Dynamics as probed by muons

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Outline

The muon spin evolution in a static field

- A reminder about the Larmor equation
- Basic examples for the two μSR geometries

The muon spin evolution in a dynamical field

- Stochastic approach: the weak and strong collision models
- Quantum approach
- Spin correlation functions
- Dynamical range of μSR

A flavor of dynamical phenomena probed by μSR

- Phase transitions, magnetic fluctuations and excitations
- Spin glasses
- Complementarity with other techniques
- Superconductors
- Diffusion of Li^+

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The evolution of the muon spin $\mathbf{S}_\mu(t)$

The Larmor equation

Basic principle of mechanics:
Time derivative of angular momentum is equal to the sum of the torques:

$$\frac{\mathrm{d}\hbar\mathbf{S}_\mu(t)}{\mathrm{d}t} = \mathfrak{m}_\mu(t) \times \mathbf{B}_{\mathrm{loc}}(t). \tag{1}$$

Since

$$\mathfrak{m}_\mu = \gamma_\mu \hbar \mathbf{S}_\mu, \tag{2}$$

by definition of the gyromagnetic ratio, we have

$$\frac{\mathrm{d}\mathbf{S}_\mu(t)}{\mathrm{d}t} = \gamma_\mu \, \mathbf{S}_\mu(t) \times \mathbf{B}_{\mathrm{loc}}(t). \tag{3}$$

$\gamma_\mu = 851.6$ Mrad s^{-1} T^{-1}.

Consequences and solution of the Larmor equation

From $\frac{\mathrm{d}\mathbf{S}_\mu(t)}{\mathrm{d}t} = \gamma_\mu \, \mathbf{S}_\mu(t) \times \mathbf{B}_{\rm loc}(t)$ we deduce:

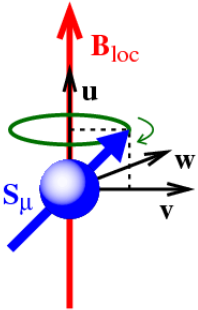
- $\frac{\mathrm{d}\mathbf{S}_\mu(t)}{\mathrm{d}t} \cdot \mathbf{S}_\mu(t) = 0$:
  $S_\mu(t)$ is a constant of the motion, *i.e.* $S_\mu(t) = S_\mu(0)$
- $\frac{\mathrm{d}\mathbf{S}_\mu(t)}{\mathrm{d}t} \cdot \mathbf{B}_{\rm loc}(t) = 0$:
  this implies $\frac{\mathrm{d}\mathbf{S}_\mu(t)}{\mathrm{d}t}$ is perpendicular to $\mathbf{B}_{\rm loc}(t)$.

Assuming $\mathbf{B}_{\rm loc}(t) = \mathbf{B}_{\rm loc}$,

$$\mathbf{S}_\mu(t) = S_\mu^{\parallel}(0)\,\mathbf{u} + S_\mu^{\perp}(0)[\cos(\omega_\mu t)\,\mathbf{v} - \sin(\omega_\mu t)\,\mathbf{w}], \quad (4)$$

with $\omega_\mu = \gamma_\mu B_{\rm loc}$.

The precession frequency only depends on $B_{\rm loc}$, not on the angle between $\mathbf{S}_\mu$ and $\mathbf{B}_{\rm loc}$!

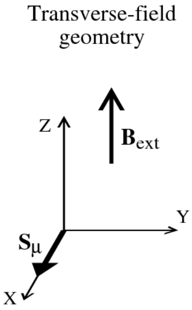


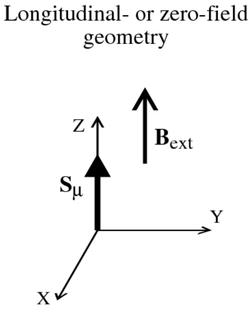
Outline

The transverse and longitudinal polarization functions

Definition

- $\mathbf{S}_\mu$: initial muon beam polarization.
- $P_\alpha(t)$: a polarization function, i.e. the evolution of the projection of the muon ensemble polarization along axis α.





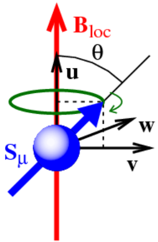
Our convention for the axes. $\mathbf{B}_{\text{ext}}$ *is always parallel to* $\mathbf{Z}$.

- in transverse field experiment: $\mathbf{S}_\mu \parallel \mathbf{X} \rightarrow P_X(t)$ or $P_Y(t)$.
- in zero-field and longitudinal field experiment: $\mathbf{S}_\mu \parallel \mathbf{Z} \rightarrow P_Z(t)$.

Transverse field experiment

Per definition, $\mathbf{S}_\mu \equiv \mathbf{S}_\mu(t=0) \parallel \mathbf{X}$.
From the solution of the Larmor equation,

$$S_\mu^X(t) = S_\mu[\cos^2\theta + \sin^2\theta\cos(\omega_\mu t)]. \tag{5}$$



Let $D_v(\mathbf{B}_{\rm loc})$ be the distribution of static fields probed by the muons,

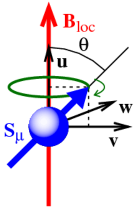
$$P_X^{\rm stat}(t) = \left\langle \frac{S_\mu^X(t)}{S_\mu} \right\rangle = \int [\cos^2\theta + \sin^2\theta\cos(\omega_\mu t)] D_v(\mathbf{B}_{\rm loc})\, \mathrm{d}^3\mathbf{B}_{\rm loc}. \tag{6}$$

Example:
if all the muons are submitted to $\mathbf{B}_{\rm loc} = \mathbf{B}_0 \parallel \mathbf{Z}$, i.e. $\theta = \pi/2$,

$$P_X^{\rm stat}(t) = \cos(\omega_0 t) \tag{7}$$

with $\omega_0 = \gamma_\mu B_0$.

Zero or longitudinal field experiment



Per definition, $\mathbf{S}_\mu \equiv \mathbf{S}_\mu(t=0) \parallel \mathbf{Z}$.
From the solution of the Larmor equation,

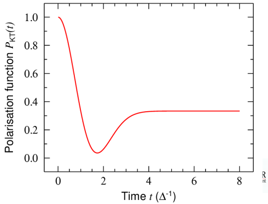
$$S_\mu^Z(t) = S_\mu[\cos^2\theta + \sin^2\theta\cos(\omega_\mu t)]. \tag{8}$$

Let $D_v(\mathbf{B}_{\rm loc})$ be the distribution of static fields probed by the muons,

$$P_Z^{\rm stat}(t) = \left\langle \frac{S_\mu^Z(t)}{S_\mu} \right\rangle = \int [\cos^2\theta + \sin^2\theta\cos(\omega_\mu t)] D_v(\mathbf{B}_{\rm loc})\, \mathrm{d}^3\mathbf{B}_{\rm loc}. \tag{9}$$

For isotropic Gaussian distributed $B_{\rm loc}^\alpha$ with rms $\Delta_{\rm G}$,

$$P_Z^{\rm stat}(t) = P_{\rm KT}(t) = \frac{1}{3} + \frac{2}{3}(1 - \gamma_\mu^2\Delta_{\rm G}^2 t^2)\exp\left(-\frac{\gamma_\mu^2\Delta_{\rm G}^2 t^2}{2}\right), \tag{10}$$



which is the so-called Kubo-Toyabe function.

Outline

Introduction to the dynamical polarization functions (1)

The Larmor equation

$$\frac{\mathrm{d}\mathbf{S}_\mu(t)}{\mathrm{d}t} = \gamma_\mu \, \mathbf{S}_\mu(t) \times \mathbf{B}_{\mathrm{loc}}(t), \tag{3}$$

is still valid.
However it is difficult to solve it when $\mathbf{B}_{\mathrm{loc}}(t)$ is a stochastic variable.

Outline

Introduction to the dynamical polarization functions (2)

Stochastic account of dynamics

We compute $P_\alpha(t)$ for two different models.

Hypothesis for both models:
$\mathbf{B}_{\rm loc}(t)$ follows a stationary Gaussian-Markovian process, i.e.

- independent of origin of time
- $B^\alpha_{\rm loc}(t)$ belongs to a Gaussian distribution
- $\mathbf{B}_{\rm loc}(t)$ evolves in jumps, with a hopping probability which does not depend on the system state before the jump.

Doob's theorem (1942):

$$\langle B^\alpha_{\rm loc}(t_0) B^\alpha_{\rm loc}(t_0+t)\rangle = \langle (B^\alpha_{\rm loc})^2\rangle \exp\left(-\nu_{\rm c}|t|\right) \tag{11}$$

where $\nu_{\rm c}^{-1} = \tau_{\rm c}$ is the field correlation time.

Dynamical polarization functions

Computation of $P_X(t)$ in an external field $B_{\rm ext}$: the weak collision model (1)

Recall, for a single static field B_0,

$$P_X^{\rm stat}(t) = \cos(\omega_0 t) \tag{7}$$

with $\omega_0 = \gamma_\mu B_0$.
For $B^Z_{\rm loc}(t)$, the phase at time t is

$$\gamma_\mu B^Z_{\rm loc}\,(t_0)\,(t_1 - t_0) + ... + \gamma_\mu B^Z_{\rm loc}\,(t_{n-1})\,(t_n - t_{n-1}) = \int_0^t \gamma_\mu B^Z_{\rm loc}(t'){\rm d}t'. \tag{12}$$

After averaging over the muon ensemble

$$P_X(t) = \mathcal{R}e\left\{\left\langle \exp\left[i\int_0^t \gamma_\mu B^Z_{\rm loc}(t'){\rm d}t'\right]\right\rangle\right\}. \tag{13}$$

Dynamical polarization functions

Computation of $P_X(t)$ in an external field $B_{\rm ext}$: the weak collision model (2)

Now, for a stationary Gaussian process,

$$\left\langle \exp\left[i\int_0^t \gamma_\mu \delta B_{\rm loc}^Z(t')\mathrm{d}t'\right]\right\rangle = \exp\left[-\int_0^t \mathrm{d}t' \int_0^t \gamma_\mu^2 \left\langle \delta B_{\rm loc}^Z \delta B_{\rm loc}^Z \left(t'-t''\right)\right\rangle \mathrm{d}t''\right], \tag{14}$$

where $\delta B_{\rm loc}^Z(t') = B_{\rm loc}^Z(t') - \langle B_{\rm loc}^Z\rangle$. Using Doob's theorem and the relation

$$\int_0^t \mathrm{d}t' \int_0^t f(t'-t'')\mathrm{d}t'' = 2\int_0^t (t-\tau)f(\tau)\mathrm{d}\tau \tag{15}$$

where $f(t)$ is an even function, we get

$$P_X(t) = \exp\left\{-\frac{\gamma_\mu^2\Delta_{\rm G}^2}{\nu_{\rm c}^2}\left[\exp(-\nu_{\rm c}t) - 1 + \nu_{\rm c}t\right]\right\}\cos\left(\gamma_\mu\langle B_{\rm loc}^Z\rangle t\right), \tag{16}$$

with $\Delta_{\rm G}^2 = \langle (B_{\rm loc}^\alpha)^2\rangle$.
Equation 16 is the so-called Abragam formula (Anderson, 1954).

Dynamical polarization functions

The Abragam function

$$P_X(t) = \exp\left\{-\frac{\gamma_\mu^2\Delta_\mathrm{G}^2}{\nu_\mathrm{c}^2}\left[\exp(-\nu_\mathrm{c}t) - 1 + \nu_\mathrm{c}t\right]\right\}\cos\left(\gamma_\mu\langle B_\mathrm{loc}^Z\rangle t\right) \qquad (16)$$

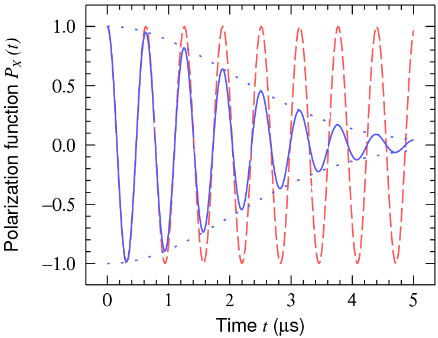
- For $\nu_\mathrm{c} \ll \gamma_\mu\Delta_\mathrm{G}$,

$$\begin{aligned} P_X(t) &= \exp\left(-\gamma_\mu^2\Delta_\mathrm{G}^2 t^2/2\right) \\ &\times \cos\left(\gamma_\mu\langle B_\mathrm{loc}^Z\rangle t\right). \end{aligned}$$

- For $\nu_\mathrm{c} \gg \gamma_\mu\Delta_\mathrm{G}$,

$$\begin{aligned} P_X(t) &= \exp\left(-\lambda_X t\right) \\ &\times \cos\left(\gamma_\mu\langle B_\mathrm{loc}^Z\rangle t\right), \end{aligned}$$

with $\lambda_X = \gamma_\mu^2\Delta_\mathrm{G}^2/\nu_\mathrm{c} = \gamma_\mu^2\Delta_\mathrm{G}^2\tau_\mathrm{c}$. This is the so-called motional narrowing limit (NMR language).



Examples of Abragam function

Dynamical polarization functions

Computation of $P_Z(t)$: the strong collision model (1)

- Let ℓ be the number of changes for $\mathbf{B}_{\rm loc}(t)$ during the muon life time,

$$P_Z(t) = \sum_{\ell=0}^{+\infty} R_\ell(t), \tag{17}$$

where $R_\ell(t)$ is the contribution to $P_Z(t)$ of muons which have experienced ℓ field changes between 0 and t.

- Now,

$$R_0(t) = P_Z^{\rm stat}(t) \exp(-\nu_{\rm c} t), \tag{18}$$

since the probability for $\mathbf{B}_{\rm loc}(t)$ to be unchanged between 0 and t is $\exp(-\nu_{\rm c} t)$.

Dynamical polarization functions

Computation of $P_Z(t)$: the strong collision model (2)

- For $\ell = 1$ field change and since the process is Gaussian-Markovian,

$$\begin{aligned} R_1(t) &= \left\langle \int_0^t \frac{S^Z_{\mu,j}(t-t')}{S_\mu} \exp[-\nu_c(t-t')]\nu_c \frac{S^Z_{\mu,i}(t')}{S_\mu} \exp(-\nu_c t')\mathrm{d}t' \right\rangle_{ij} \\ &= \nu_c \int_0^t R_0(t-t')R_0(t')\mathrm{d}t'. \end{aligned} \tag{19}$$

- Recursion relation:

$$R_{\ell+1}(t) = \nu_c \int_0^t R_\ell(t-t')R_0(t')\mathrm{d}t'. \tag{20}$$

- From Eq. 20 and the definition $P_Z(t) = \sum_{\ell=0}^{+\infty} R_\ell(t)$,

$$\sum_{\ell=0}^{+\infty} R_{\ell+1}(t) = \nu_c \int_0^t P_Z(t-t')R_0(t')\mathrm{d}t' = P_Z(t) - R_0(t), \tag{21}$$

...

Dynamical polarization functions

Computation of $P_Z(t)$: the strong collision model (3)

which can be rewritten as the integral equation

$$P_Z(t) = P_Z^{\mathrm{stat}}(t)\,\mathrm{exp}(-\nu_{\mathrm{c}}t) + \nu_{\mathrm{c}}\int_0^t P_Z(t-t')P_Z^{\mathrm{stat}}(t')\,\mathrm{exp}(-\nu_{\mathrm{c}}t')\mathrm{d}t', \tag{22}$$

or in terms of Laplace transforms ($f(s) = \int_0^t f(t)\,\mathrm{exp}(-st)\mathrm{d}t$),

$$P_Z(s) = \frac{P_Z^{\mathrm{stat}}(s+\nu_{\mathrm{c}})}{1-\nu_{\mathrm{c}}P_Z^{\mathrm{stat}}(s+\nu_{\mathrm{c}})}. \tag{23}$$

Dynamical polarization functions

$P_Z(t)$ in zero external field for an isotropic Gaussian distribution of field

Recall

$$P_Z^{\mathrm{stat}}(t) = P_{\mathrm{KT}}(t) = \frac{1}{3} + \frac{2}{3}(1 - \gamma_\mu^2 \Delta_{\mathrm{G}}^2 t^2) \exp\left(-\frac{\gamma_\mu^2 \Delta_{\mathrm{G}}^2 t^2}{2}\right), \qquad (10)$$

- For $\nu_{\mathrm{c}} \ll \gamma_\mu \Delta_{\mathrm{G}}$,

$$P_Z(t) \simeq \frac{1}{3} \exp\left(-\frac{2}{3}\nu_{\mathrm{c}} t\right) + \frac{2}{3}(1 - \gamma_\mu^2 \Delta_{\mathrm{G}}^2 t^2) \exp\left(-\frac{\gamma_\mu^2 \Delta_{\mathrm{G}}^2 t^2}{2}\right). \qquad (24)$$

High sensitivity to slow dynamics.

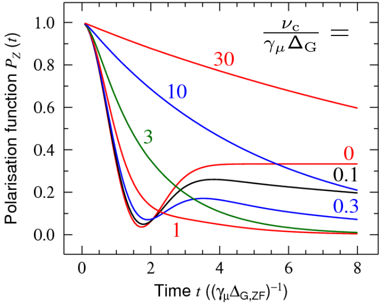
- For $\nu_{\mathrm{c}} \gg \gamma_\mu \Delta_{\mathrm{G}}$,

$$P_Z(t) = \exp\left(-\lambda_Z t\right), \qquad (25)$$

with

$$\lambda_Z = 2\gamma_\mu^2 \Delta_{\mathrm{G}}^2 / \nu_{\mathrm{c}}. \qquad (26)$$

(motional narrowing limit).



Dynamical polarization functions

$P_Z(t)$ in a longitudinal field for an isotropic Gaussian distribution of field

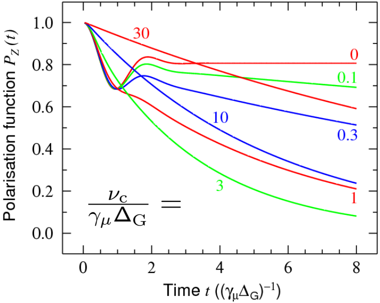
- For $\nu_c \gg \gamma_\mu \Delta_G$,

$$P_Z(t) = \exp\left(-\lambda_Z t\right), \qquad (27)$$

with

$$\lambda_Z = \frac{2\gamma_\mu^2 \Delta_G^2 \nu_c}{\nu_c^2 + \omega_\mu^2} \qquad (28)$$

(Redfield formula) and $\omega_\mu = \gamma_\mu B_{\text{ext}}$.



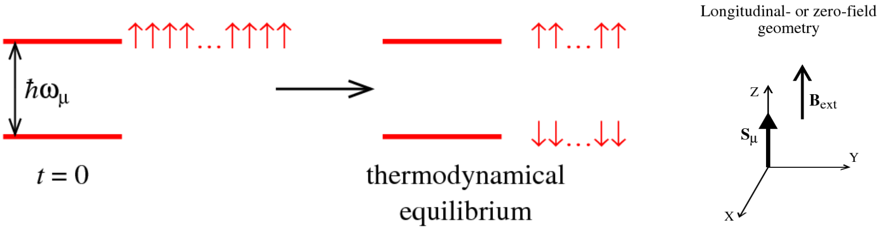
$P_Z(t)$ for $B_{\text{ext}} = 3\Delta_G$.

Outline

The polarization functions from a quantum approach

A flavor for zero and longitudinal field experiments

μ^+: spin 1/2.



At thermodynamical equilibrium, the populations of the two states are equal since $\hbar\omega_\mu \ll k_{\rm B} T$.

Indeed, for $B_{\rm loc} = 1$ T, $\hbar\omega_\mu = 0.56$ μeV ($= k_{\rm B} T$ for $T = 6.5$ mK).

The polarization functions from a quantum approach

Derivation of $P_Z(t)$ (1)

$$P_Z(t) = 2\,\mathrm{Tr}\left[\rho_{\mathrm{s}} S_\mu^Z S_\mu^Z(t)\right] \tag{29}$$

with

$$S_\mu^Z(t) = \exp\left(i\frac{\mathcal{H}t}{\hbar}\right) S_\mu^Z \exp\left(-i\frac{\mathcal{H}t}{\hbar}\right) \tag{30}$$

where ρ_{s} is the density operator and $\mathcal{H}$ is the Hamiltonian for the muon-system ensemble.

The polarization functions from a quantum approach

Derivation of $P_Z(t)$ (2)

After some computation,

$$P_Z(t) \simeq \exp[-\psi_Z(t)] \tag{31}$$

with

$$\psi_Z(t) = 2\pi\gamma_\mu^2 \int_0^t (t-\tau)\cos(\omega_\mu \tau)\left[\Phi^{XX}(\tau) + \Phi^{YY}(\tau)\right] \mathrm{d}\tau. \tag{32}$$

where $\Phi^{\alpha\beta}(\tau) = \frac{1}{4\pi}\left[\left\langle \delta B_{\mathrm{loc}}^{\alpha}(\tau)\delta B_{\mathrm{loc}}^{\beta}\right\rangle + \left\langle \delta B_{\mathrm{loc}}^{\beta}\delta B_{\mathrm{loc}}^{\alpha}(\tau)\right\rangle\right]$ is the field correlation function and $\omega_\mu = \gamma_\mu B_{\mathrm{ext}}$.

The polarization functions from a quantum approach

Derivation of $P_Z(t)$ (3)

Assuming $\Phi^{\alpha\beta}(\tau)$ to decay rapidly on the μSR time t scale, we get $\psi_Z(t) = \lambda_Z t$ with

$$\lambda_Z = \pi\gamma_\mu^2 \left[\Phi^{XX}(\omega_\mu) + \Phi^{YY}(\omega_\mu)\right]. \tag{33}$$

$\Phi^{\alpha\beta}(\omega_\mu)$ is the *time* Fourier transform of $\Phi^{\alpha\beta}(\tau)$.

If $\Phi^{\alpha\alpha}(\tau) = \frac{1}{2\pi}\langle(\delta B^\alpha_{\rm loc})^2\rangle \exp\left(-\nu_{\rm c}|\tau|\right)$ and $B_{\rm ext} = 0$,

$$\lambda_Z = \gamma_\mu^2 \left(\langle(\delta B^X_{\rm loc})^2\rangle + \langle(\delta B^Y_{\rm loc})^2\rangle\right)/\nu_{\rm c}, \tag{34}$$

which can be identified to

$$\lambda_Z = 2\gamma_\mu^2 \Delta_{\rm G}^2/\nu_{\rm c}. \tag{26}$$

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The magnetic field at the muon site

The dipolar field arising from localized spins $\mathbf{J}_j$ with Landé factors g is

$$\mathbf{B}_{\rm dip} = -\frac{\mu_0}{4\pi} g\mu_{\rm B} \sum_j \left[-\frac{\mathbf{J}_j}{r_j^3} + 3\frac{(\mathbf{J}_j \cdot \mathbf{r}_j)\mathbf{r}_j}{r_j^5} \right]. \tag{35}$$

$\mathbf{r}_j$ is the vector distance from the spin to the muon.

When a Polaris ed electron density is present at the muon, an additional contribution is present, the hyperfine field:

$$\mathbf{B}_{\rm hyp} = -\frac{\mu_0}{4\pi} g\mu_{\rm B} \sum_{j\in{\rm NN}} H_j \mathbf{J}_j. \tag{36}$$

Only the muon nearest neighbors (NN) usually contribute to $\mathbf{B}_{\rm hyp}$.
When both $\mathbf{B}_{\rm dip}$ and $\mathbf{B}_{\rm hyp}$ contribute to $\mathbf{B}_{\rm loc}$ (*i.e.* in metals) they generally have the same order of magnitude.
Altogether

$$\mathbf{B}_{\rm loc} = -\frac{\mu_0}{4\pi} \frac{g\mu_{\rm B}}{v_{\rm c}} \sum_j \boldsymbol{G}_j \mathbf{J}_j. \tag{37}$$

$\boldsymbol{G}$ is the muon-system coupling tensor.

Spin-lattice relaxation rate λ_Z and spin-correlation function

From

$$\lambda_Z = \pi\gamma_\mu^2 \left[\Phi^{XX}(\omega_\mu) + \Phi^{YY}(\omega_\mu)\right], \tag{33}$$

introducing the *space* Fourier transform,

$$\mathbf{J}(\mathbf{q}) = \frac{1}{\sqrt{n_\mathrm{c}}} \sum_j \mathbf{J}_j \exp(-i\mathbf{q}\cdot\mathbf{j}), \tag{38}$$

we get

$$\lambda_Z = \frac{\mathcal{D}}{2} \int \sum_{\alpha\beta} \mathcal{A}^{\alpha\beta}(\mathbf{q}) \Lambda^{\alpha\beta}(\mathbf{q}, \omega_\mu) \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}. \tag{39}$$

$$\Lambda^{\alpha\beta}(\mathbf{q},\omega) = \frac{1}{2}\left[\left\langle \delta J^\alpha(\mathbf{q},\omega)\delta J^\beta(-\mathbf{q})\right\rangle + \left\langle \delta J^\beta(-\mathbf{q})\delta J^\alpha(\mathbf{q},\omega)\right\rangle\right] \tag{40}$$

is the spin correlation tensor,

$$\mathcal{A}^{\alpha\beta}(\mathbf{q}) = G^{X\alpha}(\mathbf{q})G^{X\beta}(\mathbf{q}) + G^{Y\alpha}(\mathbf{q})G^{Y\beta}(\mathbf{q}) \tag{41}$$

is the muon-system coupling factor, and $\mathcal{D} = \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_\mu^2 (g\mu_\mathrm{B})^2 / v_\mathrm{c}$.

Spin-lattice relaxation rate λ_Z and spin-correlation function

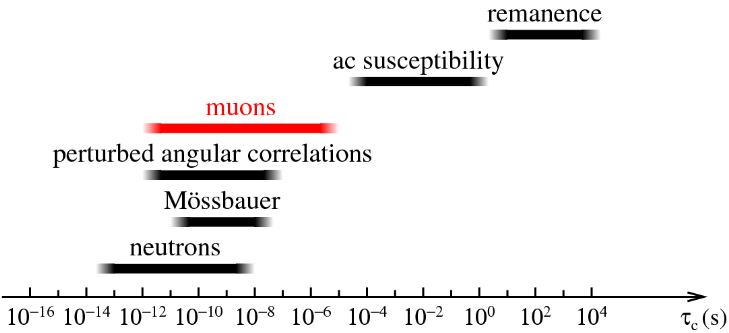
Recall

$$\lambda_Z = \frac{\mathcal{D}}{2} \int \sum_{\alpha\beta} \mathcal{A}^{\alpha\beta}(\mathbf{q}) \Lambda^{\alpha\beta}(\mathbf{q}, \omega_\mu) \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}. \tag{39}$$

λ_Z is an integral of the spin-correlation function taken near 0 energy (neV range) over the Brillouin zone with a weighting factor depending on the muon site.

Outline

Comparison of dynamical ranges accessible to different techniques



Outline

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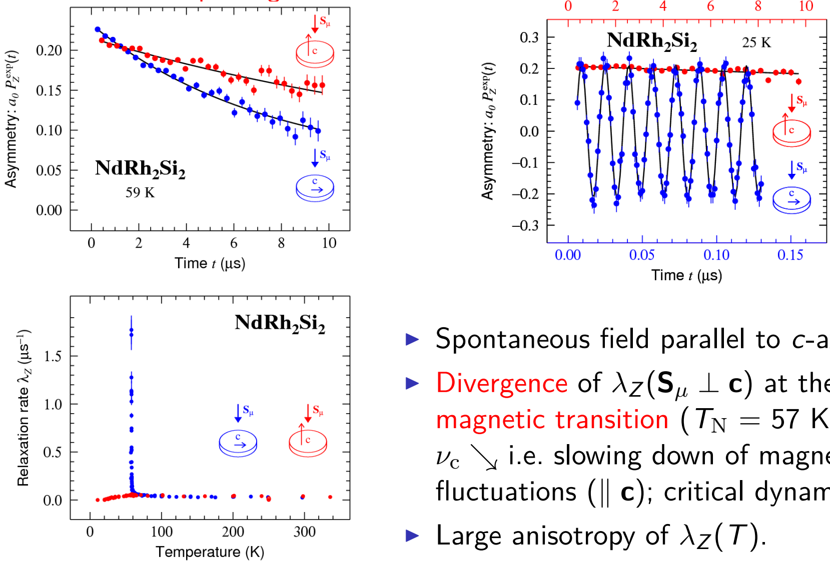
Spin dynamics in magnets

Case of an anisotropic magnet

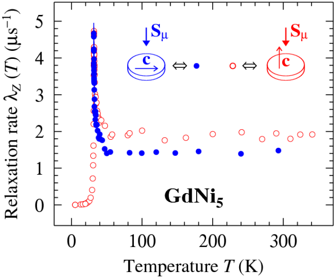


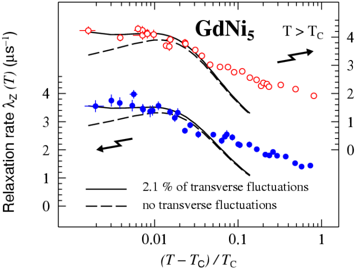
- Spontaneous field parallel to c-axis.
- Divergence of $\lambda_Z(\mathbf{S}_\mu \perp \mathbf{c})$ at the magnetic transition ($T_\mathrm{N} = 57$ K): $\nu_\mathrm{c} \searrow$ i.e. slowing down of magnetic fluctuations ($\parallel \mathbf{c}$); critical dynamics.
- Large anisotropy of $\lambda_Z(T)$.

Gubbens *et al.*, Hyp. Int. **85**, 245 (1994).

Spin dynamics in magnets

Case of a weakly anisotropic magnet





- Magnetic transition at $T_{\mathrm{C}} \simeq 32$ K.
- $\lambda_Z(T)$ nearly isotropic.
- Dipolar interaction between the spins responsible for $\lambda_Z(T)$ saturation close to T_{C}.

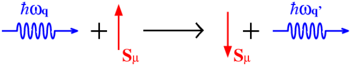
Yaouanc *et al.*, PRB **53** 350 (1996); see also Yaouanc *et al.*, PRB **47** 796 (1993).

Muon spin relaxation induced by excitations

Recall

$$\lambda_Z = \frac{\mathcal{D}}{2} \int \sum_{\alpha\beta} \mathcal{A}^{\alpha\beta}(\mathbf{q}) \Lambda^{\alpha\beta}(\mathbf{q}, \omega_\mu) \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}. \tag{39}$$

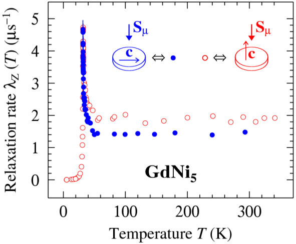
- λ_Z probes $\Lambda^{\alpha\beta}(\mathbf{q}, \omega_\mu)$ at an energy $\hbar\omega_\mu$ in the neV range.
- Since any gap in the excitation spectrum is normally much larger, a process involving a single excitation cannot relax the muon spin.
- If an excitation at $\mathbf{q}$ is, say, annihilated while a second one at $\mathbf{q}'$ is created satisfying $\omega_{\mathbf{q}} - \omega_{\mathbf{q}'} - \omega_\mu = 0$, the energy conservation is ensured and a two excitation (Raman) process can relax the muon spin.

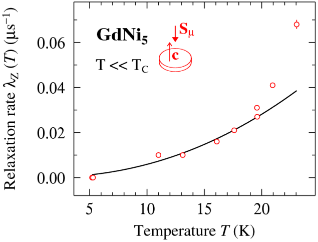


- Example: for a ferromagnet with $\hbar\omega_q = D_m q^2 + \Delta_{\rm gap}$,
  $\lambda_Z(T) \propto \frac{T^2}{D_m^3} \ln\left(\frac{k_B T}{\Delta_{\rm gap}}\right)$ for $k_{\rm B} T \gg \Delta_{\rm gap}$.
- No relaxation at low temperature is expected for a "large" spin gap ($\Delta_{\rm gap} \gg k_{\rm B} T$).

Dalmas de Réotier and Yaouanc, PRB **52**, 9155 (1995).

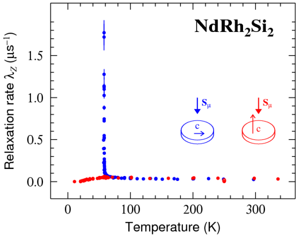
Muon spin relaxation induced by excitations

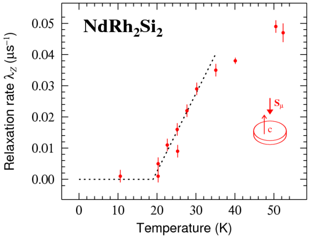




Relaxation through a Raman process:

$$\lambda_Z(T) \propto \frac{T^2}{D_m^3} \ln\left(\frac{k_B T}{\Delta_{\rm gap}}\right) \textit{ with } D_m = 3.2\,(1)\ \mathrm{meV}\,\mathring{A}^2.$$





No relaxation at low temperature due to large anisotropy.

Outline

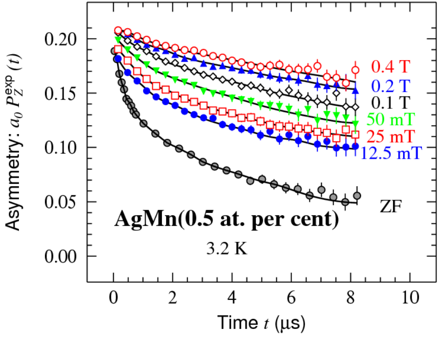
Spin dynamics in spin glasses (1)

- Spin glass: dilute magnetic impurities in a non magnetic matrix.
- Physical characteristics:
  - cusp in the low field susceptibility at T_{g},
  - broad peak in the specific heat around T_{g},
  - important dynamical effects.
- μSR in usual paramagnets (motional narrowing limit):
  - $P_Z(t) = \exp(-\lambda_Z t)$ with

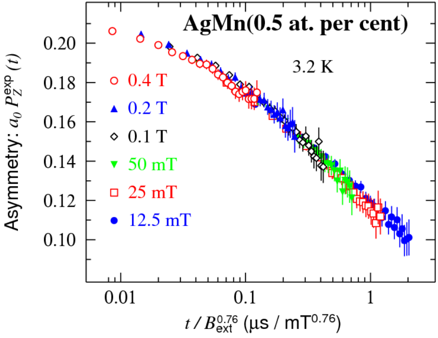
$$\lambda_Z = \frac{2\gamma_\mu^2 \Delta_{\mathrm{G}}^2 \nu_{\mathrm{c}}}{\nu_{\mathrm{c}}^2 + \gamma_\mu^2 B_{\mathrm{ext}}^2}, \tag{28}$$

    which follows from $\Lambda(\tau) \propto \exp(-\nu_{\mathrm{c}}|\tau|)$.
  - $P_Z(t, B_{\mathrm{ext}}) = P_Z(t/B_{\mathrm{ext}}^2)$ if $\gamma_\mu B_{\mathrm{ext}} \gg \nu_c$.
- μSR in spin glass above T_{g} (motional narrowing limit):
  - $P_Z(t) = \langle \exp(-\lambda_Z t) \rangle_{\Delta_{\mathrm{G}}}$.
  - if $\Lambda(\tau) \propto \exp[-(\zeta|\tau|)^\beta]$,
    $P_Z(t, B_{\mathrm{ext}}) = P_Z(t/B_{\mathrm{ext}}^\gamma)$ with $\gamma = 1 + \beta$ if $\gamma_\mu B_{\mathrm{ext}} \gg \zeta$.
  - if $\Lambda(\tau) \propto \tau^{-\alpha} \exp[-(\zeta|\tau|)^\beta]$,
    $P_Z(t, B_{\mathrm{ext}}) = P_Z(t/B_{\mathrm{ext}}^\gamma)$ with $\gamma = 1 - \alpha$ if $\zeta|\tau| \ll 1$,

Spin dynamics in spin glasses (2)



μSR spectra for different $B_{\rm ext}$.



The same spectra plotted as a function of $t/B_{\rm ext}^{\gamma}$ with $\gamma = 0.76(5)$.

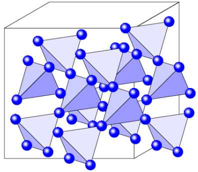
The data are only consistent with the cut-off power law:
$\Lambda(\tau) \propto \tau^{-\alpha} \exp[-(\zeta|\tau|)^{\beta}]$ with $\alpha = 0.24\,(5)$ and $\zeta|\tau| \ll 1$.

Keren *et al.*, PRL **77**, 1386 (1996).

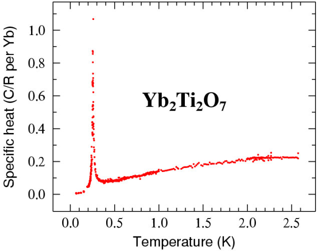
Outline

Complementarity with other techniques

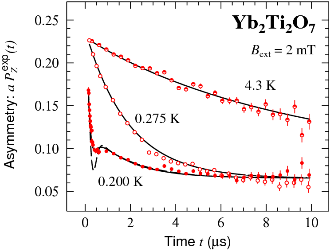
Mössbauer spectroscopy, $Yb_2Ti_2O_7$ (1)



- Pyrochlore crystal structure.
- Current interest in highly frustrated magnetism:
  - Spin ice and quantum spin ice ground states.
  - Emergent magnetic monopoles.



Specific heat: transition at 0.25 K.

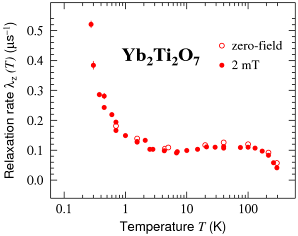


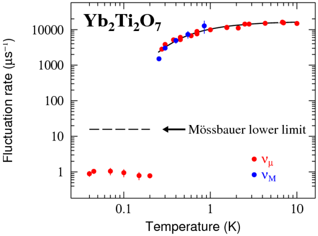
$T \geq 0.275$ K, $P_Z(t) = \exp(-\lambda_Z t)$.
$T \leq 0.200$ K, *depolarization by nearly static electronic moments:* $\nu_\mu \simeq 1$ MHz.

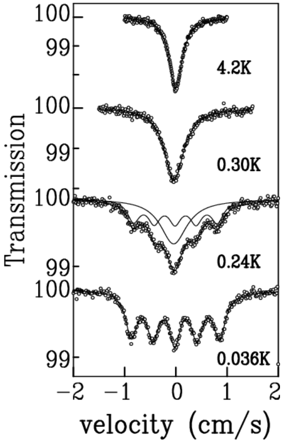
Hodges *et al.*, PRL **88**, 077204 (2002).

Complementarity with other techniques

Mössbauer spectroscopy, $Yb_2Ti_2O_7$ (2)







^{170}*Yb Mössbauer spectra.*

Comparison of the Yb^{3+} spin fluctuation rates as determined from Mössbauer (ν_{M}) and μSR (ν_μ) spectroscopies using the formula

$$\lambda_Z = 2\gamma_\mu^2 \Delta_{\mathrm{G}}^2 / \nu_\mu. \qquad (26)$$

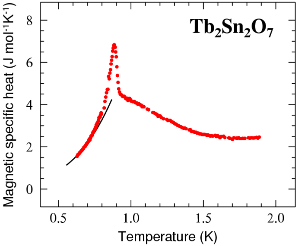
$\longrightarrow$ Good agreement found for $\Delta_{\mathrm{G}} = 80$ mT.

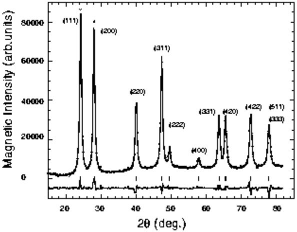
Conclusion: first order transition in the spin dynamics.

Hodges *et al.*, PRL **88**, 077204 (2002), Yaouanc *et al.*, Physica B **326**, 456 (2003).

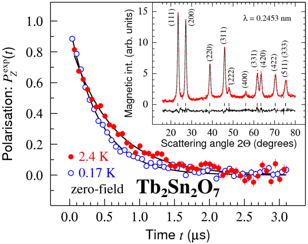
Complementarity with other techniques

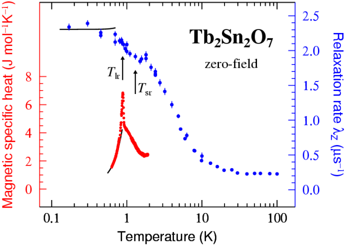
Neutron scattering, $Tb_2Sn_2O_7$ (1)





Mirebeau *et al.*, PRL **94**, 246402 (2005).





All μSR spectra are exponential, no signature for a transition.

Dalmas de Réotier *et al.*, PRL **96**, 127202 (2006).

Complementarity with other techniques

Neutron scattering, $Tb_2Sn_2O_7$ (2)

Spontaneous field at muon site is the Tb^{3+} dipolar field.
No signature of it because, either

- it cancels for symmetry reason:
  unlikely because of
  - low symmetry expected for the muon site
  - relatively complicated magnetic structure with ferromagnetic and antiferromagnetic components,
- or it is dynamical.

Complementarity with other techniques

Neutron scattering, $Tb_2Sn_2O_7$ (2)

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  unlikely because of
  - low symmetry expected for the muon site
  - relatively complicated magnetic structure with ferromagnetic and antiferromagnetic components,
- or it is dynamical.

Let's apply the result of the strong collision model:

$$P_Z(s) = \frac{P_Z^{\mathrm{stat}}(s+\nu_{\mathrm{c}})}{1-\nu_{\mathrm{c}} P_Z^{\mathrm{stat}}(s+\nu_{\mathrm{c}})}. \tag{23}$$

Complementarity with other techniques

Neutron scattering, $Tb_2Sn_2O_7$ (3)

Assumption: $\mathbf{B}_{\rm loc}$ takes two values $\pm\mathbf{B}_{\rm fl}$: $P_Z^{\rm stat}(t) = \cos(\gamma_\mu B_{\rm fl} t)$.

$$P_Z^{\rm stat}(s) = \frac{s}{s^2 + \gamma_\mu^2 B_{\rm fl}^2}; \qquad P_Z(s) = \frac{s + \nu_c}{s^2 + \nu_c s + \gamma_\mu^2 B_{\rm fl}^2}.$$

Two cases

- $\nu_c < 2\gamma_\mu B_{\rm fl}$:

$$P_Z(t) = \exp(-\nu_c t)\frac{\cos(\omega_{\rm eff} t - \varphi)}{\cos\varphi}$$

- $\nu_c > 2\gamma_\mu B_{\rm fl}$

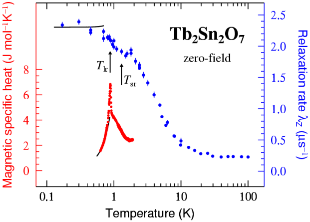
$$P_Z(t) = \exp(-\nu_c t)\frac{\cosh(\nu_{\rm eff} t - \varphi)}{\cosh\varphi}$$

In the extreme motional narrowing limit: $\nu_c \gg 2\gamma_\mu B_{\rm fl}$

$$P_Z(t) = \exp\left(-\lambda_Z t\right) \quad \text{with} \quad \lambda_Z = \frac{\gamma_\mu^2 B_{\rm fl}^2}{\nu_c}$$

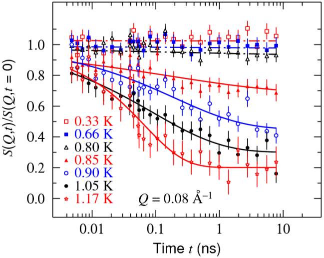
Complementarity with other techniques

Neutron scattering, $Tb_2Sn_2O_7$ (4)

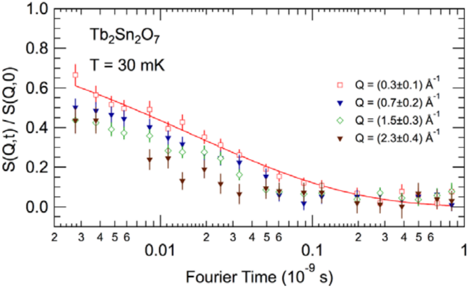


Dalmas de Réotier *et al.*, PRL **96**, 127202 (2006).

- From $\lambda_Z = \frac{\gamma_\mu^2 B_{\rm fl}^2}{\nu_c}$ and the estimate $B_{\rm fl} = 0.2$ T, we get $\nu_c \simeq 10^{10}$ s^{-1}.
- $\langle B_{\rm loc}(t) \cdot B_{\rm loc} \rangle \propto \int \mathcal{K}(Q) S(Q,t) Q^2 {\rm d}Q$.
- Neutron spin echo data:
  spin correlations are static for $Q \to 0$ and dynamical (5×10^{10} s^{-1}) for $Q \gtrsim 0.3$ Å^{-1}.



Chapuis *et al.*, JPCM **19**, 446206 (2007).

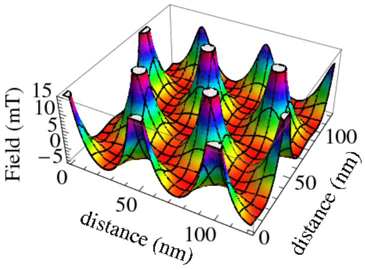


Rule *et al.*, JPCM **21**, 486005 (2009).

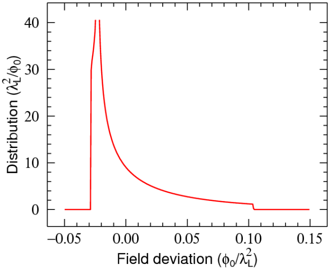
Outline

Mixed phase of superconductors

Type II superconductors submitted to a magnetic field:



Field (deviation) profile in the flux-line lattice phase.

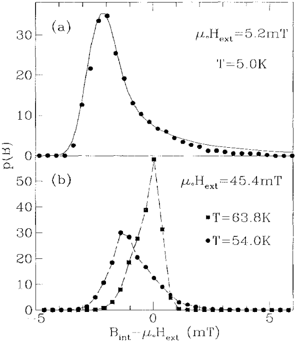


Associated field distribution.

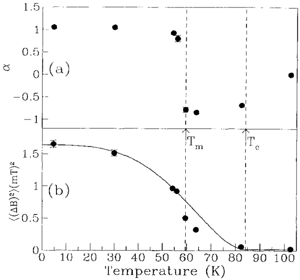
- mixed phase: $B_{c1} < B_{ext} < B_{c2}$,
- characteristic length scales
  - London penetration depth,
  - vortex core radius,
  - coherence lengths of the flux line lattice.

Mixed phase of superconductors

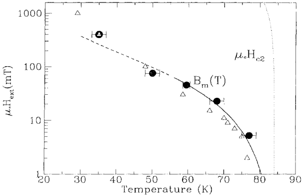
Flux-line lattice melting in $Bi_{2.15}Sr_{1.85}CaCu_2O_{8+\delta}$



Field distribution at different temperatures amd fields.



Skewness and second moment of the distribution.



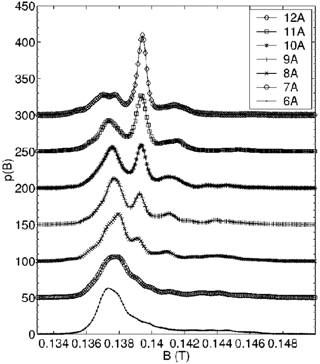
Phase diagram and comparison with a.c. susceptibility data.

First evidence from microscopic measurement of the vortex lattice melting in a superconductor.

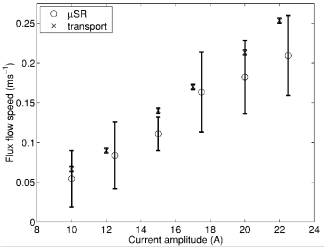
Lee *et al.*, PRL **71**, 3862 (1993); see also Cubitt *et al.*, Nature **365**, 407 (1993).

Mixed phase of superconductors

Vortex motion driven by an electrical current



Effect of a current on the field distribution measured in a Pb-In alloy.



Velocity of flux line flow vs applied current.

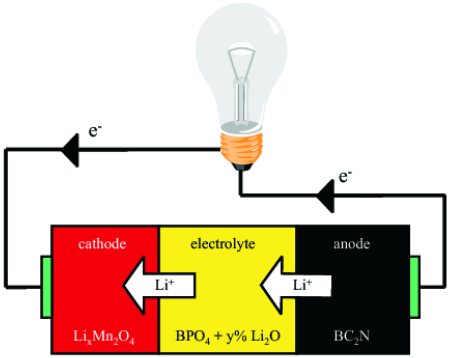
- Measure of vortex velocity.
- Influence of sample boundaries on the amount of disorder in the vortex lattice.

Charalambous *et al.*, PRB **73**, 105414 (2006).

Outline

Diffusion of Li^+

Principle of operation of a Li-ion battery



Reversible exchange of Li^+ ions between electrode materials.

The process involves the diffusion of Li^+ ions in, e.g. the positive electrode material.

Diffusion of Li^+

Diffusion coefficient D of Li^+ in the electrode material: macroscopic level

- Fick's laws

$$J = -D\frac{\partial \phi}{\partial x} \qquad \text{and} \qquad \frac{\partial \phi}{\partial t} = D\,\frac{\partial^2 \phi}{\partial x^2}$$

  in 1-dimension.
  (J is the Li^+ ion flux and ϕ the Li^+ concentration).
- Experimental determination through electrochemistry.
  Need for a functional battery with
  - a material for the second electrode,
  - an electrolyte,
  - coating for enhanced electron conductivity,
  - ...

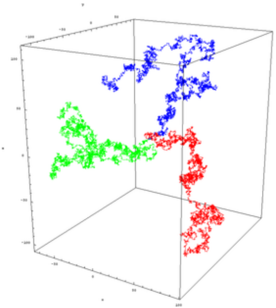
Diffusion of Li$^+$

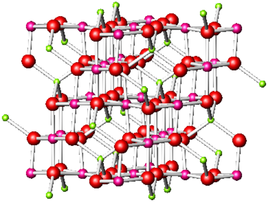
Diffusion coefficient D of Li$^+$ in the electrode material: microscopic level

- Random walk of Li$^+$ ions between lattice or interstitial sites
- $$D \propto \frac{\ell^2}{\tau}$$

  $\ell =$ distance between Li$^+$ sites

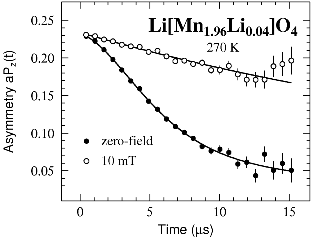
  $\tau =$ mean residence time
- Since $D \sim 10^{-9}$ - 10^{-12} cm^2 s^{-1} at RT and $\ell \sim 0.2$ - 0.3 nm, $\tau \sim 0.01$ - 10 μs.
- Microscopic techniques:
  - Neutron scattering: 1 ns - 1 ps
  - Nuclear magnetic resonance: 1 ms? Line broadening associated to paramagnetism of 3*d* element
  - Muon spin relaxation

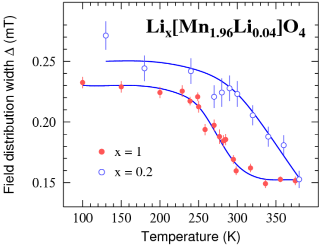


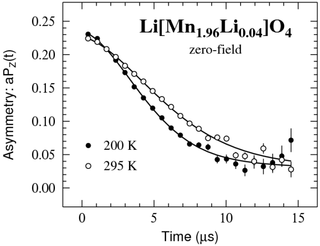


Diffusion of Li^+

μSR study of $Li_xMn_{1.96}Li_{0.04}O_4$





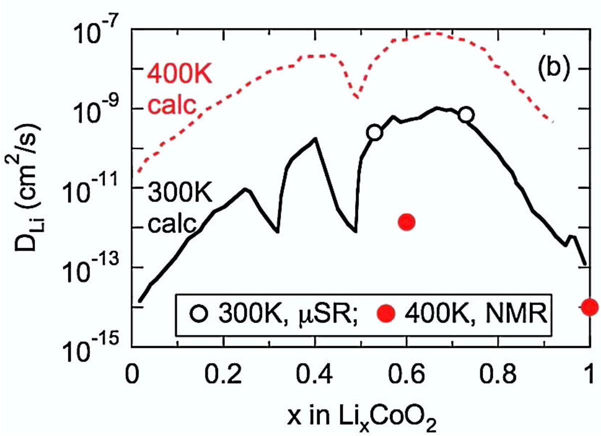


- Sensitivity to nuclear and electronic fields:
  $P_Z(t) = P_{\mathrm{KT}}(t, \Delta_{\mathrm{G}}, \nu)\,\exp(-\lambda_Z t)$
- μ^+ static from shape of $P_Z(t)$ at early times: $\nu_{\mathrm{c}} \simeq 0.1\ \mu s^{-1}$.
- Nuclear field originating from ^{55}Mn, ^{6}Li and ^{7}Li.
- Change in Δ_{G} due to Li^+ motion: $\tau < 0.1\ \mu s$.

Kaiser *et al.*, PRB **62**, R9236 (2000).

Diffusion of Li^+

Li^+ diffusion coefficient in Li_xCoO_2 determined from μSR



Experimental and theoretical values (ab initio computation) of the diffusion coefficient.

Sugiyama *et al.*, PRL **103**, 147601 (2009)

Outline

Summary

- Basic models for $P_{X,Z}(t)$ in dynamical fields.
- Examples of the use of the muon techniques for the study of dynamics in condensed matter:
  - fluctuations and excitations in magnets, critical slowing down,
  - dynamical effects in superconductors,
  - atomic diffusion.
- Not treated
  - onset of correlation involving small and dynamical spins in heavy fermions systems,
  - dynamics in thin films,
  - diffusion of muonium centers, electrons in chain polymers, or light interstitials,
  - use of muons as a spin label for information on chemical reactions,
  - ...

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• A. Amato, *Heavy-Fermion Systems Studied by μSR Techniques*, Rev. Mod. Phys. **69**, 1119 (1997)

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• A. Schenck and F.N. Gygax, *Magnetic Materials Studied by Muon Spin Rotation Spectroscopy*, in Handbook of Magnetic Materials, edited by K.H.J. Buschow, Vol. 9, p. 52 (Elsevier, Amsterdam 1995)

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Muon Spin Rotation, Relaxation, and Resonance

Applications to Condensed Matter

ALAIN YAOUANC AND
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