Structure and fluctuations of single floating bilayers

5 February 2009

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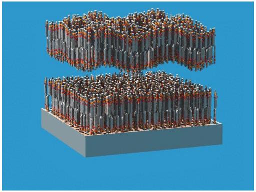
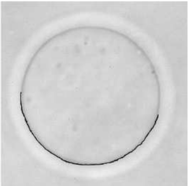


Outline

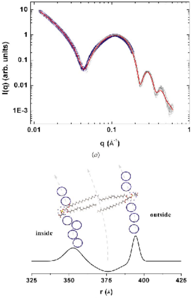
- Introduction: supported bilayers
- Fluctuations and interactions of bilayers
- X-ray scattering
- Results
  - Bilayers, protusion modes
  - Fluctuations and interaction between 2 bilayers
  - Destabilization under an electric field

Vesicles, lamellar phases

Unilamellar vesicles



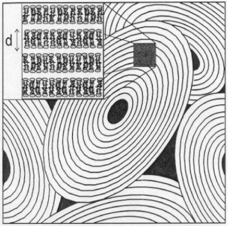
J. Pécréaux et al. *Eur. Phys. J. E* **13** 277 (2004)



40nm SOPS vesicles, Brzustowicz et al. J. Appl. Crys. 38 (2005) 126

- Normal and giant vesicles
- Fluctuations through contour analysis

MLV's, lamellar phases

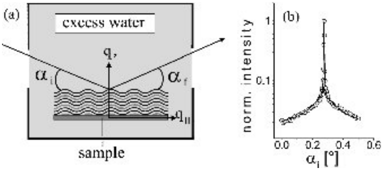


Nagle et al.

- Multilamellar vesicles (MLVs)
- Oriented samples
- Caillé theory $\rightarrow \sqrt{\kappa B}$
- Controlled osmotic pressure

R.P. Rand, V.A. Parsegian, BBA **351** 988 (1989), J.F. Nagle et al. BBA **159** 1469 (2000)

Multilamellar stacks



Vogel et al. *Phys. Rev. Lett.* **84** 390 (2000)

- Preparation: from solution + drying, spin-coating, freely suspended films,
- Well oriented samples: mosaic speading better than 0.01° by spin-coating
- Bending rigidity and compressibility from full analysis of x-ray scattering
- Unbinding

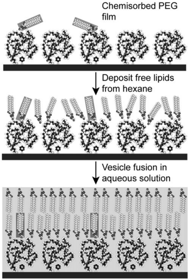
- Consistency of specular/off-specular ?
- Role of defects ?

For a recent review: T. Salditt J. Phys: Cond. Matt. 17 (2005) R287

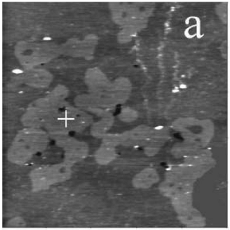
Supported bilayers I

Adsorbed bilayers

Polymeric cushions

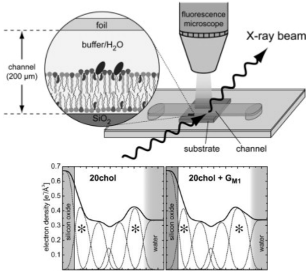


AFM:



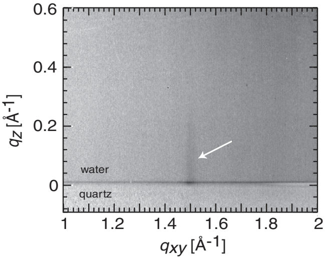
Giocondi et al. Biophys. J. 86 (2004) 861
DOPC + sphingomyelin bilayer

Reflectivity



Reich et al. *Biophys. J* **95** 657 (2008), ID01

Diffraction

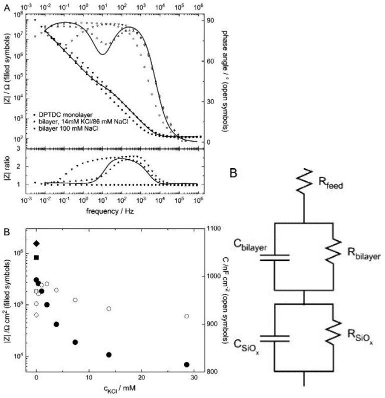


Miller et al. *Phys. Rev. Lett.* **100** 058103 (2008), APS

- Model lipid raft Cholesterol/DOPC/Sphingomyelin/DPPE 20:40:39.5:0.5 + monosialoganglioside G_{M1}
- Vesicle fusion via osmotic rupture

- DPPE bilayer

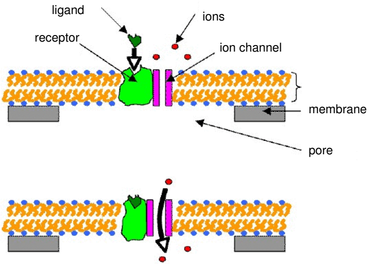
Tethered functional membranes

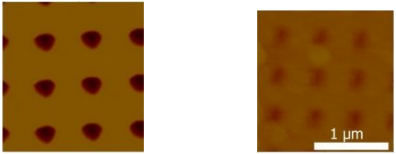


Atanasov et al. *Biophys. J* **89** 1780 (2005)

- Silane lipids (phytanyl chains)+ lipid bilayer (DPhyPC 1,2-diphytanoyl-sn-glycero-3-phosphocholine) + proteins (valinomycin, gramicidin)
- Valinomycin is a small ion carrier peptide which selectively transports K+ ions from one side to the other
- Functional tethered lipid membranes on metals or semi-conductors

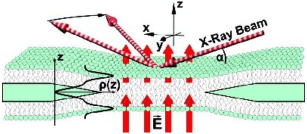
- Captors
- Resources of microelectronics, captors

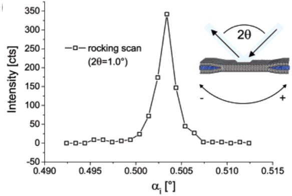




iRSTV/biopuces, LETI, CEA Grenoble

300nm pores



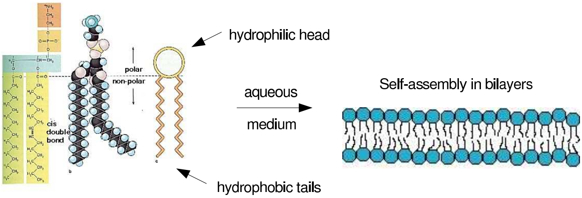


Beerlink et al. *Langmuir* **24** 4952 (2008),

BM05

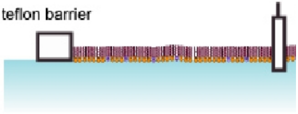
Sample preparation I

Phosphatidylcholines with C_{16}, C_{17}, or C_{18} chains

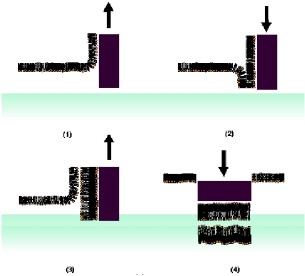


Sample preparation II

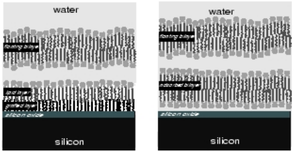
Langmuir-Blodgett + Langmuir Schaeffer deposition techniques



- "Double bilayers"



- "Grafted" or "OTS bilayers", 1rst layer is a grafted octadecyltrichlorosilane self-assembled monolayer

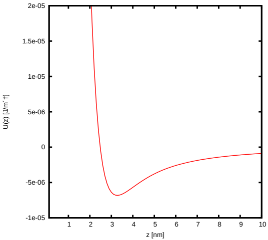


Super-polished silicon wafers $< 1\AA$ rms, SESO, Aix en Provence

Membrane elasticity

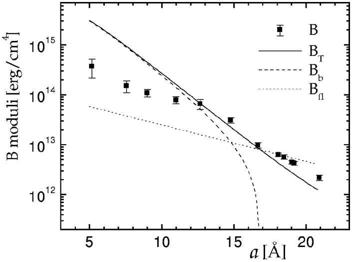
- **Tension** $\gamma < 1mN/m$?
- **bending modulus** $\kappa \approx 20 - 30k_BT$ in fluid phase
- **interaction potential** $U(z)$

$$U(z) = P_h l_h \exp(-z/l_h) - \frac{H}{12\pi}\left(\frac{1}{z^2} - \frac{2}{(z+D)^2} + \frac{1}{(z+2D)^2}\right) + c_{fl}\frac{(k_BT)^2}{\kappa z^2}$$



- $4.10^7 Pa < P_h < 4.10^9 Pa$
- $l_h = 0.1 - 0.3nm$
- $H \approx k_BT$

- Measure distance for applied osmotic pressure (Rand, Parsegian)



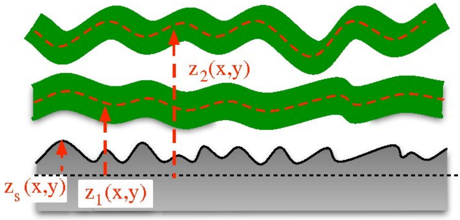
Petrache et al. *Phys. Rev. E* **57** 7014 (1998)

No agreement to experimental data with Helfrich interaction $\rightarrow$ softer potential (Podgornik, Parsegian *Langmuir* **8** 557 (1992)):

Helfrich contribution $\rightarrow \frac{\pi k_B T}{16}\left(\frac{P_h}{\kappa\lambda}\right)^{1/2} \exp(-z/2\lambda)$

Model Hamiltonian

X-ray scattering → correlation functions ($\langle \rho\rho \rangle$ or $\langle zz \rangle$)



$$\mathcal{H} = \sum_{i=1}^{2} \left[\int d^2\mathbf{r} \frac{1}{2} \left(\gamma_i \nabla^2 + \kappa_i \Delta^2 \right) (u_i(\mathbf{r})) \right] + \int d^2\mathbf{r} \left[U_{sm}(u_1 - u_0) + U_{sm}(u_2 - u_0) + U_{mm}(u_2 - u_1) \right]$$

$$\mathcal{H} = \sum_{q} \left[\frac{1}{2} \sum_{i=1}^{2} (\tilde{a}_i(q) + B) \left| \tilde{u}_i(q) \right|^2 - A_1 \tilde{u}_1(q) \tilde{u}_s(-q) - A_2 \tilde{u}_2(q) \tilde{u}_s(-q) - B \tilde{u}_1(q) \tilde{u}_2(-q) \right]$$

with $\tilde{a}(i,q) = \left(A_i + \gamma_i q^2 + \kappa_i q^4 \right)$

Correlation to the substrate (static)

Minimization of the Hamiltonian against $\tilde{u}_1(\mathbf{q})$ and $\tilde{u}_2(\mathbf{q})$:

$$\tilde{u}_1(\mathbf{q}) = \frac{A_1 \tilde{a}_2(\mathbf{q}) + B\,(A_1 + A_2)}{\tilde{a}_1(\mathbf{q})\tilde{a}_2(\mathbf{q}) + B\,(\tilde{a}_1(\mathbf{q}) + \tilde{a}_2(\mathbf{q}))}\tilde{u}_s(\mathbf{q})$$

$$\tilde{u}_2(\mathbf{q}) = \frac{A_2 \tilde{a}_1(\mathbf{q}) + B\,(A_1 + A_2)}{\tilde{a}_1(\mathbf{q})\tilde{a}_2(\mathbf{q}) + B\,(\tilde{a}_1(\mathbf{q}) + \tilde{a}_2(\mathbf{q}))}\tilde{u}_s(\mathbf{q})$$

(after Swain and Andelman, *Langmuir* **15**, 8902, 1999)

General solution:

$$\langle u_i(r)u_i(0)\rangle = \frac{1}{2\pi}\frac{A_i^2}{\kappa_i^2}\sum_{j=1}^{4}\left[\lambda_{i,j}K_0(q_j r) + \frac{1}{2}\eta_{i,j}^2 r\frac{K_1(q_j r)}{q_j}\right] \otimes \langle u_s(r)u_s(0)\rangle$$

$$\langle u_i(r)u_s(0)\rangle = \frac{1}{2\pi}\frac{A_i}{\kappa_i}\sum_{j=1}^{4}\left[\eta_{i,j}K_0(q_j r)\right] \otimes \langle u_s(r)u_s(0)\rangle$$

$$\langle u_i(r)u_j(0)\rangle = \frac{1}{2\pi}\frac{A_1 A_2}{\kappa_1\kappa_2}\sum_{j=1}^{4}\left[\tau_j K_0(q_j r) + \frac{1}{2}\nu_j r\frac{K_1(q_j r)}{q_j}\right] \otimes \langle u_s(r)u_s(0)\rangle$$

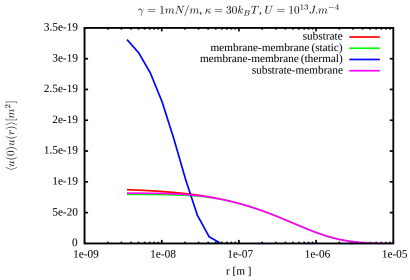
Thermal fluctuations

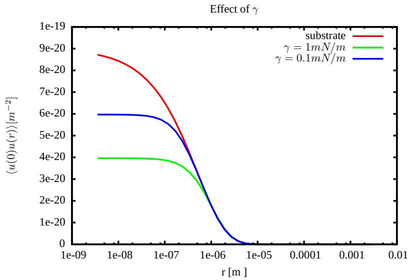
Normal modes + equipartition of energy:

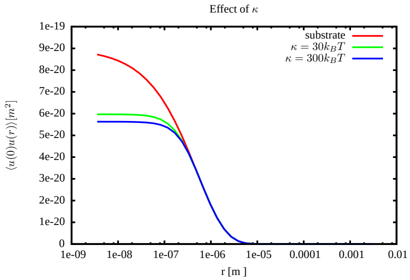
$$\begin{aligned}\mathcal{H}_q &= \frac{1}{2}\sum_{i=1}^{2}\left(\tilde{a}_i(\mathbf{q})+B\right)\left|\tilde{u}_i(\mathbf{q})\right|^2 - B\tilde{u}_1(\mathbf{q})\tilde{u}_2(-\mathbf{q}) \\ &= \begin{pmatrix} \tilde{u}_1(-\mathbf{q}) & \tilde{u}_2(-\mathbf{q}) \end{pmatrix} \begin{pmatrix} a_1(\mathbf{q}) & -B/2 \\ -B/2 & a_2(\mathbf{q}) \end{pmatrix} \begin{pmatrix} \tilde{u}_1(\mathbf{q}) \\ \tilde{u}_2(\mathbf{q}) \end{pmatrix}\end{aligned}$$

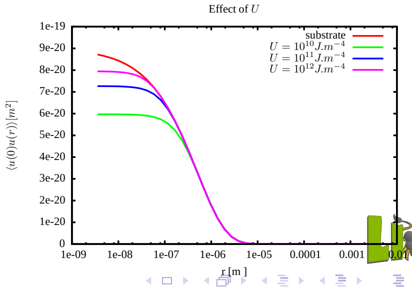
$$\begin{aligned}\langle u_i(r)u_i(0)\rangle &= \frac{k_B T}{\kappa_i}\frac{1}{2\pi}\sum_{j=1}^{4}\alpha_{i,j}K_0(q_j r) \\ \langle u_1(r)u_2(0)\rangle &= \frac{k_B T}{\kappa_1\kappa_2}\frac{B}{2\pi}\sum_{j=1}^{4}\iota_j K_0(q_j r)\end{aligned}$$

Correlation functions



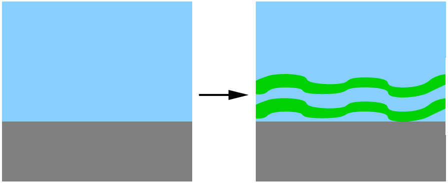




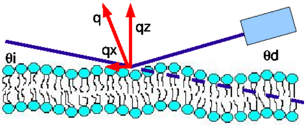


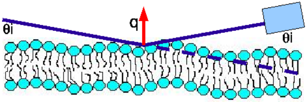
X-ray scattering - simplified DWBA

Perturbation theory (Distorted Wave Born Approximation)



X-ray scattering - simplified DWBA





$$\left(\frac{d\sigma}{d\Omega}\right) = r_e^2 \left|t^{in}\right|^2 \left|t^{sc}\right|^2 (\mathbf{e}_{in}\cdot\mathbf{e}_{sc})^2 \left\langle \left| \int d\mathbf{r}_{\|}\, e^{i\mathbf{q}_{\|}\mathbf{r}_{\|}} \left(\tilde{\rho}_{sub} e^{iq_z z_s(\mathbf{r}_{\|})} + \tilde{\rho}_{M1} e^{iq_z\left(z_1^{th}(\mathbf{r}_{\|}) + z_1^{st}(\mathbf{r}_{\|})\right)} + \tilde{\rho}_{M2} e^{iq_z\left(z_2^{th}(\mathbf{r}_{\|}) + z_2^{st}(\mathbf{r}_{\|})\right)}\right) \right|^2 \right\rangle$$

$$R(q_z) = R_F(q_z) \left| 1 + iq_z \int \frac{\delta\rho(z)}{\rho_{\mathrm{sub}} - \rho_w} e^{iq_z z} dz \right|^2$$

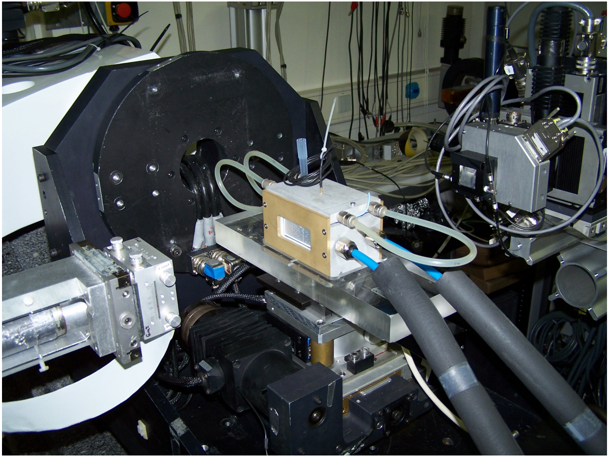
I $= R(q_z) +$ diffuse in the specular direction

$$I = \frac{I_0}{h_i w_i} \int \left[\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{ref}} + \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{pert}} \right] \mathcal{R}es\,(\Omega)\, d\Omega$$

$$= \frac{I_0}{h_i w_i} \frac{4\pi \Delta\theta \mathcal{A} r_e^2 \left|t^{in}\right|^2 \left|t^{sc}\right|^2 (\mathbf{e}_{in}\cdot\mathbf{e}_{sc})^2}{k_0} \times \int_0^{+\infty} dx \cos(q_{x0} x)\, e^{-\frac{\Delta q_x{}^2 x^2}{2}} f(x, q_z)$$

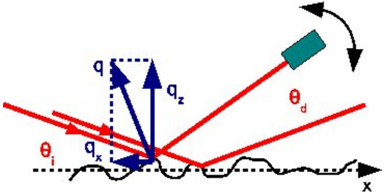
Combined treatment specular + off-specular

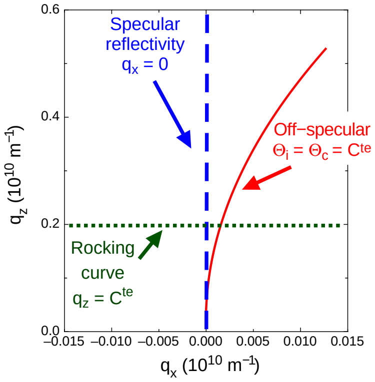
ESRF, CRG-IF BM32



E= 27keV, $\lambda = 0.46\AA$, $0.015mm \times 0.5mm$ beam

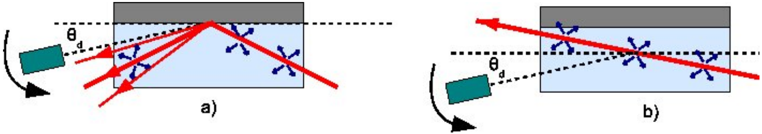
Specular and Off-specular reflectivity

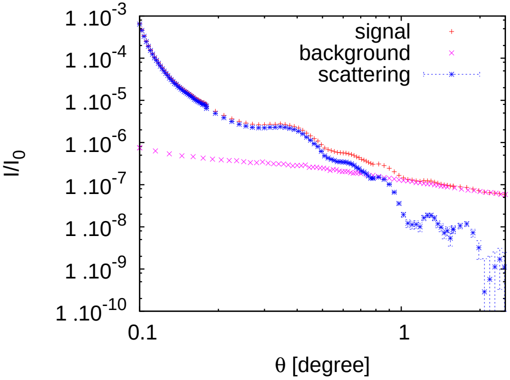




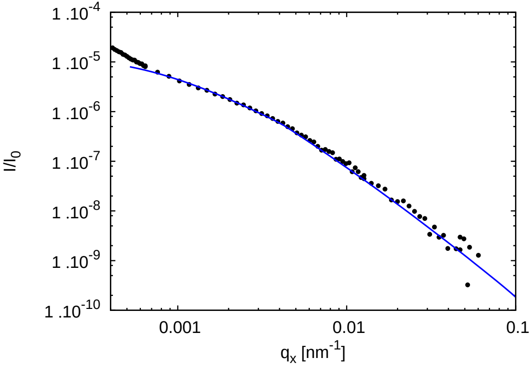
- Specular reflectivity : average structure normal to the interface
- Off-specular reflectivity : lateral inhomogeneities, elastic properties (γ,κ) and interaction potentials

Background subtraction





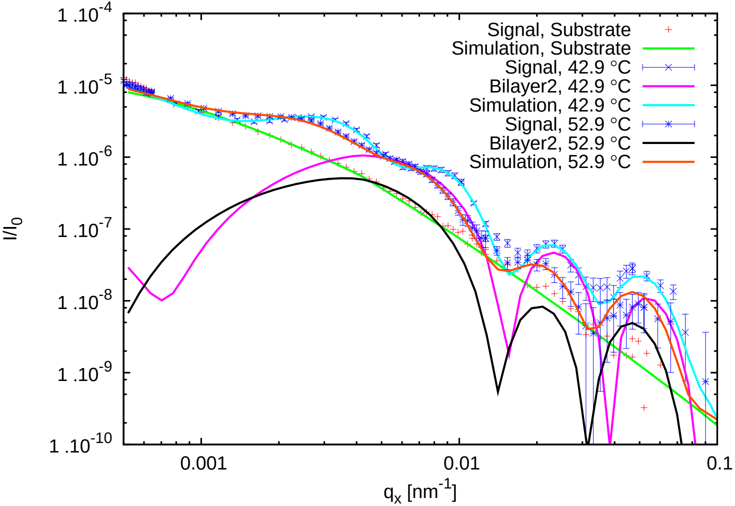
Silicon-water interface



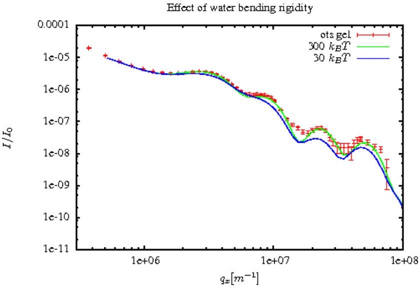
$$\langle z(\mathbf{0})z(\mathbf{r}_{\|})\rangle = \sigma^2 \exp\left({\mathbf{r}_{\|}}^2/\xi^2\right)^H$$

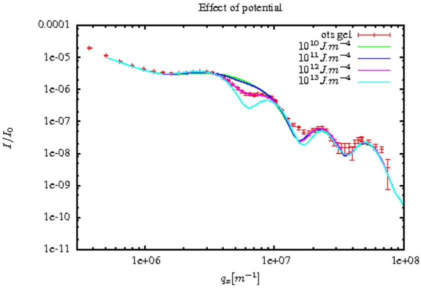
$$\sigma = 4\mathring{A},\ \xi = 1\mu,\ H = 0.4$$

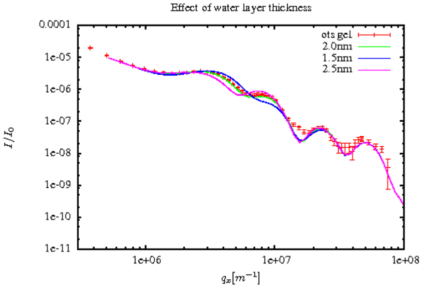
Scattered intensity



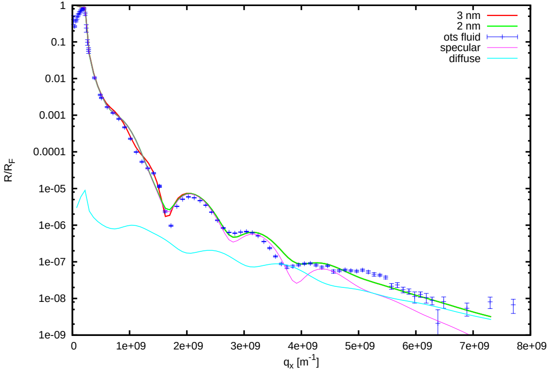
Sensitivity to parameters

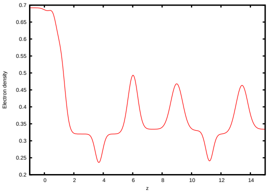






Reflectivity



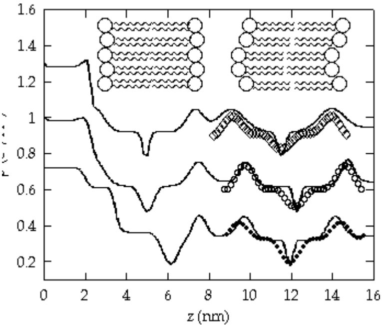


Structural parameters

Two models:

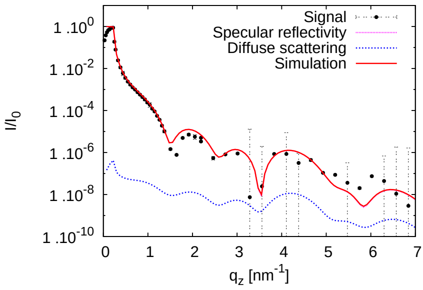
- Gaussian model: 1 Gaussian for the headgroups and 1 Gaussian trough for the methyl groups.
- Fourier development of for symmetric bilayers:

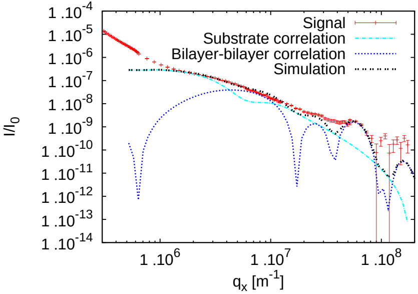
$$\rho(z) - \rho_w = \frac{F_0}{D} + \frac{2}{D} \sum_{h=1}^{h_{\max}} F_h \cos\left(\frac{2\pi h z}{D}\right)$$

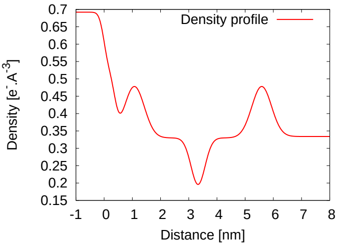


J. Daillant et al., PNAS **102**, 11639, 2005

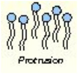
C_{18} bilayer in the gel phase: protusion modes







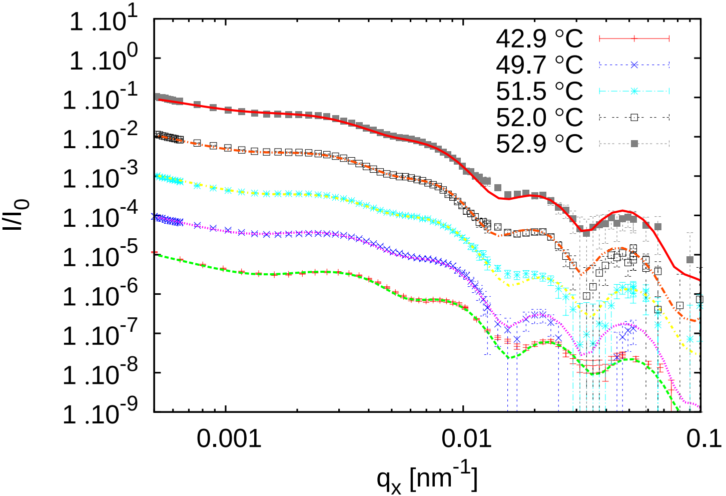
- $U'' = 2.10^{12} J.m^{-4}$
- $\kappa = 300 k_B T$
- $\boxed{\gamma = 70 mN/m}$



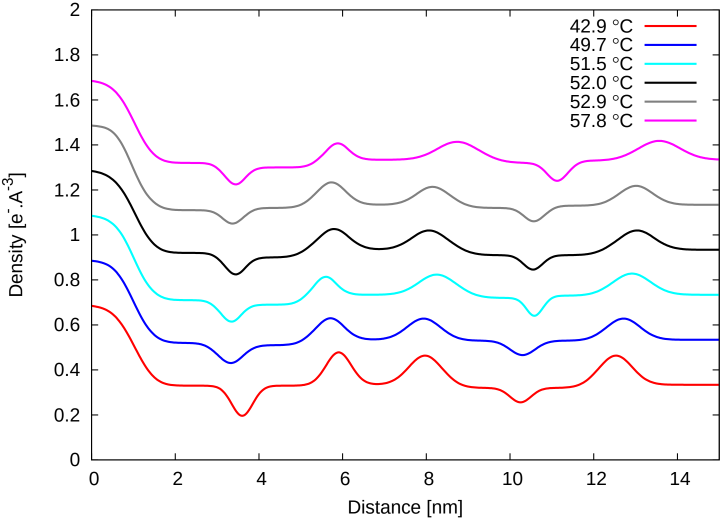
Lindhal and Edholm, *Biophys. J* **79** 426 (2000)

$\gamma_P = 50 mN/m$

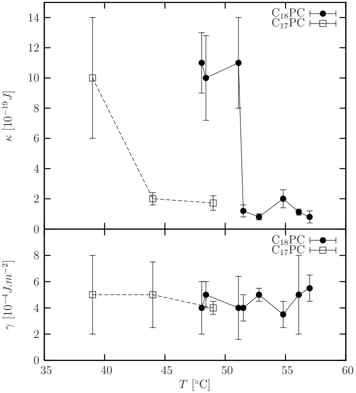
Diffuse scattering OTS bilayers



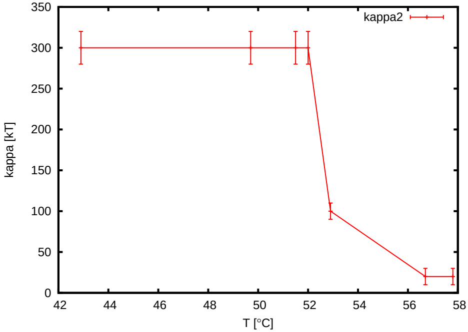
Gel to fluid transition / structure



Double bilayer

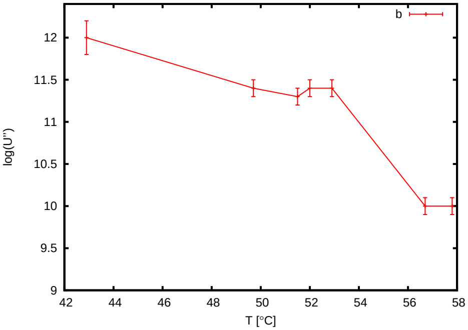


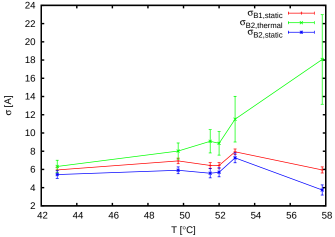
OTS bilayer



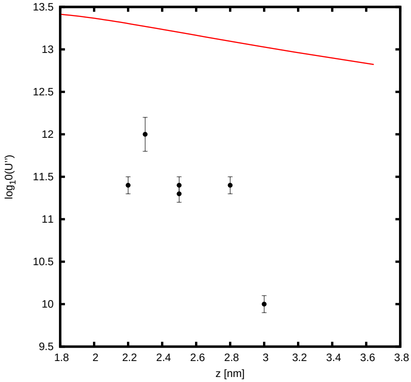
		gel		ripple		fluid
In the bulk:	C_{17}		43		48/49.8	
	C_{18}		50/52		54.6/55	

Interaction potential I





Interaction potential II



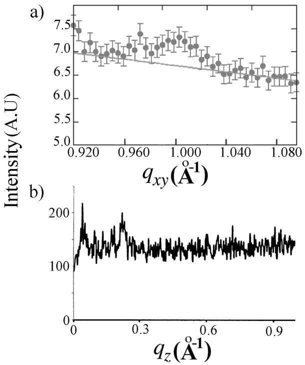
- Hydration length?
- Helfrich interaction?
- Hamaker constant?

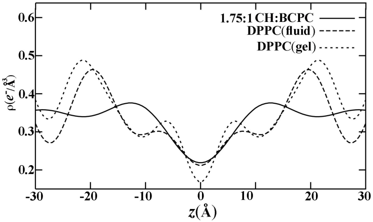
Unbinding experiments, Vogel, Münster, Fenzl, salditt, *Phys. Rev. Lett.* **84** 390 (2000): U" also determined by static defects in lamellar systems?

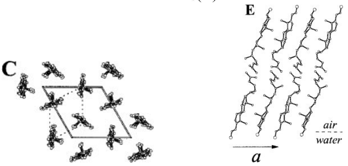
Less defects → smaller U"?

Collaboration with L. Leiserowitz, Weizmann Institute

Bovine cardiac phosphatidylcholine (BCPC), distribution for n:m acyl chains (n number of C atoms, m number of C=C bonds) of 23% 16:0; 1% 16:1; 6% 18:0; 13% 18:1; 43% 18:2; 1% 18:3; 6% 20:4 and 7% others



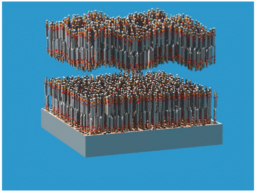




after Rapaport et al. *Biophys J* **81** 2729 (2001)

Segregated cholesterol bilayers with $10 \times 7.5 Å^2$ motif?

Summary



- Possible to study single fluctuating bilayers
- General method for x-ray scattering
- Bilayers: protusion modes
- Very soft potential
- More complicated systems can now be investigated

Thank you!