# Domain walls and density matrix

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# Fit Mn(III) based spin chain

The interactive script **MnIII-spin-chain.Rmd** computes and plots the product $\chi T$ (with $\chi$ magnetic susceptibility computed in $B=0$) for the classical Heisenberg Hamiltonian with uniaxial anisotropy

$$\mathcal{H} = -\sum_{i=1}^{N}\left[J\vec{S}_i\cdot\vec{S}_{i+1} + D(S_i^z)^2 + g\mu_B B S_i^z\right] .$$

By convention the classical spins are assumed with unitary modulus $|\vec{S}_i| = 1$. Therefore, to compare with the conventions used previously in this course, the value of the spin has to be included in the spin-Hamiltonian parameters

$$\begin{aligned} J &\to JS^2 \\ D &\to DS^2 \\ g &\to gS \end{aligned}$$

The value of the anisotropy constant has been taken from the manuscript of A.-L. Barra et al.. Angew. Chem. Int Ed. 36, **21** (1997).

• In the interactive script **MnIII-spin-chain.Rmd**, adjust the values of $gS$, $JS^2$, and $N$ till the experimental points (dots) are reasonably reproduced by the computed curve (dashed line) and copy the chosen parameters below.

$$\begin{aligned} N &= 35 \\ J \to JS^2 &= 65K \\ D \to DS^2 &= 25 \\ g \to gS &= 5.4 \end{aligned}$$

***Comment***

*The students could not know, but in each unit cell The magnetic contribution is actually provided by one $Mn^{3+}$ and one radical, the latter having the spin and the $g$ factor of a free electron. The Curie law for this pair of spins reads*

$$\chi T = \frac{g_{Mn}^2 S_{Mn}(S_{Mn}+1) + g_r^2 S_r(S_r+1)}{3k_B}$$

*Since in the high-$T$ limit the Curie law has to be recovered, the numerator of the equation above should equal the square of the $g$ factor used in our classical-spin model*

$$g^2 = \frac{g_{Mn}^2 S_{Mn}(S_{Mn}+1) + g_r^2 S_r(S_r+1)}{3k_B} = g_{av}^2\left(6+\frac{3}{4}\right) = g_{av}^2\frac{1}{4}(24+3) \simeq 27$$

*where we assumed an average $g_{av} \simeq 2$ for the electron and the Mn ion. From this calculation we would estimate the fitting parameter $g = 5.2$. The tiny correction is due to some residual orbital contribution to the magnetic moment of the Mn ion.*

- Given the fact that the product $\chi T$ theoretically is proportional to the correlation length $\xi$ why does it saturates at a constant value at low temperatures?

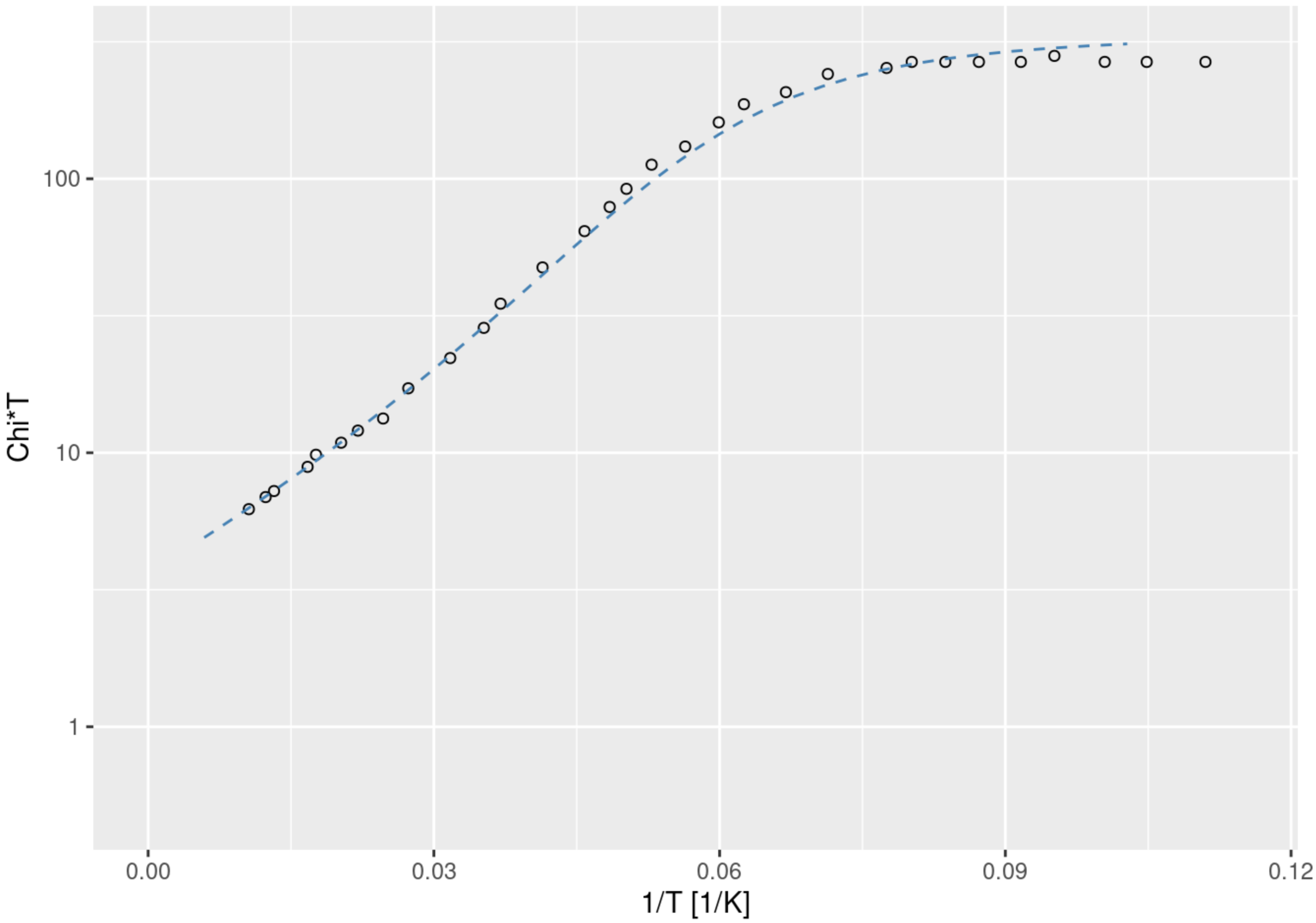
*The sample is a bulk (3D) crystal in which the exchange interaction develops only along one crystal axis so that the sample behaves in good approximation as an ensemble of spin chains. However, naturally occurring defects or lattice dislocations can easily break the exchange pathway within a given chain. In this specific sample, this effect can be accounted for assuming that it actually consists of finite chains of average length equals to $N = 35$.*

- Consistently with the values of $D$ and $J$ that better fit the experimental data, what type of DWs do you think are hosted in this spin chain, broad or sharp?

$$\frac{D}{J} = 0.38 < \frac{2}{3}$$

*therefore domain walls hosted in this spin chain are broad.*

```
##    L J_exch D*S^2 g*S Npts label
## 1 35     65    25 5.4   70    01
```




# Von Neumann entropy

In quantum mechanics the von Neumann entropy of a quantum state is defined as

$$S = -\mathrm{Tr}\left(\hat{\rho}\ln\hat{\rho}\right)$$

which can be concretely computed once the eigenvalues $\lambda_k$ of the density matrix $\hat{\rho}$ are known:

$$S = -\sum_k \lambda_k \ln \lambda_k$$

The reader probably recognizes the direct relation to the Gibbs entropy (apart from the $k_{\mathrm{B}}$ factor) and the Shannon entropy of information theory. The von Neumann entropy vanishes ($S = 0$) for a **pure state** and is larger than zero ($S > 0$) for a **mixed state.**

**Q1** Prove that for a generic state

$$|\psi(0)\rangle = a|\uparrow\rangle + b|\downarrow\rangle$$

of a two-level system the eigenvalues of $\hat{\rho}$ the are $\lambda_0 = 0$ and $\lambda_1 = 1$

$$\hat{\rho} = |\psi\rangle\langle\psi| = \begin{pmatrix} a \\ b \end{pmatrix}\begin{pmatrix} \bar{a} & \bar{b} \end{pmatrix} = \begin{pmatrix} |a|^2 & a\bar{b} \\ \bar{a}b & |b|^2 \end{pmatrix} =$$

*The eigenvalues are obtained solving the characteristic polynomial*

$$\begin{aligned} 0 =& (|a|^2 - \lambda)(|b|^2 - \lambda) - |ab|^2 = |ab|^2 - (|a|^2 + |b|^2)\lambda + \lambda^2 - |ab|^2 \\ =& \lambda^2 - \lambda = \lambda(\lambda - 1) \end{aligned}$$

*whose solutions are obviously $\lambda_0 = 0$ and $\lambda_1 = 1$ (having used the normalization condition |a|^2 + |b|^2 =1).*

**Q2** Consider the density matrix obtained for $t \to \infty$ according to the **Landau-Zener** formula

$$\hat{\rho}_{\rm LZ} = \begin{pmatrix} {\rm e}^{-\pi\gamma_{\rm LZ}} & {\rm X} \\ \bar{\rm X} & 1 - {\rm e}^{-\pi\gamma_{\rm LZ}} \end{pmatrix}$$

and determine the value that $\rm X$ should take in order that the density matrix $\hat{\rho}_{\rm LZ}$ represents a pure state.

*The characteristic polynomial reads in this case*

$$\lambda^2 - \lambda + {\rm e}^{-\pi\gamma_{\rm LZ}} - {\rm e}^{-2\pi\gamma_{\rm LZ}} - |X|^2 = 0$$

*in order for this equation to be equal to the one at the previous point, $X$ needs to be*

$$|X|^2 = {\rm e}^{-\pi\gamma_{\rm LZ}} - {\rm e}^{-2\pi\gamma_{\rm LZ}} \qquad \Rightarrow \qquad X = e^{i\theta}\sqrt{{\rm e}^{-\pi\gamma_{\rm LZ}} - {\rm e}^{-2\pi\gamma_{\rm LZ}}}$$

*where $\theta$ is a generic phase factor.*

**Q3** At **thermal equilibrium** the density matrix of a spin 1/2 in a static magnetic field $B$ takes the form

$$\rho^{\rm eq} = \begin{pmatrix} \rho^{\rm eq}_{\uparrow\uparrow} & 0 \\ 0 & \rho^{\rm eq}_{\downarrow\downarrow} \end{pmatrix}$$

where

$$\rho^{\rm eq}_{\uparrow\uparrow} = \frac{1}{\mathcal{Z}}{\rm e}^{-\beta\hbar\omega_{\rm L}/2} \qquad\qquad \rho^{\rm eq}_{\downarrow\downarrow} = \frac{1}{\mathcal{Z}}{\rm e}^{\beta\hbar\omega_{\rm L}/2}$$

$\beta = 1/(k_{\rm B}T)$, $\omega_{\rm L} = g\mu_{\rm B}B$ is the Larmor frequency and the partition function is

$$\mathcal{Z} = {\rm e}^{-\beta\hbar\omega_L/2} + {\rm e}^{\beta\hbar\omega_L/2}\,.$$

- Compute the von Neumann entropy $S^{\rm eq}$ associated with $\rho^{\rm eq}$ as a function of $\kappa = \beta\hbar\omega_L/2$

*First note that the partition function can be written as*

$$\mathcal{Z} = 2\cosh(\kappa)$$

*The von Neumann entropy takes the form*

$$
\begin{aligned}
S^{\mathrm{eq}} &= -\left[\rho^{\mathrm{eq}}_{\uparrow\uparrow}\ln\left(\rho^{\mathrm{eq}}_{\uparrow\uparrow}\right) + \rho^{\mathrm{eq}}_{\downarrow\downarrow}\ln\left(\rho^{\mathrm{eq}}_{\downarrow\downarrow}\right)\right] \\
&= -\frac{1}{\mathcal{Z}}\left[\mathrm{e}^{-\kappa}\ln\left(\frac{\mathrm{e}^{-\kappa}}{\mathcal{Z}}\right) + \mathrm{e}^{\kappa}\ln\left(\frac{\mathrm{e}^{\kappa}}{\mathcal{Z}}\right)\right] \\
&= -\frac{1}{\mathcal{Z}}\left[-\kappa\mathrm{e}^{-\kappa} + \kappa\mathrm{e}^{\kappa} - \ln(\mathcal{Z})\left(\mathrm{e}^{-\kappa} + \mathrm{e}^{\kappa}\right)\right] \\
&= -\frac{1}{\mathcal{Z}}[2\kappa\sinh(\kappa) - 2\ln(\mathcal{Z})\cosh(\kappa)] \\
&= -\frac{1}{2\cosh(\kappa)}[2\kappa\sinh(\kappa) - 2\ln(2\cosh(\kappa))\cosh(\kappa)] \\
&= -\frac{1}{2\cosh(\kappa)}[2\kappa\sinh(\kappa) - 2\ln(2\cosh(\kappa))\cosh(\kappa)] \\
&= \ln(2\cosh(\kappa)) - \kappa\tanh(\kappa)
\end{aligned}
$$

- In general, is the density matrix $\rho^{\mathrm{eq}}$ representative of a pure state?

*No. Since the off-diagonal terms are zero, the only way to get a pure state is that $\rho^{\mathrm{eq}}_{\uparrow\uparrow}$ and $\rho^{\mathrm{eq}}_{\downarrow\downarrow}$ are equal to 1 and 0, respectively, or vice versa. This not true in general, but only when just one of the two state is populated, i.e., the system is in the ground state ($T = 0$).*

- What can we conclude about the purity of states in the limits $\kappa \to \infty$ (i.e. $T \to 0$) and $\kappa \to 0$ (i.e. $T \to \infty$)?

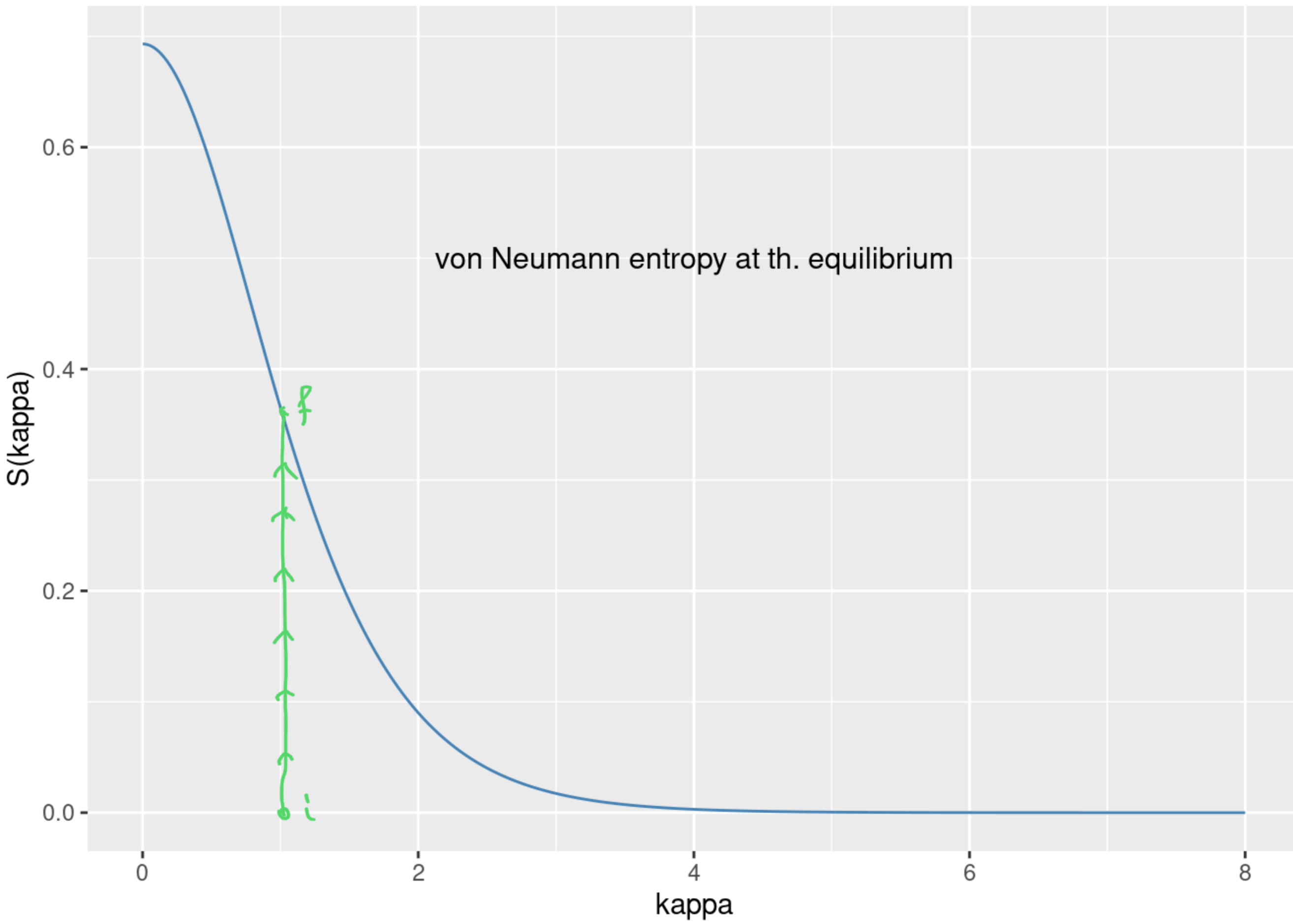
*As anticipated above, the system precipitates into the ground state for $\kappa \to \infty$ (i.e. $T \to 0$), which is a pure state. In the opposite limit $\kappa \to 0$ (i.e. $T \to \infty$), the eigenvalues of $\hat{\rho}$ are both 1/2; the system is in this case not in a pure state but in the state with maximal entropy; in particular the value $S^{\mathrm{eq}} = \ln 2$ equals the Shannon entropy for the flip of an unbiassed coin.*

- Adapt the following script to plot the expression that you have deduced analytically for $S^{\mathrm{eq}}(\kappa)$ at the first point.

*See below.*

- How would you sketch (in the plot) the time evolution of the von Neumann entropy for a system that has been prepared in the state $|\uparrow\rangle$ and evolves till it reaches thermal equilibrium?

*The initial value of the entropy will be on the horizontal axis ($S = 0$). Then the system will evolve (thermalize) till its entropy reaches the thermal equilibrium value. In the plot this time evolution is rendered as a vertical line (constant $\kappa$) starting from $S = 0$ and ending at the plotted curve $S^{\mathrm{eq}}(\kappa)$.*


von Neumann entropy at th. equilibrium
S(kappa)
kappa
0.0
0.2
0.4
0.6
0
2
4
6
8