PHOSPHOLIPID MEMBRANES AND SALT: A STRUCTURE AND DYNAMICS STUDY

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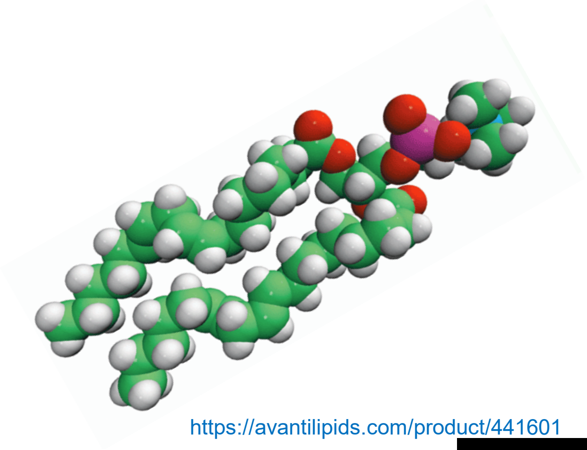
LICHTENBERGSTRASSE 1
GARCHING, GERMANY

OVERVIEW

What are we looking at?

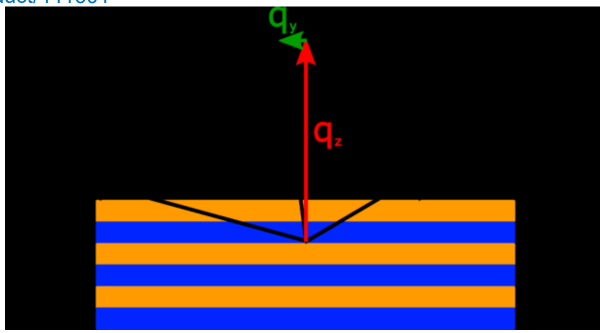
- Phospholipid model membranes
- L-α-phosphatidylcholine (SoyPC)



https://avantilipids.com/product/441601

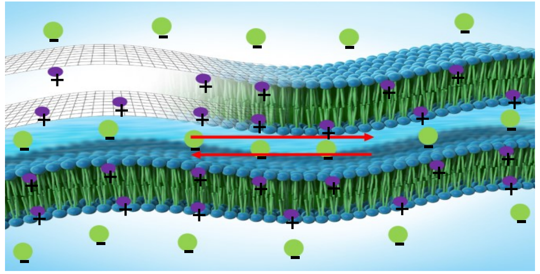
How?

- Reflectometry
- Grazing-incidence Small-Angle Neutron Scattering
- Grazing-incidence Neutron Spin-Echo Spectroscopy



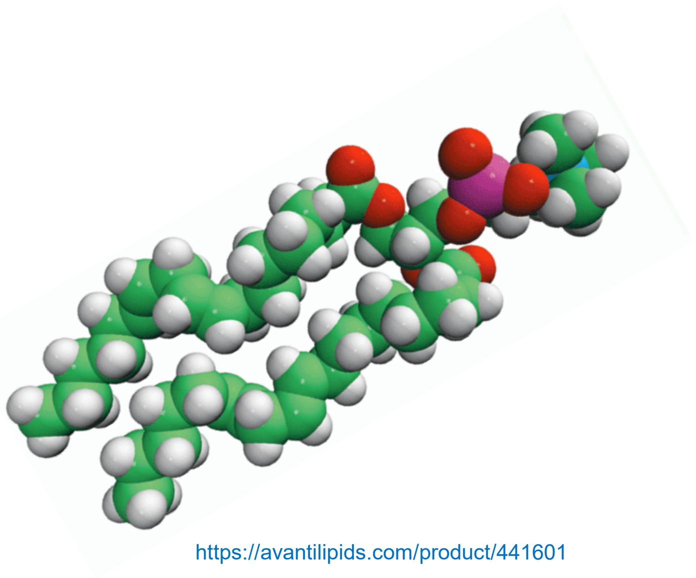
What do we see?

- Concentration of NaCl ions in specific location
- Comprehensive change in dynamics



WHY (BIOLOGICAL) MEMBRANES

- Stability and function of a cell
- Information transport
- Nutrient transport
- Waste transport
- Drug transport
- Deflection of bacteria/viruses



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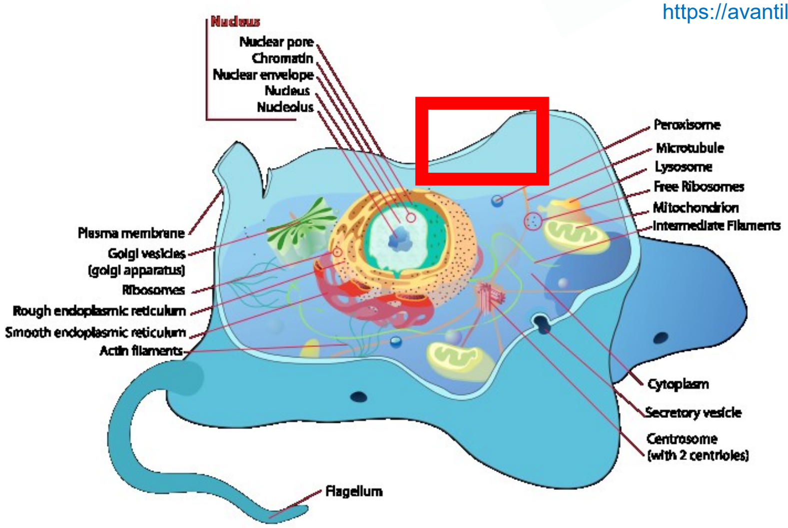
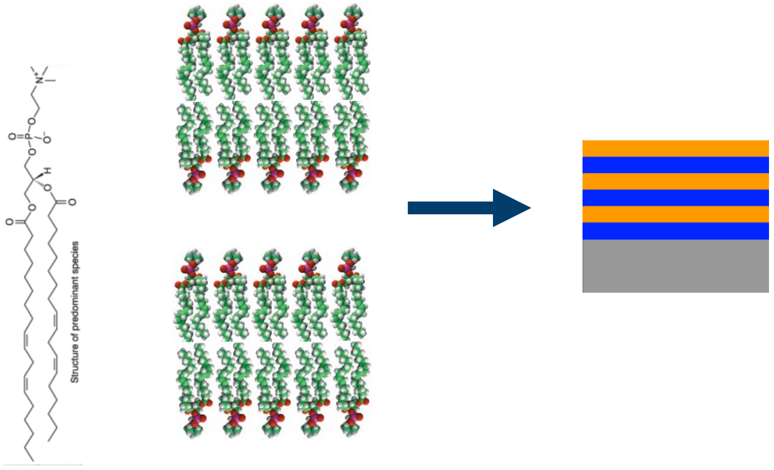


https://en.wikipedia.org/wiki/File:Animal_cell_structure_en.svg

THE SAMPLE

L-α-phosphatidylcholine
SoyPC



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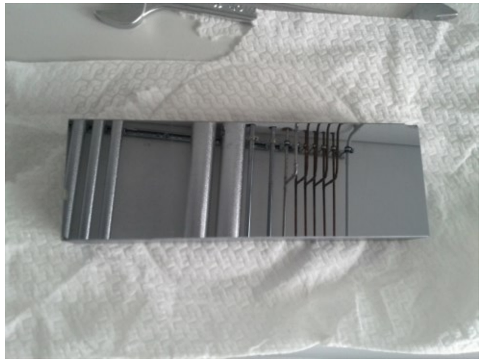
- Typical model for phospholipids
- Two-tail lipid
- Near perfect hydrocarbon tail
- Known to form multilayers
- Simple to mix with a wide range of additives



- Si-block treated to achieve hydrophilic surface
- SoyPC dissolved in isopropanol
- Solution casting on Si-block for self-assembly
- Dried under vacuum (250 mbar)

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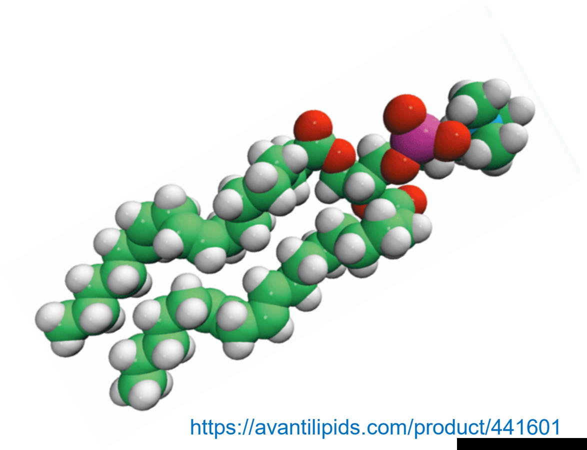

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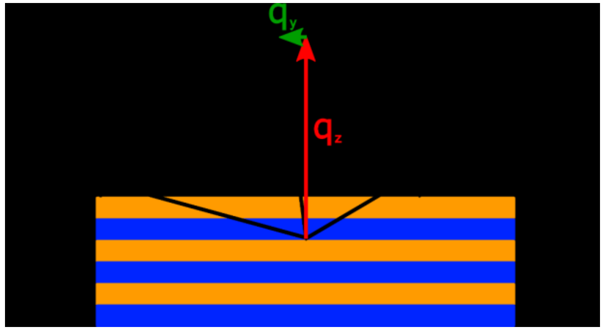

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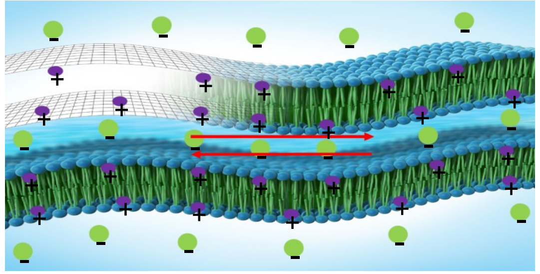
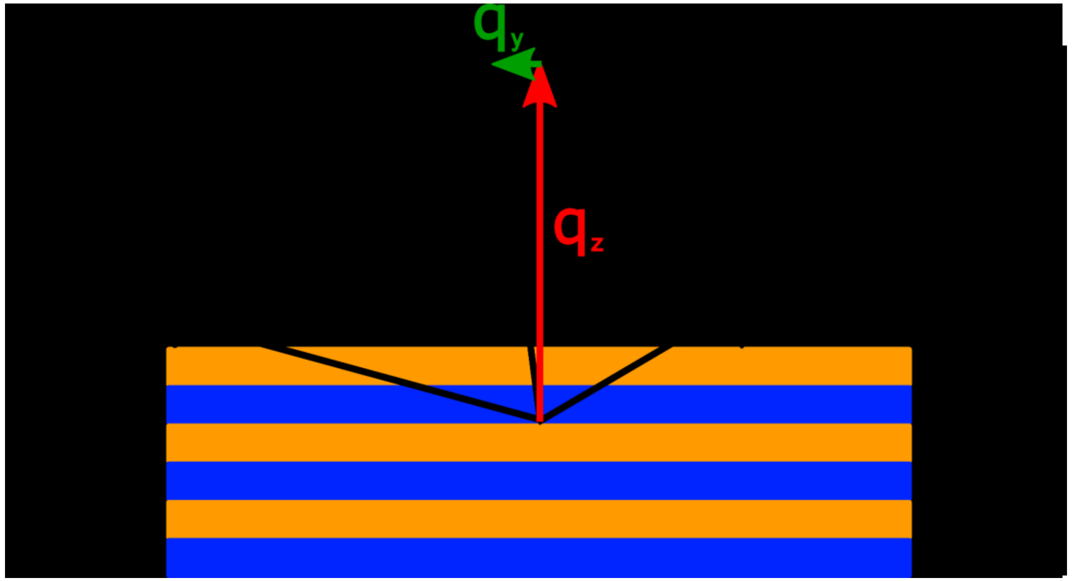
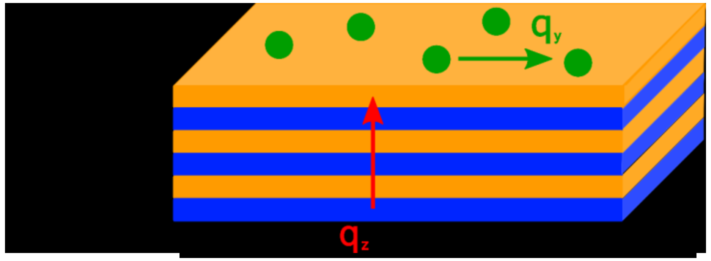


GINSES

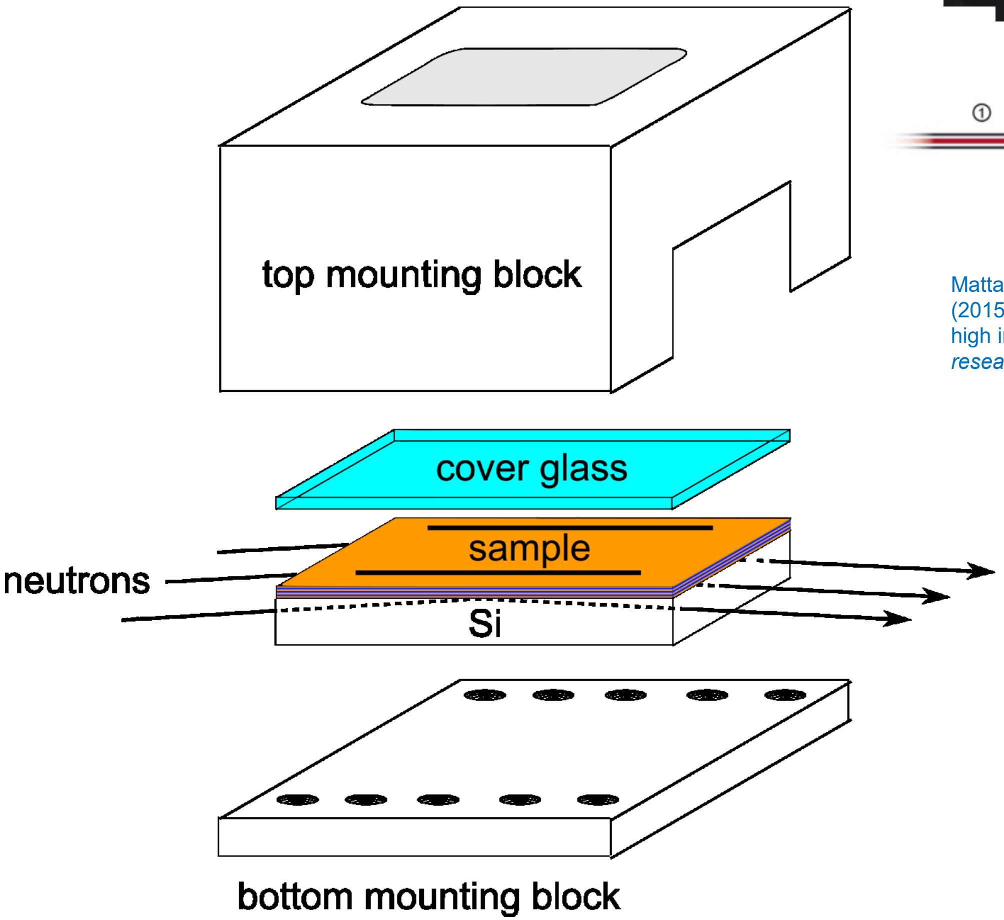
Grazing-incidence Neutron Spin-echo Spectroscopy

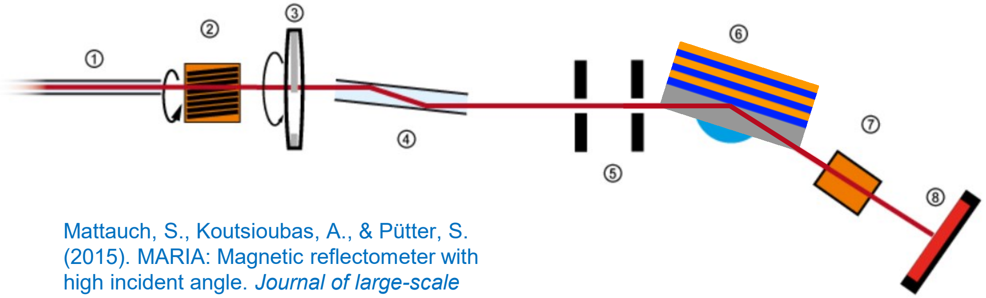




- Reflectometry geometry not feasible
- Only α_f can be used to choose q
- Both in and out of plane compenents in q
- Extremely small q in-plane, usually not accessible in NSE

THE SAMPLE





Mattauch, S., Koutsioubas, A., & Pütter, S. (2015). MARIA: Magnetic reflectometer with high incident angle. *Journal of large-scale research facilities JLSRF*, *1*, 8.

- Performed at MARIA, KWS-1, SNS-NSE, J-NSE
- Sample fully submerged in D_2O
- Cooling and heating cycle for GISANS, physiological conditions for GINSES
- Scatter through silicon to illuminate well aligned lamellae

JÜLICH Forschungszentrum

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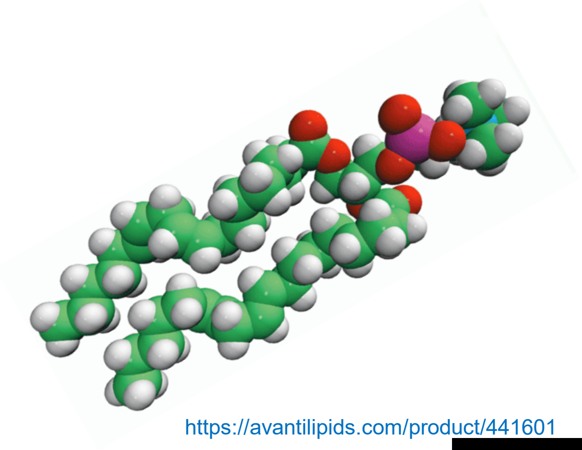

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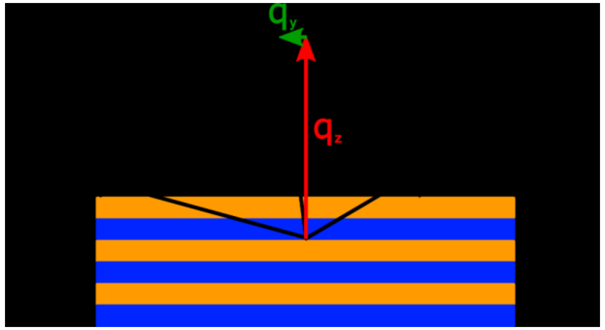

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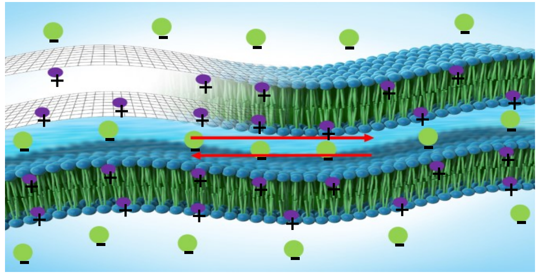
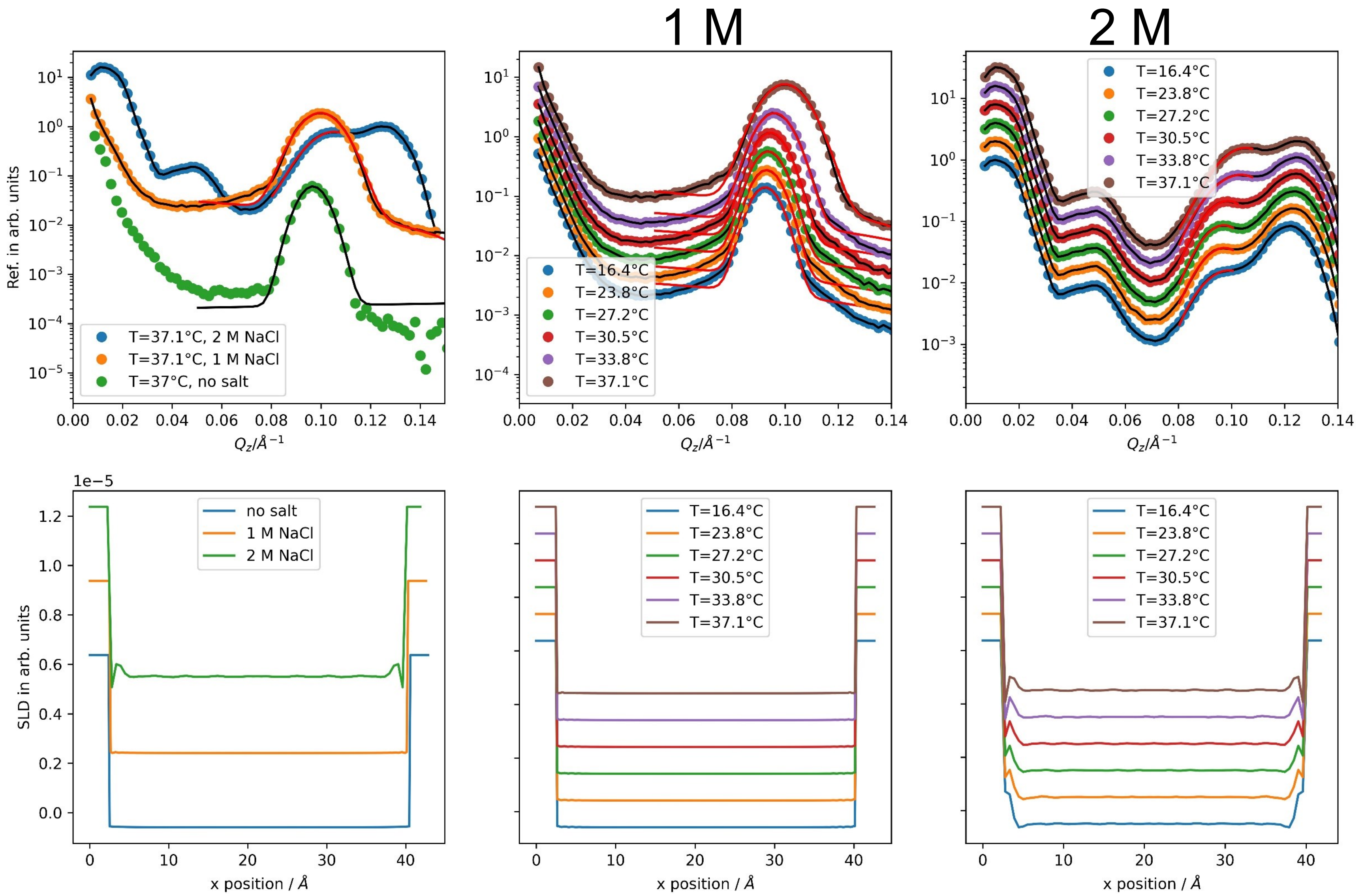
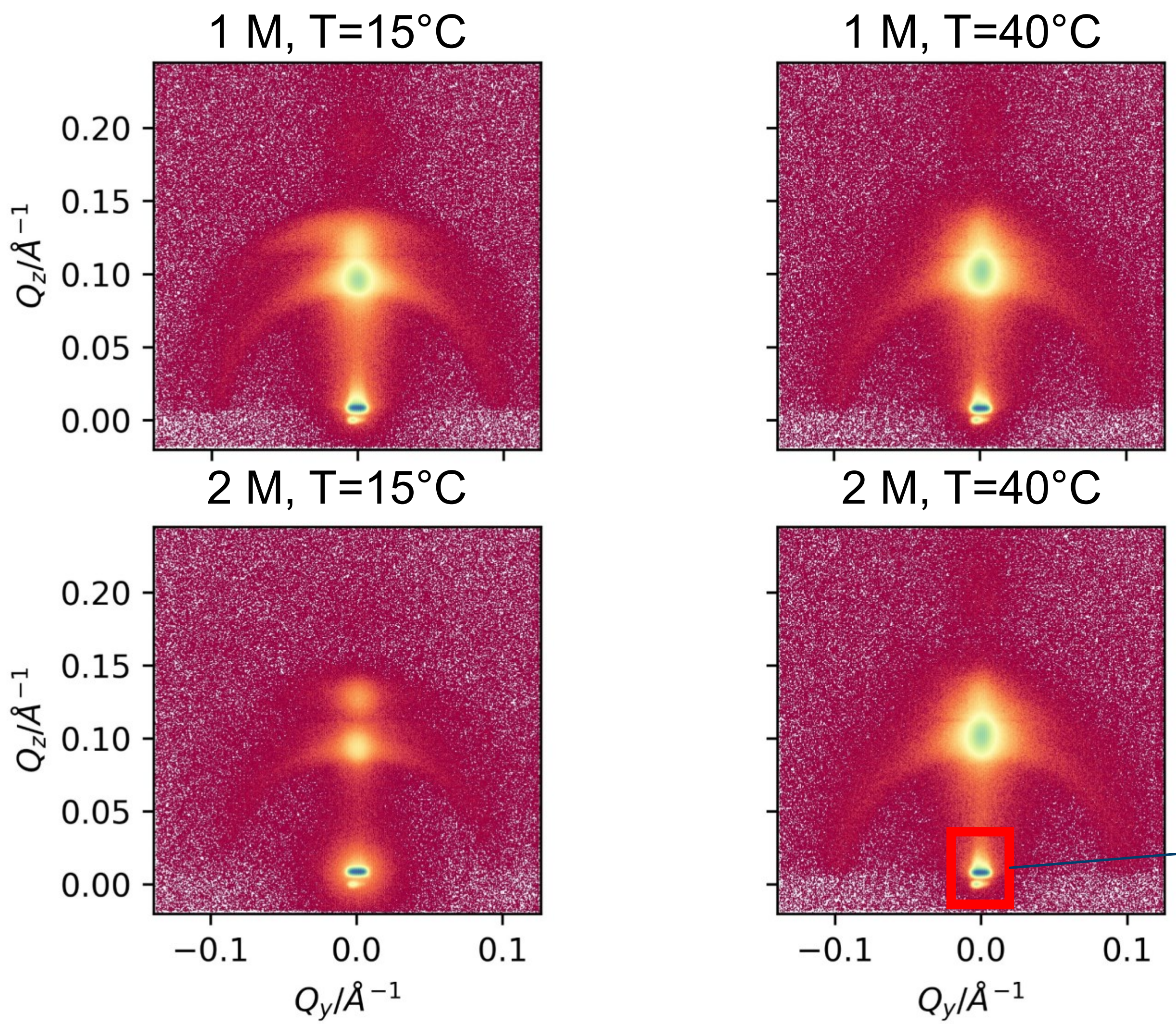


REFLECTOMETRY DATA



- Thickness decreases with temperature
- Hardly any discernible influence for 1 M sample
- Peak splitting and mostly change in the headgroup region for 2 M sample

GISANS DATA

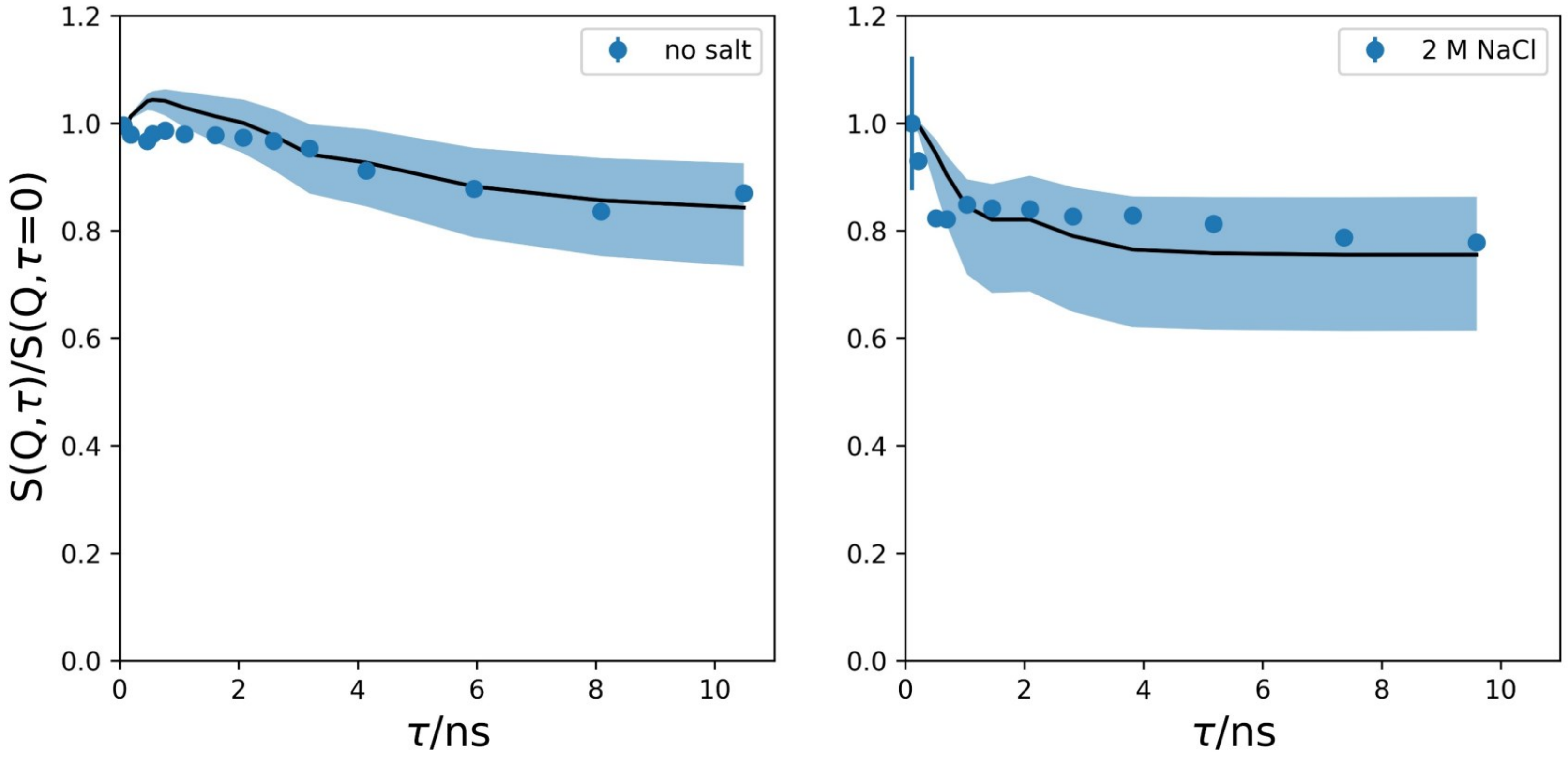


- No in-plane features
- Slight splitting for 2 M from reflectometry can be replicated
- Higher order peak better visible at high temperatures
- Slight Debye-Scherrer ring, stronger for high temperatures → more mobile membrane

Not to be caught on a tangent:
Dynamics with GISANS is here
Jaksch, S. et al., (2019). Long-range excitations in phospholipid membranes. *Chemistry and physics of lipids*, *225*, 104788.

GINSES

$Q_{in-plane} = 0.01$ Å^{-1}
T = 37°C



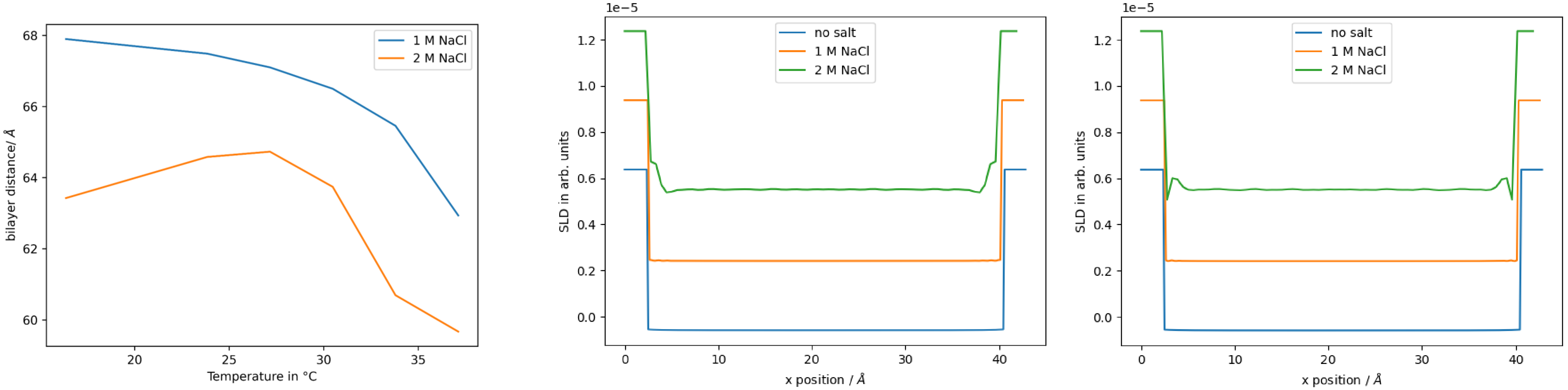
Parameter	No salt	2 M NaCl
B/Pa	3.4 10^6	3.4 10^6
γ/N m	0.01	0.01
η_3/Pa s	0.00765	0.0023
κ/k_B T	22.4	22.4
d/Å	60	60

- Fit is using a liquid crystal model by Romanov et al.
- Strong decrease at short times
- Undulations for longer times
- All parameters fixed (except for viscosity)

Jaksch, S., Holderer, O., Gvaramia, M., Ohl, M., Monkenbusch, M., & Frielinghaus, H. (2017). Nanoscale rheology at solid-complex fluid interfaces. *Scientific reports*, *7*(1), 1-7.

Romanov, V. P., & Ul'yanov, S. V. (2002). Dynamic and correlation properties of solid supported smectic-a films. *Physical Review E*, *66*(6), 061701.

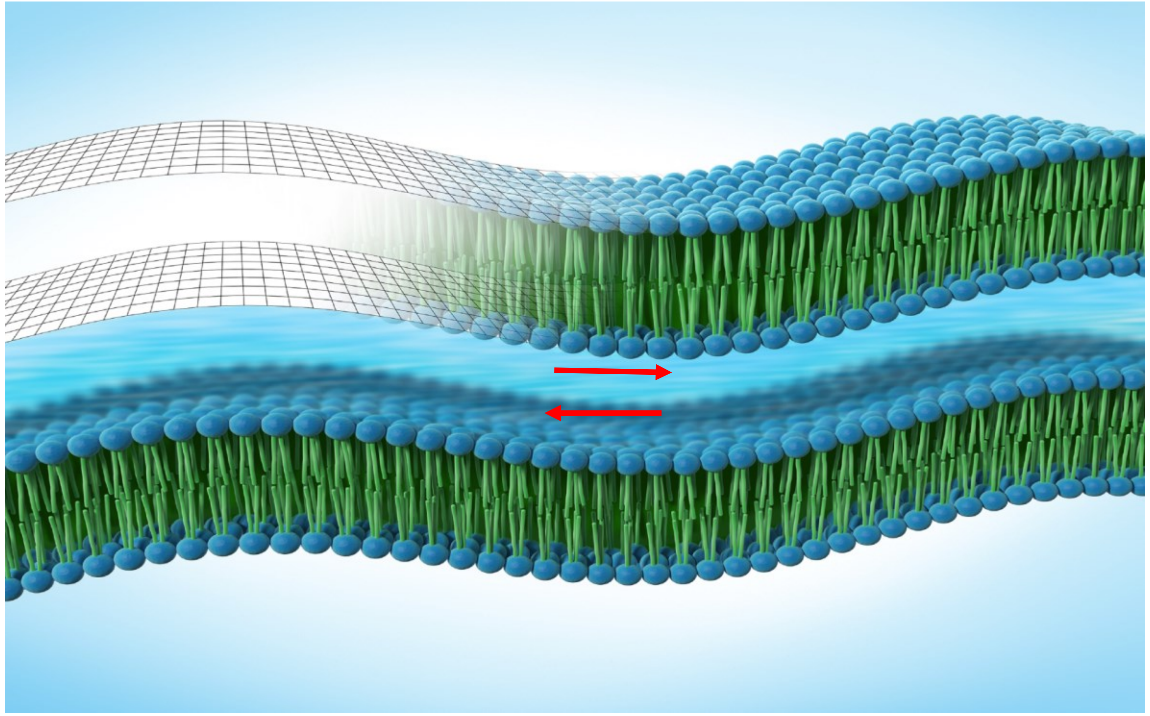
STRUCTURE



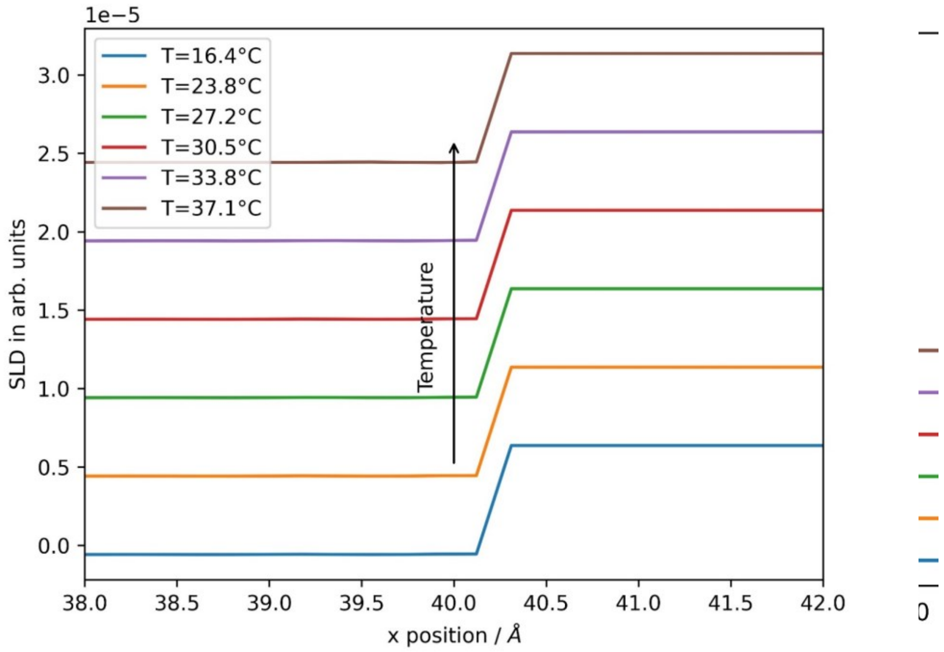
- Bilayer distance decrease with higher temperatures/Overall phase diagram agrees with literature
- No salt and 1 M NaCl are virtually identical (very slight rippling close to the phospholipid heads)
- Strong change for temperature change for 2 M NaCl → looks like Na-enrichment close to the interface

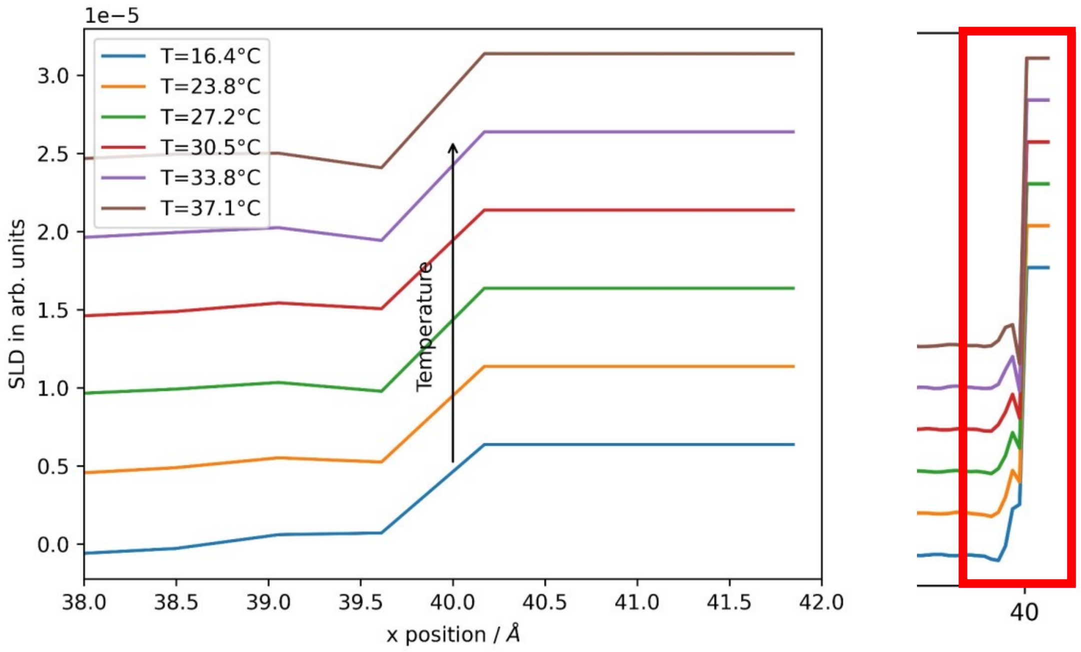
DYNAMICS

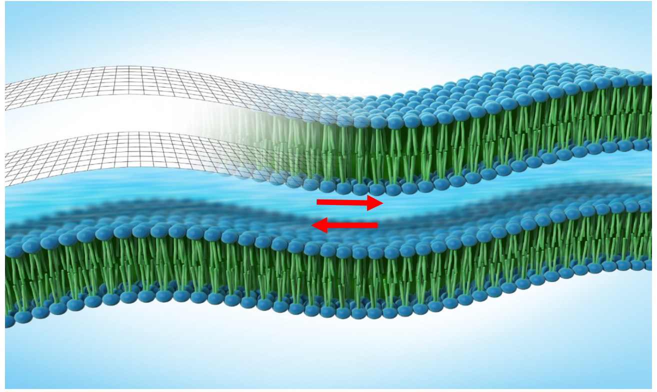
- Data can be fitted with a single parameter: Viscosity
- All other parameters are determined by common fits or external parameters
- Membranes appear to slide on a „charge cushion“ at higher NaCl concentrations
- Dynamic long-range properties are maintained (over nearly 1 µm in-plane)
- Long-range excitations (surface mode phonon → Smomon) are present both in no NaCl as well as in high NaCl conditions

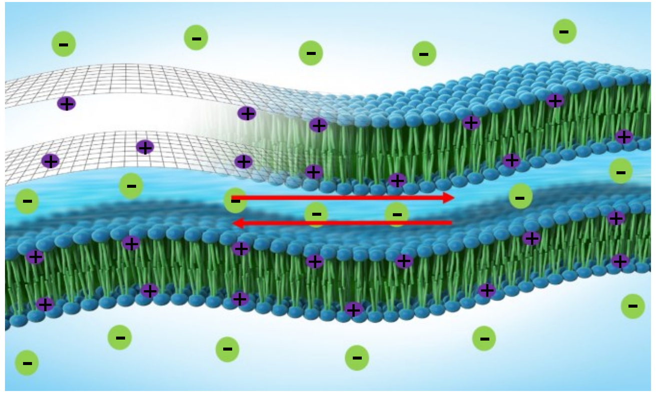


STRUCTURE & DYNAMICS





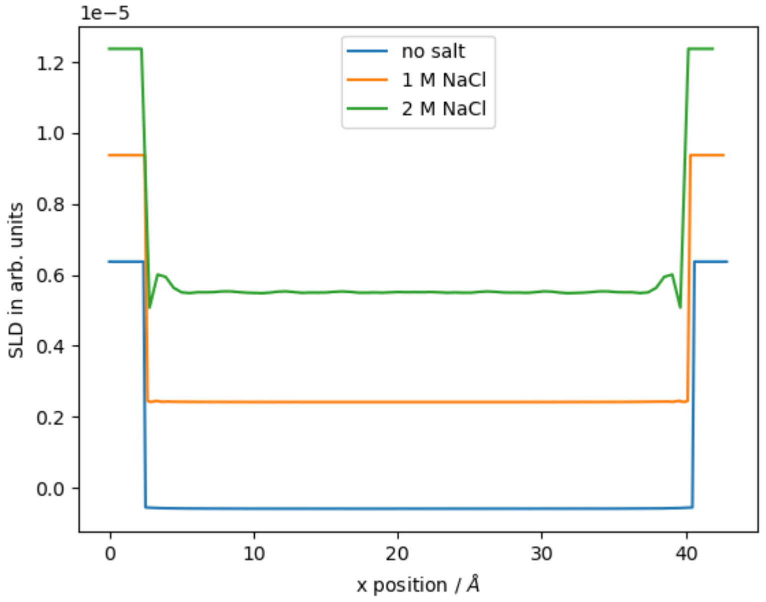




CONCLUSIONS

Structure

- Multilayer structure is maintained, also after addition of NaCl
- No additional in-plane features can be found
- NaCl ions mostly are found at the interface between headgroup and water



Dynamics

- Description as a dynamic multilayer system is maintained
- Except for in-plane viscosity all parameters are constant
- Long-range dynamic modes (smomons) are still present

CONCLUSIONS

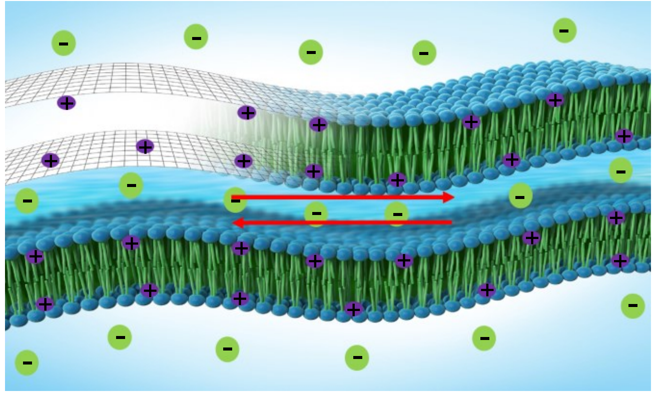
<u>Combination of structure and dynamics</u>

- Since overall structure is maintained, no extreme changes in dynamics expected
- Those changes that do occur can be directly linked both to structural and dynamic features

<u>Mobility</u>

- „Sliding cushion“ of NaCl ions increases viscosity, but only in the membrane plane

If you want the whole story:
Influence of NaCl on
the structure and dynamics of phospholipid layers,
S. Jaksch et al.,
Frontiers in Physics,
doi: 10.3389/fphy.2021.628219



Jaksch S., Holderer, O., Frielinghaus, H., Förster, S., Müller-Buschbaum, Influence of NaCl on the structure and dynamics of phospholipid layers, submitted

THANKS TO

Henrich Frielinghaus, KWS1

Olaf Holderer, J-NSE

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Stefan Mattauch, MARIA

Alexandros Koutsioumpas, MARIA

Michael Ohl, SNS-NSE

Prof. Stephan Förster, Director JCNS-1

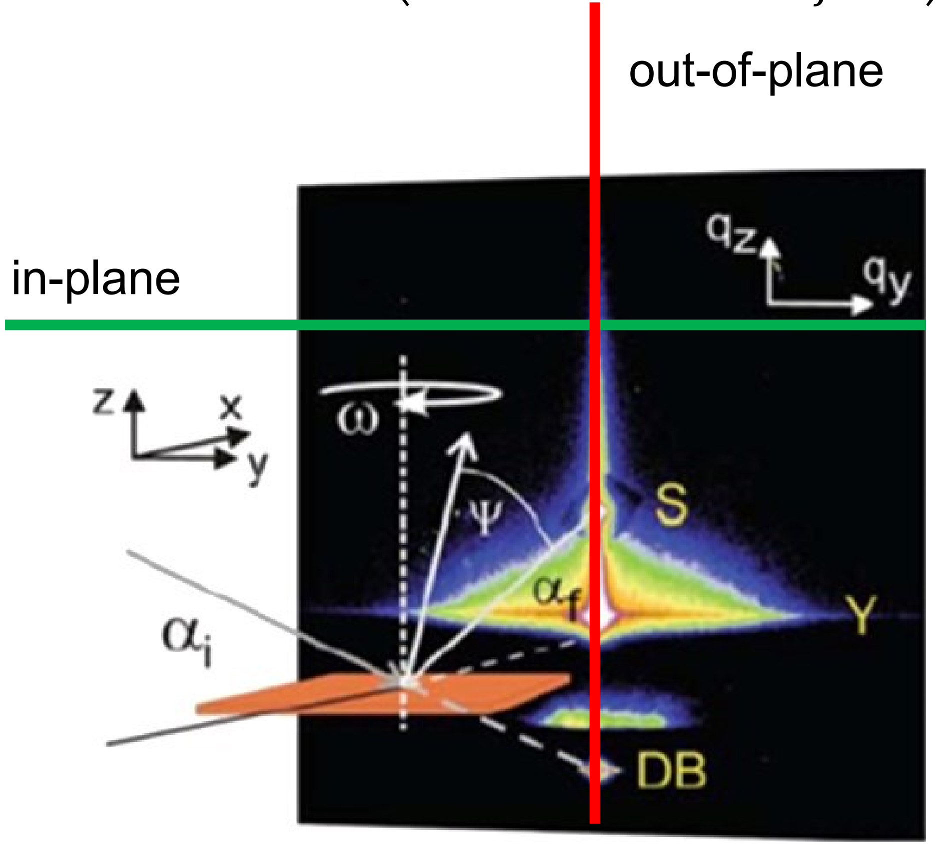
Prof. Peter Müller-Buschbaum, Director FRM2

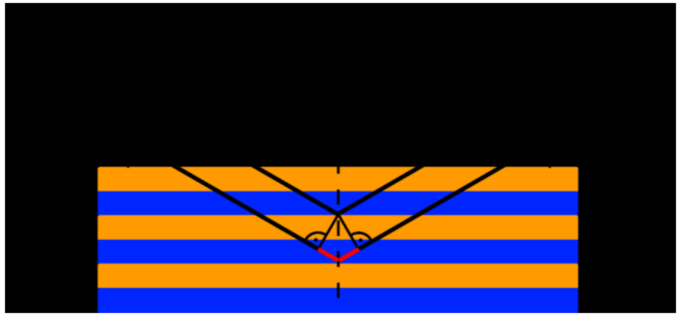
…YOU, FOR YOUR KIND ATTENTION.

GISANS

Grazing Incidence Small-Angle Neutron Scattering

$$\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \frac{2\pi}{\lambda} \begin{pmatrix} \cos\psi\cos\alpha_f - \cos\alpha_i \\ \sin\psi\cos\alpha_f \\ \sin\alpha_i + \sin\alpha_f \end{pmatrix}$$





for $\alpha_i = \alpha_f = \theta$

and $q^* = {2\pi}/{d}$

$$\Rightarrow n\lambda = 2d\sin\theta$$

Simplified for purely lamellar systems:
Bragg‘s Equation for mesoscale

Müller-Buschbaum, P. (2009). A basic introduction to grazing incidence small-angle X-ray scattering. In Applications of synchrotron light to scattering and diffraction in materials and life sciences (pp. 61-89). Springer, Berlin, Heidelberg.