photo ; Alain Jeanne-Michaud

The LiCl-RH_2O and LiBr-RH_2O Supercooled Solutions close to their Eutectic Composition

A tribute to C. A. Angell and K. A. Nelson

L. E. Bove, C. Dreyfus, R. Torre, R. M. Pick, ….

Outline

I Introduction

II Transient Grating, a recap

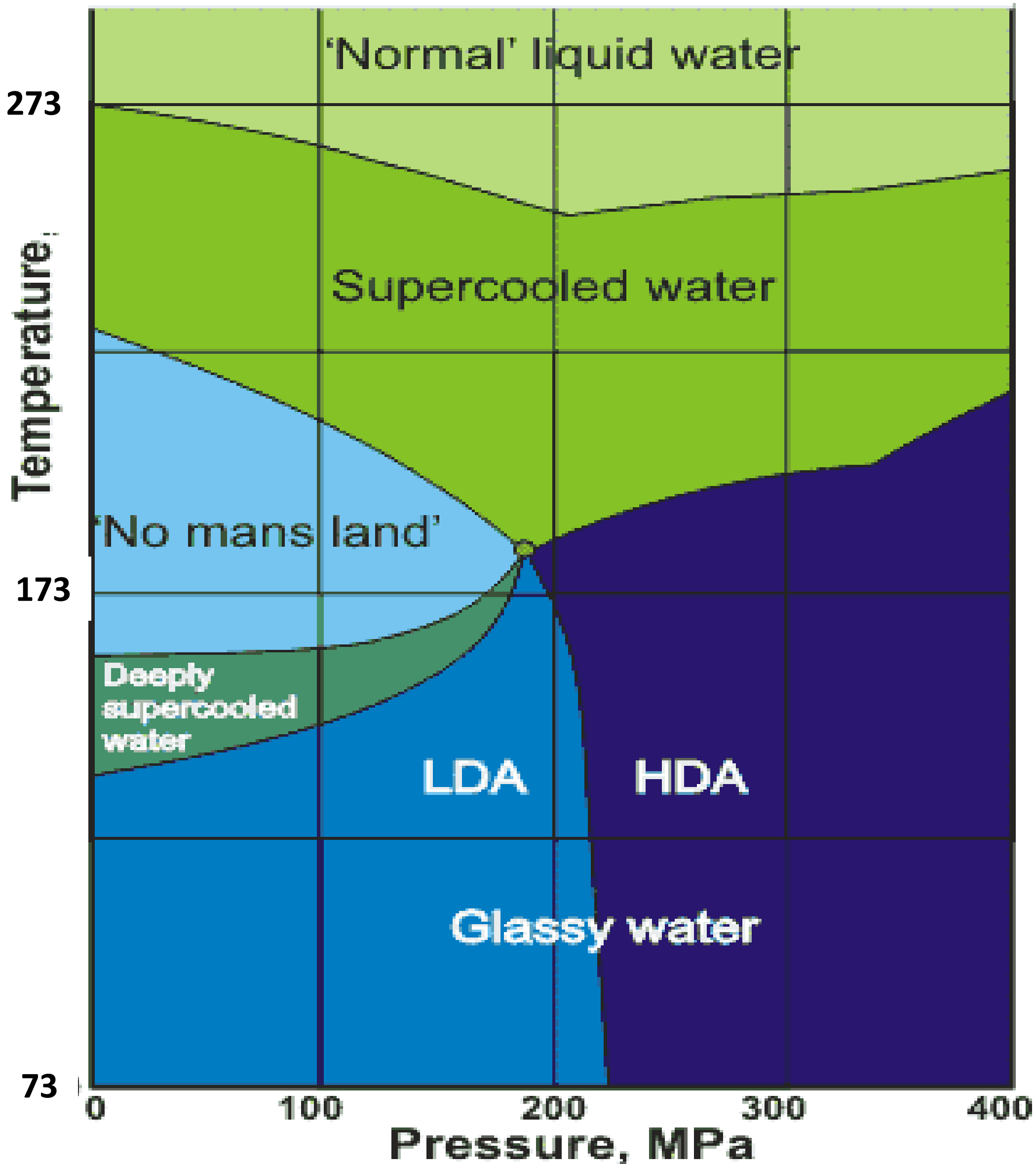
III The R=6 case

IV The $6<R<7.2$ LiCl case and its Interpretation

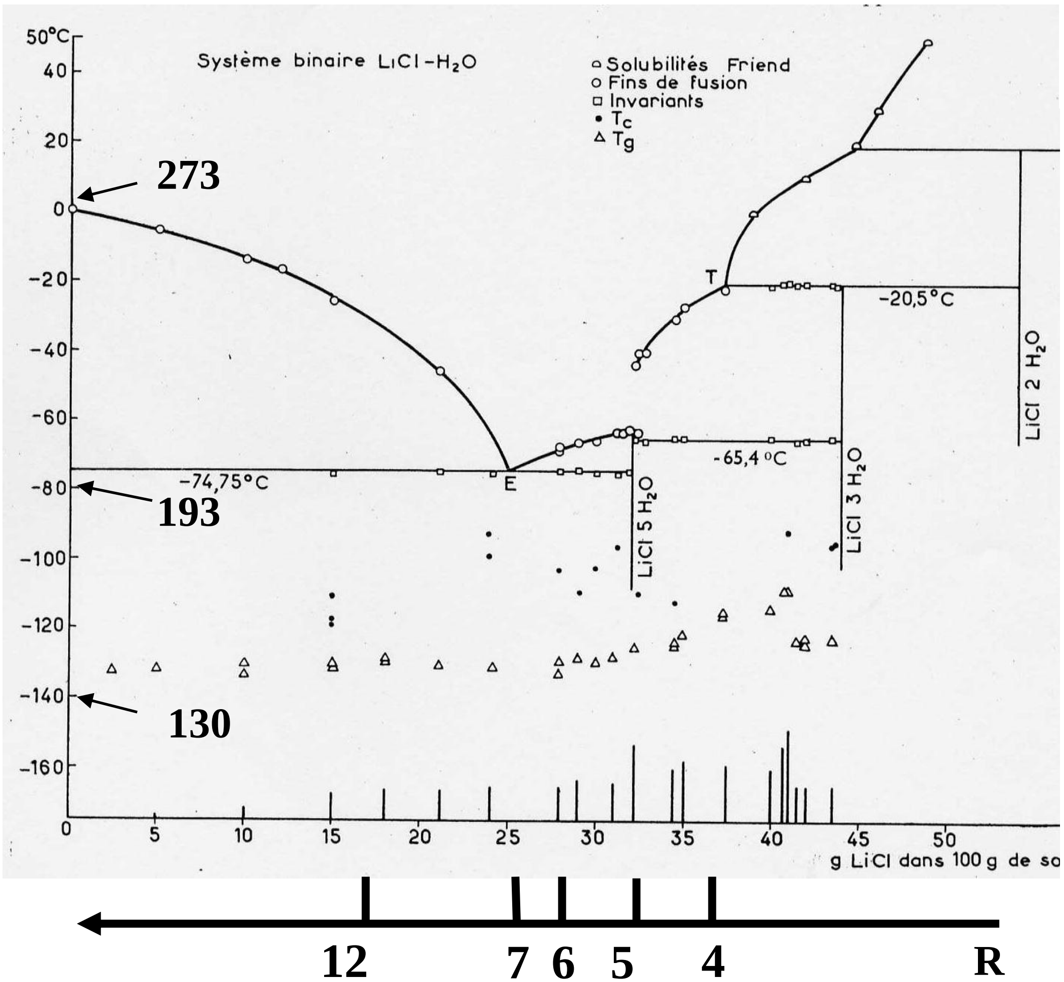
V Questions for the future

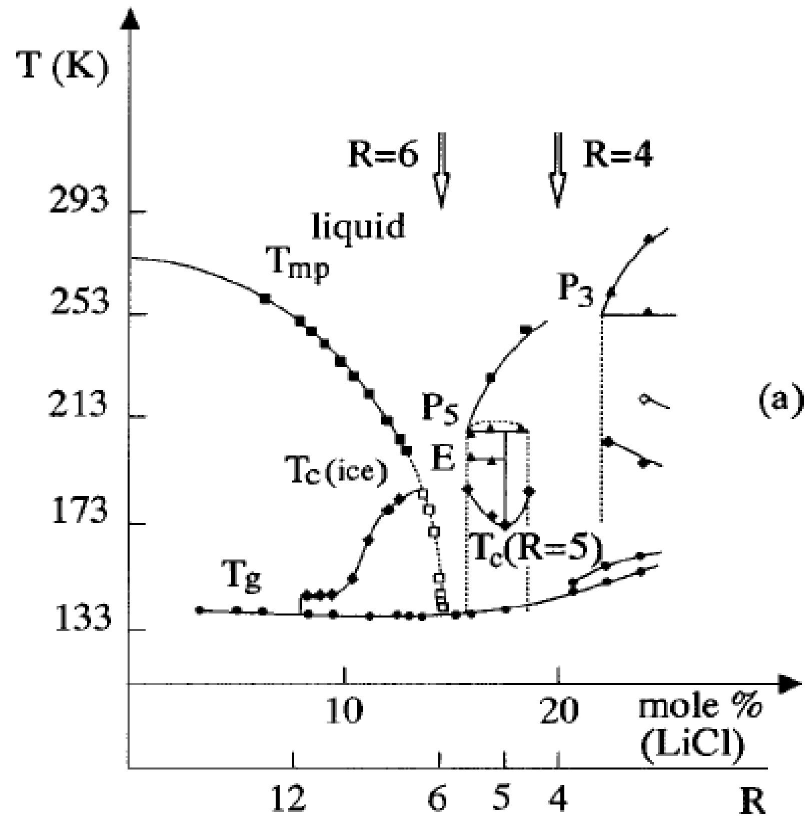
I Introduction

The water no man's land

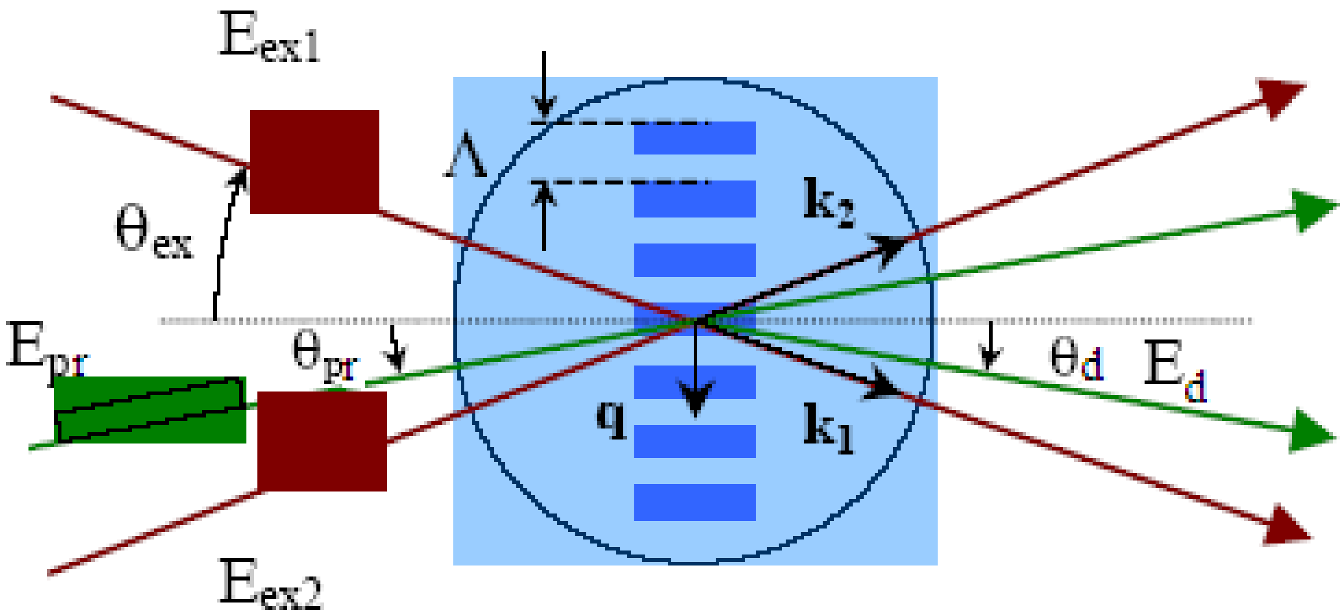


The equilibrium and non equilibrium phase diagrams of LiCl- R H_2O





II Transient Grating, a recap



$\Lambda = 10\mu m$

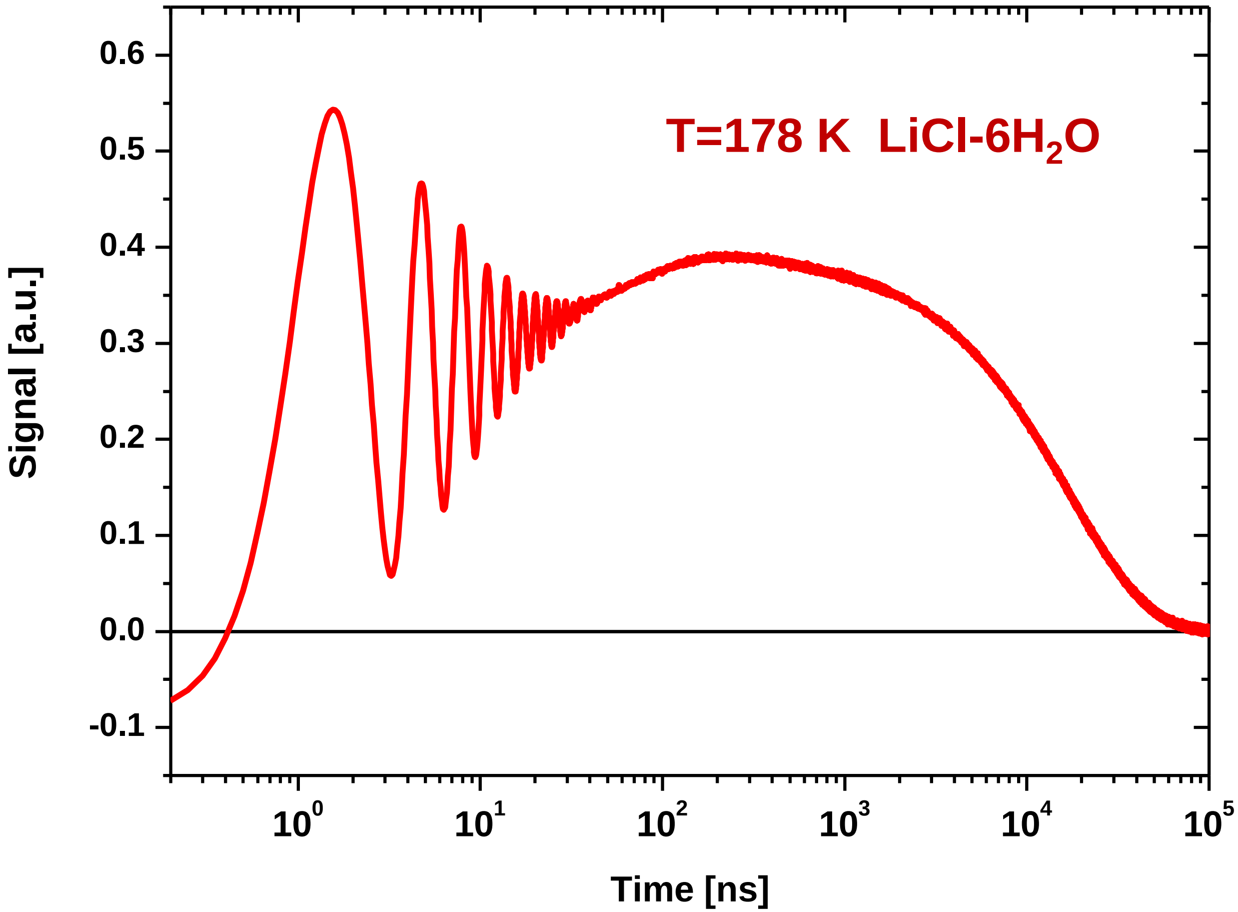
$$\text{Signal} \approx \delta n(\vec{q}_0, t) \approx \delta\rho(\vec{q}_0, t)$$

Instantaneous Heating and Electrostriction

$$\Delta T(\vec{r}, t) = \Delta T_0\, \delta(t)\left[1 + \cos(\vec{q}_0 . \vec{r})\right]$$

$$\Delta P(\vec{r}, t) = \Delta P_0\, \delta(t)\left[1 + \cos(\vec{q}_0 . \vec{r})\right]$$

Typical HD-TG signal

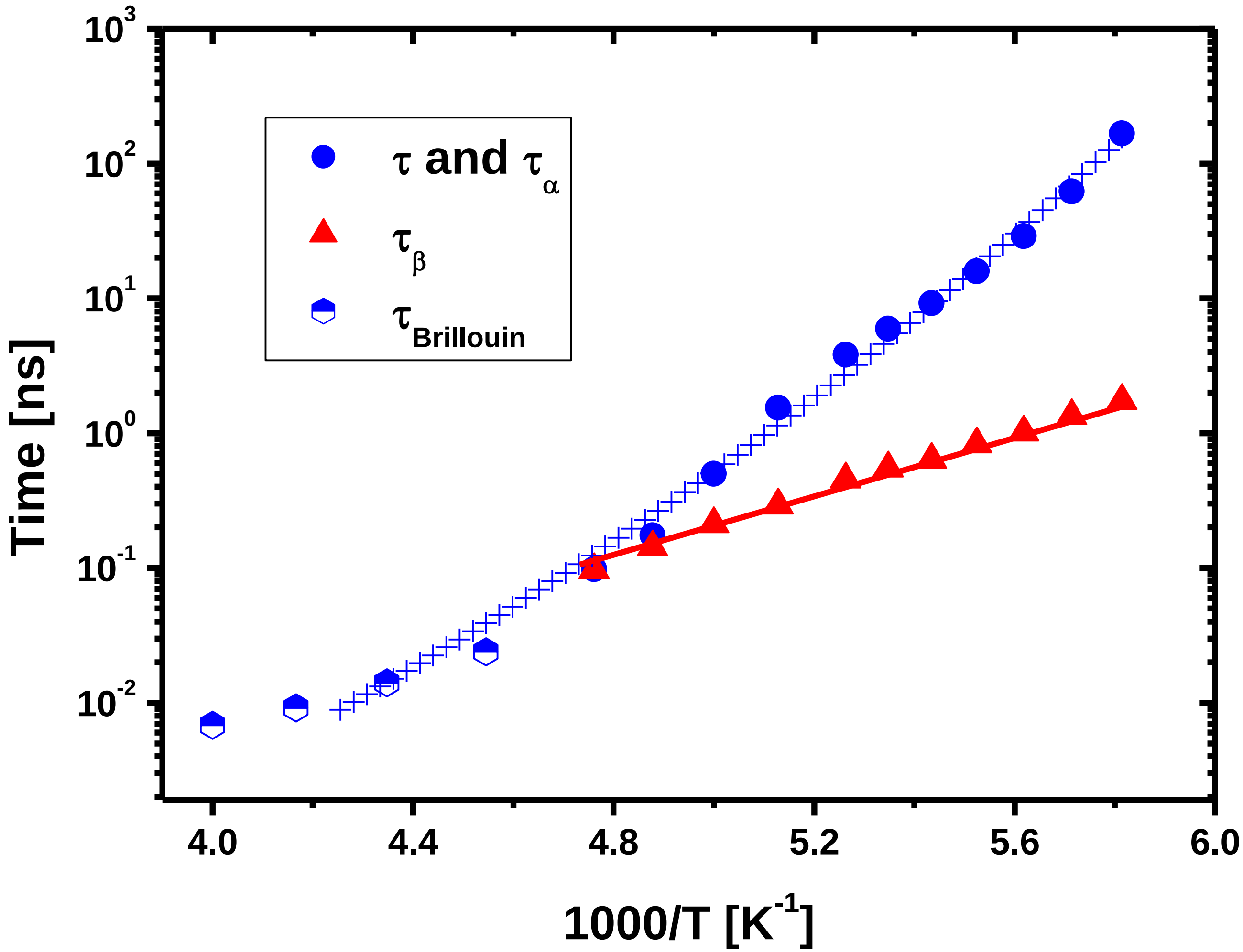


$$\delta\rho(\omega) = P_L(\vec{q}_0, \omega)\left[a\,\Delta P_0 + \frac{b\,\Delta T_0}{1 + i\omega\tau_h}\right]$$

$$\tau_h \approx q_0^{-2}$$

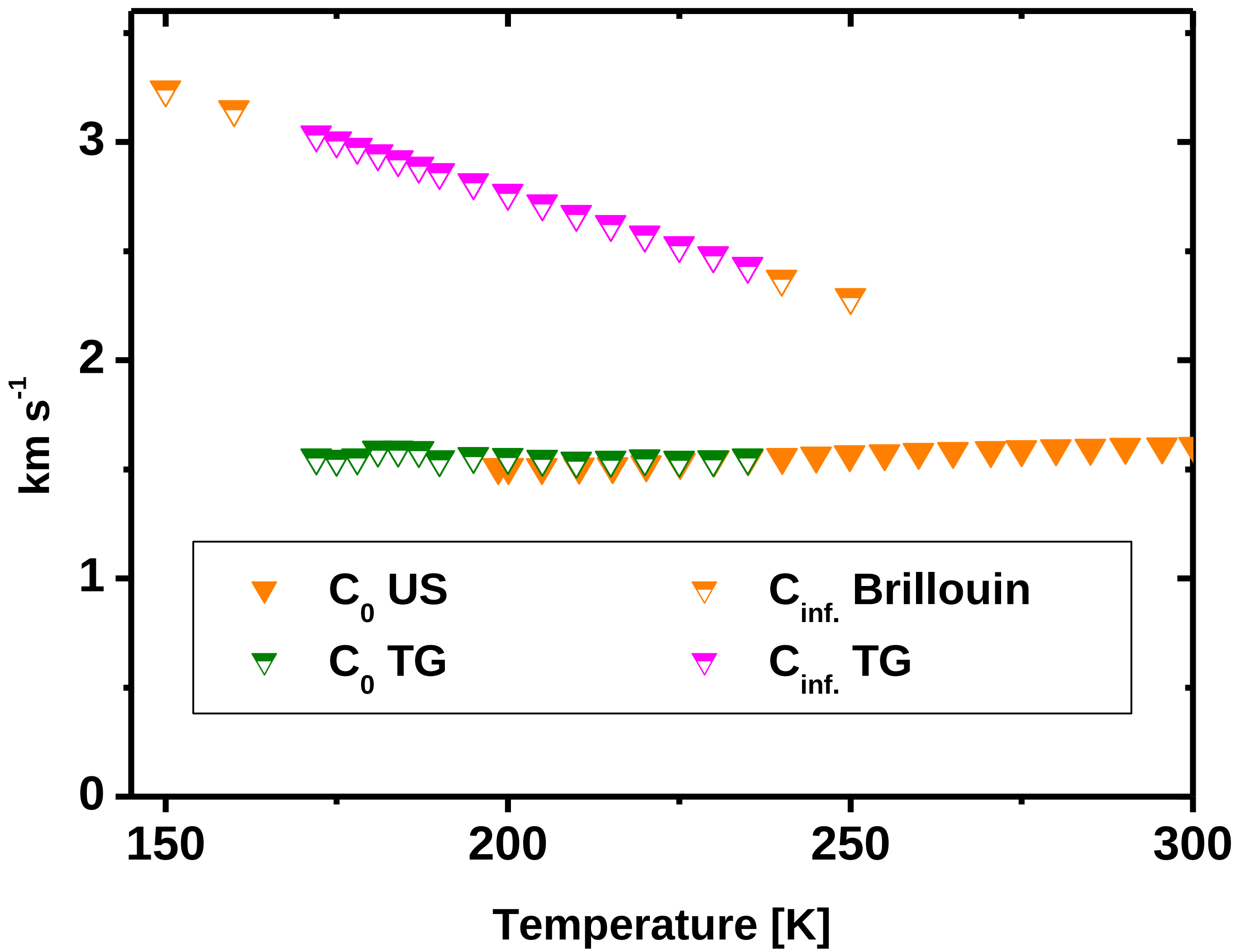
III Experimental results on LiBr-6H_2O

α and β Relaxation Times

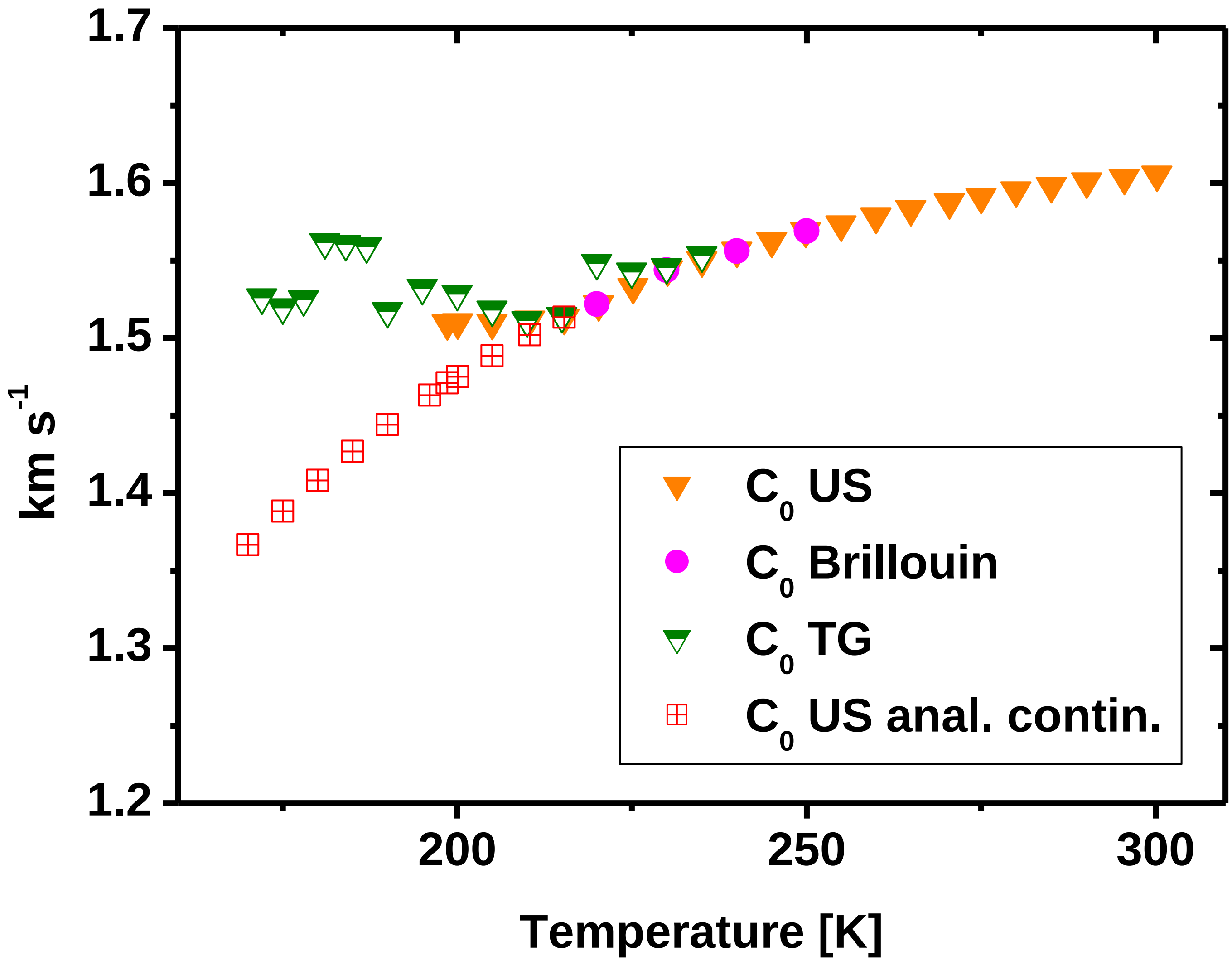


Fragility index ≈50

« Zero » and « infinite » frequency s sound velocities



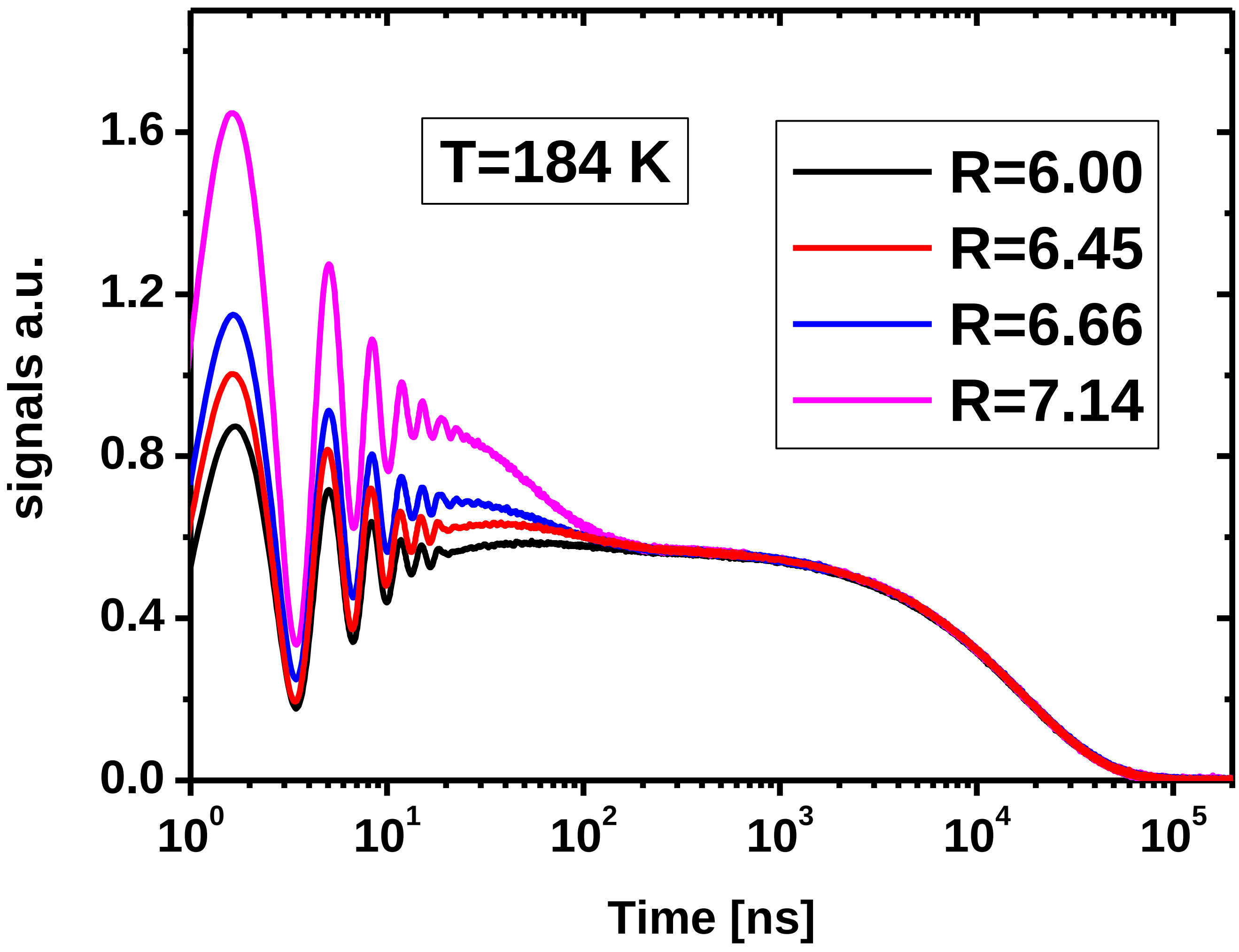
« Zero » frequency sound velocity



IV LiCl-RH_2O for 6<R<7.2
Experiments and Interpretation

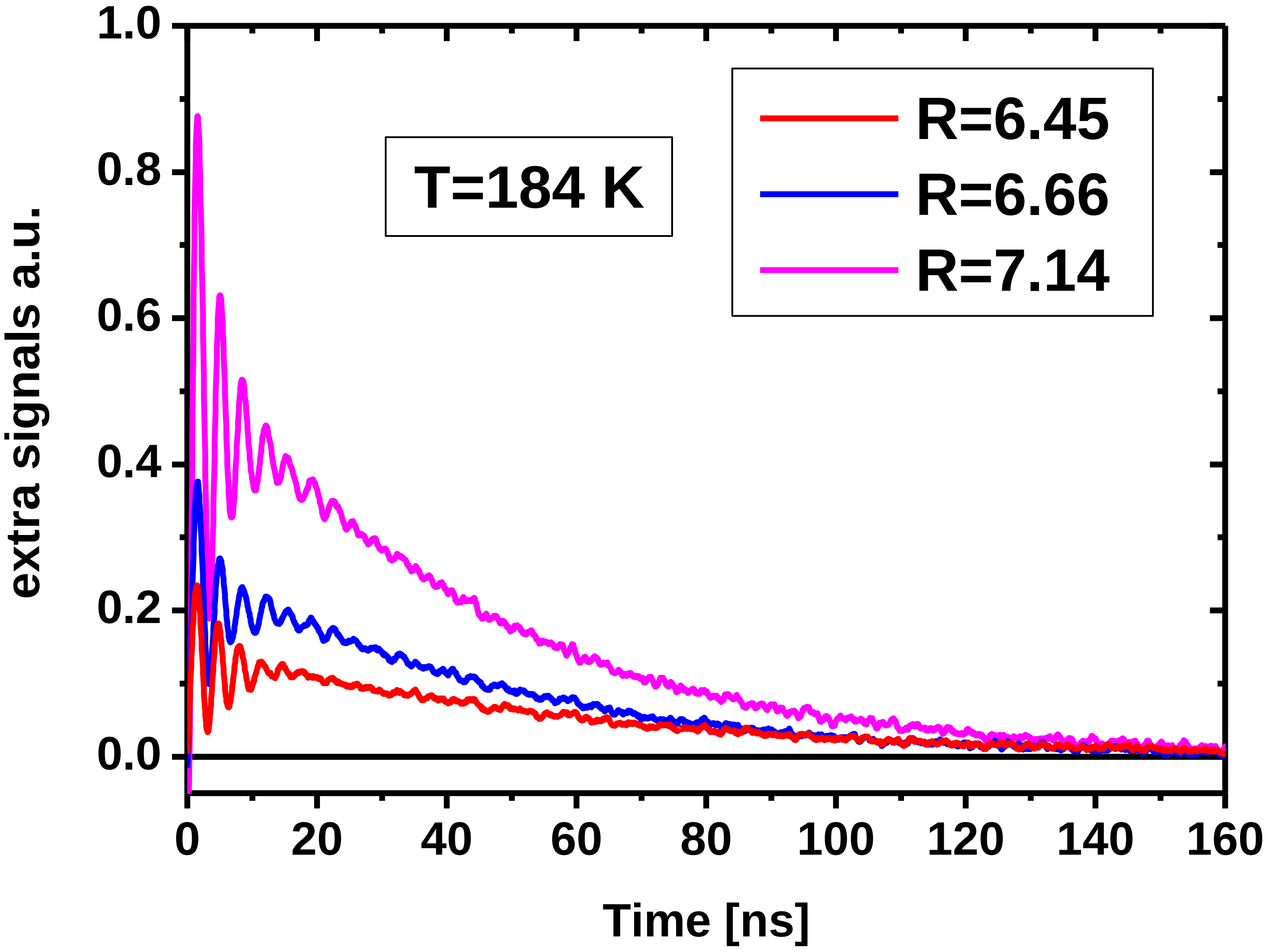
The Experimental Results

The Signals



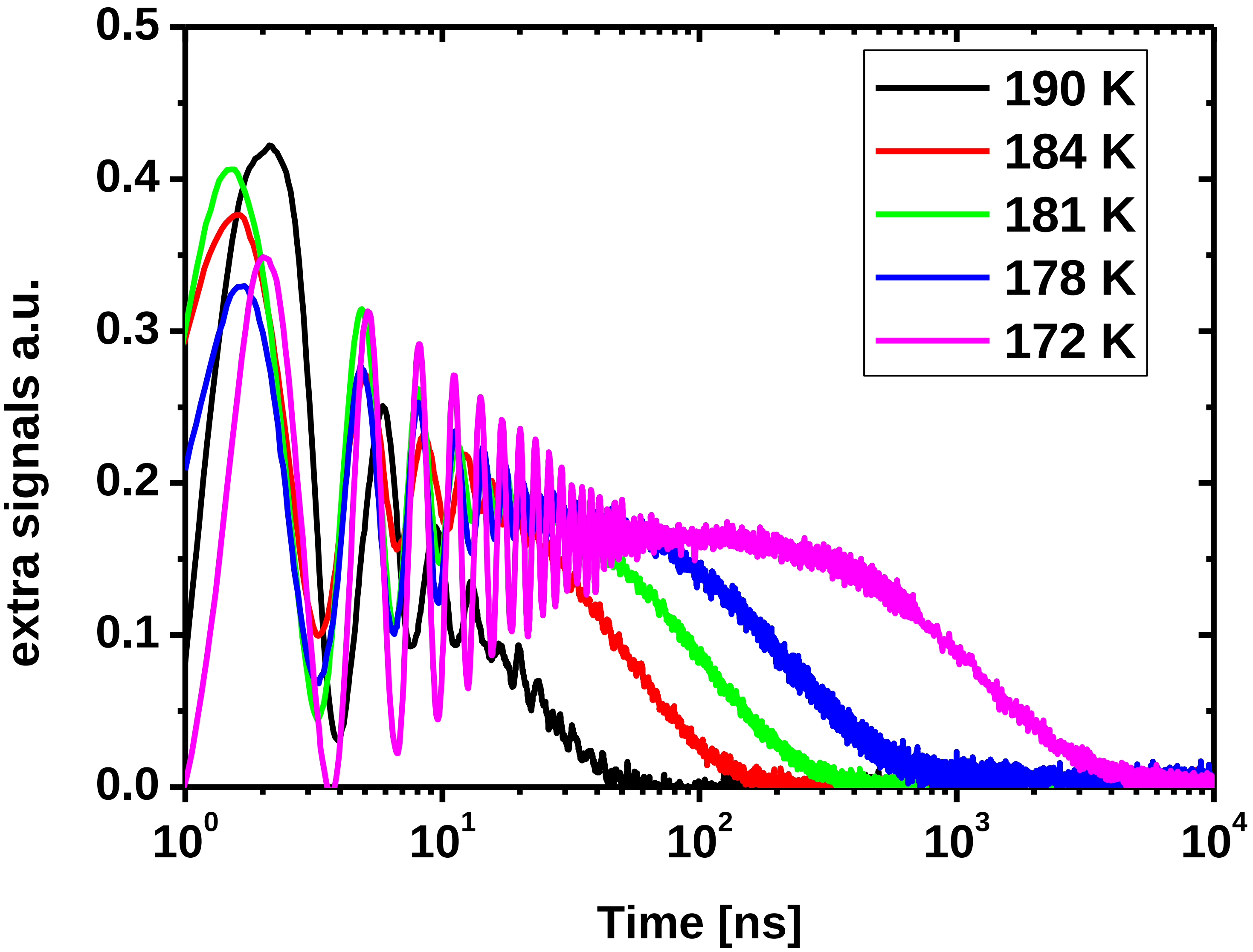
T=184 K
R=6.00
R=6.45
R=6.66
R=7.14
signals a.u.
1.6
1.2
0.8
0.4
0.0
10^0
10^1
10^2
10^3
10^4
10^5
Time [ns]

The Extra Signals

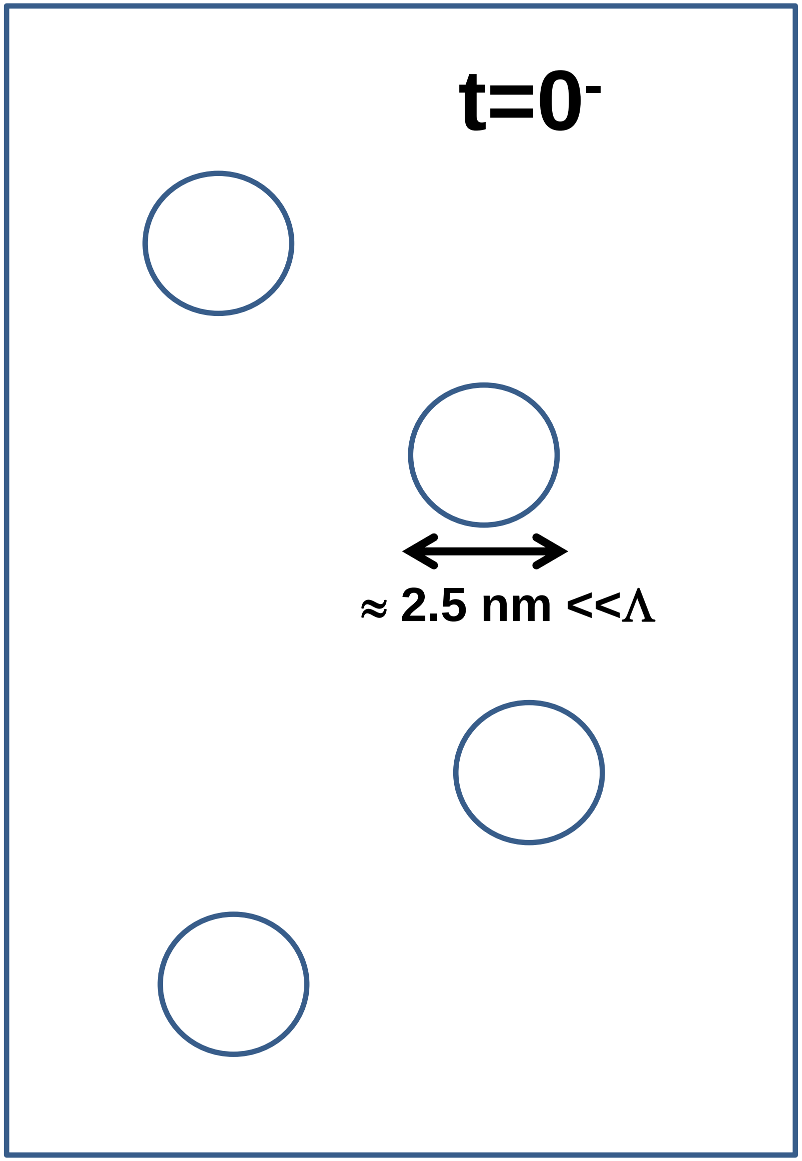


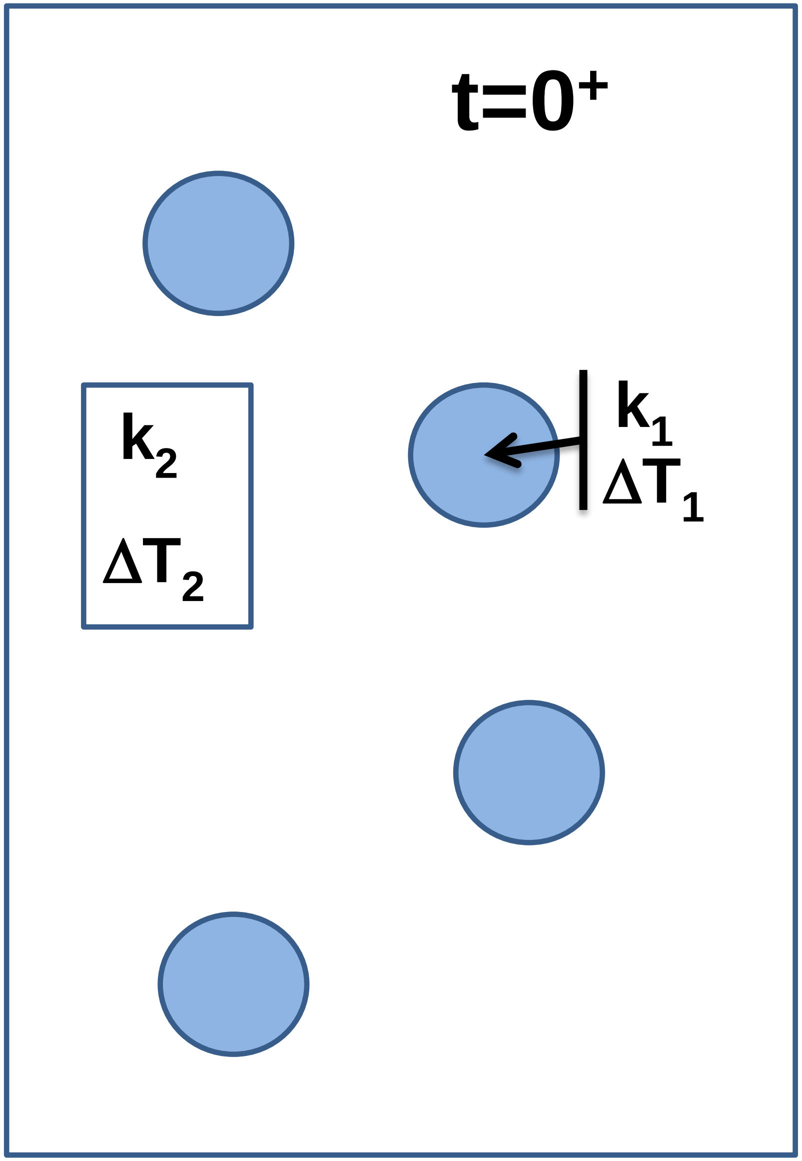
Extra signals are q_0 independent

R=6.66 - Temperature Evolution

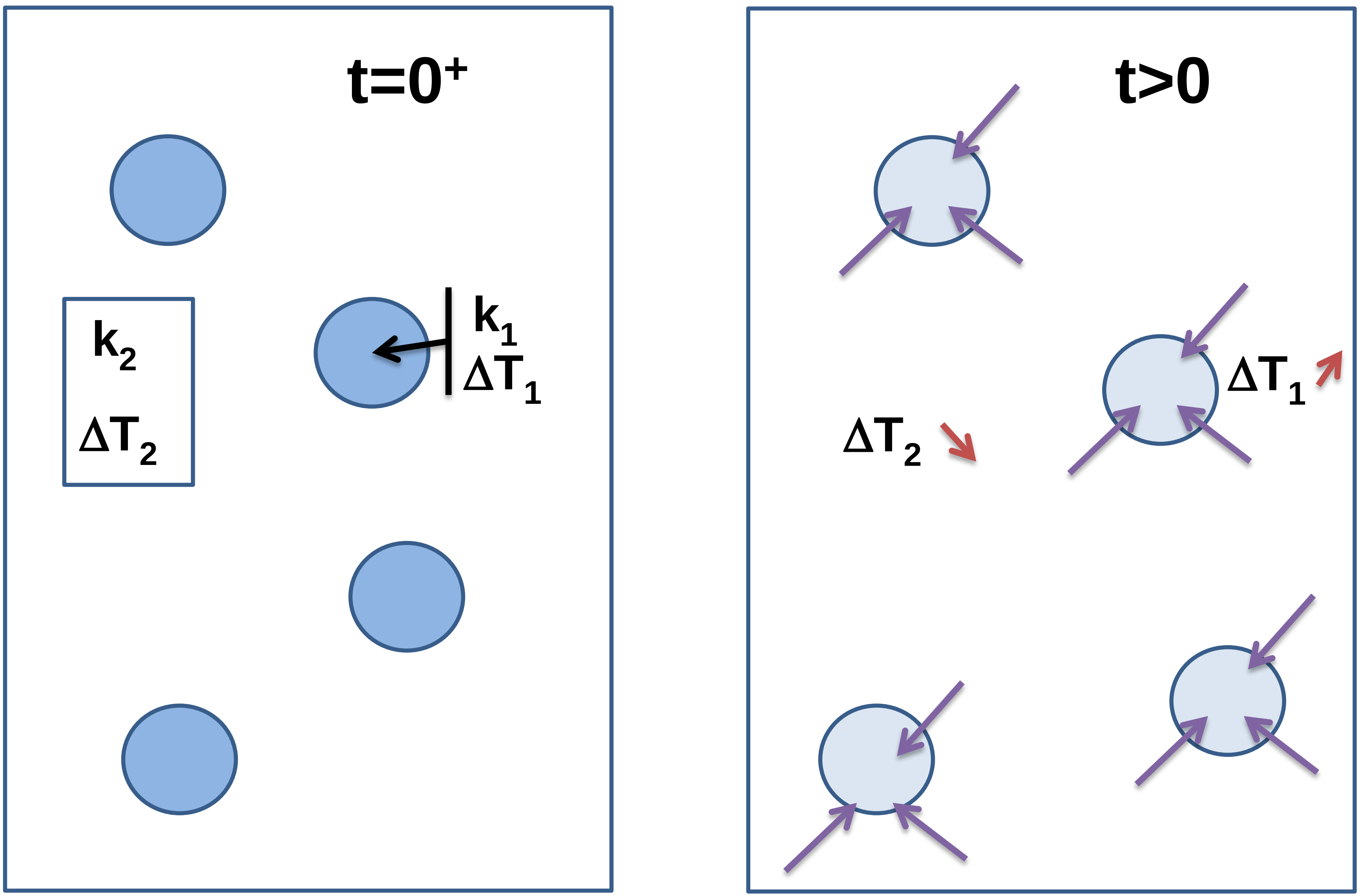


The Physical Explanation


t=0-
≈ 2.5 nm <<Λ



t=0+
k1
ΔT1
k2
ΔT2



t=0+
k1
ΔT1
k2
ΔT2
t>0
ΔT1
ΔT2

SIGNALS TO BE FITTED

5 Temperatures: 190 K≥T≥172 K
2 R values: R=6.66 and R=7.14
4 q values at T=181 K

Modelisation and Corresponding Results

$$\Delta T(\vec{r},t) = \left(\Delta T_0\, \delta(t) - \frac{\Delta T_a}{\tau_a} \exp\left(- t/\tau_a \right) \right) \left(1 + \cos \vec{q}_0 \vec{r} \right)$$

- τ_a (cluster lifetime) $\approx$ 4 τ_α (α relaxation time)

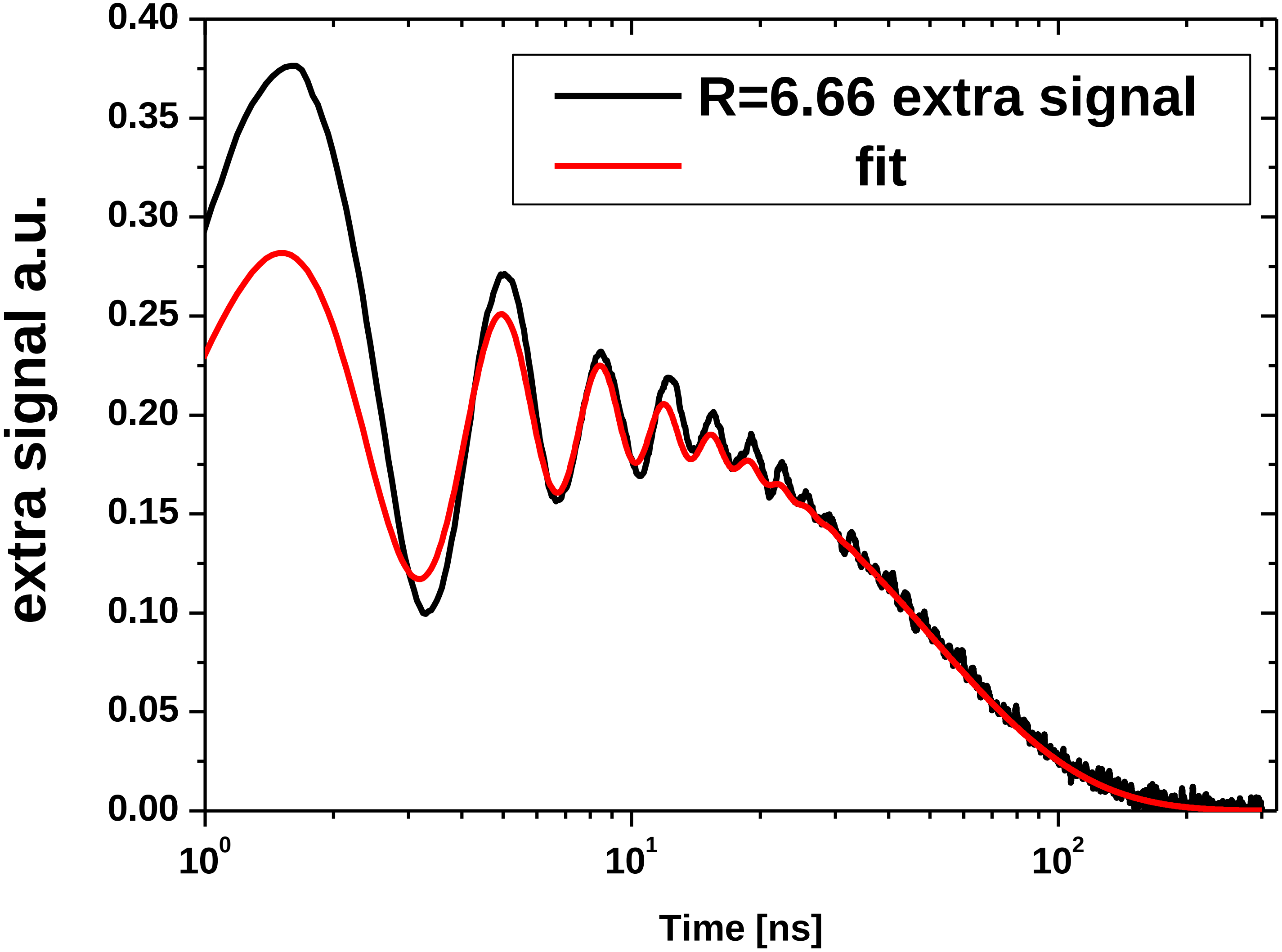
- The signal decay is due to a diffusion mechanism of the H_2O molecules

- Size of clusters $\approx$ 2.5 nm

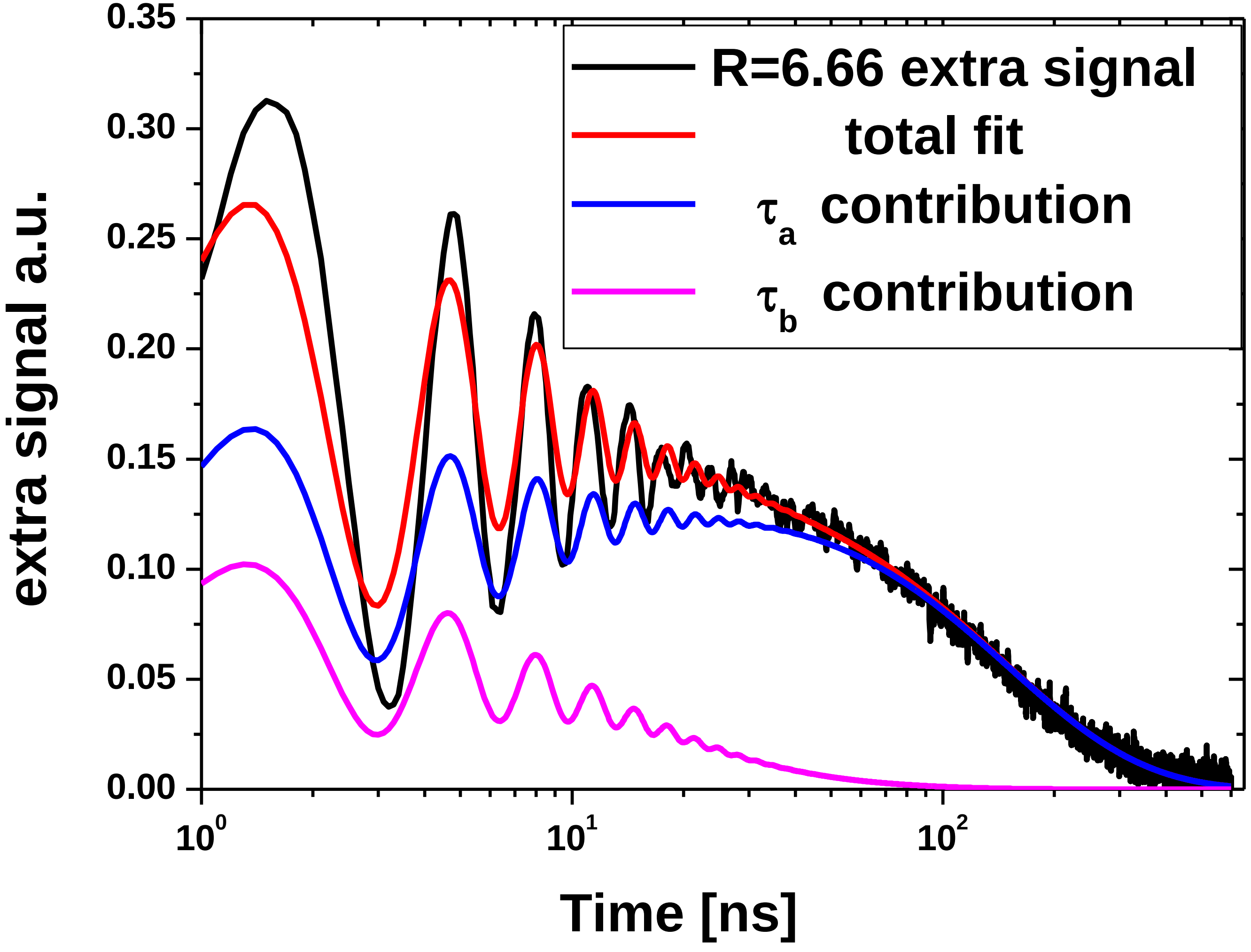
□ Size and Composition of the clusters are Temperature and R independent

Examples of fits

Fit of the T=184 K extra signal



Fit of the T=181 K extra signal



V Questions for the Future

1) Have we other evidences ?

2) - What is the cluster composition?
- Are the clusters static or dynamics?

3) Is LiCl-RH_2O a unique case?

b) The new source term in the Energy Conservation equation and its consequence

Usual case: $\Delta T(\vec{r},t) = \Delta T_0\, \delta(t)\left[1 + \cos(\vec{q}.\vec{r})\right]$

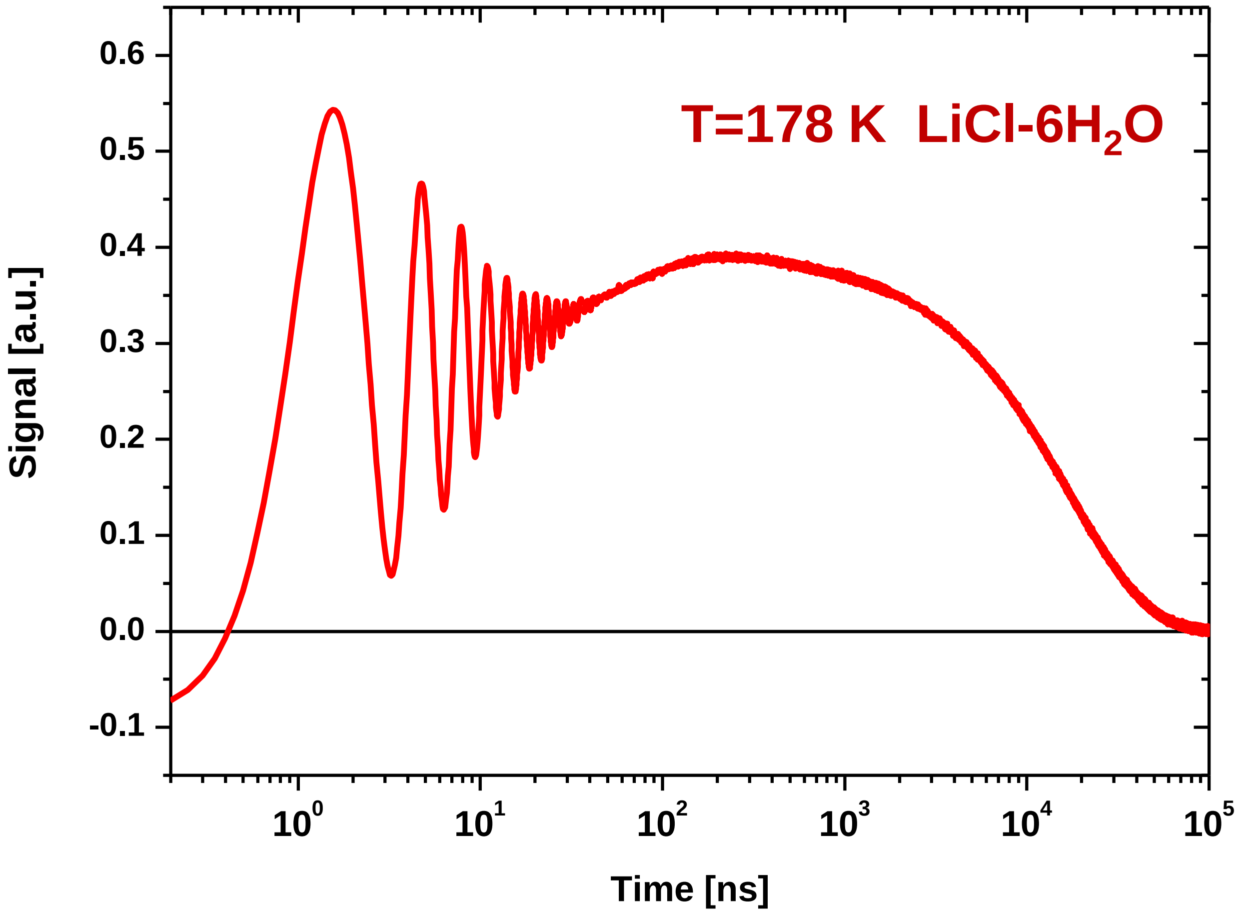
R-6 case: $\Delta T_0\, \delta(t)$ **is changed into:**

$$\Delta \tilde{T}(t) = \left(\Delta T_0\, \delta(t) - \boxed{\frac{\Delta T_a}{\tau_a} \exp\left(- t/\tau_a \right)} \right) \Rightarrow$$

$$\delta\rho(\vec{q},\omega) = P_L(\vec{q},\omega)\left[\frac{1}{1+i\omega\tau_h} + \boxed{\frac{\Delta \bar{T}_a}{\Delta T_1} \frac{1}{1+i\omega\tau_a}} \right] \Delta T_1$$

$$\Delta \bar{T}_a = \frac{\Delta T_a}{1 - \tau_a/\tau_h} \quad ; \quad \Delta T_1 = \Delta T_0 - \Delta T_a$$

Typical HD-TG signal



$$\text{Signal} \approx \delta n(\breve{q}_0, t) \approx \delta\rho(\breve{q}_0, t)$$

b) Analysis of the experiments

5 Temperatures: 190 K≥T≥172 K
2 R values: R=6.66 and R=7.14
4 $\vec{q}$ values at T=181 K

4 Parameters

$\tau_a, \tau_b, \Delta\overline{T}_a, \Delta\overline{T}_b$

- $\tau_a(T) \approx 4\,\tau_\alpha(T)$

⇛ **Size is approximately T independent, ≈ 2.5 nm**

- **Perfect scaling between R=6.66 and R=7.14**

⇛ **Only the cluster density increases with R**

- $\dfrac{\Delta\overline{T}_a}{\Delta T_1}$ or $\dfrac{\Delta\overline{T}_a + \Delta\overline{T}_b}{\Delta T_1}$ **approximately T independent**

⇛ **Cluster composition approximately constant**

Recap, next

1) $\Delta T(\vec{r},t) \Rightarrow \Delta P(\vec{r},t) \Rightarrow$

Two longitudinal phonons $\vec{q}$ and $-\vec{q} \Rightarrow$

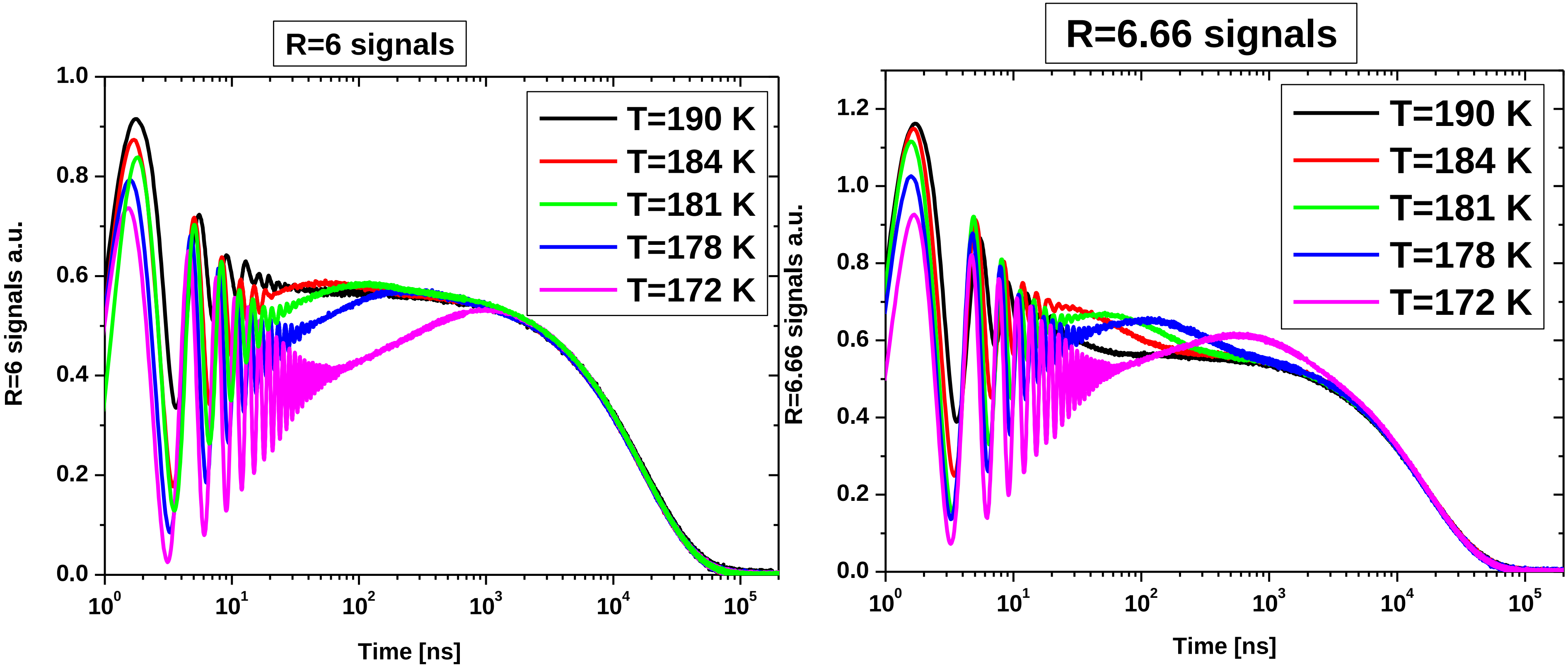
Density grating: $\delta n(\vec{r},t) = \delta n_0(t)[1+\cos(\vec{q}.\vec{r})]$

2)After the phonon decay, the density goes on equilibrating with the temperature grating $\Rightarrow$ **increase of the density grating**

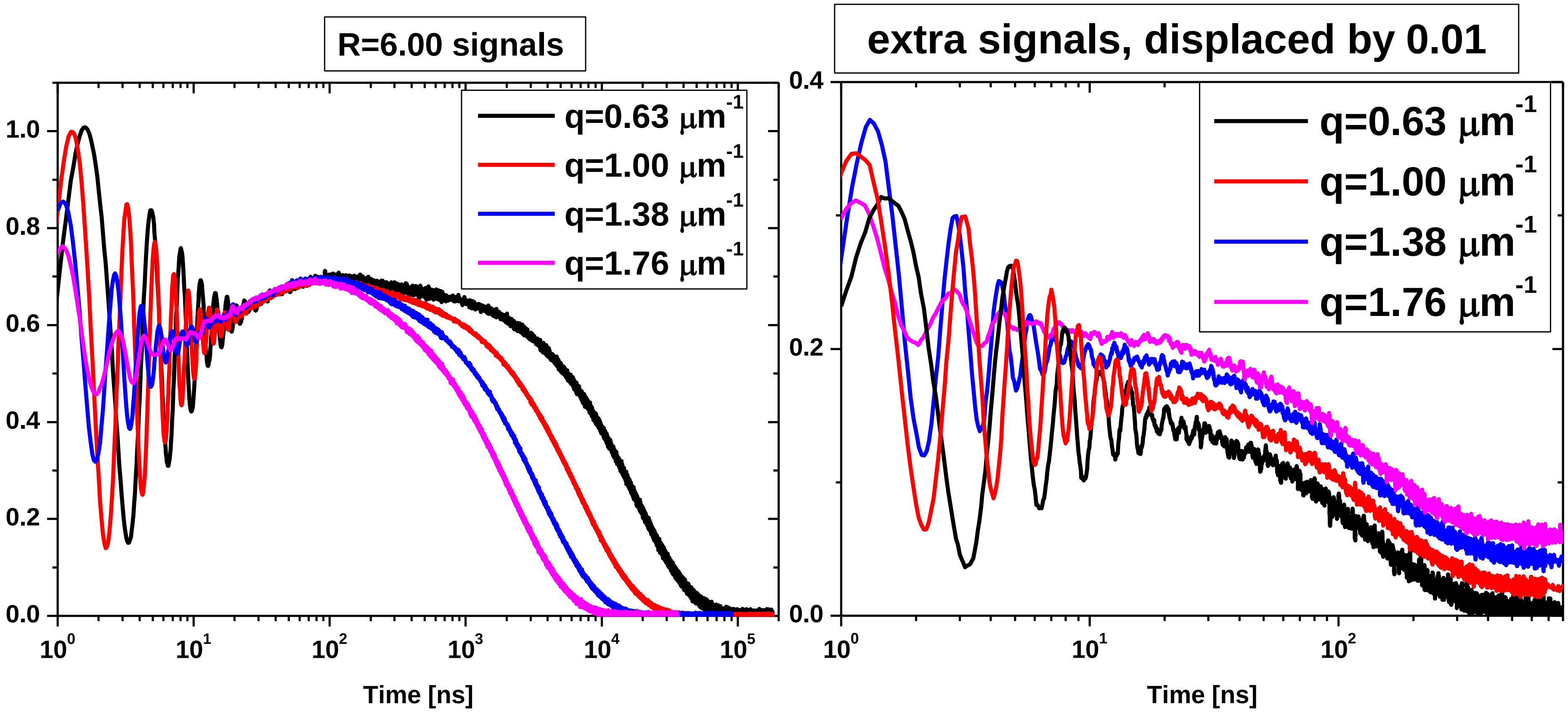
3) The temperature grating decreases by **thermal diffusion** $\Rightarrow$ **decay of the related density grating**:

$$\delta n(\vec{r},t) = \delta n_1 \exp(-t/\tau_h)[1+\cos(\vec{q}.\vec{r})]$$

T (K)	τ_{α}	τ_{a}	$\frac{\overline{T}_a}{T_0}$	τ_{β}	τ_{b}	$\frac{\overline{T}_b}{T_0}$	$\frac{\overline{T}_a+\overline{T}_b}{T_0}$	R_0
190	3.64	16	0.57	1.65			0.57	
184	21.6	38	0.55	2.6			0.55	2.0
181	32.5	120	0.35	3.3	12	0.22	0.57	2.1
178	58	220	0.31	3.4	22	0.15	0.46	2.4
172	360	1260	0.15	11.4	400	017	0.32	2.6



R=6 signals
R=6 signals a.u.
Time [ns]
T=190 K
T=184 K
T=181 K
T=178 K
T=172 K
R=6.66 signals
R=6.66 signals a.u.
Time [ns]
T=190 K
T=184 K
T=181 K
T=178 K
T=172 K



R=6.00 signals
q=0.63 μm-1
q=1.00 μm-1
q=1.38 μm-1
q=1.76 μm-1
1.0
0.8
0.6
0.4
0.2
0.0
10^0
10^1
10^2
10^3
10^4
10^5
Time [ns]
extra signals, displaced by 0.01
0.4
0.2
0.0
Time [ns]