Soft Matter Surfaces Investigated with XPCS

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Soft Matter Surfaces

Solid Surfaces

1. Introduction

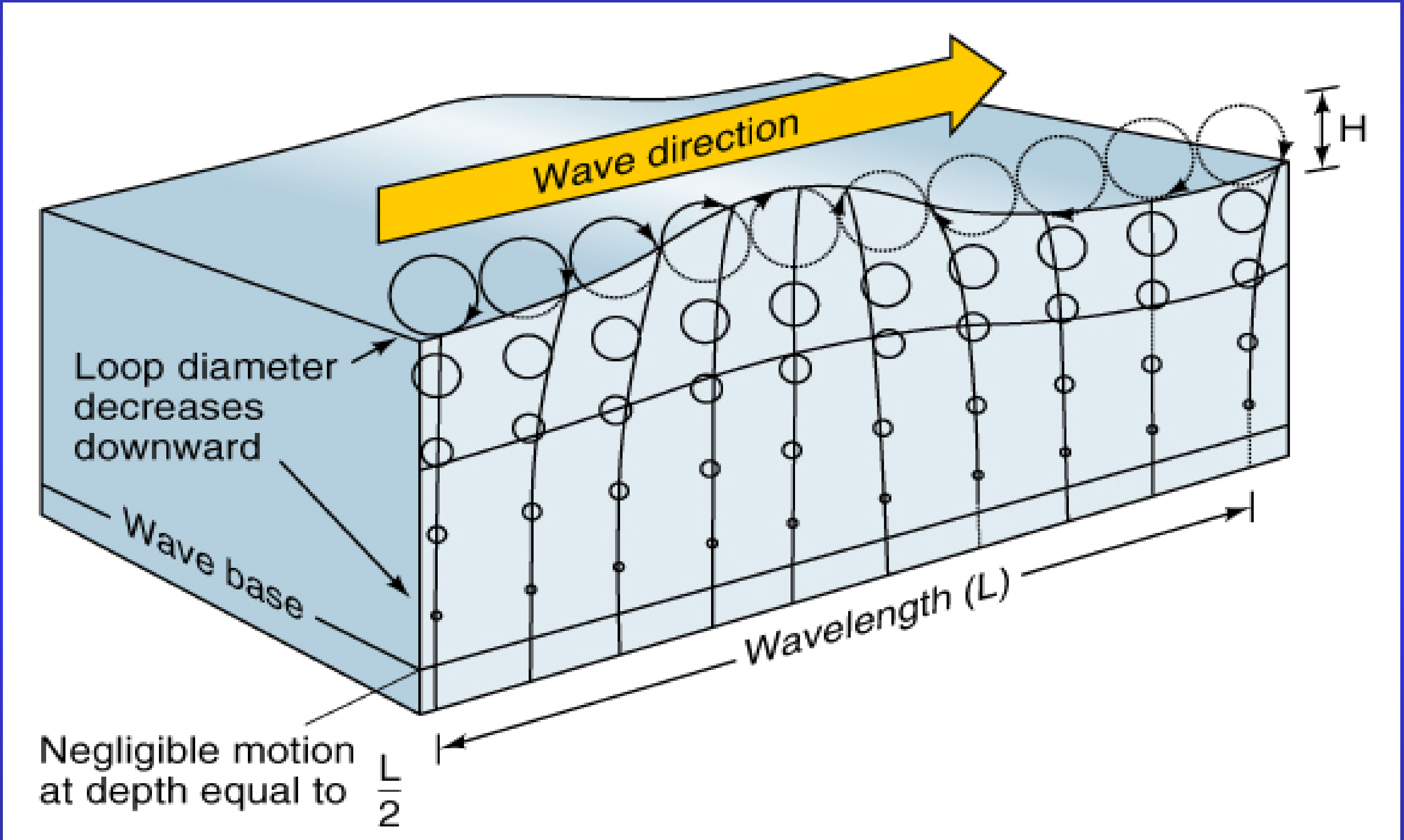
2. Bulk Liquids

3. Confined Liquids

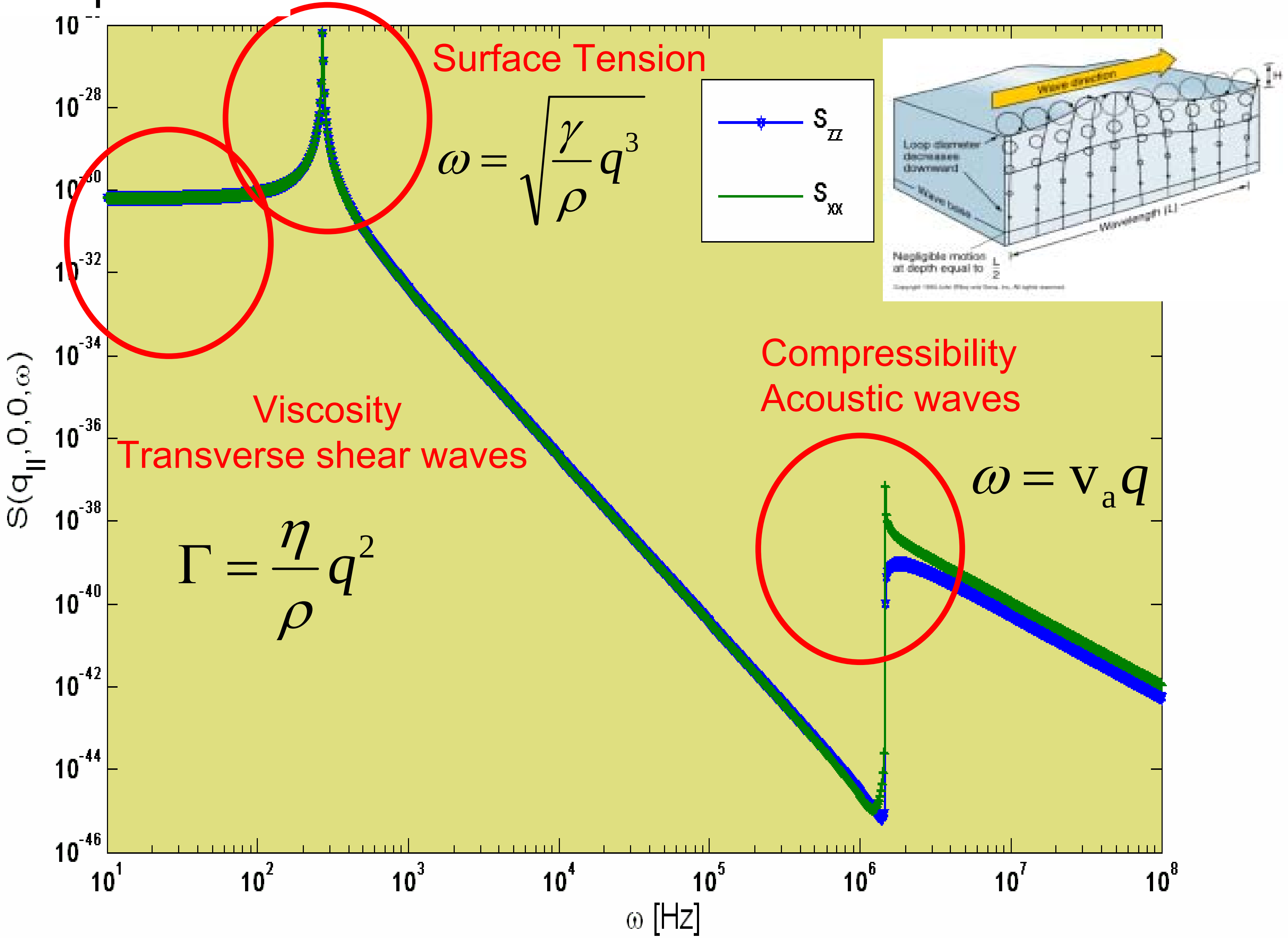
4. Glass Transition

Polymer-Metal
Composite
Systems
Poster Simone Streit

Capillary Waves



Water $q=10^{-6}$ A^{-1}



Surface Tension

$$\omega = \sqrt{\frac{\gamma}{\rho} q^3}$$

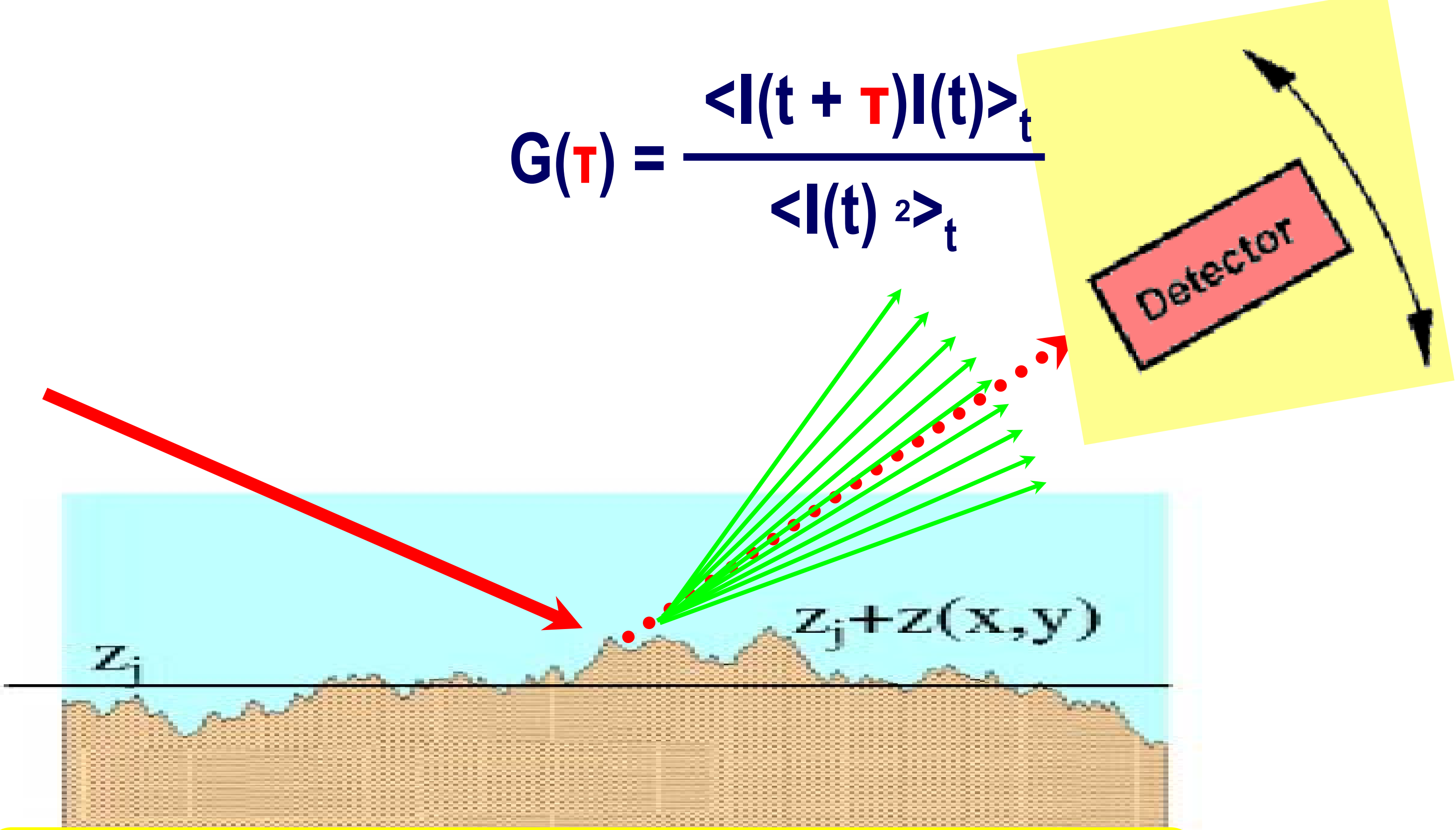
Viscosity
Transverse shear waves

$$\Gamma = \frac{\eta}{\rho} q^2$$

Compressibility
Acoustic waves

$$\omega = v_a q$$

Surface X-Ray Scattering



$$G(\tau) = \frac{\langle I(t+\tau)I(t)\rangle_t}{\langle I(t)^2\rangle_t}$$

Scattering ~ Power Spectral Density

$$I(q_x,q_y,t) \sim S(q_x,q_y,t) = FT\,(z(x,y,t))$$

Correlation functions of surface fluctuations

Homodyne detection scheme

$$\omega_s = \sqrt{\gamma / \rho}\, q^3$$

$$\Gamma = 2\, \eta / \rho\, q^2$$

$$\Gamma_{ov} = \gamma / 2\eta\, q$$

propagating CW's $G(q,\tau) = c + I_s^2 \cdot \cos^2(\omega_s \tau) \cdot e^{-2\Gamma\tau}$

over-damped CW's $G(q,\tau) = c + I_s^2 \cdot e^{-2\Gamma_{ov}\tau}$

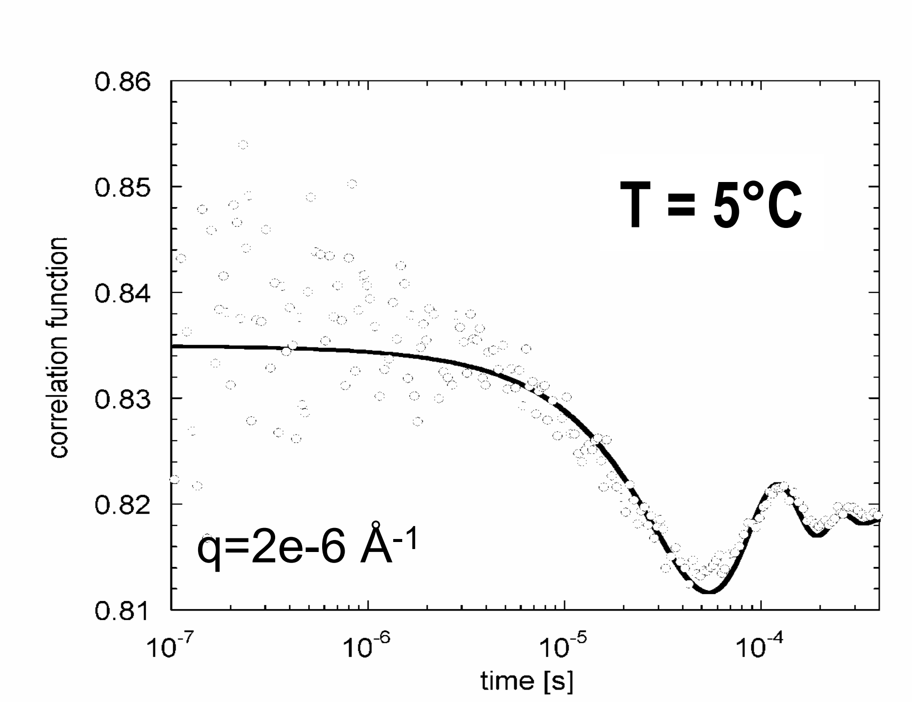
Heterodyne detection scheme

prop. CW's $G(q,\tau) = c + I_s^2 \cdot \cos^2(\omega_s \tau) \cdot e^{-2\Gamma\tau} + I_R I_S \cdot \cos(\omega_s \tau) \cdot e^{-\Gamma\tau}$

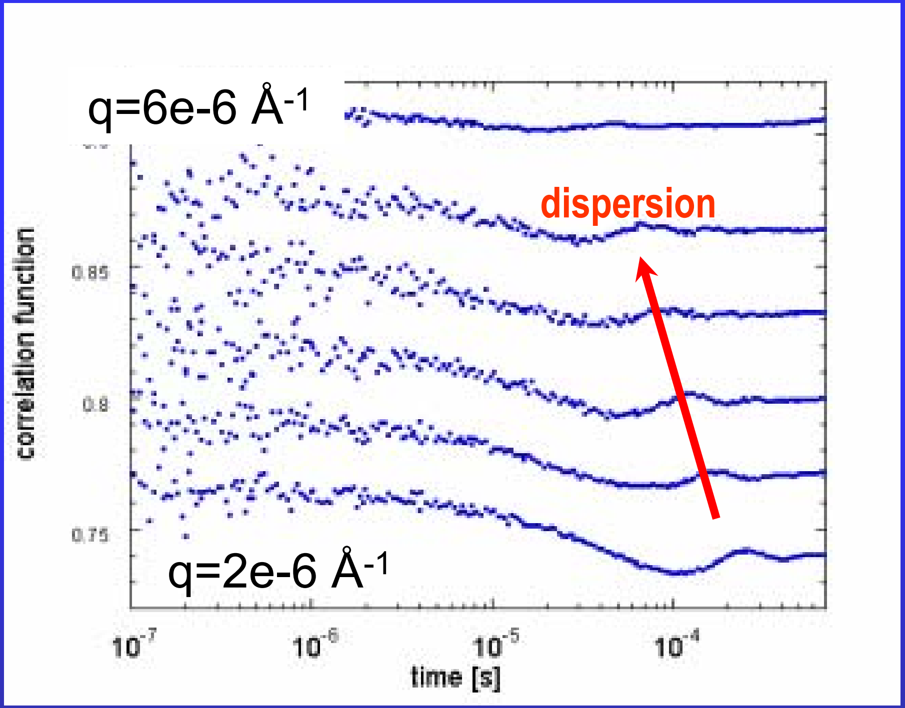
over-d. CW's $G(q,\tau) = c + I_s^2 \cdot e^{-2\Gamma_{ov}\tau} + I_R I_S \cdot e^{-\Gamma_{ov}\tau}$

C. Gutt, T.Ghaderi, V. Chamard, A. Madsen,
T. Seydel, M. Tolan, M.Sprung, G. Grübel,
S. K. Sinha; PRL 91, 076104 (2003)

Surface Dynamics of water



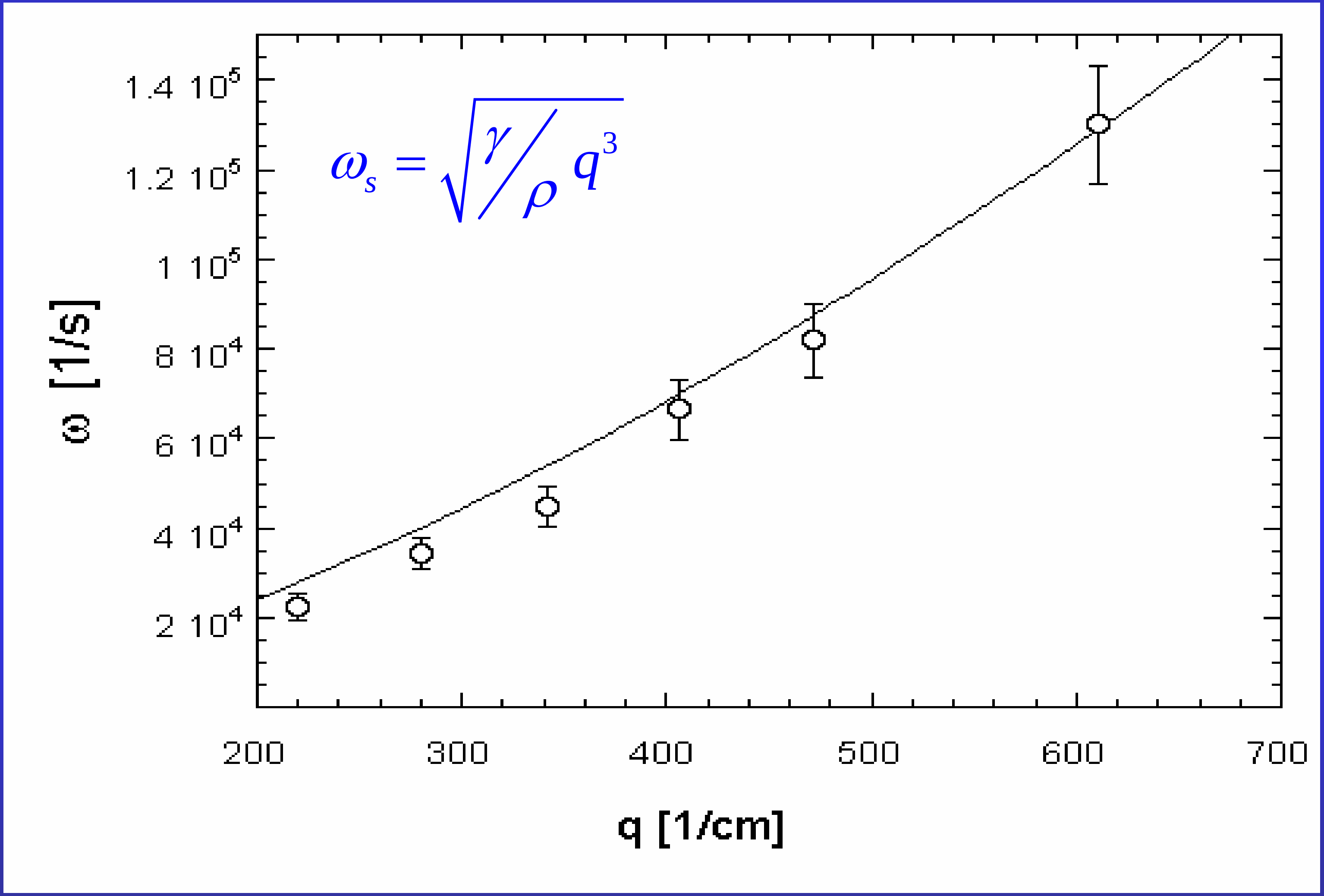
correlation functions of a water surface at T=5ºC as a function of q



!! damped cosine behavior !!
intrinsic heterodyne mixing

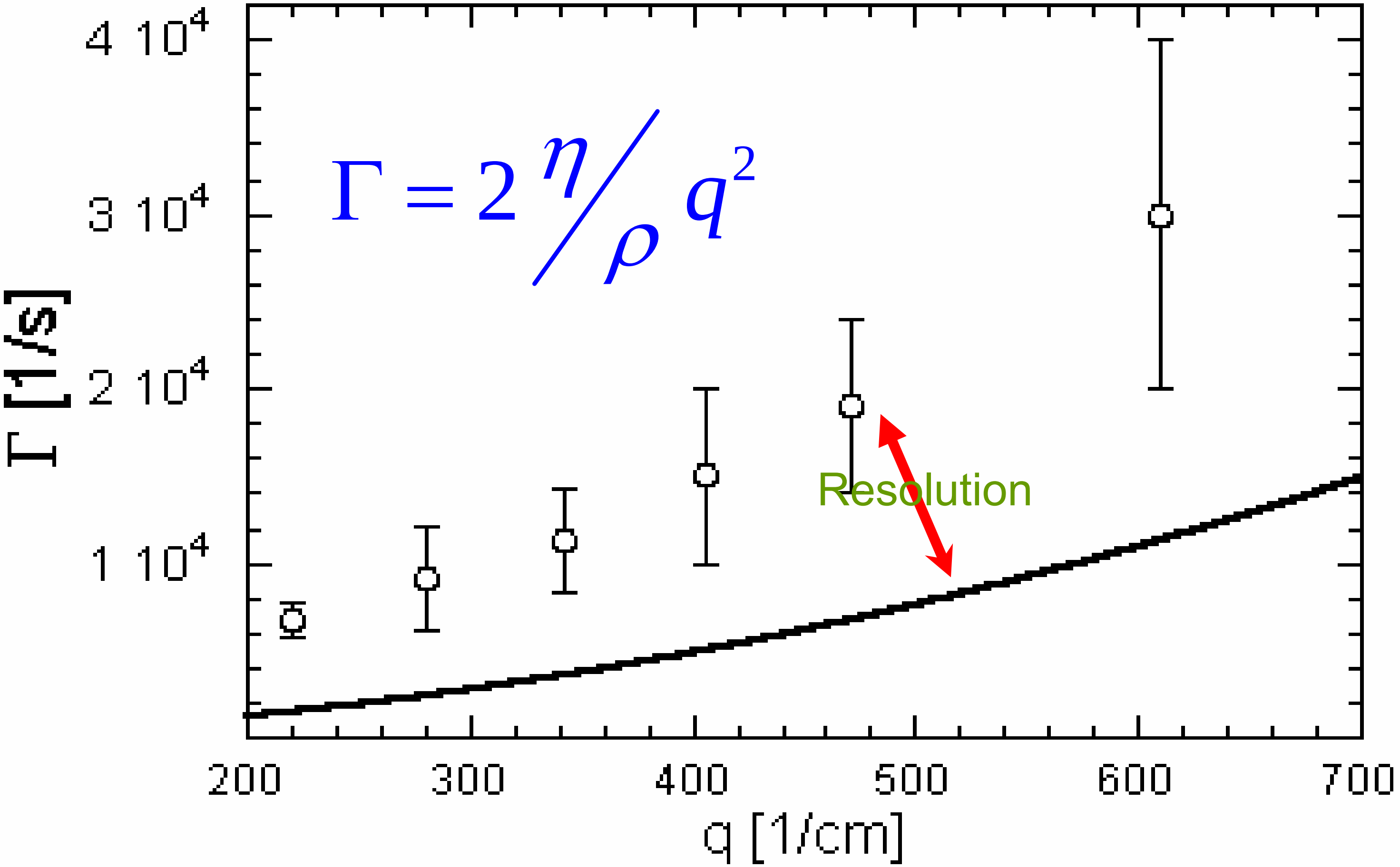
C. Gutt, T.Ghaderi, V. Chamard, A. Madsen,
T. Seydel, M. Tolan, M.Sprung, G. Grübel,
S. K. Sinha; PRL 91, 076104 (2003)

Dispersion relation of capillary waves



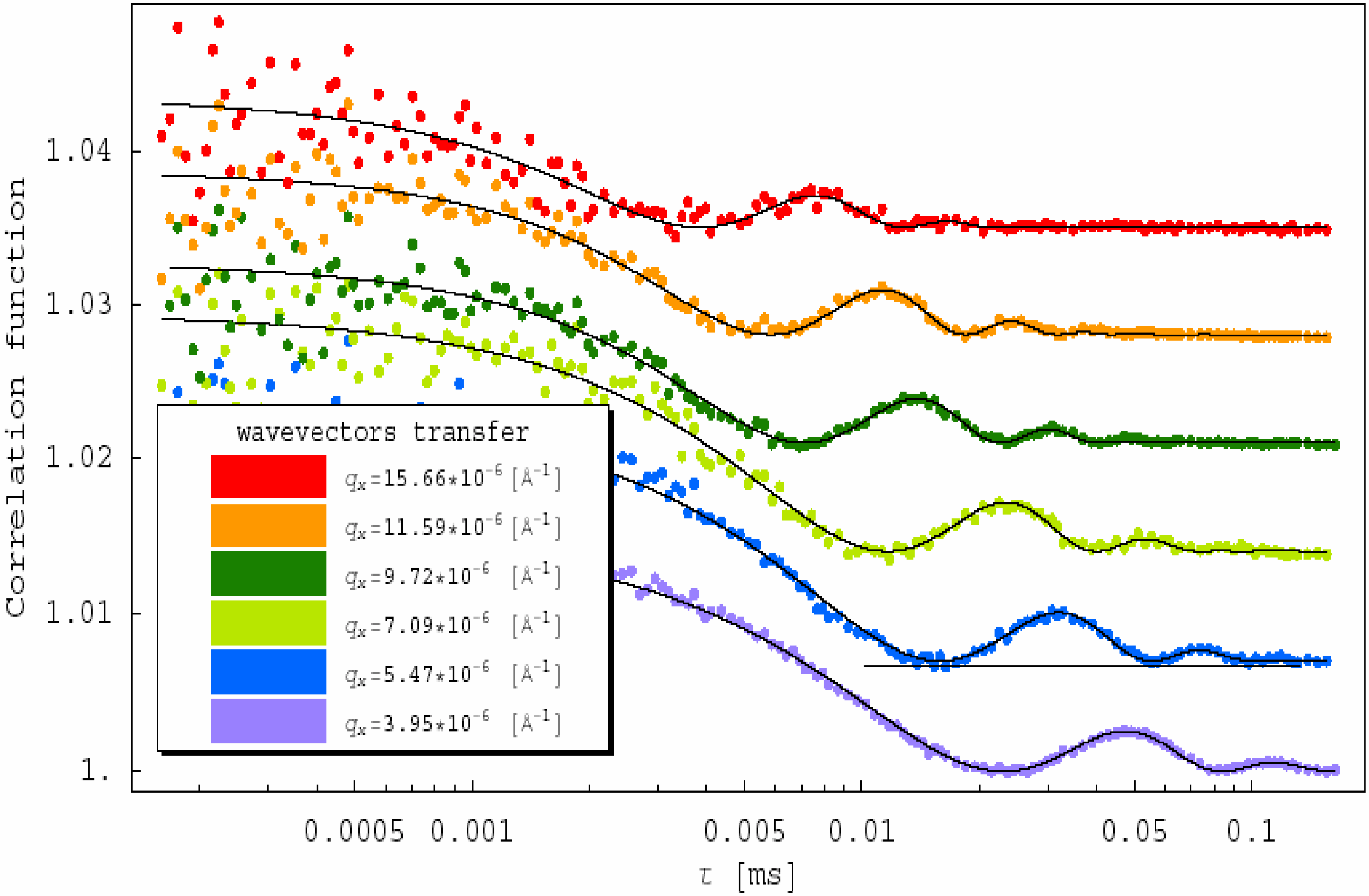
$$\omega_s = \sqrt{\gamma / \rho \, q^3}$$

Damping constants of capillary waves

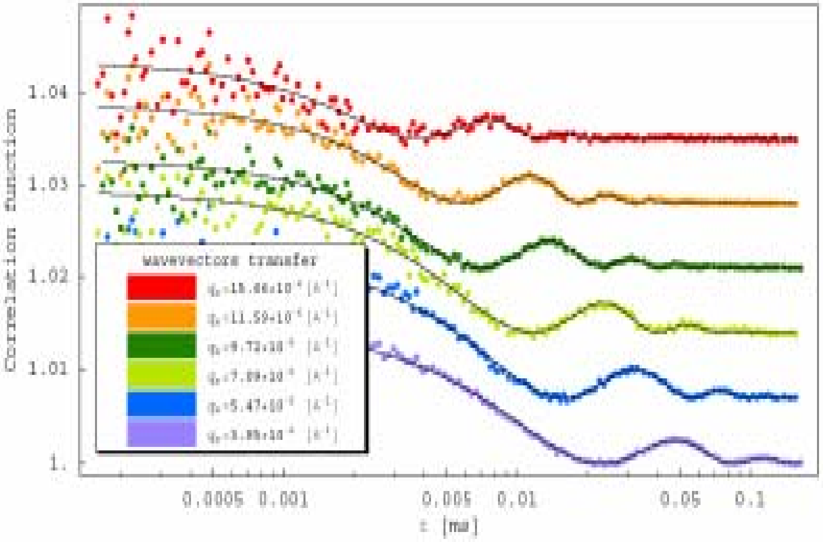


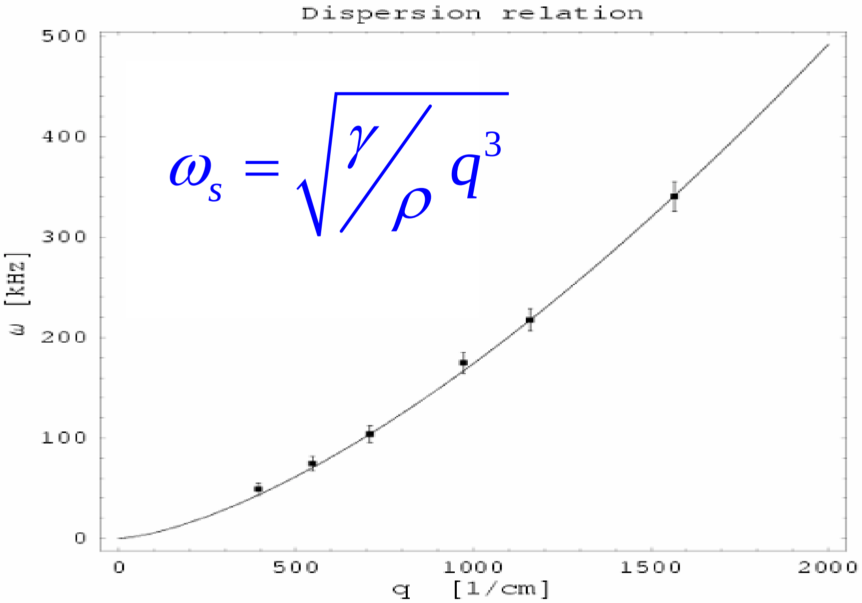
$$\Gamma = 2\,{}^{\eta}\!/_{\rho}\, q^2$$

Surface Dynamics of Hexane



Surface Dynamics of Hexane

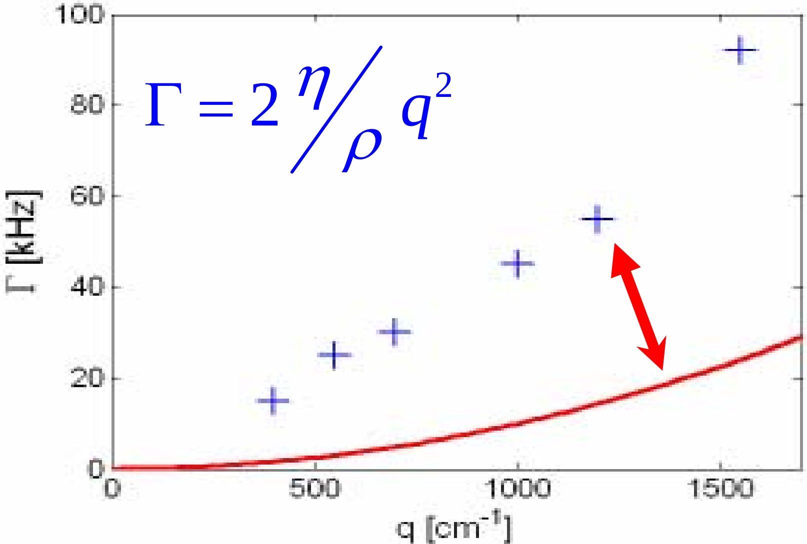




$$\omega_s = \sqrt{\gamma/\rho \, q^3}$$

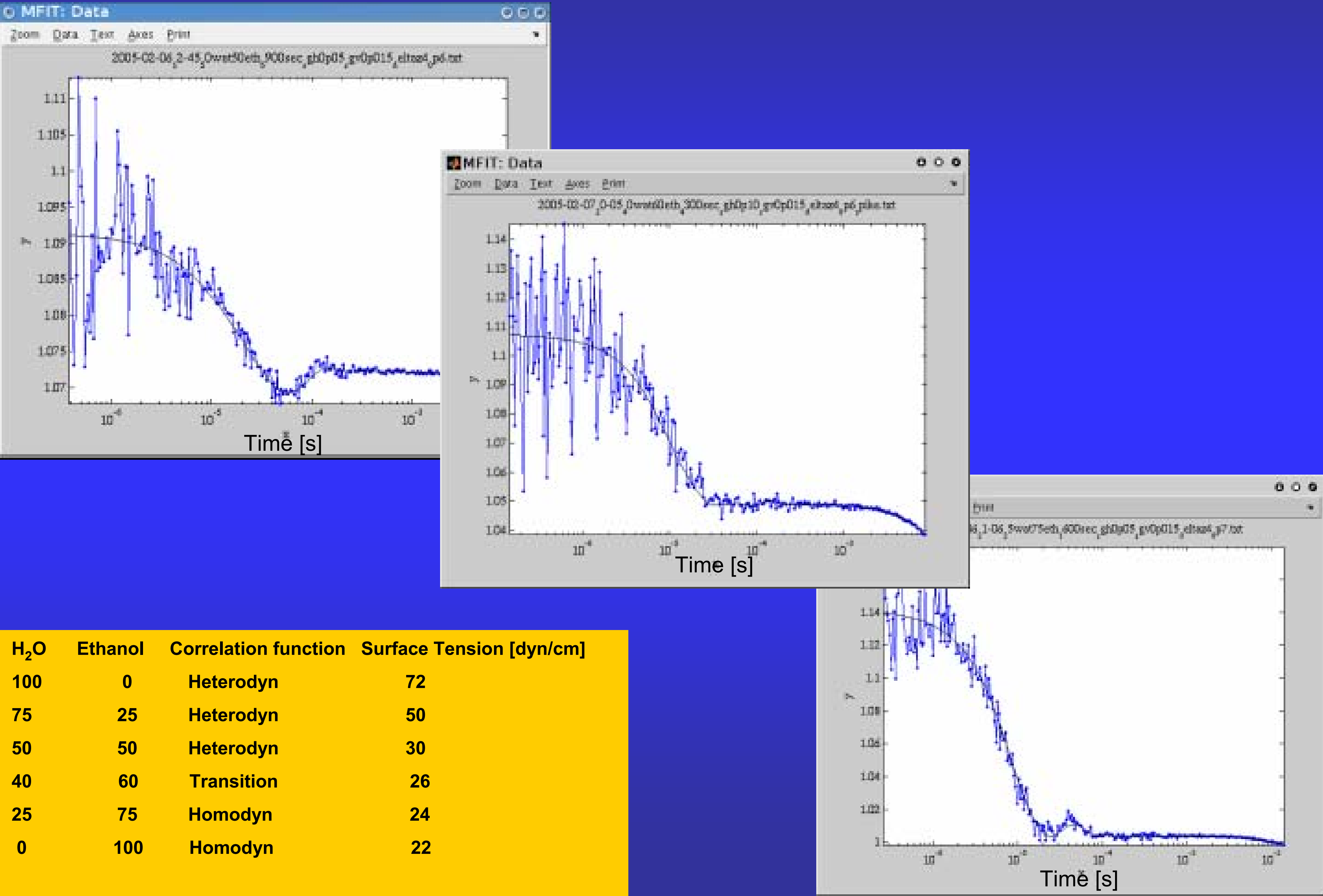
cos^2 behavior

no heterodyne mixing for hexane



$$\Gamma = 2\,\eta/\rho \, q^2$$

Homodyn-Heterodyn Transition in Water-Ethanol Mixtures

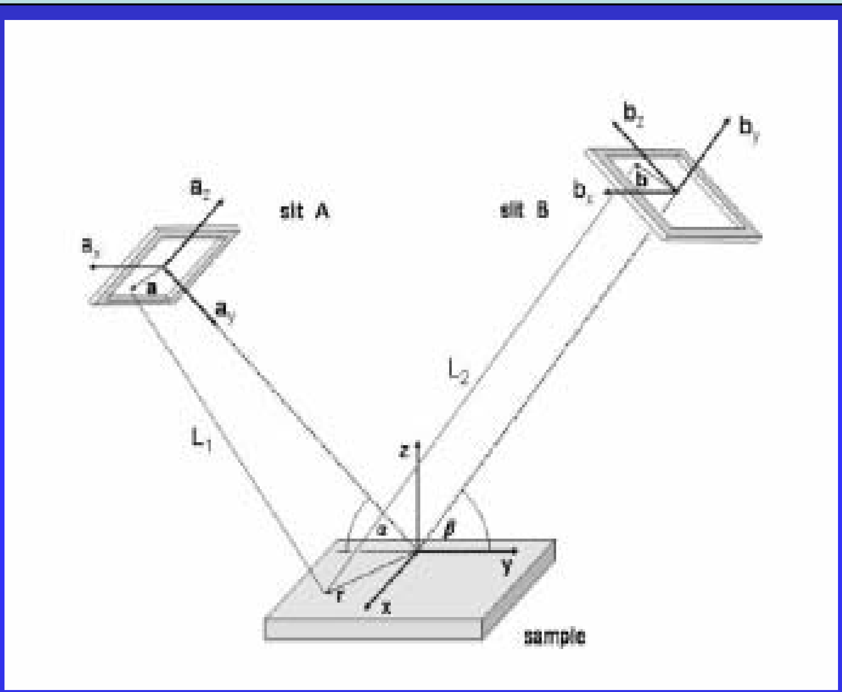


H_2O	Ethanol	Correlation function	Surface Tension [dyn/cm]
100	0	Heterodyn	72
75	25	Heterodyn	50
50	50	Heterodyn	30
40	60	Transition	26
25	75	Homodyn	24
0	100	Homodyn	22

Let´s take a closer look

Rigorous theory

$$G_1(r,\tau) = \left(\frac{k_0 r_1}{2\pi}\right)^2 \iint dr_1^3 dr_2^3 C_{\rho\rho}(\vec{r}_2 - \vec{r}_1,\tau) \iint da_1^2 da_2^2 J(\vec{a}_1,\vec{a}_2)\frac{e^{ik_0\Delta L}}{R_{a1}R_{a2}R_{b1}R_{b2}}$$



- Huygens-Fresnel
- MCF
- Aperture Integration

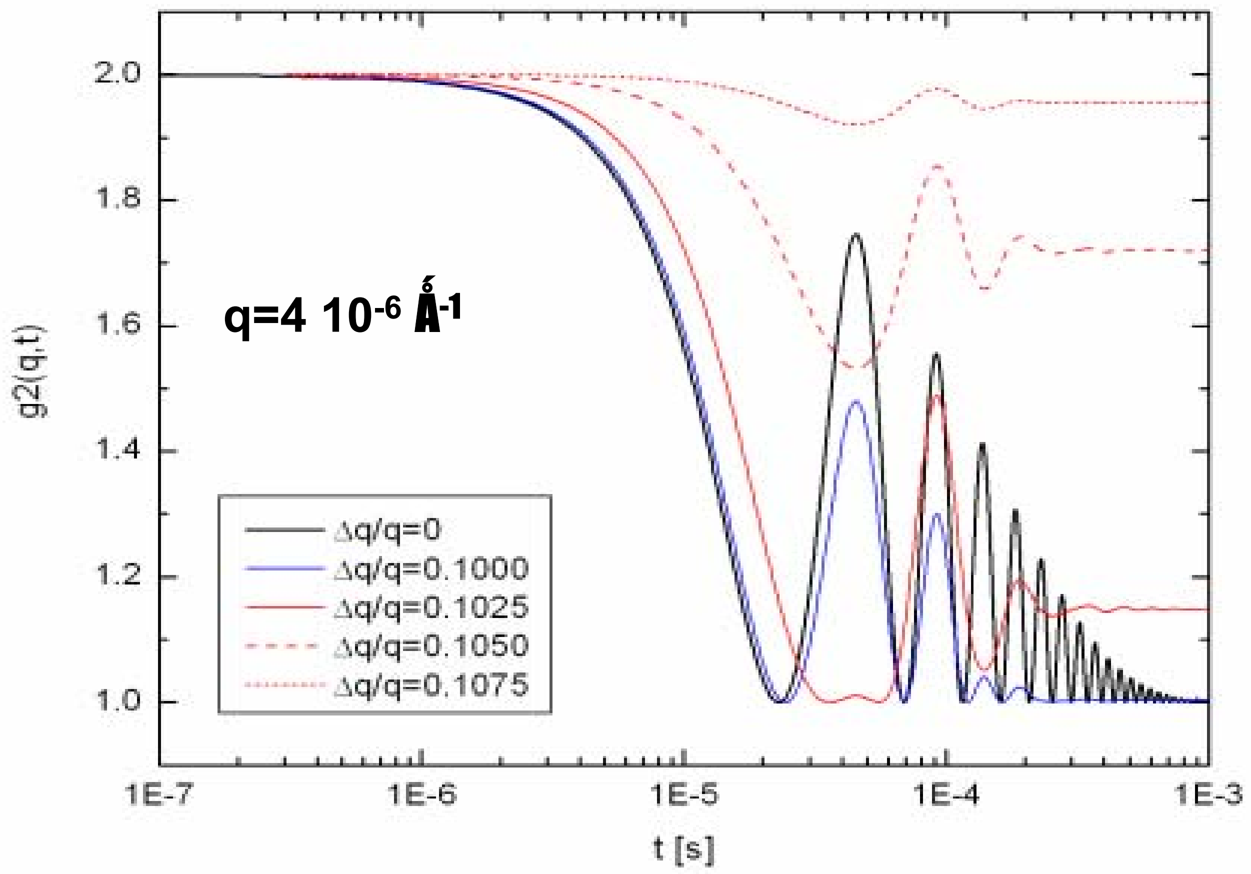
$$G_1(r,\tau) = \left(\frac{k_0 r_1 \rho}{2\pi L_1 L_2 q_z}\right) e^{-q_z^2\sigma^2}\left[F(Q_x,Q_y) + q_z^2 \iint d\tilde{Q}_x d\tilde{Q}_y C_{zz}(\tilde{Q}_x,\tilde{Q}_y,\tau) F(\tilde{Q}_x - Q_x,\tilde{Q}_y - Q_y)\right]$$

$$G_2(r,\tau) = 1 + \left|\frac{G_1(r,\tau)}{G_1(r,0)}\right|^2$$

Folding

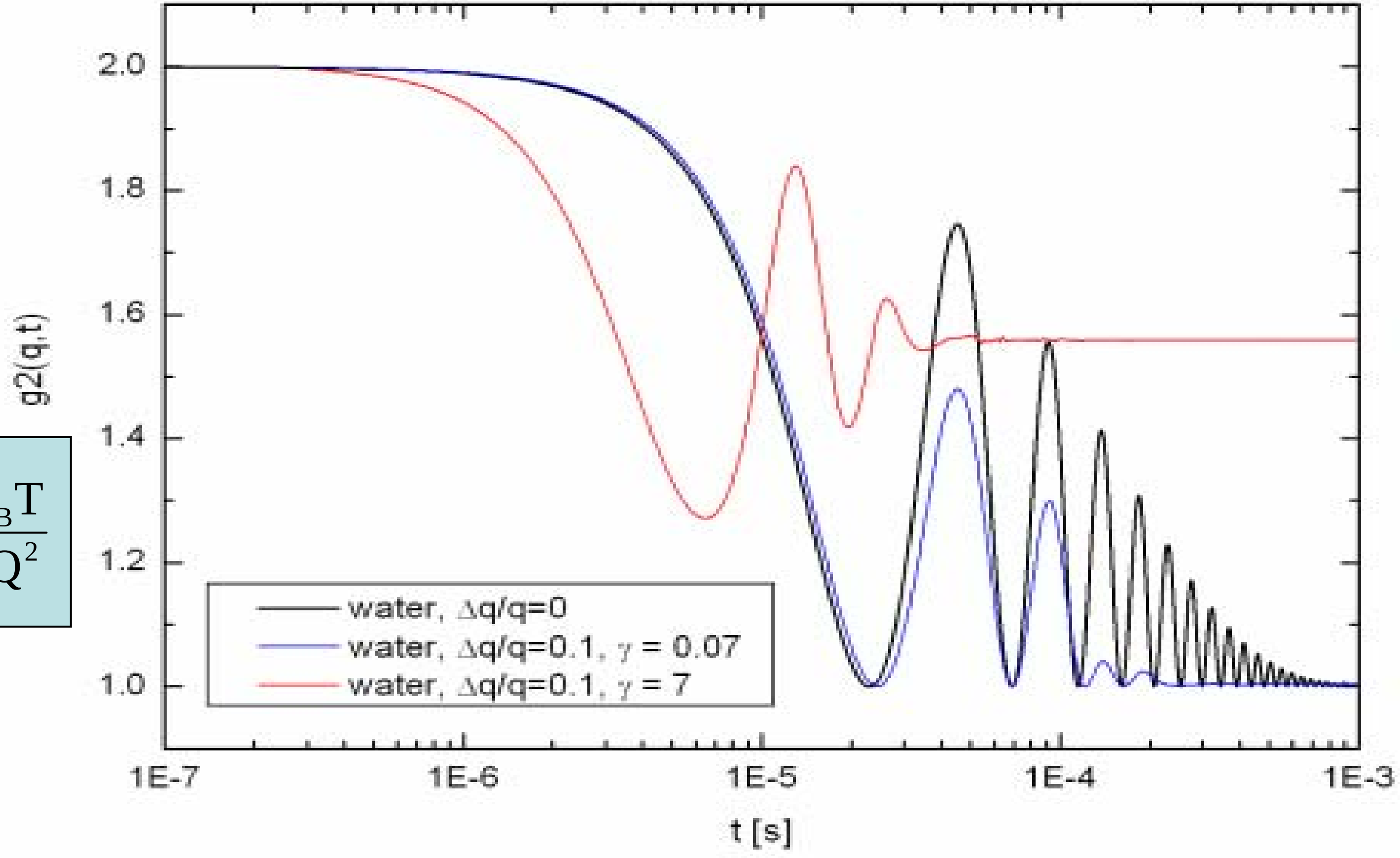
S.K. Sinha, M. Tolan, A. Gibaud PRB 57, 2740 (1998)
Tuana Ghaderi PhD Thesis 2005

Transition Homodyn-Heterodyn (i)



$$G_1(r,\tau)=\left(\frac{k_0 r_l \rho}{2\pi L_1 L_2 q_z}\right)e^{-q_z^2\sigma^2}\left[F(Q_x,Q_y)+q_z^2\iint d\tilde{Q}_x d\tilde{Q}_y C_{zz}(\tilde{Q}_x,\tilde{Q}_y)F(\tilde{Q}_x-Q_x,\tilde{Q}_y-Q_y)\right]$$

Transition Homodyn-Heterodyn (ii)

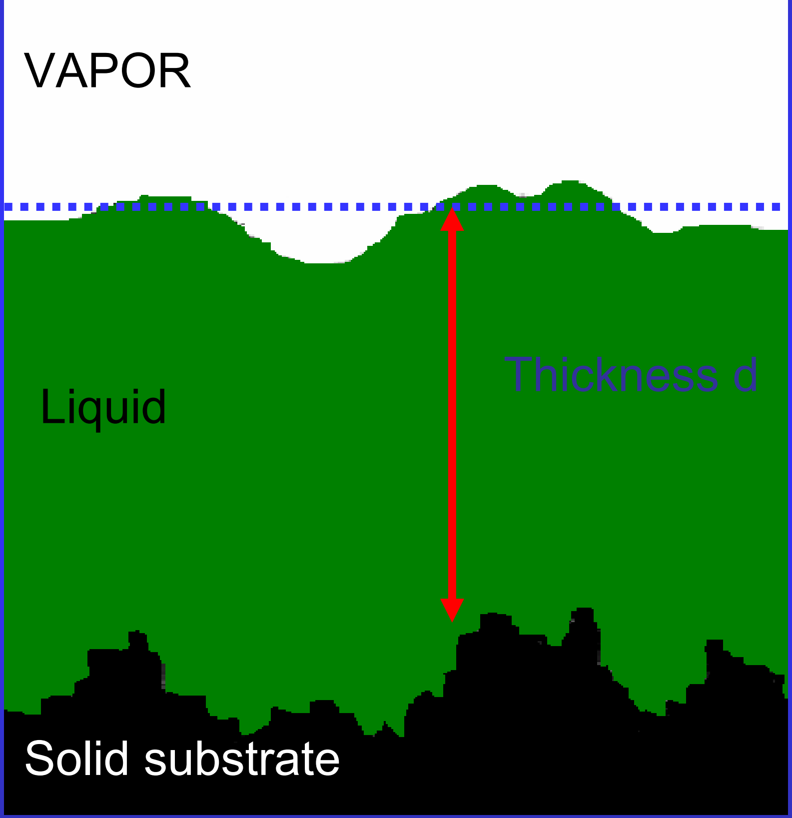


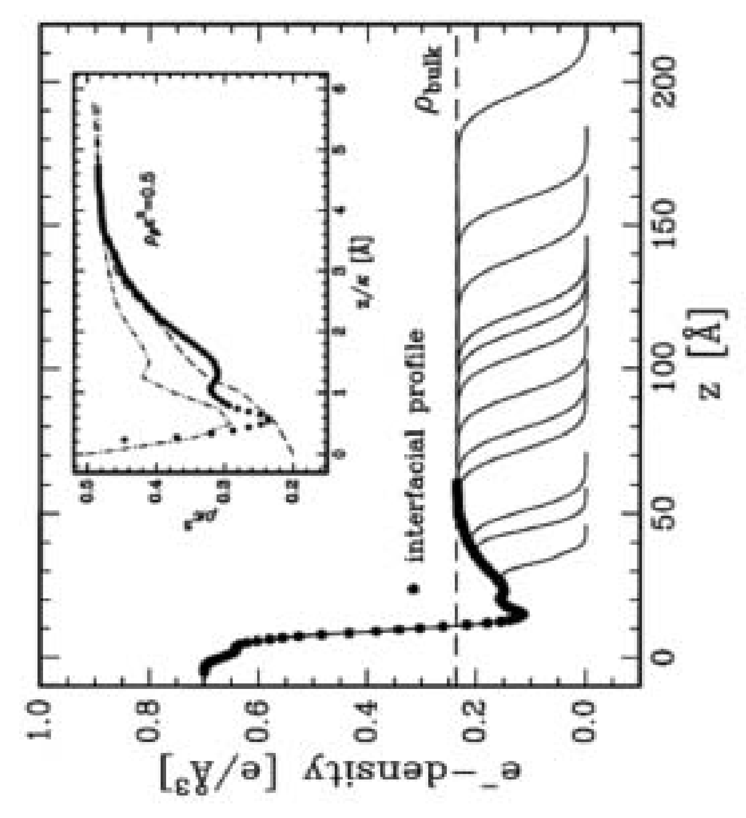
$$C_{zz}(Q,0) = \frac{k_B T}{\gamma Q^2}$$

$$G_1(r,\tau) = \left(\frac{k_0 r_1 \rho}{2\pi L_1 L_2 q_z}\right) e^{-q_z^2\sigma^2}\left[F(Q_x,Q_y) + q_z^2 \iint d\tilde{Q}_x d\tilde{Q}_y C_{zz}(\tilde{Q}_x,\tilde{Q}_y,\tau) F(\tilde{Q}_x - Q_x, \tilde{Q}_y - Q_y)\right]$$

3. Confined liquids

Surface of Liquid Thin Hexane Films



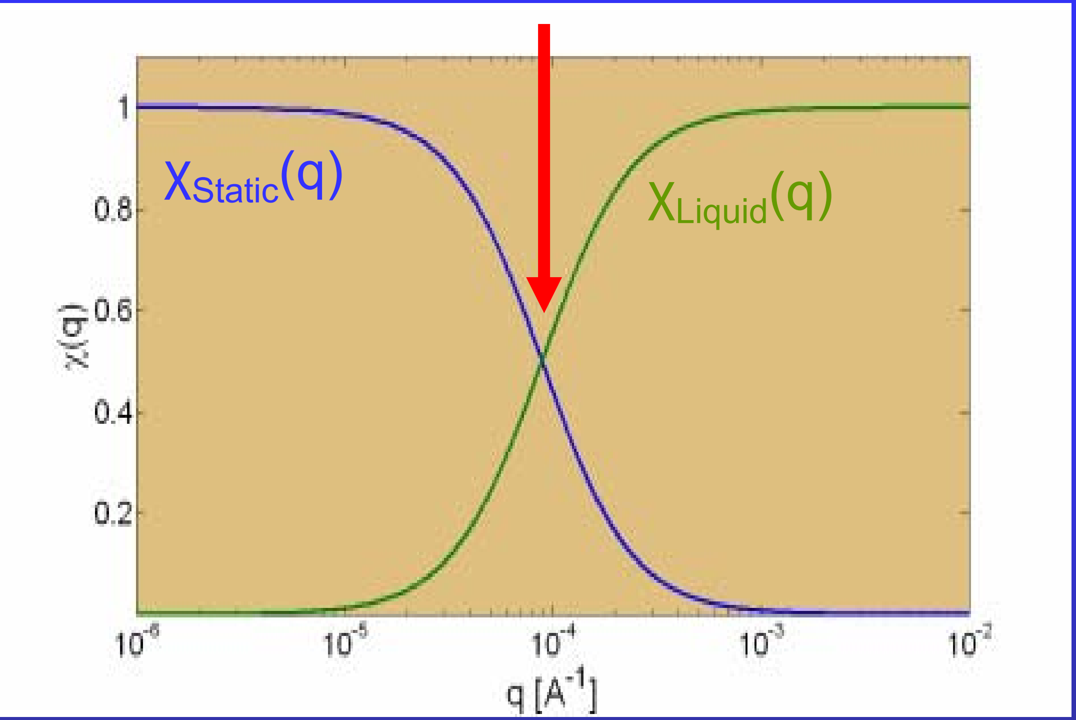


Film Thickness d = 10 Å – 600 Å

Static and Dynamic Scattering Amplitudes

$$S(q,t) \approx \chi_{\mathrm{Static}}(q) S_{\mathrm{SUB}}(q) + \chi_{\mathrm{Liquid}}(q) S_{\mathrm{Liquid}}(q,t)$$

Van der Waals cutoff qvdw d=200 A film



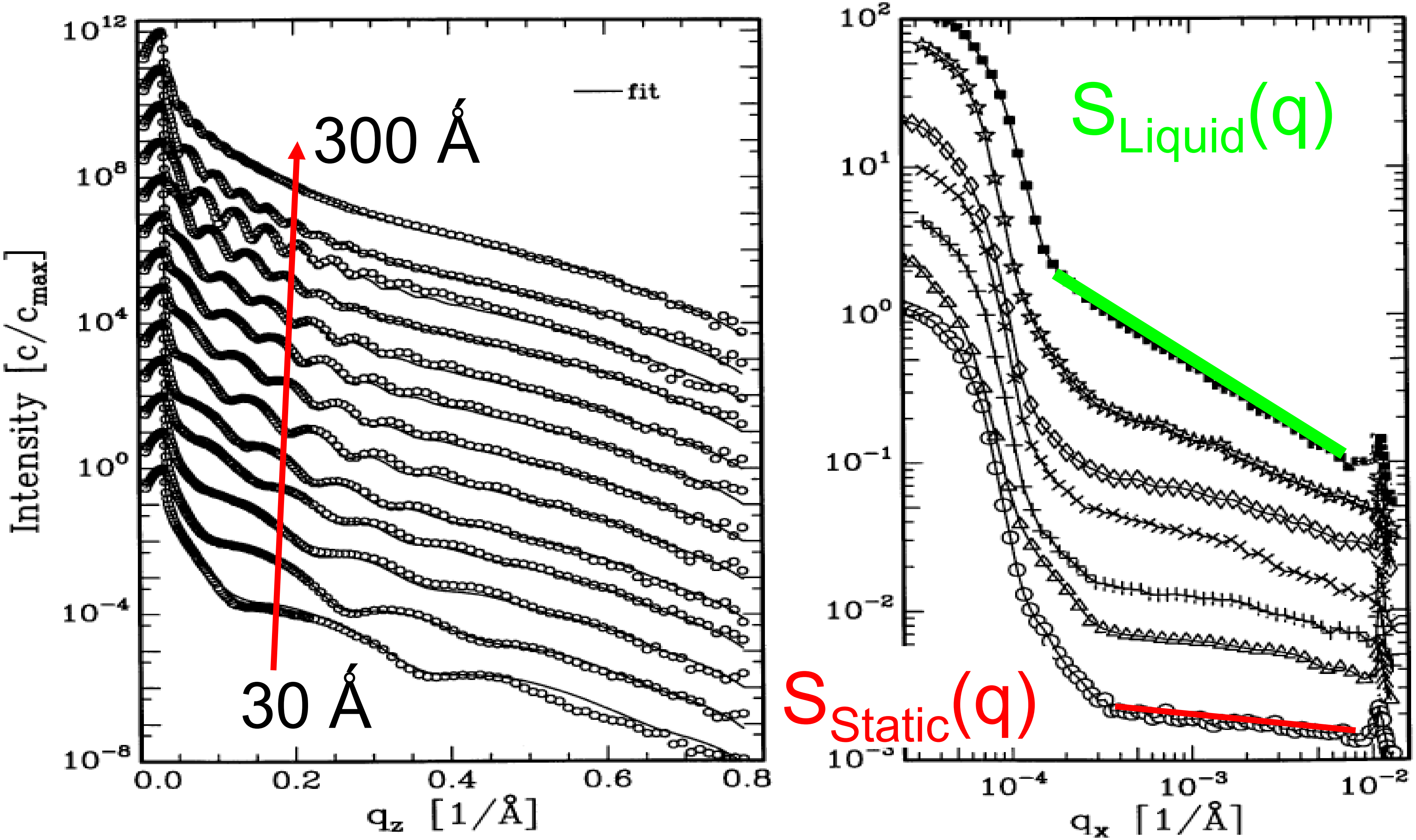
$$\chi_{static}(q) = \left(1 + \left(\frac{qd^2}{a}\right)^2\right)^{-1}$$

$$\chi_{\mathrm{Liquid}}(q) = \left(1 + \left(\frac{a}{qd^2}\right)^2\right)^{-1}$$

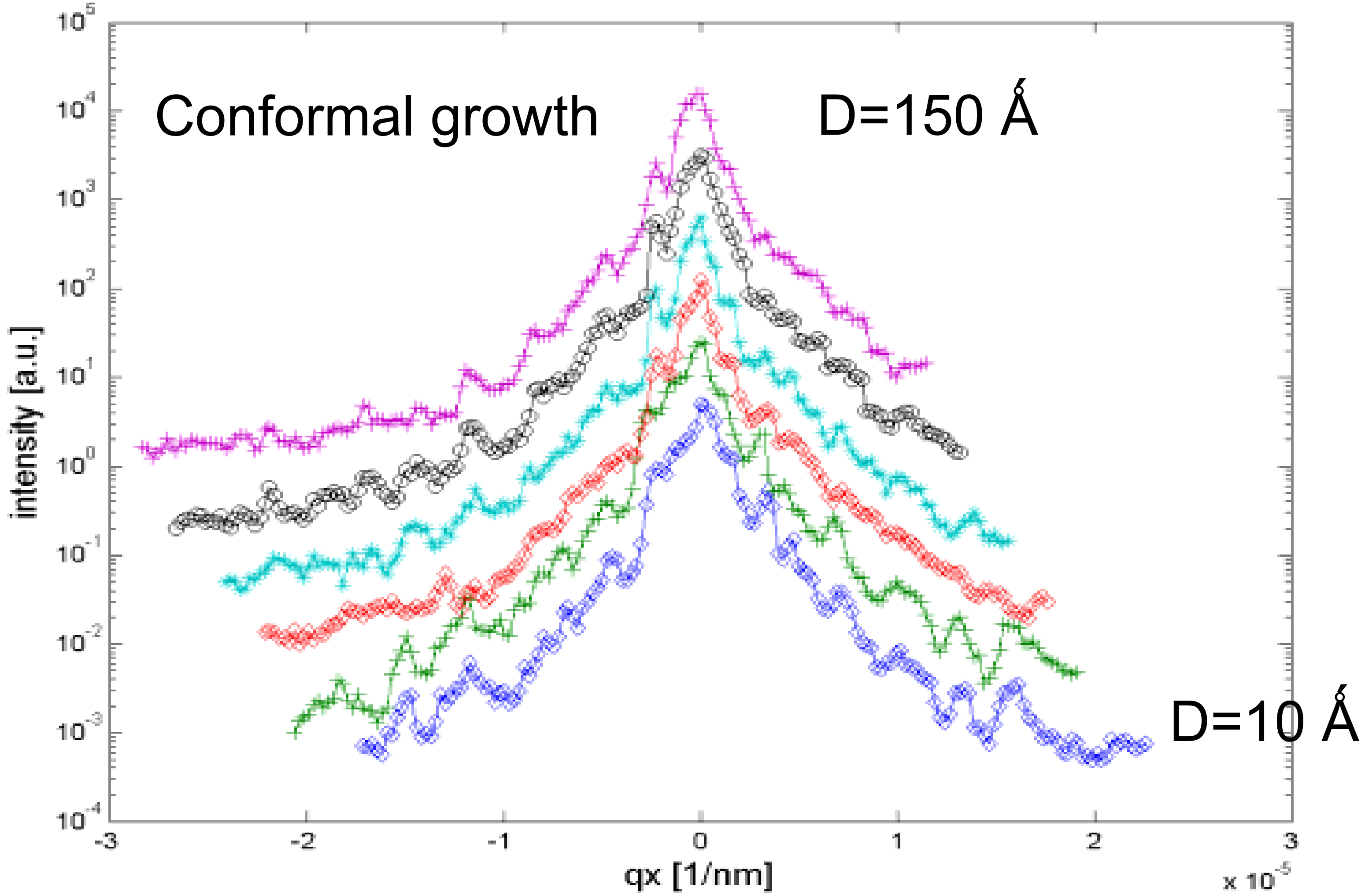
$$a = \sqrt{\frac{A_{eff}}{2\pi\gamma}} \approx 5\,\mathring{A}$$

‚Incoherent‘ Scattering

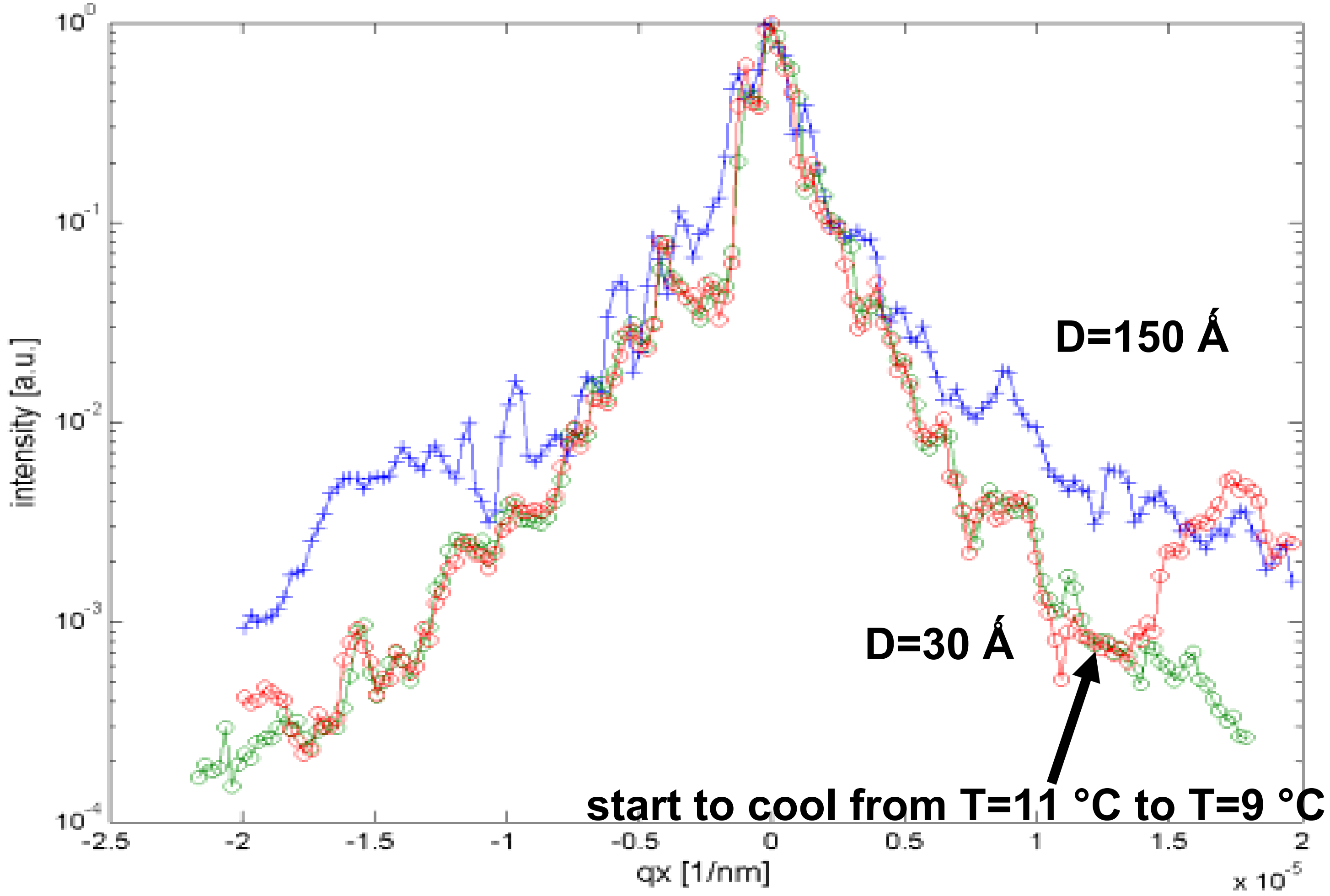
A.K. Doerr et al. / Physica B 248 (1998) 263–268



Static speckle pattern from *slowly* grown liquid thin films



Static speckle pattern from *quickly* grown liquid thin films

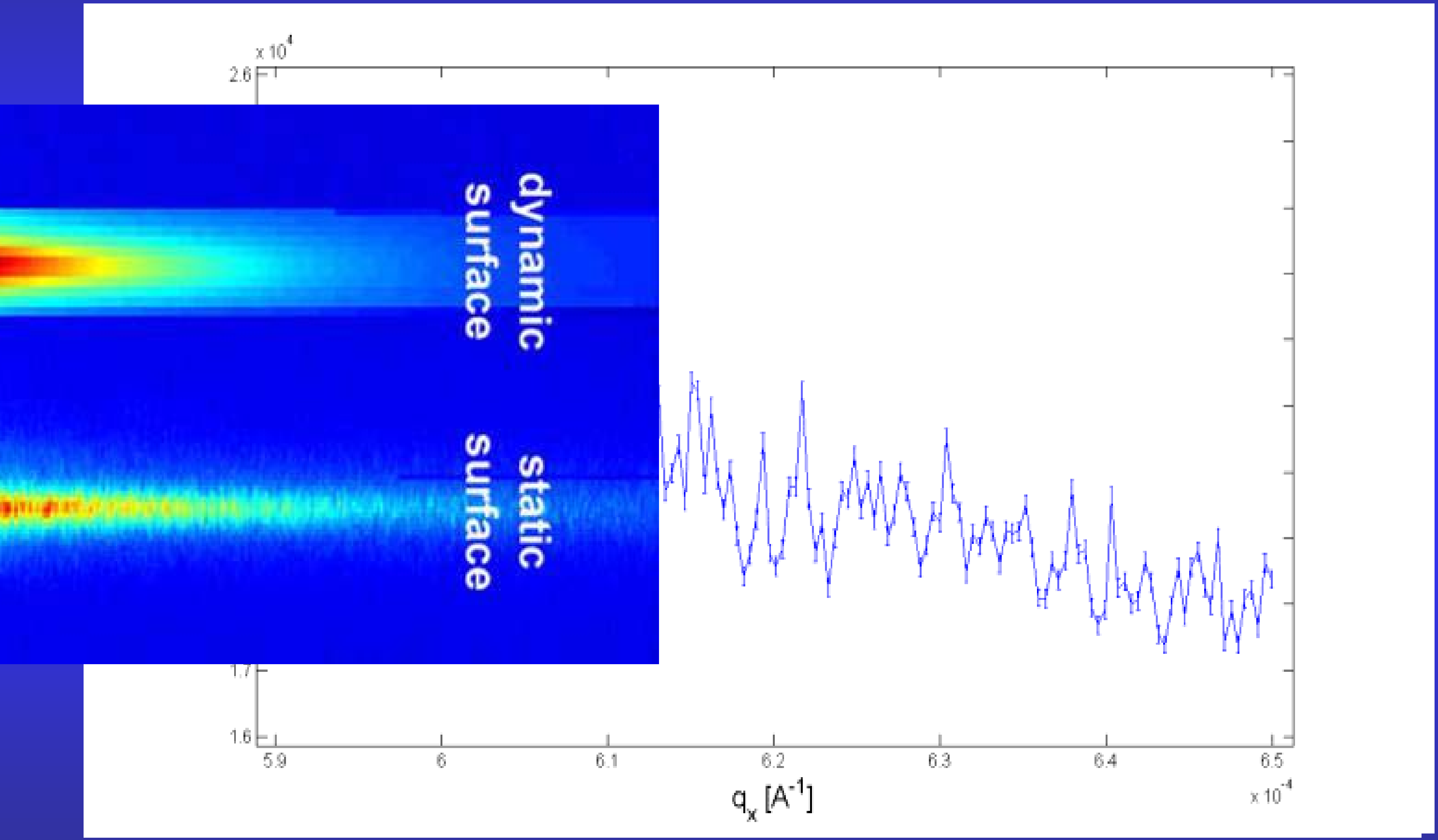


D=150 Å

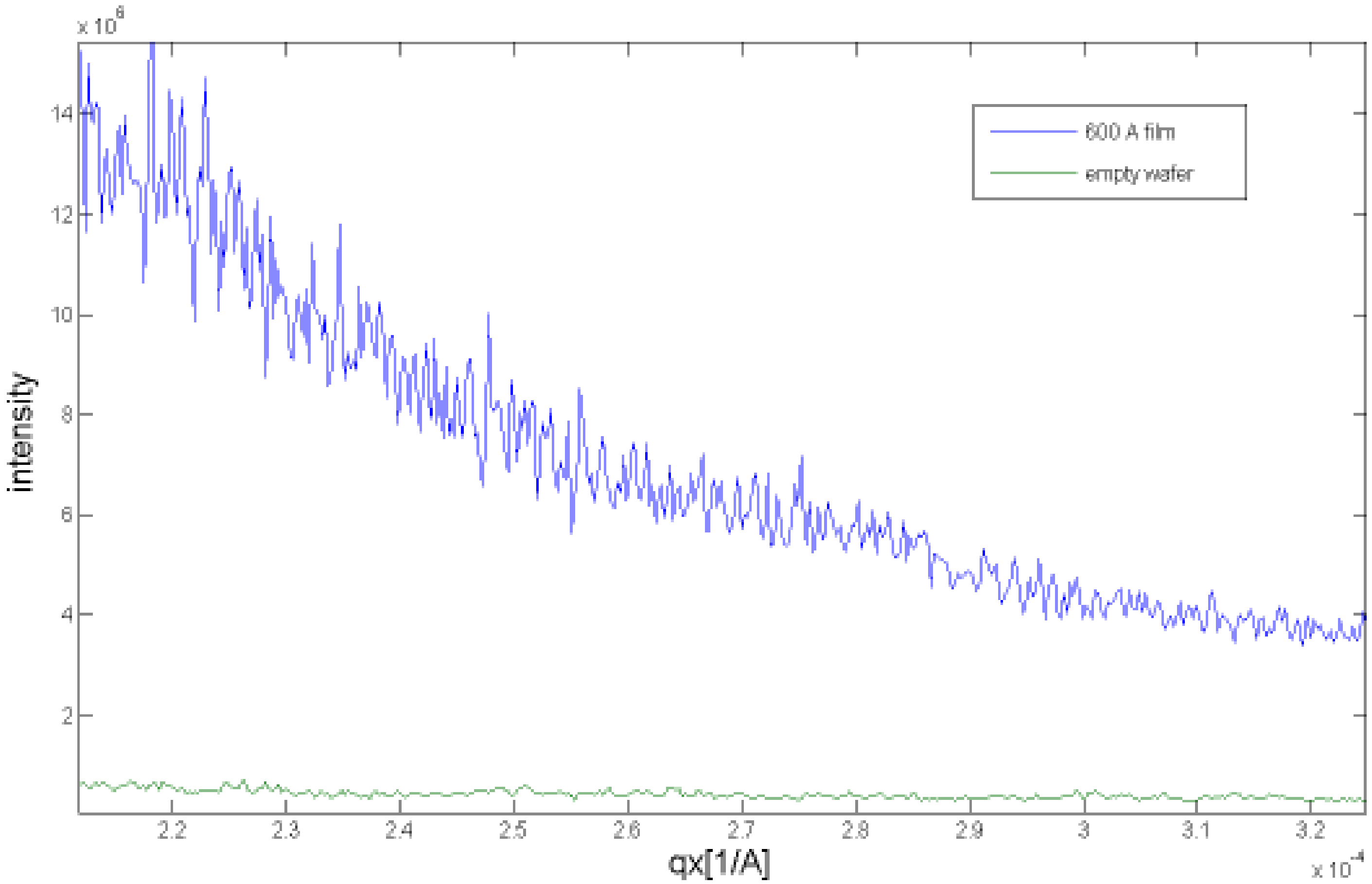
D=30 Å

start to cool from T=11 °C to T=9 °C

CCD Image - 300 Å thick film



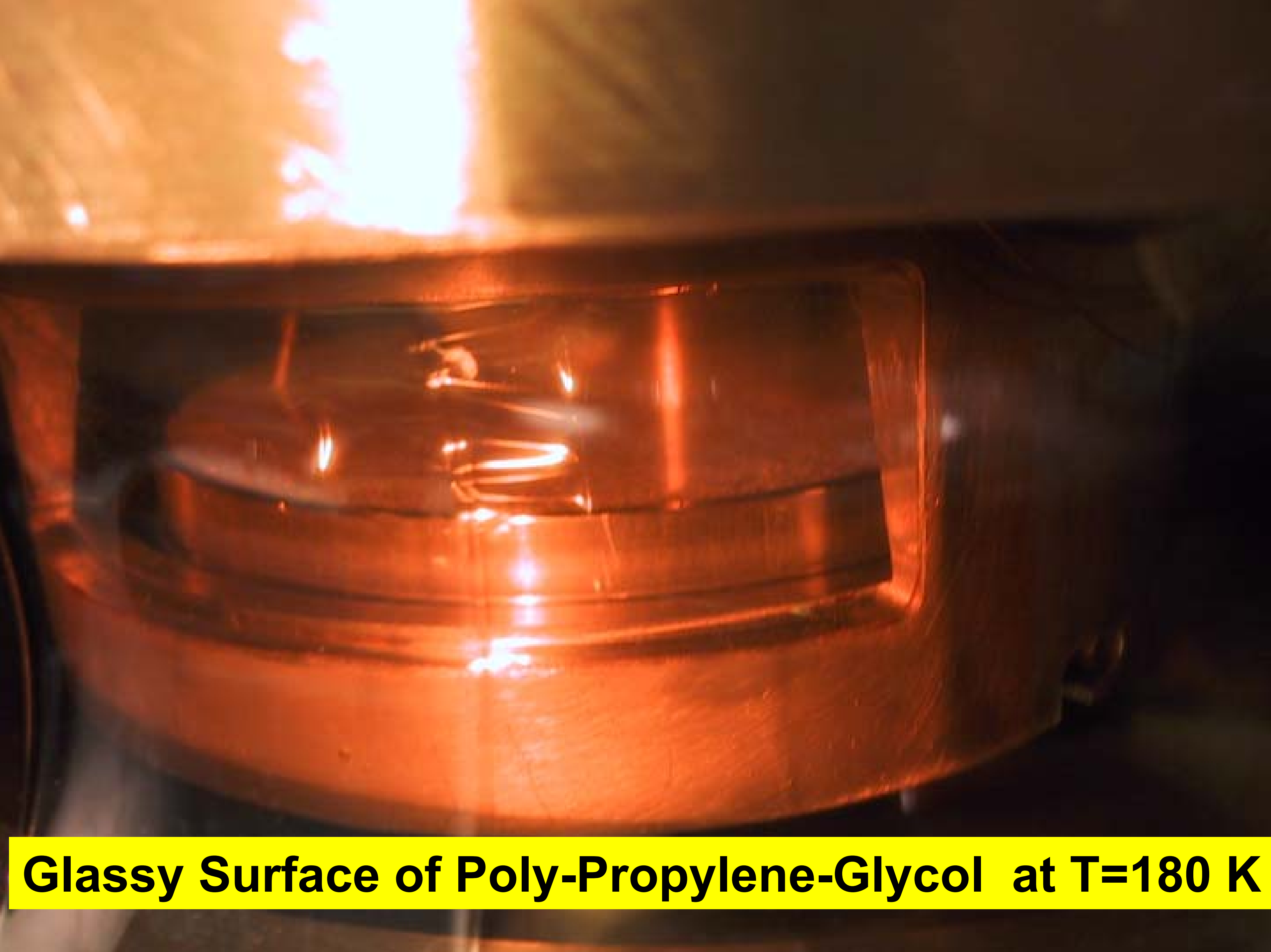
Comparison scattering intensity empty wafer – 600 Å hexane film



Thin Vapor Deposited Hexane Films

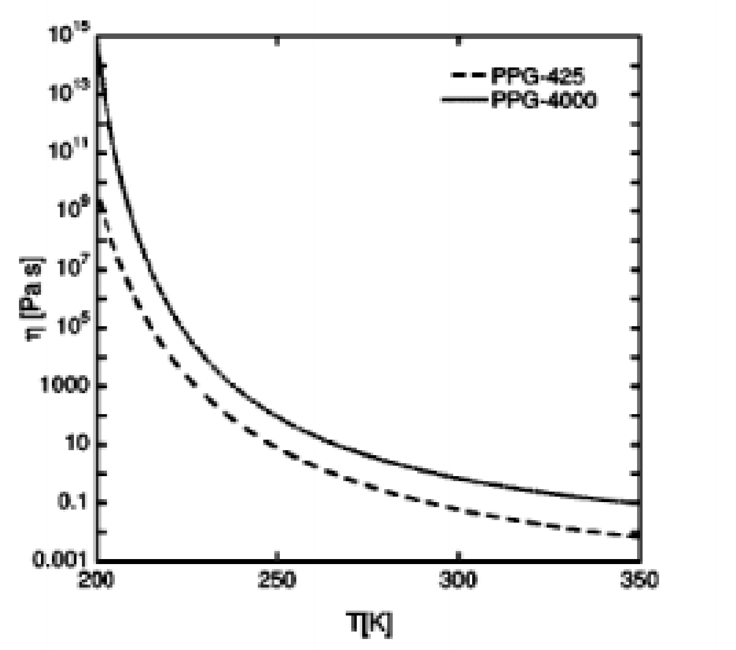
- surface dynamics basically arrested
- no capillary waves
- conformal roughness for low deposition rates
- surface roughness due to static disorder

4. Glass Transition



Glassy Surface of Poly-Propylene-Glycol at T=180 K

Surface fluctuations close to the glass transition



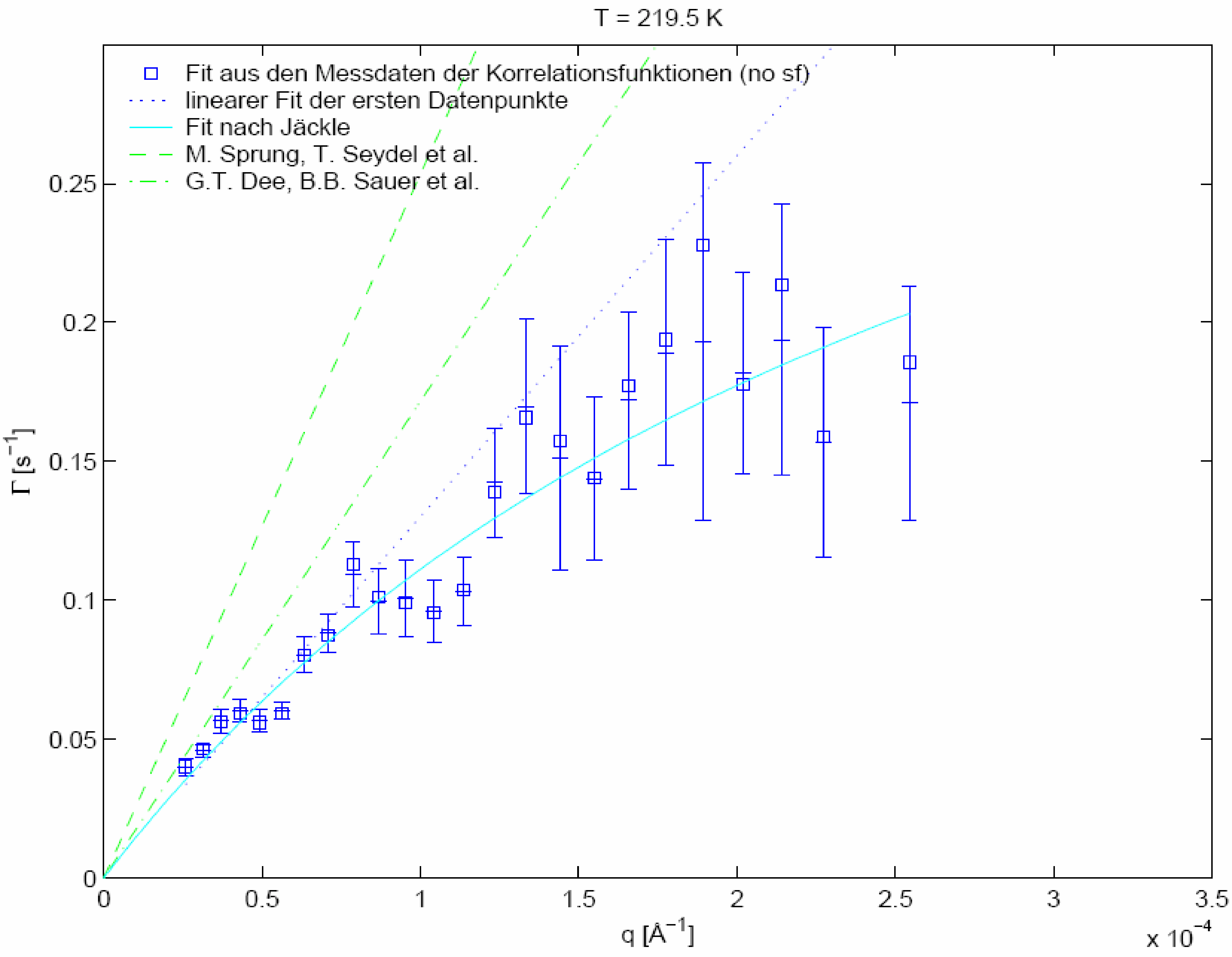
Frequency dependent viscosity

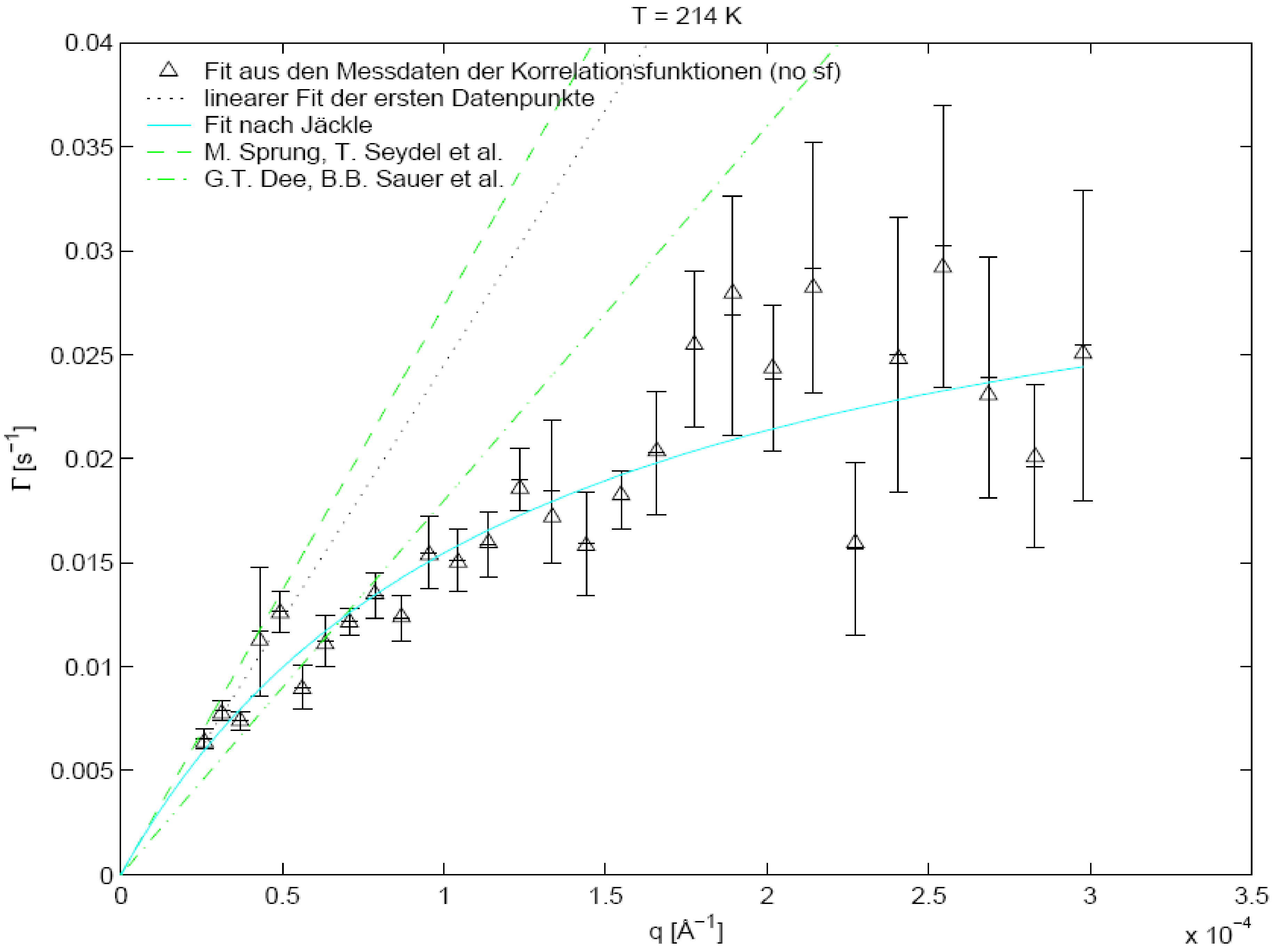
$$\eta(\omega)=\frac{\eta_0}{1-i\omega\tau}$$

Relaxation time $\tau=\frac{\eta_0\rho}{G}$

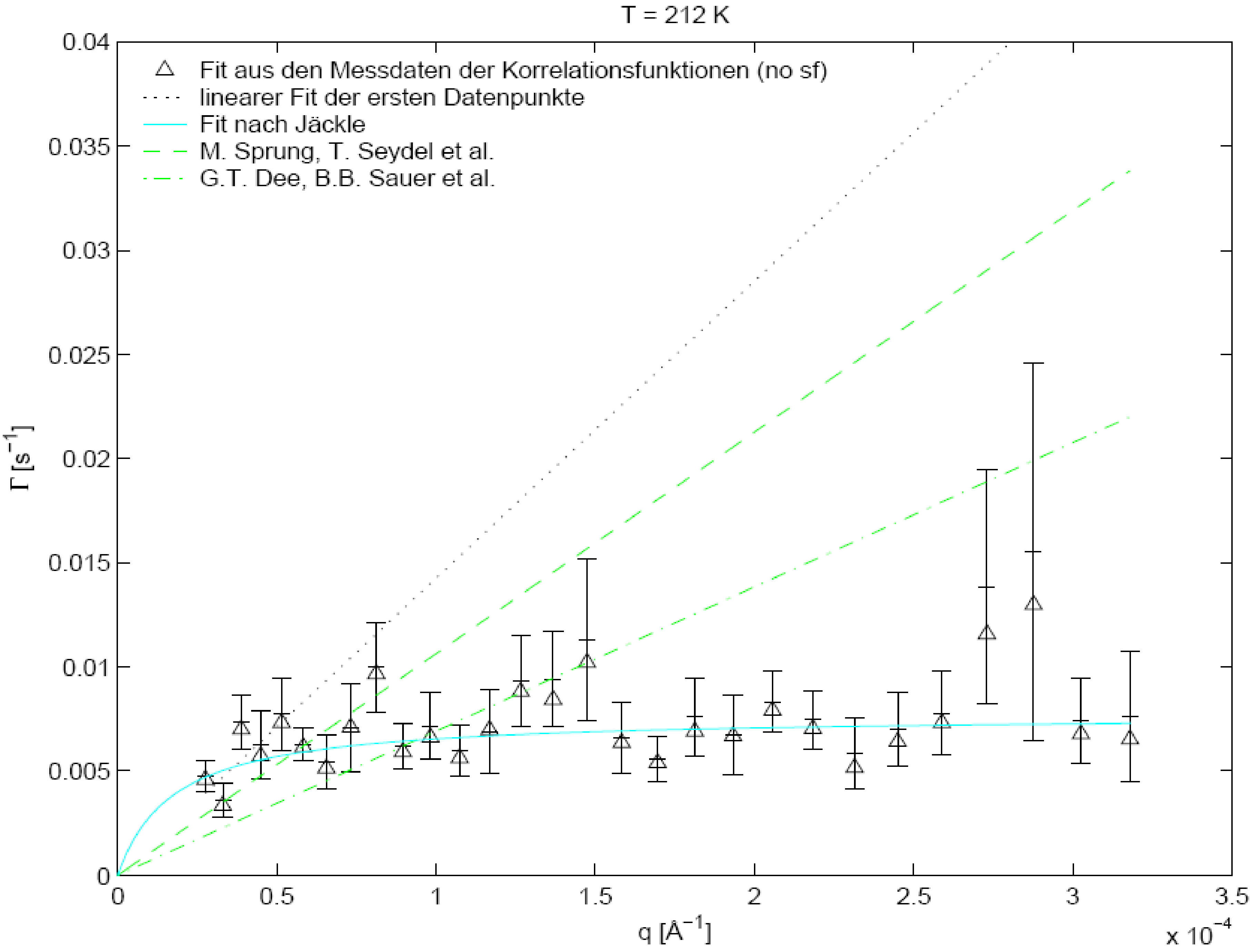
$$\boxed{\Gamma=\frac{\gamma q}{2\eta}}\xrightarrow{\text{close to Tg}}\boxed{\Gamma=\frac{\gamma q}{2\eta_0}\left(\frac{1}{1+\frac{q\gamma}{2G}}\right)}$$

Jaeckle and Kawasaki, J. Phys. : Cond. Matter 7 (1995) 4351

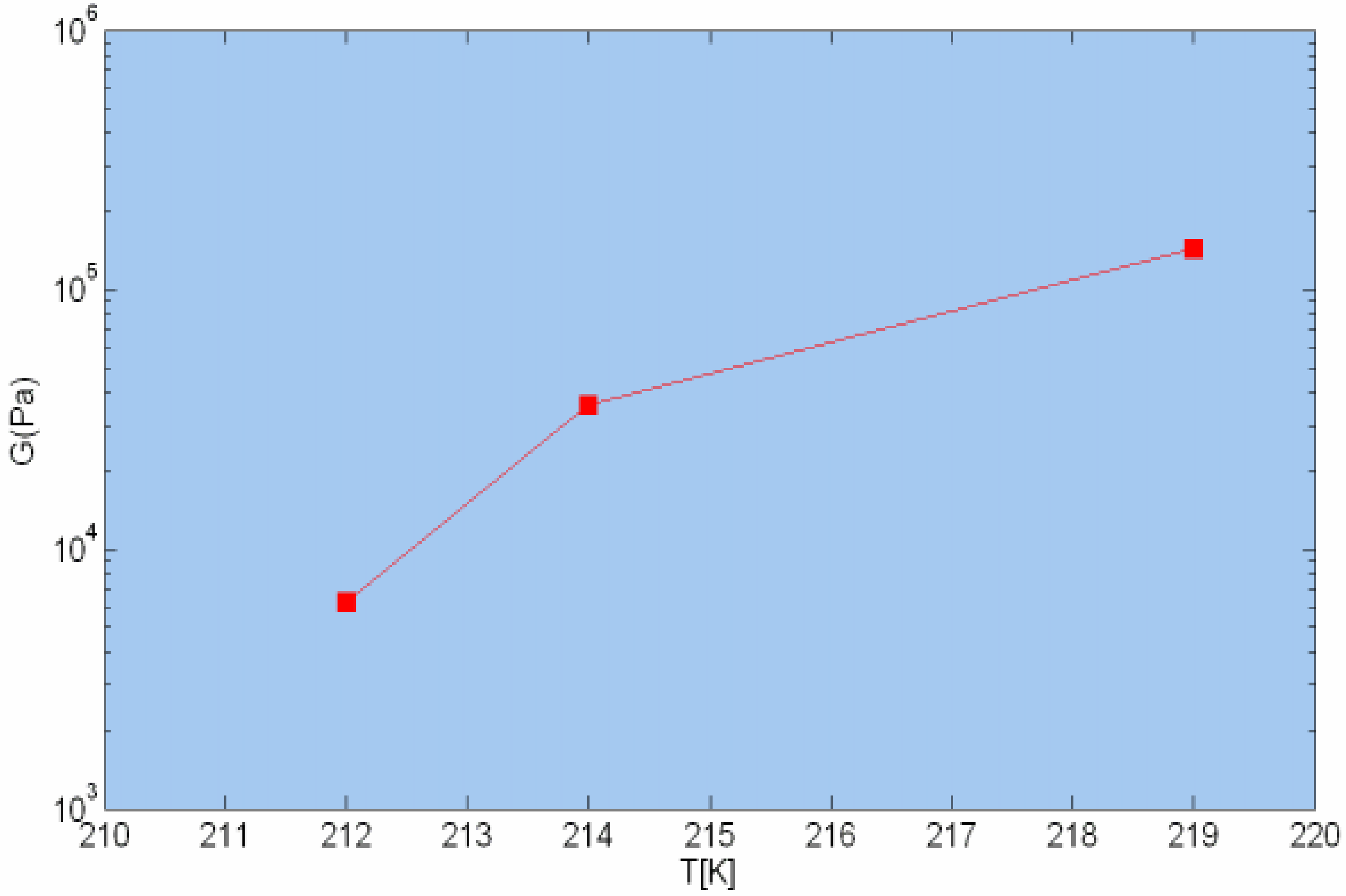

T = 219.5 K
Fit aus den Messdaten der Korrelationsfunktionen (no sf)
linearer Fit der ersten Datenpunkte
Fit nach Jäckle
M. Sprung, T. Seydel et al.
G.T. Dee, B.B. Sauer et al.
Γ [s^-1]
0
0.05
0.1
0.15
0.2
0.25
q [Å^-1]
0
0.5
1
1.5
2
2.5
3
3.5
x 10^-4



T = 214 K
Fit aus den Messdaten der Korrelationsfunktionen (no sf)
linearer Fit der ersten Datenpunkte
Fit nach Jäckle
M. Sprung, T. Seydel et al.
G.T. Dee, B.B. Sauer et al.
Γ [s^-1]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
q [Å^-1]
0
0.5
1
1.5
2
2.5
3
3.5
x 10^-4


T = 212 K
Fit aus den Messdaten der Korrelationsfunktionen (no sf)
linearer Fit der ersten Datenpunkte
Fit nach Jäckle
M. Sprung, T. Seydel et al.
G.T. Dee, B.B. Sauer et al.
Γ [s^{-1}]
q [Å^{-1}]
x 10^{-4}
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
0
0.5
1
1.5
2
2.5
3
3.5

Shear Modulus G(¶) at the Surface



Summary & Conclusions

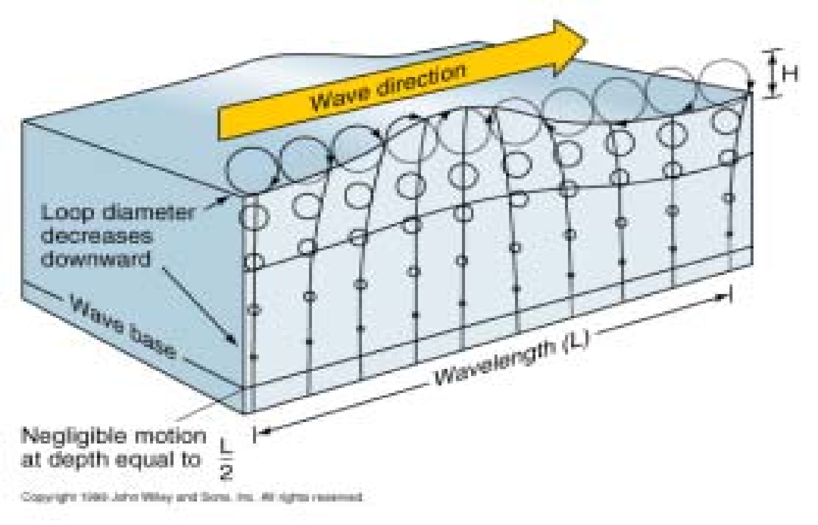
- Dynamics of Bulk liquids
- Morphology of Confined Liquids
- Surface Glass Transition

Outlook

- Dynamics of buried interfaces (e.g. Polymer-Polymer)
- Magnetic interfaces
- Bio-Systems

Development of fast 2d detectors !!

Surfaces - Static and Dynamics



Static z(x,y)
determined by free enegry F

$$\Delta \mathrm{F} \approx \frac{1}{2}\int dA\Big(\gamma(|\nabla \mathrm{z}(r)|^2 + \rho g z(r)^2 \Big)$$

Dynamic z(x,y,t) – determined by hydrodynamics

$$(1)\ \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathrm{v}) \qquad (2)\ \frac{\partial h}{\partial t} = \kappa \nabla^2 \mathrm{T}$$

$$(3)\ \rho[\frac{\partial \mathrm{v}}{\partial t} + (\mathrm{v} \cdot \nabla)\mathrm{v}] - \nabla p - \eta \nabla^2 \mathrm{v} - (\zeta + \tfrac{1}{3}\eta)\nabla(\nabla \cdot \mathrm{v}) = 0$$

$$(4)\ \sigma^{zz} = \gamma \frac{\partial^2 \mathrm{z}(r)}{\partial x^2},\ \sigma^{zx} = \sigma^{yz} = 0$$

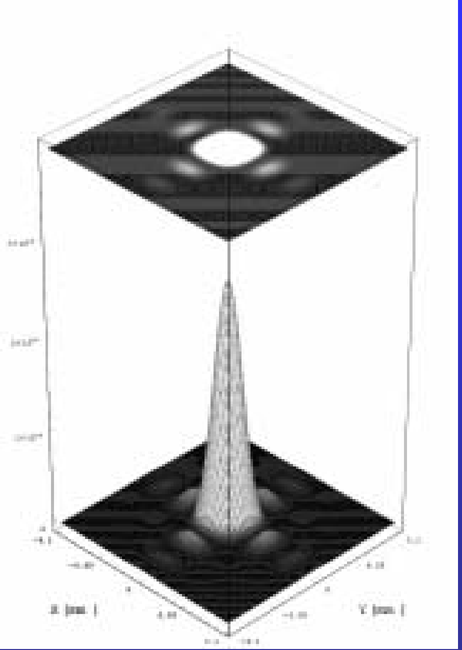
X-Ray Diffraction - Revisited

Fraunhofer vs. Fresnel

Fraunhofer-Condition $\frac{\sigma^2}{L\lambda} << 1$

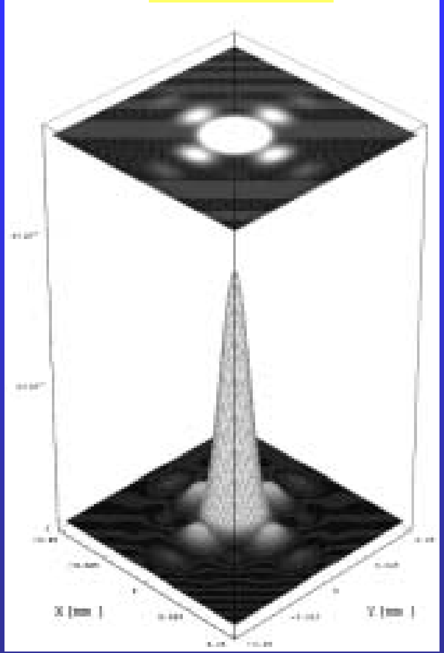
5 μm

$\frac{\sigma^2}{L\lambda} \approx 0.16$



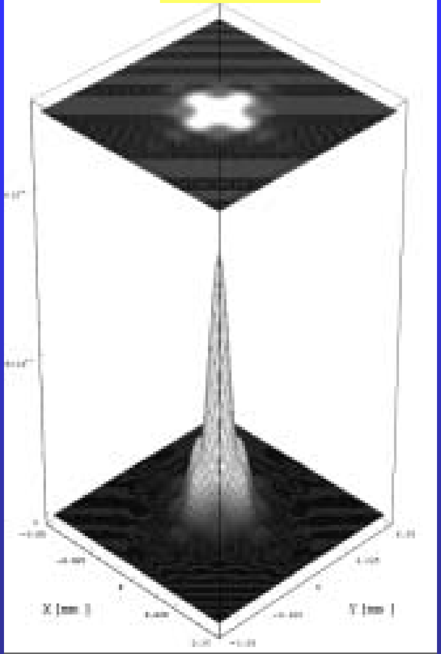
10 μm

$\frac{\sigma^2}{L\lambda} \approx 0.66$



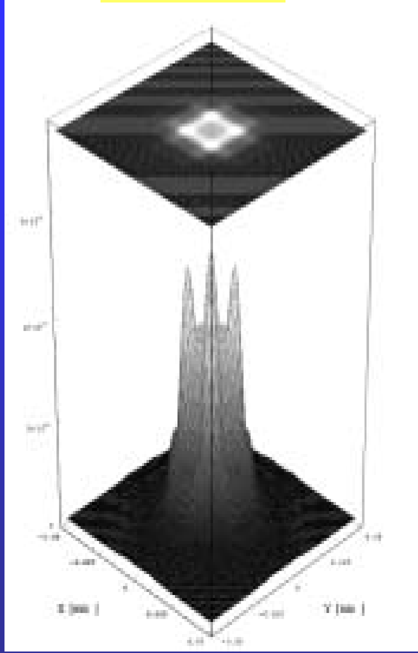
15 μm

$\frac{\sigma^2}{L\lambda} \approx 1.5$



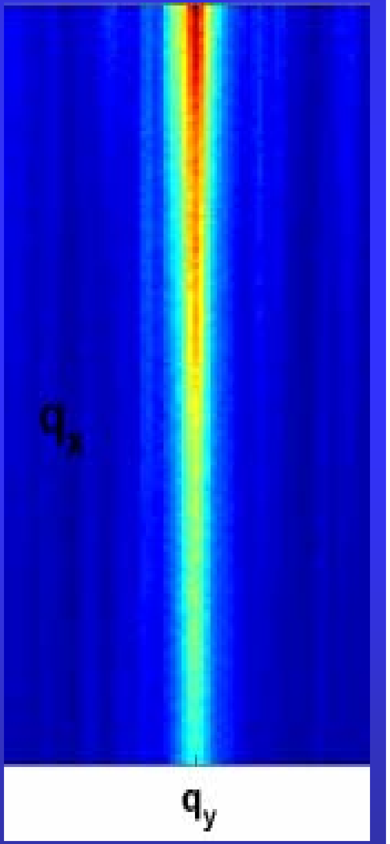
20 μm

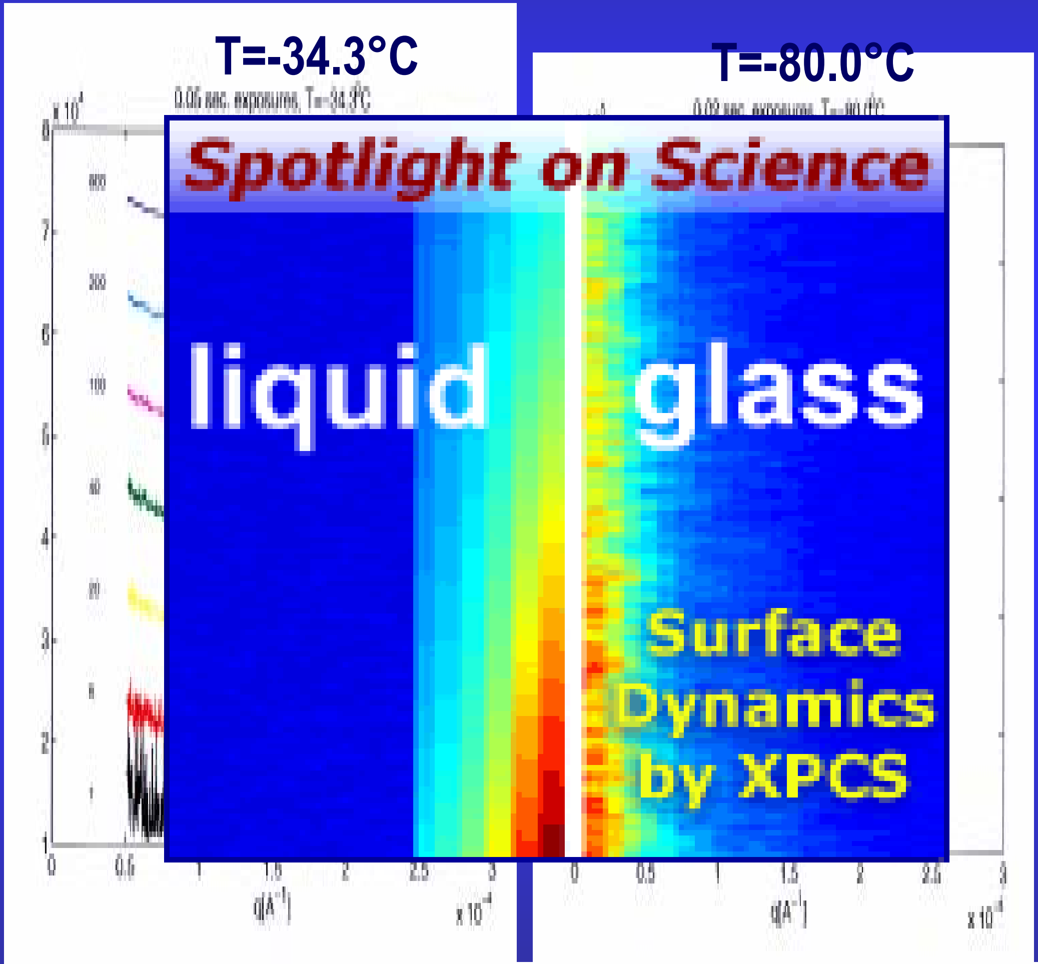
$\frac{\sigma^2}{L\lambda} \approx 2.66$

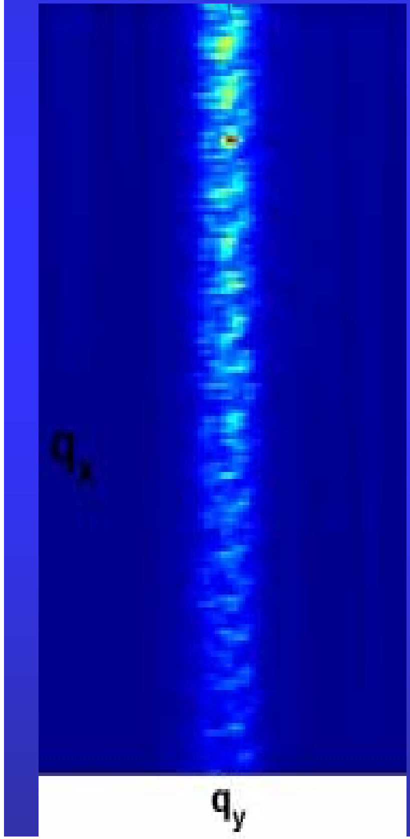


Coherent scattering from dynamic samples

Liquid surface of glycerol



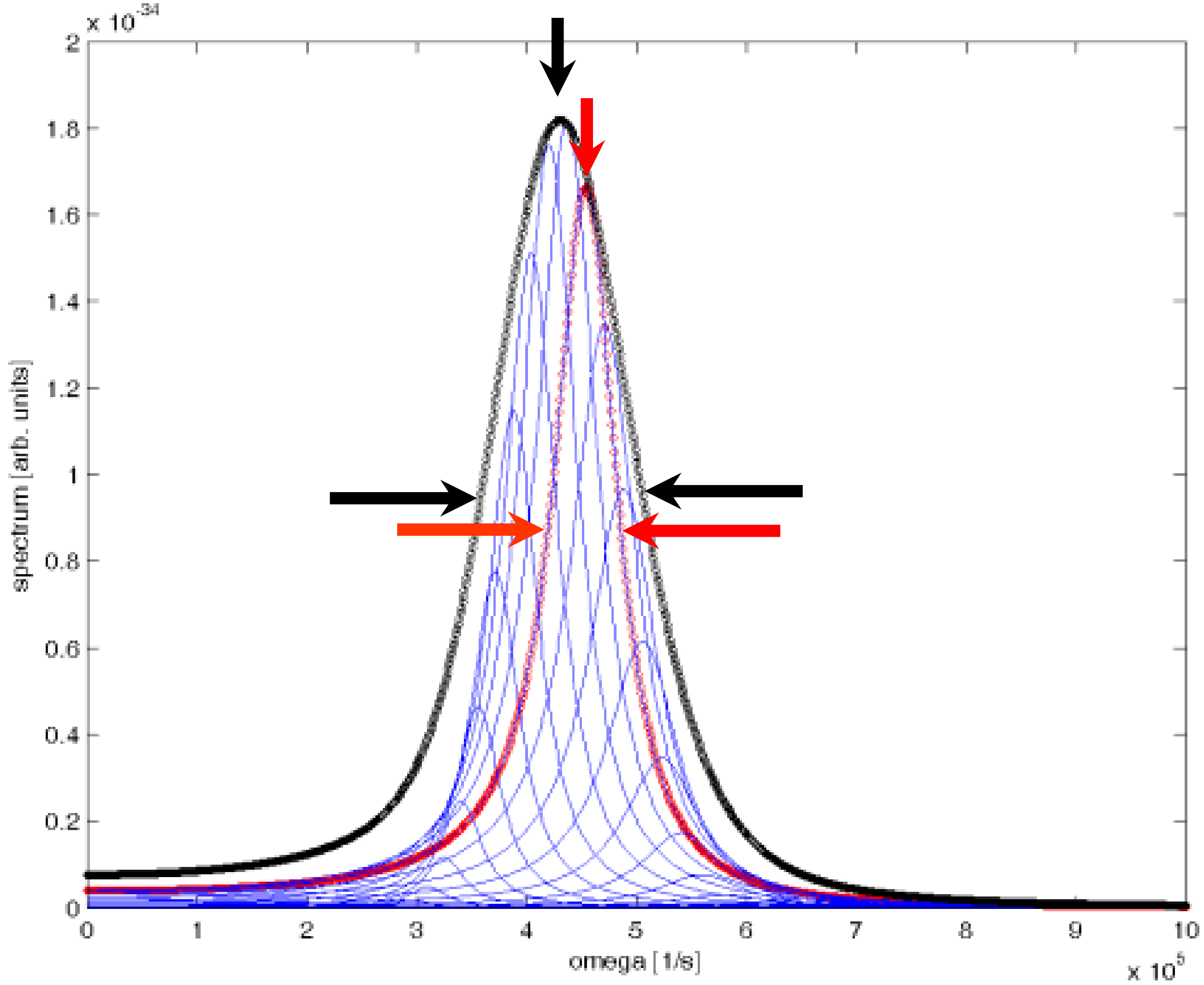




Resolution effects for propagating capillary waves

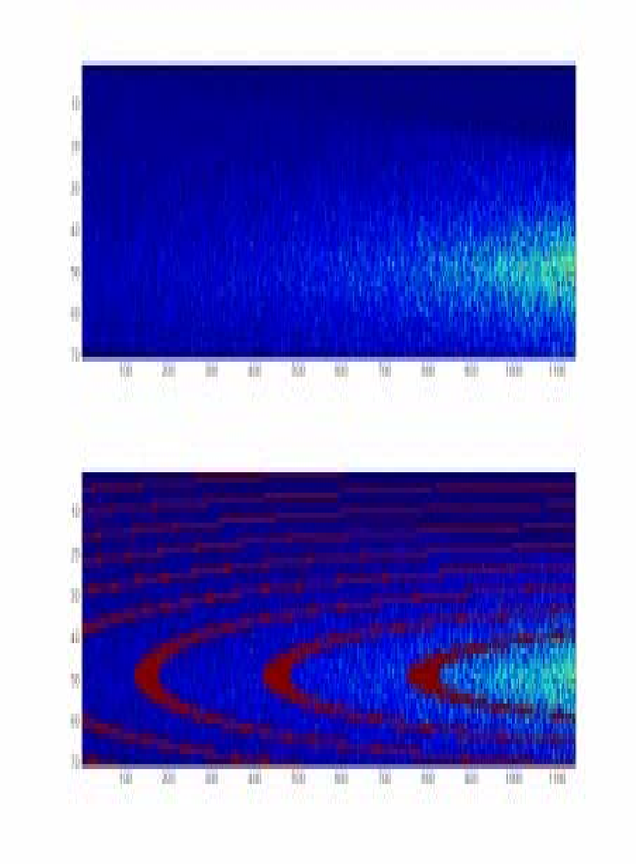
a) a small shift of the propagating frequency to lower values

b) a large increase of the damping constant



Calculation of correlation functions

YORICK (APS, MIT)
MatLab (SanDiego, APS, Dortmund)



$$g(q,\tau) = \frac{< I(q,t) I(q,t+\tau) >_t}{< I(q,t) I(q,t) >_t}$$

homodyne detection –
no reference beam

$$g(q,\tau) = 1 + \alpha \left| \frac{S(q,\tau)}{S(q,o)} \right|^2$$

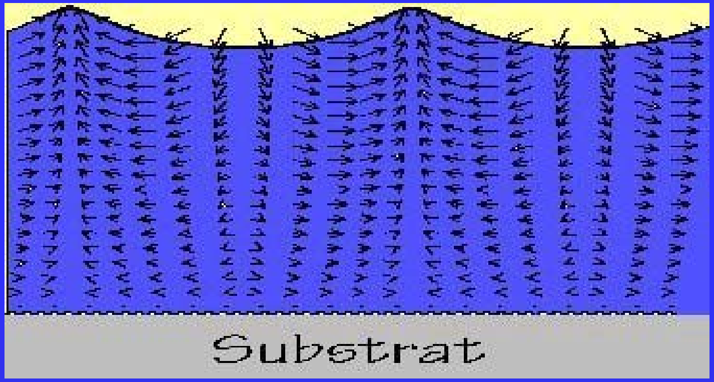
heterodyne detection
mixing with reference beam

$$g(q,\tau) = 1 + \alpha \left| \frac{S(q,\tau)}{S(q,o)} \right|^2 + \beta \frac{S(q,\tau)}{S(q,o)}$$

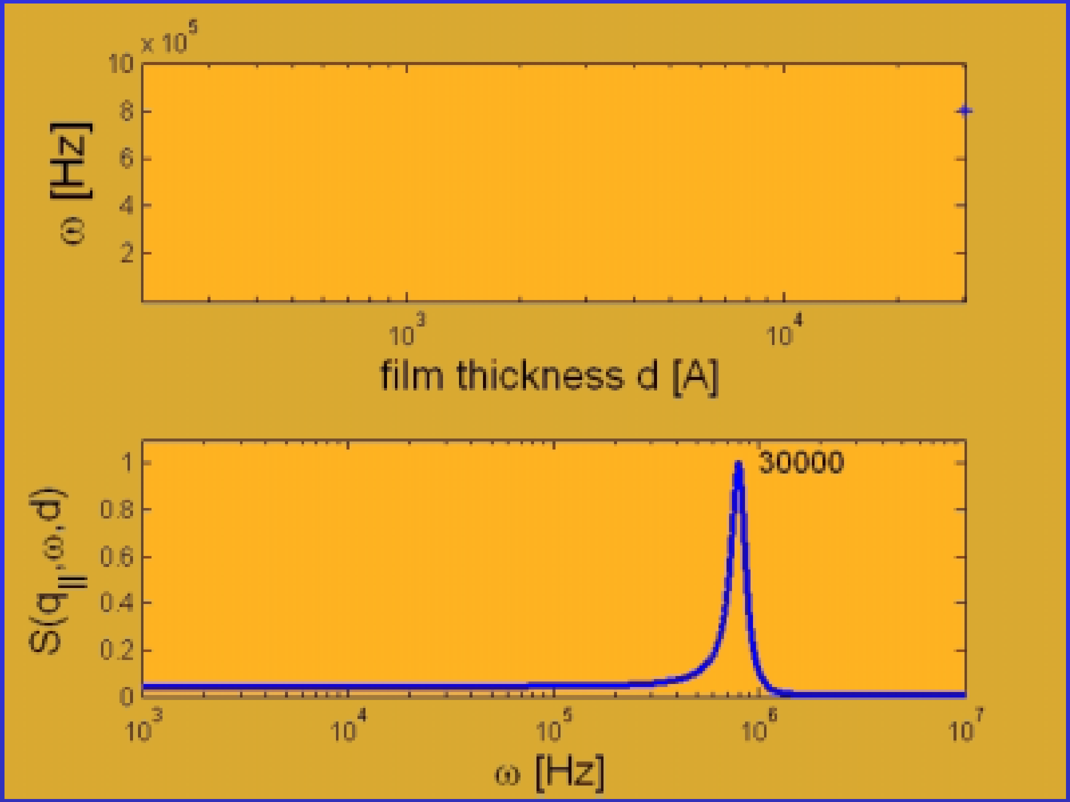
Sample correlation function

$$S(q,\tau) = \rho(-k,0)\,\rho(k,\tau)$$

Surface Spectra of Thin Liquid Films

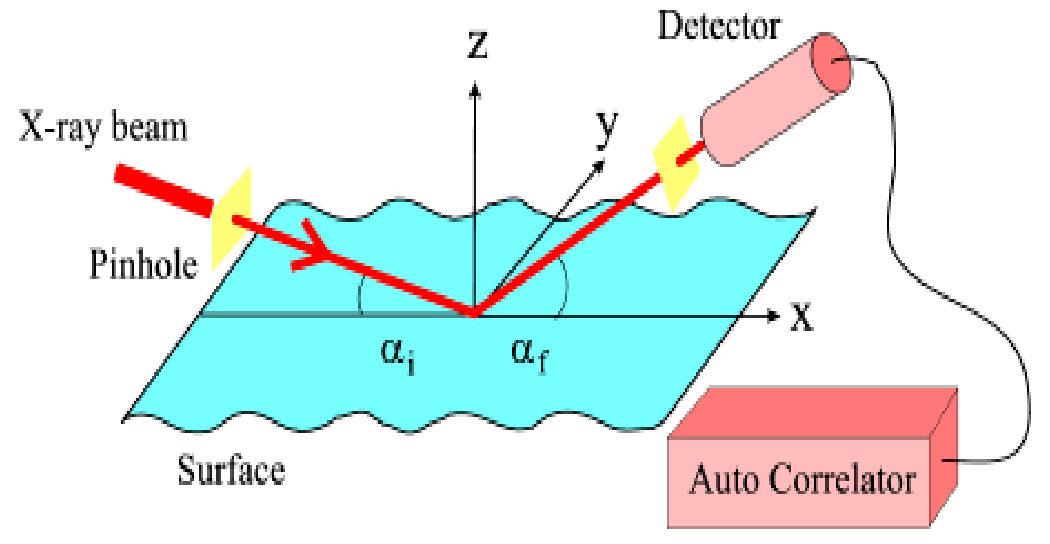


Extra boundary condition at the substrate

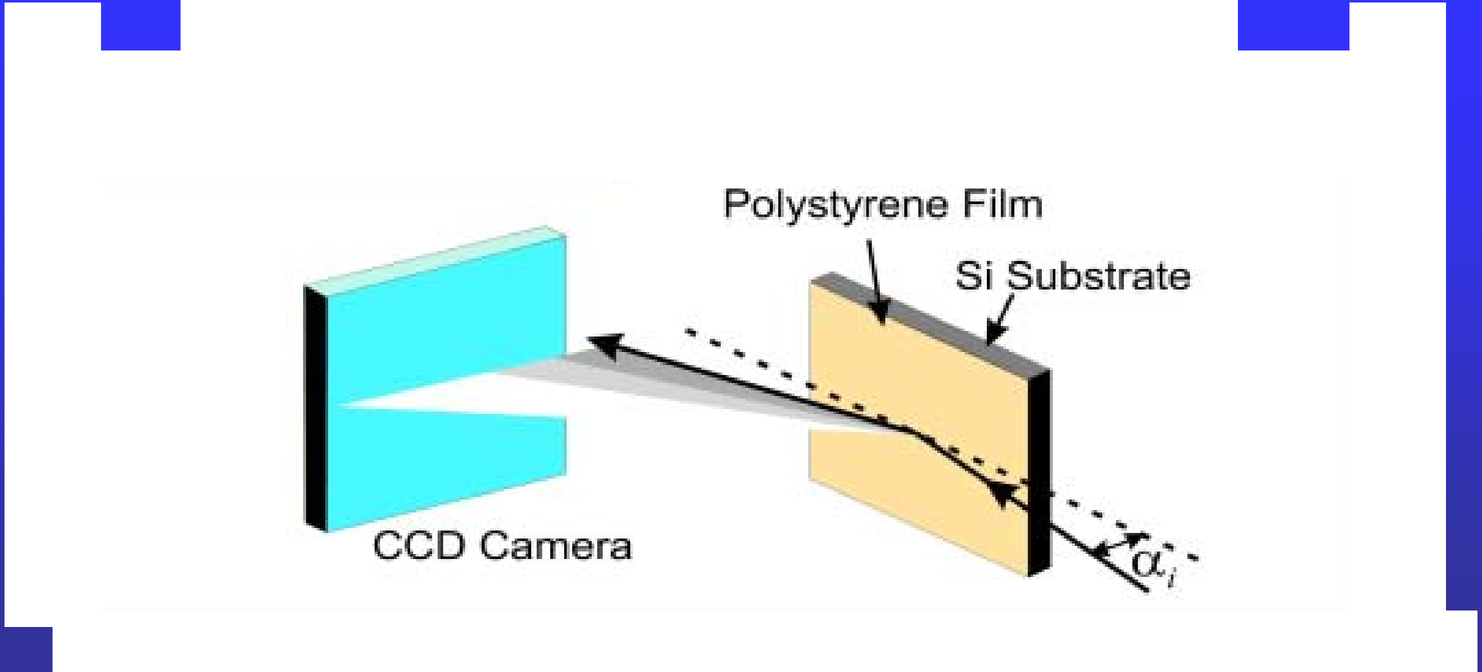


Jaeckle, J. Phys. : Cond. Matter 10 (1998) 7121

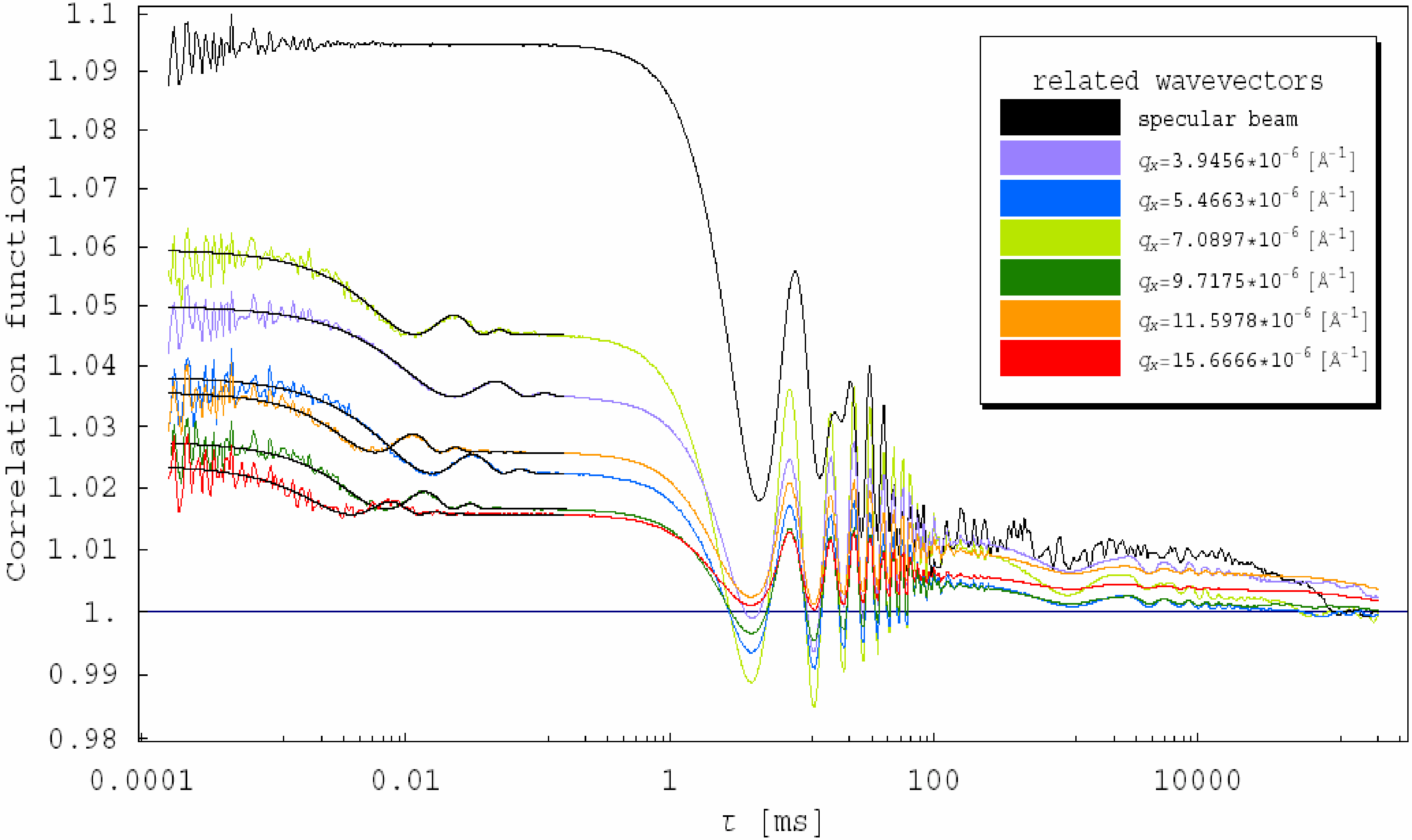
Setup for Surface XPCS



$$G(\ ) = \frac{I(t+\ )I(t)\ _t}{I(t)\ _t^{2}}$$



2. Bulk Liquids


Correlation function
1.1
1.09
1.08
1.07
1.06
1.05
1.04
1.03
1.02
1.01
1.
0.99
0.98
0.0001
0.01
1
100
10000
τ [ms]
related wavevectors
specular beam
q_x=3.9456*10^{-6} [$Å^{-1}$]
q_x=5.4663*10^{-6} [$Å^{-1}$]
q_x=7.0897*10^{-6} [$Å^{-1}$]
q_x=9.7175*10^{-6} [$Å^{-1}$]
q_x=11.5978*10^{-6} [$Å^{-1}$]
q_x=15.6666*10^{-6} [$Å^{-1}$]