# Brillouin scattering in glasses

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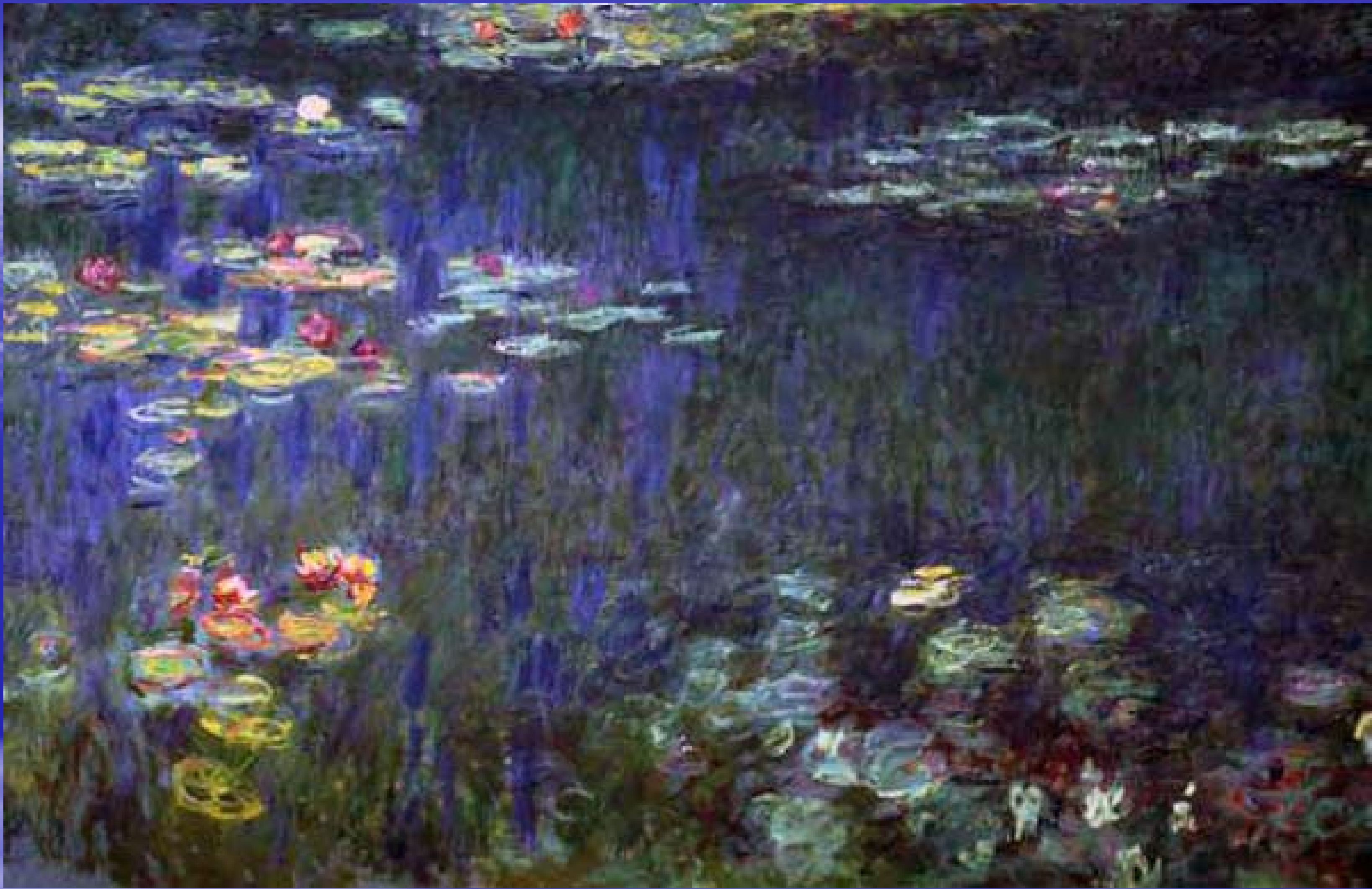

*« La lumière est le principal personnage dans le tableau »*
*(Light is the main subject of the picture)*


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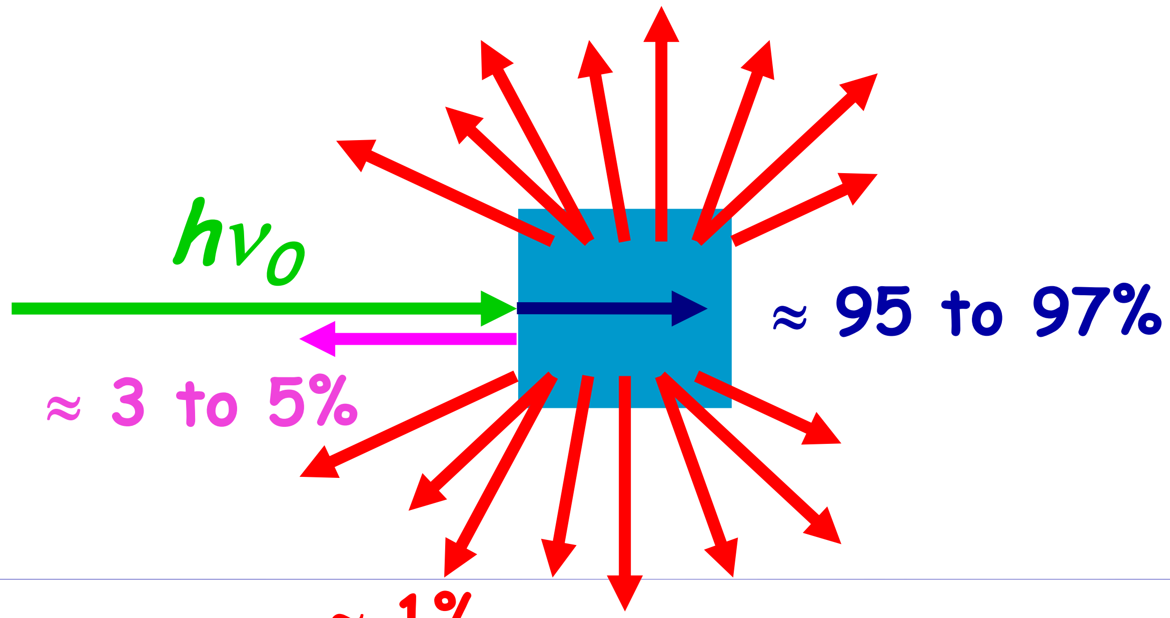
# I. Light scattering




**Scattered light**

$I_{scatt} \propto \nu_0^4$



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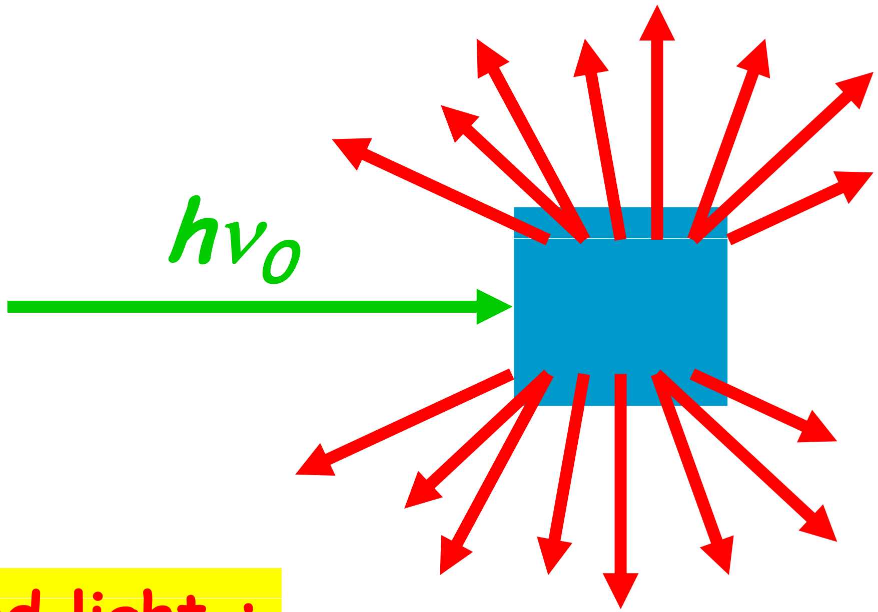


**Scattered light :**

$$I_{scatt} = I(\nu_0) + I(\nu \neq \nu_0)$$

≈ 90 to 99 %

Rayleigh scattering

≈ 1 to 10%

Raman effect



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# II. The Raman effect

$$I_{scatt} = I_{Rayl}(\nu_0) + I_{Raman}(\nu)$$

$$\nu_{Raman} = \nu_0 \pm \nu_i$$

$\nu_0$ : incident light frequency

$\nu_i$ : *i* vibrational mode frequency


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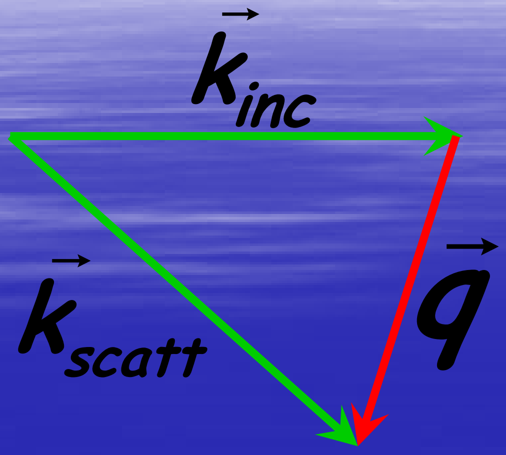
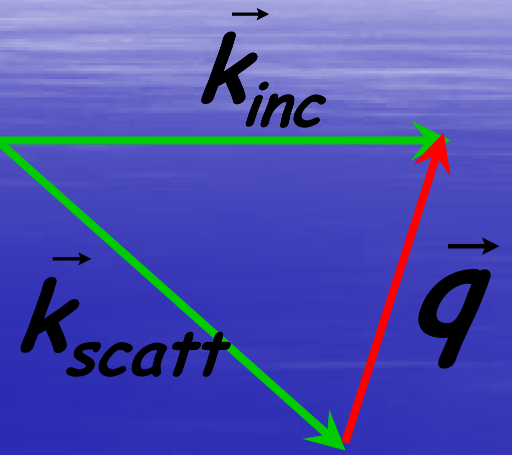
- Scattering by vibrational modes :




Annihilation of a vibrational mode

$\nu_s = \nu_0 + \nu_{phonon}$

antistokes

creation of a vibrational mode

$\nu_s = \nu_0 - \nu_{phonon}$

stokes

$$\left\|\vec{q}\right\| \cong \left\|\vec{k}_{inc}\right\| \cong \left\|\vec{k}_{scatt}\right\|$$



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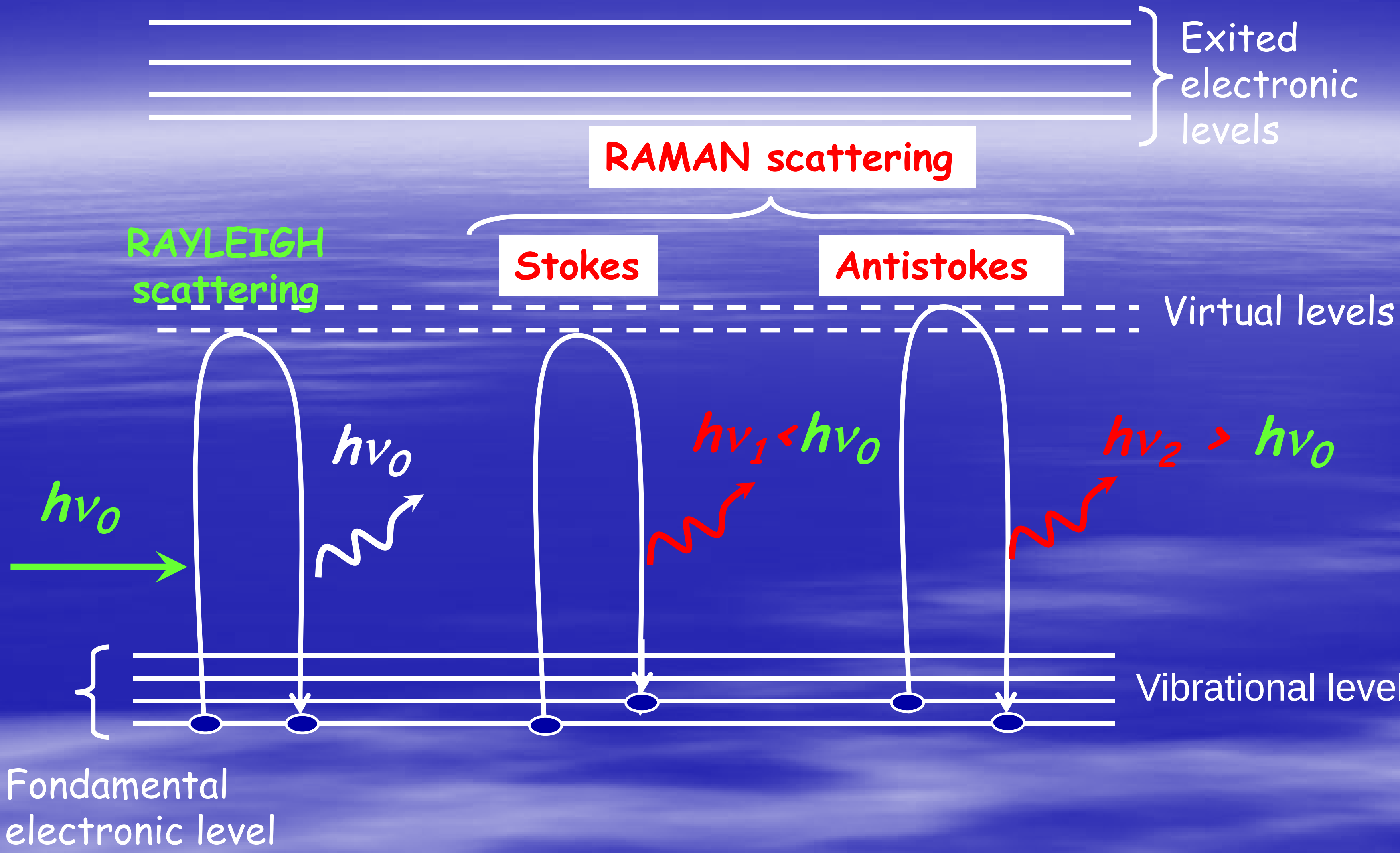


Maxwell – Boltzmann ⇒ Raman Stokes et anti-Stokes lines have not the same intensities



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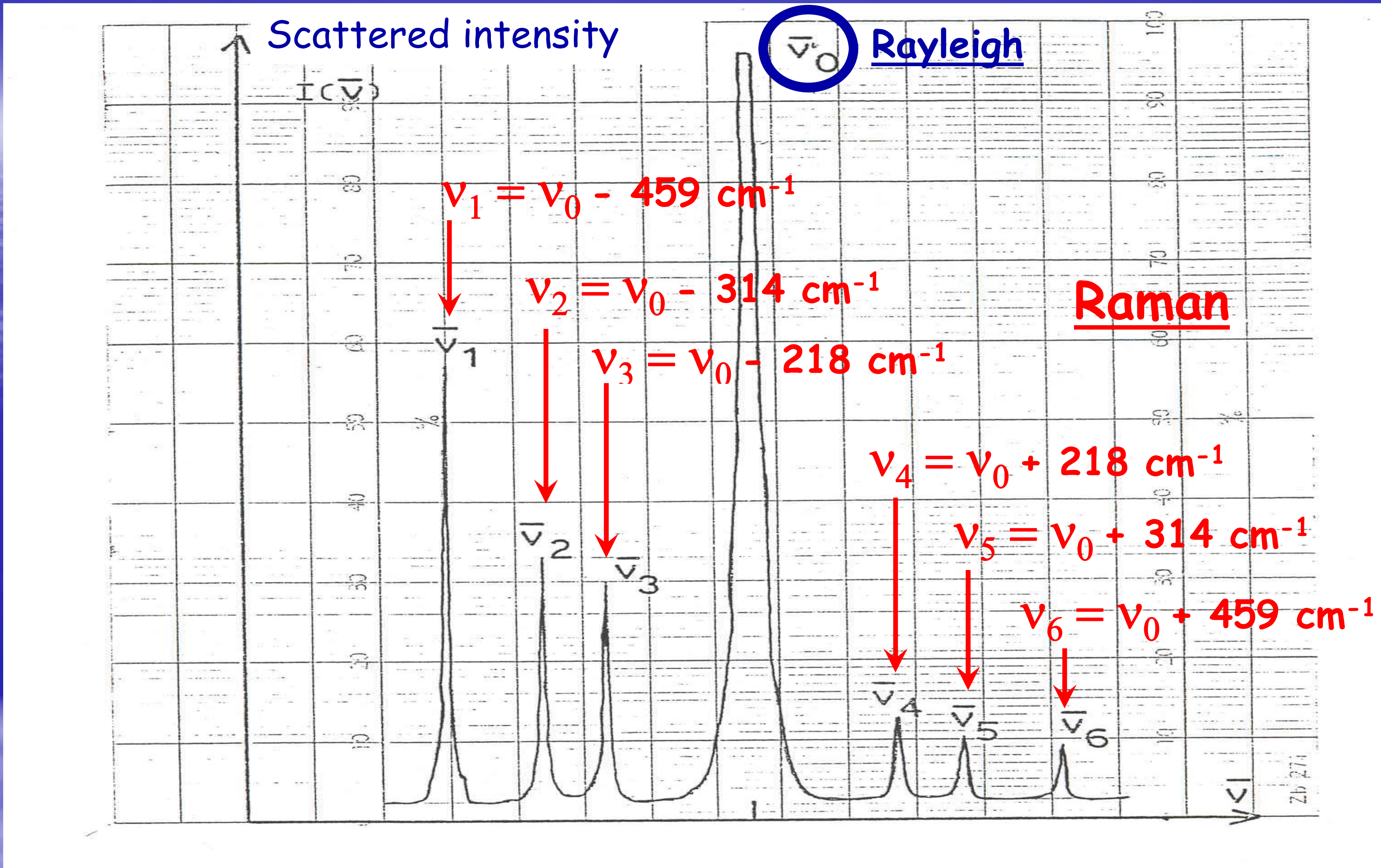


$CCl_4$ Raman spectrum at room temperature



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# III. The different types of light scattering

- Rayleigh scattering
- Raman scattering
- Brillouin scattering


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- Scattering by density inhomogeneities :

  **Rayleigh** scattering (**static**)

  **Brillouin** scattering (**dynamic**)

$$I_{id} = I_0 \left( \frac{8\pi^3}{3\lambda_0{}^4} \right) n^8 \left( \frac{\beta_{id}}{\rho} \right)^2 \left\langle |\Delta\rho|^2 \right\rangle V_0 \, k_B T$$

*J. Shroeder JACS 1973 ; K. Saito APL 1997*

$$\left\langle |\Delta\rho|^2 \right\rangle$$

- Static fluctuations : structural or chemical fluctuations
- Dynamical fluctuations : acoustical modes of vibration


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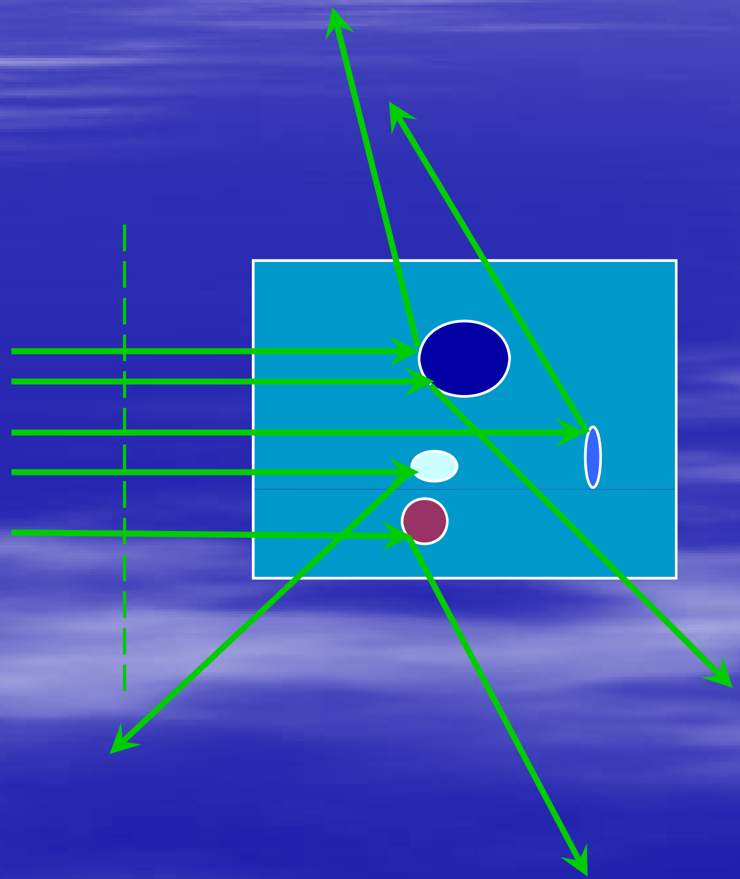
# Rayleigh scattering : due to the static fluctuations of refractive index

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# The case of a diatomic linear lattice, periodicity : *a*

$$\left\|\vec{q}\right\| \cong \left\|\vec{k}_{inc}\right\| \cong \left\|\vec{k}_{scatt}\right\| \cong \frac{2\pi}{\lambda_0} << \frac{\pi}{a}$$

**Raman scattering**

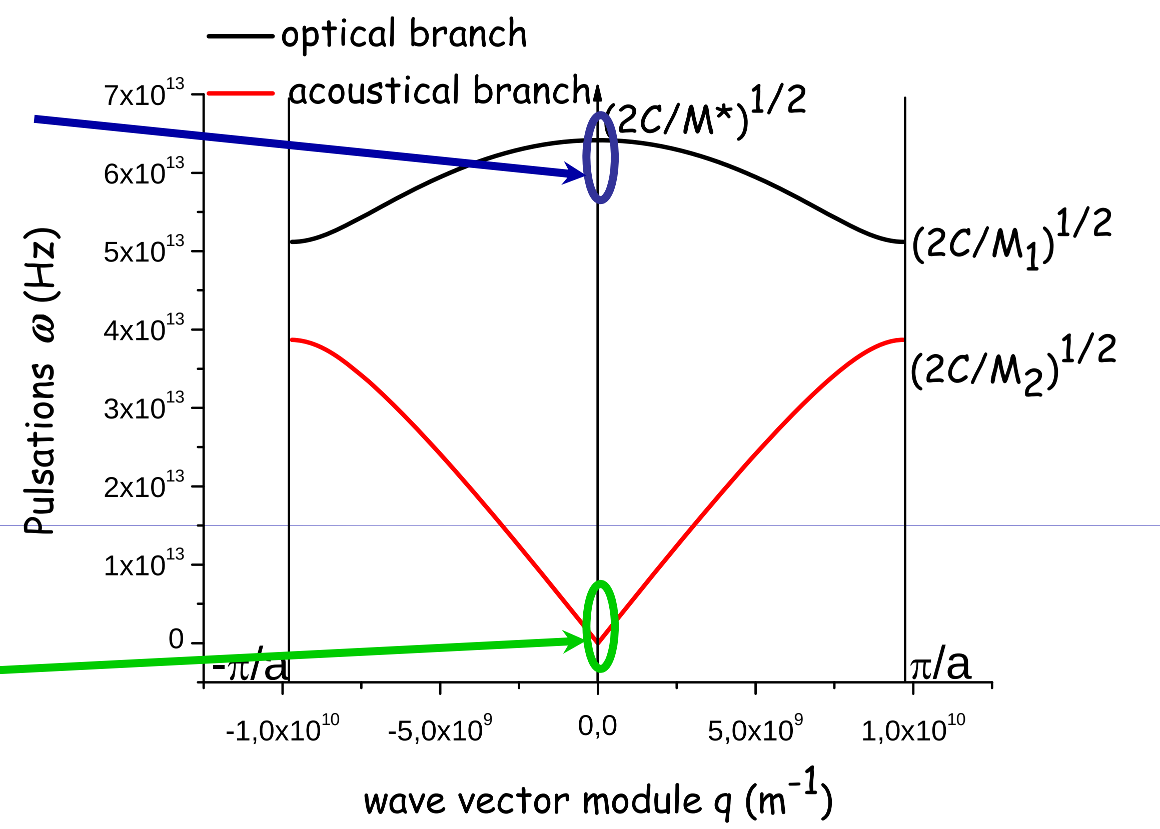
$50\ cm^{-1} < \nu < 2000\ cm^{-1}$

$1.5\ THz < \nu < 60\ THz$

**Brillouin scattering**

$\nu < 2\ cm^{-1}$

$\nu < 60\ GHz$





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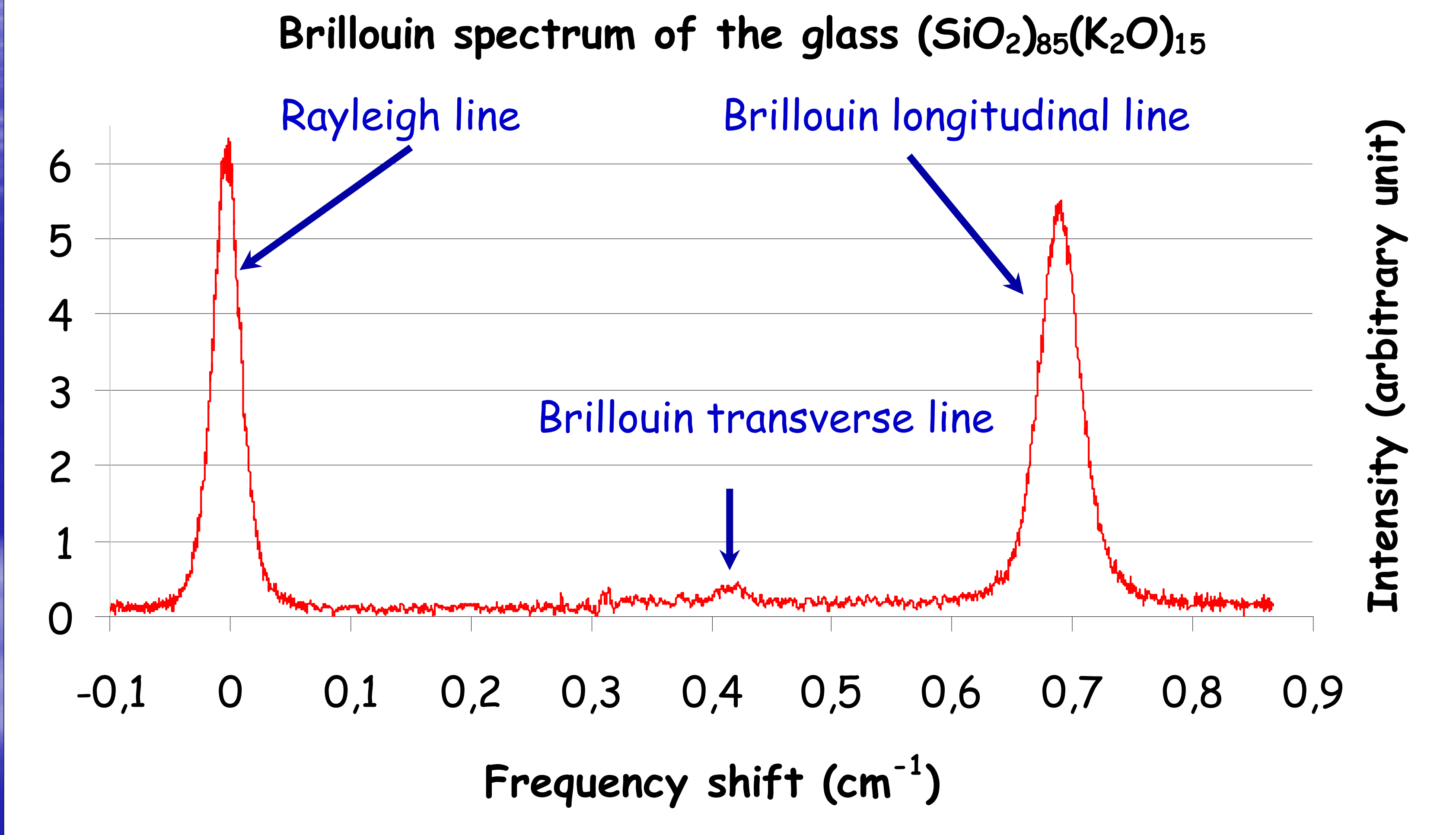
# IV. Brillouin and Rayleigh scattering





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## 1. Lines frequencies

For a right scattering configuration $\vec{k}_{inc} \perp \vec{k}_{scatt}$

$$\nu_\ell = \frac{\nu_0}{c} n\sqrt{2}V_\ell = \frac{\nu_0}{c} n\sqrt{\frac{2C_{11}}{\rho}}$$

Longitudinal acoustic mode of vibration

$$\nu_t = \frac{\nu_0}{c} n\sqrt{2}V_t = \frac{\nu_0}{c} n\sqrt{\frac{2C_{44}}{\rho}}$$

Transverse acoustic mode of vibration


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# From the Brillouin frequencies we deduce

The elastic properties of materials

*(see for example A.K. Varshneya 2006, or Y. Vaills web page)*

- $n$ and $\rho$ : measured by classical methods
- in an isotrope material : 2 independent elastic constants

Brillouin scattering $v_\ell$ $v_t$ $\Rightarrow C_{11}$ and $C_{44}$

$C_{12} = C_{11} - 2C_{44}$

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$$ Young's modulus

$$\chi = \frac{3}{3\lambda + 2\mu} = K^{-1}$$ compressibility

$\lambda = C_{12}$

$\mu = C_{44}$

Lame's constants

$$\sigma_p = \frac{\lambda}{2(\mu + \lambda)}$$ Poisson ratio


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## 2. Lines intensities

Scattering by density fluctuations :

Rayleigh scattering (static)

Brillouin scattering (dynamic)

**Freezing of density fluctuations at the glass transition**

$$I_{id} = I_0 \left( \frac{8\pi^3}{3\lambda_0^4} \right) n^8 \left( \frac{\beta_{id}}{\rho} \right)^2 \left\langle |\Delta\rho|^2 \right\rangle V_0 \, k_B T$$

*J. Shroeder JACS 1973 ; K. Saito APL 1997*

$T > T_g$

$$I_{id} = I_0 \left( \frac{8\pi^3}{3\lambda_0^4} \right) n^8 \, \beta_{id}^2 \, \chi_T(T) \, k_B T$$

# T < Tg

$$I_{id} = I_0\left(\frac{8\pi^3}{3\lambda_0^{\,4}}\right) n^8 \beta_{id}^{\,2}\left[\chi_{T,rel}(T_g)k_B T_g + \chi_{S,\infty}(T)k_B T\right]$$

*(J. Shroeder JACS 1973)*

**Rayleigh scattering :**

- static density inhomogeneities (elastic scattering)
- Incoherent atoms motions, non propagating excitations (quasielastic scattering)

*(R. Vacher JCP 1985)*

**Brillouin scattering** : inelastic scattering (dynamic density fluctuations : mechanical waves)



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## Landau-Placzek ratio

$$R_{L-P} = I_R / 2 I_{B_L}$$

In a viscoelastic material : *(N. Laberge JACS 1973)*

$$I_{Rayleigh} \propto \left\langle \Delta\rho_k^2 \right\rangle_{\nu=0} = (\rho_0^2 / V) k_B T [(\chi_T - \chi_S) + \chi_S^r]$$

Isobaric-entropy fluctuations

Fluctuations associated with structural variations in adiabatic-pressure fluctuations ⇔ relaxational compressibility

After quenching fluctuations are frozen into the material at the equilibrium structural configuration corresponding to the fictive temperature $T_f$

$$I_{Rayleigh} \propto \left\langle \Delta\rho_k^2 \right\rangle_{\nu=0} = (\rho_0^2 / V) k_B T_f [(\chi_T - \chi_S) + (\chi_S - C_{11}^{-1})]$$

(N. Laberge JACS 1973)

$$I_{Brillouin} \propto \left\langle \Delta\rho_k^2 \right\rangle_{\nu\neq 0} = (\rho_0^2 / V)[k_B T C_{11}^{-1}]$$


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## ⇒ Determination of a glass fictive temperature

$$R_{L-P} = \frac{T_f}{T}\left(C_{11}\chi_T - 1\right)$$

Directly deduced from by Brillouin scattering



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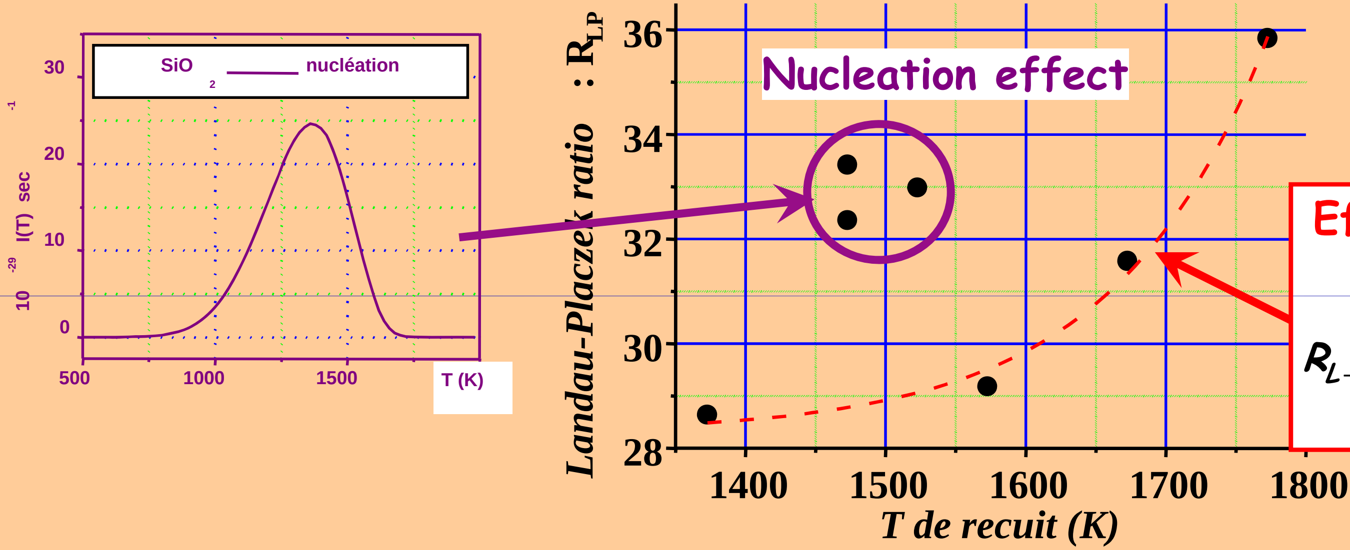
# Influence of heat treatment on silica for optical fiber

*Y. Vaills (CRMHT), P. Simon (CRMHT), G. Matzen (CRMHT),*
*H. Cattey (post-doc CRMHT-Alcatel), G. Orcel (Alcatel)*

## Effect of fictive de la temperature on light scattering in silica




**Effect of fictive temperature**

$$R_{L-P} = \frac{T_f}{T}\left(C_{11}\chi_T - 1\right)$$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- **From the Brillouin line intensities we deduce**

  - The photoelastic constants of the materials

    Coupling between elastic waves and electromagnetic waves

  - electromagnetic energy loss in materials

    Attenuation of electromagnetic wave in optical fibers

  - fictive temperature of glasses


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## 3. Lines shapes

*(See for example **R. Vacher JCP 1985, J. Schreoder JNCS 1988**)*

The experimental Brillouin line is :

a convolution of the natural Brillouin line with the apparatus function

- **natural Brillouin line** : narrow lorentzian shape
- **apparatus function** : a convolution of several contributions

  - The finite frequency width of the laser
  - The finite acceptance angle of the light gathering
  - The Airy's transmission function of the F-P interferometer

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- Extraction of the natural Brillouin line :

deconvolution of the spectrum : several technics

*(H.W. Leidecker J.A.S.A. 1967*
*D. Walton S.S.C. 1982*
*G.E. Durand IEEE J.Q.E.1968*
*A.S. Pine PR 1969)*

For example :

$$I^{exp}_{Brillouin}(\nu) = S_{nat}(\nu) * I_{app}(\nu)$$

**Lorentzian** ($S_{nat}(\nu)$)

**Gaussian** ($I_{app}(\nu)$)


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**Experimental Brillouin linewidth** : convolution of

- Natural Brillouin linewidth $\Delta\Gamma_B$ ($\approx$ 0.1 GHz)
- Instrumental linewidth ($\approx$ 1 GHz)

Phonon liftime $\tau$ :

$$\tau = 1/\Delta\Gamma_B$$

Phonon attenuation coefficient $\alpha$ :

$$\Delta\Gamma_B = \frac{\alpha V_\ell}{\pi}$$


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## From the Brillouin line shapes we deduce

- Structural informations via the lifetime of vibrational waves
- Characterization of relaxation phenomenons bonded to rearrangements of the structure
- Properties controlled by vibrational waves
  - Thermal expansion coefficient and its anomalies
  - Anharmonicity

*(R. Vacher ,communication at this Conference 8$^{th}$ ESG 2006, and PRB 2005)*


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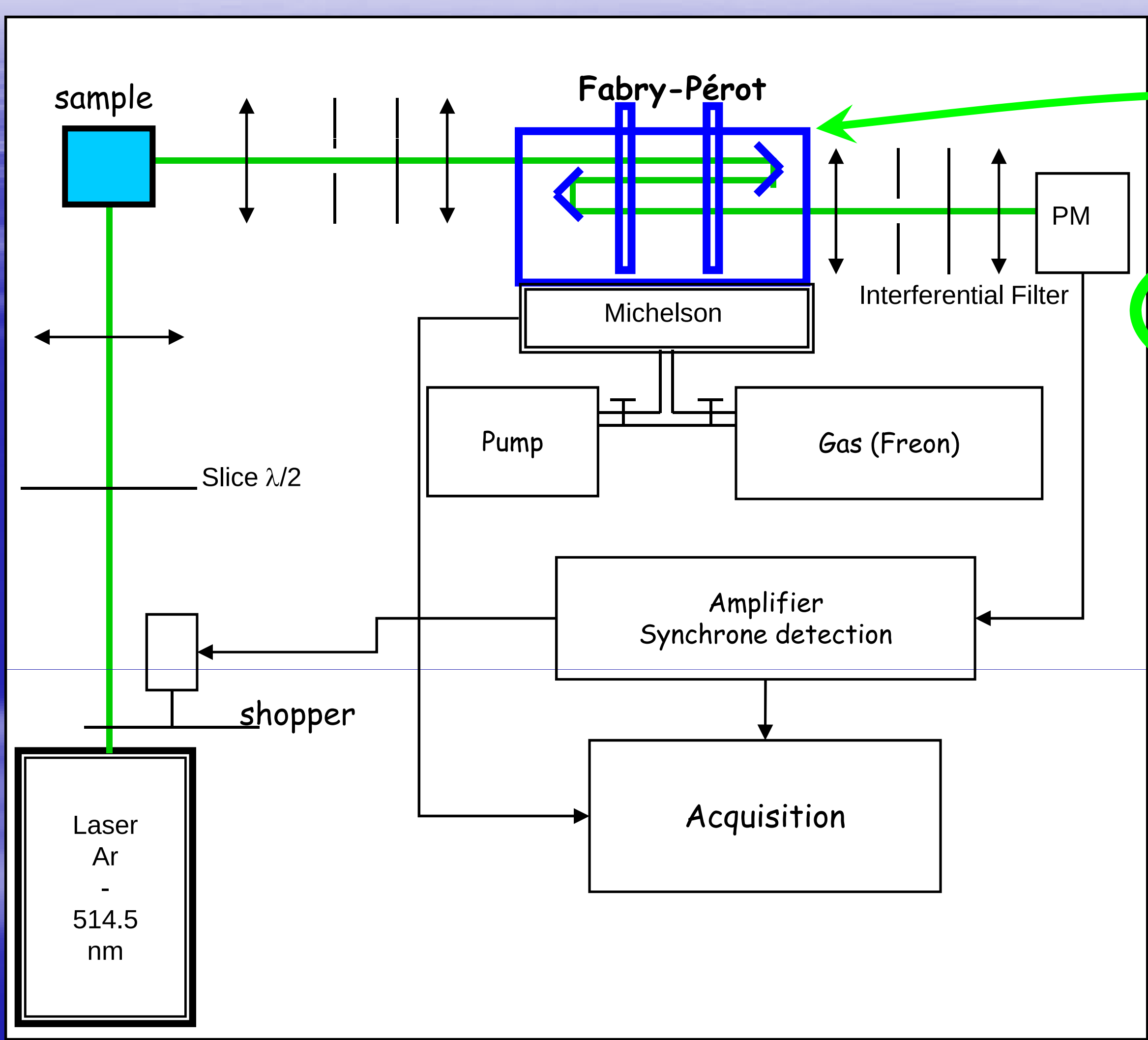
# V. Brillouin scattering apparatus




Pressure scanned Fabry-Pérot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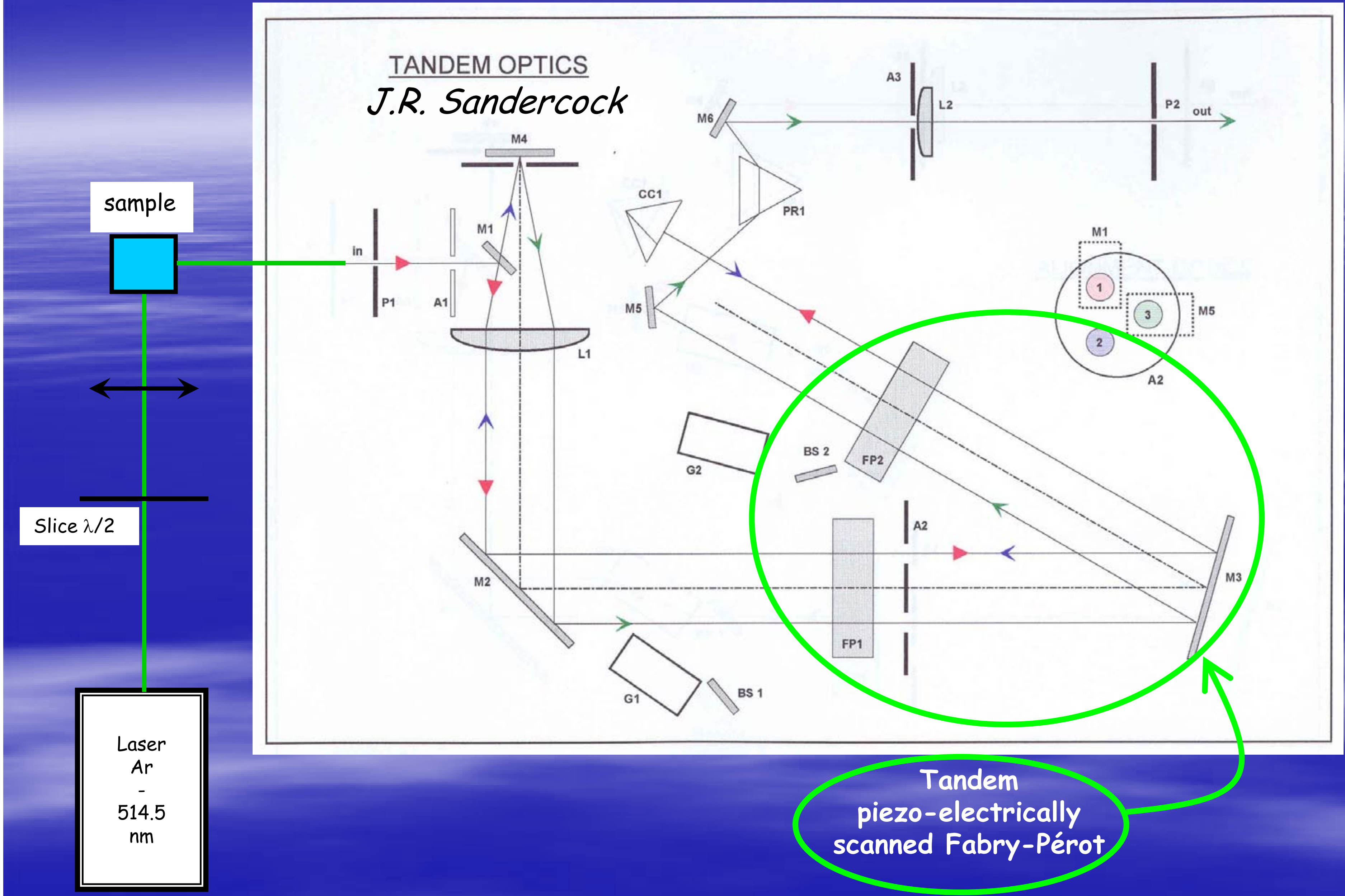



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# Comparison of the two devices

| Low Raman frequencies | Triple passed pressure scanned Pérot-Fabry | Tandem Triple passed FP piezo-el$^{ly}$ controlled |
|---|---|---|
| Contrast | 3 $10^{6}$ | $10^{11}$ |
| Finesse | 70 | 80 |
| Instrumental linewidth | 770 MHz | 500 MHz |
| Resolution | 770 MHz at $e$ = 2.76 mm<br>$R$ = 760 000 | 500 MHz at $e$ = 2 mm<br>$R$ = 1 170 000 |
| Accessible frequency range | 5 - 50 GHz<br>0,2 - 2 $cm^{-1}$ | 5 - 1500 THz<br>0,2 - 500 $cm^{-1}$ |
| Acquisition time for 1 scan | 45 minutes for 4 $cm^{-1}$ | 30 seconds for 500 $cm^{-1}$ |
| Spectra accumulations | Impossible | Possible |

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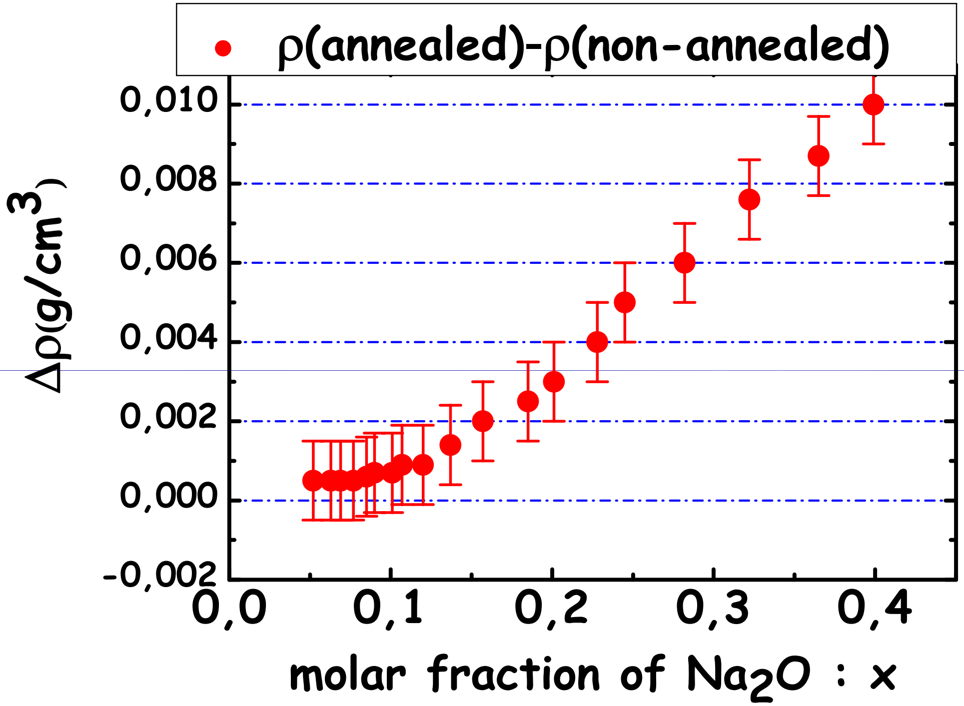
# VI. Brillouin scattering in glasses

- **Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$**

*(Y. Vaills JNCS 2001)*





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## Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$

### Hypotheses for calculation of elastic energy

- 1) We have considered that the variations of Na-O length could be the unique cause of the density change on annealing.
- 2) Consequently, **most of the elastic energy due to residual stress before annealing is located in the sodium atoms neighbourhood**.


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# Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$

- 3) In order to simplify the evaluation of the deformation tensor we suppose that the residual stresses are of hydrostatic type. Then the relative dilatation can be calculated from the relative variation of the density :

$$\theta = -\frac{\Delta\rho}{\rho}$$

- 4) We neglect the variations of interatomic bond strengths induced by the interatomic bond length variations.


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## Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$

Consequently the elastic energy stored in the non-annealed glass is given by :

$$\Phi = \frac{\theta^2}{6}(3C_{11} - 4C_{44})$$

$\Phi$ is the elastic energy per unit of volume, $C_{11}$ and $C_{44}$ are the elastic constants of the annealed glass (undeformed glass).


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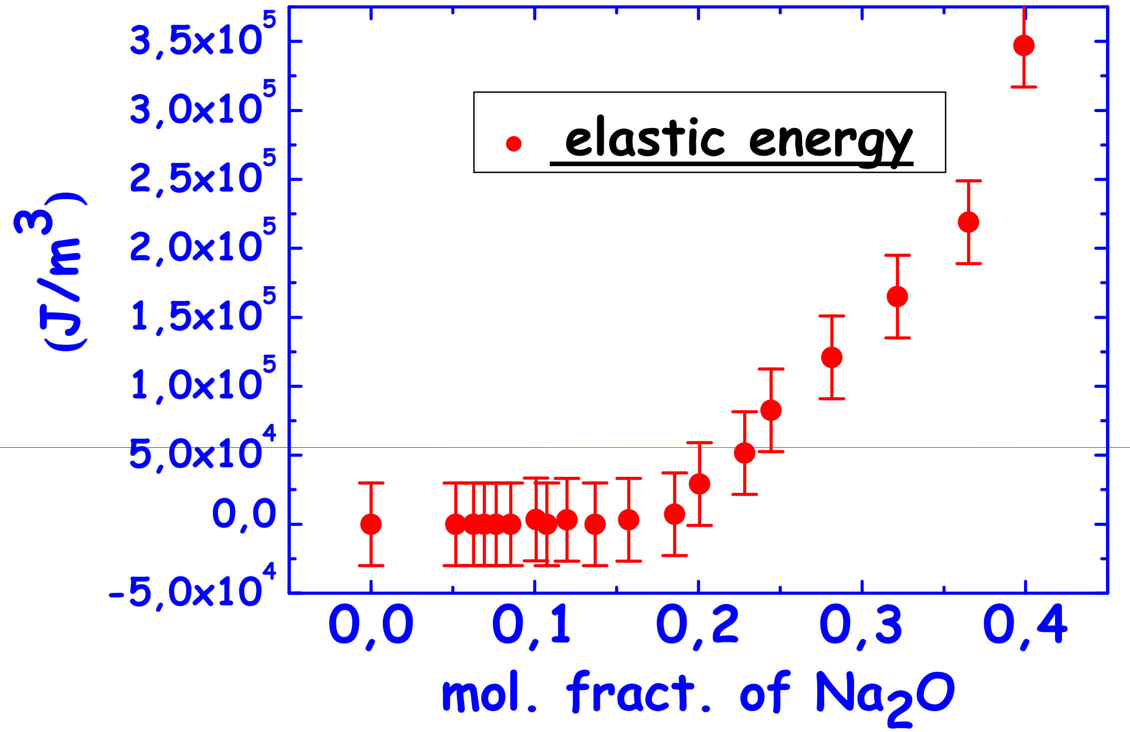




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## Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$

- If we write the total volume of the glass as :

$$V = V_{Na-O} + V_{SiO_2} = n\alpha\, a^3 + V_{SiO_2}$$

- where $a = r_{Na-O}$, then we can calculate $\delta a$ through annealing by :

$$\delta a = -\frac{\Delta\rho}{\rho}\frac{V}{n\,\alpha\, 3a^2}$$


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# Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$

Using

- the $\delta(r_{Na-O})$,
- the elastic energy variations through annealing
- and the fact that Na is known to be fivefold coordinated in $Na_2O$-$SiO_2$ glasses,

we calculated :

1) the elastic energy for each Na-O pair
2) the force constant of Na-O bond
3) the frequency associated to the Na vibrational mode


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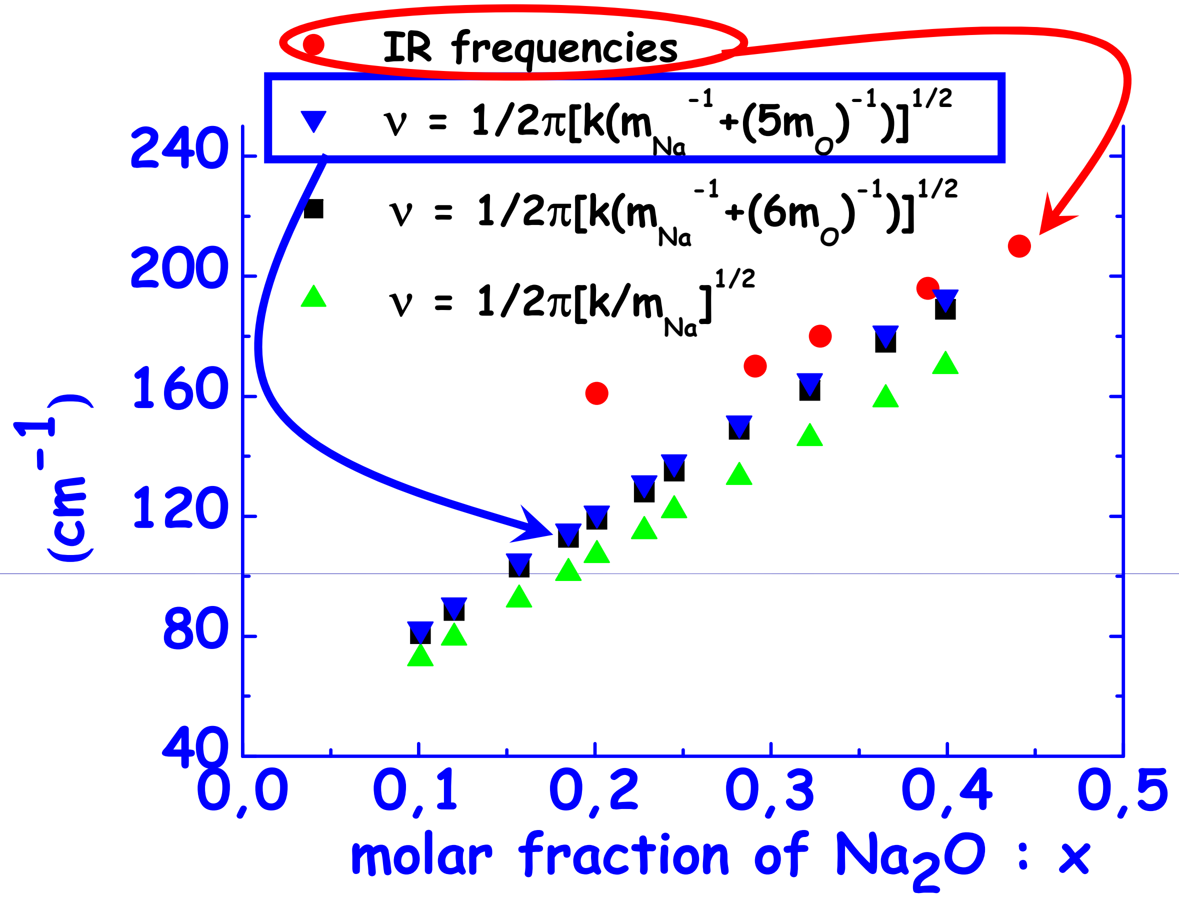
## Localisation of residual stresses in silicate binary glasses $(SiO_2)_{1-x}(Na_2O)_x$





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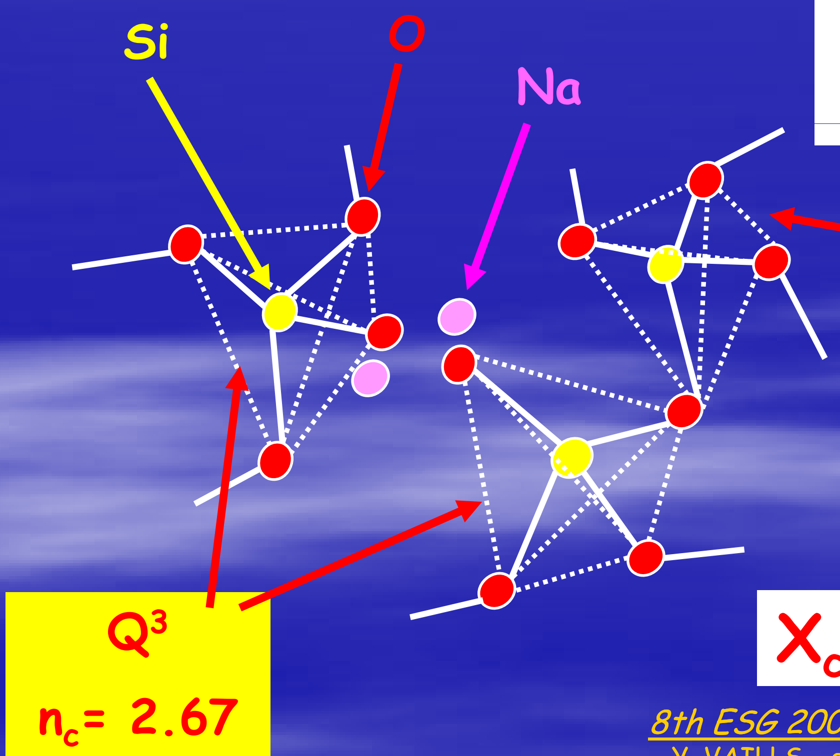
# constraint theory

(J.C. Phillips JNCS 1979)

Binary glasses $(SiO_2)_{1-x}(Na_2O)_x$




Na increases ⇒ connectedness decreases

$\bar{n}_c = 3$

⇓

$x = x_c$ Elastic phase transition from rigid to floppy phase

$X_c = 0.2$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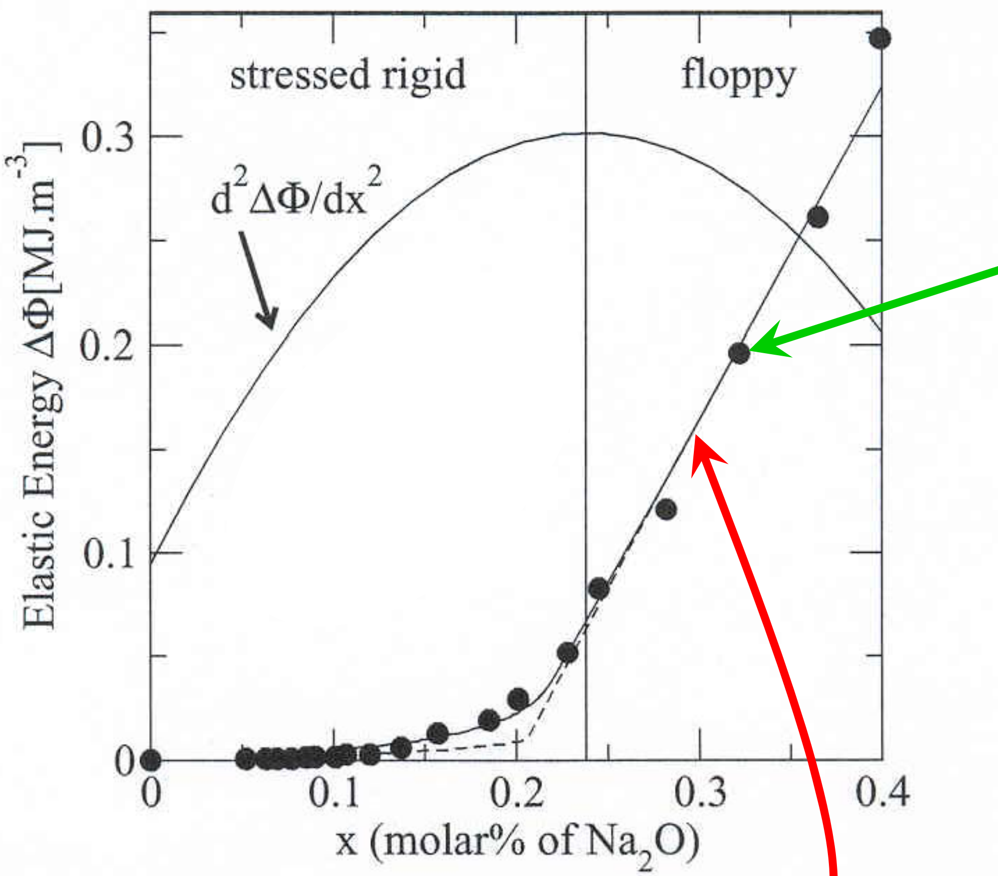
# Unsteady state and elastic free energy throw annealing : $\Delta\Phi$

*(Vaills J. Phys. C 2005)*




$$\Delta\Phi = \frac{1}{6}\left(\frac{\Delta\rho}{\rho}\right)^2 (3C_{11} - 4C_{44})$$

Random networks within mean-field theory : *f(x)= (10x-3)/3* floppy modes

x < 0.2 ⇒ 0 floppy modes

x > 0.2 ⇒ $\Delta\Phi$ parallels f(x)

In amorphous silica $d^2\Delta\Phi/dx^2$ :

Cusp at x = 0.211

*(Thorpe JNCS 2000)*

*Floppy modes fraction f(x)*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