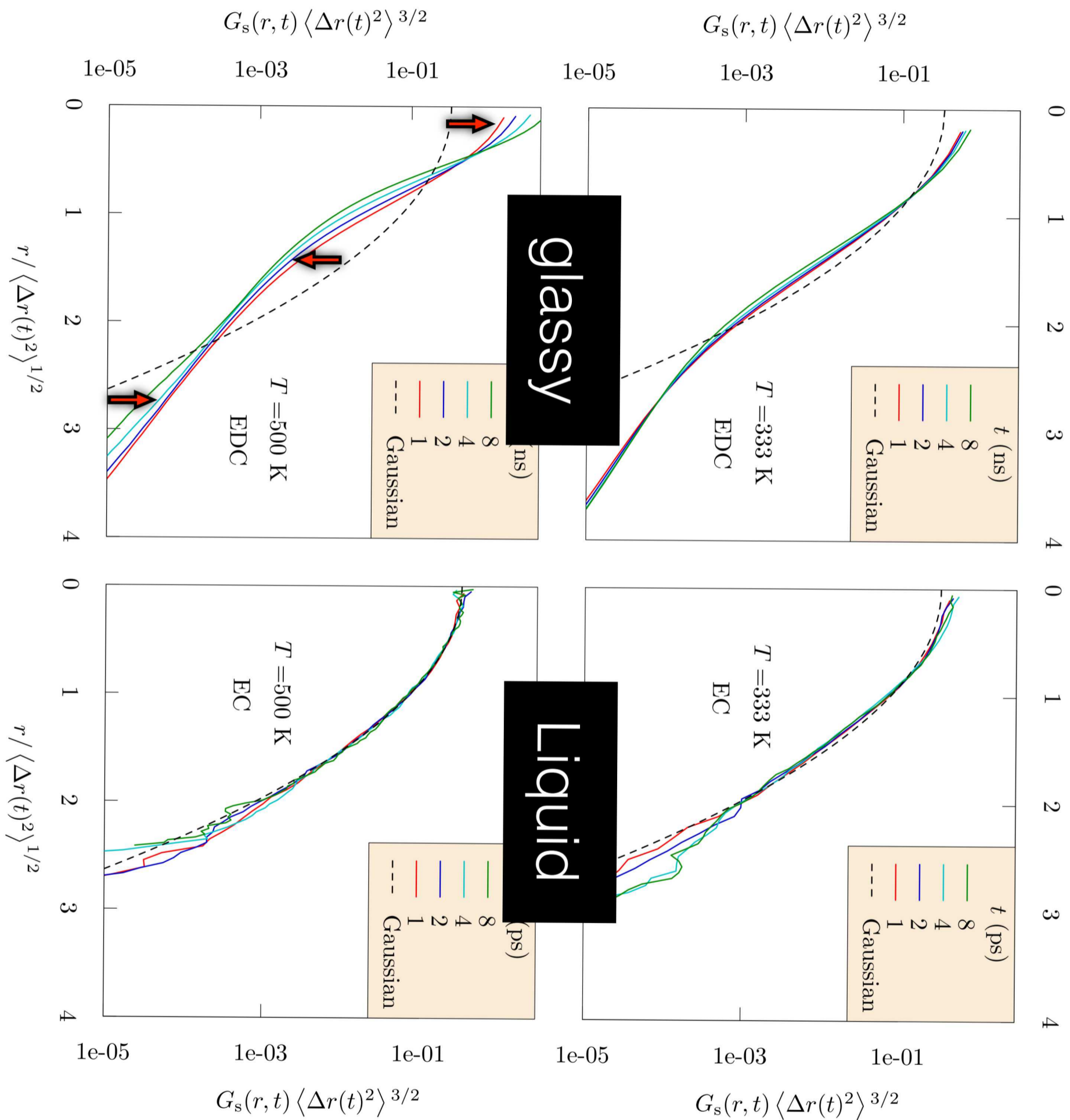
Self Distinct

- Experimental access: Neutron scattering

Self part - Jump probability

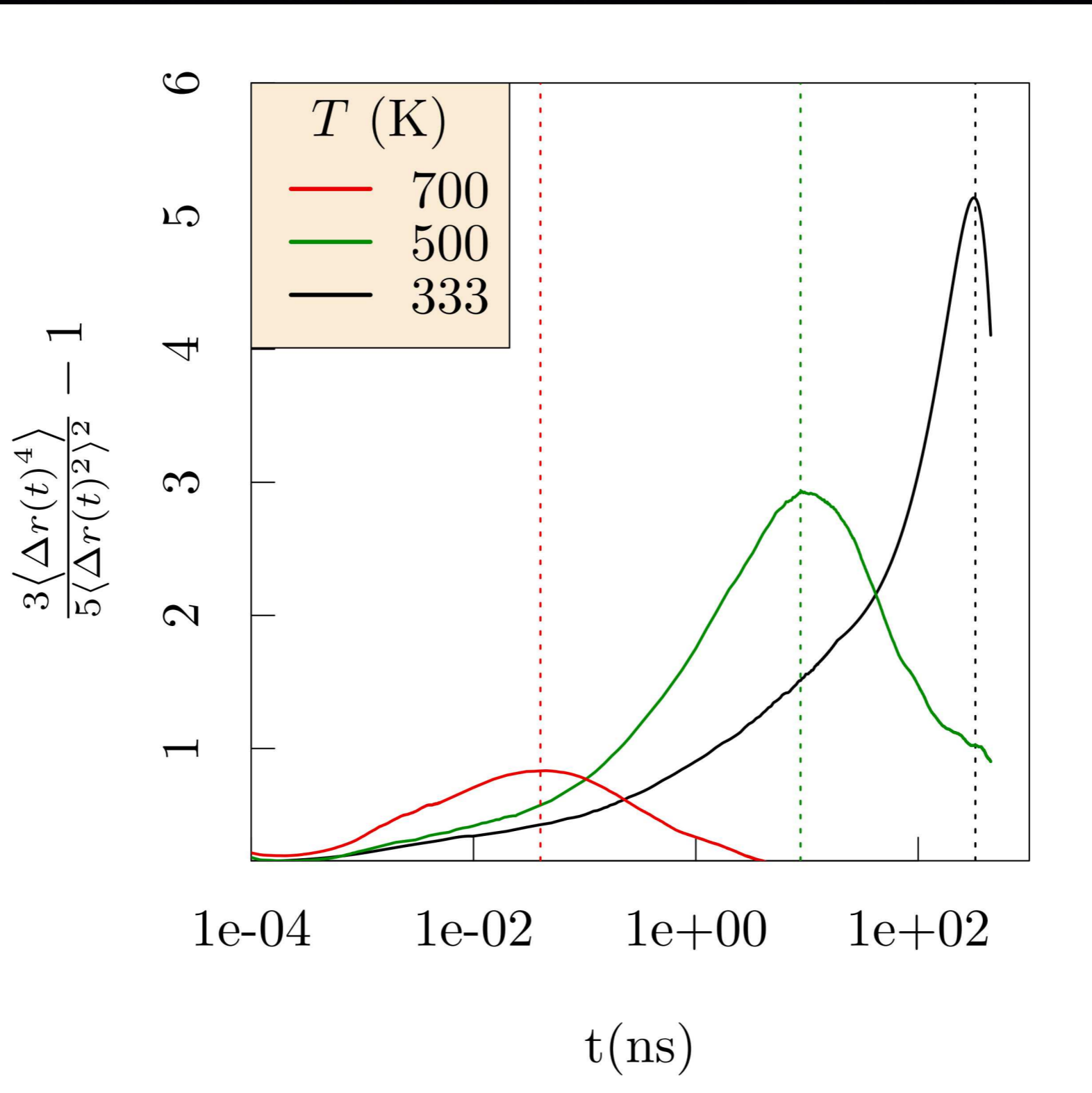


Self part of van Hove function

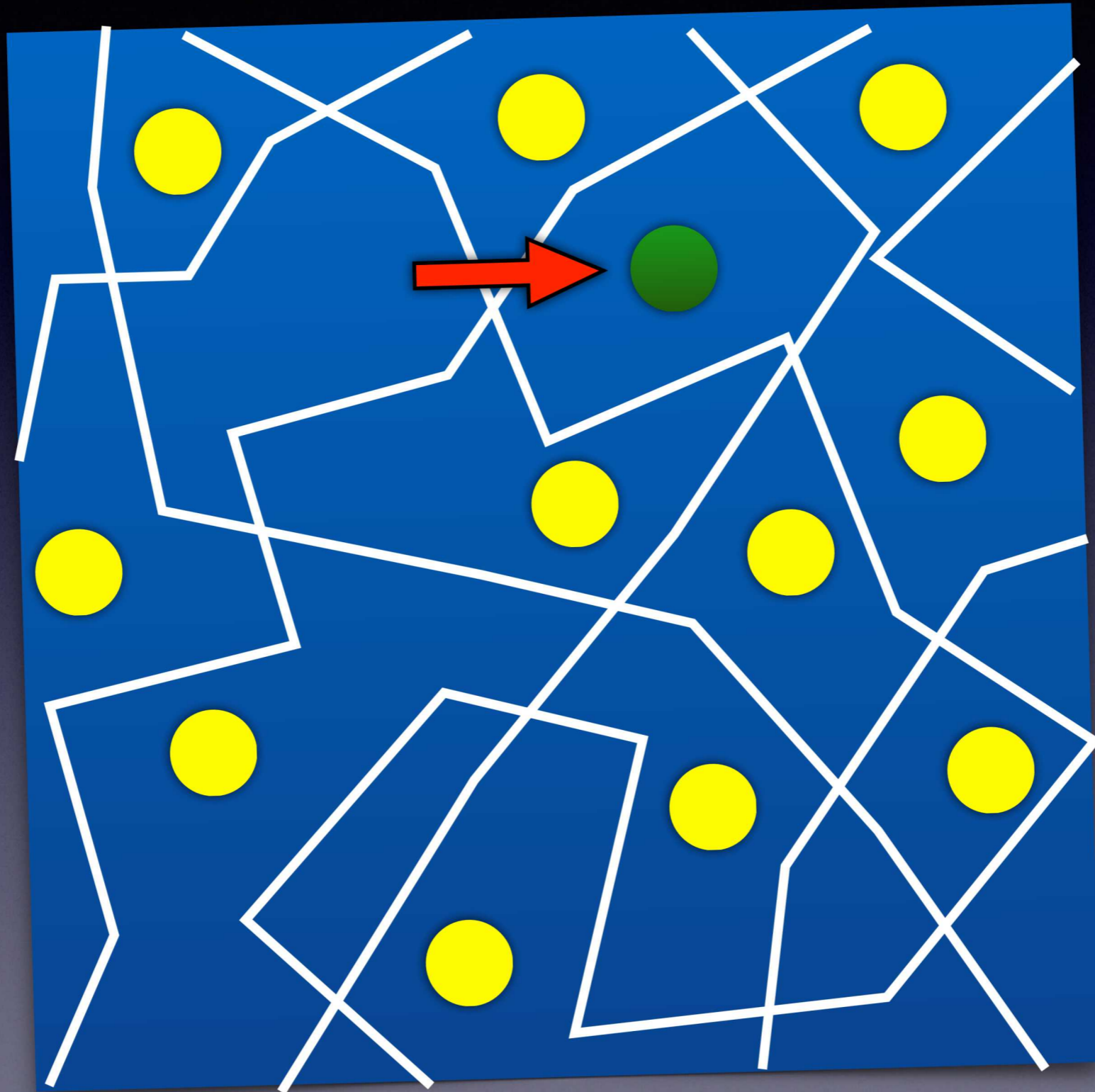


$$\alpha(t) = \frac{3\langle\Delta r(t)^4\rangle}{5\langle\Delta r(t)^2\rangle^2} - 1$$

Non Gaussian parameter for Li (EDC)



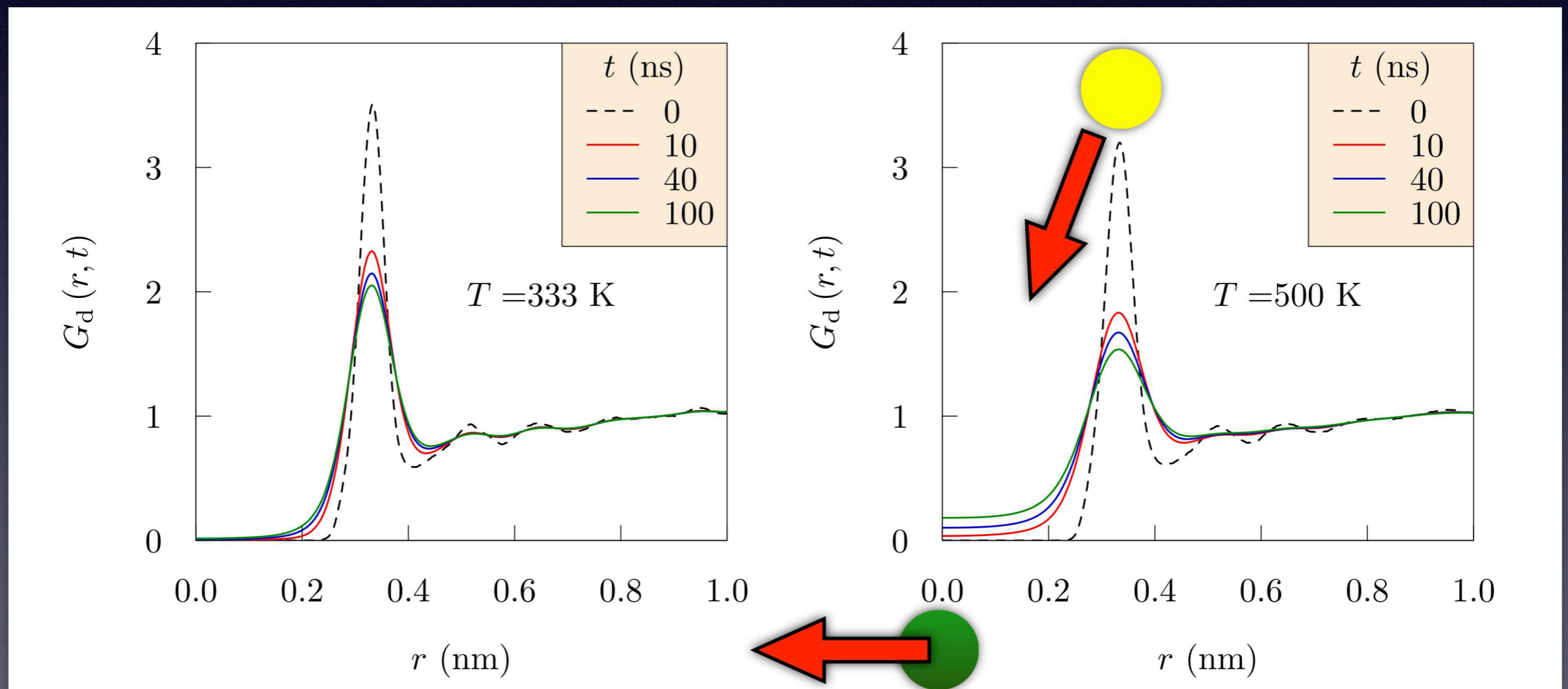
Distinct part



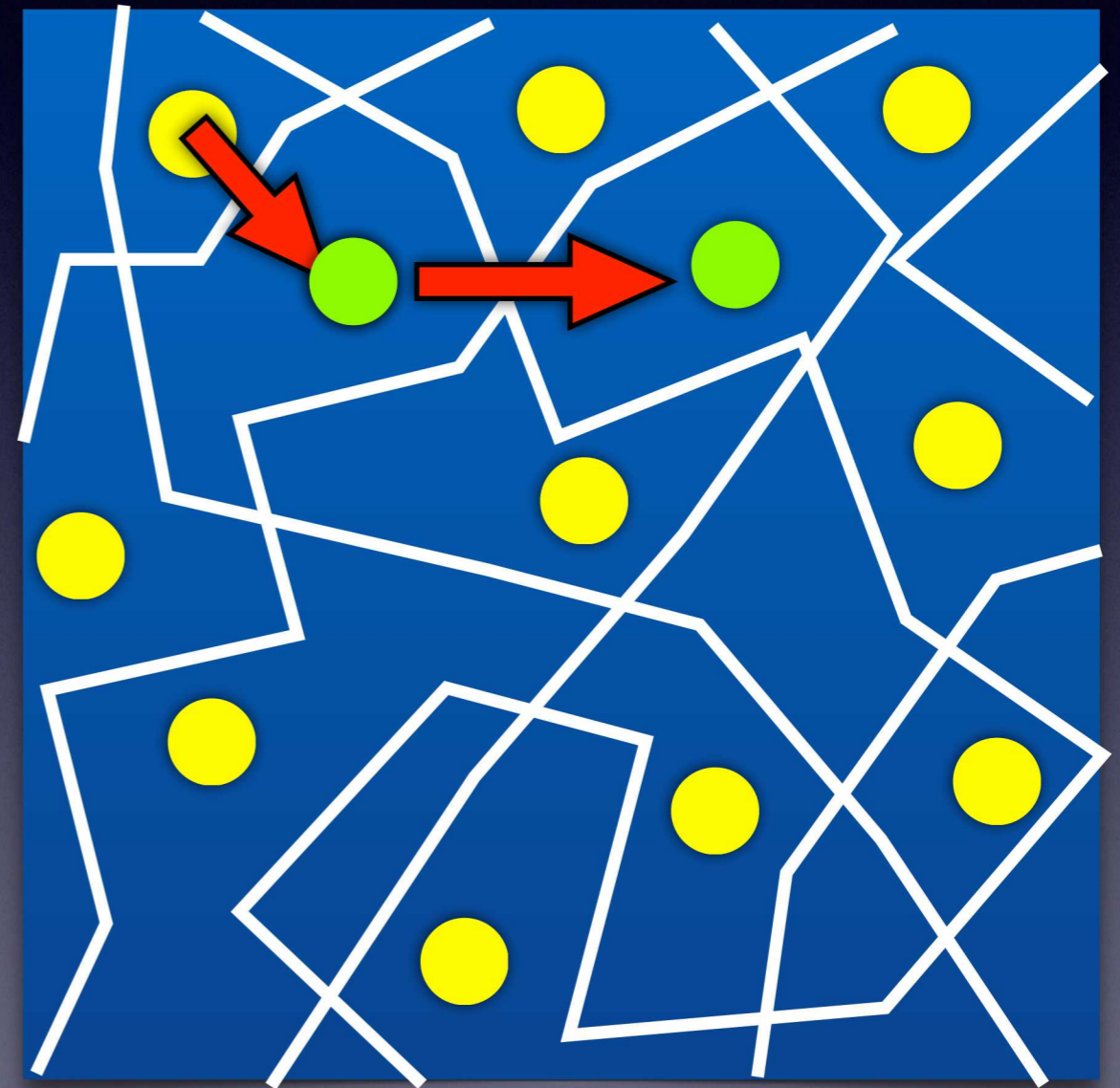
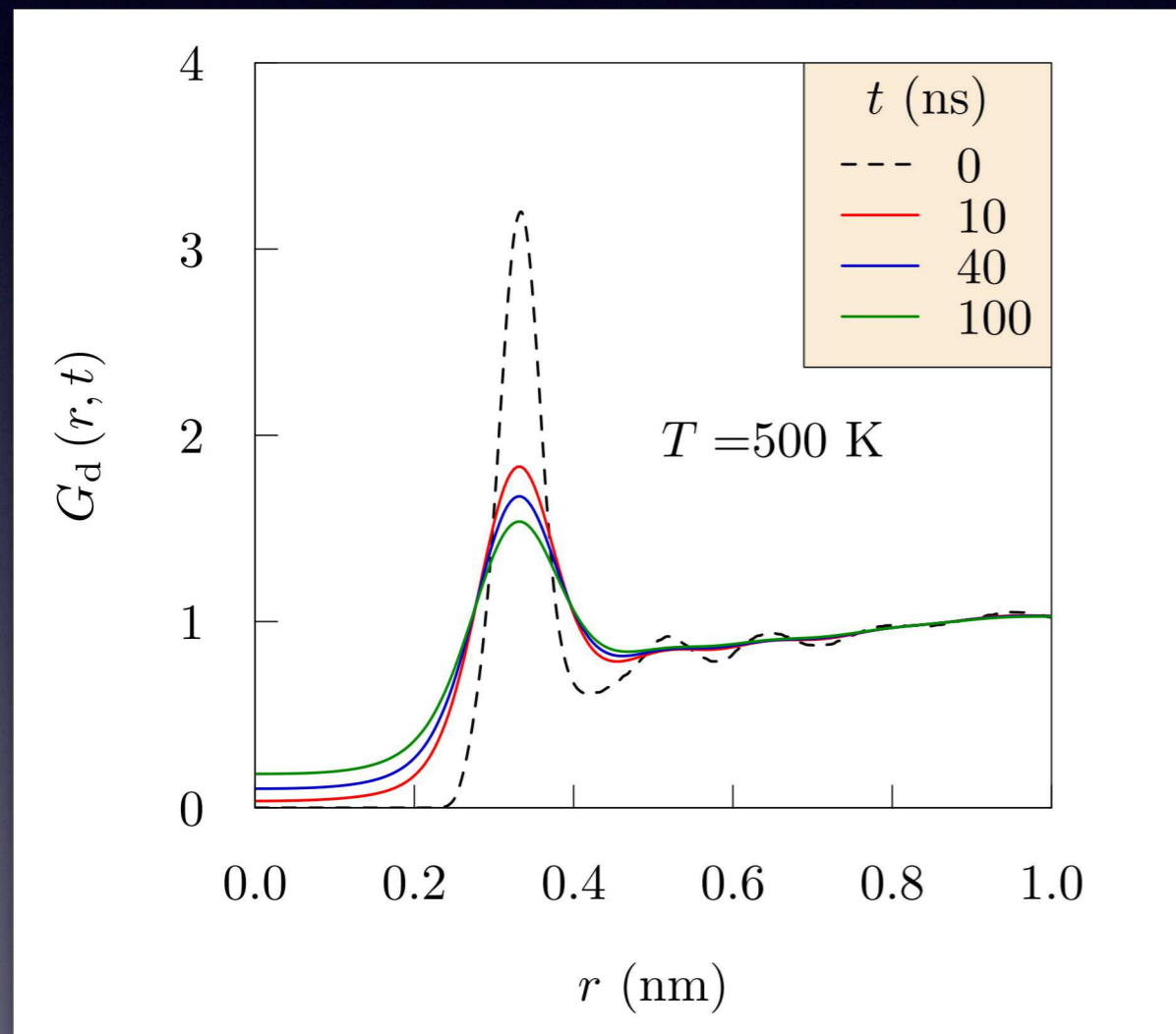
Distinct part of van Hove function

Vineyard approximation,

$$G_d(r, t) \approx \int d^3 r' g(r') G_s(|\mathbf{r} - \mathbf{r}'|, t)$$



Hopping of Li-ions



Summary

- Li^+ is trapped in cages formed by EDC matrix.
- Huge trapping lifetimes (>10 ns at 333 K).
- Frequencies of the trapped Li^+ : 436 & 681 cm^{-1}
- Non-Gaussian Li^+ jump probabilities.
- Li^+ jumps are correlated.

Acknowledgements

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