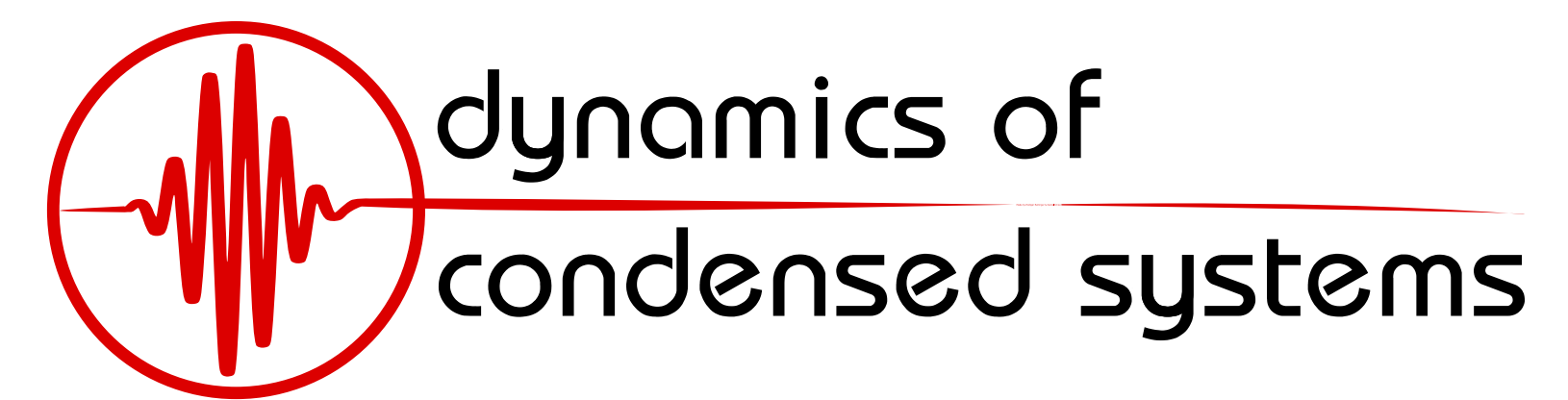


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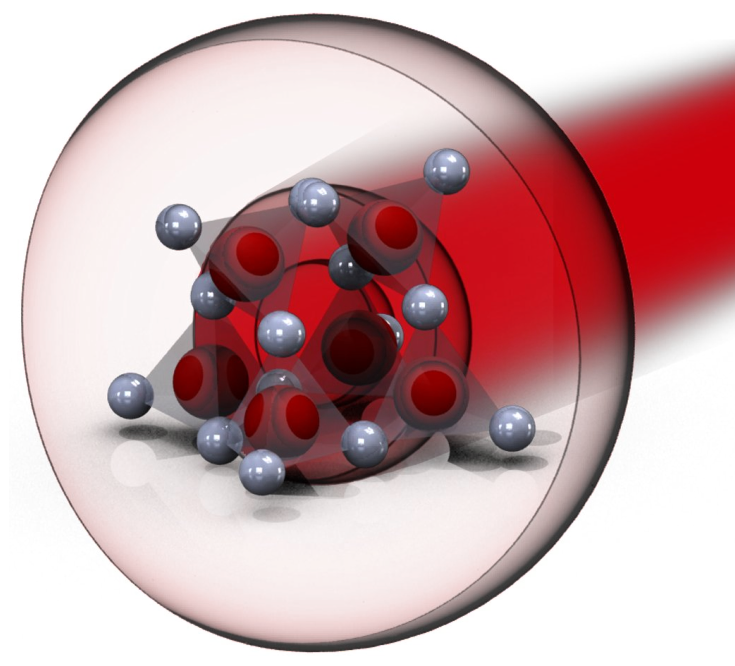
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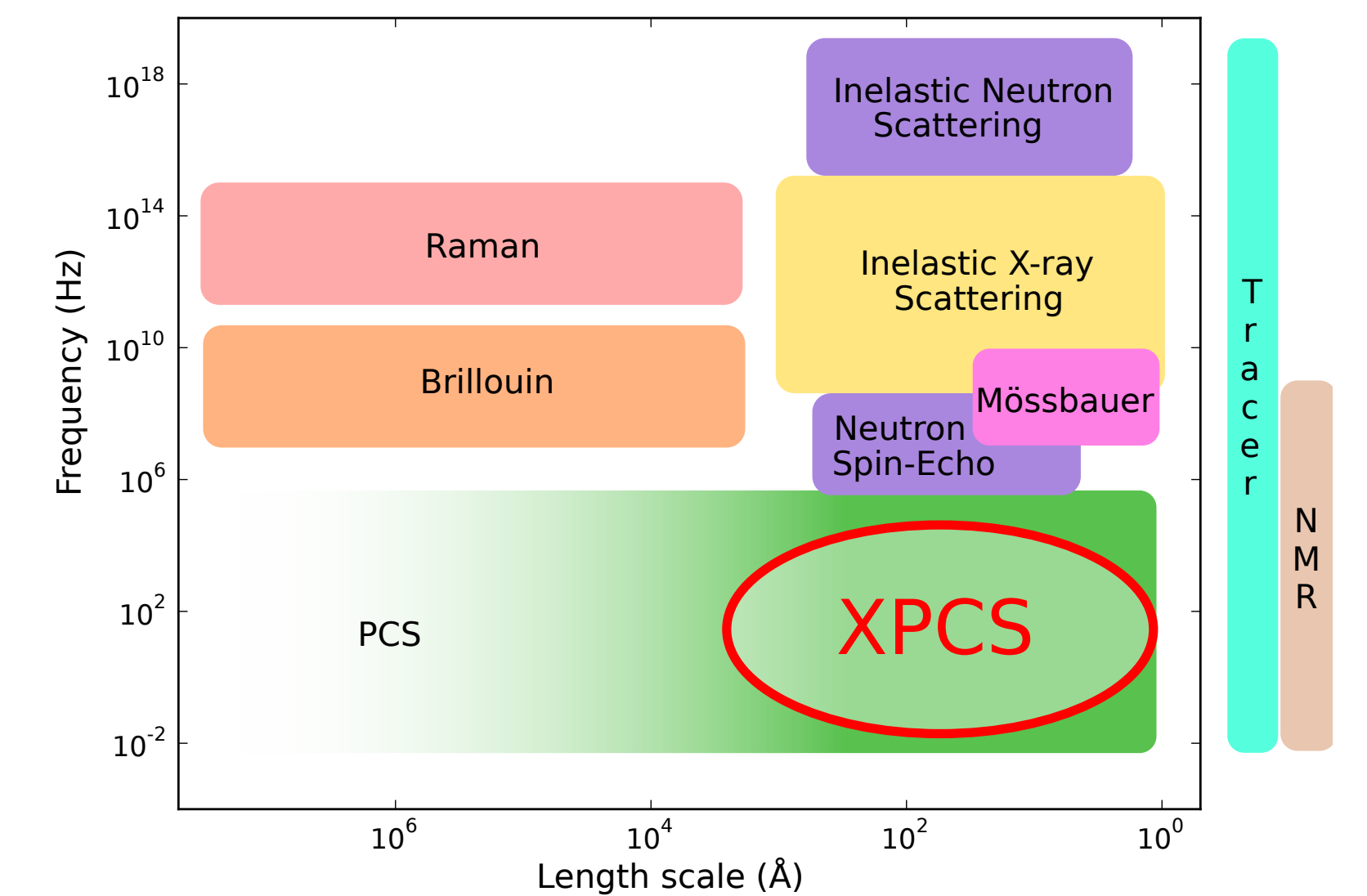
Introduction

Despite the fact that glasses have been studied for many decades, they stay enigmatic at the atomic level and refuse to reveal their underlying dynamics to a satisfactory level. Many of these materials like fast ionic conducting glasses are relevant both on the theoretical and on the technological level. With the avail-



ability of synchrotron sources like the ESRF, new techniques became possible. We extended one of the most promising methods to the sub-nanometre range, obtaining insight into dynamics on atomic length scales. This technique is called atomic X-ray Photon Correlation Spectroscopy (aXPCS) [1,2].

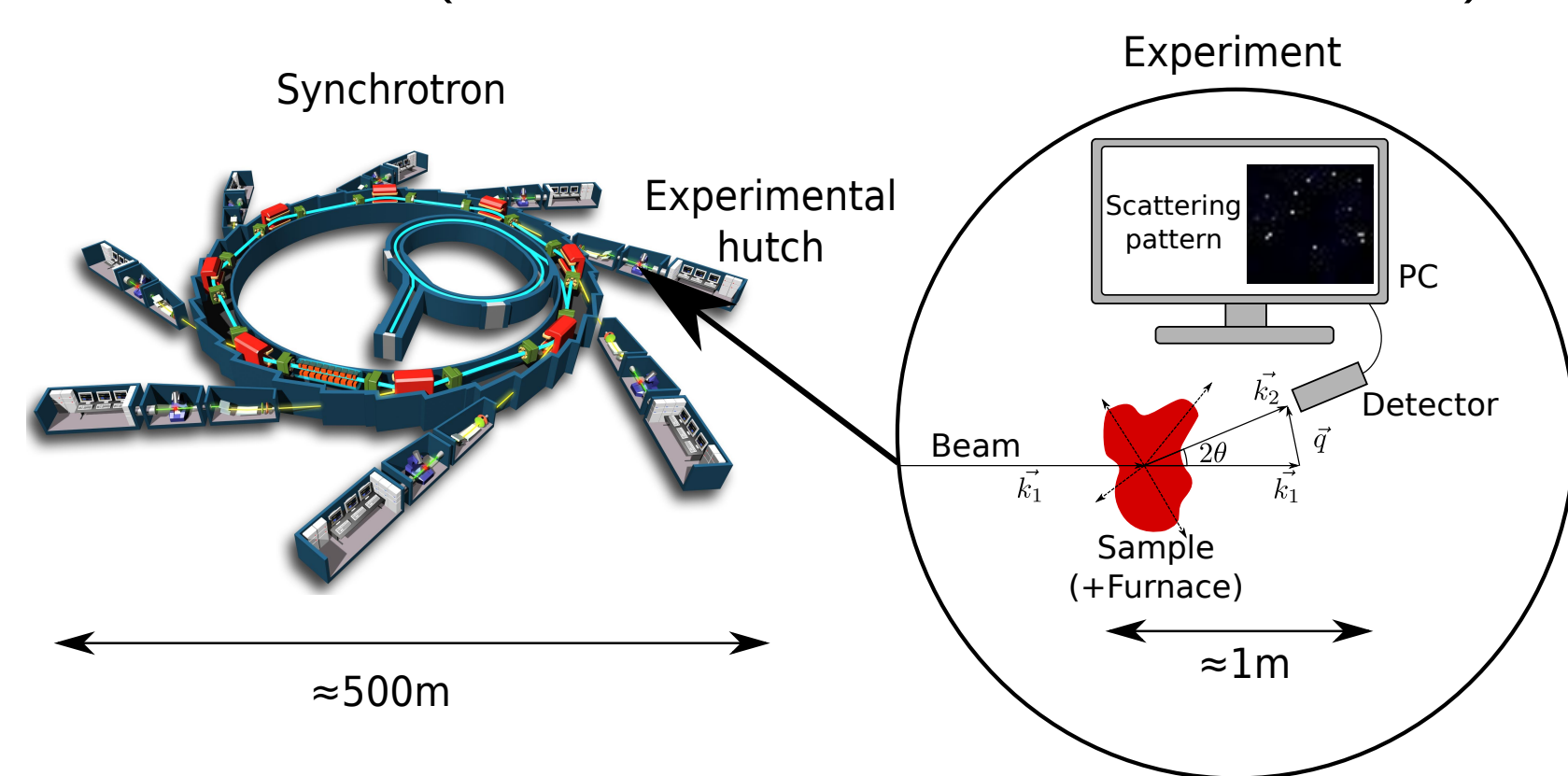
We now aim at gaining deeper insight into the dynamics of the physically interesting case of non-crystalline materials. One of physics' unsettled questions are the dynamic properties of these amorphous materials.



Setup and Sample Preparation

Aim: look at **atomic** movements

Experiment: measure intensities of coherently scattered X-ray radiation (corresponds to atomic distances)



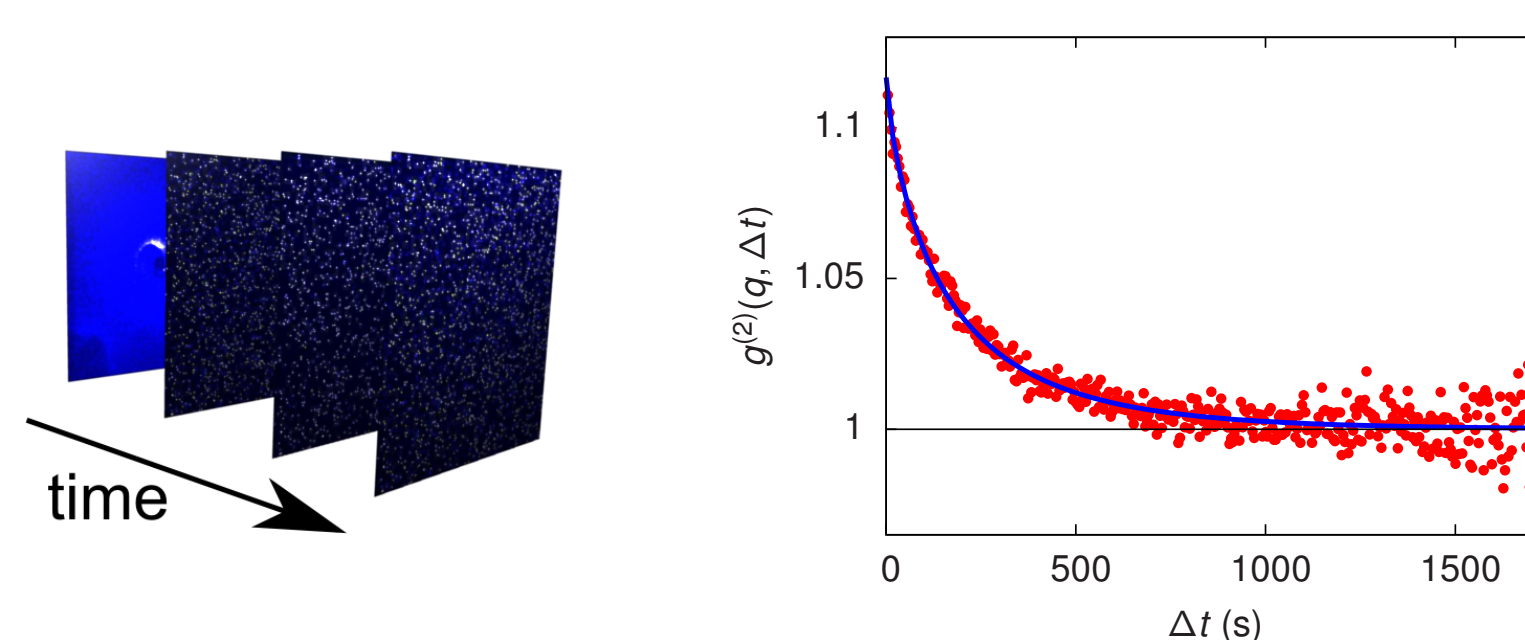
Samples: lead silicate oxide glasses $(\text{PbO})_x(\text{SiO}_2)_{1-x}$, with mixing ratios of

- ▶ $x = 30$ mole % (low-lead glass),
- ▶ $x = 60$ mole % (high-lead glass).

Lead silicate glass systems are of fundamental interest due to the fact that both components can act as network formers, depending on composition.

Theory in a Nutshell

Extract information on dynamics: correlate intensity patterns



Intensity autocorrelation function:

$$g^{(2)}(\vec{q}, \Delta t) = \langle I(\vec{q}, t) I(\vec{q}, t + \Delta t) \rangle / \langle I(\vec{q}, t) \rangle^2$$

with intensity $I(\vec{q}, t)$, scattering vector \vec{q} , time t
Gaining real space information on dynamics:

$$g^{(2)}(\vec{q}, \Delta t) = 1 + \beta \exp \{ -2 (\Delta t / \tau(\vec{q}))^\alpha \}$$

with coherence factor β , stretching parameter α

With the obtained correlation time $\tau(\vec{q})$, atomic diffusion models can be applied to draw conclusions on the atomic dynamics.

Atomic Diffusion Model

Chudley-Elliot model:

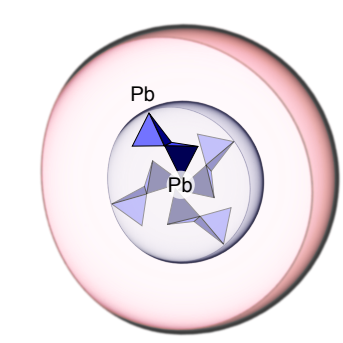
- ▶ isotropic diffusion ($q = |\vec{q}|$)
- ▶ fixed distance d of movement

These assumptions lead to correlation time τ :

$$\tau^{-1}(q) = \tau_0^{-1} \left(1 - \frac{\sin(qd)}{qd} \right)$$

with τ_0 mean residence time.

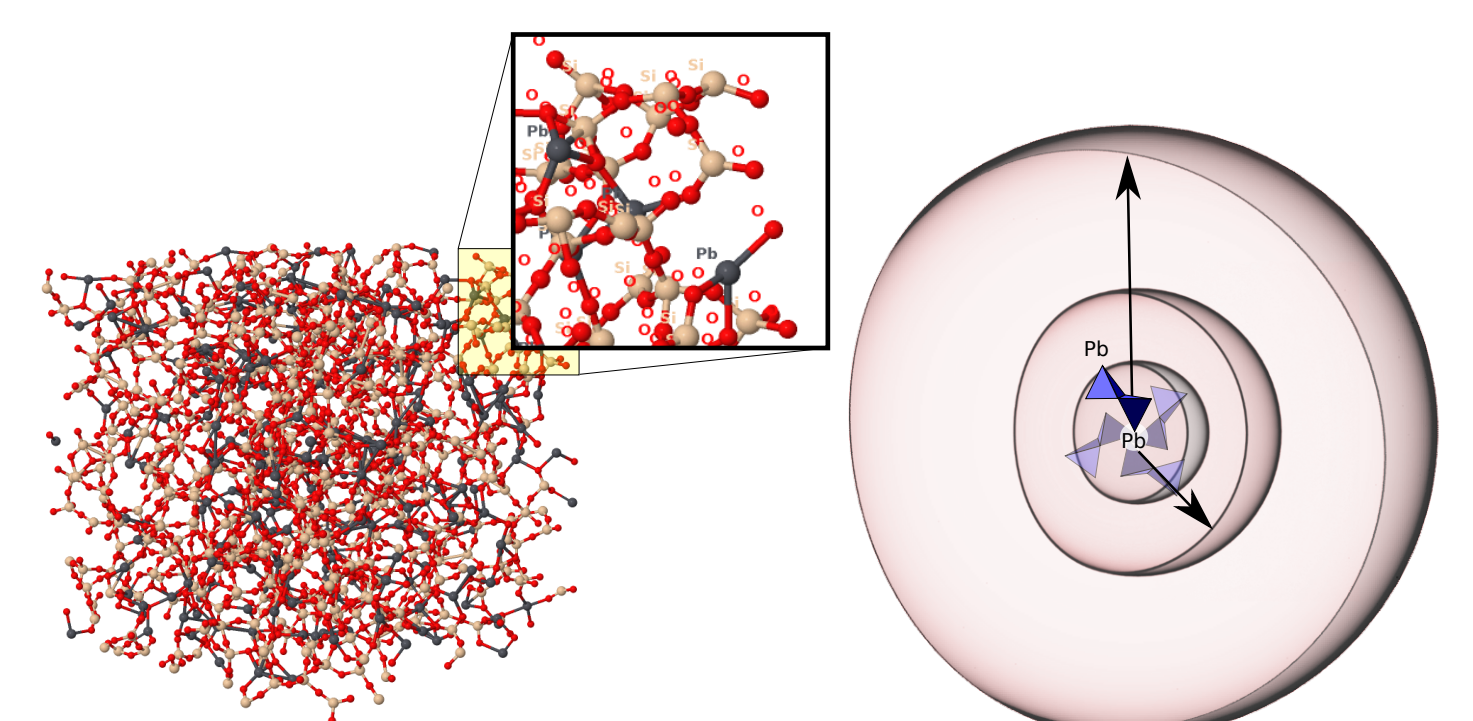
Diffusivity (Einstein relation): $D = \frac{\langle d^2 \rangle}{6\tau_0}$



Chudley-Elliot model extended to 2 jump processes:

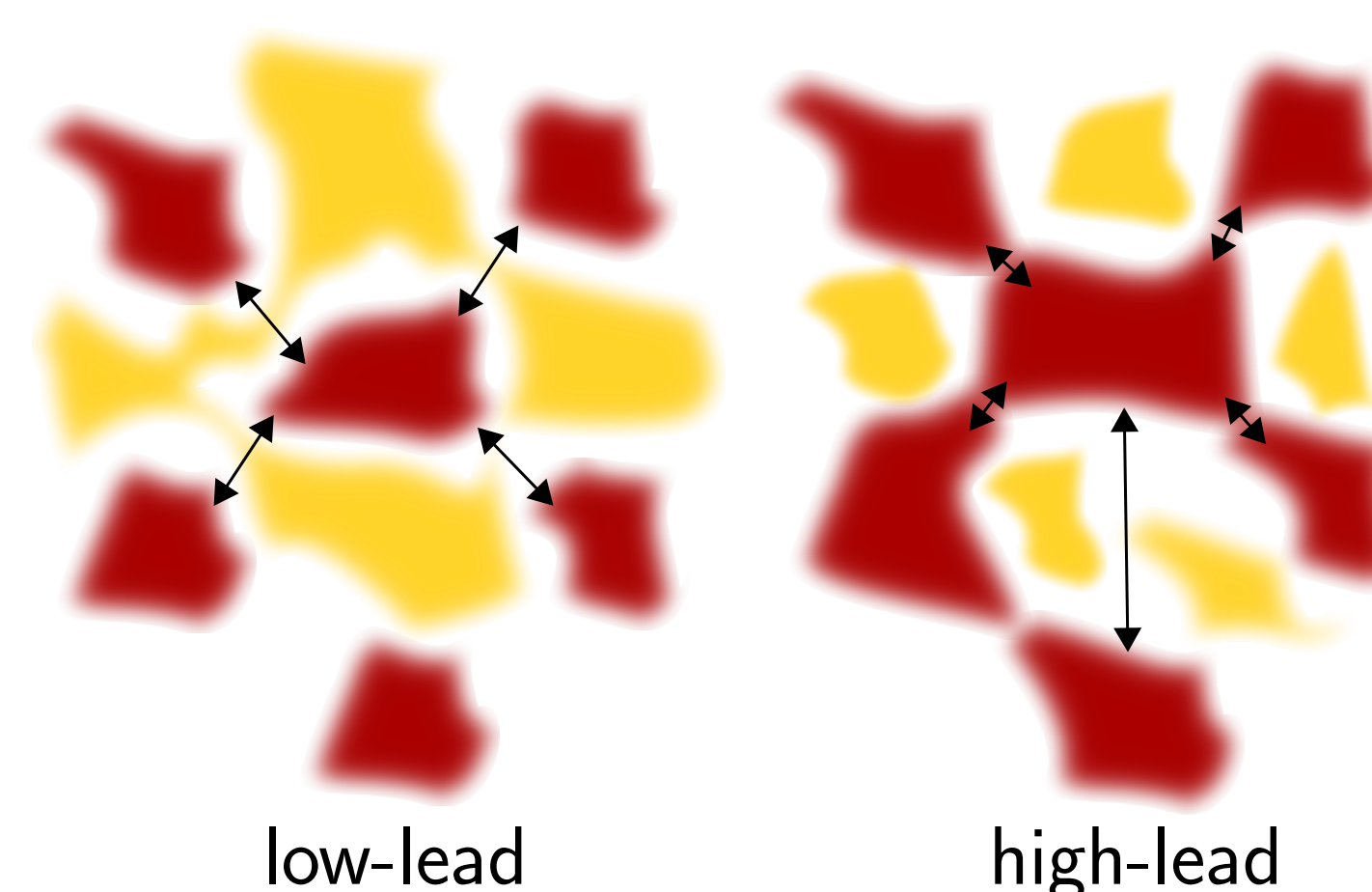
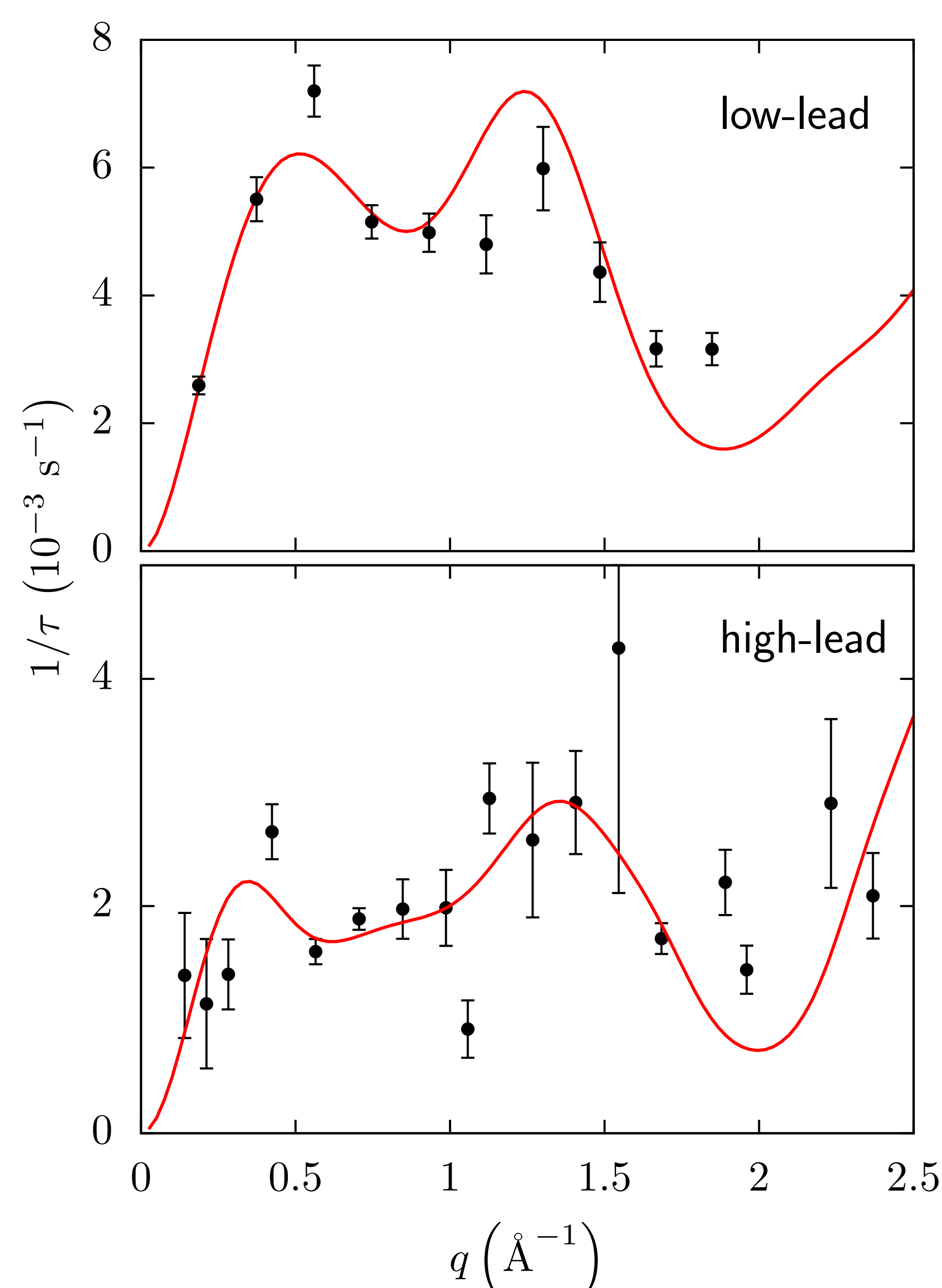
$$\tau^{-1}(q) = \tau_0^{-1} \left(1 - \omega_1 \frac{\sin(qd_1)}{qd_1} - (1 - \omega_1) \frac{\sin(qd_2)}{qd_2} \right)$$

with $\tau_0^{-1} = \tau_1^{-1} + \tau_2^{-1}$ and jump ratio $\omega_i = \frac{\tau_i^{-1}}{\tau_0^{-1}}$



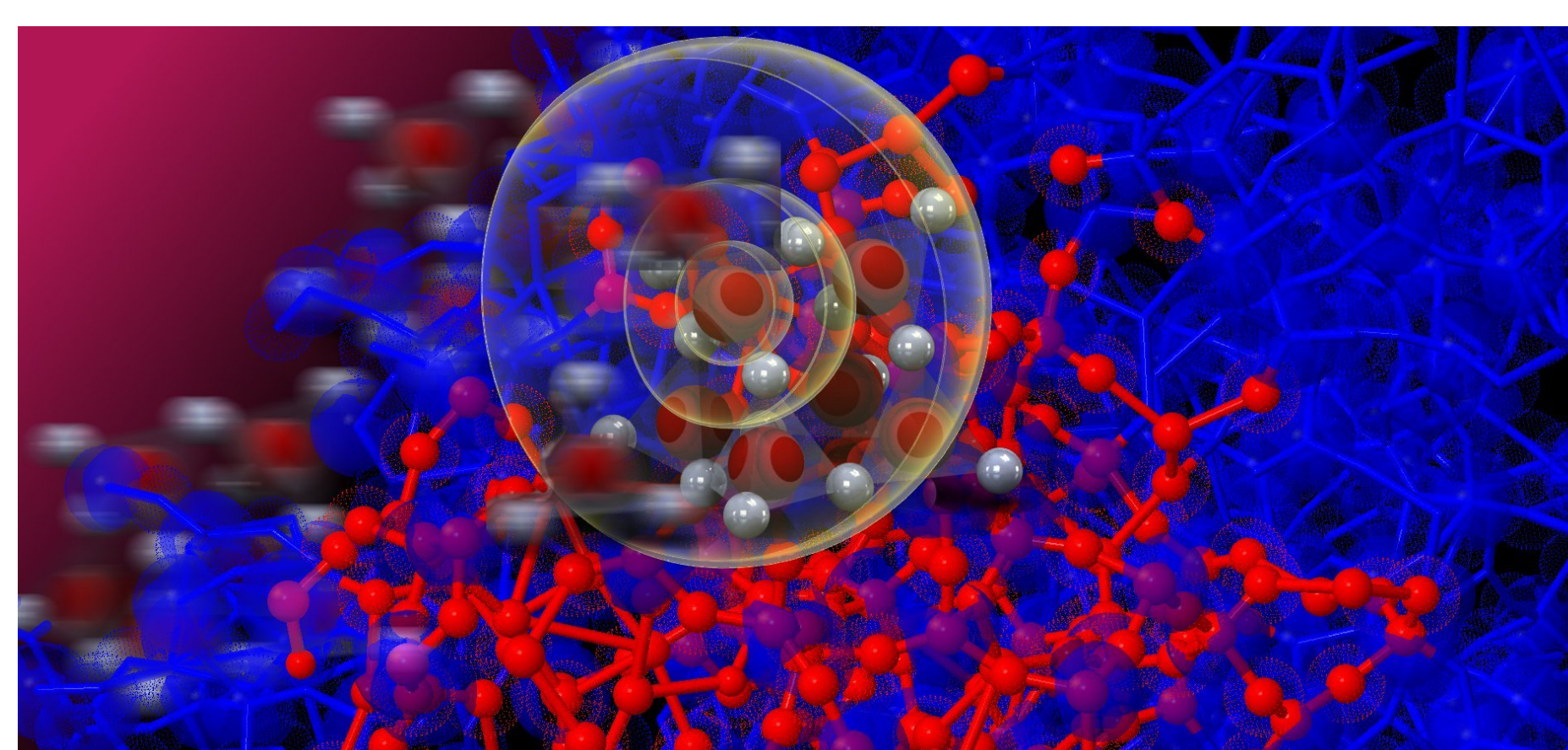
Results

We find a clear transition in atomic motion from a single jump process in low-lead to a two-jump process in high-lead glass. In low-lead glass, the fit of the Chudley-Elliot model to the data yields a jump distance of about $l \approx 8$ Å and a mean residence time of $\tau_0 \approx 370$ s. We calculate a diffusivity of $D \approx 3 \cdot 10^{-22} \text{ m}^2 \text{ s}^{-1}$. In high-lead glass, the extended Chudley-Elliot model fit yields $l_1 \approx 1$ Å, $l_2 \approx 13$ Å, $\omega_1 \approx 0.9$ and $\tau_0 \approx 435$ s. From that, we calculate diffusivities of $D_1 \approx 0.5 \cdot 10^{-23} \text{ m}^2 \text{ s}^{-1}$, $D_2 \approx 5.1 \cdot 10^{-23} \text{ m}^2 \text{ s}^{-1}$ and an overall diffusivity of $D \approx 5.6 \cdot 10^{-23} \text{ m}^2 \text{ s}^{-1}$. Thus about 90% of the atomic jump processes take place on a very short range, while longer range jumps comparable to the situation in the low-lead glass still exist.



Jump processes of lead oxide in lead silicate glass. Regions in red colour are clusters of lead oxide, regions in yellow colour represent silica oxide structures. For low-lead glass, the diffusive motion is due to jumps between lead oxide clusters. In high-lead glass, two distinct types of jump processes drive the dynamics. The network connectivity enables a short-range diffusion along network paths, also jump processes through the voids over longer distances contribute to the diffusion.

This indicates a change in the dynamics hand in hand with the change in structure. The existence of jump processes on distinctly different length scales can be attributed to two structural features. First, the longer range jumps indicate a still existing partial clustering of lead in high-lead silicate glass and resulting voids in between these clusters. Secondly, the much more frequent short range jumps show that by the percolation of the PbO network structure, diffusion is now possible along the strongly connected PbO clusters.



Conclusion

Our recent study in metallic glass [3] at temperatures around the glass transition revealed highly non-equilibrium atomic mobility which was independently confirmed by another group [4, 5]. We now succeeded in measuring true atomic diffusion in a glass system, revealing the characteristic jump distances and the connection between the structural heterogeneity of different glass compositions and the change in the diffusion processes. Thus a consistent description of transport properties in lead silicate glasses can be achieved. Studying further glass systems with aXPCS promises to yield deeper insight and enhance the understanding of atomic diffusion in amorphous systems. We further investigate into the low-temperature dynamics of alkali borate ionic conducting glasses, where the network structure influences the way ions diffuse and thus the conductivity of the material. These materials are well known for their fast diffusive motion and thus also promising for pushing the limits of the accessible range for aXPCS.

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FWF

Der Wissenschaftsfonds.

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