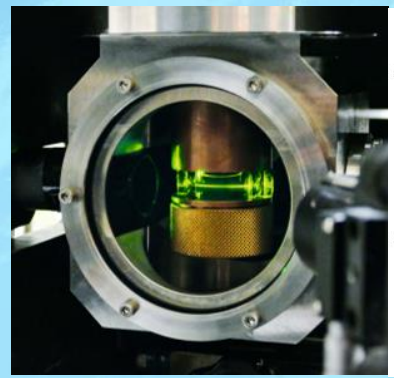

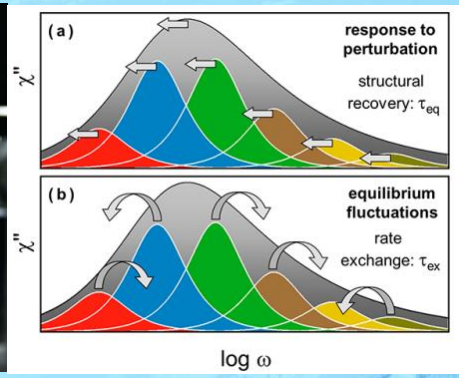

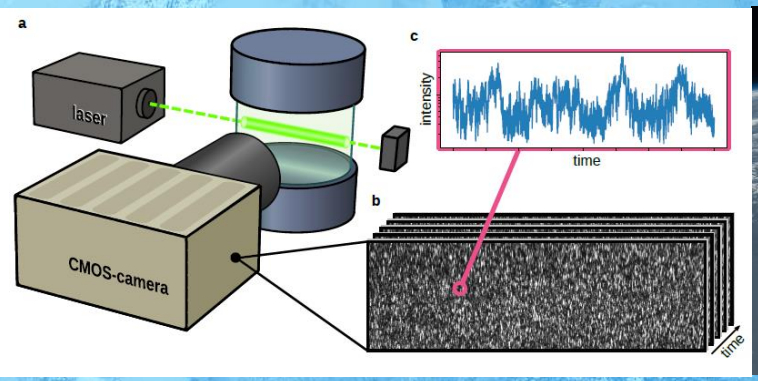

RELAXATION AND AGING DYNAMICS IN GLASSY SOFT MATTER

Jan P. Gabriel[1,2,3,4], Christopher Mayo[1], Marlo Kunzner[1], Matthias Sperl[1], Till Böhmer[1,2,3], Florian Pabst[2], Rolf Zeißler[2], Thomas Blochowicz[2], Tina Hacksher[3], Jeppe Dyre[3] , Ranko Richert[4] , Marceau Hénot[5]

1 Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany

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10IDMRCS, Barcelona 22. Juli 2025

Structural Relaxation and Recovery: A Dielectric Approach

Ranko Richert,* Jan P. Gabriel, and Erik Thoms

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 8465–8469

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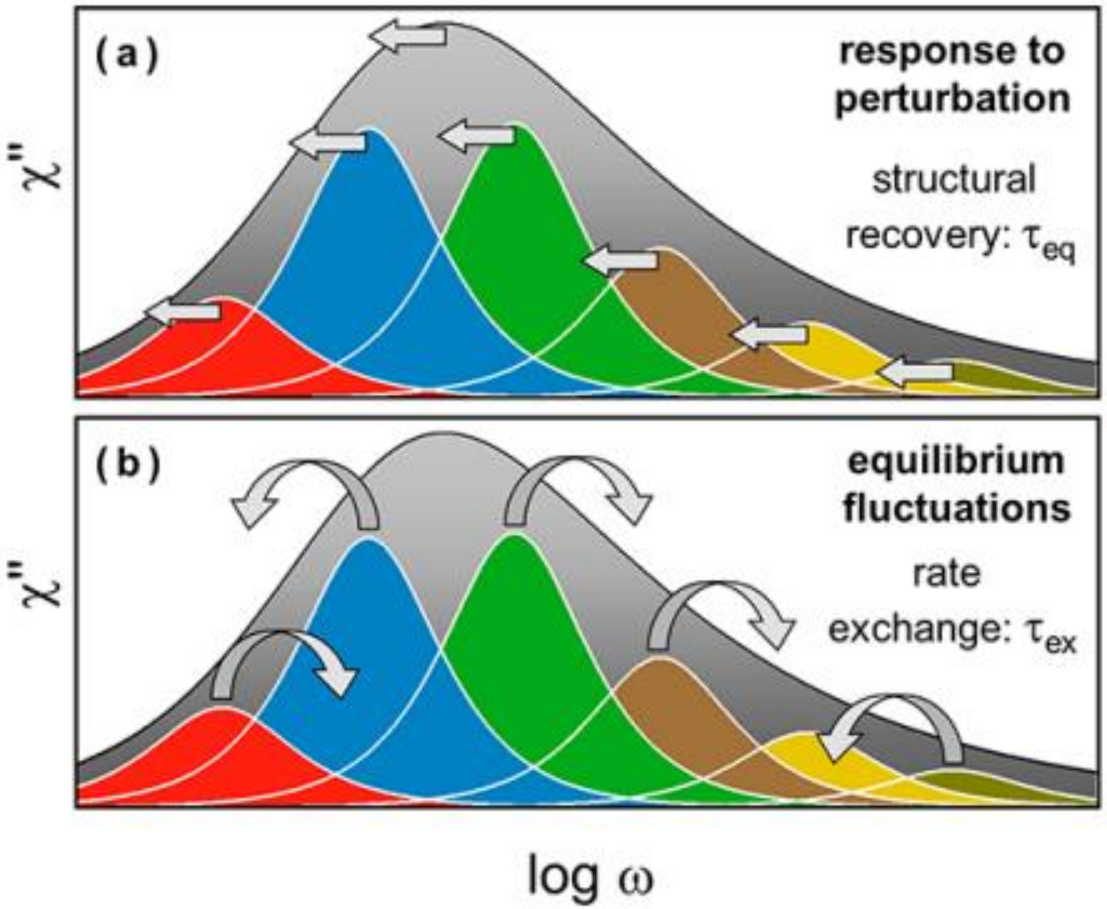
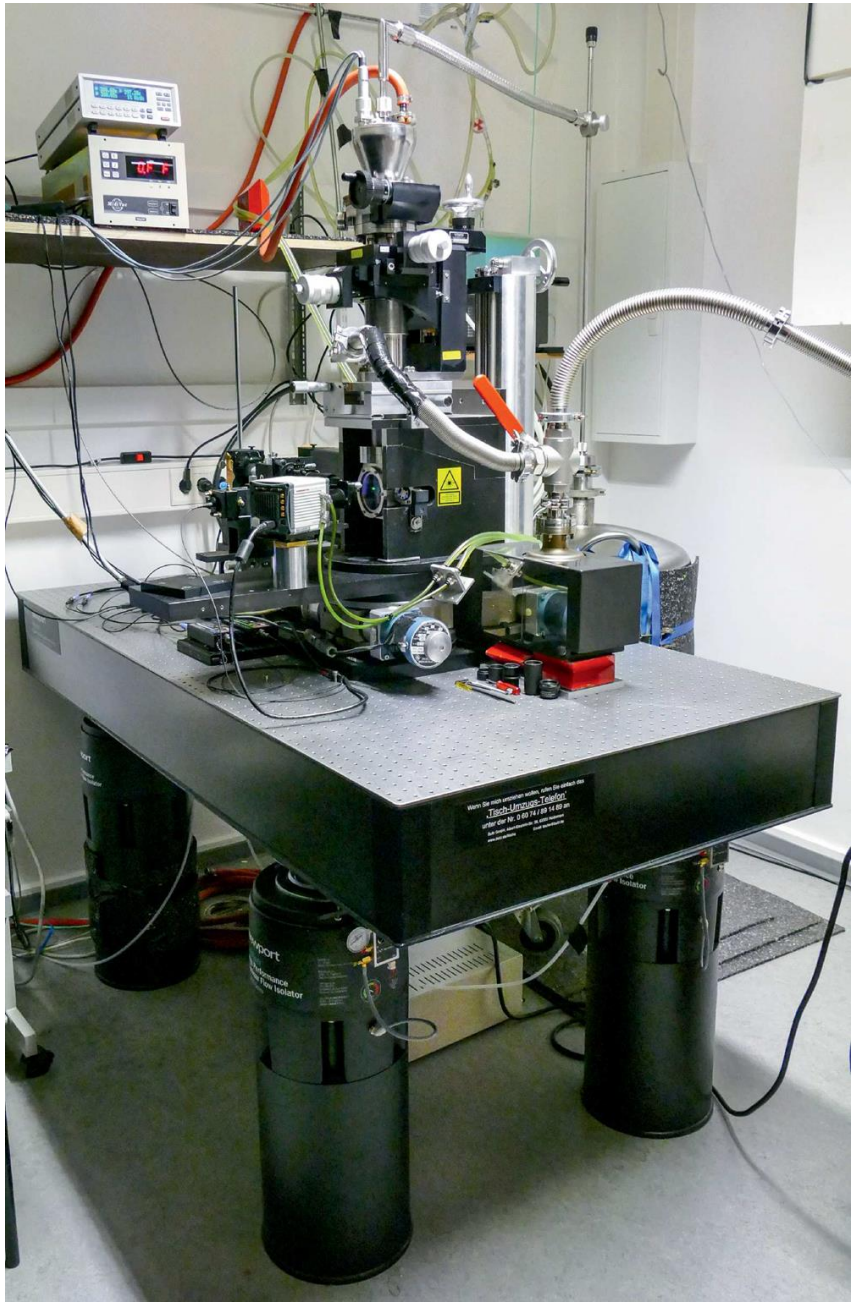
physical aging

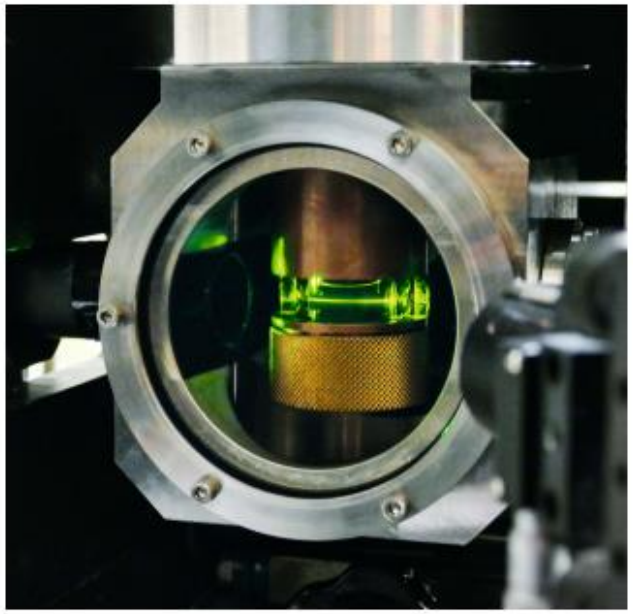
relaxation

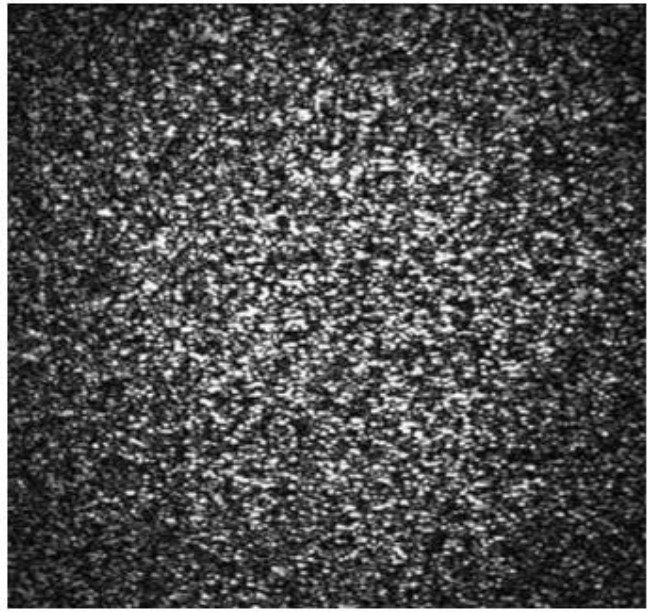


rotational dynamics

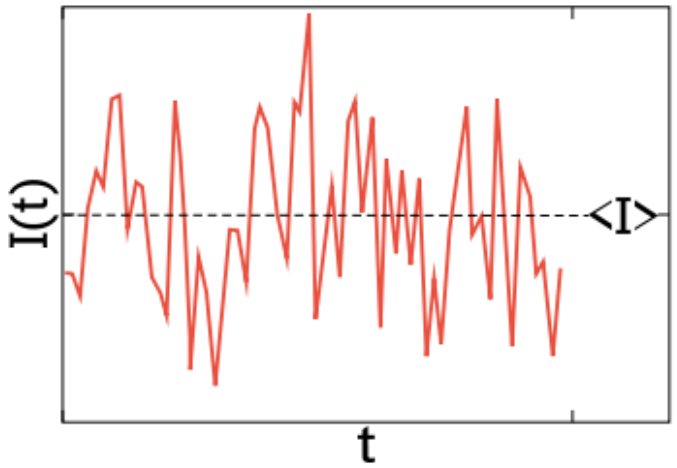
depolarised photon correlations spectroscopy (PCS)



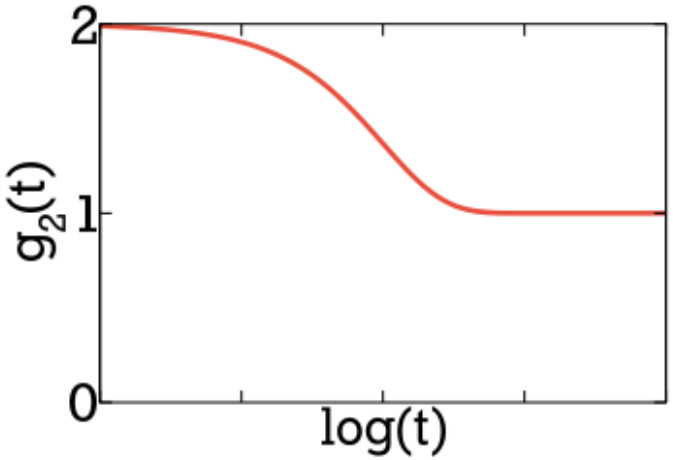


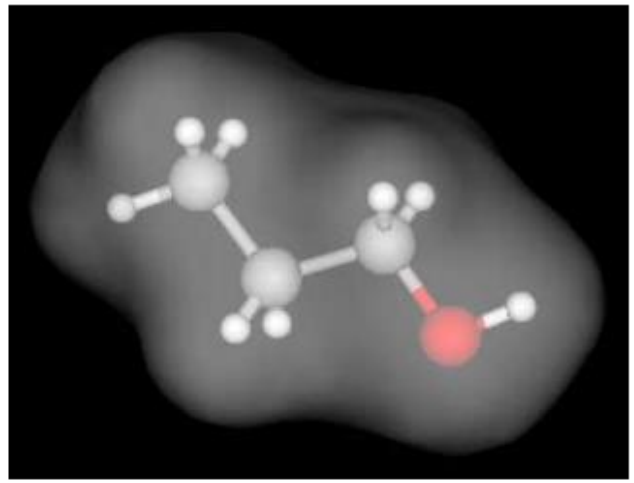


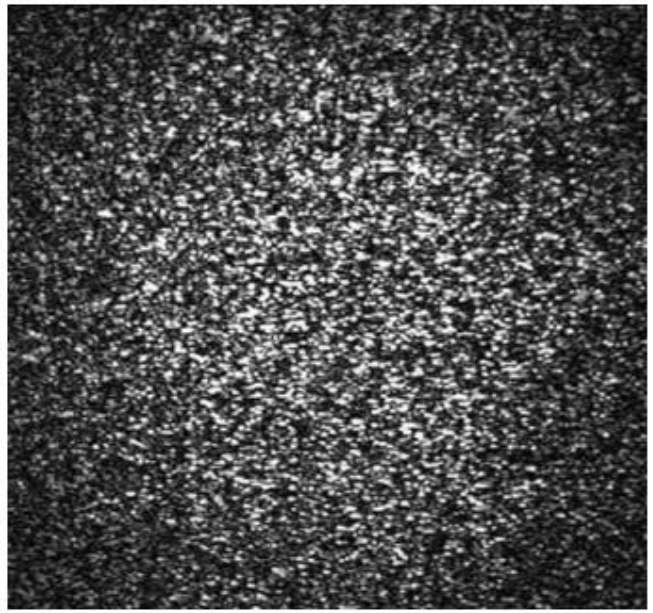
optical anisotropy

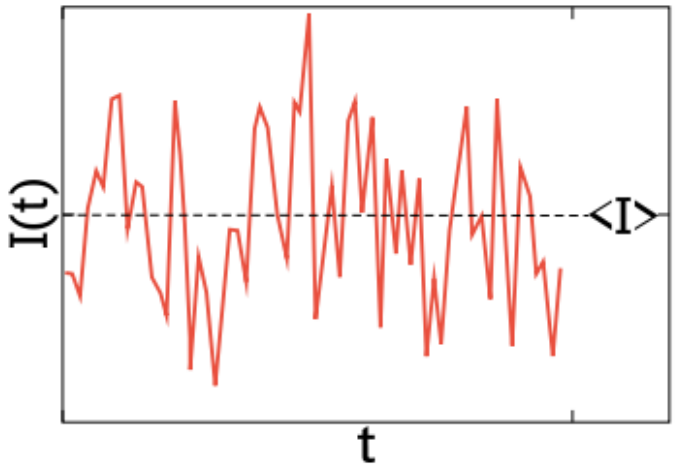


$$g_2(t) = \frac{\langle I(0)I(t)\rangle}{\langle I^2\rangle}$$









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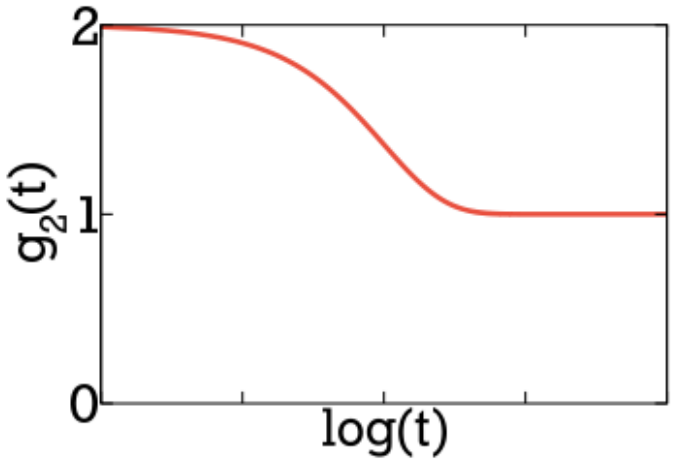
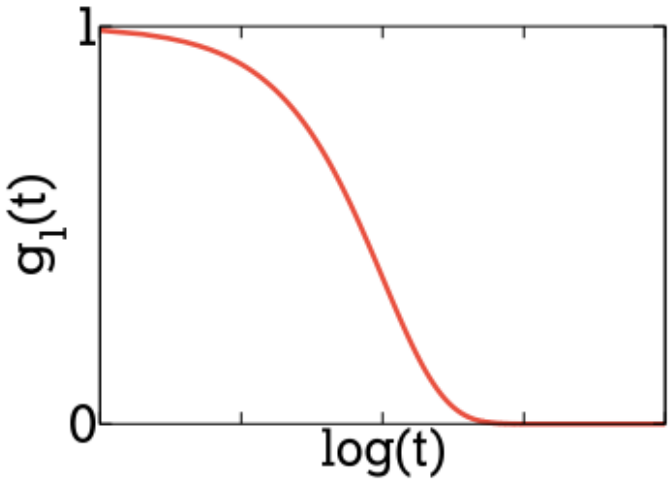
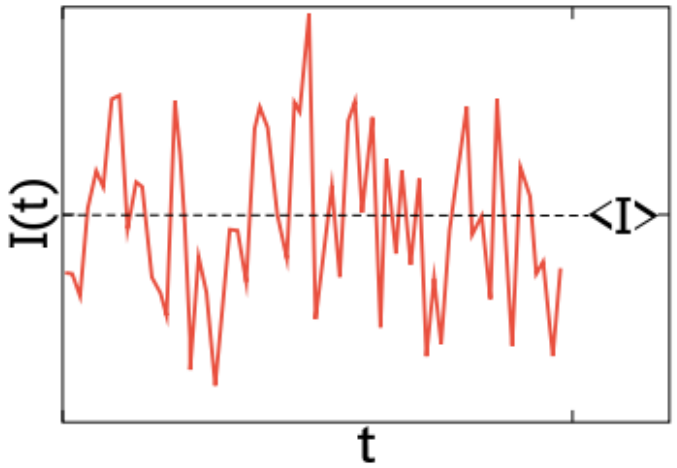


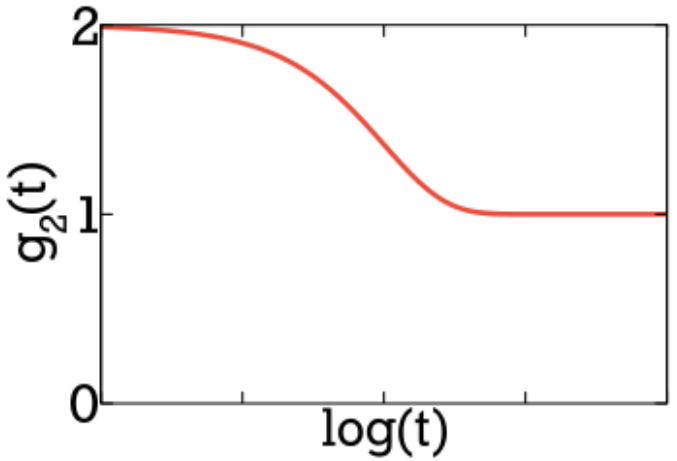
$$g_2(t) = 1 + |g_1(t)|^2$$

$$g_1(t) = \phi_2^{\mathrm{PCS}} \propto \langle P_2(\cos(\theta))\rangle$$





$$g_2(t) = \frac{\langle I(0)I(t)\rangle}{\langle I^2\rangle}$$



$$g_2(t) = 1 + |g_1(t)|^2$$

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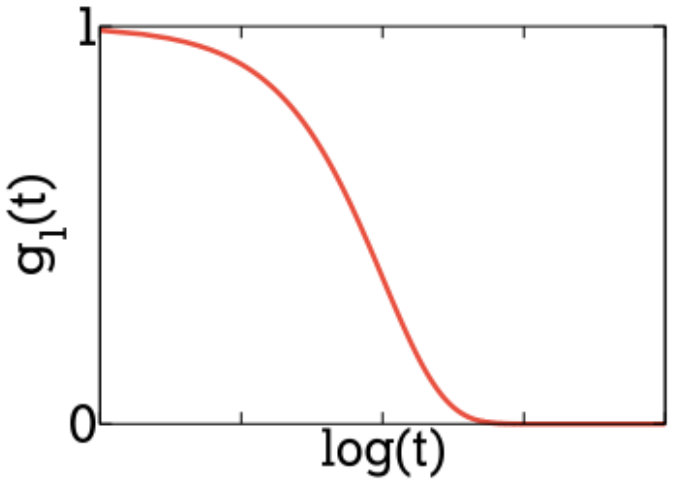


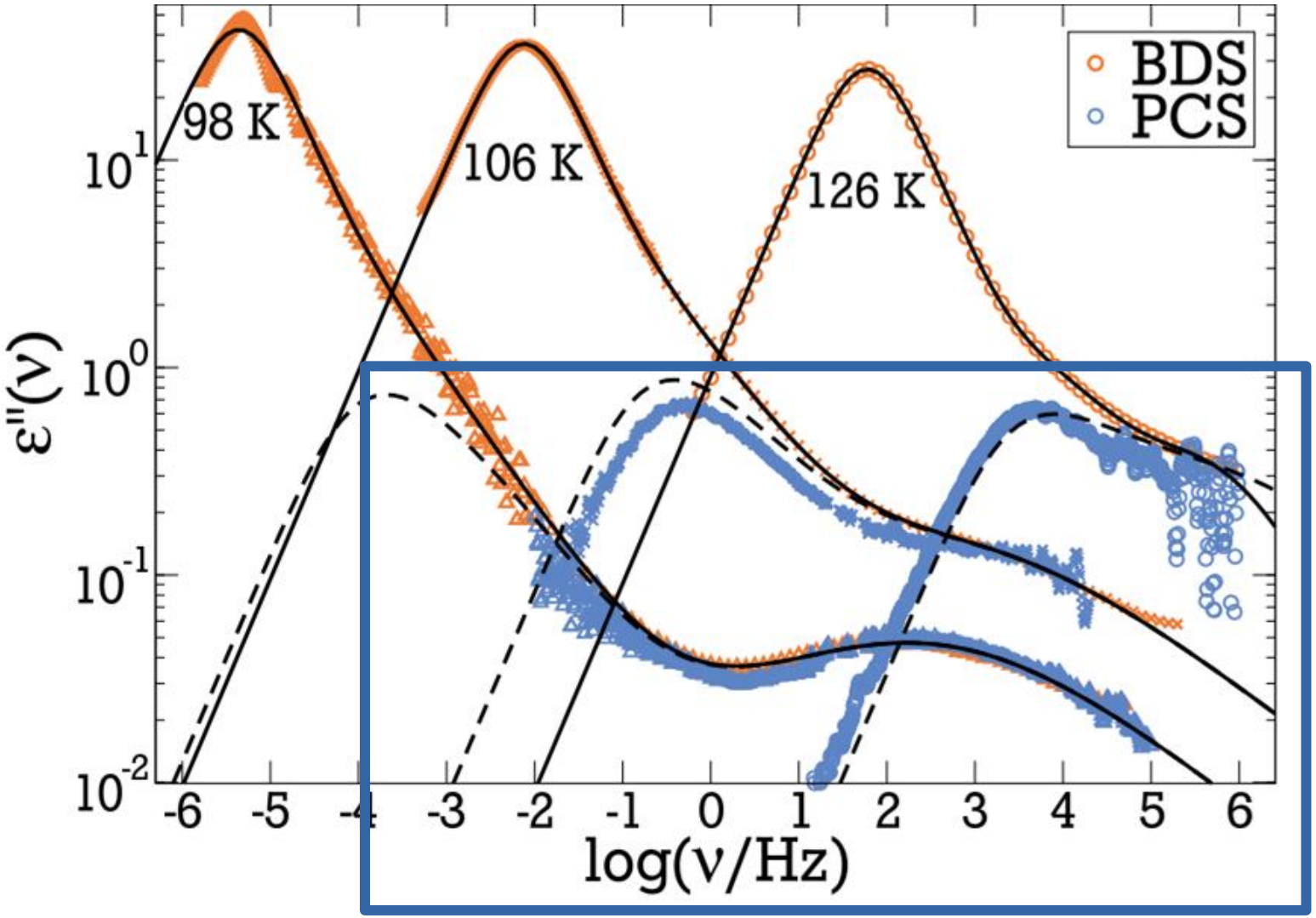
Fourier transform

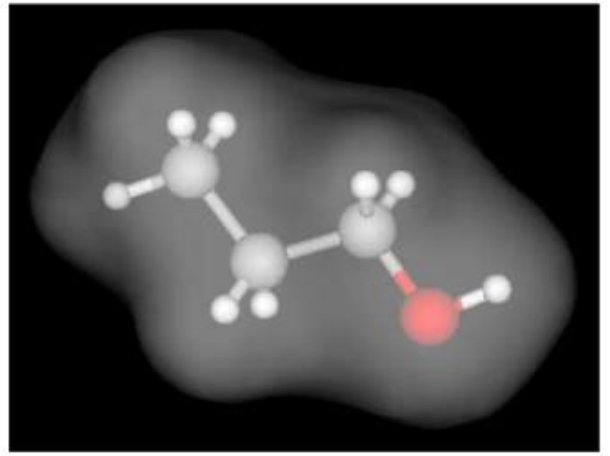
$$\hat{S}(\omega) = \int_0^\infty \Phi(t)\, e^{-i\omega t}\, \mathrm{d}t$$

$$\Im(\omega\hat{S}(\omega)) \circ Im(\omega) \propto \epsilon''(\omega)$$

dipole moment vs. optical anisotropy tensor

J. Gabriel et al., J. Phys. Chem. B, 121, 37 (2017)

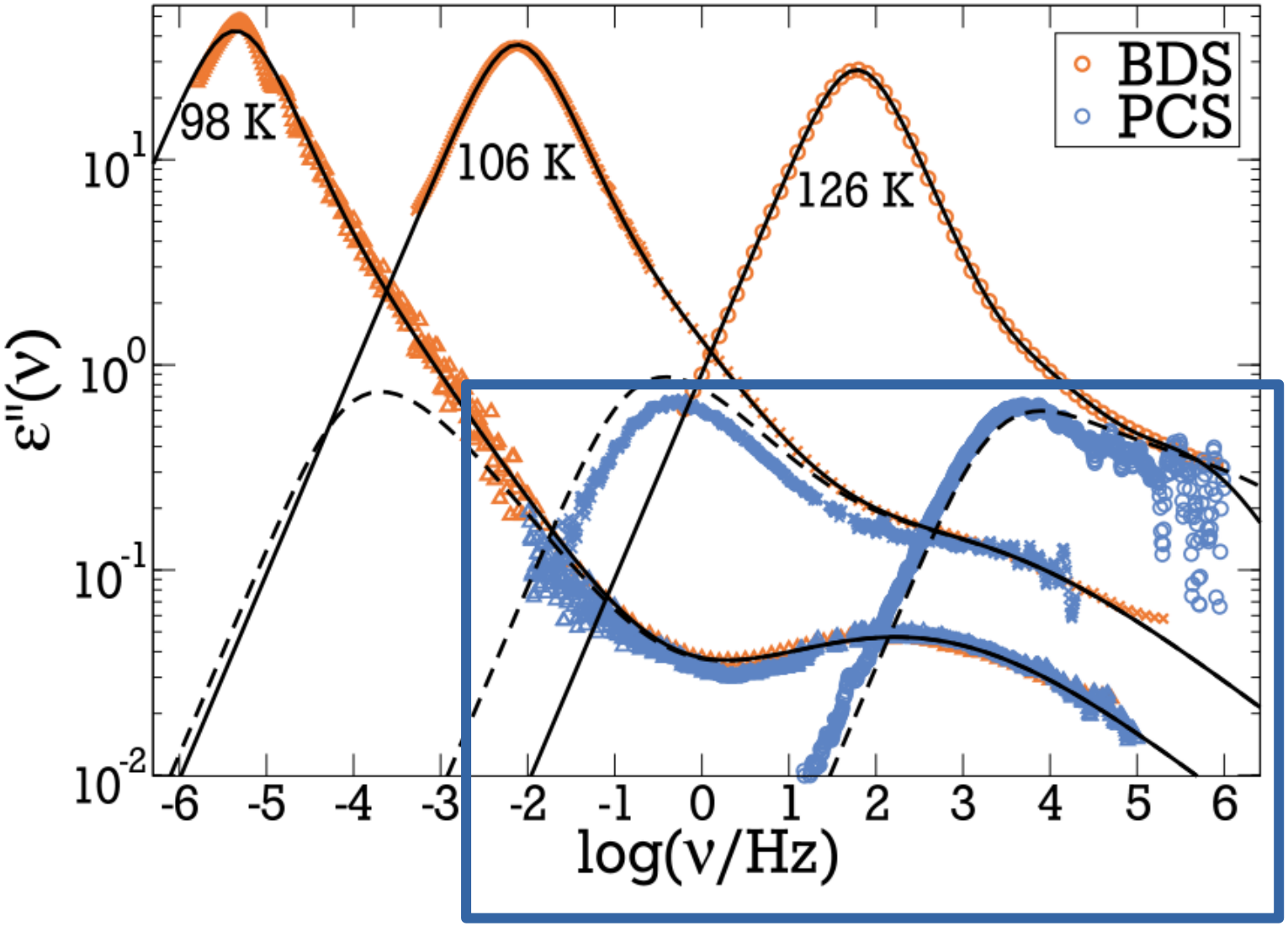




$$\phi_2^{\mathrm{PCS}} \propto \langle P_2(\cos(\theta)) \rangle$$

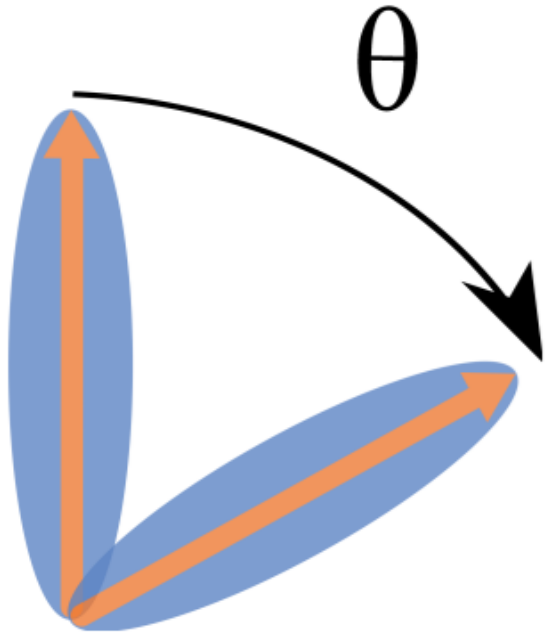
dipole moment vs. optical anisotropy tensor

J. Gabriel et al., J. Phys. Chem. B, 121, 37 (2017)



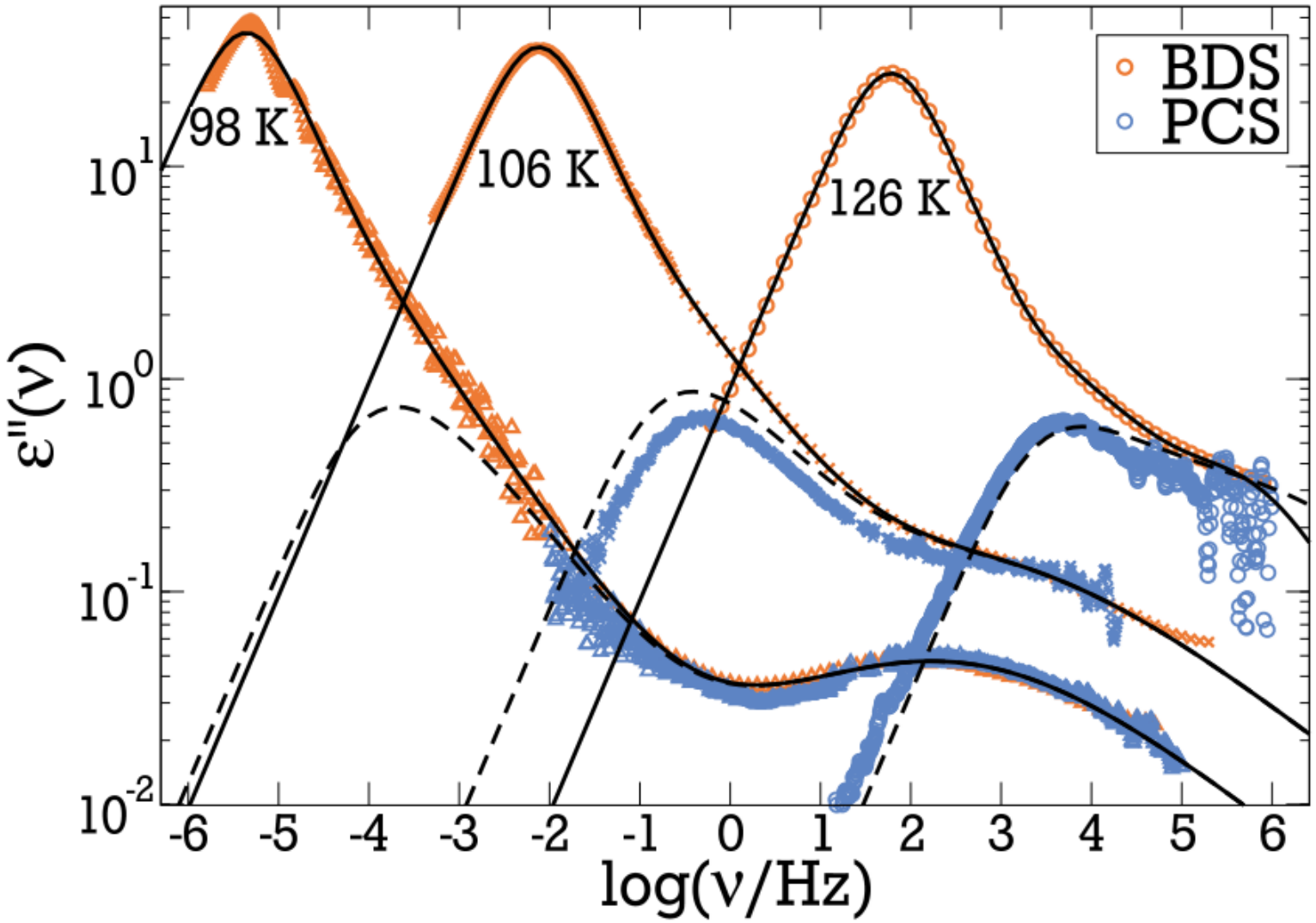
large angle jump

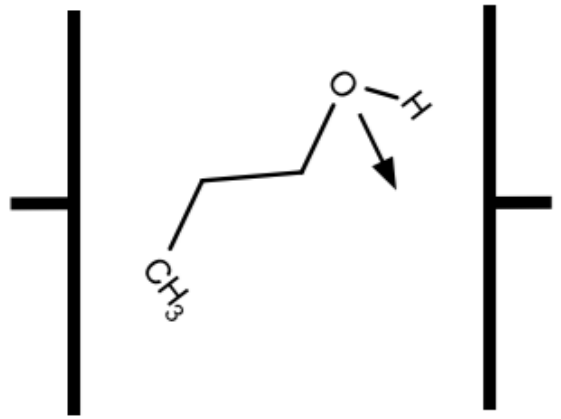
$$\phi_2^{PCS} = \phi_1^{BDS}$$



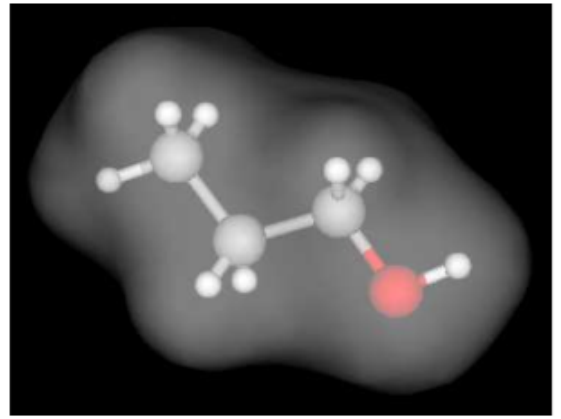
dipole moment vs. optical anisotropy tensor broadband dielectric spectroscopy (BDS) and PCS

J. Gabriel et al., J. Phys. Chem. B, 121, 37 (2017)





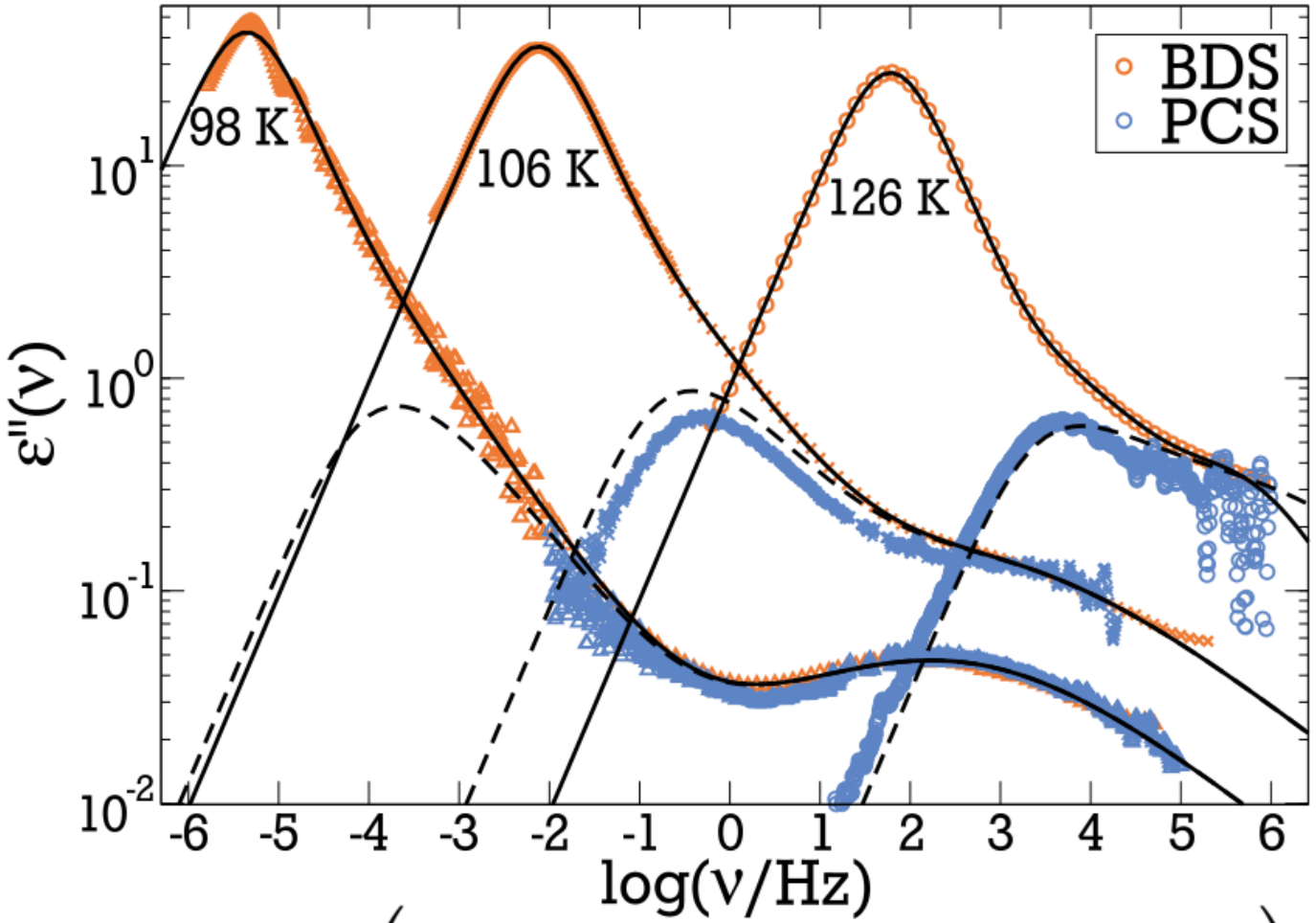
$$\phi_1^{BDS} \propto \langle P_1(\cos(\theta)) \rangle$$



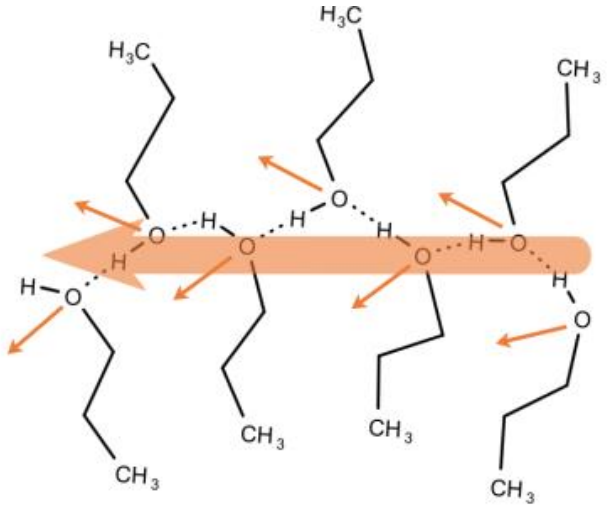
$$\phi_2^{PCS} \propto \langle P_2(\cos(\theta)) \rangle$$

cross-correlations between dipoles and anisotropy tensor

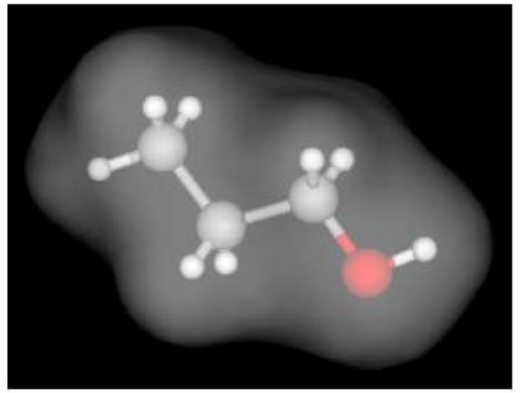
J. Gabriel et al., J. Phys. Chem. B, 121, 37 (2017)



$$\Phi_{mik} = \frac{1}{g_K \, \mu^2} \left(\left\langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \right\rangle + \left\langle \vec{\mu}_i(0) \cdot \sum_{i \neq j} \vec{\mu}_j(t) \right\rangle \right)$$

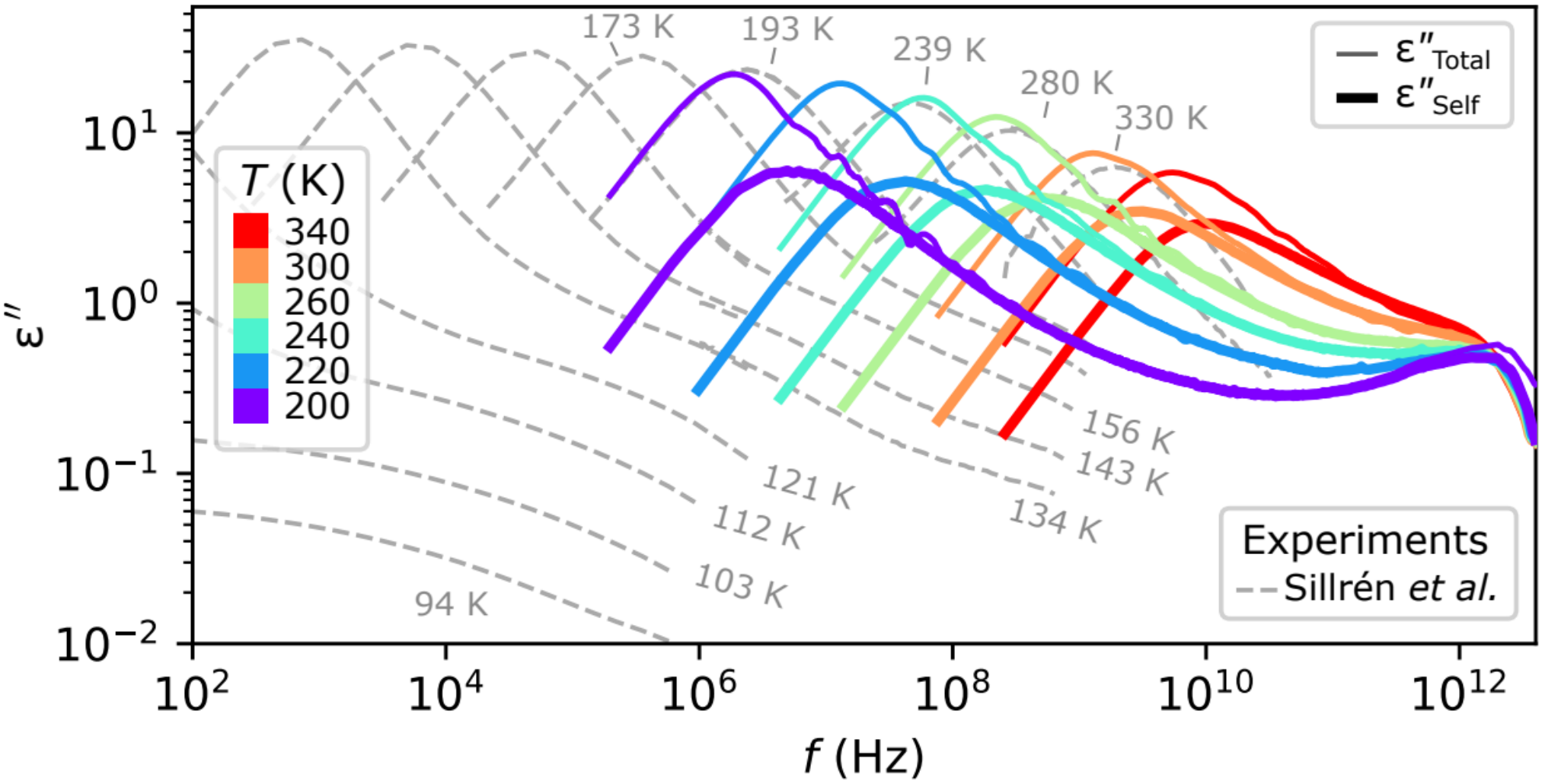


$$g_K^{BDS} = 1 + \langle P_1(\cos(\theta_{ij})) \rangle$$



$$g_K^{PCS} \approx 1$$

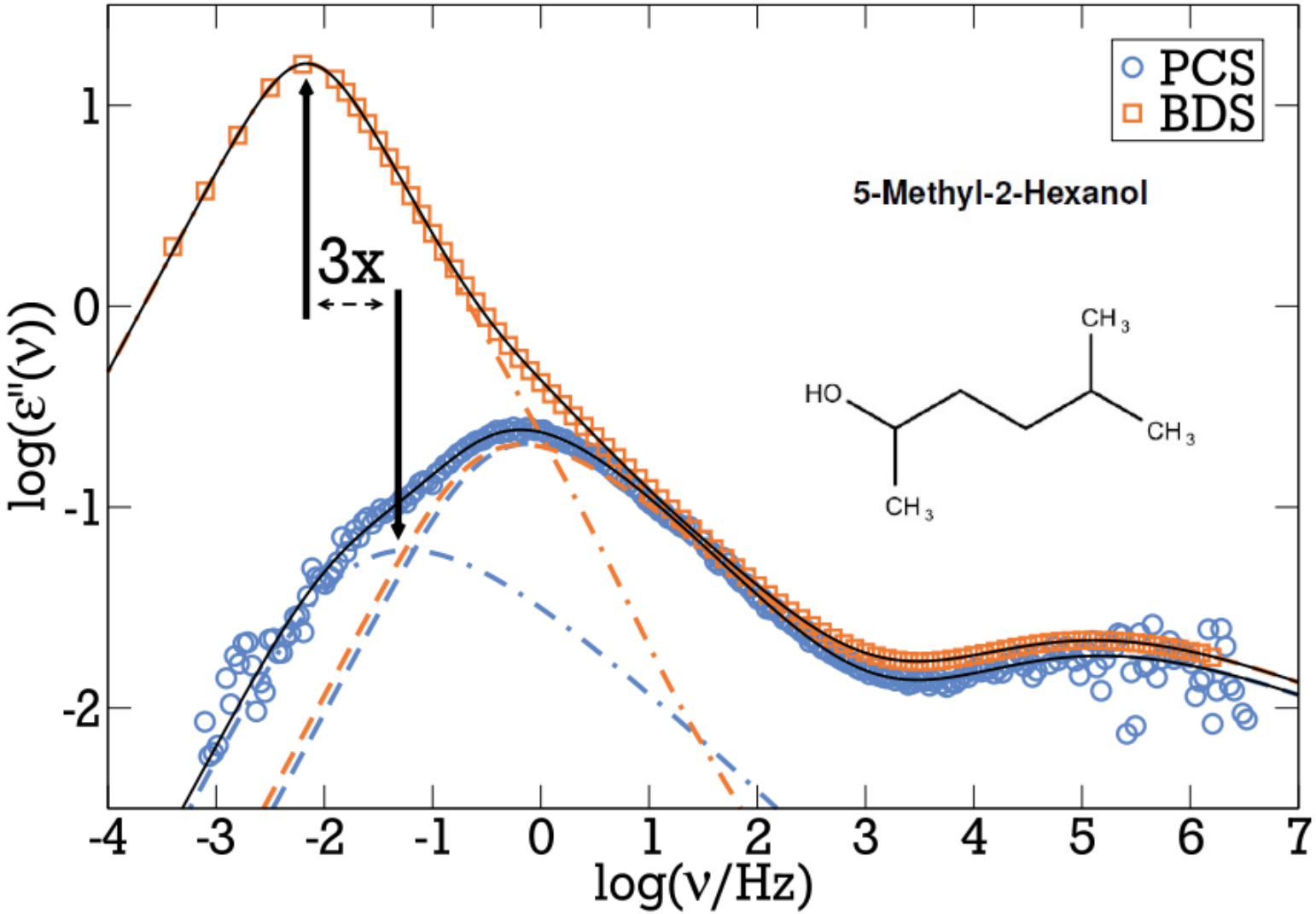
Propanol simulations by Marceau Hénot



Marceau Hénot

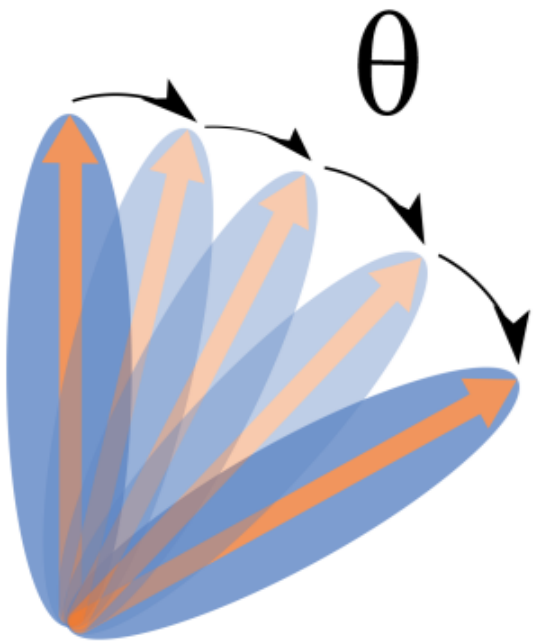
5-methyl-2-hexanol anisotropic alpha relaxation

J. Gabriel et al., Phys. Rev. Lett. B, 121 (2018)



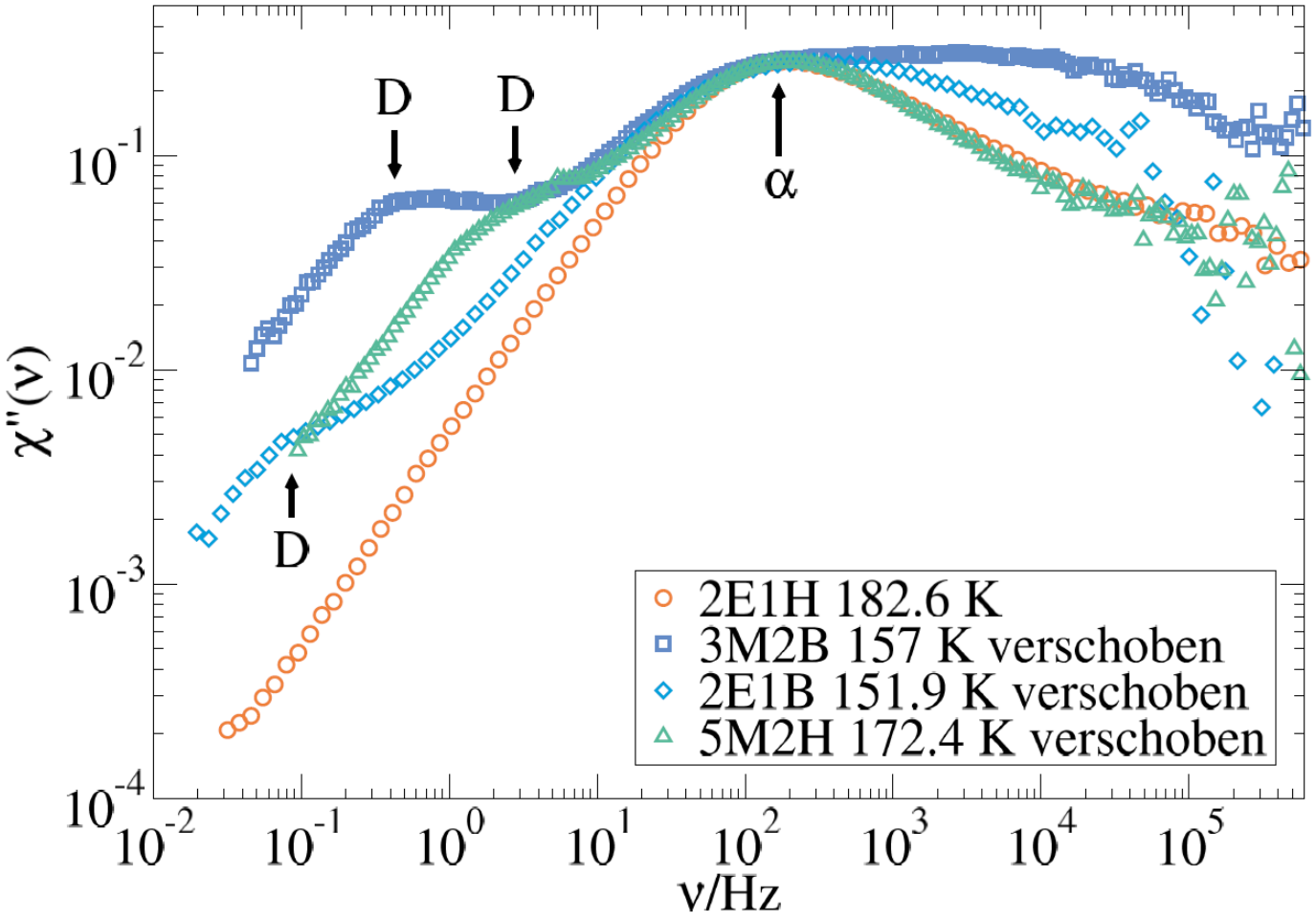
continuous rotation

$$\phi_\ell \propto \langle P_\ell(\cos(\theta)) \rangle$$

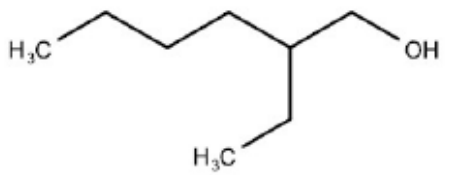


non unique anisotropic alpha relaxation

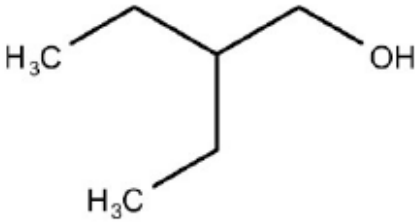
J. Gabriel et al., Phys. Rev. Lett. B, 121 (2018)



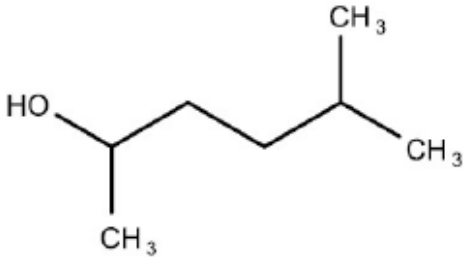
2-Ethyl-1-Hexanol



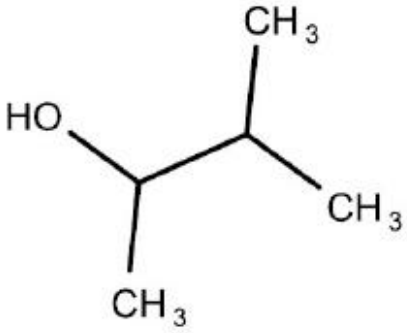
2-Ethyl-1-Butanol



5-Methyl-2-Hexanol

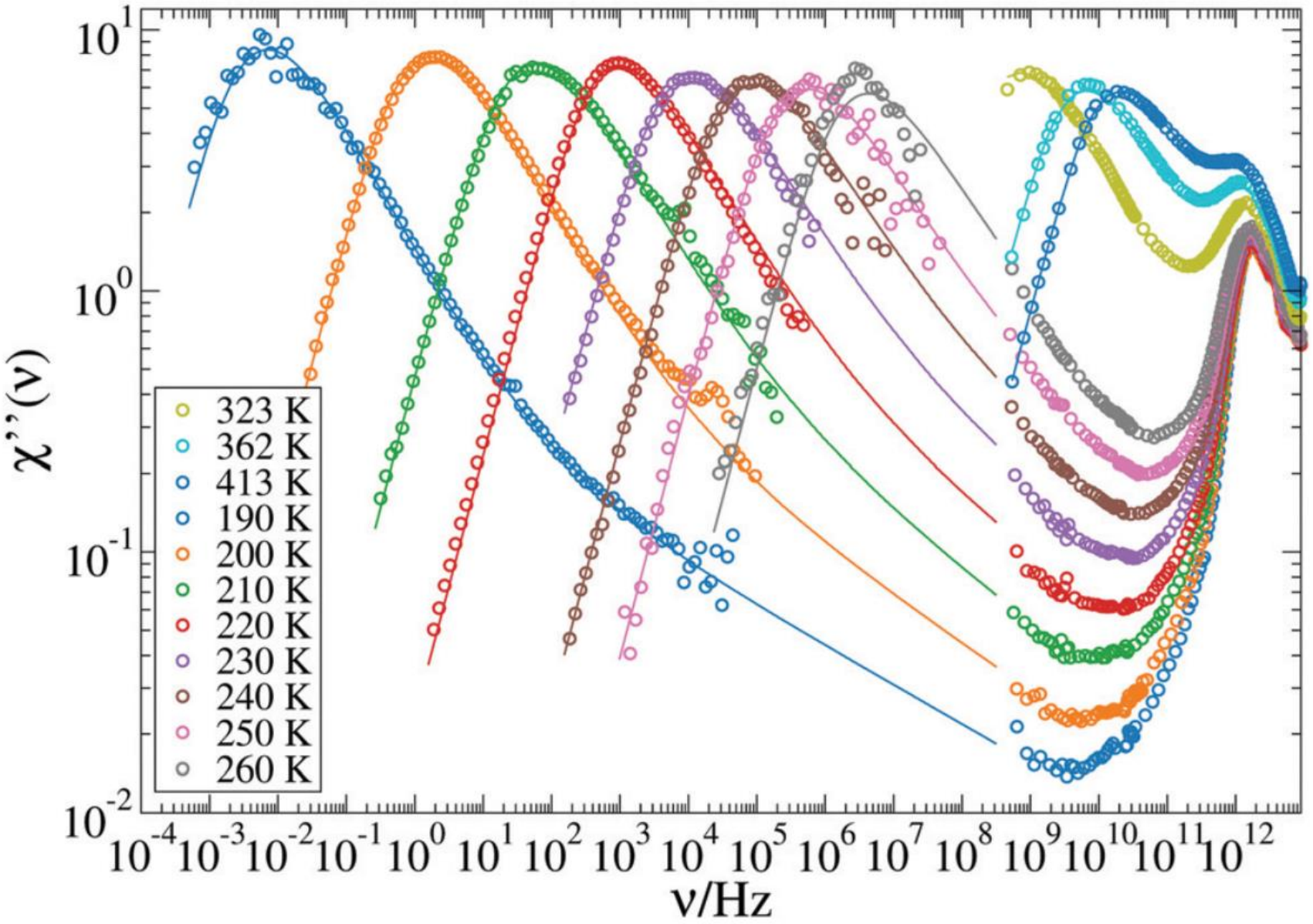


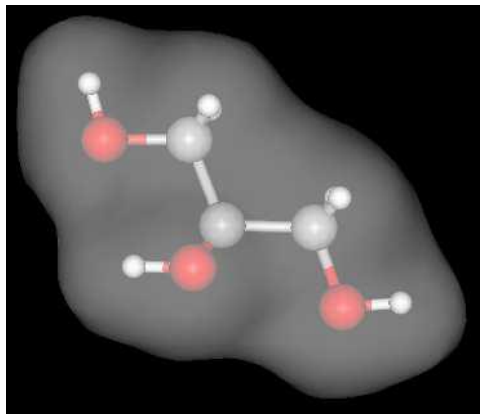
3-Methyl-2-Butanol



Light scattering on polyalcohol glycerol

TFPI: A Brodin and E.A. Rössler, Eur. Phys. J. B, **44** (2005)
PCS: J. P. Gabriel et al., Phys. Chem. Chem. Phys., **22** (2020)





→weak scattering

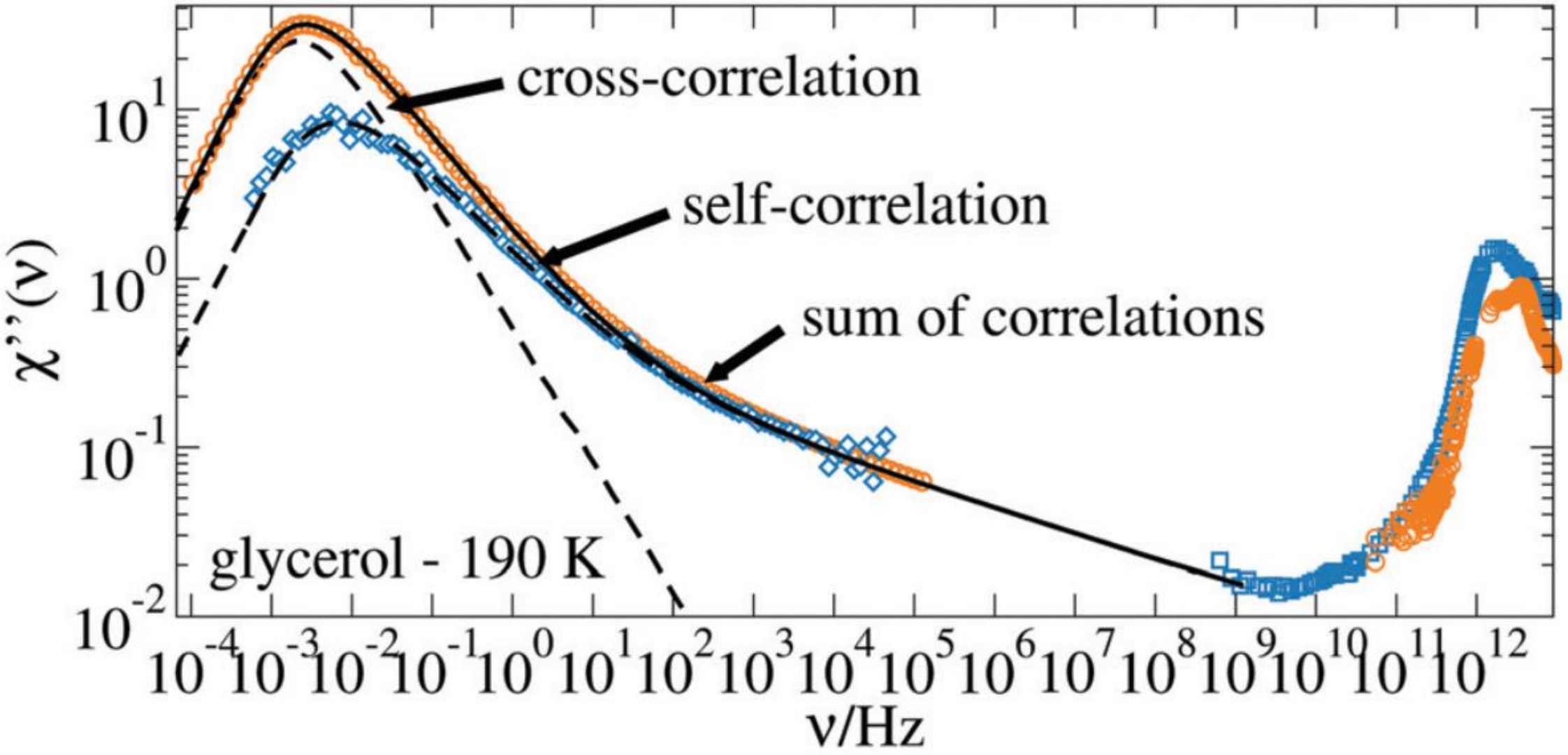
→17 decades in frequency

→3 decades in magnitude

→absolut intensity by Curie law 1/T

combining light scattering and dielectric spectroscopy

High frequency BDS: U. Schneider, P. Lunkenheimer, B. Brand and A. Loidl, J. Non-Cryst. Solids, 235-237, (1998)
TFPI: A Brodin and E.A. Rössler, Eur. Phys. J. B, 44 (2005)
PCS: J. P. Gabriel et al., Phys. Chem. Chem. Phys., 22 (2020)



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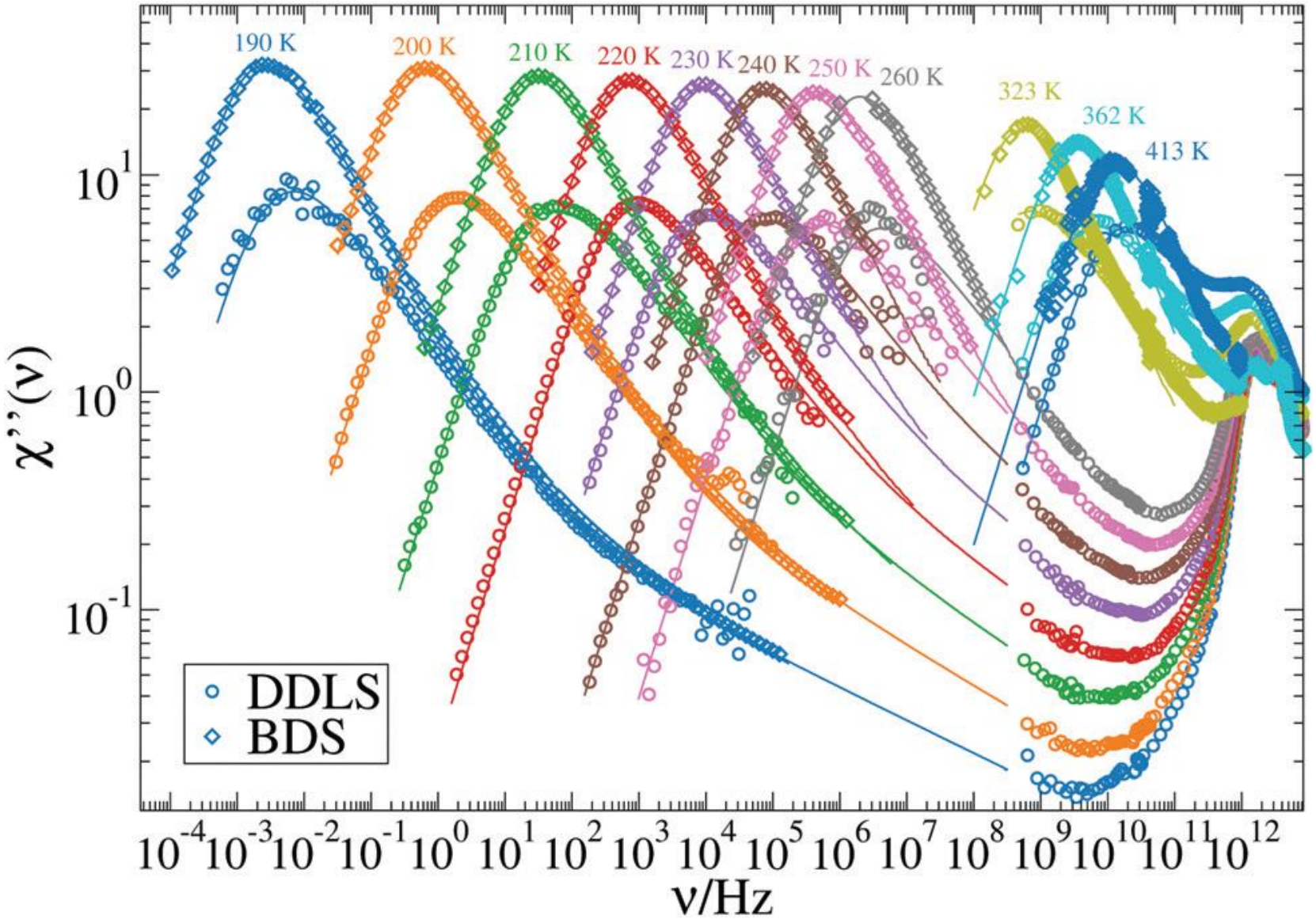
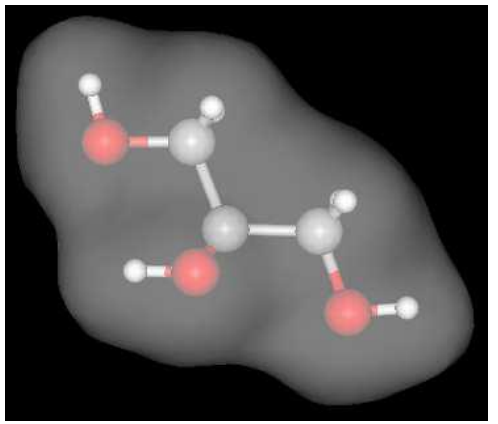
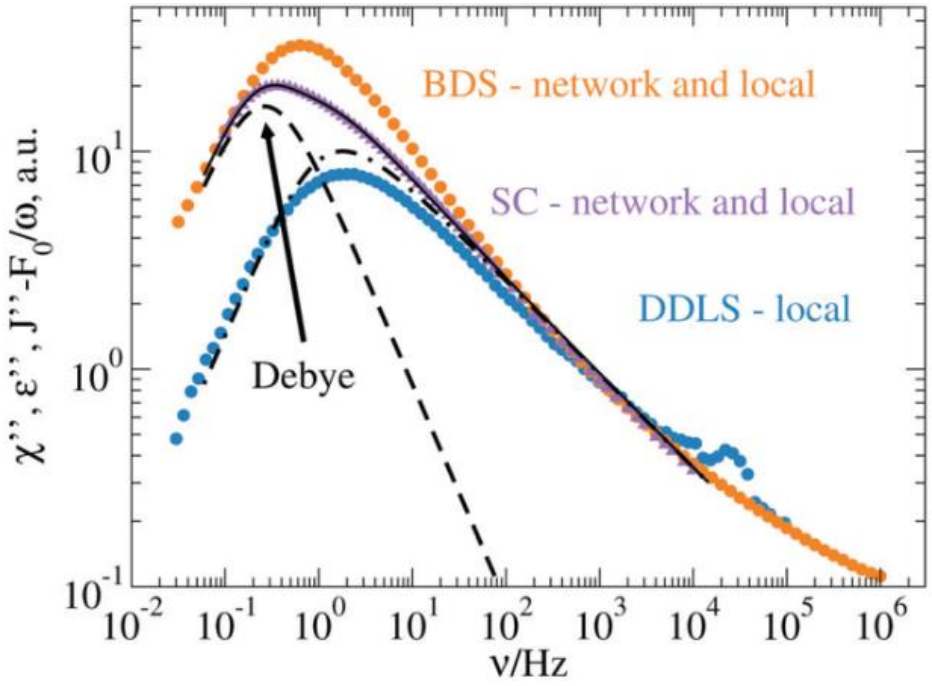


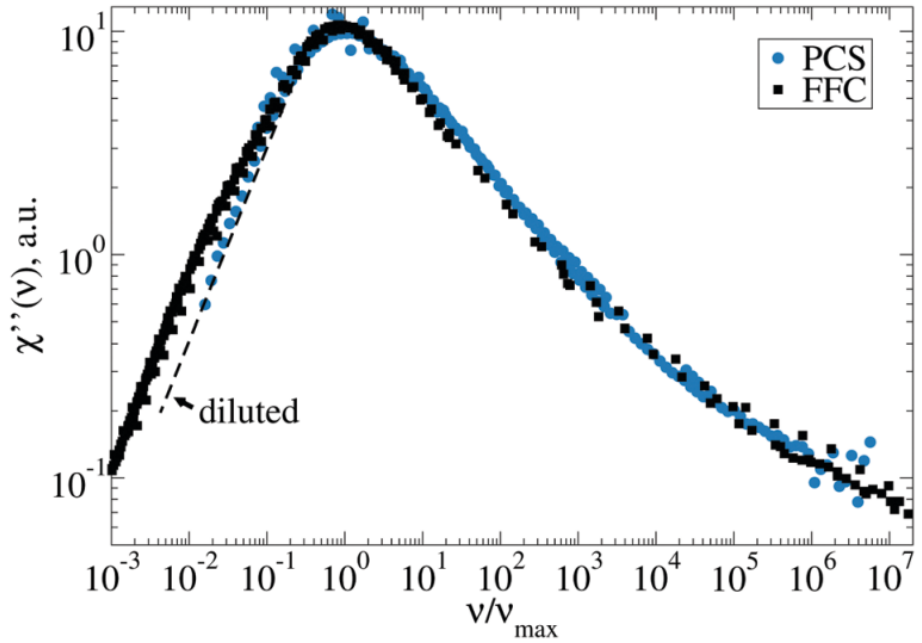


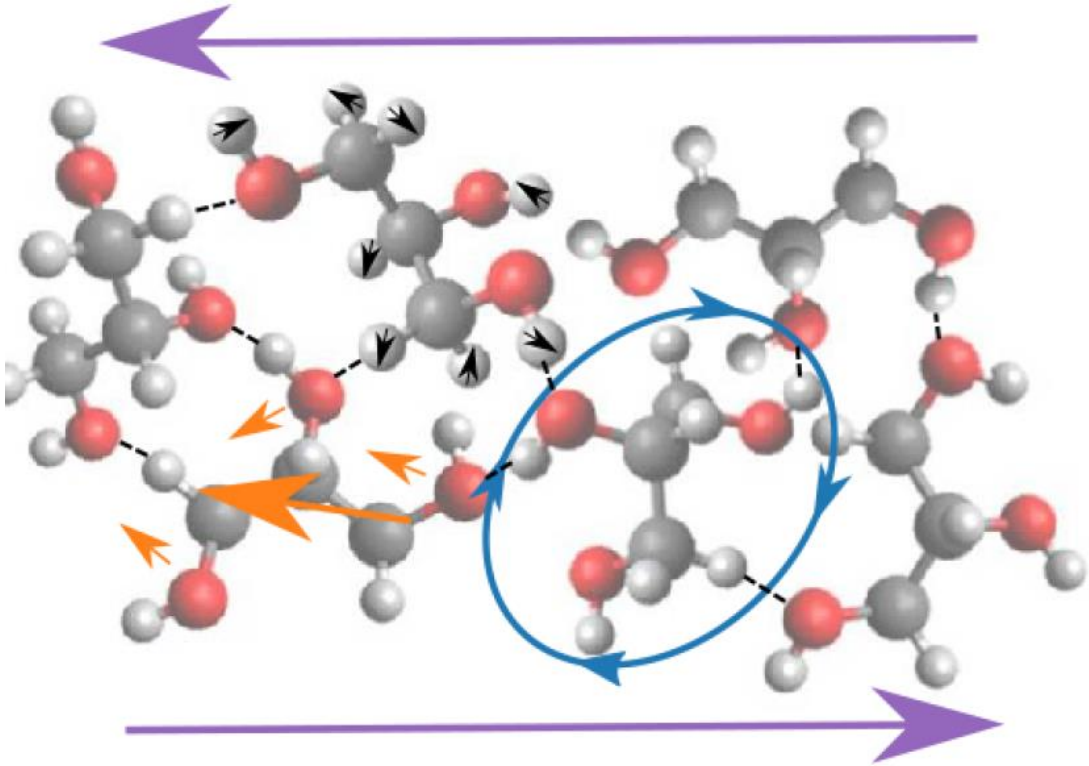
→extra cross-correlation contribution

→coinciding secondary relaxation

J. P. Pabst et al., Phys. Chem. Chem. Phys. (2020)







F. Pabst et al., J. Phys. Chem. Lett. (2021)

On the spectral shape of the structural relaxation in supercooled liquids

Cite as: J. Chem. Phys. 162, 120902 (2025); doi: 10.1063/5.0254534
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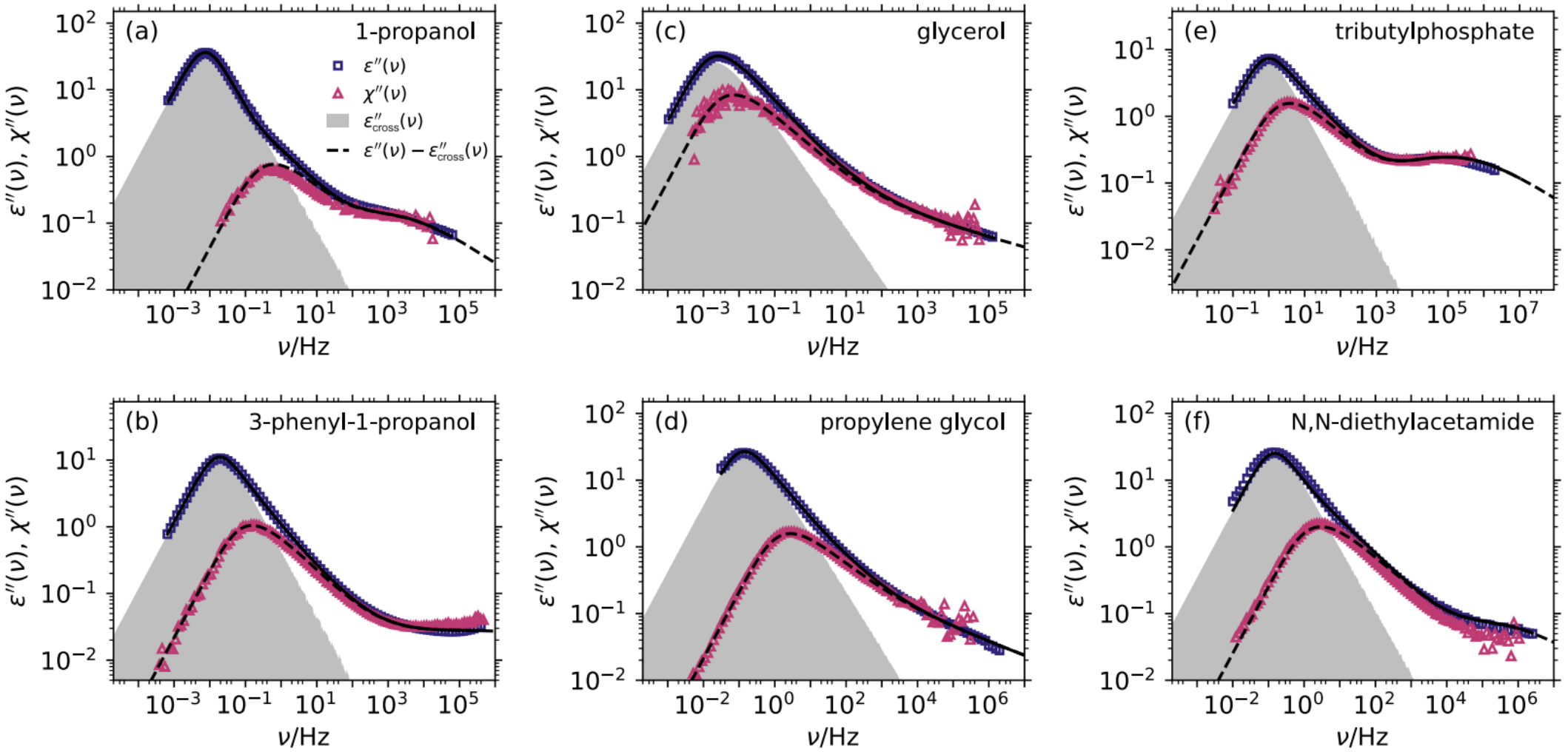
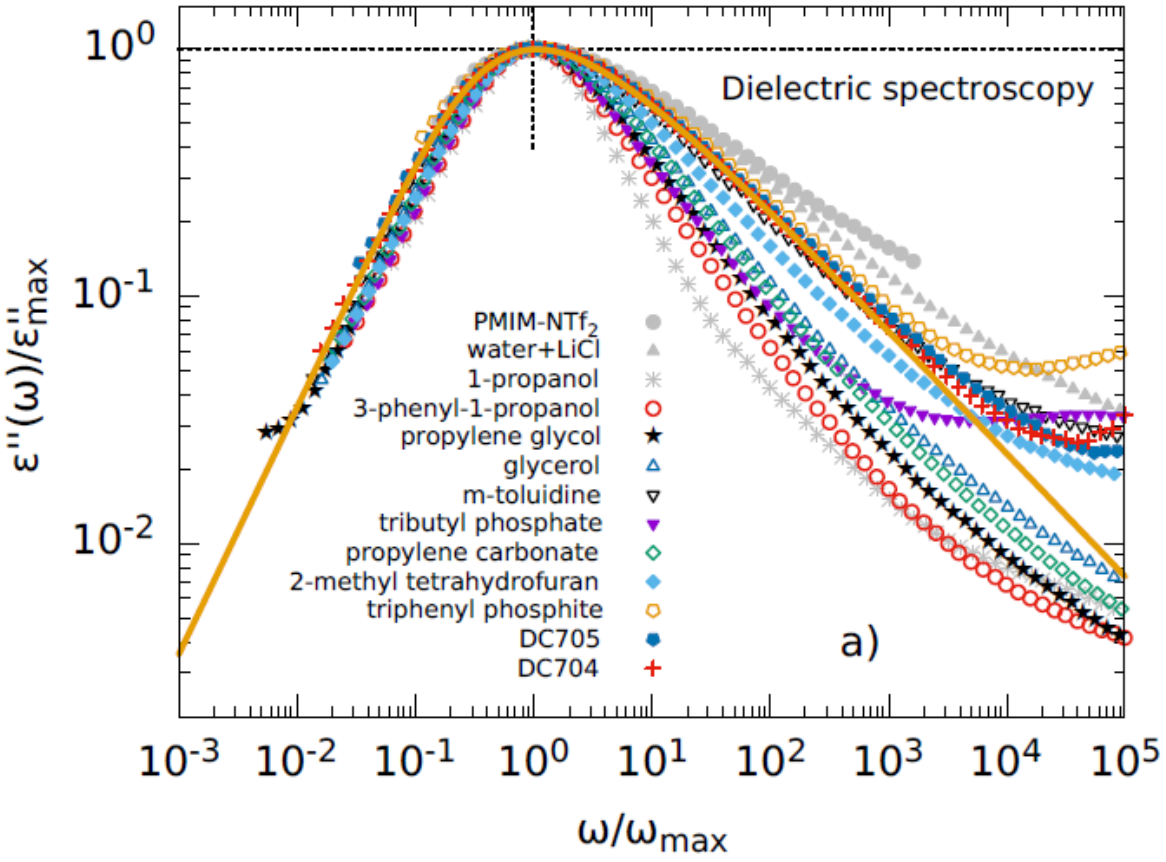
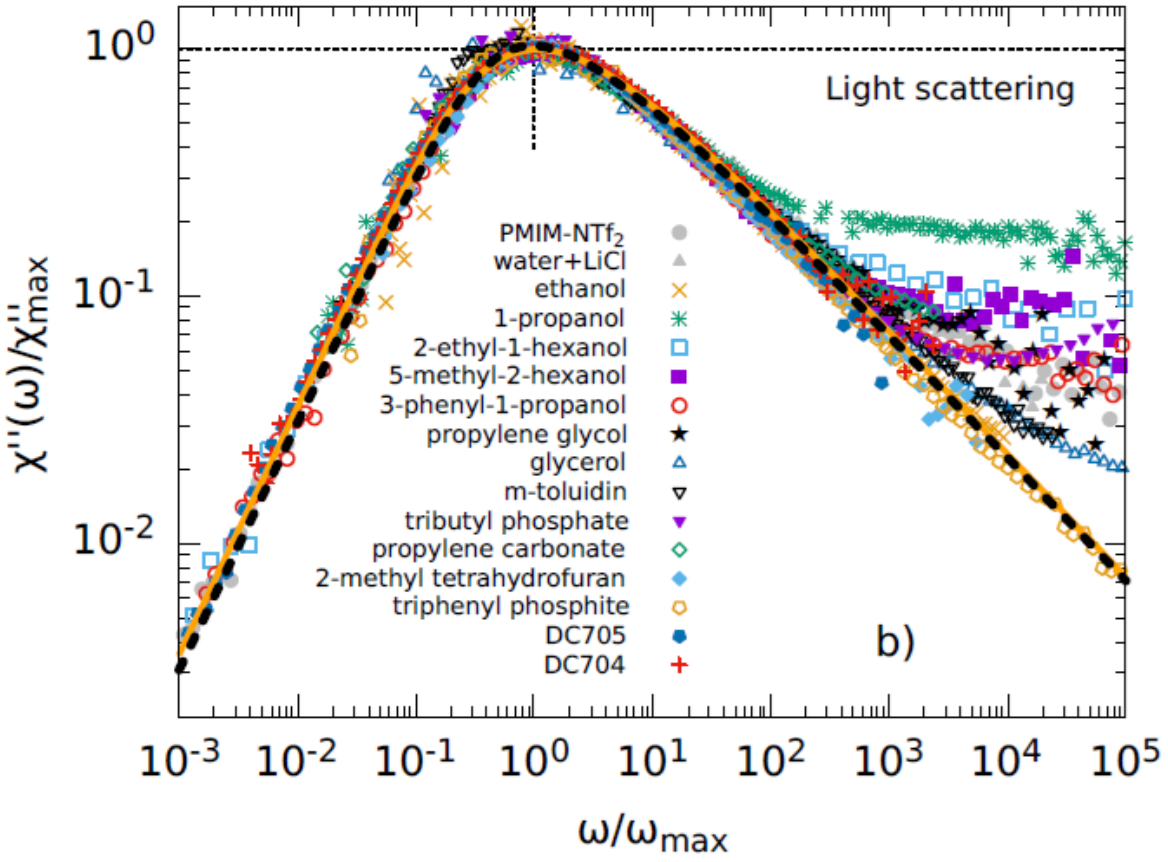
Till Böhmer,[1,a] Florian Pabst,[2,b] Jan Philipp Gabriel,[3] Rolf Zeißler,[4] and Thomas Blochowicz[4,c]



strong cross-correlations in dielectric spectroscopy

F. Pabst et al., J. Phys. Chem. Lett. (2021)

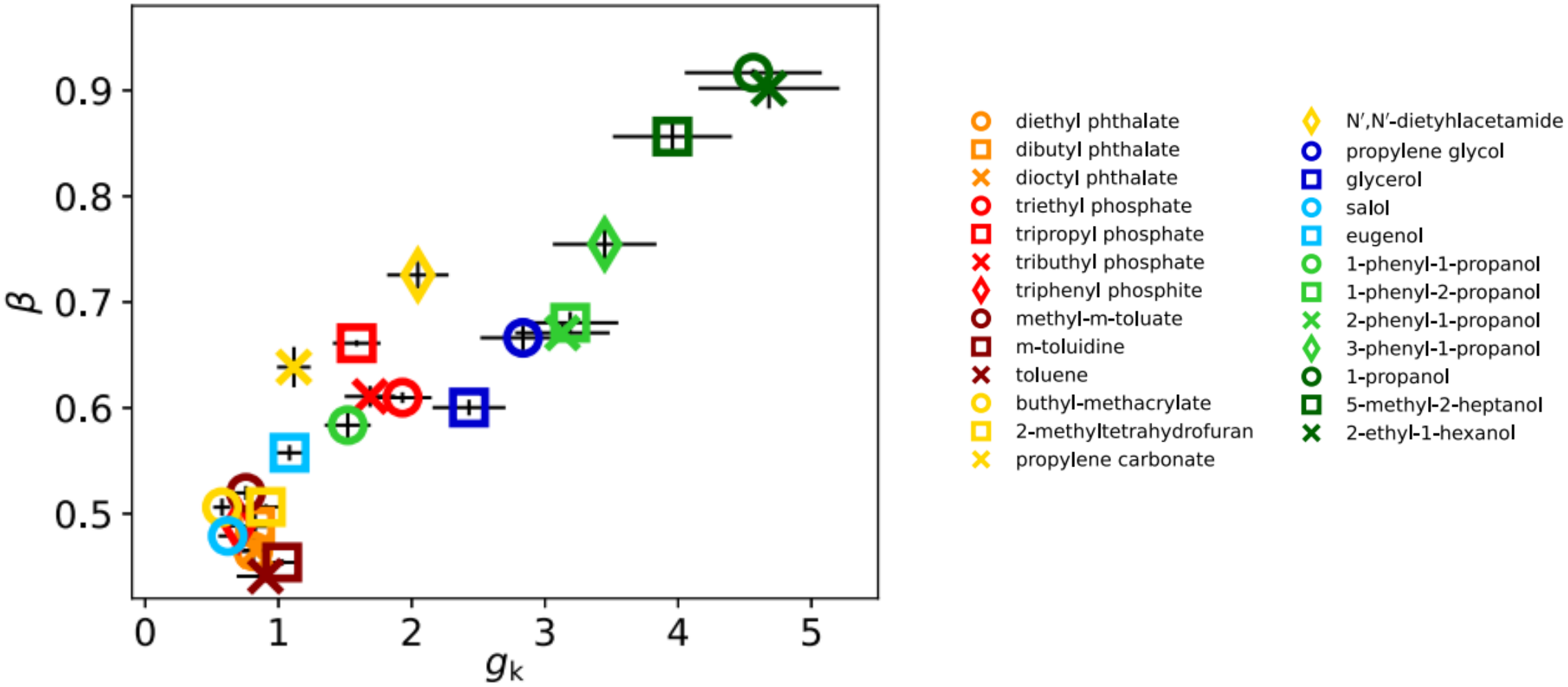




DLR

Dipolar Order Controls Dielectric Response of Glass-Forming Liquids

Till Böhmer,[1] Florian Pabst,[1,2] Jan P. Gabriel,[3,4] and Thomas Blochowicz[1]



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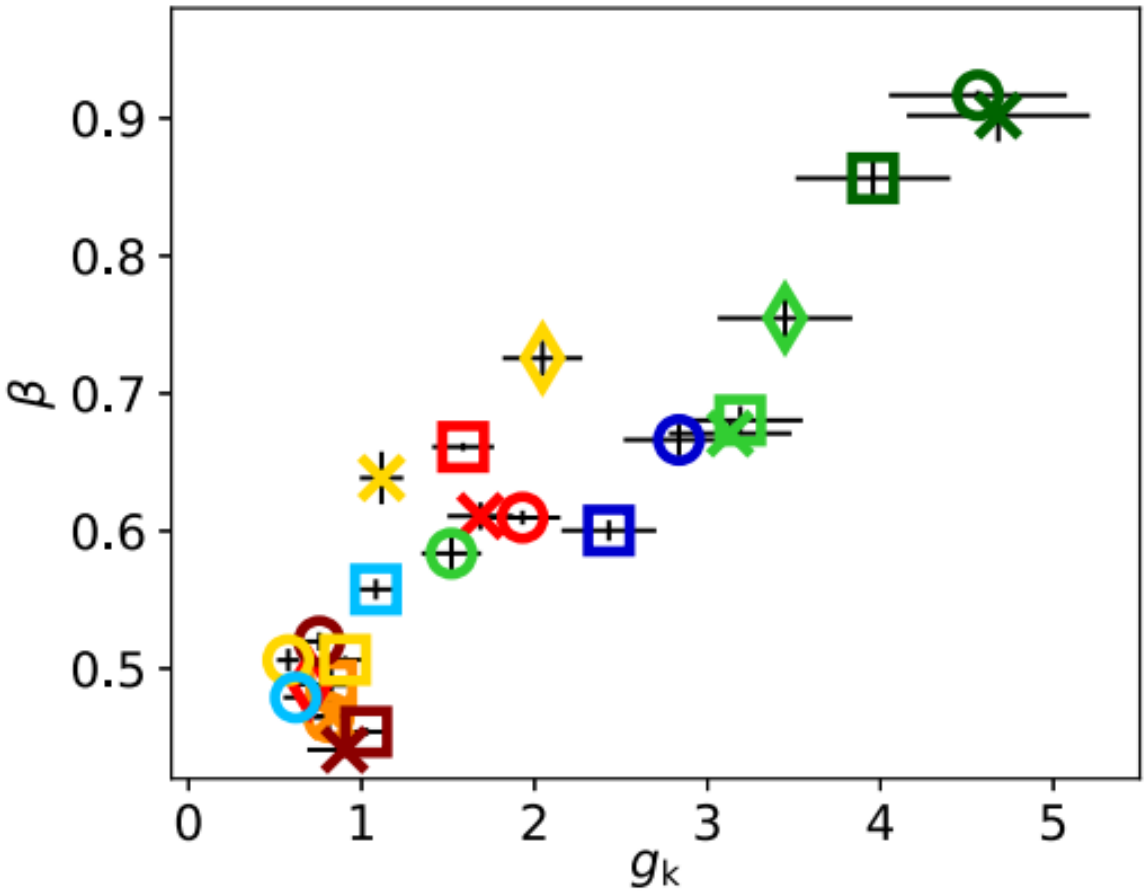
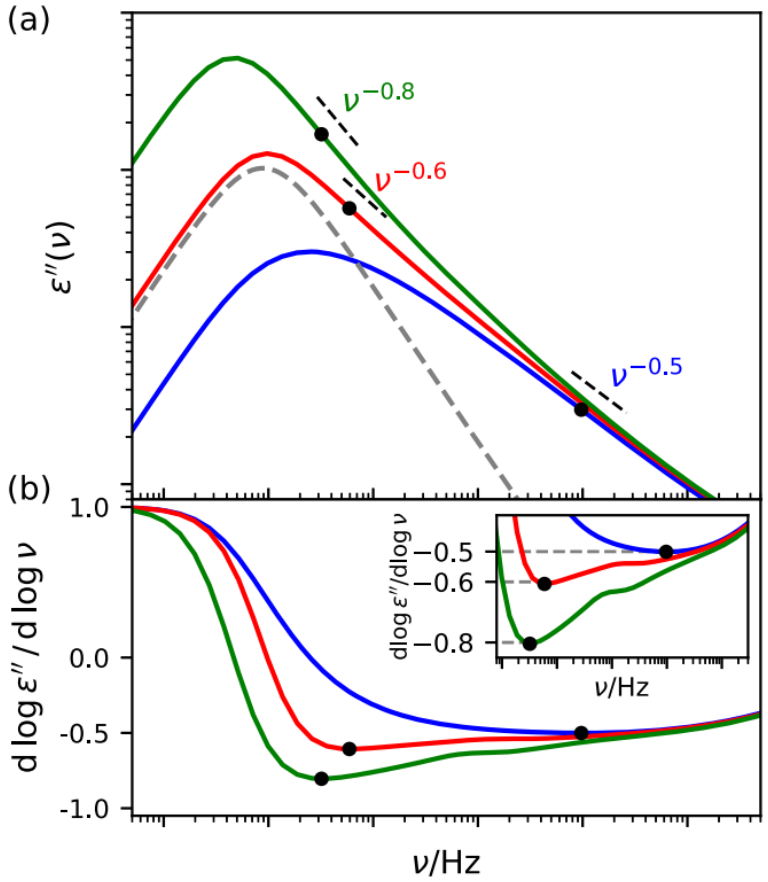
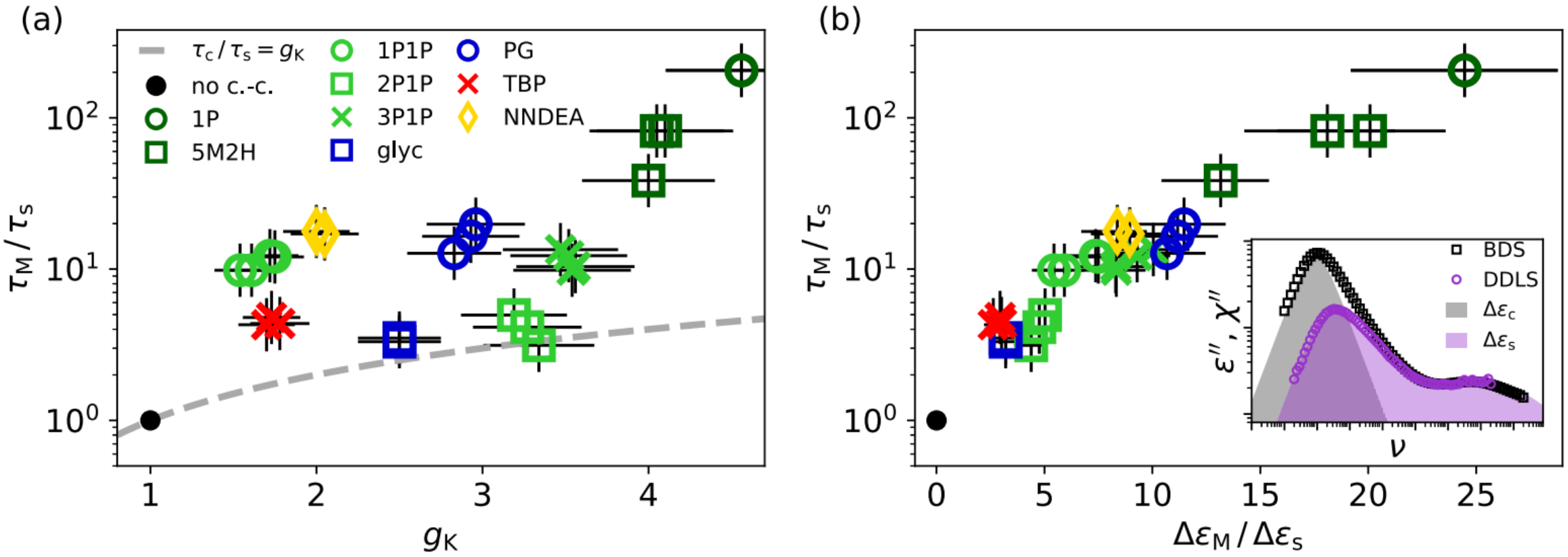




Dipolar Order Controls Dielectric Response of Glass-Forming Liquids

Till Böhmer,[1] Florian Pabst,[1,2] Jan P. Gabriel,[3,4] and Thomas Blochowicz[1]



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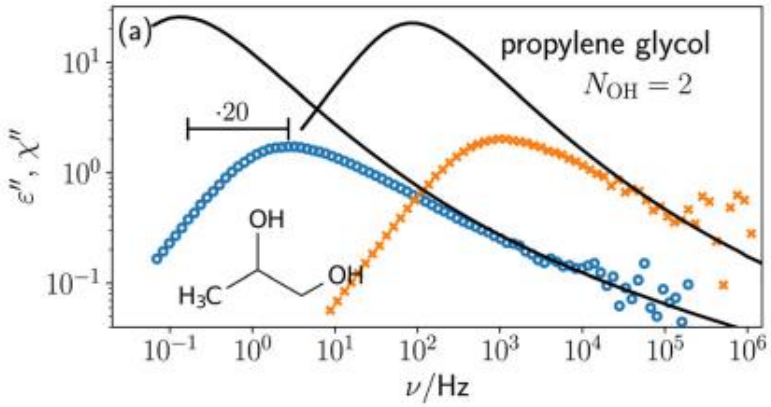
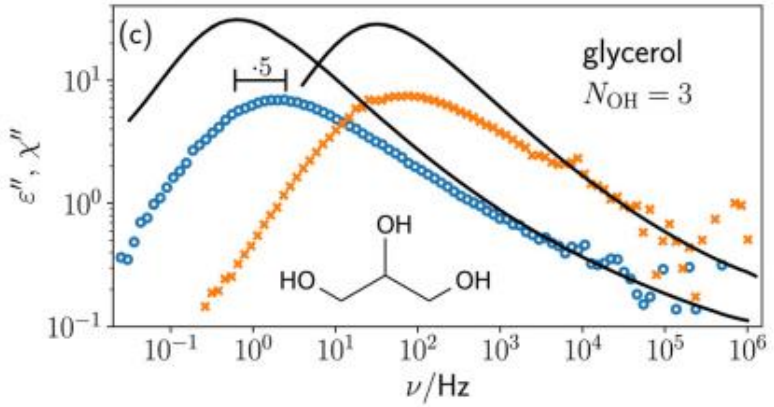
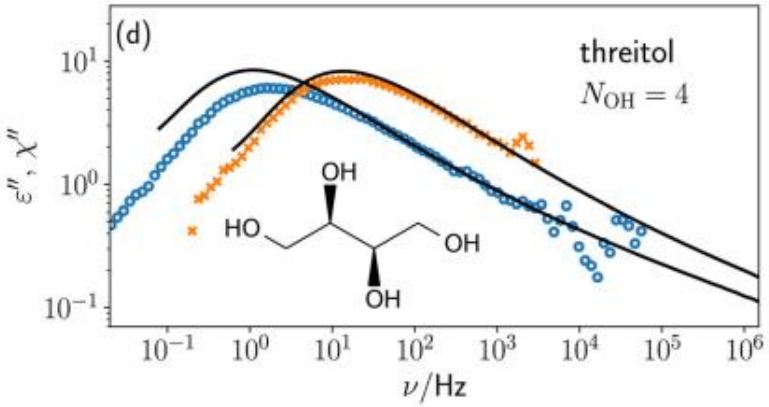
Glassy dynamics in polyalcohols: intermolecular simplicity *vs.* intramolecular complexity†

Till Böhmer, *[a] Jan Philipp Gabriel, [b] Rolf Zeißler, [a] Timo Richter[a] and Thomas Blochowicz *[a]

DLR



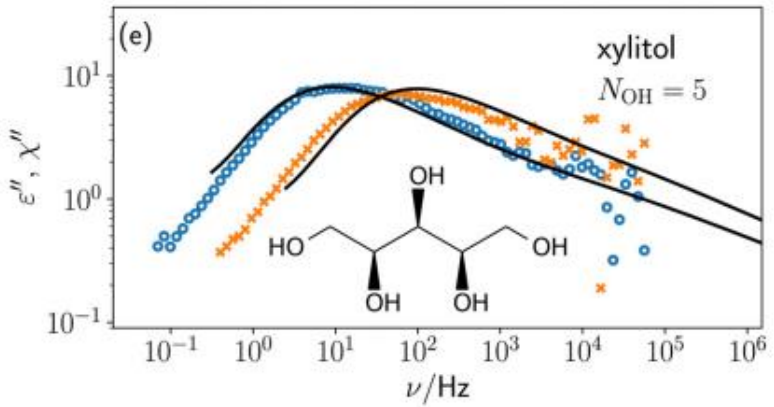


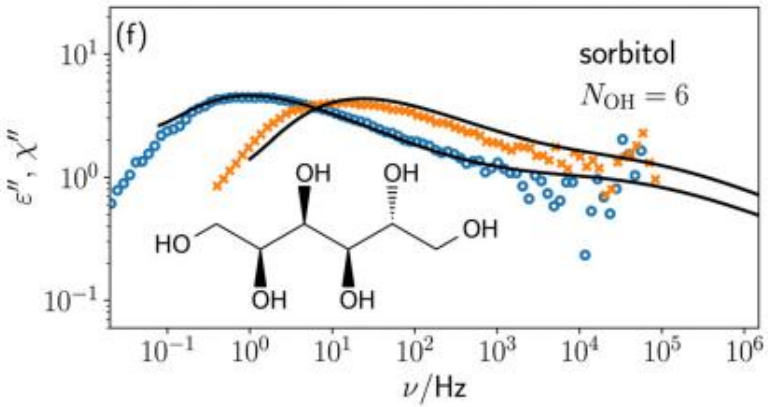


(b)

BDS
PCS

N_{OH}	T
2	175 K, 190 K
3	200 K, 210 K
4	235 K, 240 K
5	255 K, 260 K
6	275 K, 280 K





On the spectral shape of the structural relaxation in supercooled liquids

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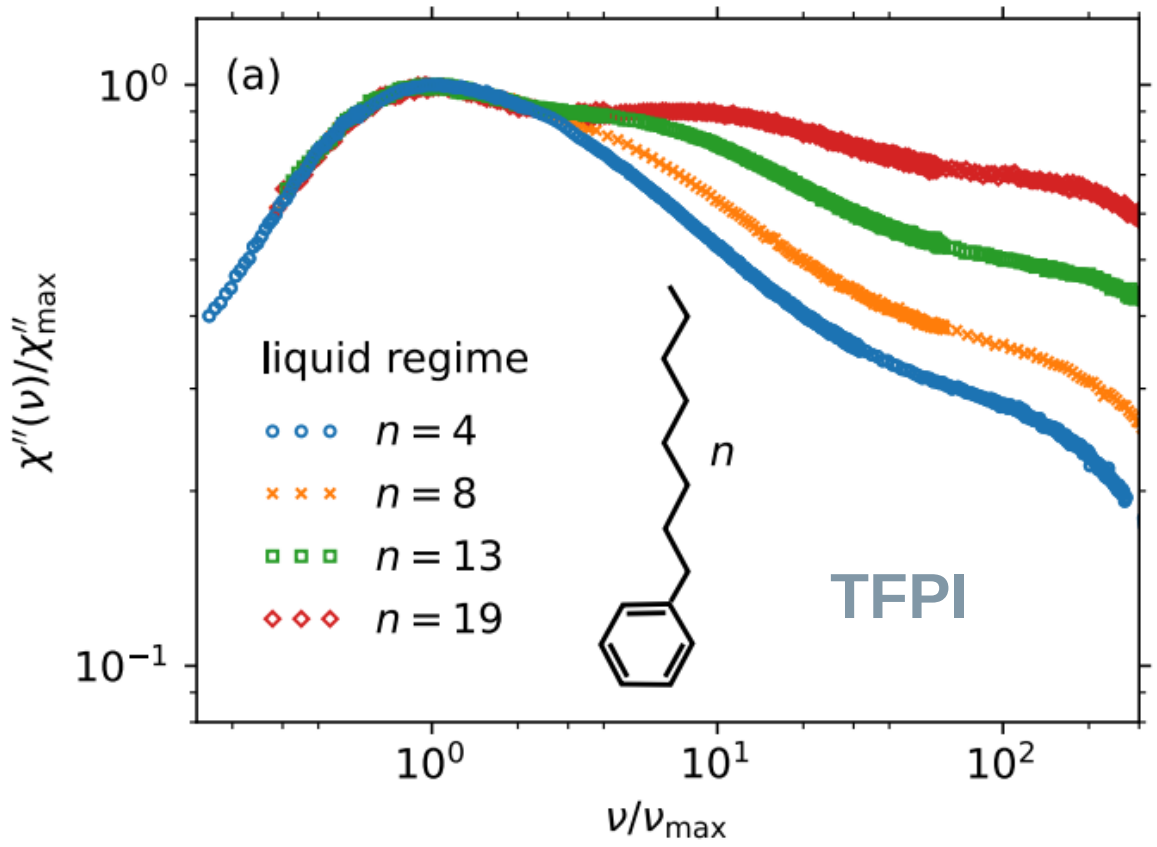
Till Böhmer,[1,a] Florian Pabst,[2,b] Jan Philipp Gabriel,[3] Rolf Zeißler,[4] and Thomas Blochowicz[4,c]

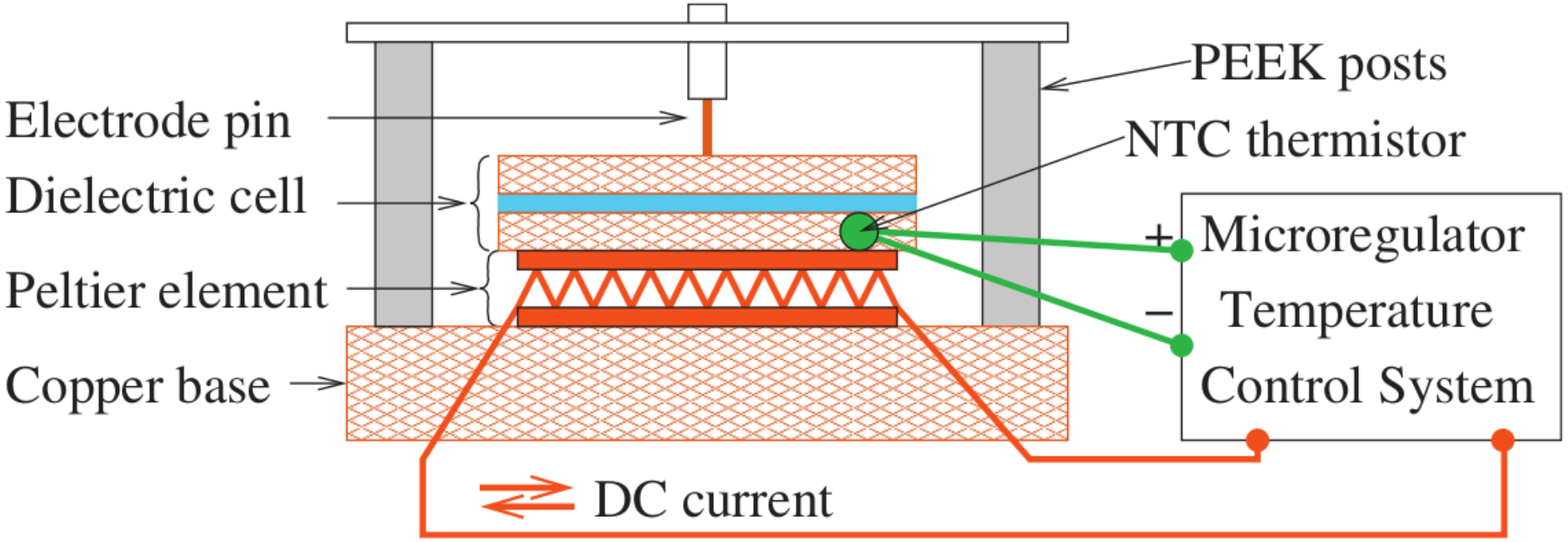


physical aging

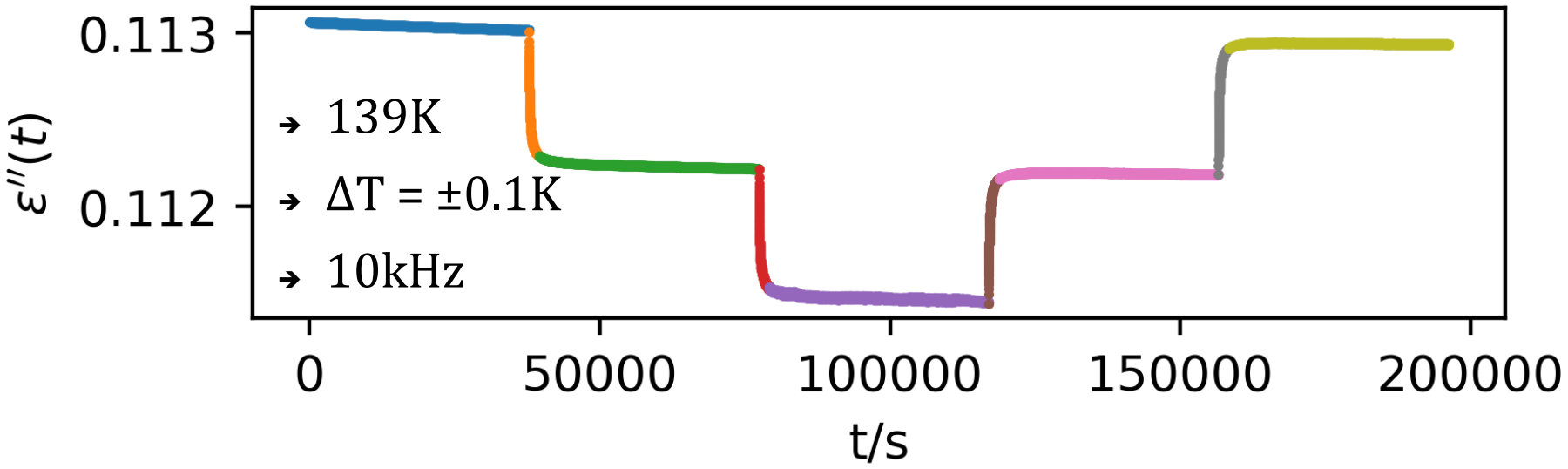
(from non equilibrium to equilibrium response)

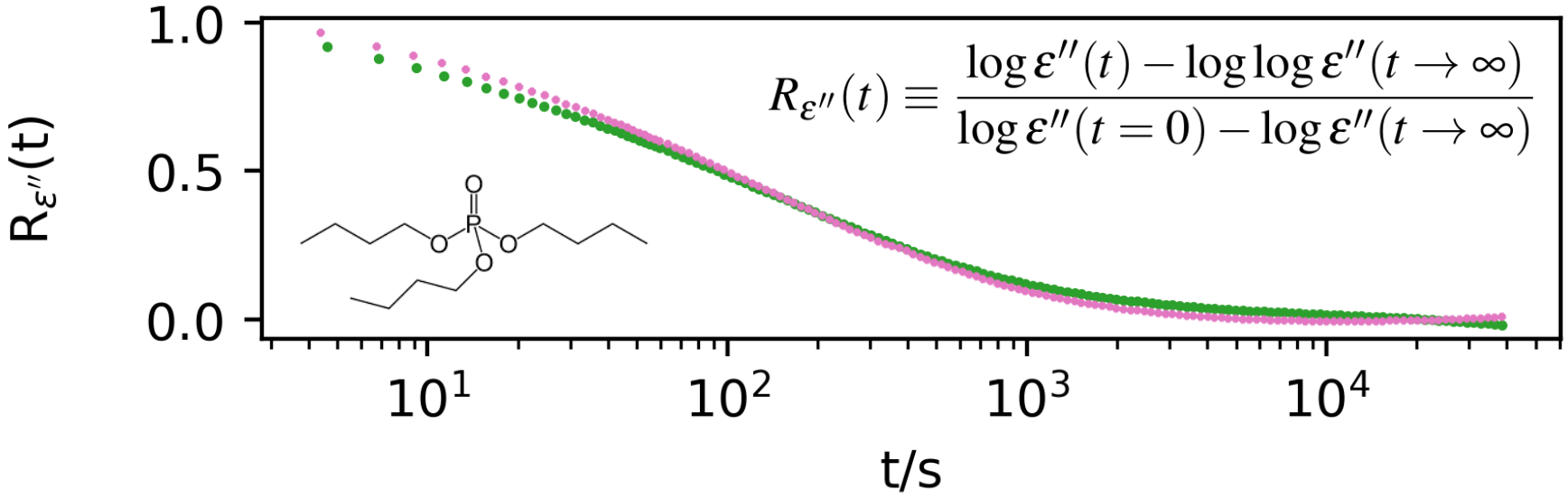
linear structural recovery - dielectric spectroscopy with a microregulator

T. Hecksher et al., J. Chem. Phys. (2010)



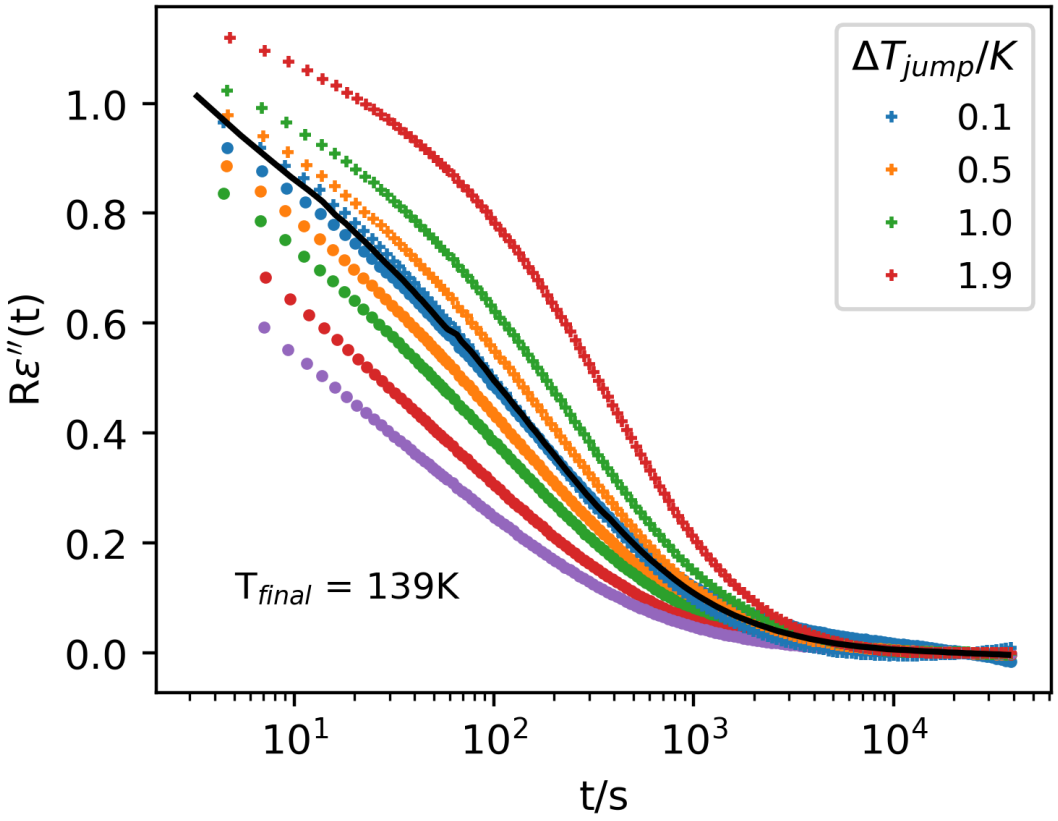
dielectric structural recovery

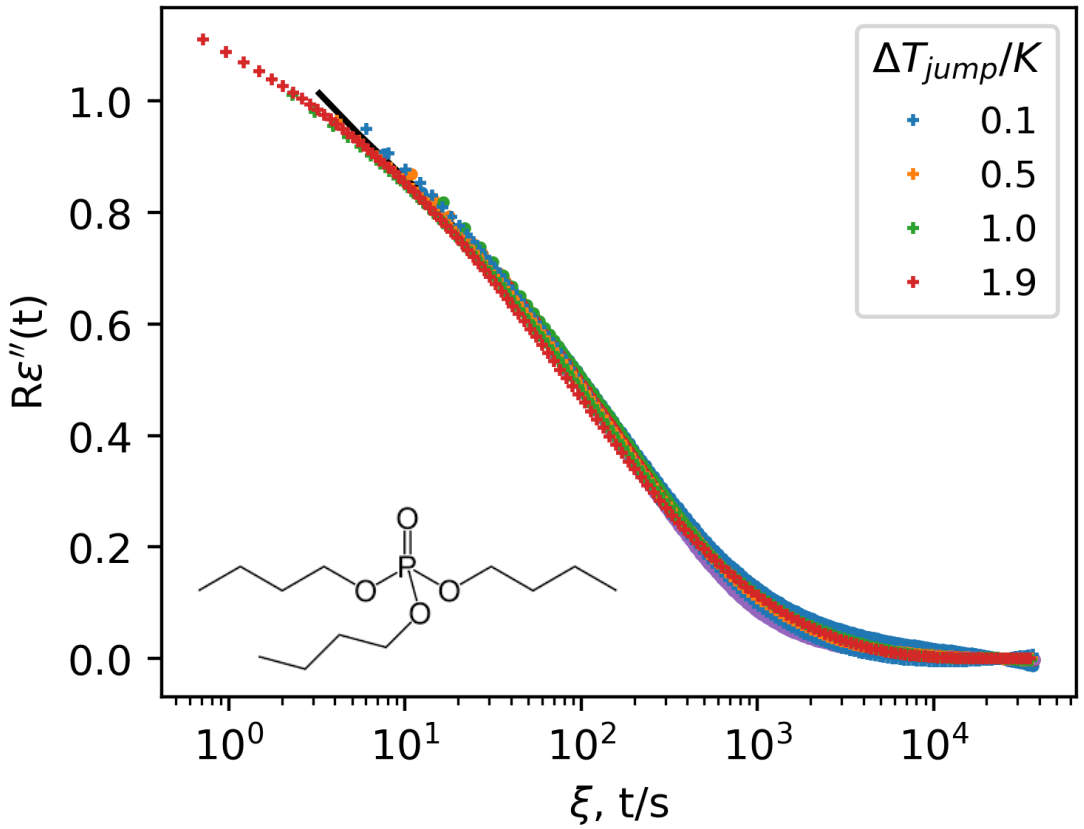




material time – single parameter

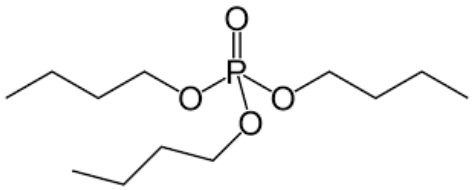
T. Hecksher et al., J. Chem. Phys. (2015)



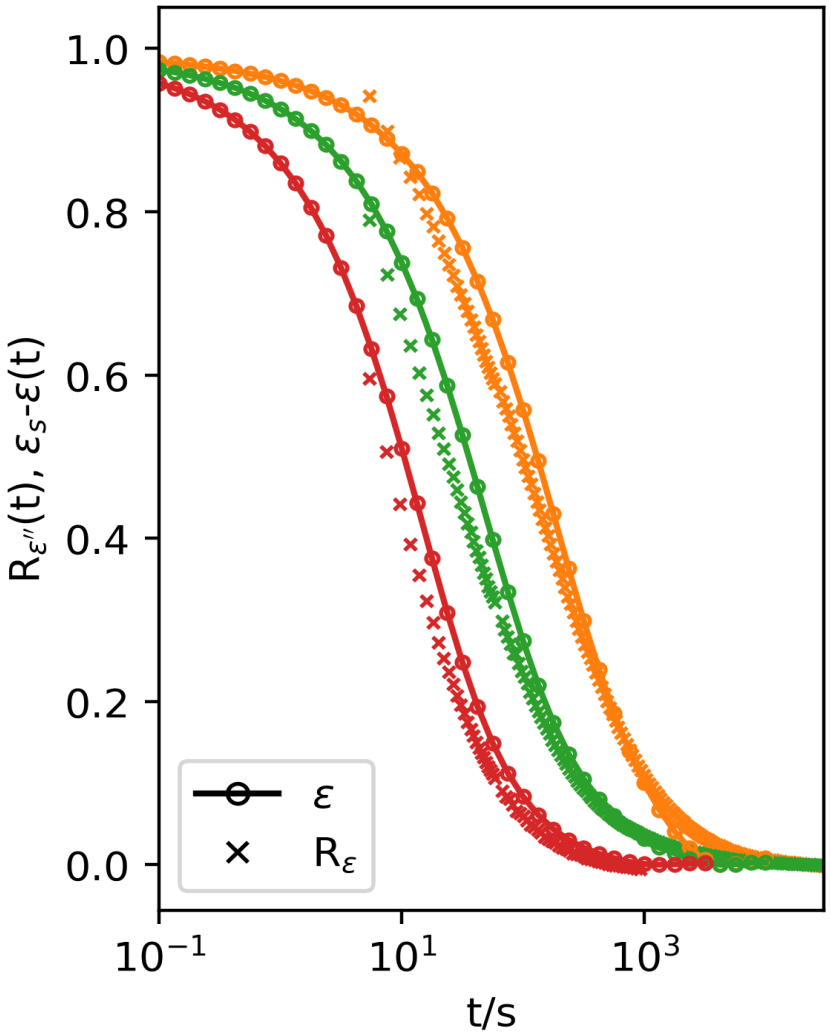


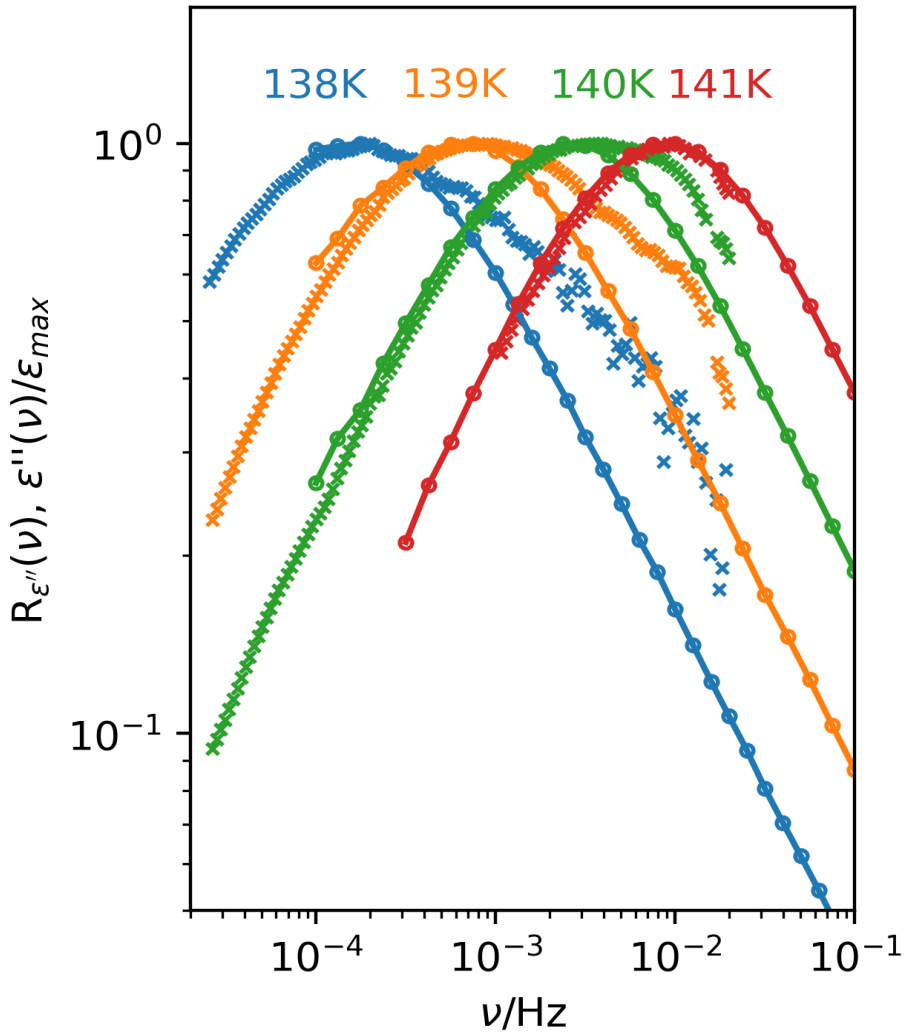
$$d\xi = \gamma(t)\,dt \quad , \Lambda_{12}=a\cdot\Delta T\,, \quad t_2(R) = \int_0^{t_1(R)} \exp\left(\Lambda_{12} R(t_1)\right)\,dt_1$$

TBP - tributylphosphate



- same terminal mode
- cross-correlations aging relevant
- recovery broader spectral shape



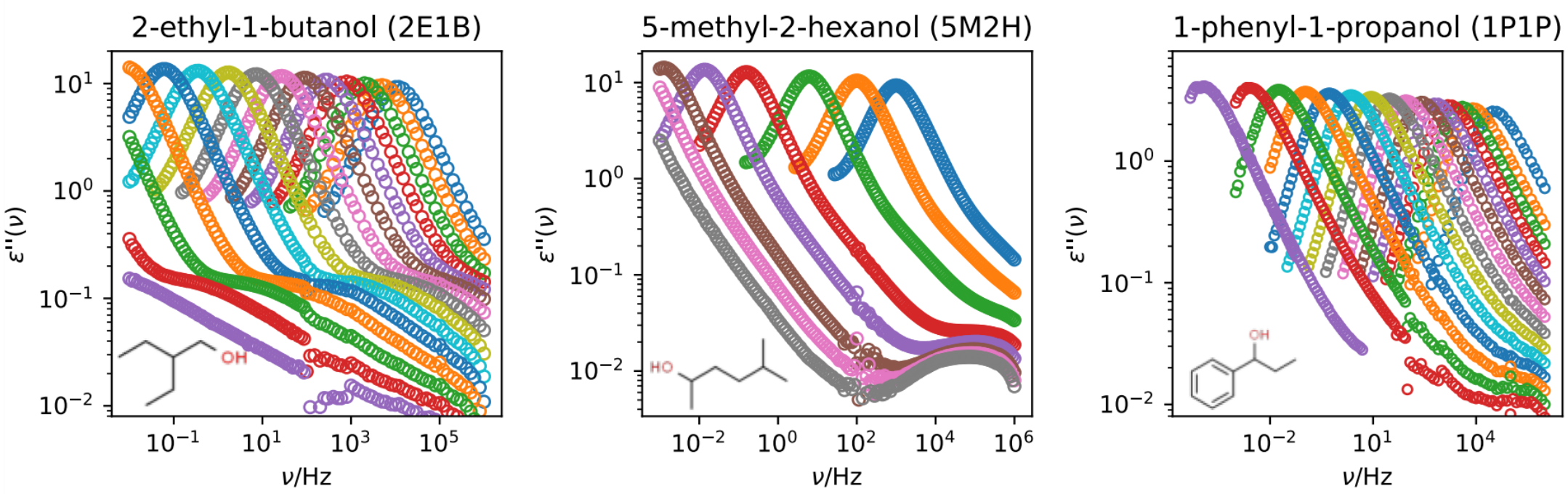


J. P. Gabriel et al., J. Phys. Chem. B (2025)

Linear-Limit Aging Times of Three Monoalcohols

Published as part of The Journal of Physical Chemistry B special issue "Mark Ediger Festschrift".

Jan Philipp Gabriel,* Jeppe C. Dyre,* and Tina Hecksher*



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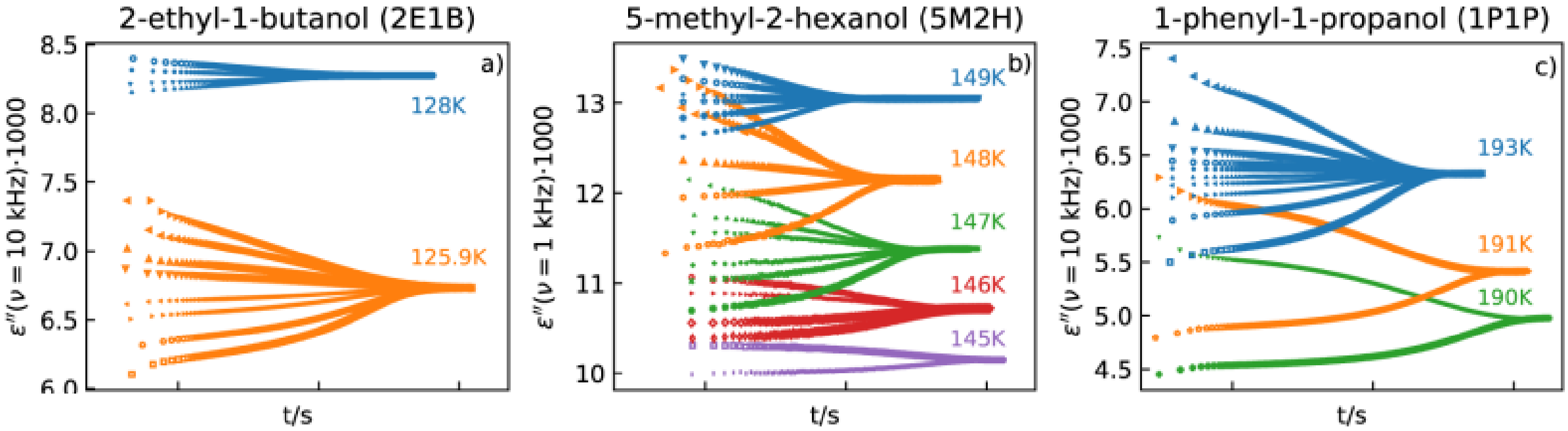
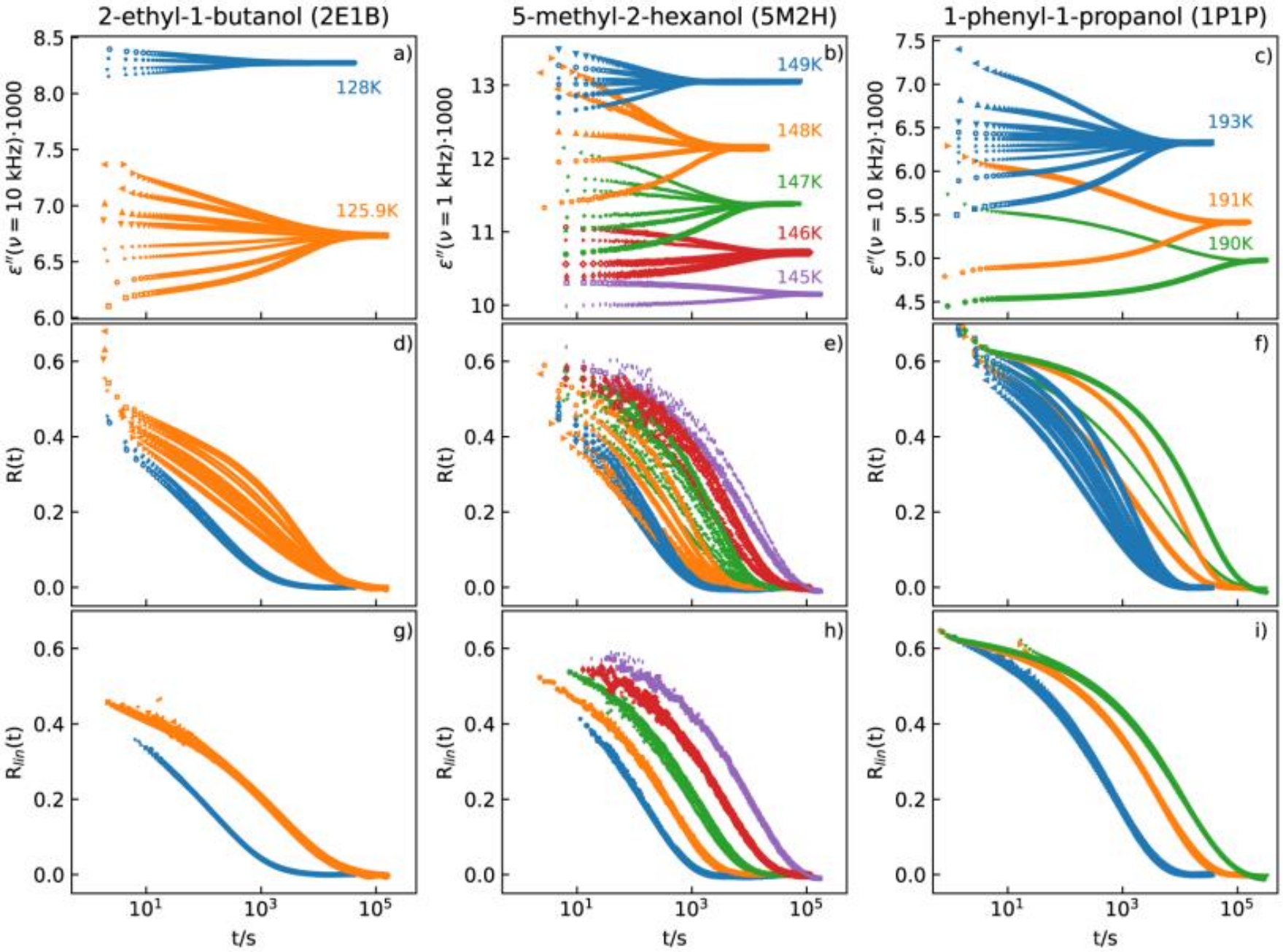
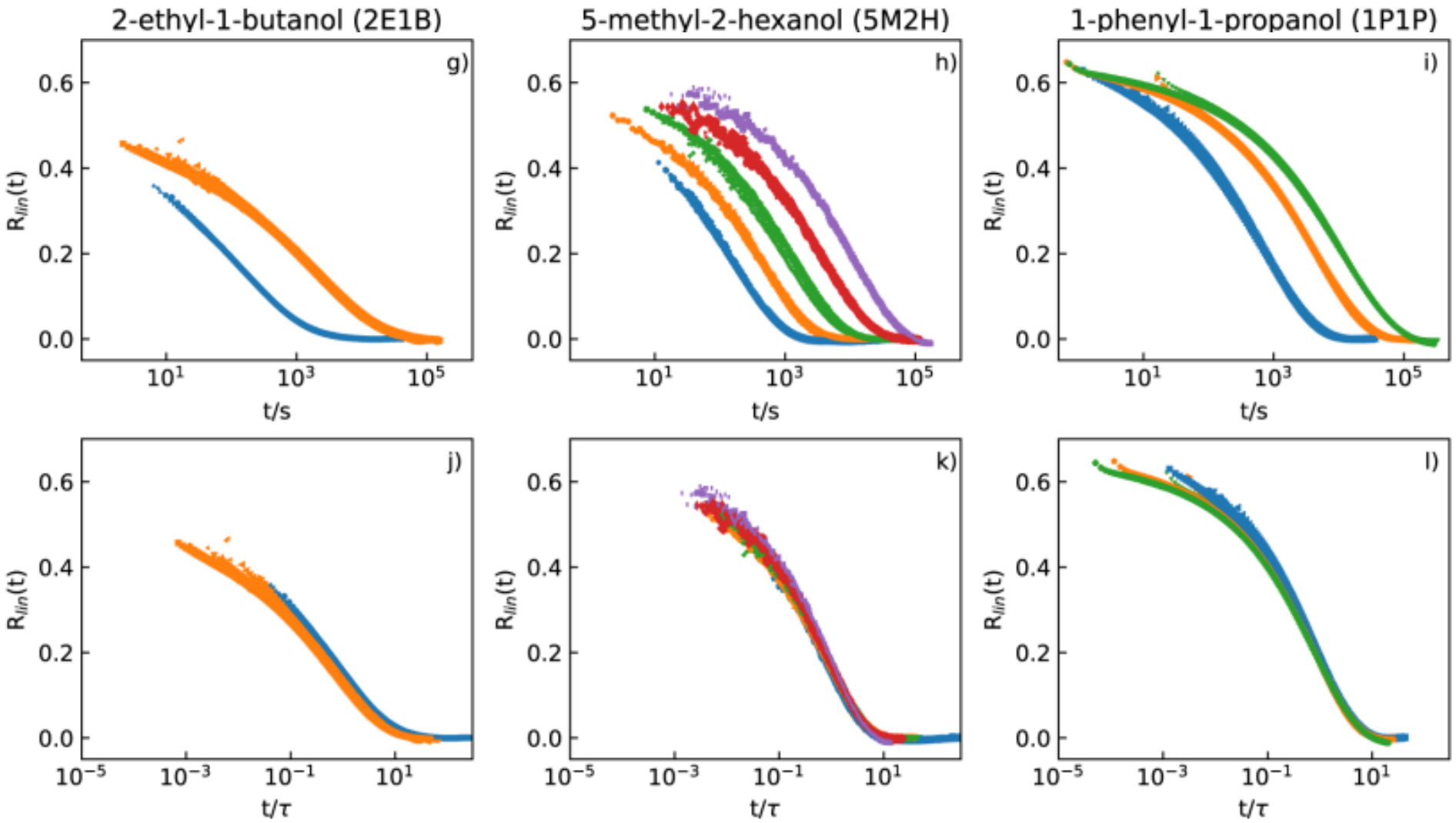


J. P. Gabriel et al., J. Phys. Chem. B (2025)



J. P. Gabriel et al., J. Phys. Chem. B (2025)



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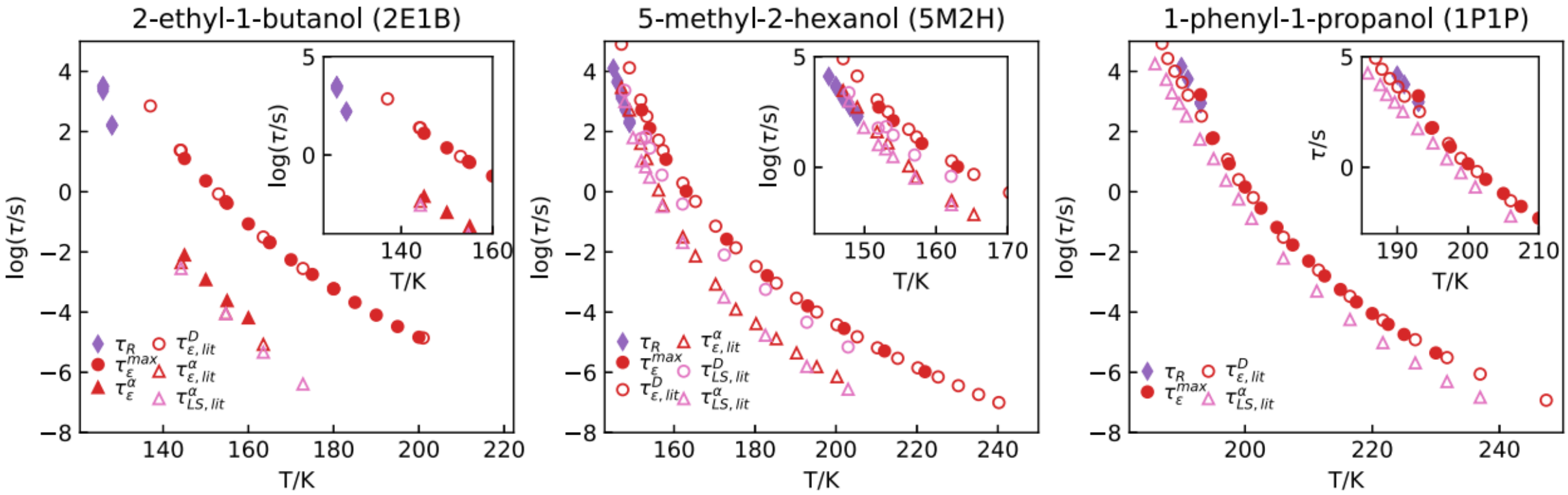
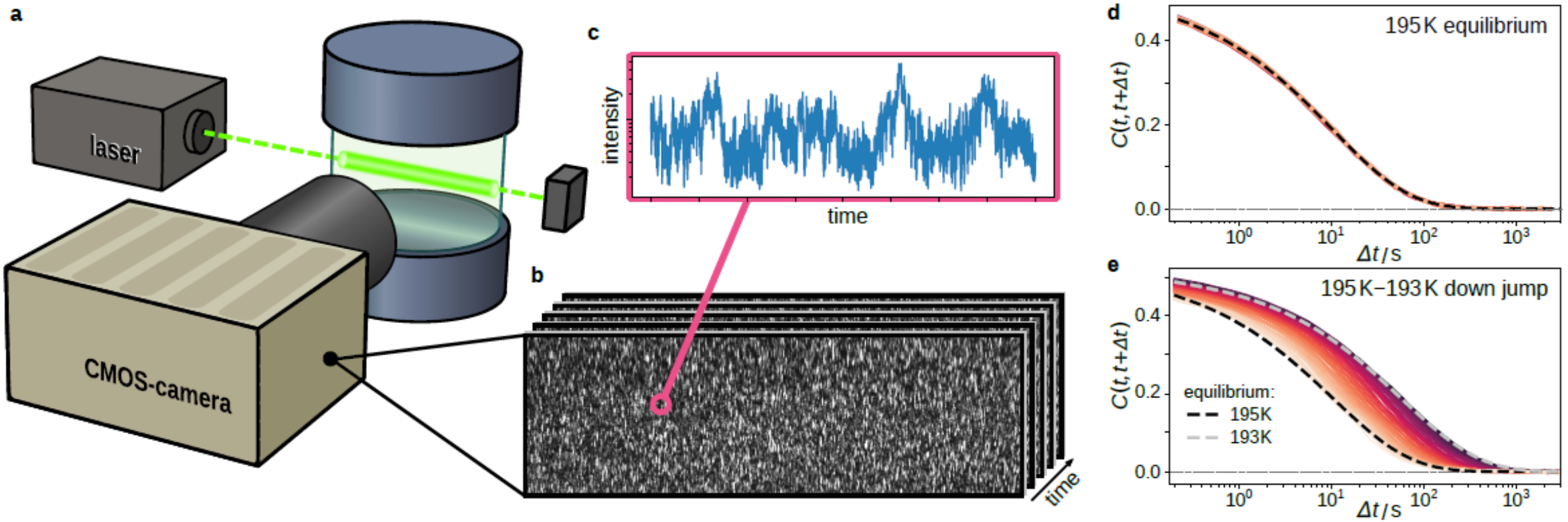


time resolved correlation functions

T. Böhmer et al., Nature Physics (2023) accepted

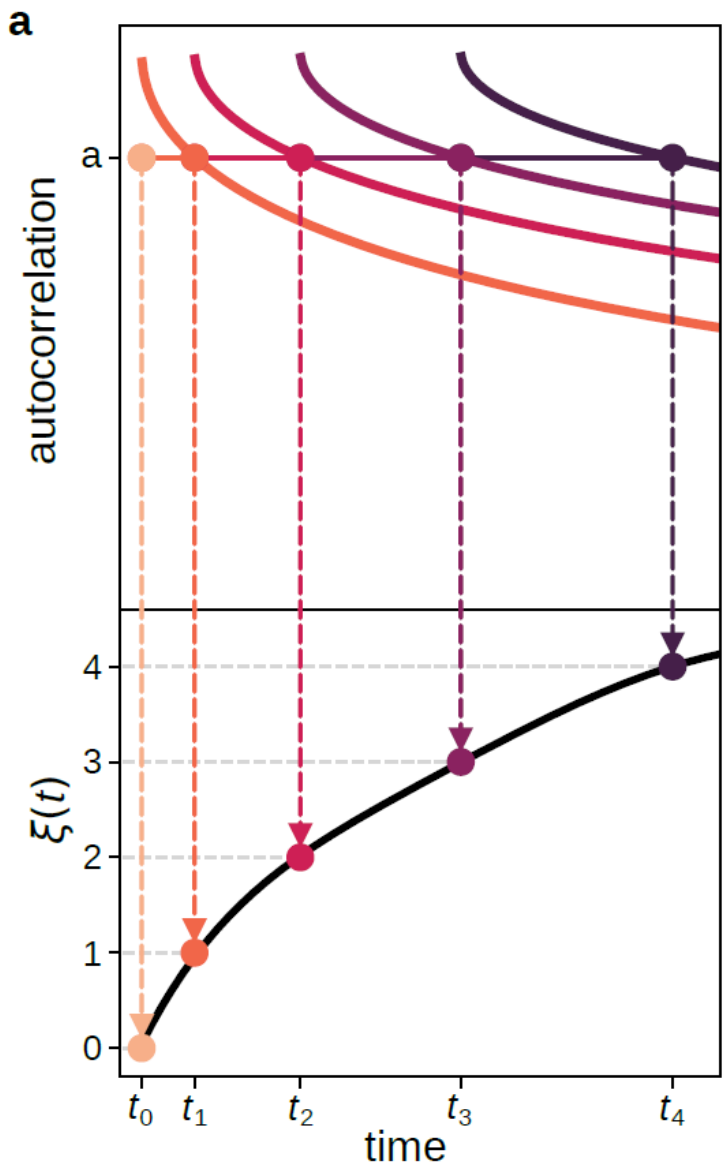


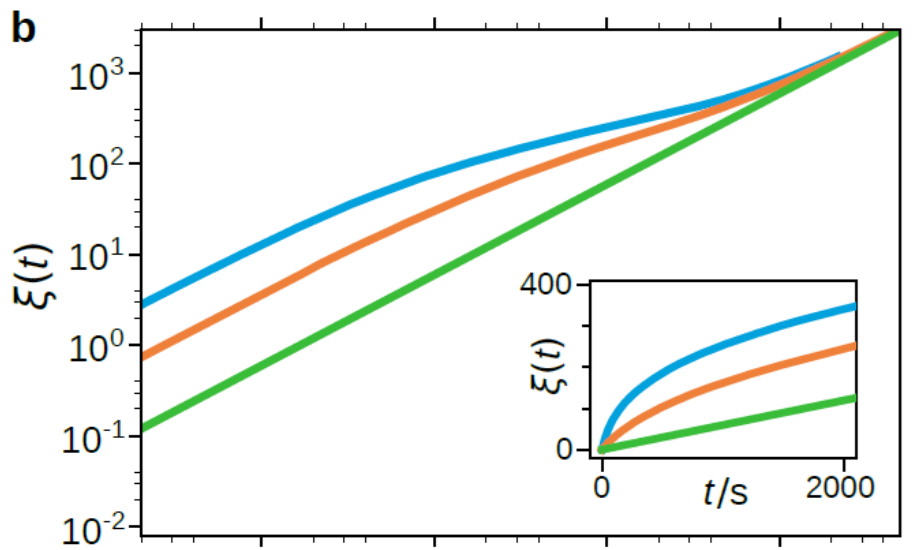
$$C(t, t+\Delta t) = \frac{N}{M} \sum_{j=1}^{M} \left[\frac{\sum_{i=1}^{N} I_{ij}(t) I_{ij}(t+\Delta t)}{\left(\sum_{i=1}^{N} I_{ij}(t)\right)\left(\sum_{i=1}^{N} I_{ij}(t+\Delta t)\right)} \right] - 1$$

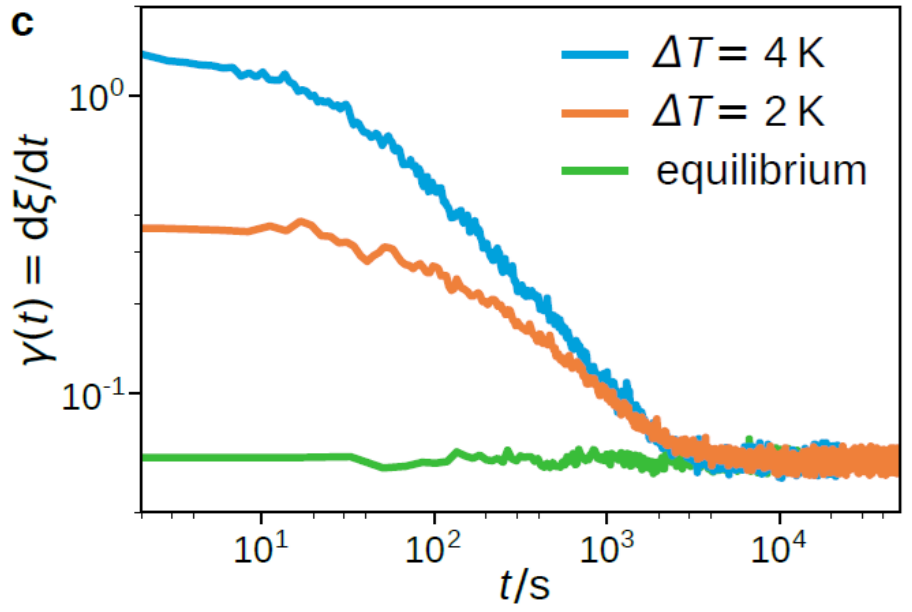
material time linearises dynamics

T. Böhmer et al., Nature Physics (2023) accepted

$$\gamma = \left| \frac{d\xi}{dt} \right|$$

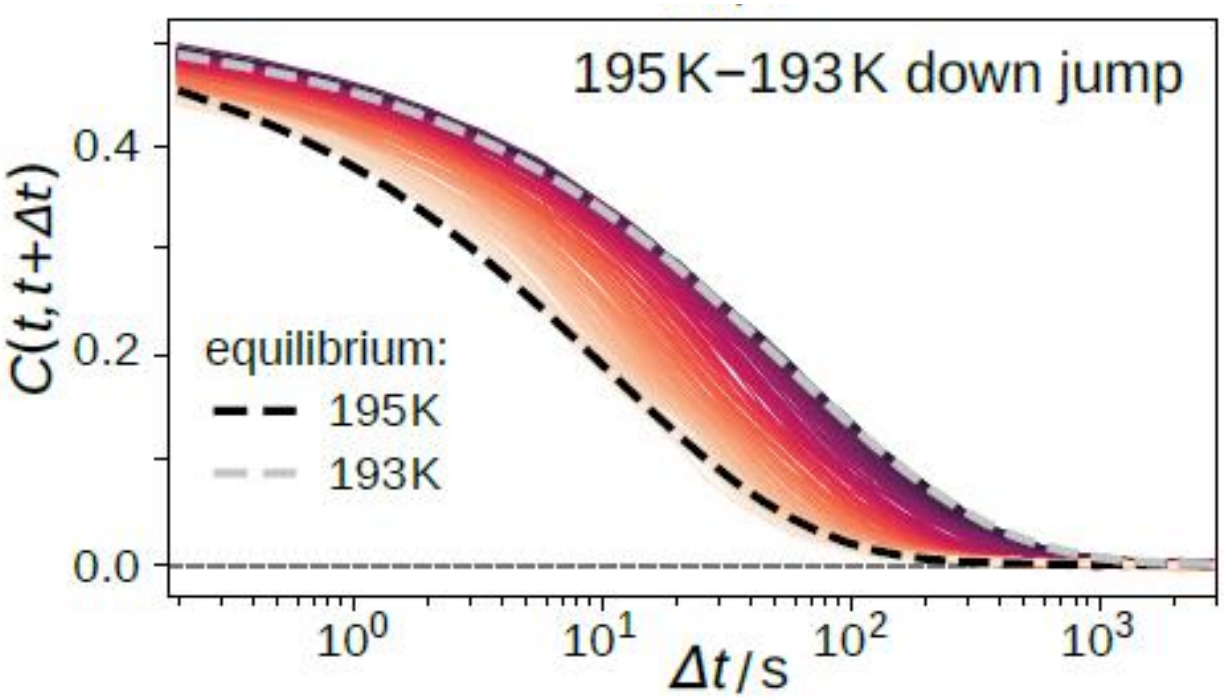


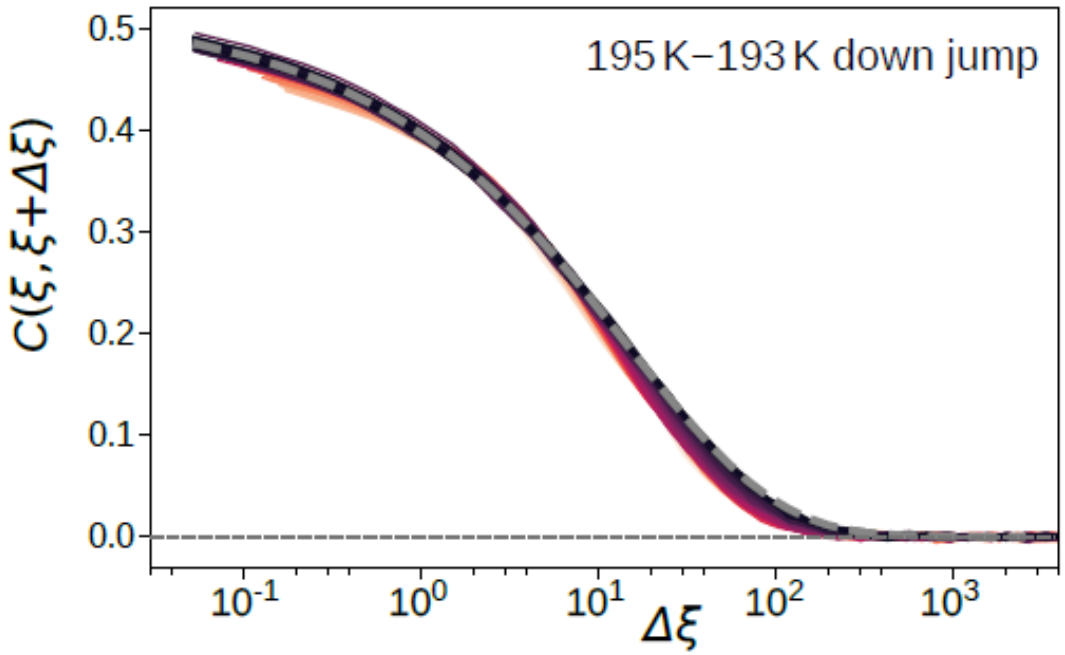




material time application 1P1P

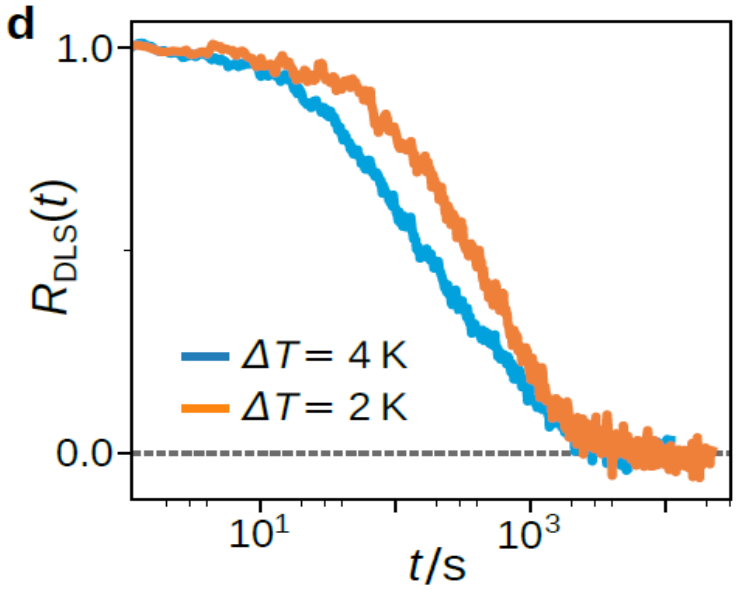
T. Böhmer et al., Nature Physics (2023)

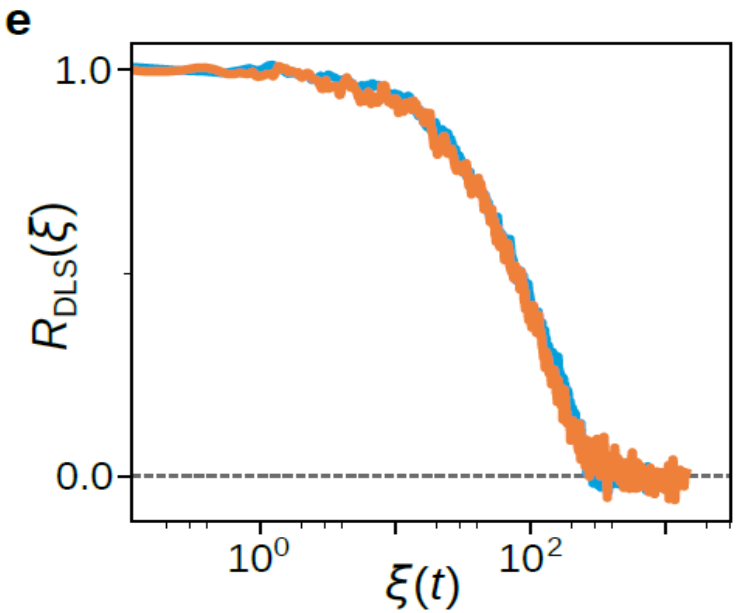


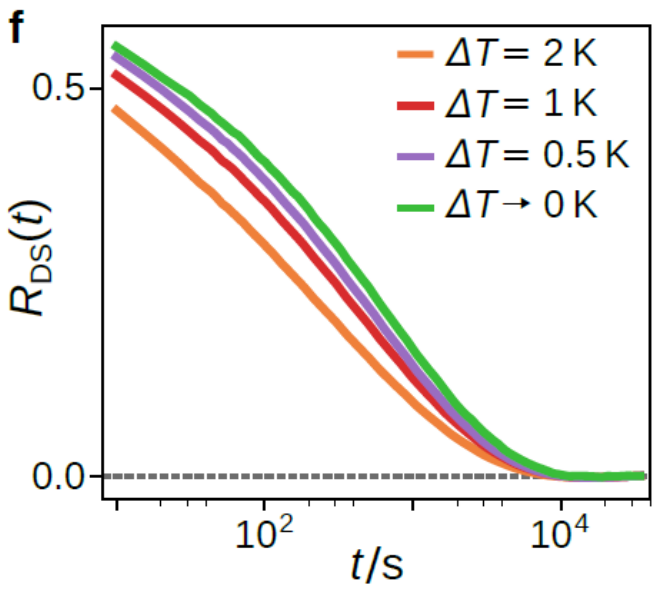


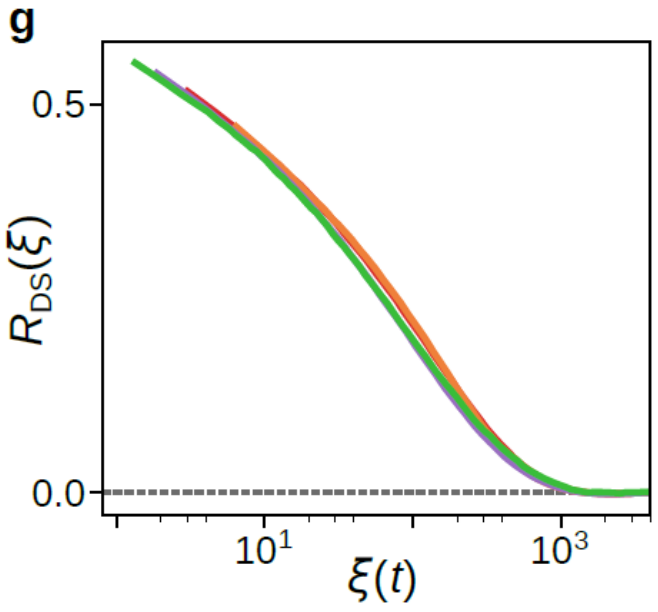
$$R(t) \equiv \frac{g_1(t) - g_1(t \to \infty)}{g_1(t=0) - g_1(t \to \infty)}$$

$$R^X_{\varepsilon''}(t) = \frac{\varepsilon''(\nu_0, t) - \varepsilon''(\nu_0, t \to \infty)}{\varepsilon''(\nu_0, t \to 0^-) - \varepsilon''(\nu_0, t \to \infty)}$$







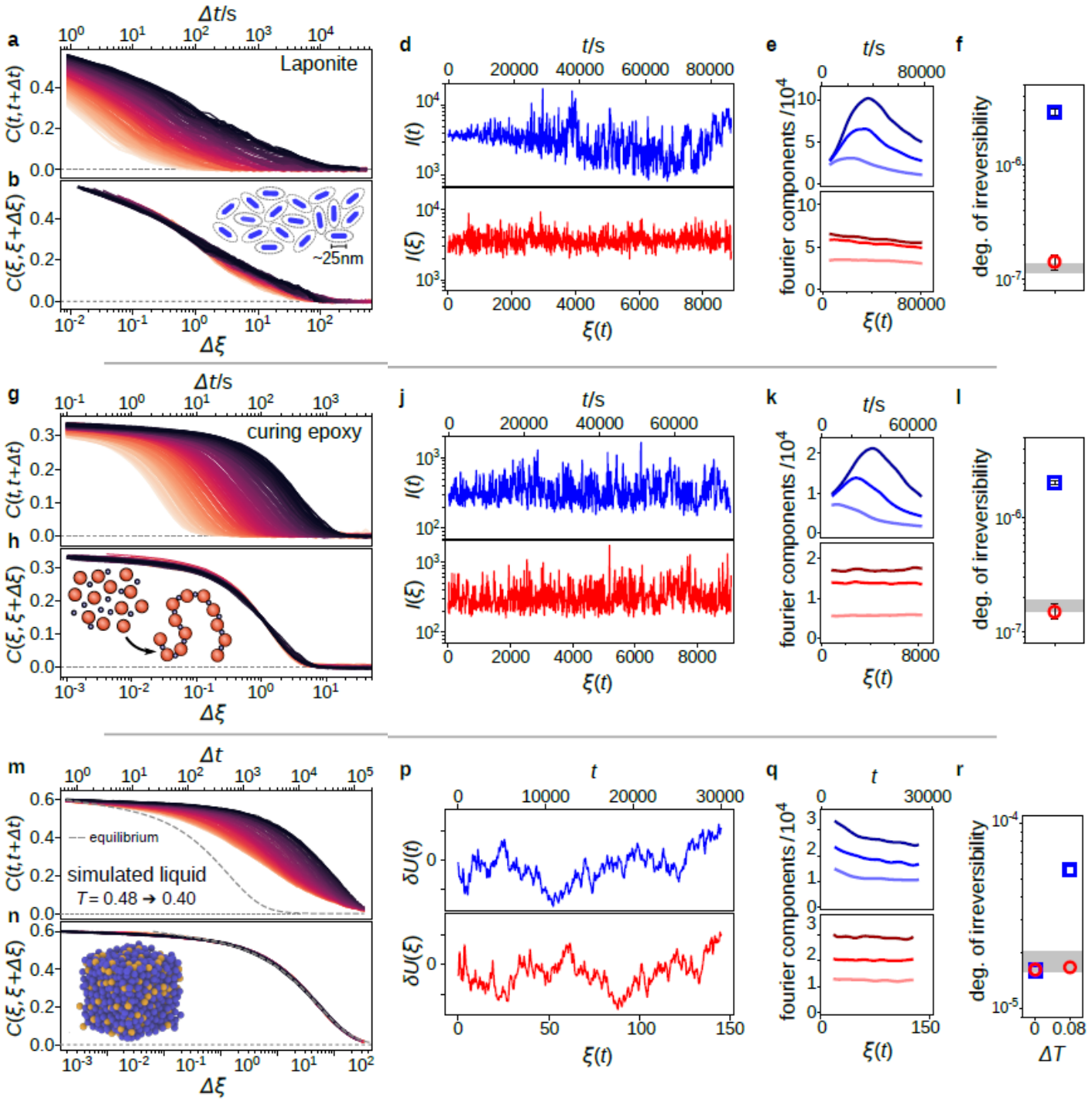


T. Böhmer et al., Nature Physics (2023)

Colloid

Polymerizing liquid

Simulated liquid



athermal

(glass and jamming)

properties are time and energy dependent…

Gas

Fluid

Soft/Solid

compaction of grains …

Cereal

Roman Street

Old Roman road between Cologne and Neus

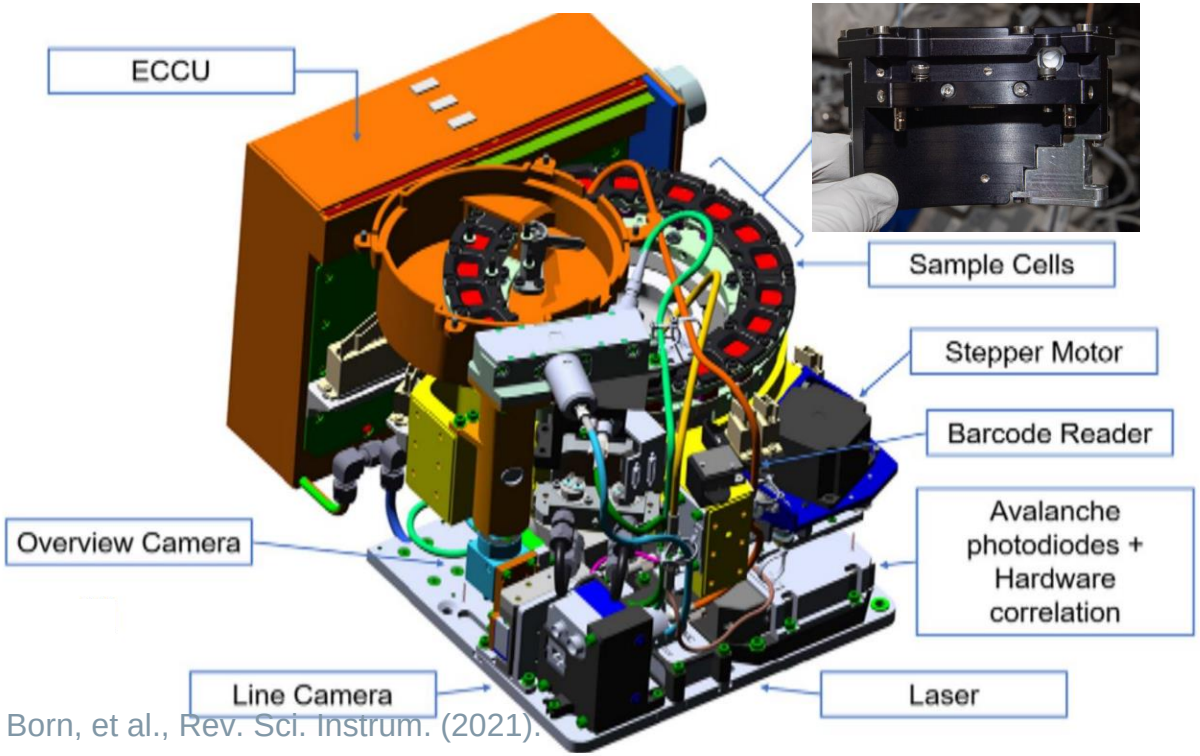
Swiss road

Switzerland road deformation

Moon

how do particles compact without gravity?

Soft Matter Dynamics Module (SMD) on the ISS
Foams - Emulsions - Grains



Born, et al., Rev. Sci. Instrum. (2021).

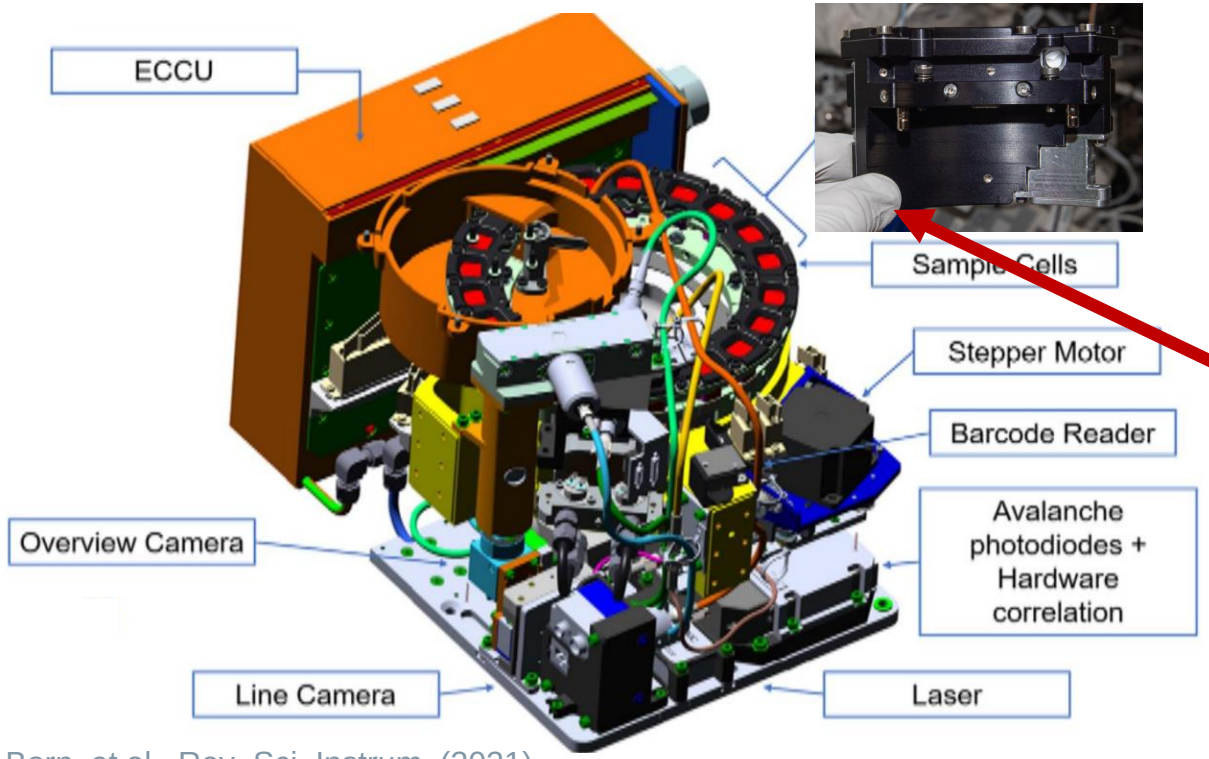
Alexander Gerst installing the SMD

ISS and SMD provide long-term low gravity for the investigation of slow processes

how do particles compact without gravity?

Soft Matter Dynamics Module (SMD) on the ISS

Foams - Emulsions - Grains

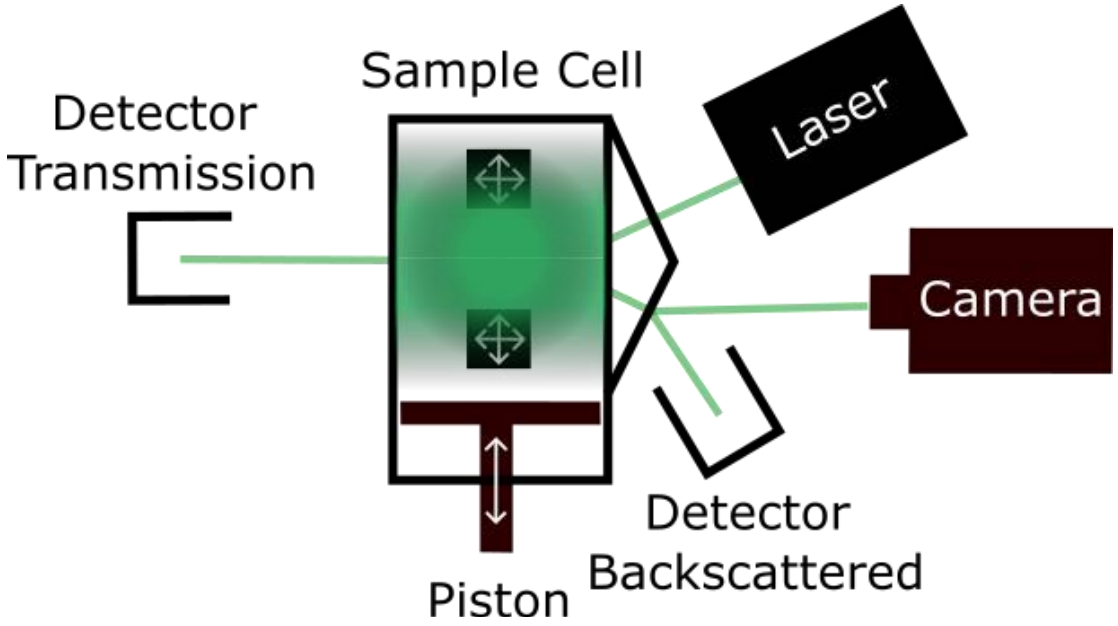


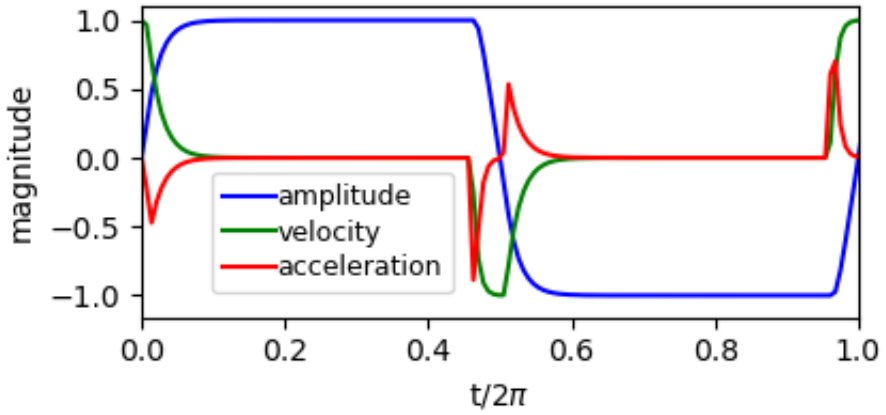
Born, et al., Rev. Sci. Instrum. (2021).

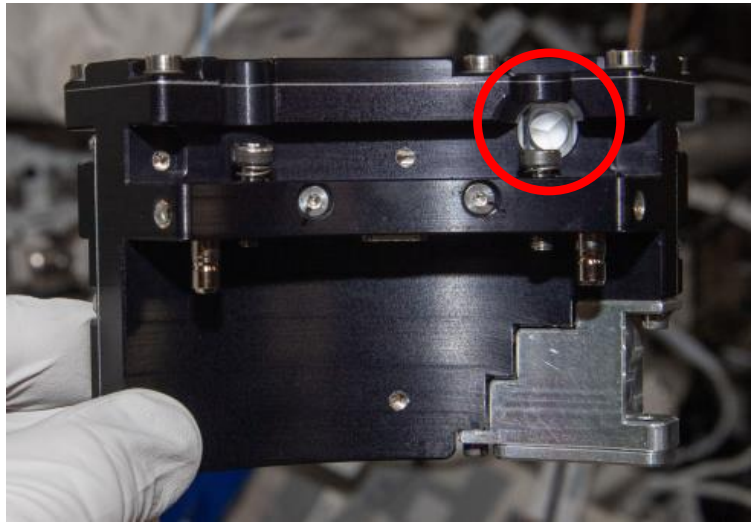
Andreas Mogensen

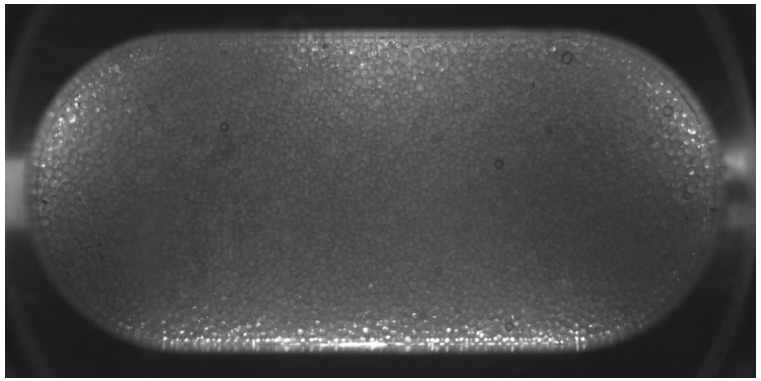
ISS and SMD provide long-term low gravity for the investigation of slow processes

four piezo crystals generate a pulsed excitation of approx. 1g

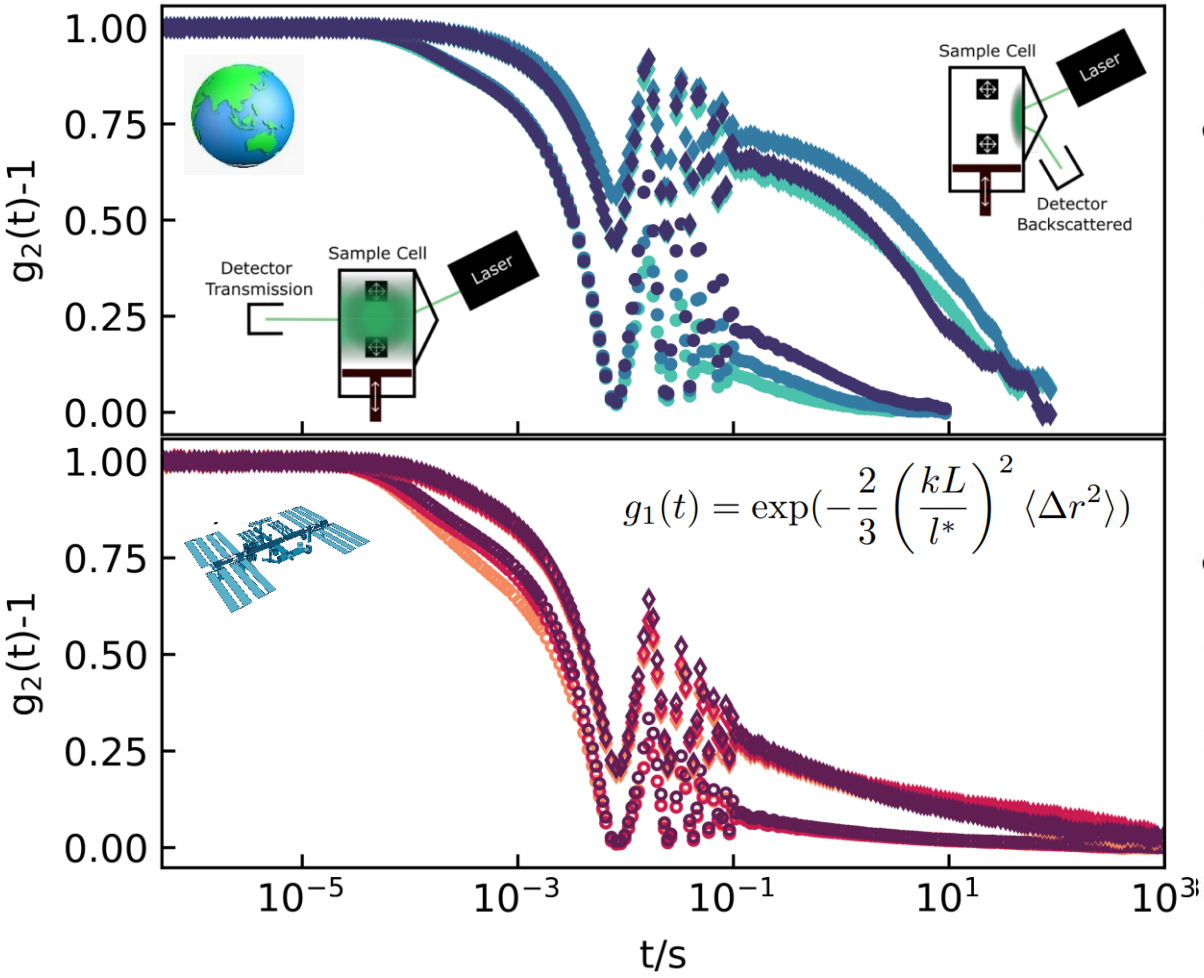


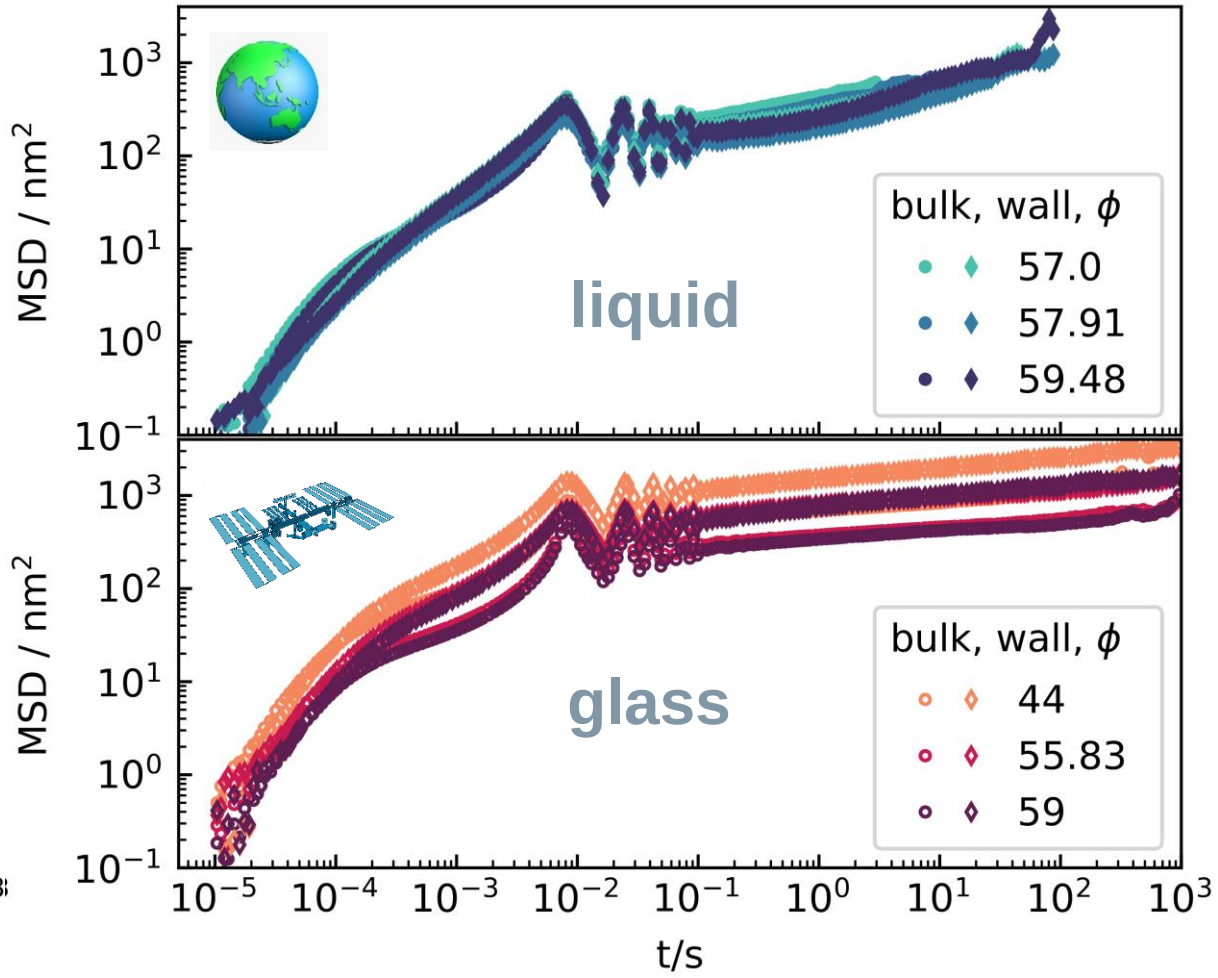




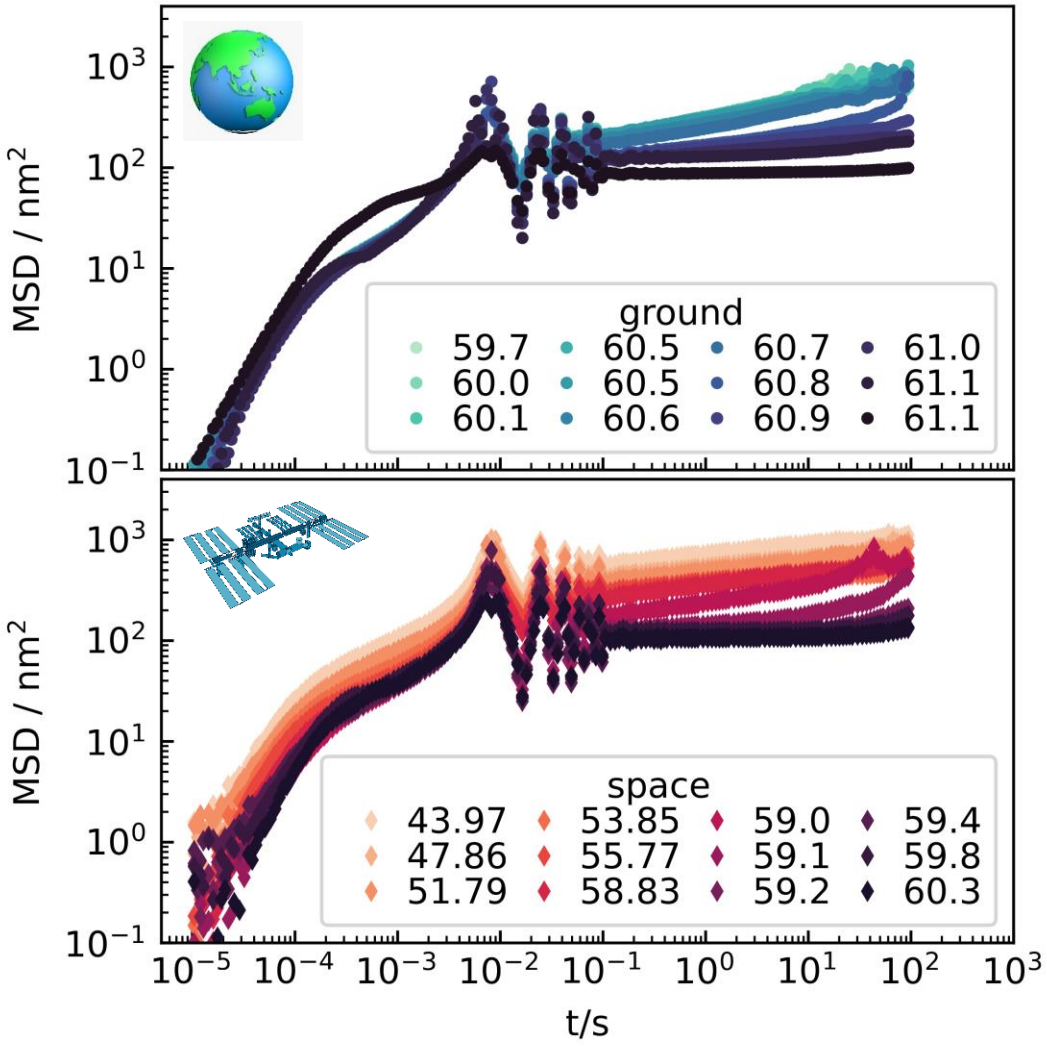


Granule mobility on Earth and on the ISS





the glass transition takes place earlier without gravity



Earth:

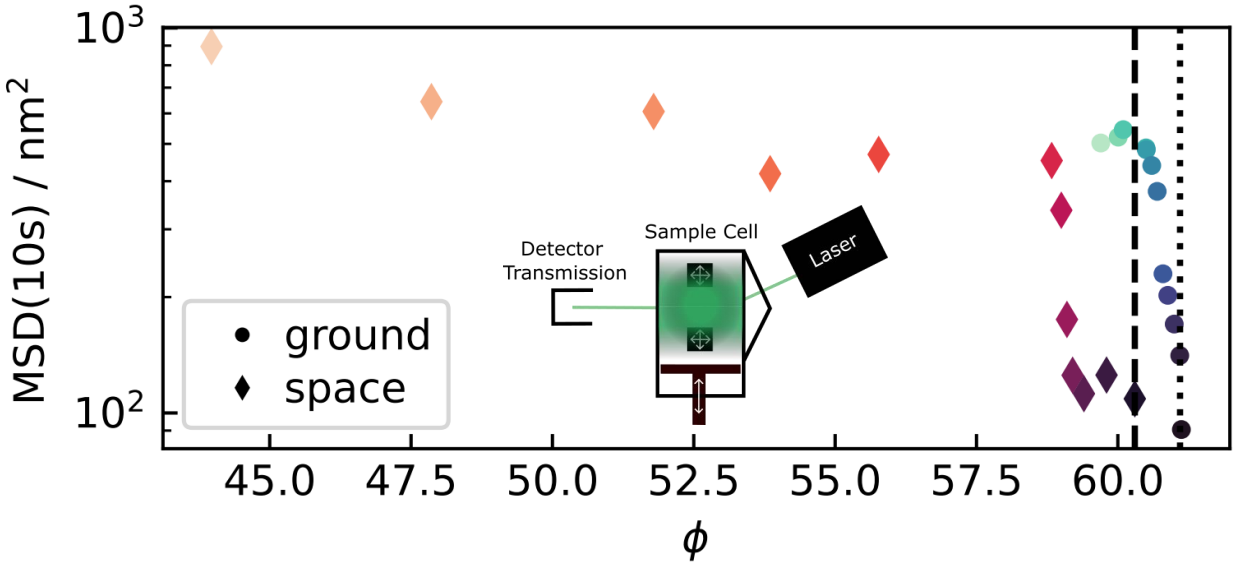
Glassy 60.6%

Jamming 61.1%

ISS:

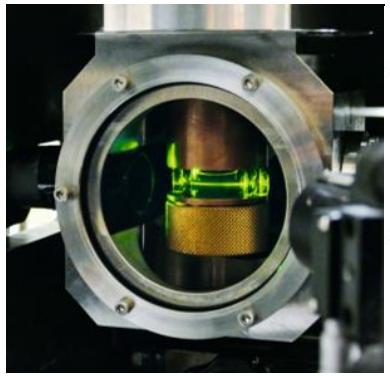
Glassy 59.0%

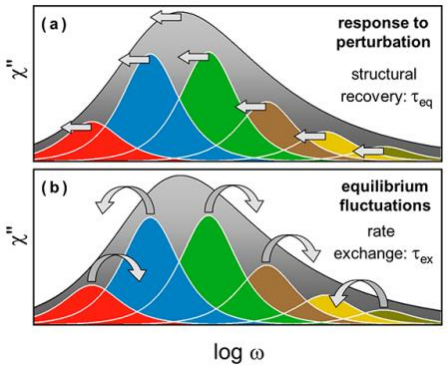
Jamming 60.3%.

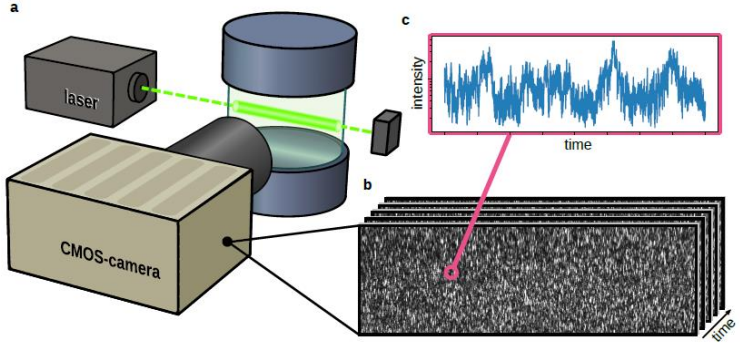


Summary

- The spectral shape is related to the Kirkwood factor and dipole density.
- The spectral shape and cross-correlations depend on the molecular specifics. (polymer-like, asymmetries in shape, H-bound positions).
- Material time works in many systems and method independent.
- Densification in space is less efficient, and the spectra are similar to those of liquids.
- Consistent with: Simulations, solvation dynamics, mechanical spectroscopy, NMR, etc.

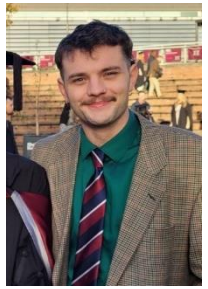






Acknowledgment

German Aerospace Center


Christopher Mayo,


Marlo Kunzner,


Philip Born,


Matthias Sperl,

Roskilde University


Jepper Dyre,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Thomas Blochowicz,


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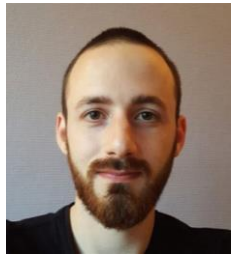
Rolf Zeißler,

Université Paris-Saclay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