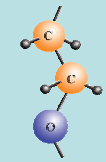
VERSATILE FIBER-COUPLED SYSTEM DESIGN FOR SIMULTANEOUS PHOTON CORRELATION SPECTROSCOPY (PCS) AND FABRY-PEROT INTERFEROMETRY

R. B. Bogoslovov, D. P. Shelton, J. C. Selser, S. Peng and G. Piet, University of Nevada, Las Vegas, Las Vegas, NV 89154-4002

Introduction

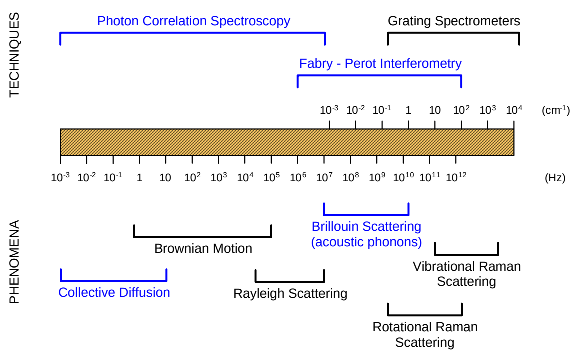
Polymer "solid" electrolytes have been studied for years for their potential application in high energy density rechargeable batteries. One of the most promising systems is based on poly(ethylene oxide) (PEO) in complexes with lithium perchlorate ($LiClO_4$) salt. It has been shown that the transport of lithium ions in such an electrolyte occurs in the amorphous phase of the polymer host. Therefore, we have focused our research on the structure and dynamic properties of molten PEO and PEO/$LiClO_4$ compositions. Our light scattering results have revealed the presence of a transient physical network formed by the polymer in the melt.

In the present work we apply Fabry-Perot interferometry to study the Brillouin spectra which will reveal another dynamic aspect of the system – the propagation of acoustic modes in the media. The classical F-P interferometer is extended by applying fiber-optic coupling. That would allow simultaneous PCS and F-P measurements without changing the state or disturbing the sample. We address some interesting practical issues related to the experimental design and performance of the instruments.



Poly(ethylene oxide) (PEO)

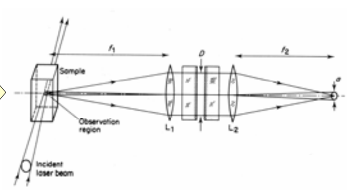
Laser Spectroscopy



Fabry-Perot Interferometer

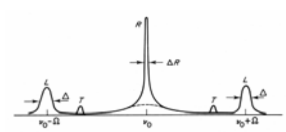
Fabry-Perot Classic Geometry

The scattered light is collimated by the first lens and then passes through the two parallel F-P mirror plates with adjustable spacing. The second lens collects the light and the signal is detected through a pinhole *a*. The diameter of the pinhole determines the scattering volume in the sample.



Brillouin Spectra

The central peak *R* with half-width *ΔR* is centered at the laser frequency ν_0. The two Brilouin peaks *L* corresponding to longitudinal acoustic waves are shifted by frequency Ω and are characterized by half-width Δ. In some occasions, the peaks T corresponding to transverse acoustic waves can be observed.



Some useful relations

- Reflected and transmitted intensities:
  (no absorption, perfect flatness and collimation)

$$\frac{I_r}{I_i}=\frac{Q_R\sin^2\frac{\delta}{2}}{1+Q_R\sin^2\frac{\delta}{2}} \qquad \frac{I_t}{I_i}=\frac{1}{1+Q_R\sin^2\frac{\delta}{2}}$$

$$\frac{\delta}{2}=\frac{2\pi D}{\lambda}\cdot\cos\varphi$$

- Finesse coefficient (coeff. of finesse):

$$Q_R=\frac{4R}{(1-R)^2}=\left(\frac{2}{\pi}F_R\right)^2$$

- Free spectral range (in Hz):

$$\Delta\nu_{FSR}=\frac{c}{2D}$$

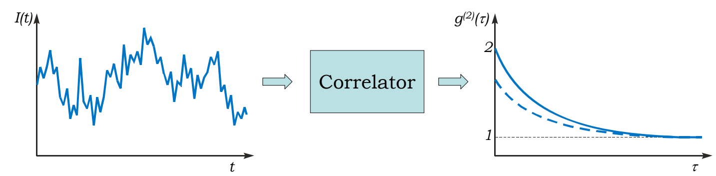
- Contrast:

$$C=Q_R+1=\frac{(1+R)^2}{(1-R)^2}$$

- Reflectivity finesse: $F_R=\frac{\pi\sqrt{Q_R}}{2}=\frac{\pi\sqrt{R}}{1-R}$
- Flatness finesse: $F_F=\frac{M}{2}$
- Aperture limited finesse: $F_P=\frac{\lambda}{d}\frac{4f^2}{a^2}=\frac{\lambda}{d}\cdot\theta^2$
- Total finesse: $\frac{1}{F_{Total}^2}=\frac{1}{F_R^2}+\frac{1}{F_F^2}+\frac{1}{F_P^2}+\ldots$
- Measured finesse: $F=\frac{\Delta\nu_{FSR}}{\Delta\nu_{FWHM}}$

R - reflectivity of the plates; *D* - spacing of the plates; *c* - speed of light in vacuum; λ - laser wavelength; *f* - focal length; *a* - aperture diameter; θ - numerical aperture ($\theta=a/2f$); *M* – rms flatness; φ – angle of incidence

Dynamic Light Scattering



The technique is also known as *quasi-elastic light scattering* (QLS) or *photon correlation spectroscopy* (PCS). It measures fluctuations of the random interference pattern created by coherently illuminated, randomly moving scatterers. Therefore, the fluctuations in the intensity of the scattered light (left) are a signature of the dynamics of the system. From the correlation function one can deduce, for example, the diffusion coefficient.
The correlator forms in real time the autocorrelation function $G^{(2)}(\tau)=\langle I(t)I(t+\tau)\rangle$. Normalized to the baseline that gives the *normalized autocorrelation function:*

$$g^{(2)}(\tau)=\frac{\langle I(t)\cdot I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

which is shown on the right.
Ideally, the initial value of the autocorrelation function amounts to twice its limiting value at large correlation lag times (solid line). In practice, the amplitude of the correlation function decreases with decreasing angular resolution (dashed line). For Brownian motion of non-interacting particles in suspension with diffusion coefficient *D*:

$$g^{(2)}(\tau)=1+e^{-2q^2D\tau}$$

Siegert relation:

$$g^{(2)}(\tau)=1+f\left|g^{(1)}(\tau)\right|^2$$

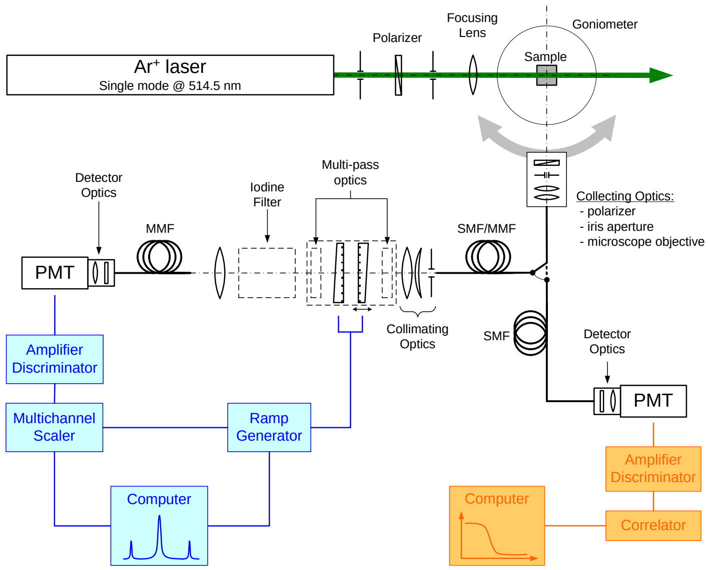
The factor *f* in front of the dynamic part of the autocorrelation function is called *coherence factor*. Typical values of *f* in the classic pinhole setup are in the range 0.5 – 0.8. It has been shown theoretically and experimentally that in the case of a single-mode fiber receiver *f=1* (assuming proper alignment). Furthermore,

$$f_{pinhole}<f_{MM\ fiber}<f_{SM\ fiber}$$

Advantages and disadvantages of fiber-coupling

Fabry-Perot Interferometer	Dynamic Light Scattering
Single mode fiber: Selection of a single coherence area is not essential (+) Very small effective illuminating aperture improves the resolution of the F-P interferometer (-) Small aperture means lower light-collection efficiency	**Single mode fiber:** Coherence factor is essential for the quality of the correlation function (+) Perfect selection of a single coherence area leads to high SNR (Very high coherence factors with corresponding high light-collection efficiency)
Multimode fiber: (+) Higher collection efficiency can be achieved (-) Increasing the fiber core diameter lowers the instrument's resolution	**Multimode fiber:** (-) Does not improve the light-collection efficiency without significantly degrading the coherence factor thus resulting in lower SNR
(+) Allows for simultaneous (2-way splitter) or sequential (2-way switch) measurements with both techniques without changing the condition or disturbing the sample	
(+) Compact detection optics independent of the rest of the instrument's components: - easy to position and align - heavy and bulky components (such as F-P, iodine filter, photodetectors, MCS and correlator electronics, etc.) may be arranged at convenient location and distance - expandable; portable	

Experimental set-up

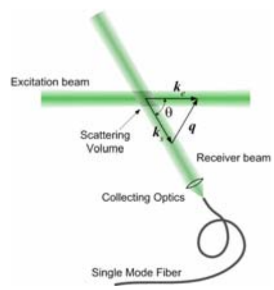


Scattering geometry

The excitation and receiver beams are approximated by Gaussian beams and we assume that both have well defined wave vectors $\vec{k}_e$ and $\vec{k}_s$ inside the scattering volume. Angle θ between the excitation and the observation beam determines the scattering vector $\vec{q} = \vec{k}_s - \vec{k}_e$

$$|\vec{q}| = \frac{4\pi n}{\lambda} \cdot \sin\frac{\theta}{2}$$

The collection optics usually consists of a polarizer and focusing lens (we used microscope objective with 10x magnification).

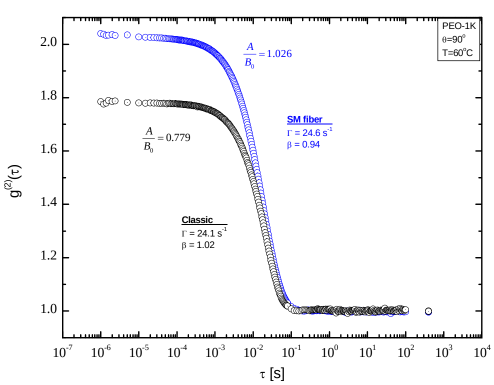


Dynamic light scattering with single-mode fiber receiver

Siegert relation: $$g^{(2)}(\tau) = 1 + f\left|g^{(1)}(\tau)\right|^2$$

Kohlrausch-Williams-Watts (KWW) "stretched exponential" fit: $$g^{(2)}(\tau) = 1 + \frac{A}{B_0} e^{-2(Dq^2\tau)^\beta}$$

f – coherence factor; D – diffusion coefficient; $\Gamma = Dq^2$ – relaxation rate; A – amplitude; B_0 – baseline; $\beta \sim 1$ – "single exponential" relaxation



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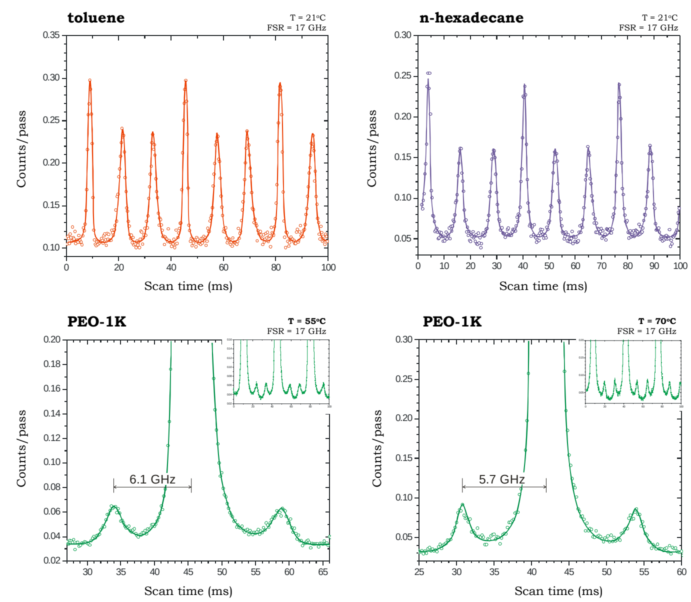
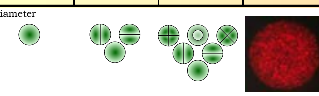
Brillouin scattering with single-mode fiber receiver

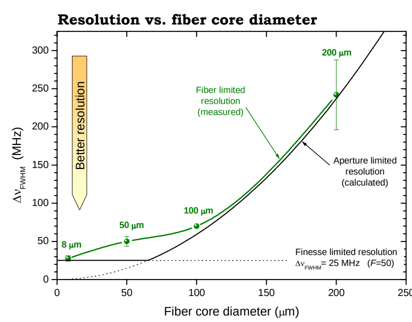


Effects of multimode fibers on the resolution

Fiber	SM – 3.5	MM – 4	MM – 8	MM – 50	MM – 100	MM – 200	MM - 400
Core Diameter	3.5 μm*	4 μm*	8 μm*	50 μm	100 μm	200 μm	400 μm
Specified cutoff wavelength	430 nm	620 nm	850 nm	—	—	—	—
Numerical aperture	0.13	0.12	0.12	0.22	0.22	0.22	0.22
Number of modes @ 514.5 nm	1	3	6	~ 2,260	~ 9,000	~ 36,000	~ 145,000
	single mode	"few modes"		"true" multimode			
Supplier	Nufern (ThorLabs)	3M (ThorLabs)	Ocean Optics	Ocean Optics	Ocean Optics	Ocean Optics	Ocean Optics

*MFD – Mode field diameter





- Aperture limited resolution:

$$\Delta\nu_{FWHM} = \frac{ca^2}{8\lambda f^2}$$

- Finesse limited resolution:

$$\Delta\nu_{FWHM} = \frac{\Delta\nu_{FSR}}{F}$$

We tested some of the fibers listed in the table above to see if the mode structure degrades the resolution beyond the limit of equivalent aperture with the same diameter as the core of the fiber. Overall, the resolution was not appreciably affected by the fiber.

Conclusions and prospects

A fiber-coupled system for light scattering experiments was designed and tested. The set-up combines Fabry-Perot interferometry and photon correlation spectroscopy in a very useful way allowing for simultaneous or consecutive measurements. In both cases, measurements are conducted without changing the conditions or disturbing the sample.

The system was tested using toluene, n-hexadecane and poly(ethylene oxide) and its performance was excellent in both PCS and F-P modes. While in PCS single mode detection has intrinsic advantages and showed dramatic improvement in the quality of the correlation function it is not essential for the operation of F-P. If the signal is weak and high resolution is not required, one can choose to work with multimode fibers.

Our research will continue as we apply the described set-up in systematic studies of the dynamic properties of the polymer electrolyte PEO/$LiClO_4$ at various concentrations, temperatures and scattering angles.