Experimental Heat-Bath Cooling of Spins

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Abstract

Algorithmic cooling is a novel technique to generate ensembles of highly polarized spins, which could significantly improve the signal strength in Nuclear Magnetic Resonance (NMR) spectroscopy. It combines reversible (entropy-preserving) manipulations and irreversible controlled interactions with the environment, using simple quantum computing techniques to increase spin polarization far beyond the Shannon entropy-conservation bound. Notably, thermalization is beneficially employed as an integral part of the cooling scheme, contrary to its ordinary destructive implications. We report the first cooling experiments bypassing Shannon’s entropy-conservation bound, performed on a standard liquid-state NMR spectrometer. We believe that this experimental success could pave the way for the first near-future application of quantum computing devices.

Introduction

An efficient technique to generate ensembles of highly-polarized spins is a Holy Grail for Nuclear Magnetic Resonance (NMR) spectroscopy and imaging (MRI). The resulting enhancement of the signal-to-noise ratio (SNR) permits faster data acquisition, or reduces the amount of material required, thus enabling more efficient analysis of chemicals and visualization of tissues. Methods to overcome the low sensitivity of nuclear magnetic resonance \cite{1,2} include high magnetic fields (limited to about 20 T), signal averaging (time consuming), and temperature reduction (impractical for many samples). Another solution is to cool the spins without cooling the environment: spin-half particles in magnetic fields have steady-state polarization biases inversely proportional to the temperature and so spins exhibiting polarization biases in excess of the equilibrium bias are considered cool, even when their environment is warm \cite{2}. Such spin-cooling is an important

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Abbreviations: AC, algorithmic cooling; NMR, nuclear magnetic resonance; SNR, signal to noise ratio; PT, polarization transfer; POTENT, polarization transfer via environment thermalization
method of increasing SNR: at room temperature in a constant magnetic field, a polarization enhancement by a factor of $M$ improves the SNR by the same factor, and reduces the required signal averaging time by a factor of $M^2$.

Spin-cooling techniques are not a new concept. Many NMR studies rely on a variety of methods to transfer polarization from high bias spins to low bias spins (see 2 and references therein) increasing the latter’s signal intensity. Alternatively, several more recent approaches are based on the creation of very high polarizations, e.g. dynamic nuclear polarization 4, para-hydrogen in two-spin systems 5, and hyperpolarized xenon 6. In addition, there are other spin-cooling methods that are based on general unitary transformations 3, and on (closely related) data compression methods in closed systems 7. A different effective-cooling method, algorithmic cooling (AC), makes use of entropy manipulations in an open system 8, 9. These entropy manipulation techniques in closed and open systems employ simple NMR quantum computing tools.

Nuclear Magnetic Resonance Quantum Computing (NMRQC) 10, 11, 12, 13 was proposed and demonstrated in 1996 14, 15, 16. NMRQC researchers have subsequently implemented several quantum algorithms, using standard NMR equipment, on spin systems (molecules) containing up to 7 quantum bits (that is, two-level quantum systems, also called qubits) 17. The system is commonly a solution containing an ensemble of identical molecules. Each molecule acts as an independent quantum computer, and the same algorithm is run in parallel on all computers. A qubit is represented by a spin-half nucleus in each molecule. For instance, trichloroethylene (TCE) molecules (see figure 1) with two $^{13}$C nuclei and one $^1$H nucleus provide three-qubit registers. Gate operations are implemented by sequences of radio frequency pulses, as in conventional NMR. Two key aspects of such ensemble quantum computing are the highly mixed initial state and the fact that when measuring a qubit one obtains a sum of values for that qubit, averaged over the ensemble. The application of conventional quantum algorithms to such mixed-state computers suffers from a severe scalability problem 16, 18, 7, 11, 8. To resolve this problem, and to prove the potential scalability of NMRQC, Schulman and Vazirani 7 suggested the use of reversible (entropy preserving) spin-cooling schemes. The practicality of such unitary schemes 3, 7 is highly limited due to the Shannon entropy-conservation bound and the Sørensen unitarity bound. For instance, the spin temperature of a single spin (qubit) in an $n$-qubit molecule (at room temperature) cannot be decreased by more than a multiplicative factor of $\sqrt{n}$ due to the entropy-conservation bound (namely, Shannon’s bound on reversible entropy manipulations — the source coding theorem 19, 20). The Sørensen bound is tighter than the Shannon bound as Shannon does not prohibit the use of non-unitary transformations.

Algorithmic Cooling of Spins

To increase spin polarization far beyond these two bounds, Boykin, Mor, Roychowdhury, Vatan and Vrijen 5 suggested a novel technique, algorithmic cooling of spins, which combines reversible manipulations with controlled irreversible interactions with the environment. The reversible steps consist of compressing entropy, then transferring it to “reset” spins, that is spins that reach thermal equilibrium rapidly (qubits with very short relaxation times). Consequently, these reset spins (reset bits) thermalize and lose their excess entropy irreversibly to the environment.

More recently, Fernandez, Lloyd, Mor, and Roychowdhury 9 have designed improved cooling algorithms that can be applied to short molecules, thus greatly expanding the potential for near-future application to high-sensitivity magnetic resonance spectroscopy; a polarization improvement by a factor of about $(3/2)^{(n-1)/2}$ on a single spin is obtained using a simple algorithm applied to $n$ spins (of which one is a reset spin). For more details, and several interesting algorithms and bounds see 9, 21.

The reversible manipulations required have already been demonstrated experimentally 3, 22.

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‡The total entropy of such a molecule, $H(n) \approx n(1 - \epsilon^2 / \ln 4)$, is compressed so that $n - 1$ spins have full entropy; the remaining spin satisfies $H(\text{single}) \geq 1 - (\sqrt{\epsilon})^2 / \ln 4$.

§We use the term “bit” and not “qubit”, as our cooling algorithms are classical. We refer to “qubits” when appropriate. Furthermore, we use the term “spin” to mean a spin-half nucleus.
while the irreversible step of AC has not been previously reported. Here we show experimentally, for the first time, controlled entropy extraction from a spin system, to bypass Shannon’s entropy-conservation bound. To do so, we implement a restricted form of AC called heat-bath cooling, where polarization transfer steps (but no compression steps) are combined with controlled interactions with the environment (reset steps) to achieve this entropy reduction. This experimental implementation presents a major step in the development of open-system spin-cooling techniques, and therefore paves the road for the full 3-bit algorithmic cooling process, and for more dramatic cooling as suggested in [8,9,21].

Materials and methods

In our AC experiment we employ the 3-qubit heteronuclear molecule TCE, shown in Figure 1, in which the hydrogen has relatively fast relaxation and can function as a reset bit. Furthermore, at thermal equilibrium, the polarization of both $^{13}$C nuclei is approximately the same, say $\varepsilon$, and that of the proton is very close to $4\varepsilon$. Therefore it is also useful for conventional (entropy preserving) polarization transfer (PT). When PT is combined with fast relaxation (reset) of the proton and with polarization compression, cooling of TCE beyond Shannon’s and Sørensen’s bounds can be achieved in various ways, based on algorithms described in [9,21], positioning this molecule as a good testbed for various cooling experiments. The bound we bypass in this work is the Shannon bound regarding the conservation of the full entropy of the 3-bit system. The Shannon entropy of the system at thermal equilibrium is approximately $H \sim 3 \times (4^{1/2} + 1^{1/2}) \varepsilon^2 \ln 4 = 3 - 18\varepsilon^2 / \ln 4$, in bit units. The information content of the molecule, that is the difference from full entropy, is given in this case by $I = 3 - H \sim 18\varepsilon^2 / \ln 4$. Here we shall be interested in increasing this value, $I$, thus decreasing the total entropy $H$, and cooling the entire system. We take advantage of two properties of the $^1$H in relation to the $^{13}$C: greater polarization at thermal equilibrium, and sufficiently smaller T$_1$ relaxation time. The cooling procedure we report here is very simple, involving no compression step. While a system is usually heated by “thermalization”, this partial AC presents a simple demonstration of “heat-bath cooling”, one of the two building blocks of the full algorithmic cooling. It has four steps: (1) transfer polarization from H to the far carbon (C1); (2) wait for a suitable time, $t_1$, for H to repolarize; (3) transfer polarization from H to the adjacent carbon (C2); (4) wait again for a second duration, $t_2$, for H to repolarize. Although polarization transfer is used widely, sometimes also combined with fast relaxation of the more polarized spins, this heat-bath cooling is the first experiment reporting bypassing Shannon’s entropy-conservation bound.

From an algorithmic point of view, a transfer of polarization can be achieved by exchanging the states of the two spins, using a SWAP gate. The required PT, however, is unidirectional and therefore simpler than SWAP. Implementation of such a unidirectional PT from proton to adjacent carbon has some freedom as we do not care about any residual polarization of the proton (after PT), which is to be reset. It is normally inefficient to implement directly a PT gate between non-adjacent spins due to weak scalar couplings. Step 1 above thus comprises two sequential steps: PT(H → C2) and PT(C2 → C1). A simple way of implementing PT is to use the refocused INEPT sequence, which is an extension of the well-known INEPT sequence [22]. Refocused INEPT (for an illustration of the sequence see Figure 5 of supporting information) may be considered as a unidirectional SWAP, in which the polarization of the proton is fully transferred to the carbon. We refer to this practical implementation of cooling by thermalization as POTENT: POlarization Transfer via ENvironment Thermalization.

First consider an ideal case, where the T$_1$ ratio between each $^{13}$C nucleus and $^1$H is infinite, the resonance frequencies are in exact ratios of 1:1:4, all SWAP gates are implemented perfectly and the long-lived spins are not prone to relaxation or errors. Starting from equilibrium biases $\{\varepsilon, \varepsilon, 4\varepsilon\}$ scaled up by $\varepsilon$ and denoted as $\{1, 1, 4\}$ for C1, C2 and H, respectively, this would result in

\[ I = 3 - H = 3 - \frac{18\varepsilon^2}{\ln 4} = 3 - \frac{18\varepsilon^2}{\ln 4} \]

Note that conventional entropy preserving algorithms (common in data compression, and in NMR polarization manipulations) cannot decrease the total entropy of the three bits.

\*The ln 4 emerges from the 2nd order term in the Taylor approximation.

\*Note that conventional entropy preserving algorithms (common in data compression, and in NMR polarization manipulations) cannot decrease the total entropy of the three bits.
in the following sequence of polarizations:

\[
\{1, 1, 4\} \xrightarrow{PT} \{1, 4, 1\} \quad \xrightarrow{reset} \{4, 1, 4\} \quad \xrightarrow{PT} \{4, 1, 1\} \quad \xrightarrow{reset} \{4, 4, 1\}
\]

which would result in a final information content of

\[ I = (4^2 + 4^2 + 4^2) e^2 / \ln 4 = 48 e^2 / \ln 4, \]

a more than two-fold increase, which clearly bypasses the entropy-conservation bound.

However, one must account for the finite ratio in \( T_1 \) values. We performed a numerical simulation of the POTENT pulse sequence using a standard relaxation model and \( T_1 \) relaxation rates measured in the laboratory, to obtain the expected final bias values of each spin. The same simulation model also provided optimal values of the two free parameters in the experiment, \( t_1 \) and \( t_2 \), the first and second \( H \) repolarization delays, which maximize the final information content (see details of the simulation method in supporting information).

The POTENT experiments were initially performed at Université de Montréal and later on at the Technion and Oxford. In some of the experiments a paramagnetic relaxation agent was added to the sample to increase the ratios of \( T_1 \) relaxation times between the \( ^1H \) and both \( ^13C \), as suggested in [24, 25]. See supporting information for details regarding the relaxation agent. The simulation and experimental results presented in this paper correspond to a sample that contains this relaxation agent.

## Results

We acquired spectra of TCE at equilibrium and after the cooling pulse sequence. Figure 2 displays \(^{13}C \) and \(^1H \) NMR spectra for TCE. Figures 2(a) and 2(c) were obtained at thermal equilibrium and serve as a reference point for \(^{13}C \) and \(^1H \), respectively. For both \(^{13}C \) nuclei, the increase in polarization can be observed by looking at the noticeably higher peaks compared with the reference spectrum, while the \(^1H \) intensity is only slightly reduced. Experimentally acquired resonance frequencies and temperature were used to calculate equilibrium biases of \( 1 \pm 0.003 \) for the carbons and \( 3.98 \pm 0.01 \) for the proton, leading to initial information content of \( I = 17.8 \pm 0.1 \) (in units of \( e^2 / \ln 4 \)) and ideal final information content of \( I = 47.44 \). Precise values for the final polarization of each nucleus were obtained by comparing the integrals of the peaks (see supporting information for details regarding data analysis), as shown in Table 1. The table also includes simulated final values, accounting for actual \( T_1 \) relaxations. In terms of information capacity, a final value of \( 20.70 \pm 0.06 \) was observed, compared with \( 17.8 \pm 0.1 \) at thermal equilibrium (in units of \( e^2 / \ln 4 \)), resulting in an increase of \( 16% \pm 1% \). The ideal value of 47.44 is devoid of relaxation constraints, while the simulated value of 29.59 accounts for experimental \( T_1 \) values; for details on the simulation results see supporting information. This discrepancy between actual and simulated values can largely be ascribed to inevitable imperfections in polarization transfer steps, arising from many sources**. A more subtle factor is that the relaxation model used is naive, as the spins do not relax completely independently but rather show significant cross-relaxation. Because of this effect, the final observed polarizations were lower than expected under our single-spin \( T_1 \) relaxation model.

## Discussion

We have successfully implemented experimental cooling of a spin system, using an essential step of Algorithmic Cooling, “heat-bath cooling”. Our POTENT experiment combined well-controlled spin polarization transfer on three qubits and relatively fast thermal relaxation of the “reset bit”. We thus increased the polarization of two \(^{13}C \) nuclei using one \(^1H \) proton in trichloroethylene.

**A practical simulation, which takes these imperfect PTs into account, yields results much closer to our experimental 20.70, see supporting information for more details.
This is the first reported experiment bypassing Shannon’s bound on entropy manipulation and in particular on polarization enhancement††. This also complements the previously implemented steps of Algorithmic Cooling, polarization compression [3, 22], and polarization transfer. Thus, our experiment shows that AC is viable in practice as a technique for increasing spin polarization in NMR. AC is readily usable with current off-the-shelf technology and is directly applicable to a wide range of molecules. Full AC protocols promise very significant SNR improvement if performed on longer molecules, if the reset bits thermalize much faster, or if AC is combined with other techniques for improving the SNR. It is important to compare our experiment to some common polarization transfer techniques. Some specialized NMR techniques (such as continuous CP, DNP, NOE or ENDOR [1, 2]) may be able to bypass Shannon’s entropy-conservation bound under certain circumstances. However, to the best of our knowledge, such bypassing has not been previously claimed in the literature ‡‡. The high level of controlled quantum operations typical of NMR quantum computing, and the potential to reach highly polarized states without access to an initial low temperature heat-bath, further distinguishes AC from the above NMR methods.

While AC is a classical algorithm, its implementation (via qubits) makes use of novel tools recently developed in the evolving field of NMR quantum computing. This algorithm holds the potential to significantly improve NMR spectroscopy. Therefore, our experimental success may pave the road to the first practical application of quantum computing.

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††Note that a simpler experiment with one proton and one carbon could also bypass Shannon’s entropy-conservation bound; we chose 3-spin POTENT because it is a necessary building block for the implementation of the full AC technique.

‡‡In contrast, the easier task of bypassing Sørensen’s unitarity bound was discussed theoretically long before AC was suggested, see [26].
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Figure 1: Trichloroethylene labeled with two $^{13}$C. We denote the leftmost $^{13}$C in this figure as C1 and the other, neighboring $^1$H, as C2. In our experiments, the resonance frequencies were 125.773354, 125.772450 and 500.133245 MHz for C1, C2 and H respectively. The scalar coupling constants were 201, 103 and 9 Hz between C2-$^1$H, C1-C2, and C1-$^1$H, respectively, while $T_1$ relaxation times were measured at 43 ± 4.0s and 20 ± 2.0s for C1 and C2 respectively, and 3.50 ± 0.05s for H.

Table 1: Initial and final polarizations and spin temperatures for each qubit in TCE for the AC experiment shown in figure.

|       | Initial bias ($\varepsilon$) | Simulated bias ($\varepsilon$) | Observed bias ($\varepsilon$) | Spin temperature (K) |
|-------|-----------------------------|--------------------------------|------------------------------|----------------------|
| C1    | 1 ± 0.003                   | 2.965                          | 1.74 ± 0.01                  | 170 ± 1              |
| C2    | 1 ± 0.003                   | 2.602                          | 1.86 ± 0.01                  | 159 ± 1              |
| H     | 3.98 ± 0.01                 | 3.734                          | 3.77 ± 0.01                  | 312 ± 1              |

The resonance frequency of each nucleus is used to compute its natural bias at thermal equilibrium at the room temperature of 295.7 ± 1.0 K at which the experiment was run. A maximum bias of 3.98 could be achieved for all three spins if the $T_1$ gaps were infinite and the polarization transfers were implemented by perfect unitary transformations. The simulated values were computed by taking into consideration $T_1$ relaxation measured in the laboratory but ignoring imperfections in the transfers.
Figure 2: Spectra of TCE before and after the AC experiment. Figs. (a) and (b) are the $^{13}$C spectra before and after the experiment, respectively, with the left multiplet being C1 and the right one C2. Figs. (c) and (d) are the corresponding $^1$H spectra before and after the experiment, respectively. The spectrum in Fig. (d) was obtained by running the AC experiment a second time with the exact same parameters as in Fig. (b), this time observing the $^1$H instead of the $^{13}$Cs by reversing the spectrometer channels.

A Supporting Information

The heat-bath cooling experiment (POTENT) was first performed at the Université de Montréal in March 2002 on a Bruker DMX-400. Initial and final carbon spectra of the original experiment are presented in Figure 3. Proton polarizations were calculated via the simulation model, as only carbon spectra were recorded. The resulting information content showed that Shannon's entropy bound was bypassed, but we did not have experimental results for the proton to support that conclusion.

The experiment has since been repeated at the Technion on a Bruker Avance-500 and at Oxford University on a Varian Inova-600. $^{13}$C$_2$-trichloroethylene (TCE) was obtained from CDN Isotopes (99.2%$^{13}$C) or from Cambridge Isotope Laboratories (99%$^{13}$C, diisopropylamine stabilized). In Montréal and in Haifa, the same Bruker pulse sequence programs were used on samples of TCE dissolved in deuterated chloroform (Aldrich, 99.9%D). In Oxford, functionally equivalent pulse programs were used on TCE in deuterated chloroform as well as in deuterated acetone. Some experiments, including the first one and those shown in this paper, were carried out with addition of a paramagnetic relaxation reagent, Cr(III)acetylacetonate, obtained from Alfa Aesar (97.5+% pure), at a final concentration of about 0.2 mg/mL.

To evaluate the expected efficiency of our AC procedure, we wrote a Matlab program that simulates the conditions of the TCE POTENT experiment. Originally, the simulation model did not account for imperfections in the three polarization transfers (H to C2, C2 to C1, and final H to...
C2). This simulation model assumes perfect polarization transfers, and includes experimentally-obtained $T_1$ relaxation of all spins, applied by the program during the two waiting periods, $t_1$ and $t_2$. The simulation yields a two-dimensional surface of expected Information Capacity (IC) values, normalized by $\varepsilon^2/\ln 4$ as a function of both waiting periods, as shown in Figure 4. Note the broad maximum region encompassing a large extent of $t_1$ values.

It is not simple to take inevitable imperfections into account theoretically, but it is possible to do so in practice by using transfer efficiency rates obtained experimentally. A “practical” simulation model can thus account for imperfections in the three PTs. We obtained the results $92\% \pm 2\%$, $69\% \pm 1\%$ and $74\% \pm 1\%$ for the three PTs, resulting in an information content of $22.4 \pm 0.9$. These transfer efficiency rates were obtained by measuring the relative peak integrals after various intermediate stages in laboratory conditions identical to the AC experiment.

Only “hard”, high-power, non-selective pulses were used for the $^{13}$C. In the single case where addressing only one of them was necessary, we induced a phase separation by employing the chemical shift, while adequately refocusing coupling evolutions. We chose not to use time-averaging or phase cycling, in order to study the effect of AC independently of all other techniques. A block diagram depicting the various stages of our experiment is shown in Figure 5. The three transfer sequences, from H to C2, from C2 to C1, and finally from H to C2 again, use different refocusing schemes to compensate for unwanted couplings and chemical shifts (the $^{13}$C channel was chosen to be in resonance with C2). In addition, the third transfer is designed to leave intact any polarization already stored on C1 (indicated by the $^*$ sign in Figure 5). In this case, we employ refocusing to prevent unwanted polarization transfer out of C1. The first two polarization transfers jointly consist of two overlapping refocused INEPT sequences, while the third transfer is a single refocused INEPT. The INEPT sequences are shorter and consist of fewer pulses than the corresponding SWAP sequences, facilitating implementation.

The POTENT sequence was run with various combinations of $t_1$ and $t_2$ delays. To obtain statistical information several spectra were acquired for each combination of delays. Reported values were obtained for five separate single-scan measurements.

In order to validate the sequence and estimate transfer efficiencies, truncated versions of the complete pulse sequence were acquired, each version terminating at a different stage. Intermediate spectra obtained in this manner are shown in Figure 6.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{before_after.pdf}
\caption{Carbon spectra before and after POTENT sequence from an experiment performed at Montréal in 2002.}
\end{figure}
Figure 4: A simulation of information capacity (IC) as a function of the H repolarization delay times $t_1$ and $t_2$, with the IC represented on the z-axis. In this simulation we assume perfect polarization transfers. The maximum IC value was numerically found at $t_1 = 8.25$ s and $t_2 = 9.6$ s.

Figure 5: A block diagram of the complete experiment, with C1 represented at the top line. The arrow boxes denote polarization transfers in the direction of the arrow. The periods $t_1$ and $t_2$ are the variable delay times in which we wait for H to repolarize.
| Step | Spectrum after the step |
|------|------------------------|
| 1    | ![Image of step 1]     |
| 2    | ![Image of step 2]     |
| 3    | ![Image of step 3]     |
| 4    | ![Image of step 4]     |
| 5    | ![Image of step 5]     |

Figure 6: The steps of the cooling experiment and the resulting $^{13}$C spectra after each step.