DYNAMIC LIGHT SCATTERING AT LIQUID INTERFACES

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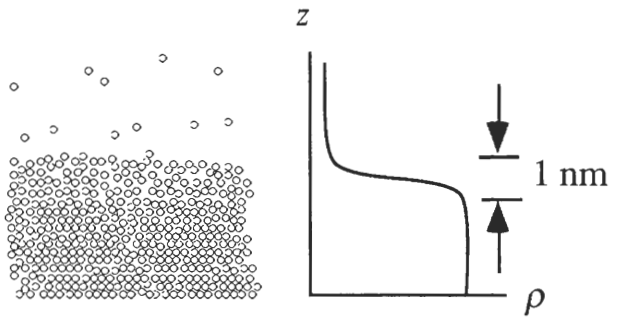
Lowell, April 7, 1990

HARVARD UNIVERSITY
Quantum Electronics and Molecular Physics Group

SURFACES & SURFACE WAVES

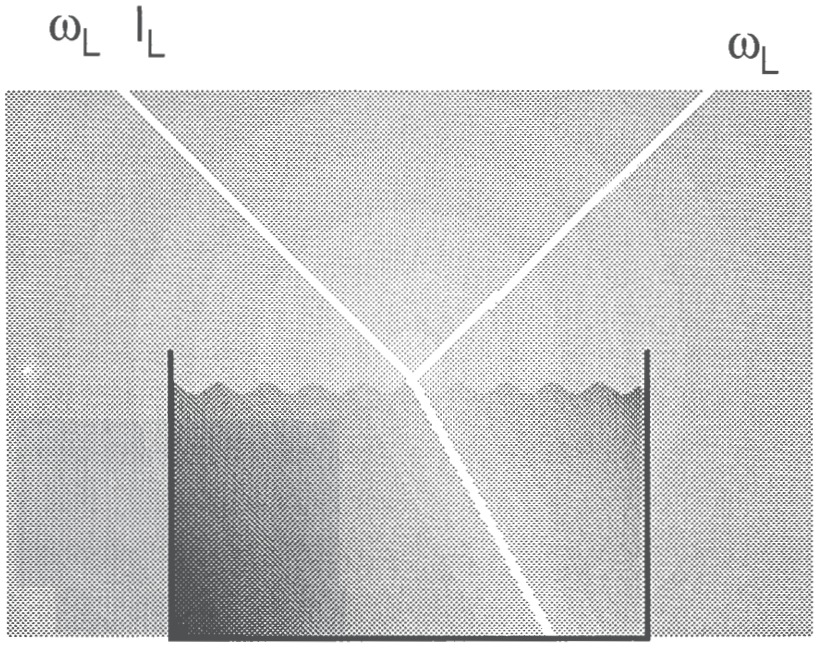


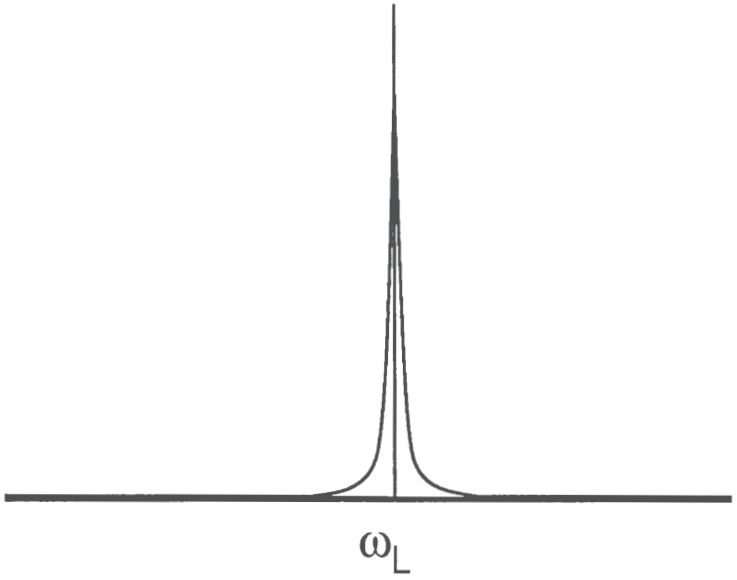
Perturbations & Restoring Forces → Surface Waves (surface phonons)

Gravity: gravity waves (long wavelength)

Surface Tension: capillary waves or ripplons (short wavelength)

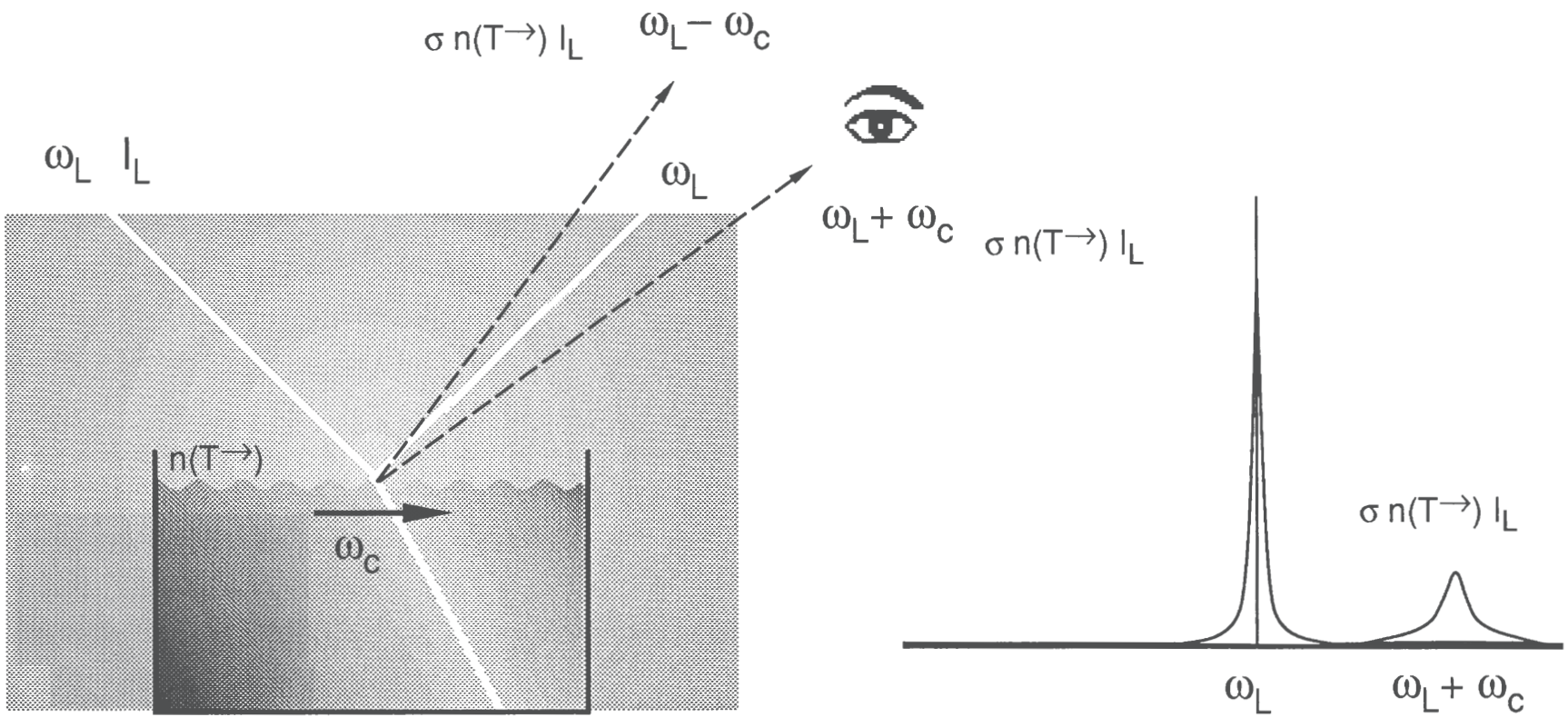
LIGHT SCATTERING FROM CAPILLARY WAVES





Elastic scattering from surface, bulk, and instrument

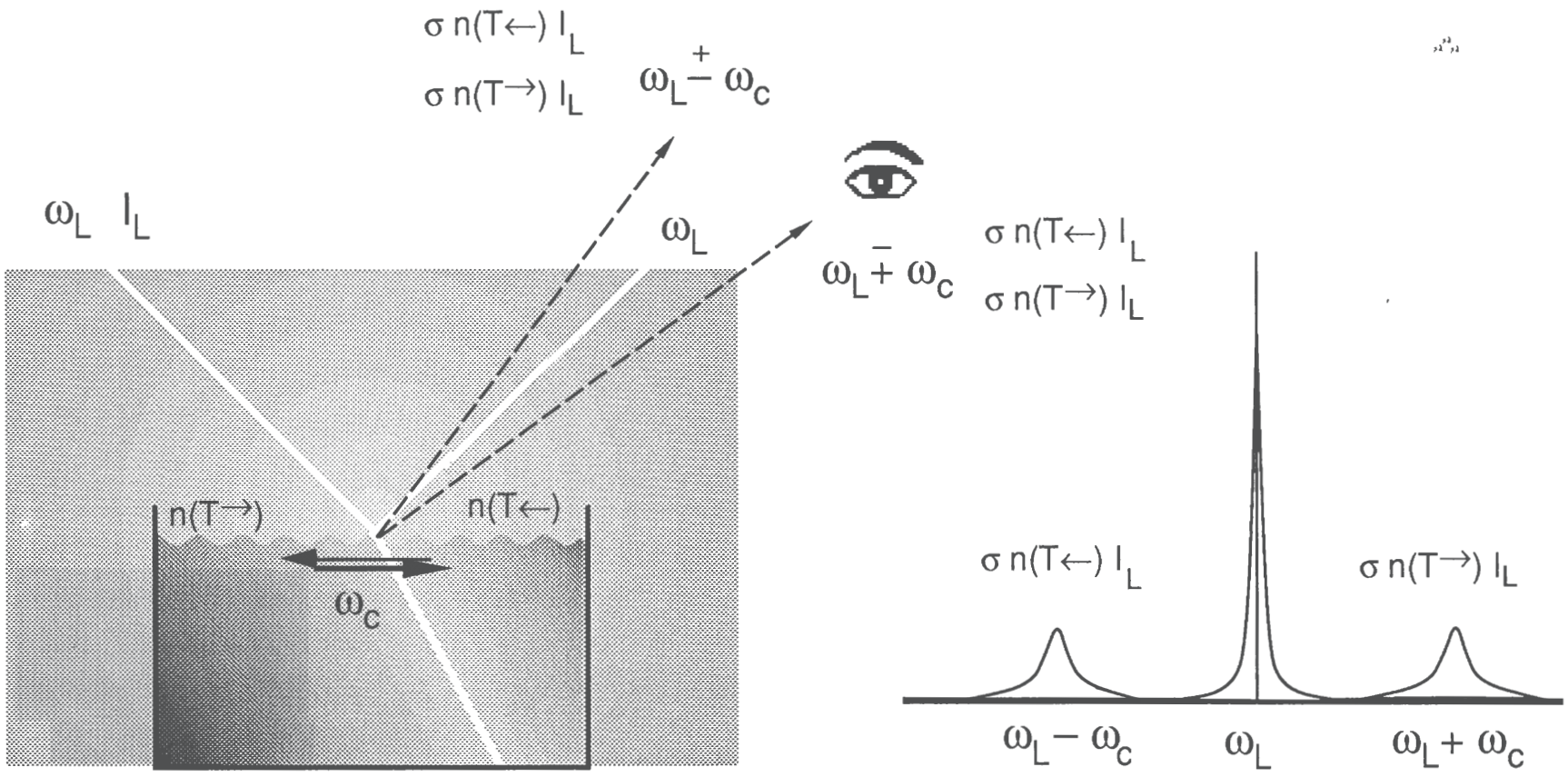
LIGHT SCATTERING FROM CAPILLARY WAVES



Elastic scattering from surface, bulk, and instrument

Inelastic scattering from surface phonon (*capillary wave, ripplon*)

LIGHT SCATTERING FROM CAPILLARY WAVES



Elastic scattering from surface, bulk, and instrument

Inelastic scattering from surface phonon (*capillary wave, ripplon*)

'BACK OF THE ENVELOPE' THEORY

Asymmetry of Stokes and anti-Stokes peaks:

$$\varepsilon \equiv \frac{I_s - I_a}{I_s + I_a} \approx \frac{n_s - n_a}{n_s + n_a} .$$

Since $n \approx 2\pi k_B T / h\omega_c$,

$$n_s - n_a \approx \frac{2\pi k_B}{h\omega_c} \Delta T^* = \frac{2\pi k_B}{h\omega_c} \vec{l}_c \bullet \vec{\nabla} T,$$

where $\vec{l}_c = l_c \hat{q}$. Then,

$$\varepsilon \approx \frac{n_s - n_a}{2n} \approx \frac{\vec{l}_c \bullet \vec{\nabla} T}{2T} ,$$

or, with $L_\nabla \equiv [\, \hat{q} \cdot \vec{\nabla} ln\, T \,]^{-1}$

$$\boxed{\varepsilon \approx \tfrac{1}{2}\, l_c / L_\nabla .}$$

LINEAR FLUCTUATING HYDRODYNAMICS

Fluctuating hydrodynamic theory yields

$$\boxed{\varepsilon = \tfrac{3}{2}\, l_c / L_\nabla \,.}$$

Mean free path l_c follows from dispersion relation

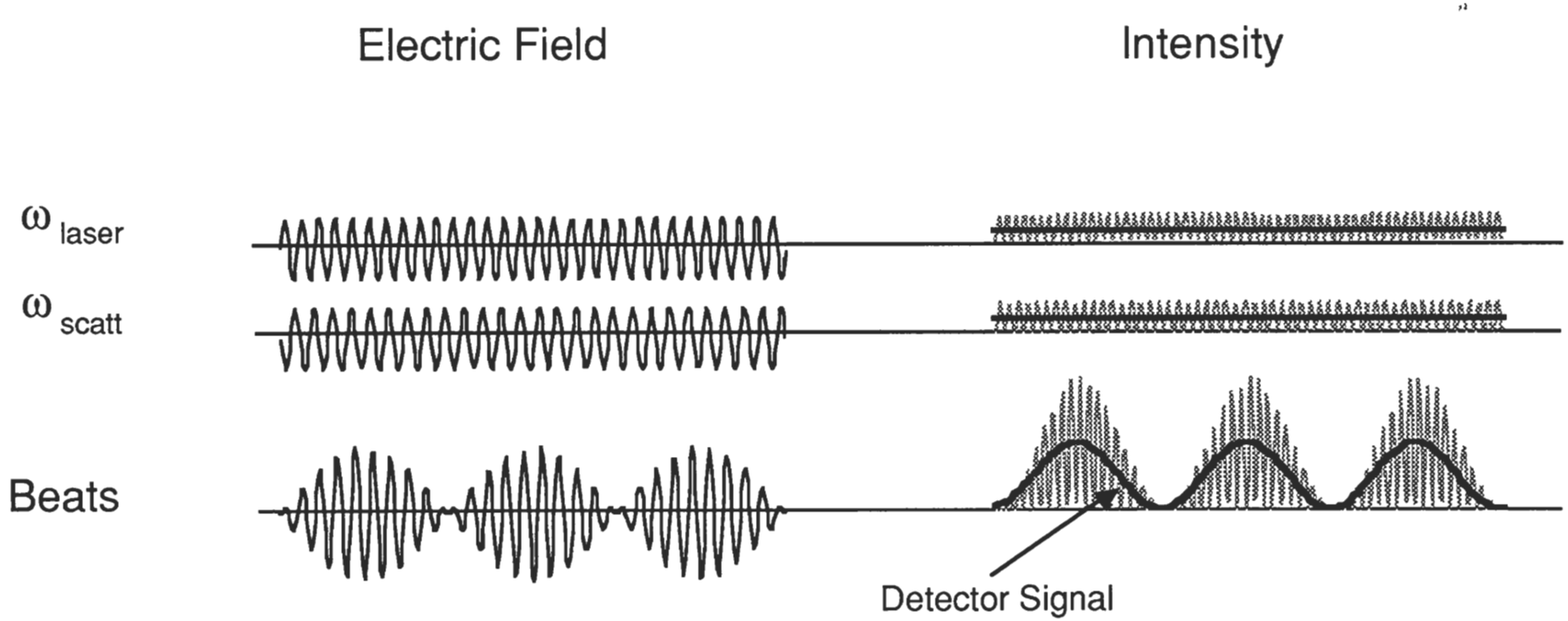
$$\omega = \sqrt{\frac{\sigma}{\rho}}\, q^{\frac{3}{2}} + 2i\frac{\eta}{\rho} q^2,$$

so that

$$\varepsilon = \frac{3}{4}\frac{\sqrt{\sigma\rho}}{\eta}\, q^{-\frac{3}{2}} \frac{\partial\, ln\, T}{\partial\, x}\,.$$

M. Grant and R.C. Desai, *Phys. Rev.* **A27**, 2577 (1983)

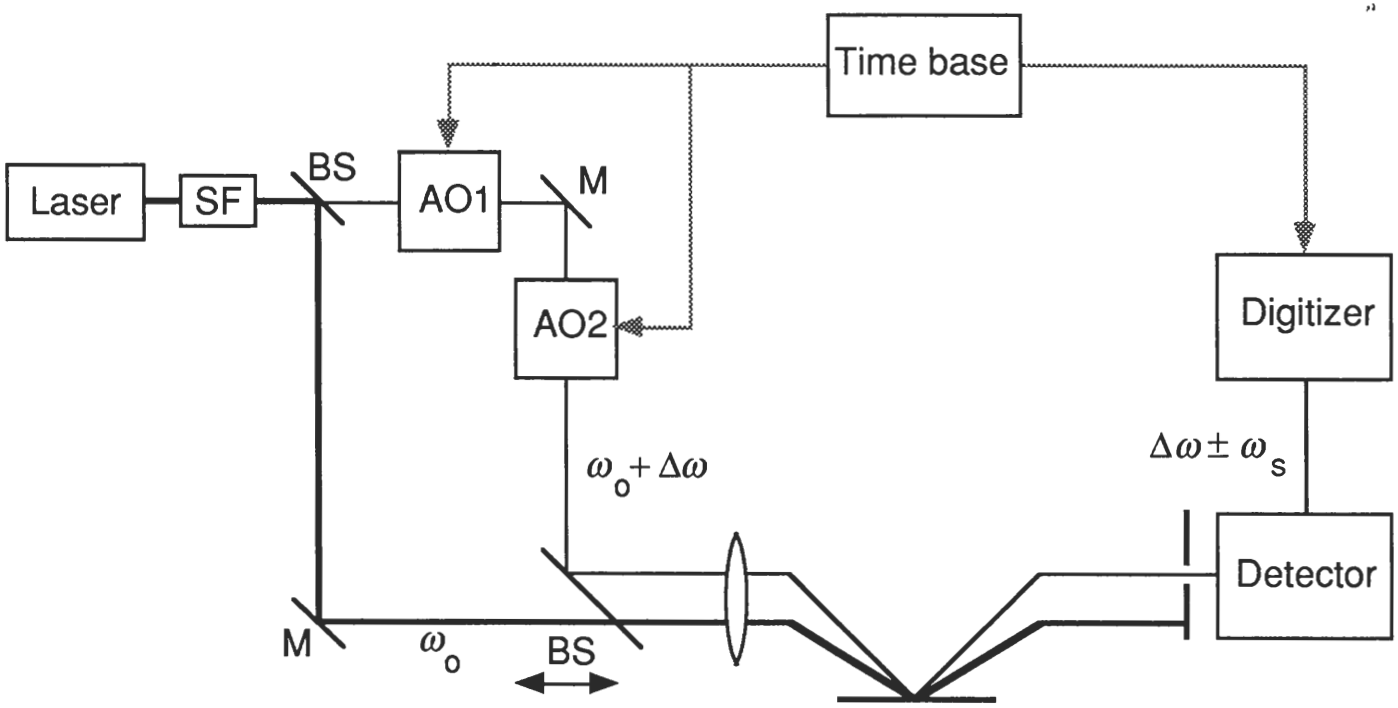
HETERODYNE SPECTROSCOPY



Detector signal is modulated with frequency $\omega_{laser} - \omega_{scatt}$

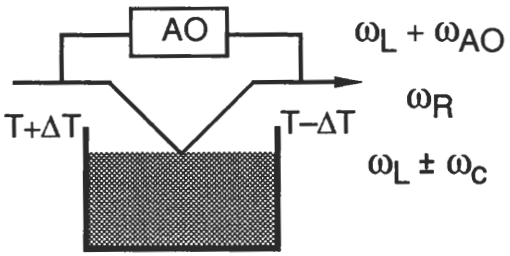
➪ Fourier transform of signal yields spectrum of ω_{scatt} !

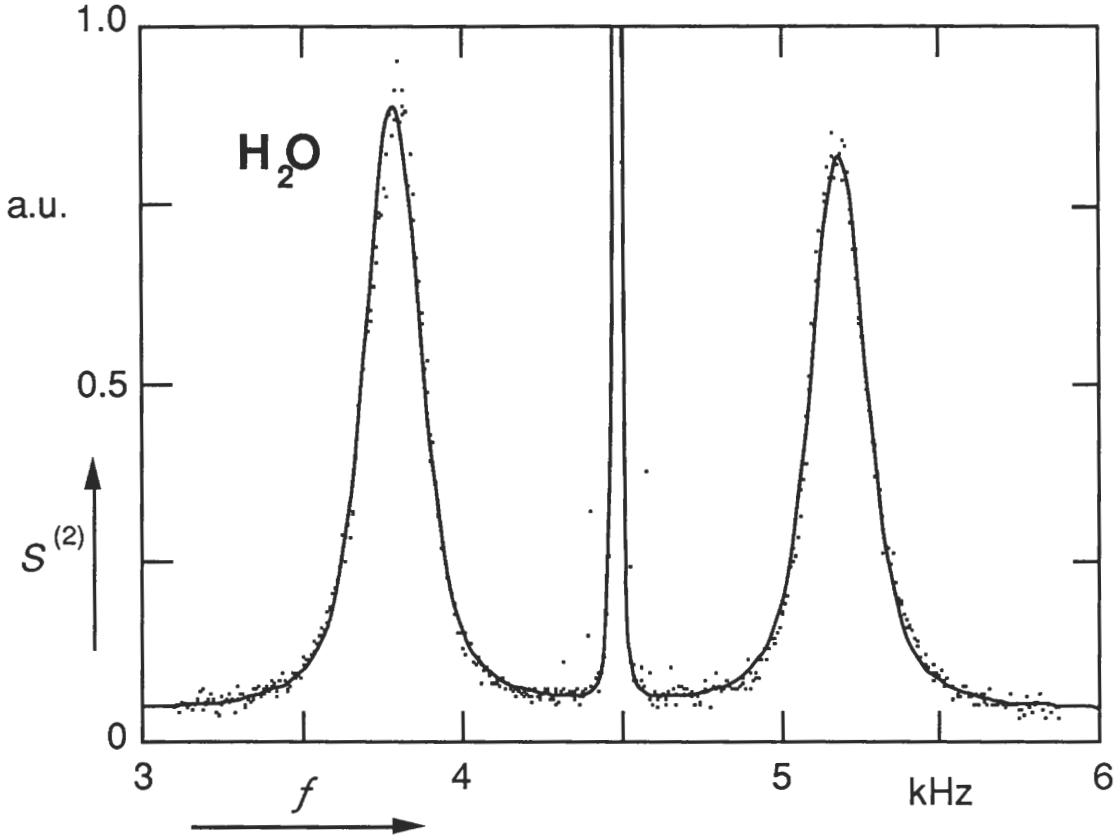
SHIFTED LOCAL OSCILLATOR



- Frequency shifted local oscillator
- Phasematched beam geometry ('premixing')
- Continuously variable *q*
- Direct FTH

NONEQUILIBRIUM ASYMMETRY





D.S. Chung, K.Y. Lee and E. Mazur, *Int. J. Thermophys.*, 9 (1988) 729.

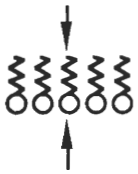
SURFACE MODES

COMPRESSIONAL MODES

lateral compression:

$\varepsilon, \varepsilon'$

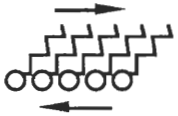
vertical compression



SHEAR MODES

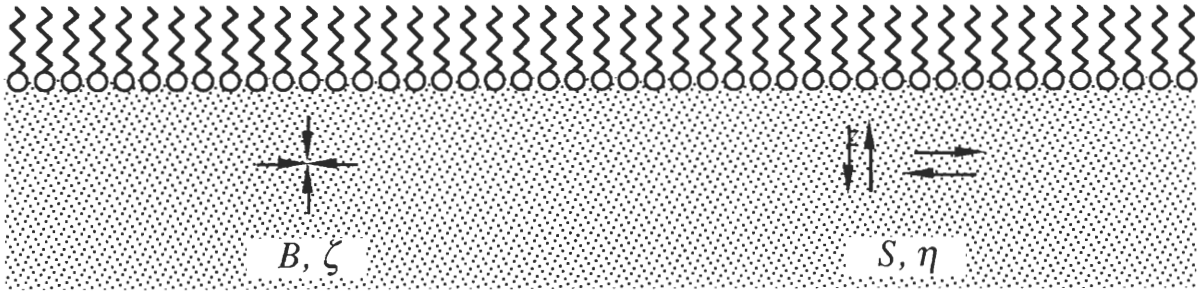
vertical shear:

σ, σ'

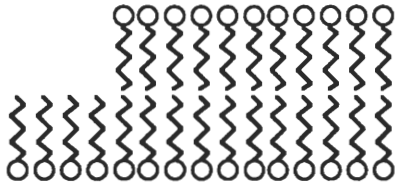


horizontal shear

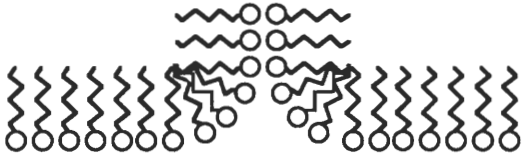
lateral shear



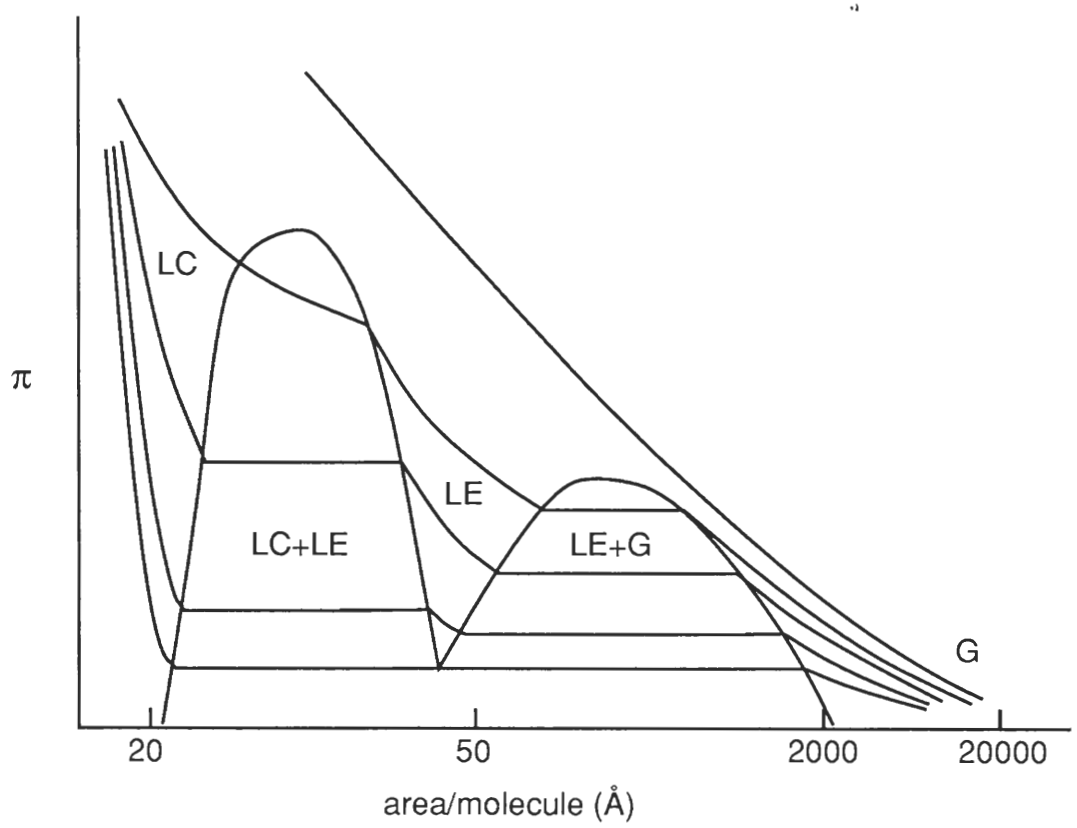
MONOLAYER PHASE DIAGRAM



collapsed



collapsing…

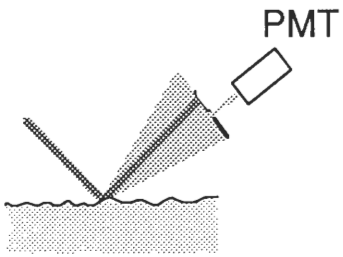


liquid condensed

liquid expanded

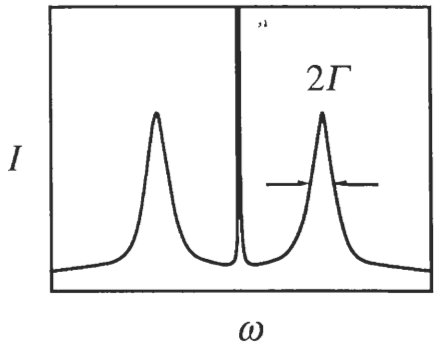
'gas'

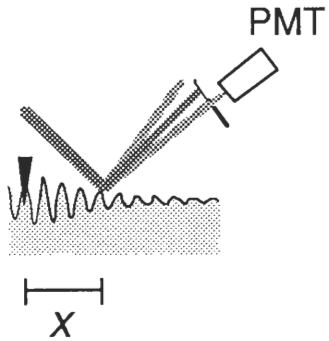
HOW TO MEASURE DAMPING



- Fixed, real q
- Variable ω

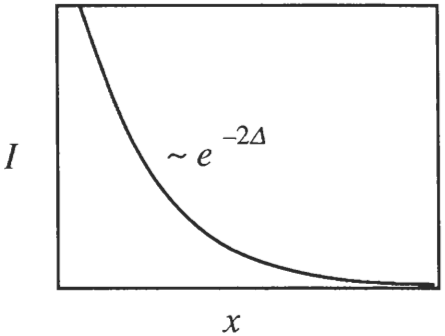
$$e^{i[qx - \Omega(q)t]} = e^{iqx - i\omega t - \Gamma t}$$

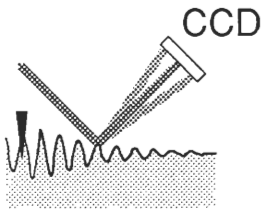




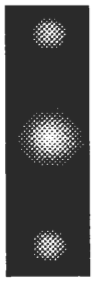
- Fixed, real ω
- Fixed, real q
- Variable x

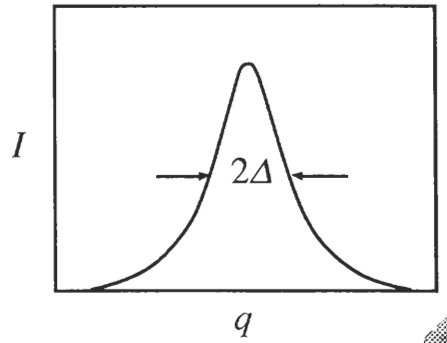
$$e^{-\Delta x} \cdot e^{i(qx - \omega t)}$$



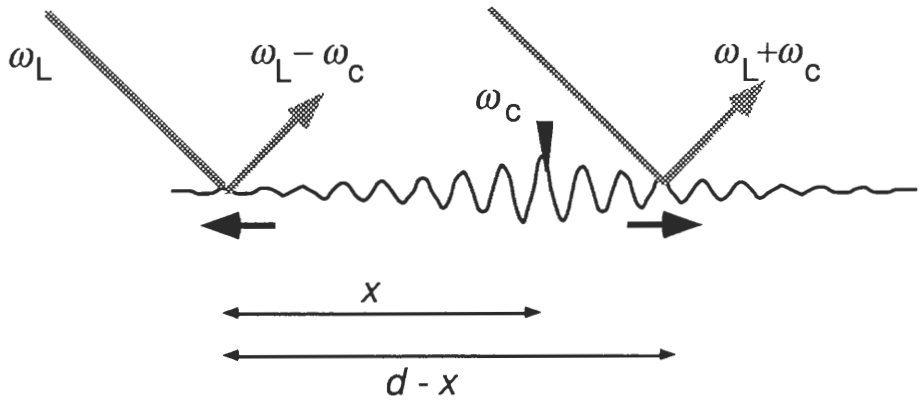


- Fixed, real ω
- Fixed x
- Variable, real q





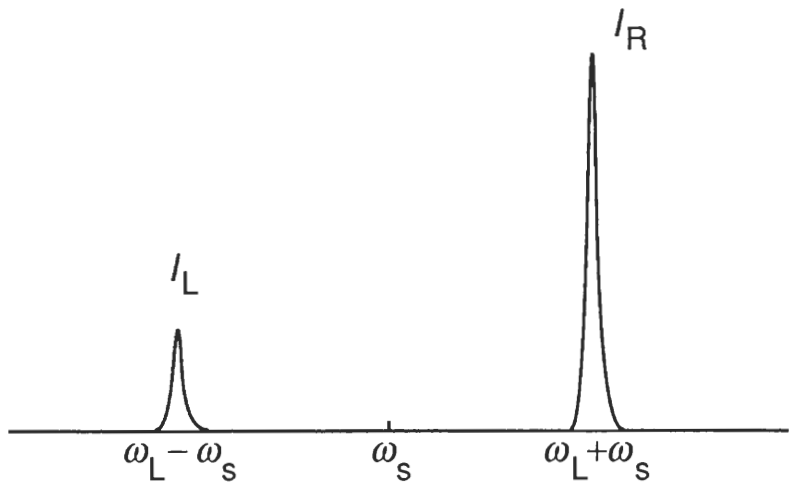
DIFFERENTIAL DAMPING MEASUREMENT

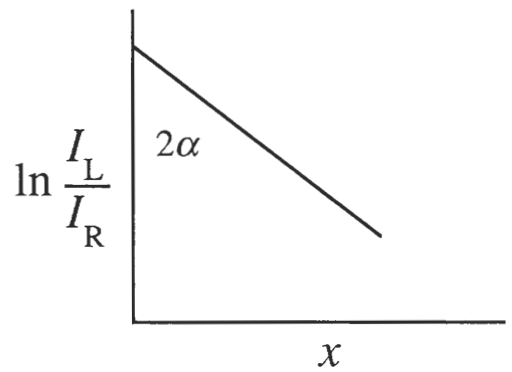


$$I_L = c_1 \zeta_o e^{-\alpha x}$$

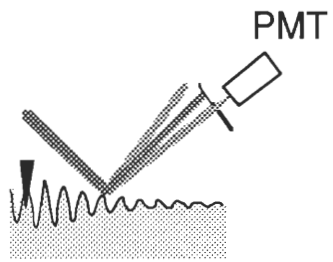
$$I_R = c_2 \zeta_o e^{-\alpha (d - x)}$$

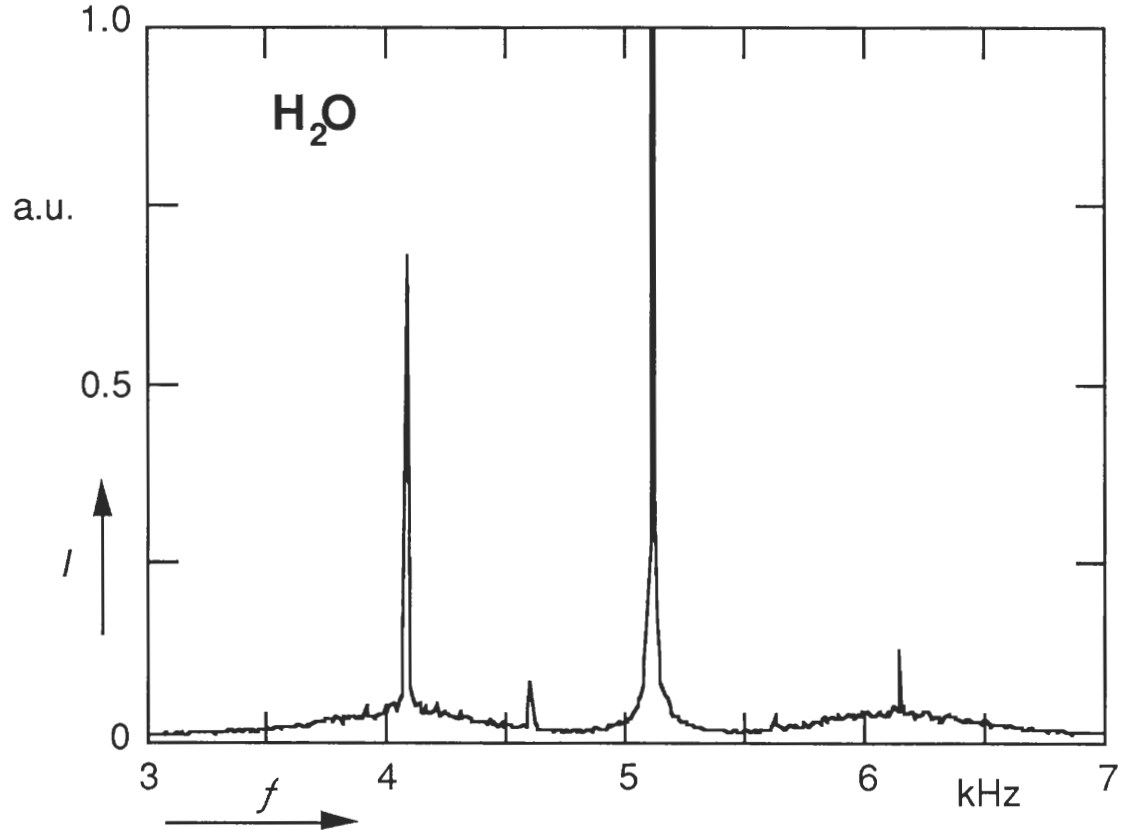
$$\frac{I_L}{I_R} = \frac{c_1}{c_2} e^{-2\alpha x} e^{+\alpha d} = c\, e^{-2\alpha x}$$



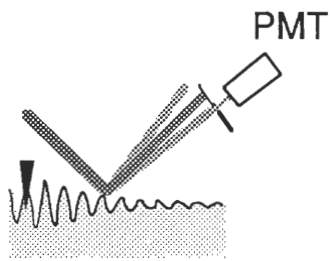


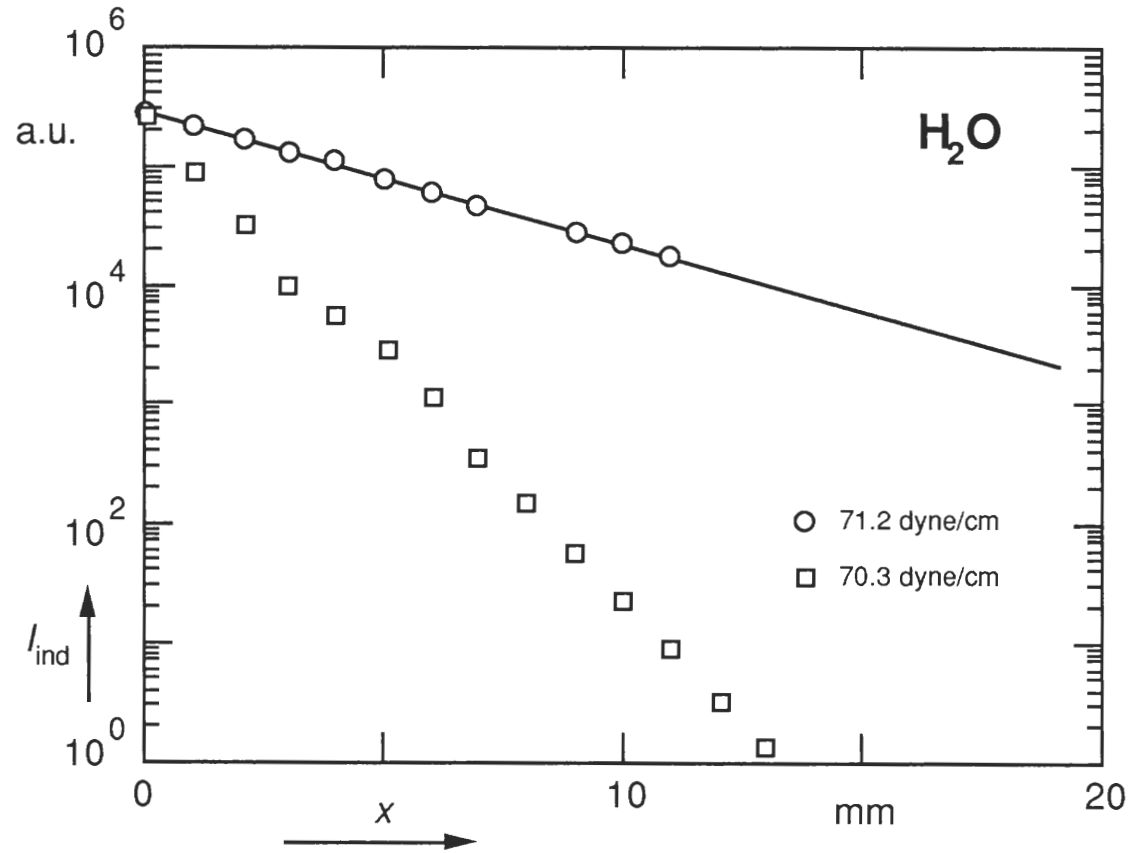
INDUCED WAVE ASYMMETRY



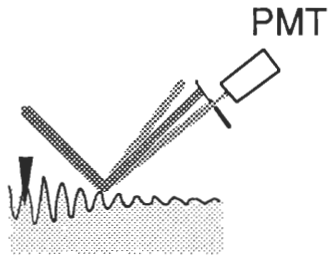


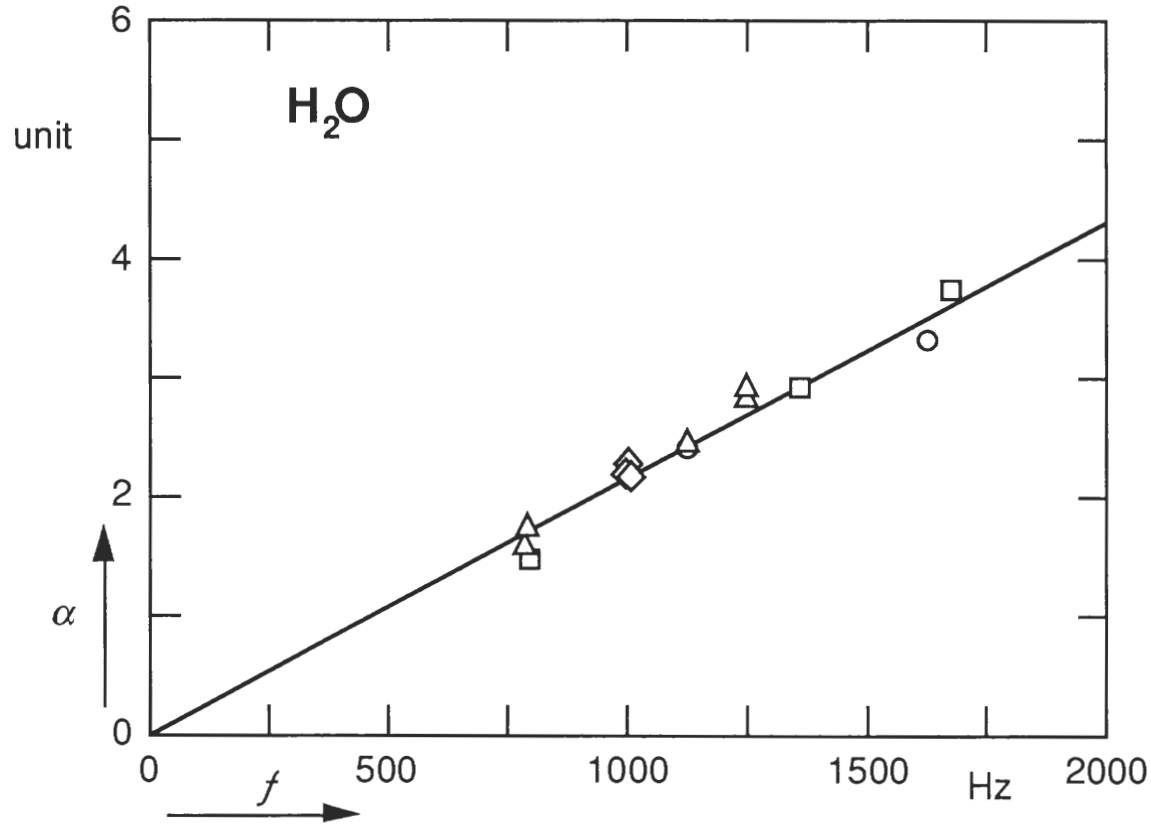
DECAY OF INDUCED SURFACE WAVE

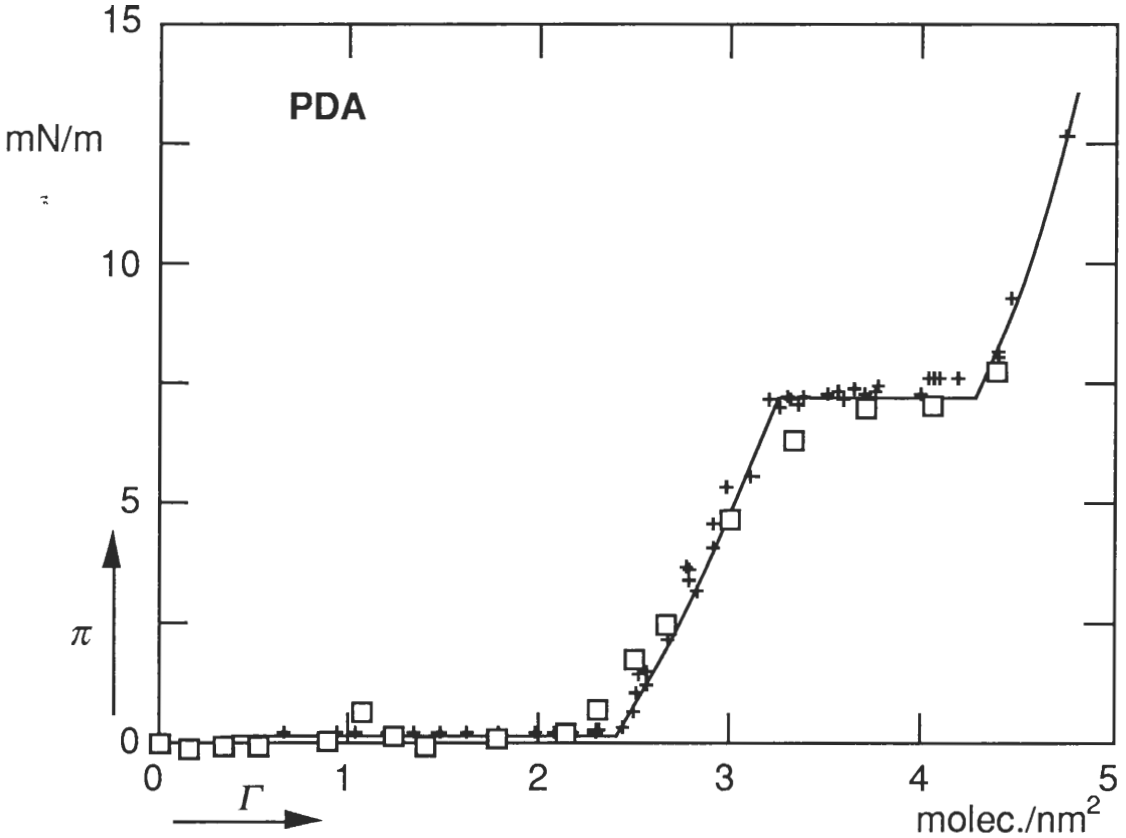


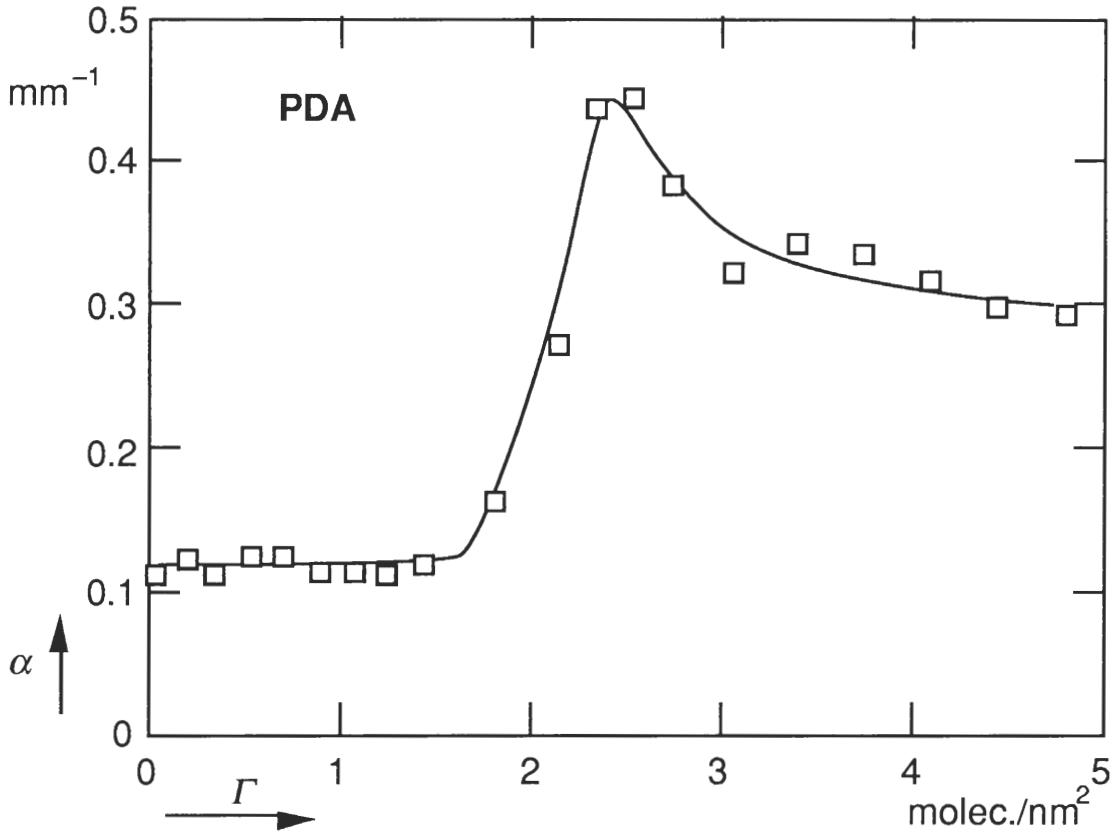


PURE LIQUIDS



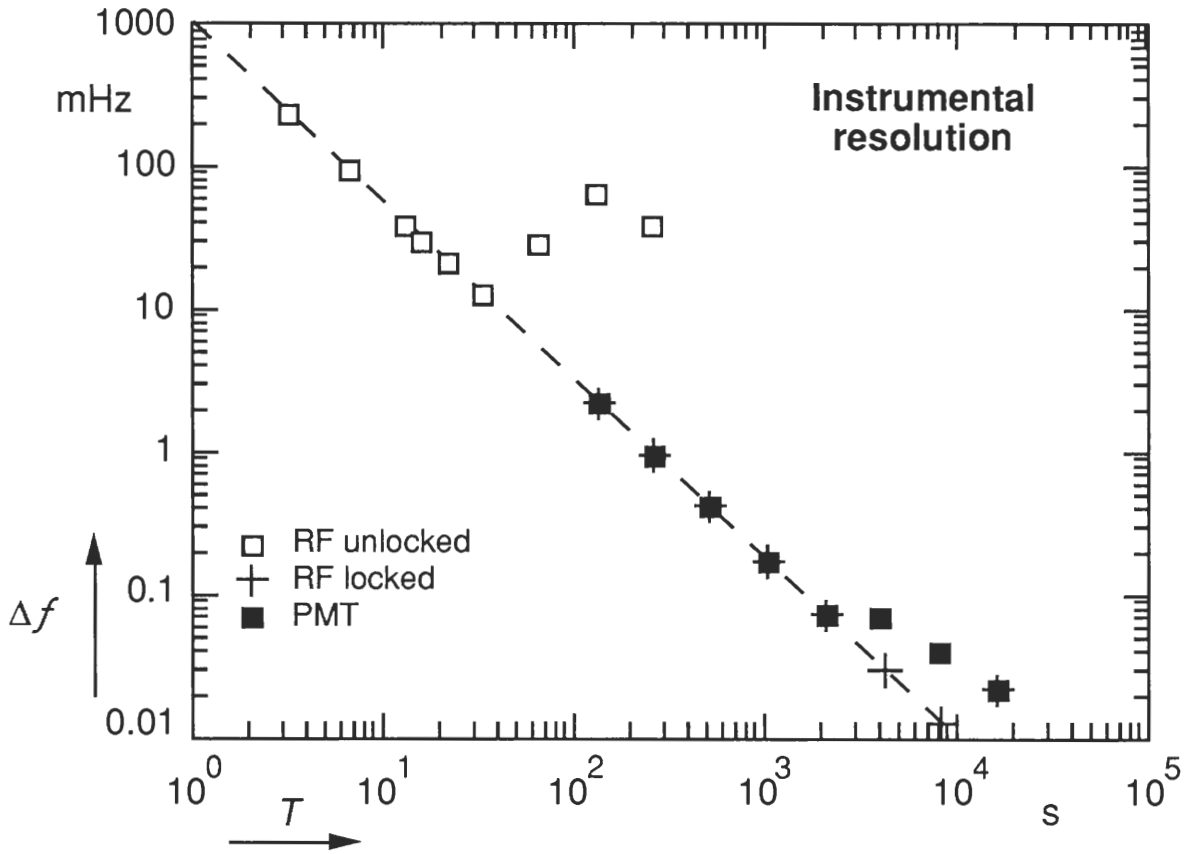



PDA
mN/m
15
10
5
0
π
0
1
2
3
4
5
Γ
molec./nm²


PDA
mm⁻¹
0.5
0.4
0.3
0.2
0.1
0
α
0
1
2
3
4
5
Γ
molec./nm²

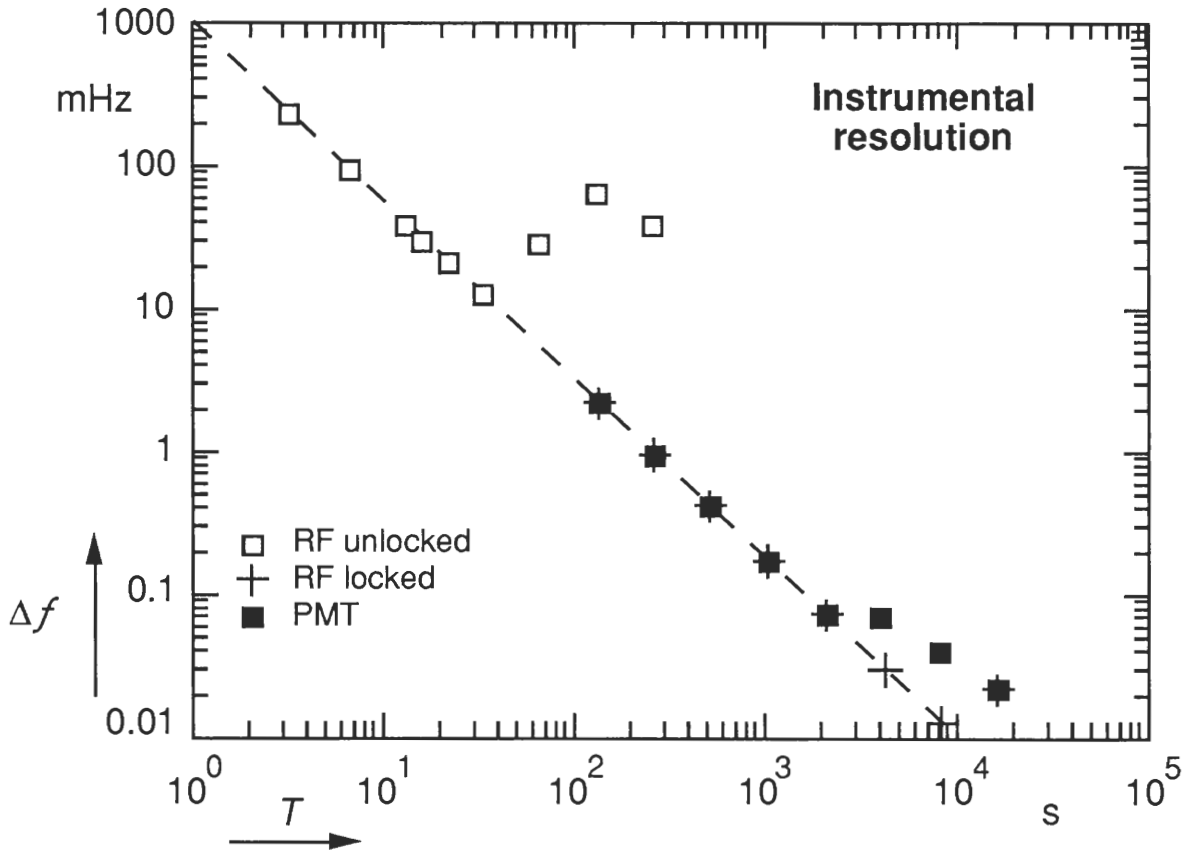
I53–89–18

20 μHz RESOLUTION



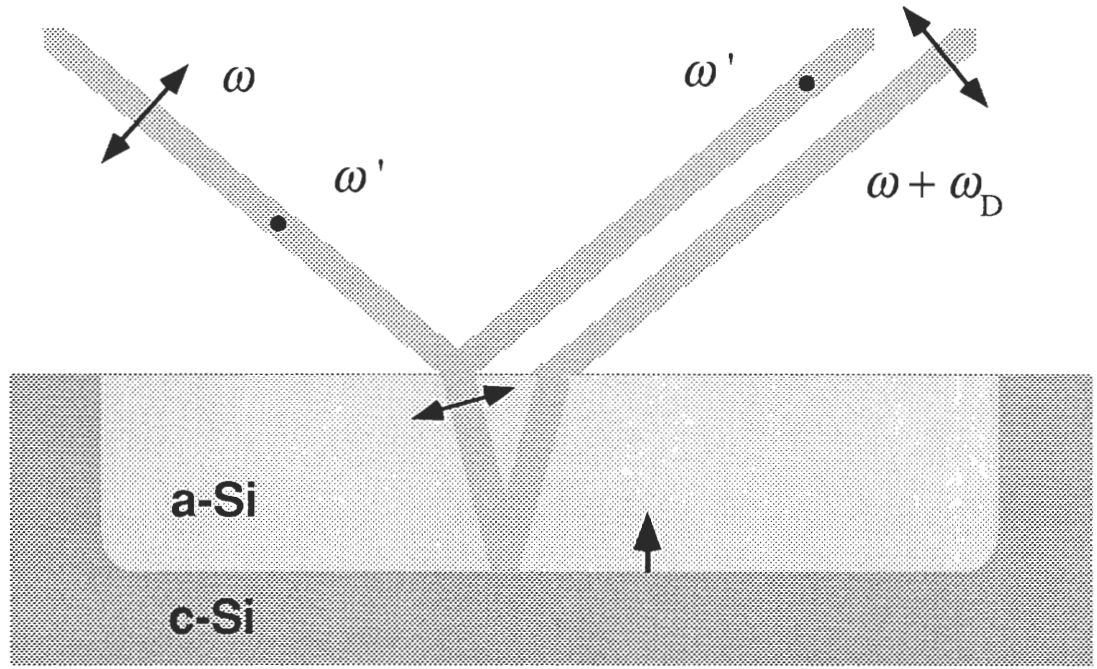
I53–89–19

20 μHz RESOLUTION

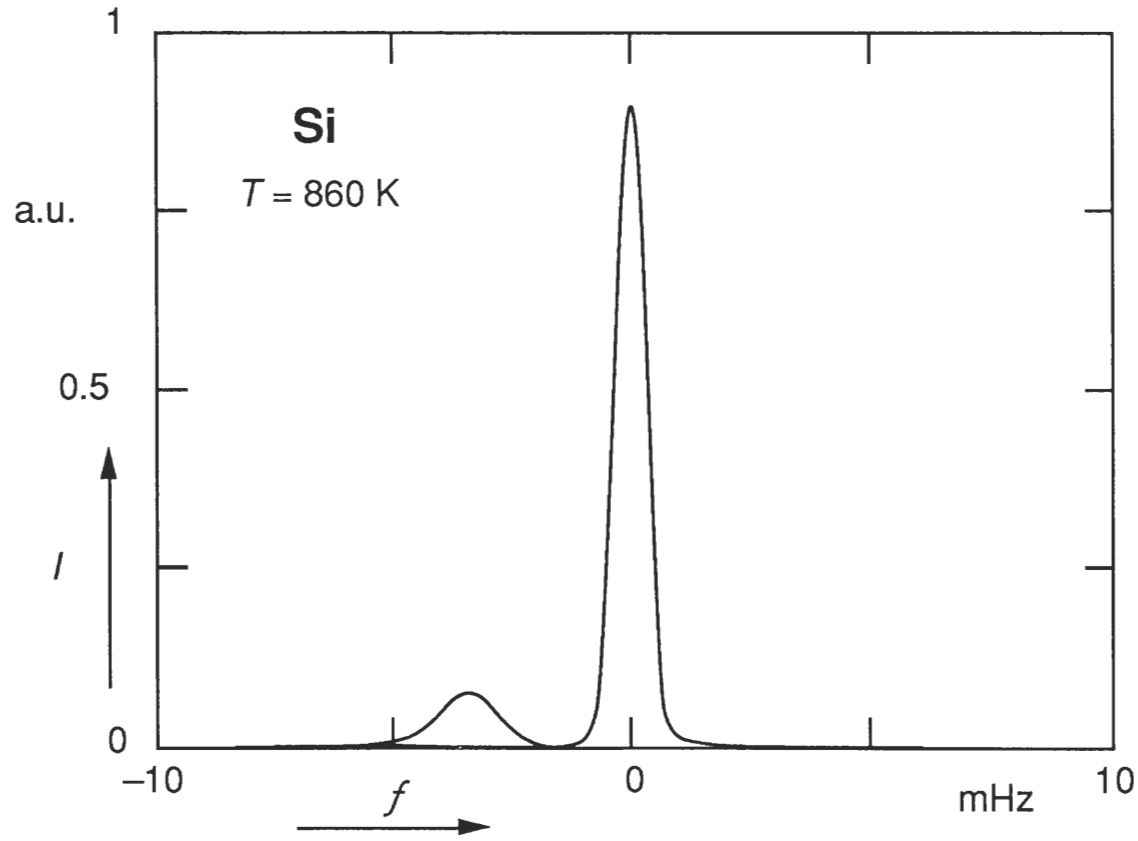


I53–89–19

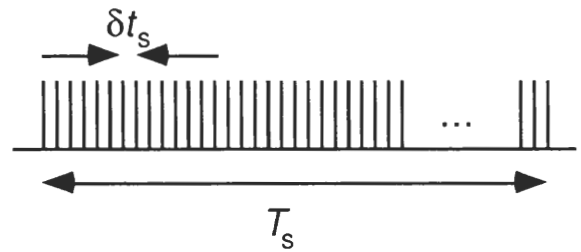
LASER VELOCIMETRY OF A GROWING CRYSTAL



SILICON DOPPLER SHIFT



LIMITS



		Now	Limit	Limiting Process
Resolution	$\Delta f = 1/T_s$	$T_s \leq 4$ hrs.	20 μHz	stability
Spectral Range	$F = 1/2\delta t_s = f_s/2$	$f_s \leq 100$ kHz	1 GHz	detection time
Number of points	$n = f_s\ T$	65,000	?	transform time
Transform time	$n \log_2 n$	45 s (float)	?	CPU/FPU

SUMMARY

- Nonequilibrium asymmetry of interfacial light scattering spectrum
- Direct measurement of monolayer effects
- Simple technique with 20 μHz resolution
- Possible to measure small Doppler shift from growing Si crystal

Acknowledgments

Experiment:

Doo Soo Chung

Ka Yee Lee

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Rashmi Desai

Irwin Oppenheim

Mike Aziz

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