Algorithmic Cooling in Liquid-state NMR

Yuval Elias / Gilles Brassard Group

↑NTR↓Q Meeting November 2015

Château Bromont
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Château Bromont
Bonne-Fête Anniversaire Gilles!

http://menouummm.centerblog.net/6123670-Bonne-Fete-Anniversaire-
QUANTUM MECHANICS
IN THE REAL-WORLD TODAY!

Our tribute to Erwin Schrödinger on his 126th birthday

https://s3.amazonaws.com/uploads.startups.fm/wp-content/uploads/2013/08/erwin-schrodinger.jpg
Overview

Novel Spin Cooling from Quantum Computing

- Spin cooling: enhancing polarization in NMR
- Polarization compression: generalized polarization transfer
- Open systems: heat-bath cooling, algorithmic cooling

Heat-bath Cooling Experiments

- Model system: $^{13}$C-labeled trichloroethylene (TCE)
- $^{13}$C-labeled glutamate and glycine (Glu, Gly)

Algorithmic Cooling Experiments

- AC in solid-state NMR
- AC in liquid-state NMR - building blocks
- AC in liquid-state NMR – process 1 (cooling C1)
- AC in liquid-state NMR – processes 2, 3 (cooling C2, C3)

Future prospects – Carbon-based Brain Spectroscopy
The advent of NMR quantum computing in the late 1990s led to renewed interest in entropy manipulations for spin cooling.
Spin Cooling – Enhancing Polarization in NMR

**Polarization bias** \( \varepsilon \): excess polarization of spins aligned with field

\[
\rho = \begin{pmatrix}
\frac{1+\varepsilon}{2} & 0 \\
0 & \frac{1-\varepsilon}{2}
\end{pmatrix}, \quad \varepsilon = \tanh\left(\frac{E_{\downarrow}-E_{\uparrow}}{2kT}\right) \xrightarrow{T \to 0} \frac{E_{\downarrow}-E_{\uparrow}}{2kT} = \frac{\hbar \gamma B_0}{2kT}
\]

**Effective spin temperature**: for any bias (also non-thermal)

11.7T (500 MHz), 25°C \( \Rightarrow \varepsilon \sim 10^{-5} \)

🌟 *Spin-cooling*: transient increase in polarization, beyond thermal

Abragam and Goldman, Nuclear Magnetism: Order and Disorder (1982)
Polarization Compression

**Shannon’s bound** on total entropy

Shannon, *Bell Syst. Tech. J.* (1948)

\[ H(X) = \sum p_i \log_2 \frac{1}{p_i} \]

**Coin flip:** \( H(\text{fair}) = 1; \) \( H(\frac{1}{4}, \frac{3}{4}) = 0.811; \) \( H(\text{heads}) = 0 \)

**Fair biased coin:** flip twice, use first toss if different

J. von Neumann, *Appl. Math. Ser.* (1951).

**NMR:** rf pulses for optimal polarization transfer

Sørensen, *Prog. Nucl. Mag. Res. Spec.* (1989)

**“Molecular scale heat engine”:** loss-less data compression

Schulman & Vazirani, *Proc. 31st ACM Symp. Theory Comput.* (1999)
Polarization Compression – Shannon’s Bound

\[H(1) = p_\downarrow \log \frac{1}{p_\downarrow} + p_\uparrow \log \frac{1}{p_\uparrow} = \varepsilon \rightarrow 1 \rightarrow 1 - \frac{\varepsilon^2}{\ln 4}\]

\[\text{Shannon’s bound for } n \text{ spin-system:} \]

\[H(n) = nH(1) = n\left(1 - \frac{\varepsilon^2}{\ln 4}\right) = 1 \cdot \left(1 - \frac{\varepsilon_{\max}^2}{\ln 4}\right) + (n - 1) \cdot 1 \Rightarrow \varepsilon_{\max} = \sqrt{n\varepsilon}\]

★ Over a billion spins required to produce one pure spin!
**3-Bit Polarization Compression**

3-bit compression with non-uniform bias: \( \varepsilon'_a = \frac{\varepsilon_a + \varepsilon_b + \varepsilon_c}{2} \)

Elias, Fernandez, Mor & Weinstein, *Isr. J. Chem.* (2006)

| abc       | \( P(abc) \) |
|-----------|--------------|
| |000\>      | \( p_3 = p_{\uparrow}^3 \) |
| |001\>      | \( p_2 \) |
| |010\>      | \( p_2 \) |
| |011\>      | \( p_1 \) |
| |100\>      | \( p_2 \) |
| |101\>      | \( p_1 \) |
| |110\>      | \( p_1 \) |
| |111\>      | \( p_0 = p_{\downarrow}^3 \) |

\[ P'(a = 0) = p_{\uparrow}^3 + 3p_{\uparrow}^2p_{\downarrow} \xrightarrow{\varepsilon_{\downarrow}} \frac{1+3\varepsilon_0/2}{2} \Rightarrow \varepsilon_a = \frac{3\varepsilon_0}{2} \]
Spin Cooling in Open Systems

selective-reset(c→r): PT to selected computation spin c followed by reset of reset spin r

Assumption: computation spins relax infinitely faster than reset spins
Heat-bath Cooling of Spins

*Heat-bath cooling*: one or more selective-reset steps \(\rightarrow\) cool spin-system entirely or partially

Reset spin \((^1H)\), \(\varepsilon_{eq} \cong 4\varepsilon_0\)

Computation spins \((^{13}C)\), \(\varepsilon_{eq} = \varepsilon_0\)

\[ SR(H \rightarrow C1) \]

\[ SR(H \rightarrow C2) \]

* Improved cooling of both \(^{13}C\) by avoiding final reset*

Fernandez, Lloyd, Mor & Roychowdhury, *Int. J. Quant. Inf.* (2004)
Algorithmic Cooling of Spins

**Heat-bath algorithmic cooling**: bypass entropy bound
combine polarization compression and heat-bath cooling!

\[ \varepsilon_{eq} = 4\varepsilon_0 \]

Reset spin \( (^1H) \), \( \varepsilon_{eq} \equiv 4\varepsilon_0 \)

\[ \varepsilon = 6\varepsilon_0 \rightarrow \text{beyond } H(3)! \]

Computation spins \( (^{13}C) \), \( \varepsilon_{eq} = \varepsilon_0 \)

\* **PAC** – practicable algorithmic cooling

Boykin, Mor, Roychowdhury, Vatan & Vrijen, *PNAS* (2002)
Fernandez, Lloyd, Mor & Roychowdhury, *Int. J. Quant. Inf.* (2004)
Mor, Roychowdhury, Fernandez, Lloyd & Weinstein, US Patent #6,873,154 (2005)
Algorithmic Cooling – Second Cooling Level

Reset spin \( (^1H) \), \( \varepsilon_{eq} \approx 4\varepsilon_0 \)

Computation spins \( (^{13}C) \), \( \varepsilon_1 = 6\varepsilon_0 \)

\( \varepsilon_2 = 9\varepsilon_0 (16\varepsilon_0) \)

\( \text{PAC with } n \text{ spins } \rightarrow (3/2)^n [2^n] \)

Fernandez, Lloyd, Mor & Roychowdhury, Int. J. Quant. Inf. (2004)
Spin-cooling Algorithms

For $n$ spins, one reset spin and $2Q = n-1$ computation spins, ideally:

- **leftmost** - reset spin;
- **rightmost** - coldest

**Optimal** algorithm (PPA): \[ \{1, 1, 2, 4, 8, 16, 32, \ldots, 2^{n-2}\} \]

“Fibonacci” algorithm: \[ \{1, 1, 2, 3, 5, 8, 13, \ldots, F_n\} \]

“Tribonacci” algorithm: \[ \{1, 1, 2, 4, 7, 13, 24, \ldots, T_n\} \]

**Semi-optimal** 4PAC: \[ \{1, 1, 1.94, 1.94, 3.75, 3.75, 7.27\} \Rightarrow 911 \text{ resets} \]

**Semi-optimal** 4Fib: \[ \{1, 1, 1.88, 2.70, 4.28, 6.54, 10.2\} \]

Fernandez, Lloyd, Mor & Roychowdhury, *Int. J. Quant. Inf.* (2004)
Schulman, Mor & Weinstein, *Phys. Rev. Lett.* (2005)
Elias, Fernandez, Mor & Weinstein, *Isr. J. Chem.* (2006)
Elias, Mor & Weinstein, *Phys. Rev. A*, (2011)
Relaxation-Time Ratios

- Reset spins should repolarize much faster than computation spins relax
- Preserve enhanced polarization during reset

\[ \mathcal{R}(c,r) = \frac{T_1(c)}{T_1(r)} \gg d \times Nr \text{ (#reset-steps)} \]

- Preferably - \( \mathcal{R}(c,r) > 10 \times Nr \) (typically \( d \sim 1-5 \))

Elias, Mor & Weinstein, *Phys. Rev. A*, (2011)
Brassard, Elias, Mor & Weinstein, *EPJ+* (2014)
Heat-bath Cooling Model System

$13\text{C}_2$-TCE

Non-selective ("hard") pulses

- chloroform-d / acetone-d$_6$
- Paramagnetic reagent Cr(acac)$_3$

$R(13\text{C}, 1\text{H}) \cong 10$

$T_2 >> 1/J$

$\Delta \omega < 1 \text{ kHz} \Rightarrow$ hard pulses

Fernandez, Mor & Weinstein, *Int. J. Quant. Inf.* (2005)
Brassard, Elias, Fernandez, Gilboa, Jones, Mor, Weinstein & Xiao, *arXiv:quant-ph/0511156* (2005)
Heat-bath Cooling – POTENT pulse sequence

1) 1\textsuperscript{st} Selective Reset(C1$\rightarrow$H)
2) 2\textsuperscript{nd} Selective Reset(C2$\rightarrow$H)

**POTENT** pulse sequence: POlarization Transfer via ENvironment Thermalization

\[
\begin{align*}
1^1\text{H} & \quad \quad 1^3\text{C} \\
1^3\text{C} & \quad \quad 1^3\text{C} \\
\text{C}2 & \quad \quad \text{C}2 \\
\text{C}2 & \quad \quad \text{C}1
\end{align*}
\]

\[T_1(H) < d_2, d_3 < T_1(C2) < T_1(C1)\]

Brassard, Elias, Fernandez, Gilboa, Jones, Mor, Weinstein & Xiao, arXiv:quant-ph/0511156 (2005), EPJP (2014)
Annotated POTENT pulse sequence

Brassard, Elias, Fernandez, Gilboa, Jones, Mor, Weinstein & Xiao, *EPJP* (2014)
Heat-bath Cooling of TCE – Entropy Reduction

After POTENT:

Equilibrium:

Entropy of spin-system reduced by 16% ± 1%

Brassard, Elias, Fernandez, Gilboa, Jones, Mor, Weinstein & Xiao, EPJP (2014)
Heat-bath Cooling – Amino Acids (Gly, Glu)

1) Selective Reset (C1 → H)
2) PT (C2 → H)

13C2-Glu/Gly

Gd-DTPA (Magnevist)

D2O, K3PO4, pH~8

Glutamate (Glu) – major excitatory neurotransmitter, Alzheimer’s disease
Glycine - inhibitory neurotransmitter (low conc.)

T1(H) ~ T1(C2) < d2 << T1(C1)
T2 >> 1/J
Short spin-selective pulses (1 ms BURP)

Elias, Gilboa, Mor & Weinstein, Chem. Phys. Lett. (2011)
Cooling Amino Acids Beyond the Entropy Bound

After cooling

Equilibrium

Both spin-systems cooled (C1 by 1.90 ±0.01)

Elias, Gilboa, Mor & Weinstein, *Chem. Phys. Lett.* (2011)
Heat-bath Cooling of Both Backbone Carbons

Both carbons cooled about 2.5-fold (to ~120K)

Elias, Gilboa, Mor & Weinstein, Chem. Phys. Lett. (2011)
Algorithmic Cooling in Solid State NMR

- Spin diffusion – fast repolarization (msec), $T_1(13C) > 100$ s 😊
- Numerically optimized pulses

- Single crystal, ~3% labeled
- Heat-bath – protons in crystal

$13C_3$-malonic acid

- $1^\text{st}$ Selective Reset ($C_1$→$Hm_1$)
- $2^\text{nd}$ Selective Reset ($C_2$→$Hm_1$)
- Selective PT($C_m$→$Hm_1$)
- 3-Bit Compression ($C_1,C_m,C_2$)

C1 cooled by factor of $4.0 \pm 0.1$
C2 cooled beyond heat-bath (4.59, …, 5.58)

Baugh, Moussa, Ryan, Nayak & Laflamme, *Nature* (2005)
Ryan, Moussa, Baugh & Laflamme, *Phys. Rev. A* (2008)
Algorithmic Cooling in Liquid-state NMR – Building Block 1

- Initial state: $I_z^{C1} + I_z^{C2} + 4I_z^H \propto \text{diag}(6, -2, 4, -4, 4, -4, 2, -6)$
- Final state: $I_z^{C1} + 4I_z^{C2} + I_z^H \propto \text{diag}(6, 4, -2, -4, 4, 2, -4, -6)$
- Max RF: 2 kHz
- Duration: 6 msec

Numerically-optimized pulses (GRAPE)
SIMPSON open source simulation package

PE (polarization exchange) : C2 cooled by $3.76 \pm 0.02$

Glaser, Reiss, Kehlet & Schulte-Herbrüggen, *J. Magn. Reson.* (2005)
Tosner, Vosegaard, Kehlet, Khaneja, Glaserd & Nielsen, *J. Magn. Reson.* (2009)
Atia, Elias, Mor & Weinstein, *Int. J. Quant. Inf.*
Algorithmic Cooling in Liquid-state NMR – Building Block 2

- Initial state: $I_{z}^{C1} + I_{z}^{C2} + I_{z}^{H} \propto \text{diag}(3, 1, 1, -1, 1, -1, -1, -3)$
- Final state: $\frac{3}{2} I_{z}^{C1} + \frac{1}{2} I_{z}^{C2} + \frac{1}{2} I_{z}^{H} + 2I_{z}^{H} I_{z}^{C2} I_{z}^{C1} \propto \text{diag}(3, 1, 1, 1, -1, -1, -1, -3)$
- Max RF: 2 kHz
- Duration: 13 msec

Numerically-optimized pulses (GRAPE)
SIMPSON open source simulation package

COMP : C1 cooled by $2.76 \pm 0.02$

Glaser, Reiss, Kehlet & Schulte-Herbrüggen, *J. Magn. Reson.* (2005)
Tosner, Vosegaard, Kehlet, Khaneja, Glaserd & Nielsen, *J. Magn. Reson.* (2009)
Atia, Elias, Mor & Weinstein, *Int. J. Quant. Inf.*
AC in Liquid-state NMR – Process 1 Overview

Atia, Elias, Mor & Weinstein, *arXiv:1411.4641v2 [quant-ph]*, submitted to *Phys. Rev. A*
AC in Liquid-state NMR – Process 1

Process 1: $D_1=150\text{s}$, $D_2=5\text{s}$, $D_3=3\text{s}$

Atia, Elias, Mor & Weinstein, arXiv:1411.4641v2 [quant-ph], submitted to Phys. Rev. A
AC in Liquid-state NMR – Process 1 Buildup

| Round | Polarization | Carbon’s IC         |
|-------|--------------|---------------------|
| 0     | 1.00         | 1.00 ± 0.04         |
| 1     | 3.40         | 11.56 ± 0.14        |
| 2     | 3.98         | 15.84 ± 0.16        |
| 3     | 4.34         | 18.84 ± 0.17        |
| 4     | 4.49         | 20.16 ± 0.18        |
| 5     | 4.55         | 20.70 ± 0.18        |
| 6     | 4.59         | 21.07 ± 0.18        |
| 7     | 4.61         | 21.25 ± 0.18        |
| 10    | 4.59         | 21.07 ± 0.18        |
AC in Liquid-state NMR – Process 1 (7 Rounds)

C1 cooled by factor of about 4.6, IC\textsubscript{C1} = 21.25 ± 0.18

Atia, Elias, Mor & Weinstein, arXiv:1411.4641v2 [quant-ph], submitted to Phys. Rev. A
AC in Liquid-state NMR – Process 2

Process 2: $D_1 = 150\text{s}$, $D_2 = 5\text{s}$, $D_3 = 3\text{s}$, $D_4 = 5\text{s}$

Atia, Elias, Mor & Weinstein, *arXiv:1411.4641v2 [quant-ph]*, submitted to *Phys. Rev. A*
AC in Liquid-state NMR – Process 2 Results (7 Rounds)

C1, C2 cooled by factors of 3.8, 3.4 (IC_{C1,C2}=25.9 \pm 0.2)

Atia, Elias, Mor & Weinstein, arXiv:1411.4641v2 [quant-ph], submitted to Phys. Rev. A
AC in Liquid-state NMR – Process 3

Process 3: D1=150s, D2=5s, D3=3s, D4=6s, D5=6s

Atia, Elias, Mor & Weinstein, arXiv:1411.4641v2 [quant-ph], submitted to Phys. Rev. A
AC in Liquid-state NMR – Process 3 Results (7 Rounds)

\[
\{C_1, C_2, H\} = \{2.87, 2.64, 3.58\} \pm 0.02, \quad IC=28.0 \pm 0.2
\]

Atia, Elias, Mor & Weinstein, \textit{arXiv:1411.4641v2 [quant-ph]}, submitted to \textit{Phys. Rev. A}
Future Prospects – Carbon-based Brain Spectroscopy

- Suitable isotopomers
- Moderate cooling
- *In vivo* – replenish
- Monitor slow metabolism

Review: Rodrigues & Cerdán, *Concepts Magn. Reson.* (2005)
Future Prospects – Carbon-based Brain Spectroscopy

- Dorith Goldsher MD (Rambam) - 3T MRI
- Dr. Itamar Kahn (Technion) - 9.4T MRI
- Dr. Andrew Webb (Leiden) - 7T MRI

Sailasuta, Robertson, Harris, Gropman, Allen & Ross, *J. Mag. Res.* (2008)
Collaborators

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Thanks for listening!
NMR Quantum Computing (NMRQC)

- Experiments since 1997
  leading QC implementation – 13 qubits (2010)
- **Qubits**: nuclear spins, usually spin-$\frac{1}{2}$ ($^1H$, $^{13}C$, $^{15}N$, $^{19}F$, $^{31}P$)
- **Single qubit gates**: spin-selective rf pulses
- **Multi-qubit gates**: J-coupling, dipolar coupling
- **Algorithm**: pulse sequence – **universal set of gates**
- **Sample**: ensemble of many identical molecules
- **Pseudopure state** – not scalable!

*Review*: Jones, “Quantum Computing with NMR” preprint *arXiv:1011.1382v1* (2010)
HCC relay using soft vs hard pulses

Elias, Gilboa, Mor & Weinstein, *Chem. Phys. Lett.* (2011)
Brassard, Elias, Fernandez, Gilboa, Jones, Mor, Weinstein & Xiao, *EPJP* (2014)