Modulación de Coherencias Cuánticas Intermoleculares debido a difusión molecular restringida en materiales porosos.

Rodolfo Acosta

Imágenes por RMN (MRI)

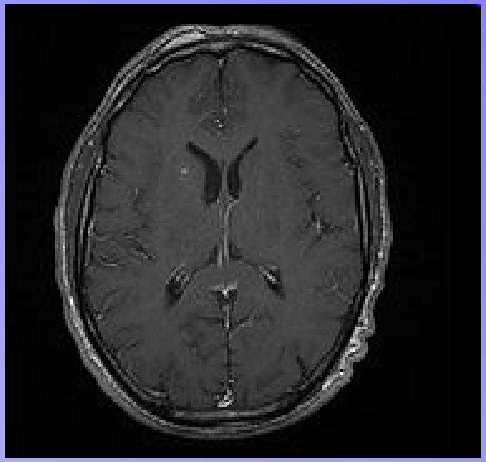
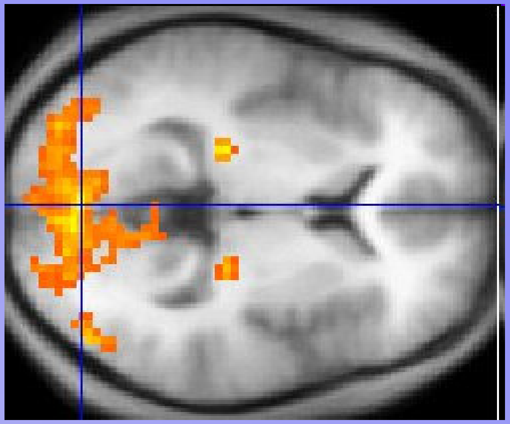


Imagen con secuencia sin contraste

Imagen con contraste de T_1

Imagen con contraste de T_2



Functional MRI

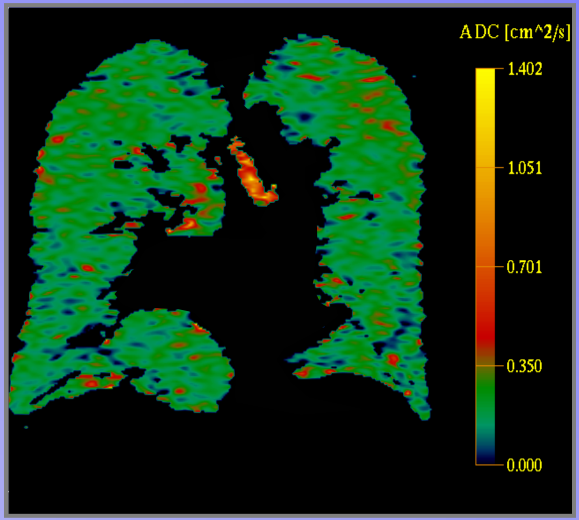
Gas MRI

Imágenes de pulmones con gases hiperpolarizados

^{3}He (^{129}Xe, $S^{19}F_6$)

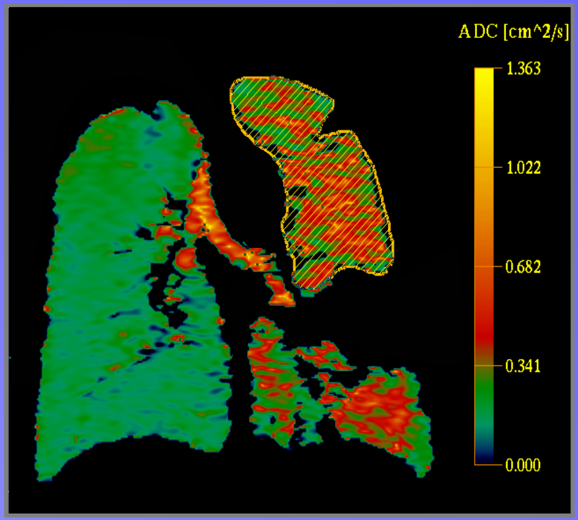
^{1}H

^{3}He

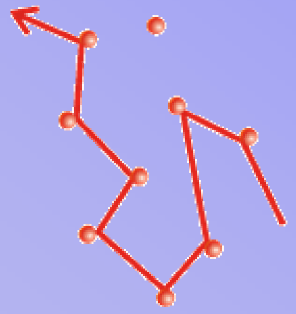


Pulmon sano

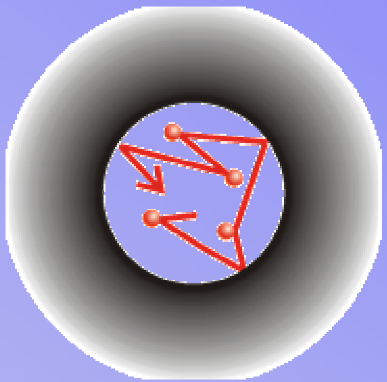
Mapas de Difusión



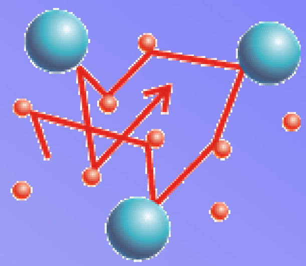
Pulmón con enfisema



Difusión libre



restringida

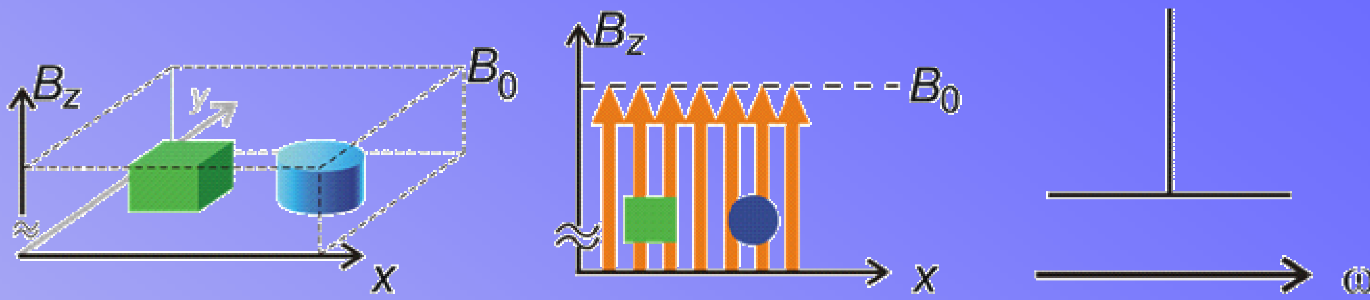


en presencia de otros gases

RMN – conceptos – Imágenes por RMN

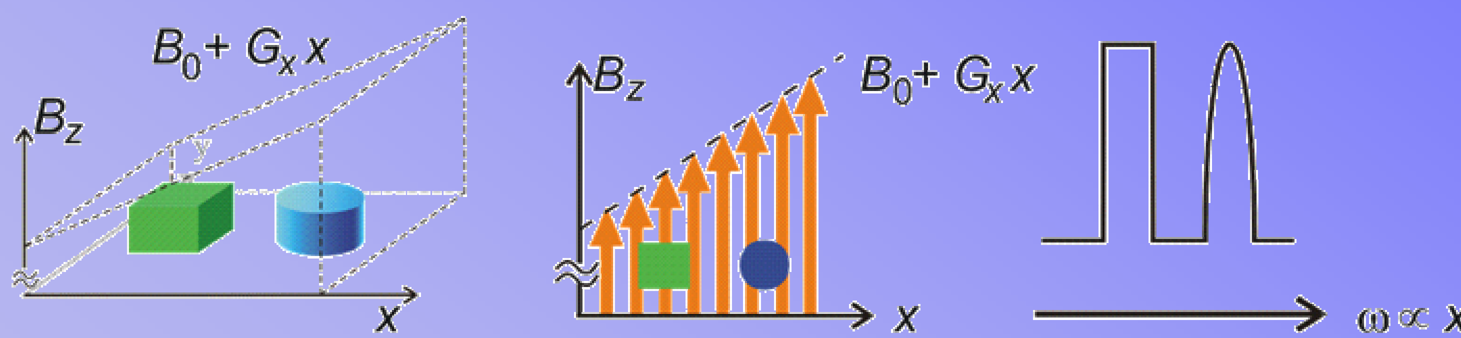
Espectroscopía

$$\omega = \gamma \boldsymbol{B}$$

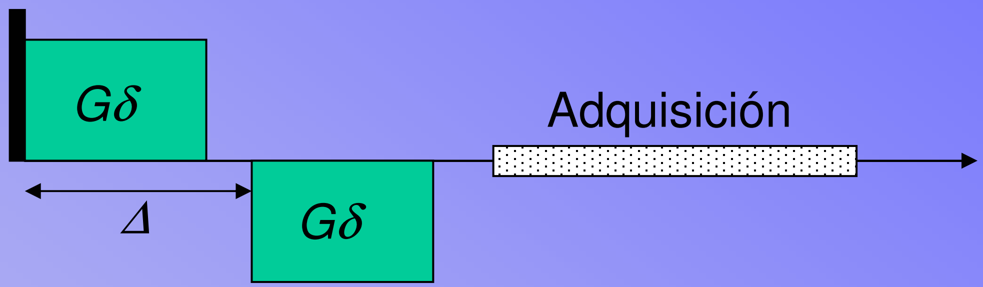


MRI

$$G_x = \frac{\partial B_z}{\partial x}$$

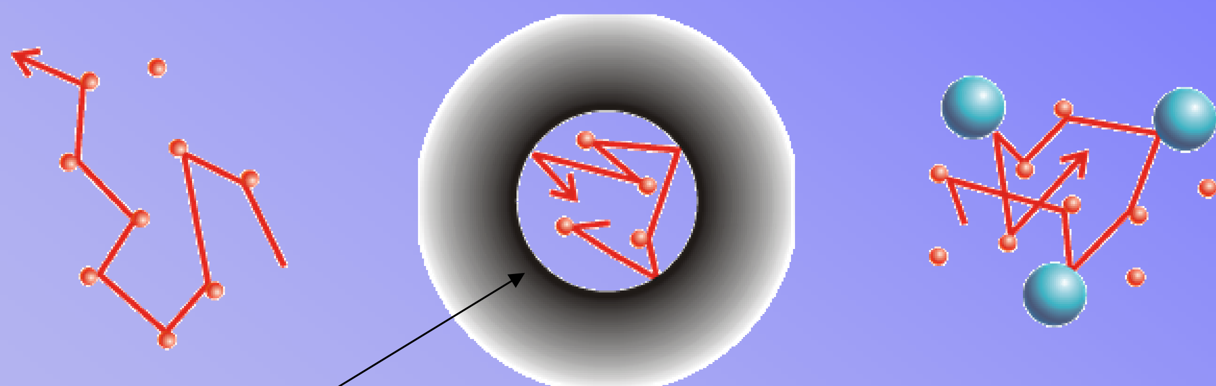


Atenuación debido a Difusión



$$\frac{S(D,G,\delta,\Delta)}{S_0} = \exp\left(-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D\right)$$

$$\left\langle \left[\vec{r}(t) - \vec{r}(0)\right]^2 \right\rangle = 2dD(t)t$$

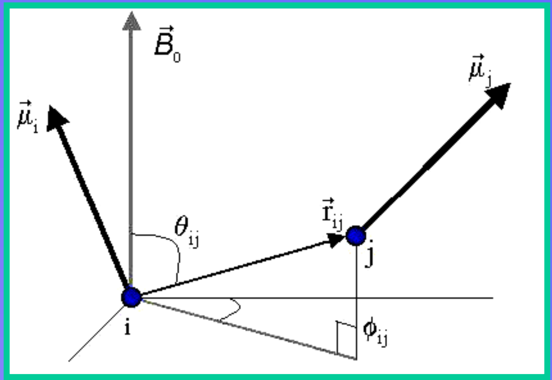


Diferencias de susceptibilidad magnética en las interfases introducen gradientes internos

$D(0)$: medición de tamaño de poro

$D(t)$: Interconectividad entre poros

Interacción Dipolar de largo alcance en líquidos



La energía de interacción entre pares de momentos magnéticos

$$H_d = \frac{\mu_i \mu_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5}$$

Hamiltoniano secular

$$H_d^{(0)} = \sum_{i<j} \frac{\mu_0 \gamma^2 \hbar}{4\pi} \frac{1}{r_{ij}^3} \frac{1}{2} \left(1 - 3\cos^2\theta_{ij}\right)\left(3 I_{iz} I_{jz} - \vec{I}_i \cdot \vec{I}_j\right)$$

Normalmente se asume que se promedia por movimientos moleculares

SI SE ROMPE LA SIMETRIA EL PROMEDIO ANGULAR NO SE CANCELA PARA MOLECULAS LEJANAS

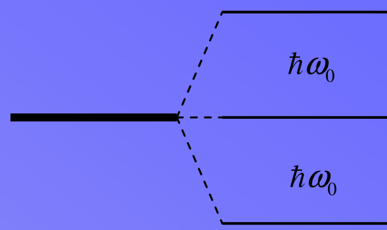
$\longrightarrow$ Agua T_{amb} difunde 150 μm en 5 seg.

GRADIENTES DE CAMPO ESTATICO

Construcción de la Matriz Densidad en líquidos

Despreciando cualquier interacción salvo Zeeman

$$\rho_{eq} = \frac{\exp(-\mathrm{H}/kT)}{\mathrm{Tr}\{\exp(-\mathrm{H}/kT)\}} = \frac{\prod_i \exp(-\hbar\omega_0 I_{zi}/kT)}{\mathrm{Tr}\{\exp(-\mathrm{H}/kT)\}}$$



Asumiendo distribución Gaussiana

$$\rho_{eq} = 2^{-N} \exp\left(-\sum_i \frac{\hbar\omega_0}{kT} I_{zi}\right)$$

APROXIMACION DE ALTA TEMPERATURA

$$\rho_{eq}^{HT} = 2^{-N}\left(1 - \frac{\hbar\omega_0}{kT}\sum_i I_{zi}\right)$$

No funciona para campos magnéticos lo suficientemente altos   Warren S. Warren, Science, **262**, 2005 (1993)

Solución exacta

$$\rho_{eq} = \sigma_{1,eq} \otimes \sigma_{2,eq} \otimes \cdots \otimes \sigma_{N,eq}$$ Matrices reducidas de espines individuales

$$\boxed{\begin{gathered}\sigma_{i,eq} \propto \exp\left(-\frac{\hbar\omega_0}{kT} I_{zi}\right) = \cosh\left(-\frac{\hbar\omega_0}{2kT}\right) 1 - 2\sinh\left(-\frac{\hbar\omega_0}{2kT}\right) I_{zi} \\ \mathrm{Tr}\left[\exp\left(-\frac{\hbar\omega_0}{kT} I_{zi}\right)\right] = 2\cosh\left(-\frac{\hbar\omega_0}{2kT}\right)\end{gathered}}$$

EXACTA $$\rho_{eq} = 2^{-N} \prod_i \left(1 - \Im I_{zi}\right), \quad \text{donde} \quad \Im = 2\tanh\left(\frac{\hbar\omega_0}{2kT}\right)$$

HT $$\rho_{eq}^{HT} = 2^{-N}\left(1 - \frac{\hbar\omega_0}{kT} \sum_i I_{zi}\right)$$ Coinciden a primer orden

Introduce términos del tipo: $\Im^2 I_{zi} I_{zj} \xrightarrow{90^\circ_y} \Im^2 I_{xi} I_{xj}$ CCD

Evolución con ecuación de Liouville y Hamiltoniano Dipolar

Coherencias cuánticas múltiples

$$
\rho(t)=\begin{array}{c}
\\
\langle +++| \\ \langle ++-| \\ \langle +-+| \\ \langle +--| \\ \langle -++| \\ \langle -+-| \\ \langle --+| \\ \langle ---|
\end{array}
\begin{array}{c}
\begin{array}{cccccccc}
|+++\rangle & |++-\rangle & |+-+\rangle & |+--\rangle & |-++\rangle & |-+-\rangle & |--+\rangle & |---\rangle
\end{array}\\
\begin{bmatrix}
\rho_{11} & \rho_{12} & \rho_{13} & \rho_{14} & \rho_{15} & \rho_{16} & \rho_{17} & \rho_{18}\\
\rho_{21} & \rho_{22} & \rho_{23} & \rho_{24} & \rho_{25} & \rho_{26} & \rho_{27} & \rho_{28}\\
\rho_{31} & \rho_{32} & \rho_{33} & \rho_{34} & \rho_{35} & \rho_{36} & \rho_{37} & \rho_{38}\\
\rho_{41} & \rho_{42} & \rho_{43} & \rho_{44} & \rho_{45} & \rho_{46} & \rho_{47} & \rho_{48}\\
\rho_{51} & \rho_{52} & \rho_{53} & \rho_{54} & \rho_{55} & \rho_{56} & \rho_{57} & \rho_{58}\\
\rho_{61} & \rho_{62} & \rho_{63} & \rho_{64} & \rho_{65} & \rho_{66} & \rho_{67} & \rho_{68}\\
\rho_{71} & \rho_{72} & \rho_{73} & \rho_{74} & \rho_{75} & \rho_{76} & \rho_{77} & \rho_{78}\\
\rho_{81} & \rho_{82} & \rho_{83} & \rho_{84} & \rho_{85} & \rho_{86} & \rho_{87} & \rho_{88}
\end{bmatrix}
\end{array}
$$

± 3 Coherencias cuanticas triples

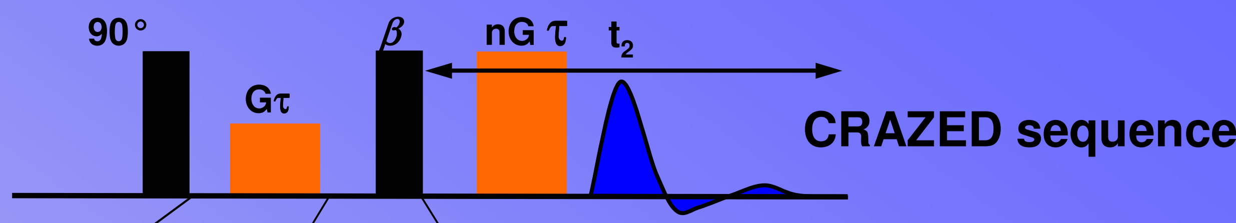
0 Poblaciones

± 1 Observables por RMN

Medición de i-MQC – Marco clásico

Fase introducida por Gradientes

$$\phi(z) = \gamma G z \tau$$



$$\rho(0^+) = I_x$$

$$\rho(\tau^-) = I_x \cos(\phi(z)) + I_y \sin(\phi(z))$$

$$\rho(\tau^+) = I_x \cos(\phi(z)) \cos\beta - I_z \cos(\phi(z)) \sin\beta + I_y \sin(\phi(z))$$

Dipolar Demagnetizing Field $$B_d = -\frac{1}{\gamma \tau_d} \cos(\phi(z)) \sin\beta$$

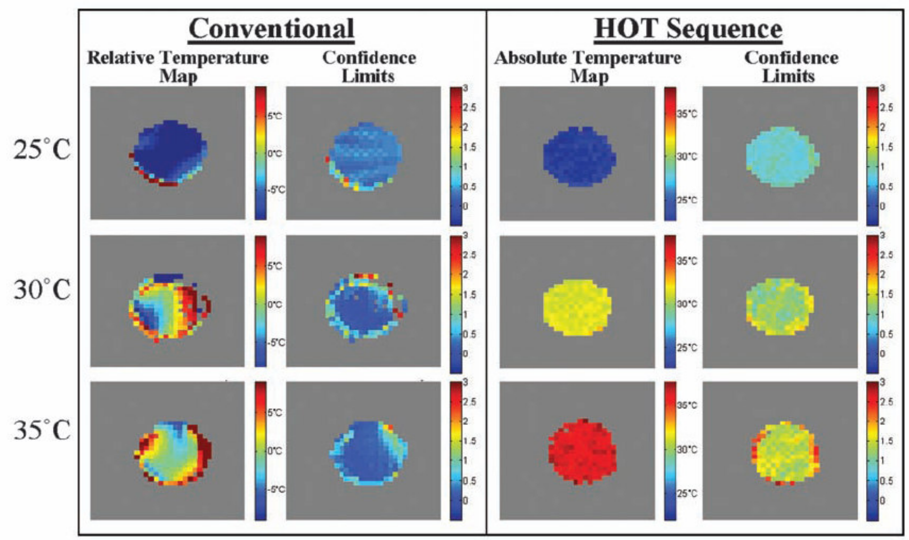
Dipolar Demagnetizing Time $$\tau_d = \frac{1}{\gamma \mu_0 M_0}$$

CONDICIONES
- **Magnetizacion alta**
- **Difusion baja**

Accurate Temperature Imaging Based on Intermolecular Coherences in Magnetic Resonance

Gigi Galiana,[1,2] Rosa T. Branca,[2] Elizabeth R. Jenista,[2] Warren S. Warren[2]*

Conventional magnetic resonance methods that provide interior temperature profiles, which find use in clinical applications such as hyperthermic therapy, can develop inaccuracies caused by the inherently inhomogeneous magnetic field within tissues or by probe dynamics, and work poorly in important applications such as fatty tissues.
suitable for imaging temperature in a wide r
resonances of intermolecular zero-quantum c
flipping down a nearby fat spin. We show th
temperatures in vivo on an absolute scale.



Temperature, one of the most fundamen
intrinsic quantities of matter, is very d
ficult to measure noninvasively benea
the surface of an object. A general method
image interior temperatures in soft matter cou
find a wide range of experimental applications

kill cancer
and numer
sensitive fo
drugs selec
In practice,
is compron
perature in
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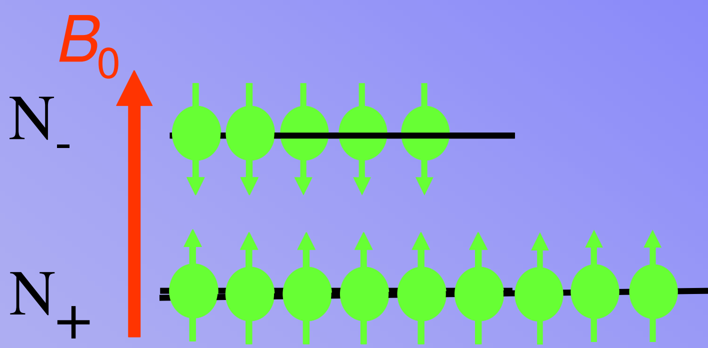
Sensitividad en RMN



Magnetization: $M_0 = \frac{1}{2} N_s \gamma\hbar P$
(I =1/2)

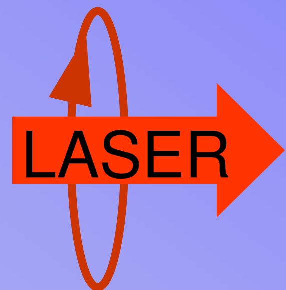
Polarization: $P = \frac{N_+ - N_-}{N_+ + N_-}$

Boltzmann: $\cancel{\frac{N_-}{N_+}} = \exp\left(-\frac{\gamma\hbar B_0}{kT}\right) \xrightarrow[\gamma\hbar B_0 << kT]{} \boxed{P \approx \frac{\gamma\hbar B_0}{2kT}}$

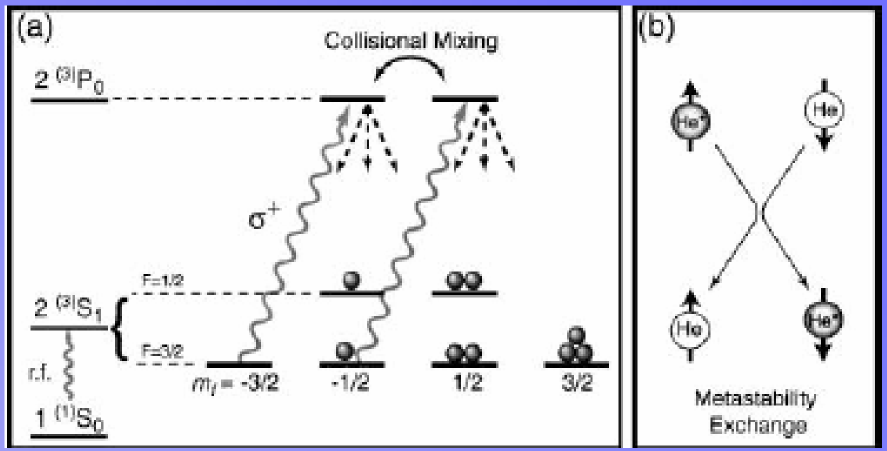
hyperpolarized gases (3He, 129Xe): $P \approx 10^{-1}$ (factor >10000)

$P \approx 5 \cdot 10^{-6}$

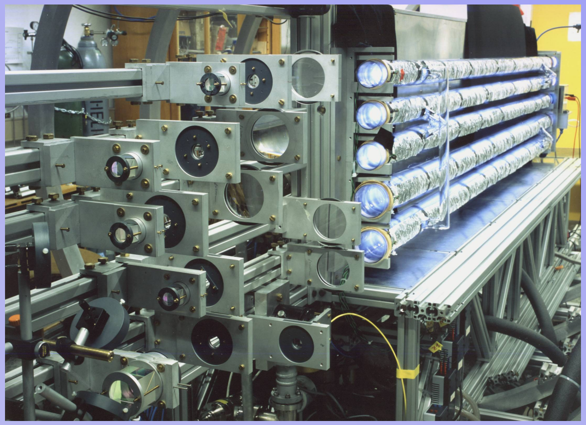
Metastable ^{3}He Pumping

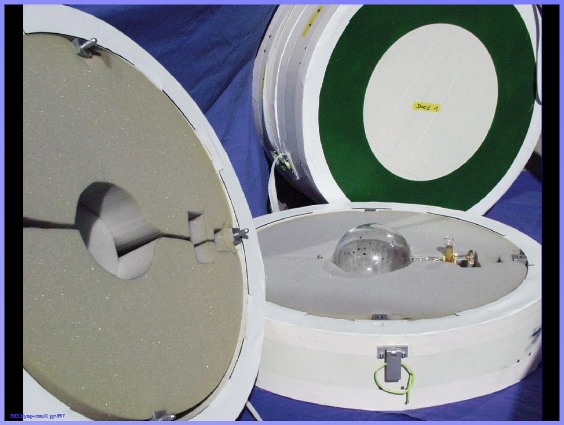


λ = 1083nm



Electronic Energy levels Polarization Transfer

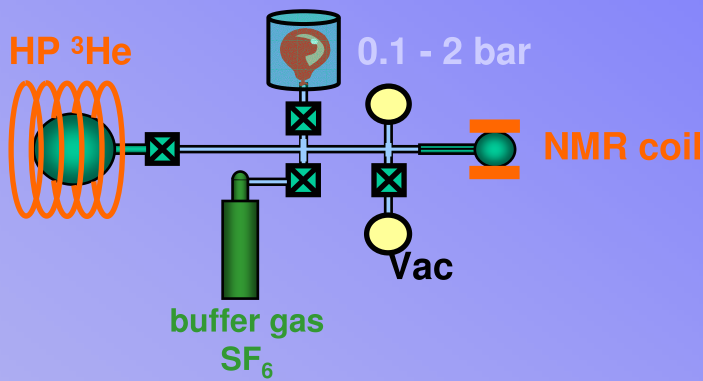


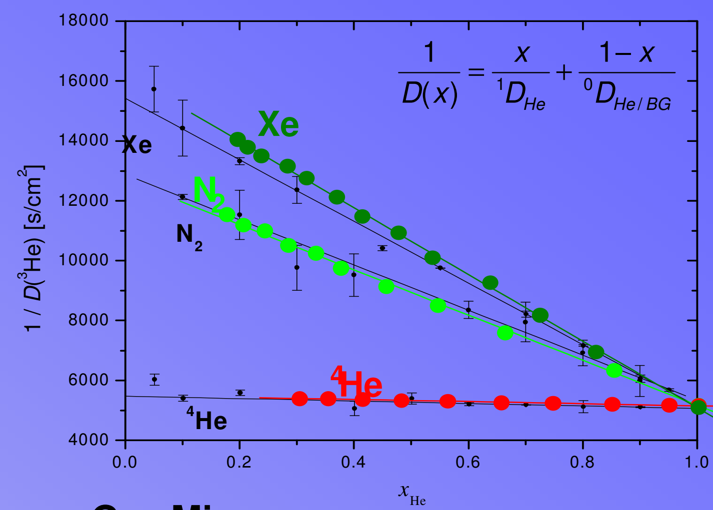


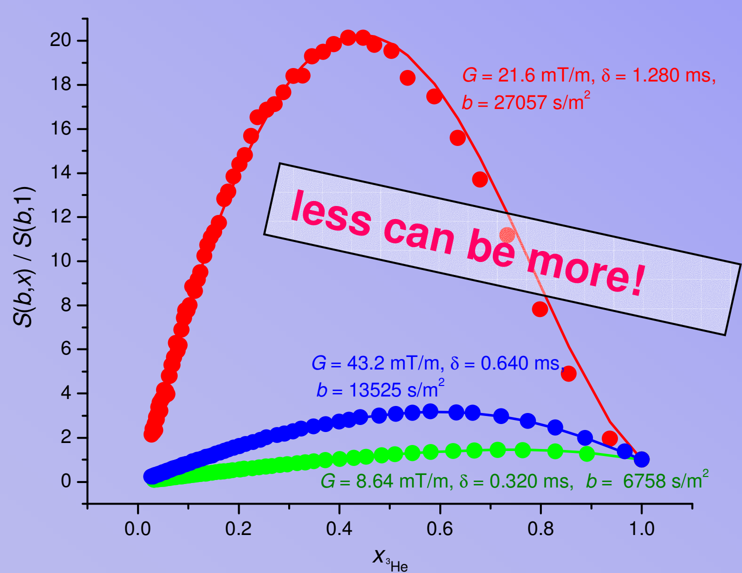
Transport box

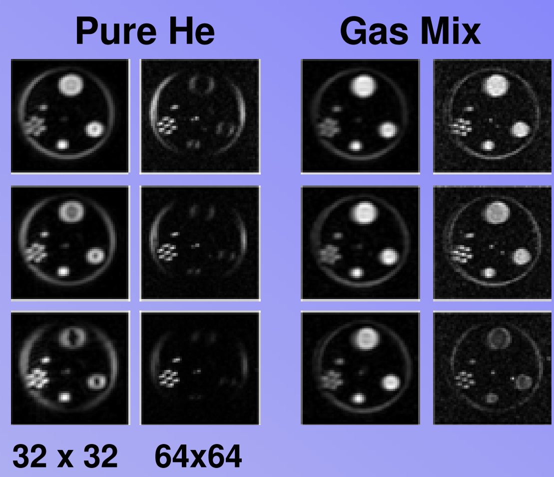
Manipulacion del coeficiente de difusión mediante mezcla de gases

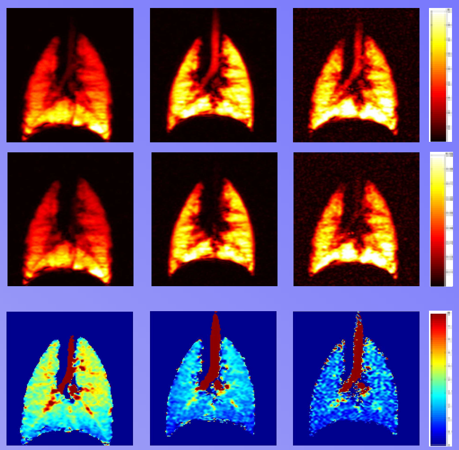
Fully automated – Matlab controlled







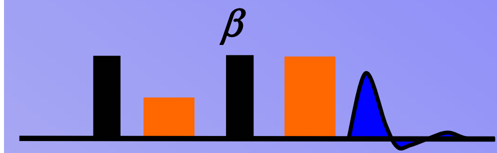


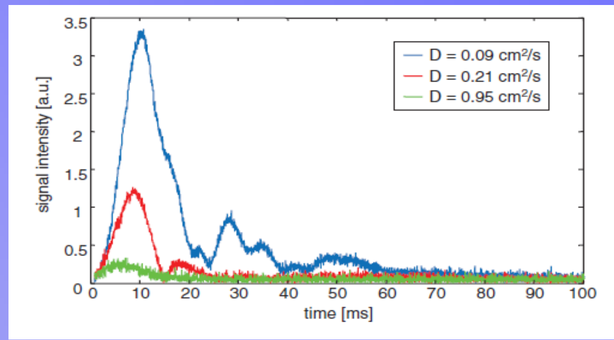


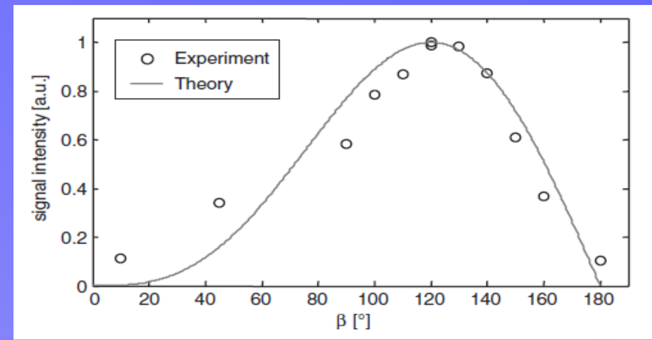
Exp. Lung. Research, **30,** 73 (2004)
Magn. Reson. Imag. **22,** 1077 (2004)
JMR. **197** 56 (2009)

PCCP, **8** 4182 (2006)
JMRI. **24** 1291 (2006)

iDQ in ^{3}He para distintos coeficientes de difusión

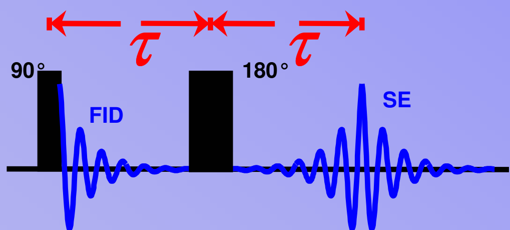


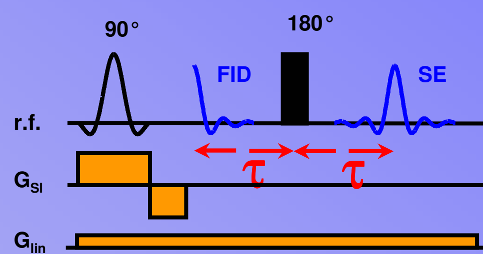


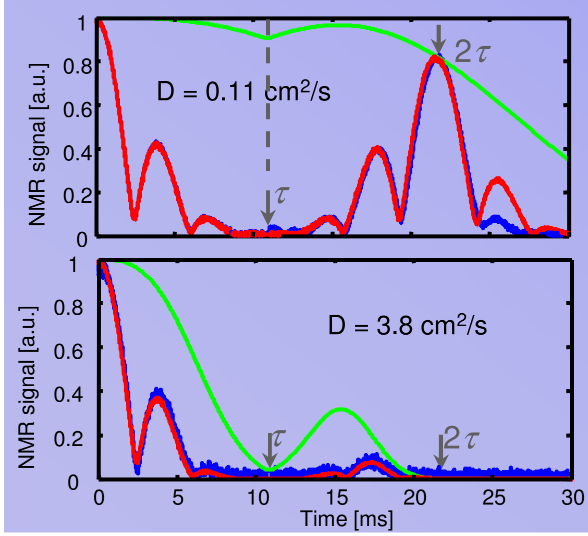


PRL **100**, 213001 (2008)

Atenuación del eco debido a difusión







Señal nuclear

$$E(t) = M(t) \cdot A_{Diff}(t)$$

Atenuacion por difusion

$$A_{Diff}(2\tau) = \exp[-\tfrac{1}{2}\gamma^2 G^2 D (2\tau)^3]$$ Formula usual

$$A_{Diff}(t) = \exp[-\tfrac{1}{2}\gamma^2 G^2 D (4\tau^3 - 4\tau^2 t + \tfrac{2}{3} t^3)] \quad , t > \tau$$

$$t_{max} = \sqrt{2}\tau$$

PRL **99**, 263001 (2007)
CPL, aceptado para publicacion

Perspectivas

Desarrollar marco teórico para influcencia de difusión restringida en i-MQC. Aplicacion a nanotubos.

Mapas de difusión del coeficiente de Difusión en pulmones a través de i-DQC.

Detección de señales intermoleculares en parahidrógeno:

$$\rho_{eq} = I_{1z} I_{2z} \qquad \rho_{eq} = I_{1z} I_{2z} + \frac{1}{2}\left(I_{1z} - I_{2z} \right)$$

Transferencia de señales i-MCQ a nucleos raros.