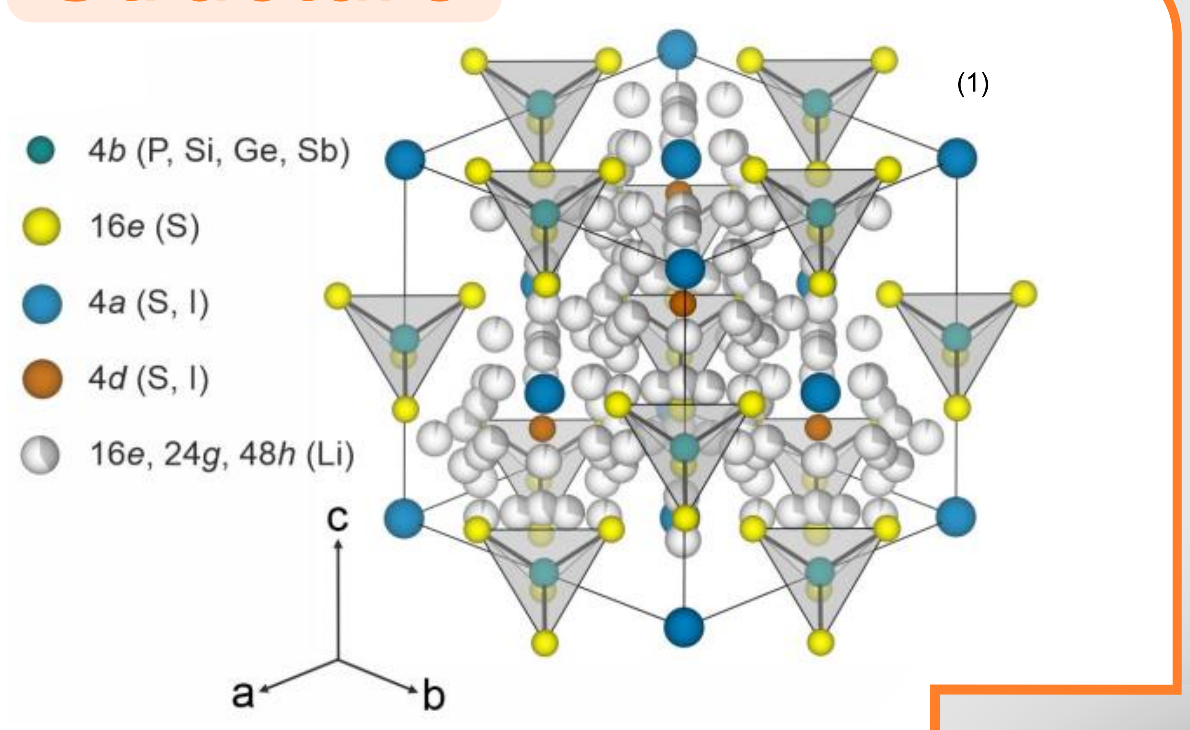
Ion dynamics of multicationic substituted High-Entropy Argyrodite Superionic Conductors

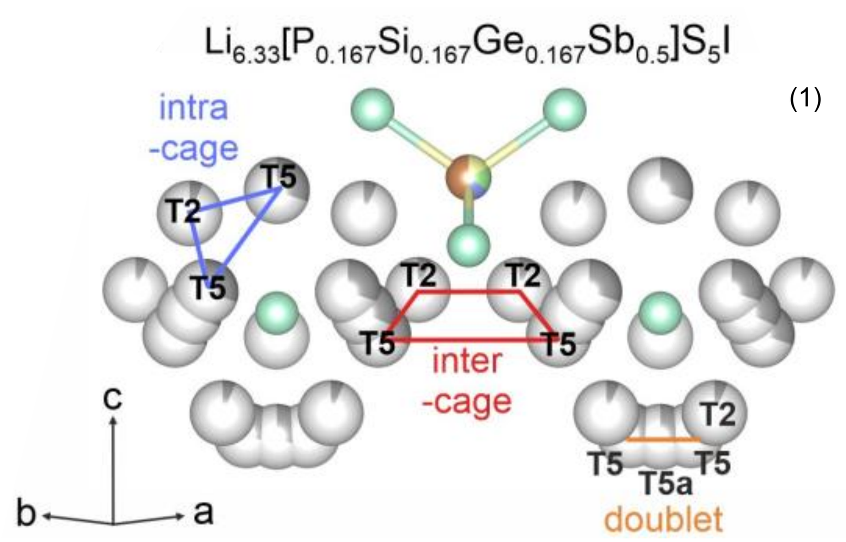
Mareen Schaller*, Jing Lin, Florian Strauss and Sylvio Indris
*mareen.schaller@kit.edu; *Karlsruher Institute of Technology, IAM-ESS

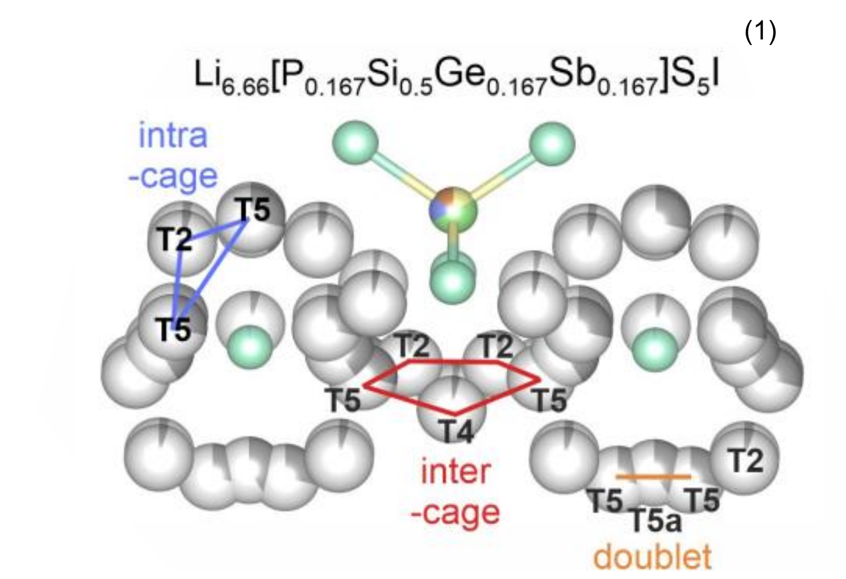
Interested?

Visit:
- Jing Lin; Tue 11:55-12:10 (Gielgud-O2)
- Florian Strauss; Tue 10:35-10:50 (Gielgud-O1)

Structure

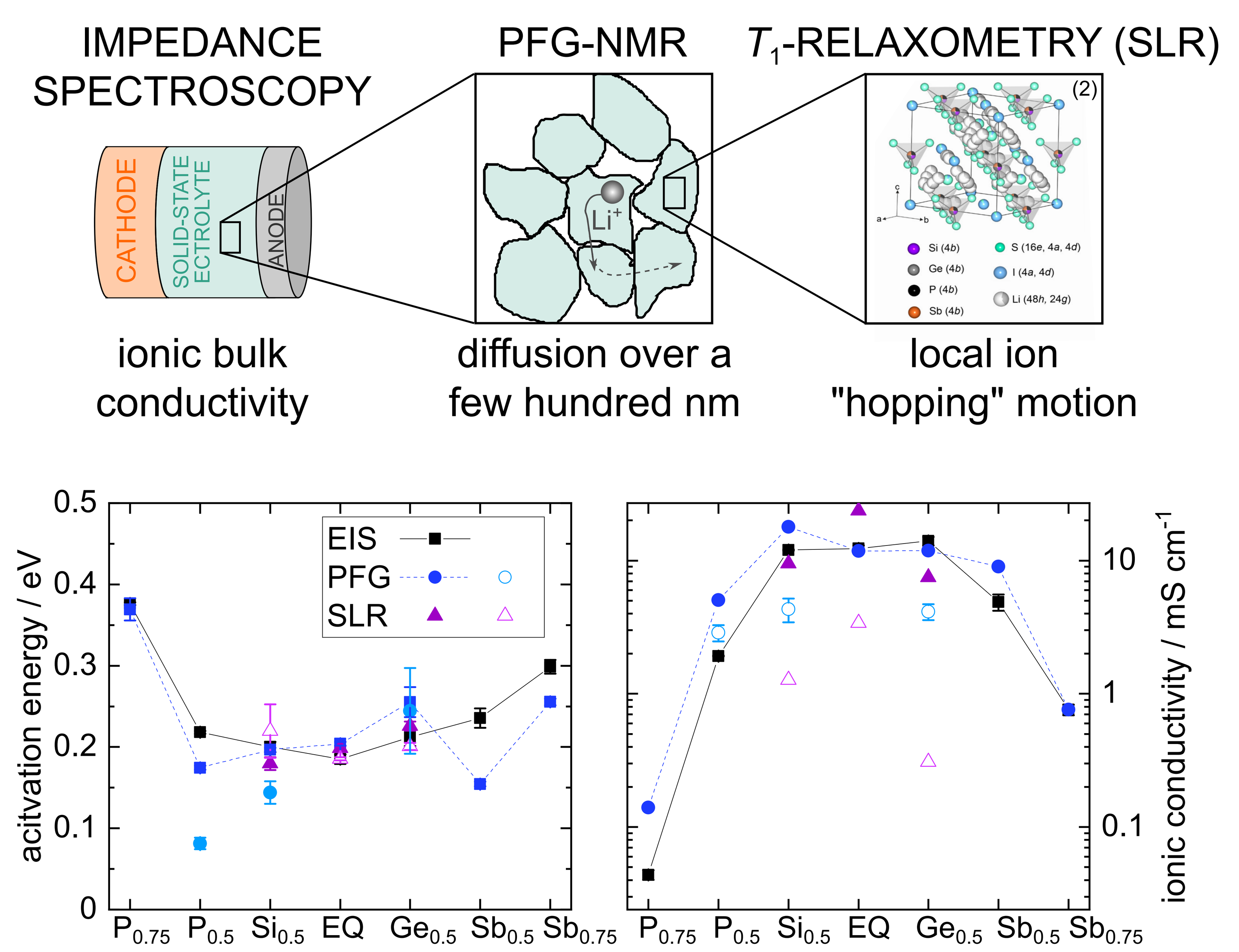




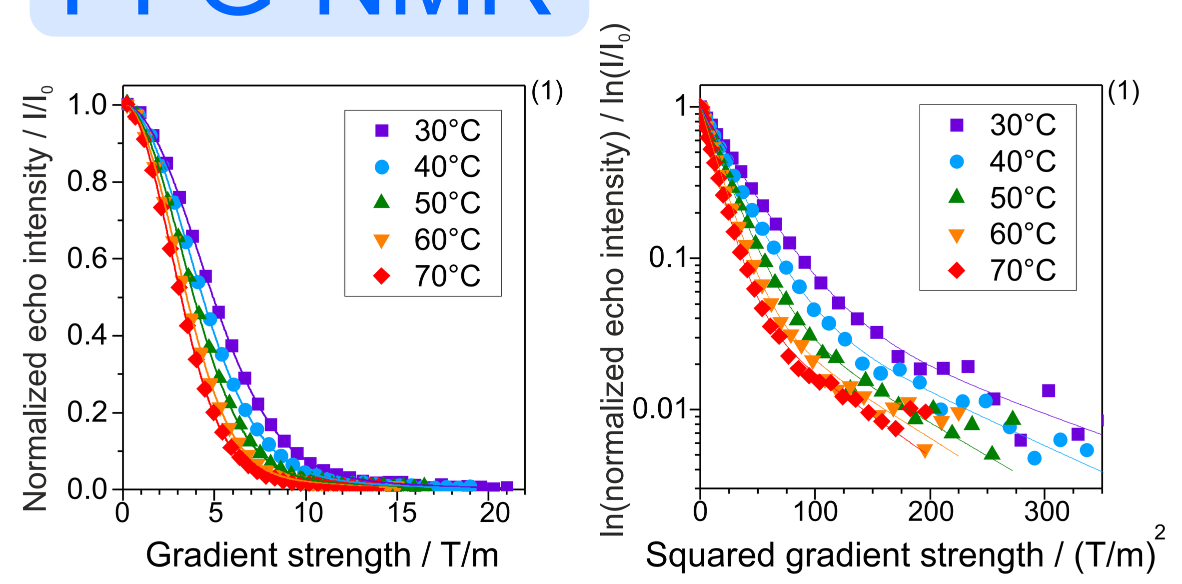


Samples

$P_{0.75}$:	$Li_{6.17}[\mathbf{P_{0.75}}Si_{0.083}Ge_{0.083}Sb_{0.083}]S_5I$
$P_{0.5}$:	$Li_{6.33}[\mathbf{P_{0.5}}Si_{0.167}Ge_{0.167}Sb_{0.167}]S_5I$
$Si_{0.5}$:	$Li_{6.66}[P_{0.167}\mathbf{Si_{0.5}}Ge_{0.167}Sb_{0.167}]S_5I$
EQ:	$Li_{6.5}[P_{0.25}Si_{0.25}Ge_{0.25}Sb_{0.25}]S_5I$
$Ge_{0.5}$:	$Li_{6.66}[P_{0.167}Si_{0.167}\mathbf{Ge_{0.5}}Sb_{0.167}]S_5I$
$Sb_{0.5}$:	$Li_{6.33}[P_{0.167}Si_{0.167}Ge_{0.167}\mathbf{Sb_{0.5}}]S_5I$
$Sb_{0.75}$:	$Li_{6.17}[P_{0.083}Si_{0.083}Ge_{0.083}\mathbf{Sb_{0.75}}]S_5I$

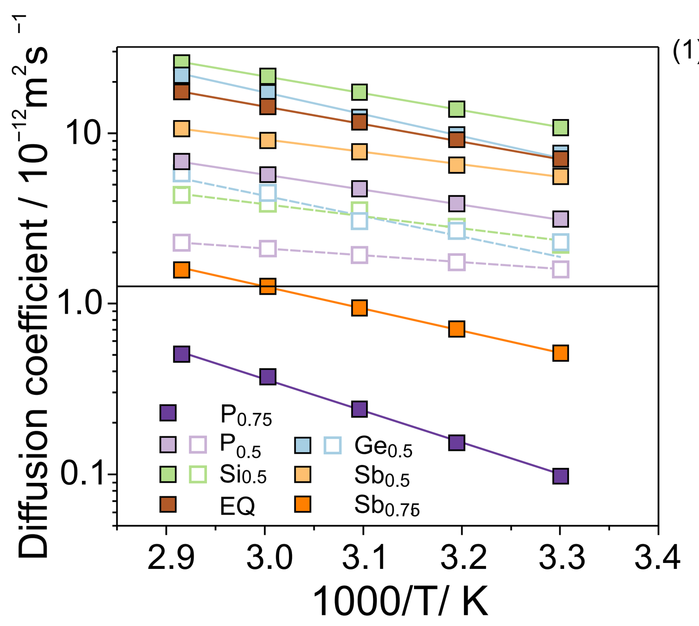


PFG-NMR



$$I/I_0 = \exp\left(-D\gamma^2\delta^2 g^2(\Delta - \delta/3)\right)$$ [3]

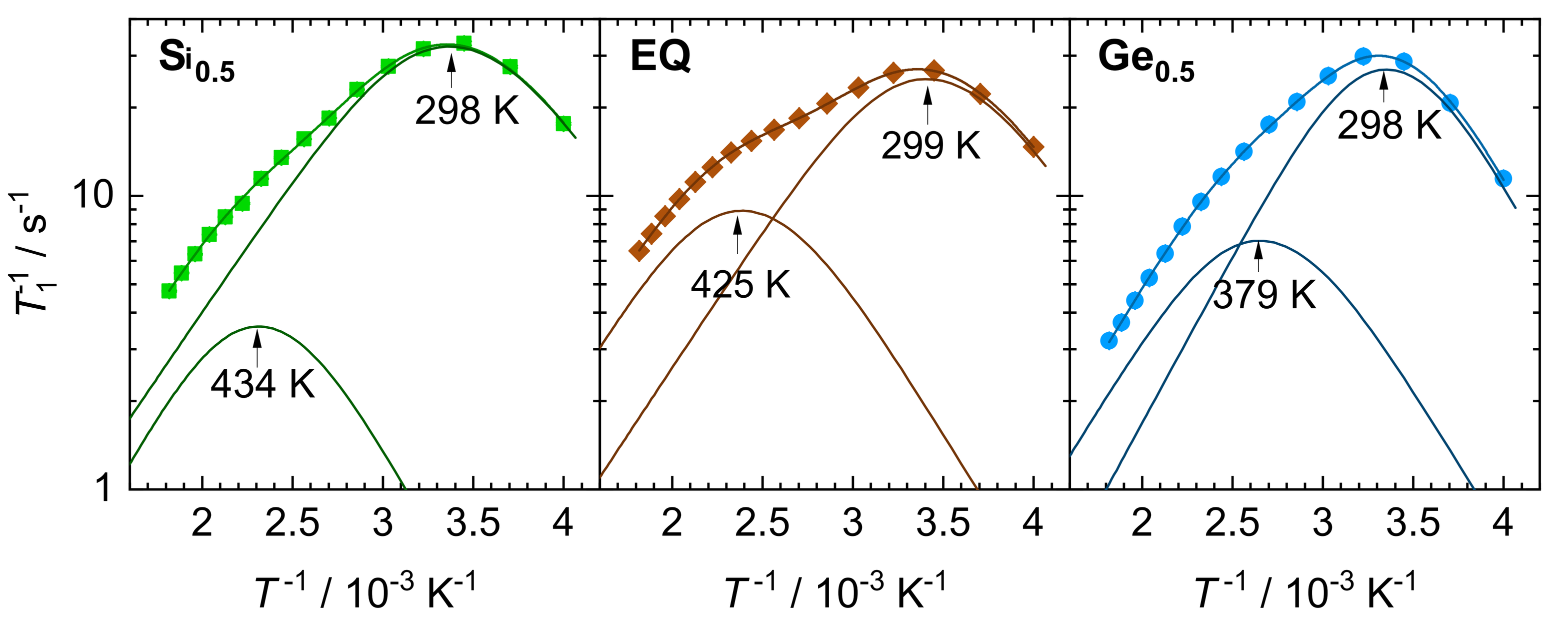
D: diffusion coefficient; γ: magnetogyric ratio; δ: gradient pulse duration; *g*: gardient strength; Δ: diffusion time



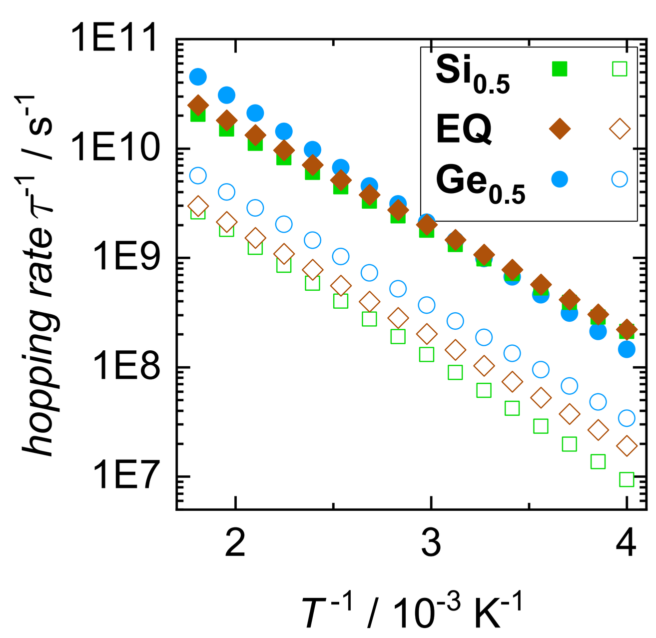
activation energy / eV

$P_{0.75}$	0.26	**EQ**	0.20
$P_{0.5}$	0.17 / 0.08	**$Ge_{0.5}$**	0.20 / 0.14
$Si_{0.5}$	0.26 / 0.24	**$Sb_{0.5}$**	0.15
		$Sb_{0.75}$	0.37

^{7}Li T_1-relaxometry



	activation energy / eV	
	fast	slow
$Si_{0.5}$	0.18	0.22
EQ	0.20	0.19
$Ge_{0.5}$	0.23	0.20



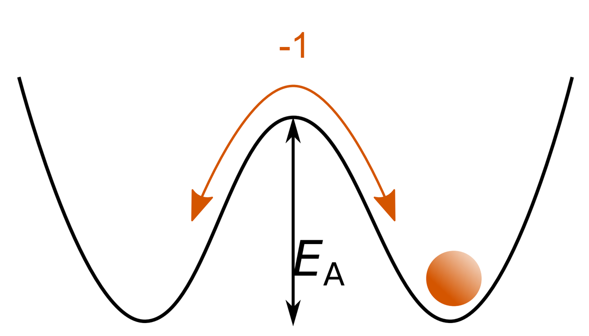
- Estimate diffusion via Einstein-Smoluchowski equation[4,5]
  $D = l^2 / (6\cdot\tau)$
  l: average jump length of Li^+-ions
- Estimate conductivity σ via Nernst-Einstein equation[5]:
  $$D = \frac{\sigma \cdot k_B \cdot T}{N \cdot q^2}$$
  N: particle concentration;
  q: charge of charge carriers

Spin-lattice relaxation - theory

- The hopping of Li^+ ions from one site to another within the crystal lattice enables fast ion diffusion
- The **local** jump motion (correlation rate τ^{-1}) can be investigated using T_1-relaxtion times and analyzed using the BPP theory[6]

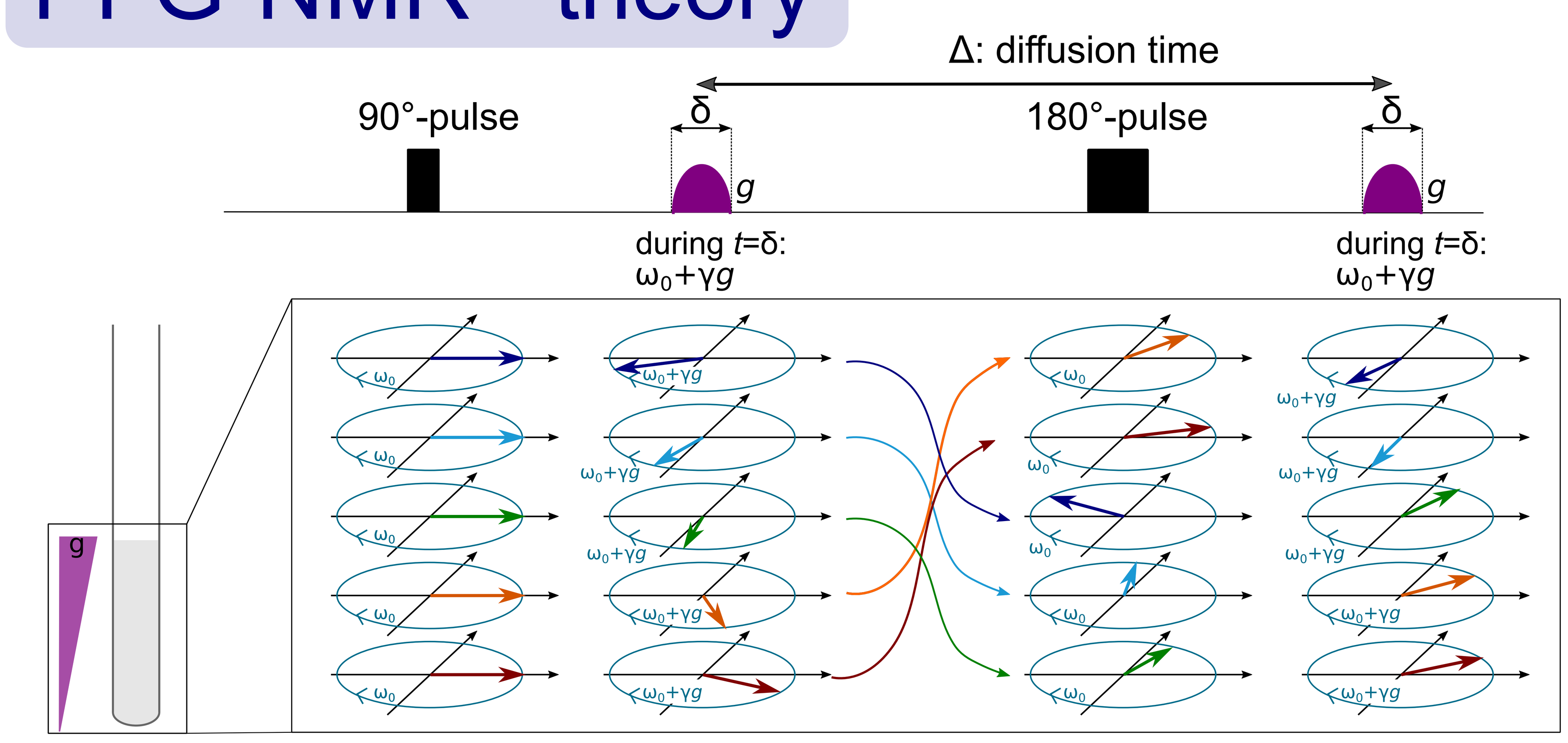
$$T_1^{-1} \sim \left(\frac{\tau}{1+\omega_L^2\tau^2} + \frac{4}{1+4\omega_L^2\tau^2}\right)$$

$$\tau^{-1} = \tau_0^{-1} \cdot \exp\left(\frac{-E_A}{k_B T}\right)$$



E_A: activation energy; k_B: Boltzmann constant; *T*: temperature; ω_L: Larmor frequency

PFG-NMR - theory



References

(1) Taken from *Angew. Chem. Int. Ed.* **2024**, e202404874 (2) Reprinted with permission from *ACS Materials Lett.* **2022**, 4, 2187-2194
(3) Stejskal, E. O. and Tanner, J. E.; *J. Chem. Phys.* **42**, 288-292 (1965) (4) von Smoluchowski, M.; *Ann. Phys.* **326**, 756-780 (1906)
(5) Einstein, A.; *Ann. Phys.* **322**, 549-560 (1905) (6) Bloembergen, H., Purcell, E. M. and Pound, R. V.; *Phys. Rev.* **72**, 679-712 (1948)