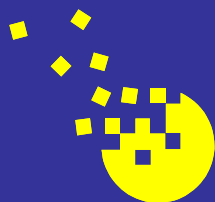


Diffusion related electrochemical noise

Can diffusion result in flicker noise?

Gábor Mészáros

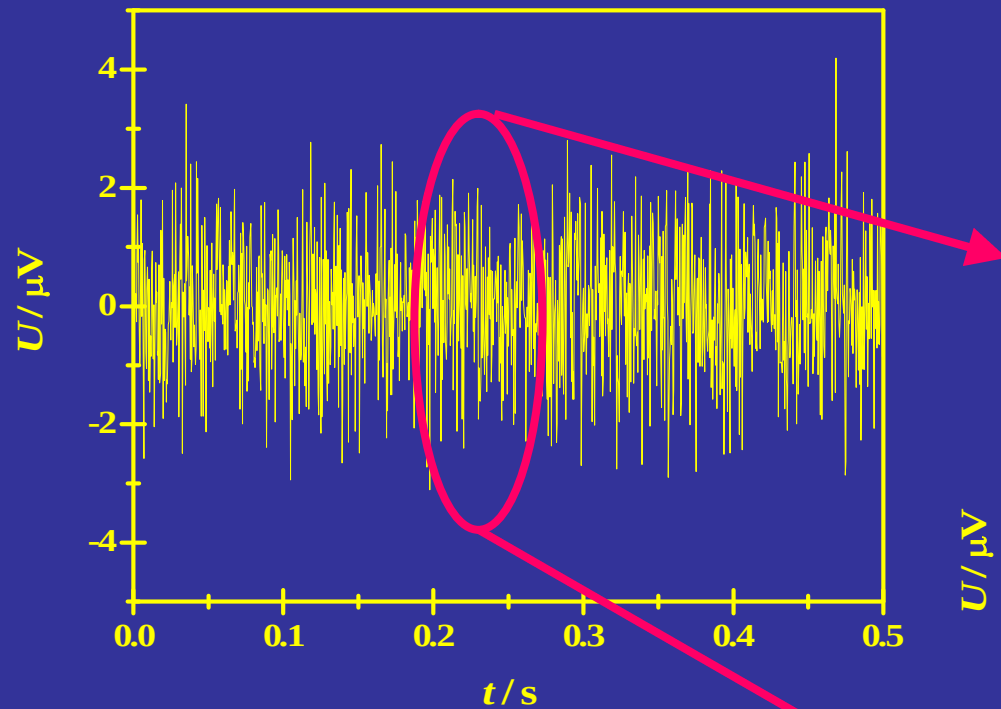


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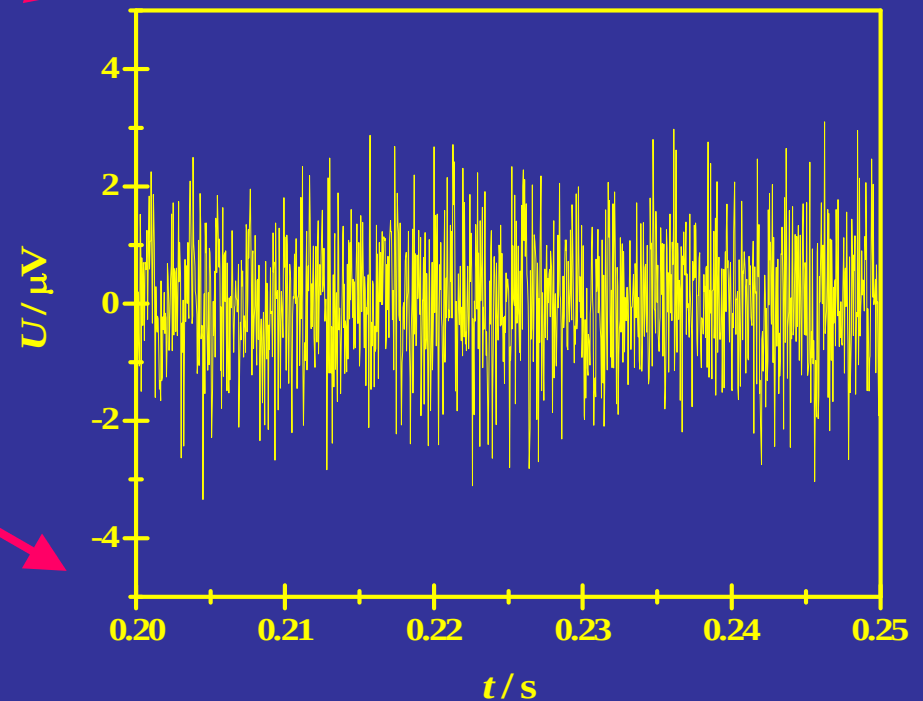
What is flicker noise – from mathematical point of you

White noise:



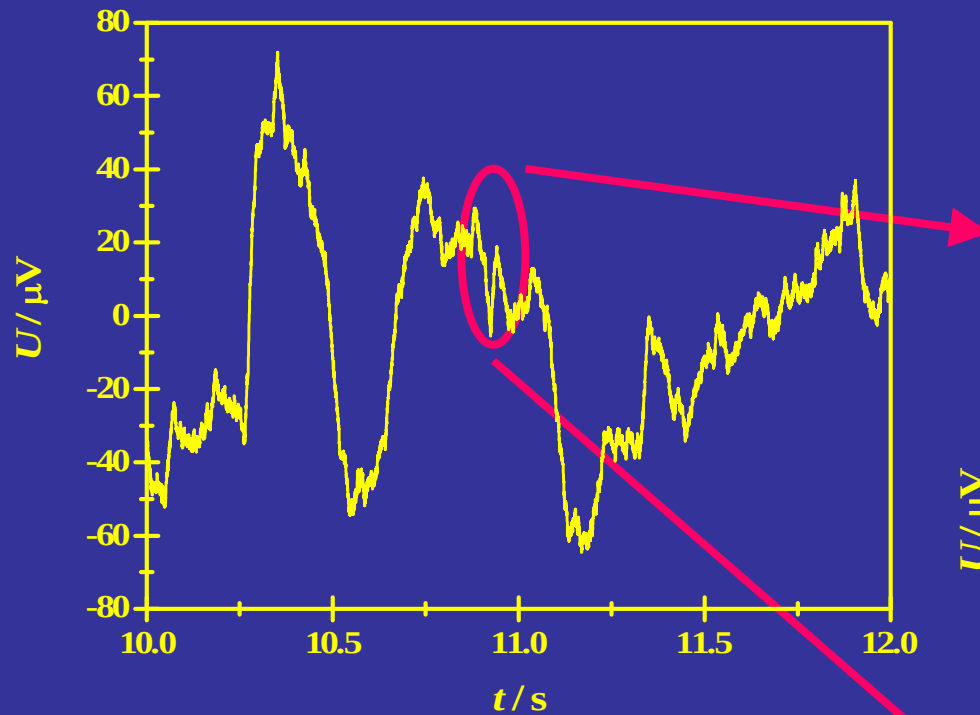
Power spectral density:

$$S = \text{const}$$



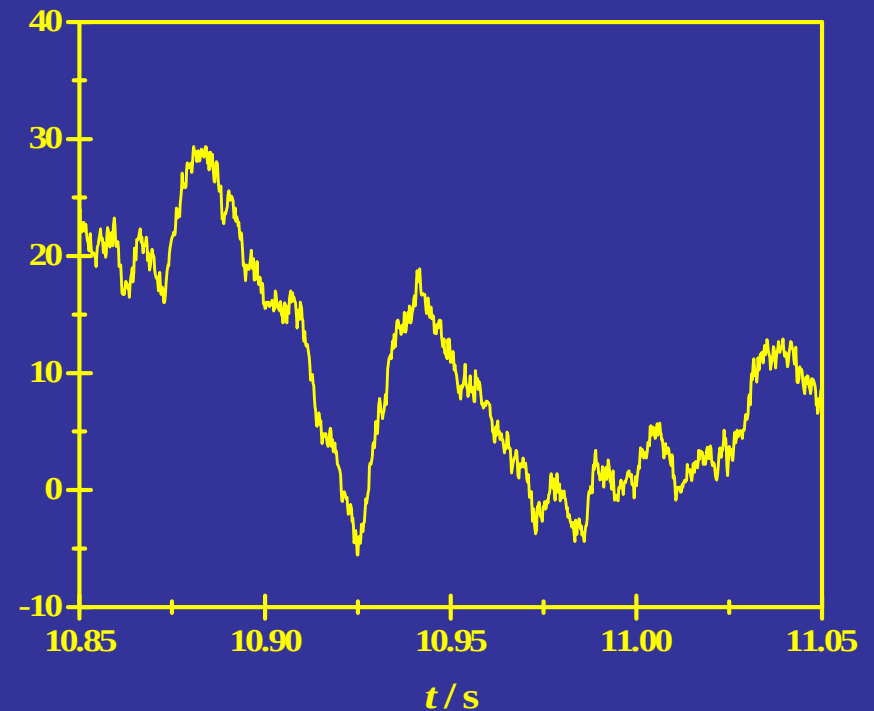
What is flicker noise – from mathematical point of you

Flicker noise:



Power spectral density:

$$S \sim 1 / f^\alpha$$



What is flicker noise – from physical point of you

Typical non-equilibrium noise

Power spectra: $S \sim 1 / f^\alpha$

Origin:
generally unknown

New definition of flicker noise – relative noise spectra

Thermal noise – “no wonder noise” :

in equilibrium noise and impedance are in one-to-one correspondence with each other !!!!

$$S_U(\omega)=4kTR \quad \text{or} \quad S_I(\omega)=4kT / R$$

$$S_U(\omega)=4kTZ'(\omega) \quad \text{or} \quad S_I(\omega)=4kT Y(\omega)'$$

New definition of flicker noise – relative noise spectra

The interesting part of noise is the deviation from the thermal (“no wonder”) noise

Relative noise spectra:

$$S_{rel}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} \equiv \frac{S_I(\omega)}{4kTY'(\omega)}$$

Measuring technique

“Noiseless” galvanostatic polarization

Measured quantities:

Voltage noise

Impedance

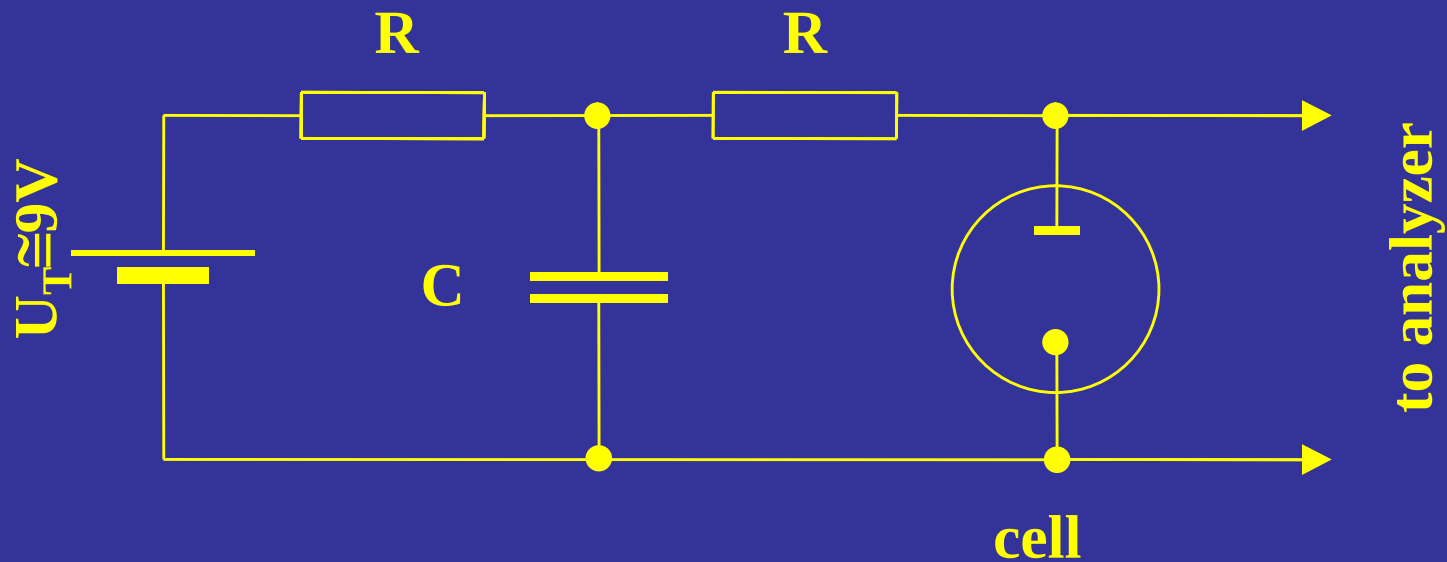
Cell: two electrodes

Working electrode : microelectrode

**Counter/reference electrode : large surface area “noiseless”
electrode (e.g. hydrogen filled Pd)**

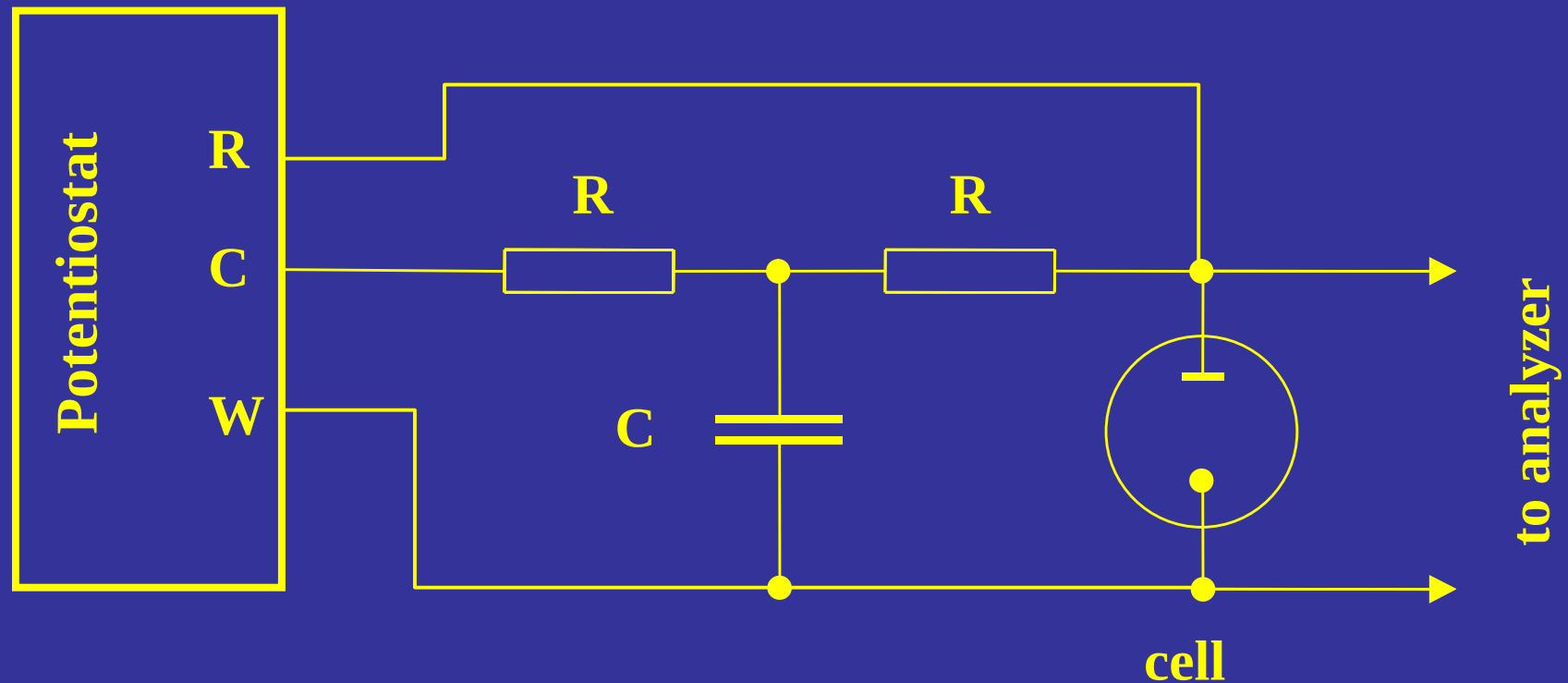
Measuring technique

“Noiseless” galvanostatic polarization

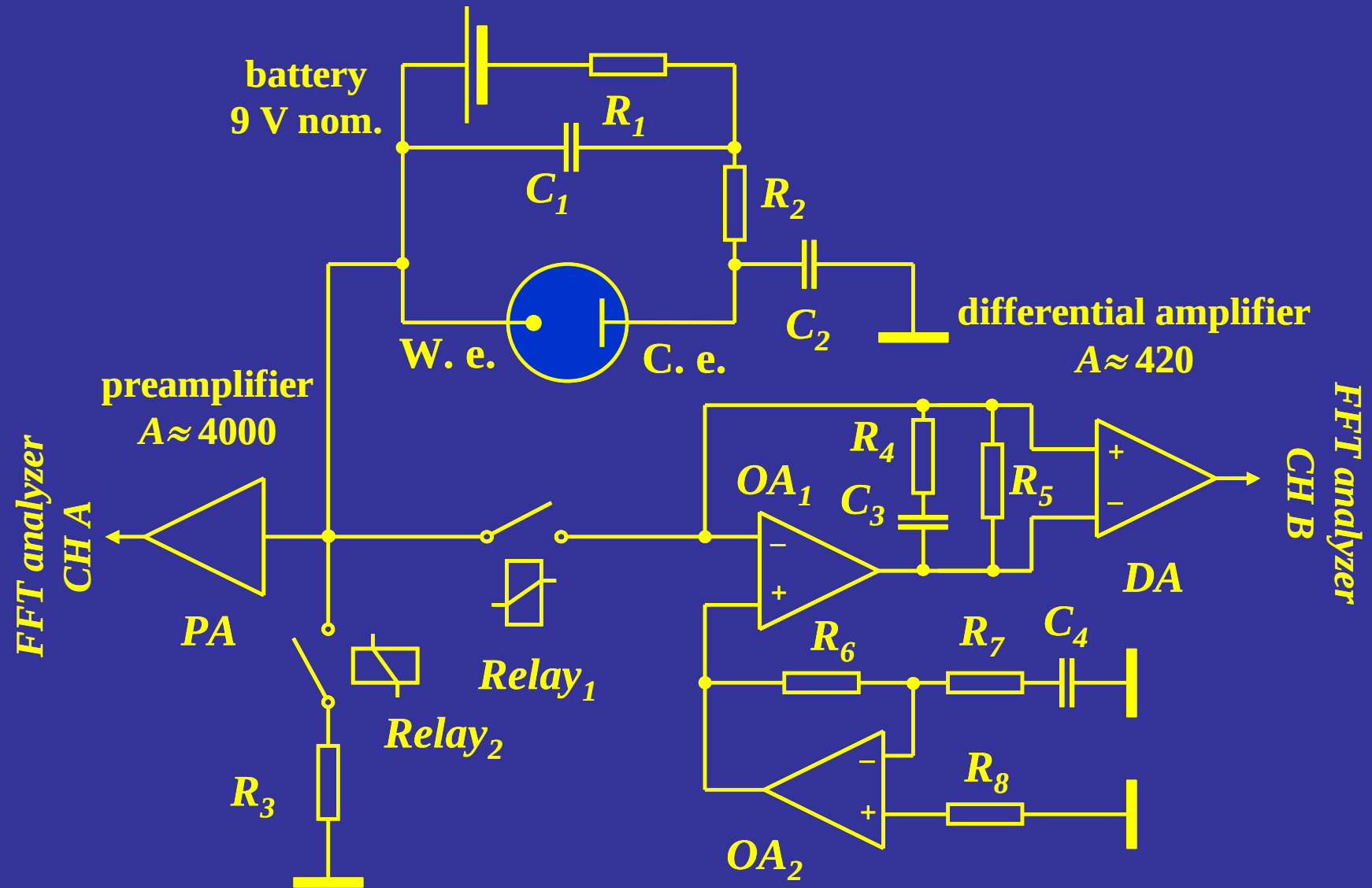


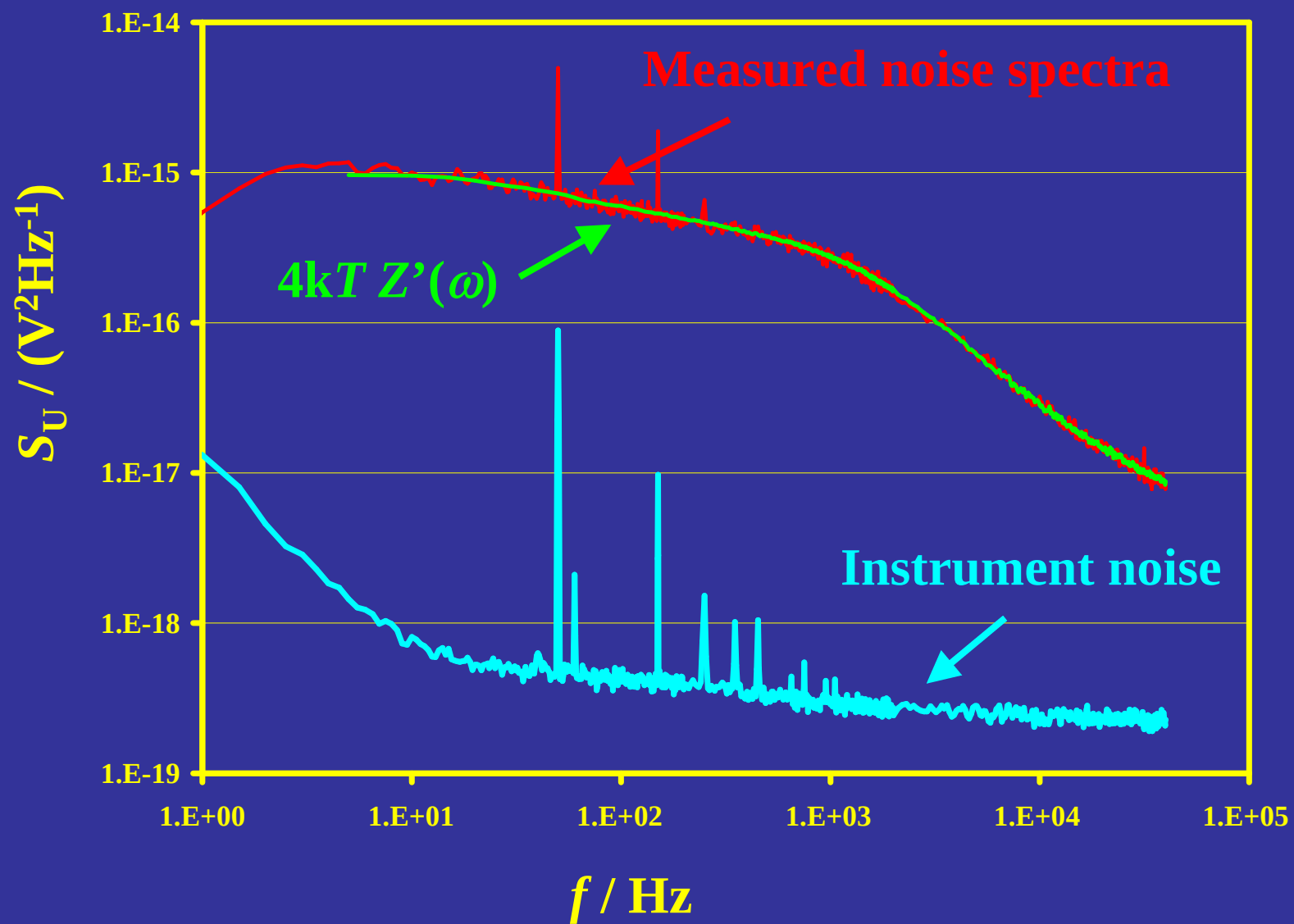
Measuring technique

“Noiseless” galvanostatic polarization

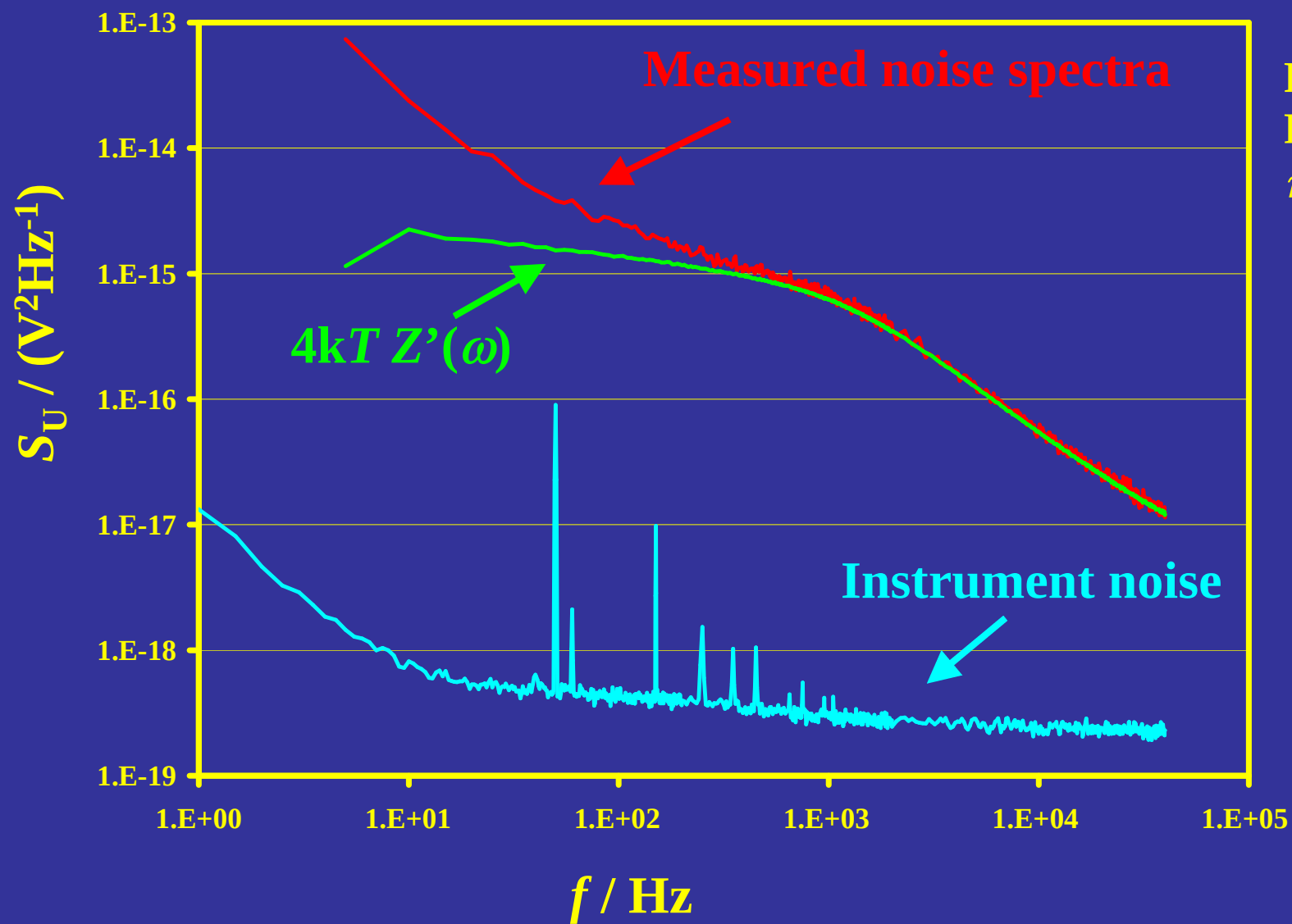


Measuring technique

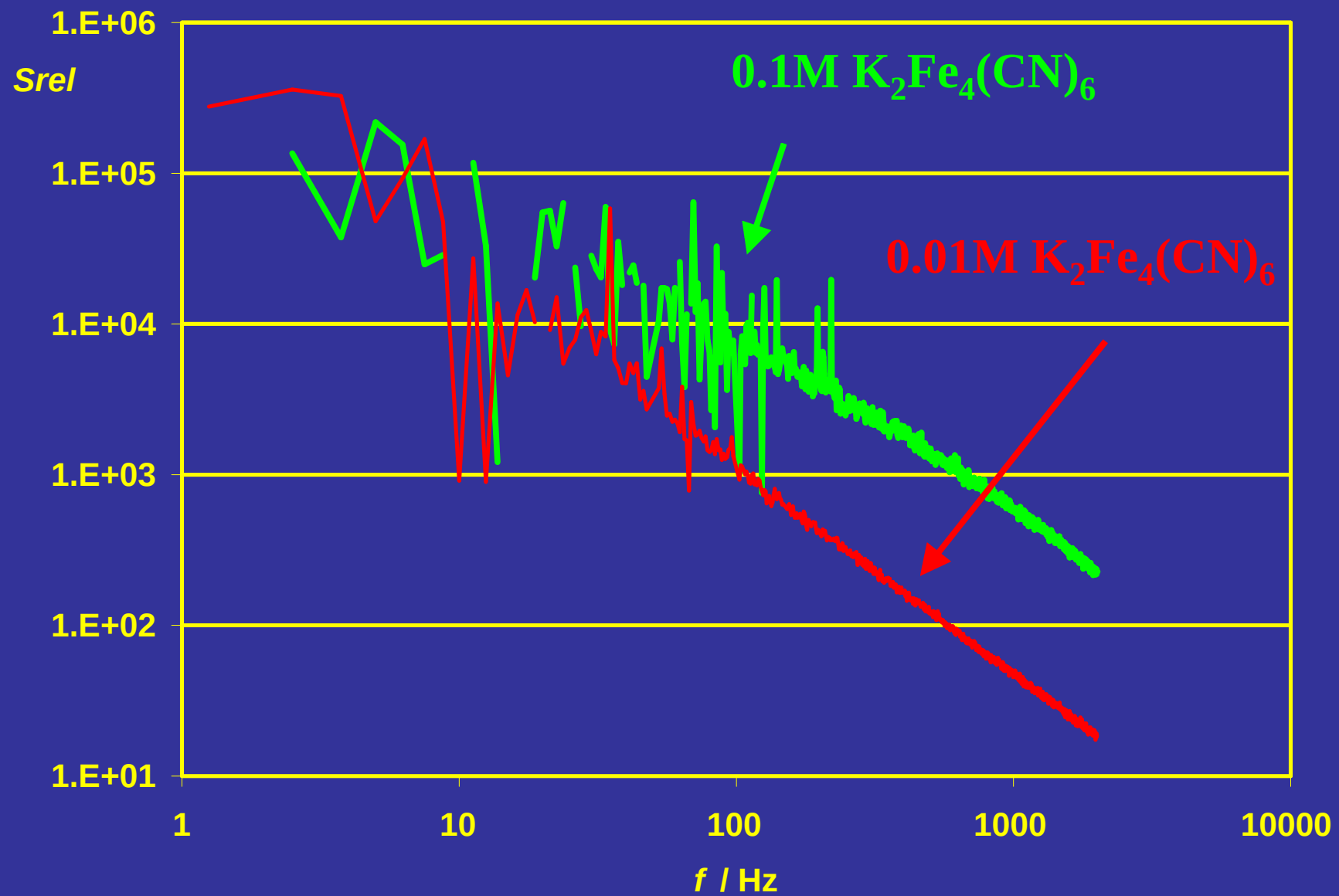




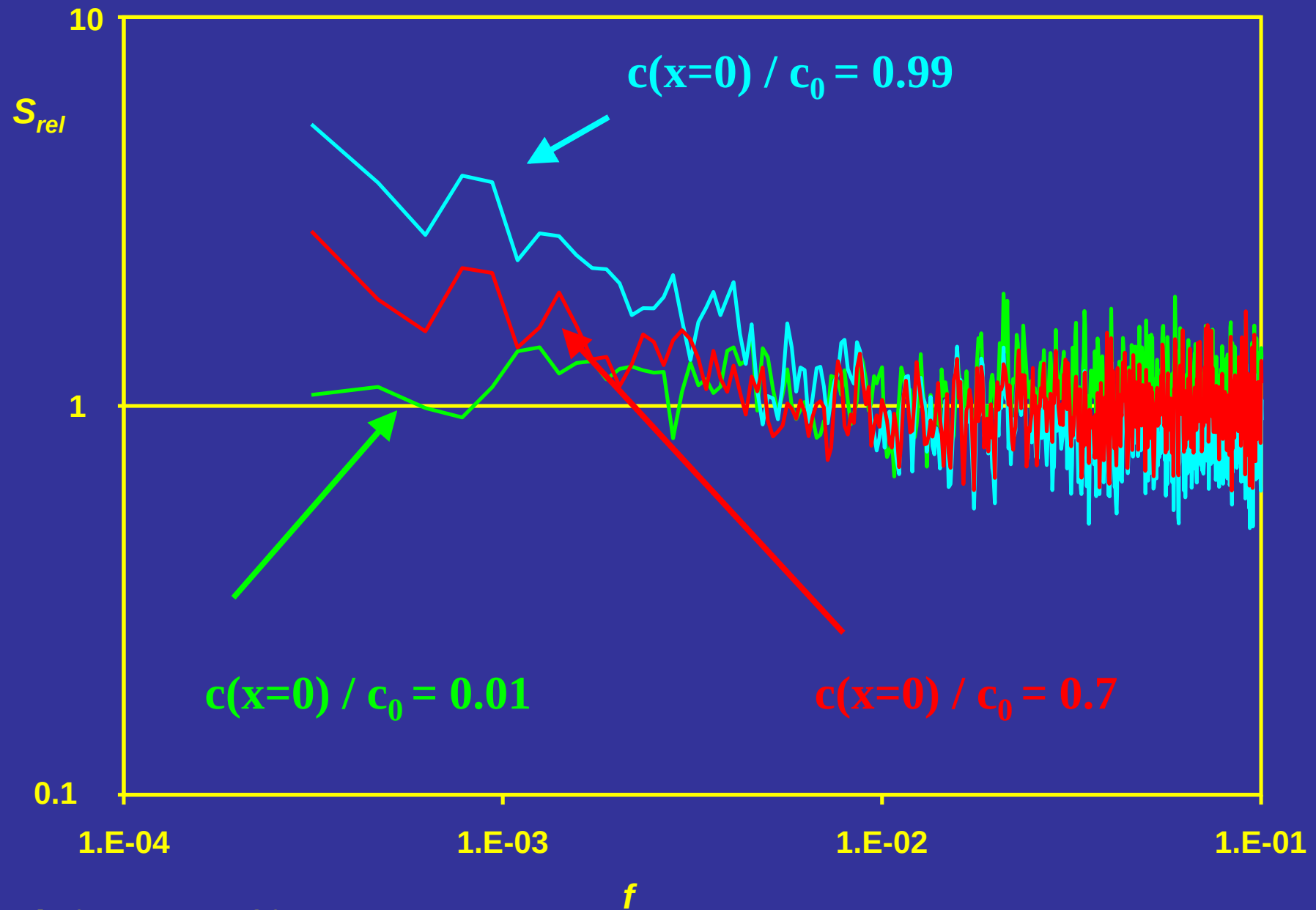
Pt $d=50\mu\text{m}$
 $\text{Fe}^{2+} / \text{Fe}^{3+}$
 $\eta = 0\text{V}$



Pt $d=50\mu\text{m}$
 $\text{Fe}^{2+} / \text{Fe}^{3+}$
 $\eta = -130\text{mV}$



Model calculation



Summary

Noise must always be measured together with impedance

Information is obtained from the deviation from the thermal (“no wonder”) noise

The relevant measure of noise : relative power density spectra

$$S_{rel}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} \equiv \frac{S_I(\omega)}{4kTY'(\omega)}$$

Diffusion control close to the limiting flux might be one of the reasons that lead to flicker noise/