Physics of polarized targets

Tapio Niinikoski
CERN (retired)
CH-1211 Geneva, Switzerland
E-mail: tapio.o.niinikoski@gmail.com

For developing, building and operating solid polarized targets we need to understand several fields of physics that have seen substantial advances during the last 50 years. We shall briefly review a selection of those that are important today. These are: 1) quantum statistical methods to describe saturation and relaxation in magnetic resonance; 2) equal spin temperature model for dynamic nuclear polarization; 3) weak saturation during NMR polarization measurement; 4) refrigeration using the quantum fluid properties of helium isotopes. These, combined with superconducting magnet technologies, permit today to reach nearly complete polarization of almost any nuclear spins. Targets can be operated in frozen spin mode in rather low and inhomogeneous field of any orientation, and in DNP mode in beams of high intensity. Beyond such experiments of nuclear and particle physics, applications are also emerging in macromolecular chemistry and in magnetic resonance imaging.

This talk is a tribute to Michel Borghini, whom we remember for his work on the equal spin temperature model at CERN, and to Franz Lehar, who promoted the frozen spin target technique and applied it in a long series of nucleon-nucleon scattering experiments in Saclay.

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1. Tributes to Michel Borghini and to Franz Lehar

1.1 Michel Borghini † 15 December 2012

Born in 1934, Michel Borghini was citizen of Monaco. He graduated from Ecole Polytechnique (Paris) in 1955 and went on to obtain a degree in electrical engineering from Ecole Supérieure d’Electricité, Paris, in 1957. He then joined the group of Anatole Abragam at what was then Centre d’Etudes Nucléaires, Saclay, where he took part in the study of dynamic nuclear polarization (DNP) that led to the development of the first polarized proton targets for use in high-energy physics experiments. It was there that he gained the experience that he was to develop further at CERN, to the great benefit of experimental particle physics.

An obituary of Michel Borghini was published in the CERN Courier of 28 March 2013 [1], with biographic information including references to his work on polarized targets and spin physics. We remind here his paper entitled “Spin temperature model of DNP” [2], which remains one of his major contributions to polarized target physics for the participants of this Workshop. This model extended the general quantum statistical (QS) treatment of magnetic resonance saturation to electron spin systems at low temperatures where the polarization is high. The QS treatment and Borghini’s model will be discussed in Sections 2 and 3. Borghini and his team at CERN proved also experimentally [3] the validity of his hypothesis that all nuclear spin species cool towards a common temperature, which is that of the dipolar energy reservoir of the electronic spin system under a saturating microwave field.

The efficient cooling of nuclear spin systems in the above model required that the spectrum of the electron spin resonance (EPR) frequencies be suitably broad. This ensures rapid transfer of the magnetic energy between the nuclear and electron spin systems, by multispin transitions that are allowed in first-order perturbation theory. Borghini was probably the first person to fully understand the benefits of this, in comparison with the “solid effect” mechanisms. The latter required such large microwave field strength that cooling was possible only by evaporation of superfluid 4He (or, more accurately, by 2-phase flow of 4He as we know now). The DNP described by the new model could benefit from lower coolant and lattice temperatures, and could be extended to a large class of new materials that are richer than LMN in hydrogen or deuterium. Moreover, the much lower temperatures available by dilution refrigeration would enable “freezing” the polarization so that a lower and more inhomogeneous “holding” field of a spectrometer would be sufficient to maintain the polarization of the target after DNP in a high and homogeneous field. Magnets designed for such spectrometers could have large acceptance, when optimized for the reaction under study. Borghini initiated the development of such target technology at CERN, where the first frozen spin target was constructed and operated in 1974 [4].

As reported in the article of CERN Courier [1], Borghini participated in a broad range of particle physics experiments with polarized targets and beams at Saclay, CERN, SLAC, and Argonne, before moving to the UA2 collider experiment at CERN. Details of these can be found in the original Courier article, together with an account of his activities as President of CERN Staff Association and as Permanent Representative of Monaco to the United Nations in New York.
1.2 Franz Lehar † 23 November 2011

Born in Bludov, about 200 km east of Prague in Czechoslovakia (now in the Czech Republic), in the same year 1934 as Michel Borghini, Franz Lehar had a turbulent transition in his career during the politically delicate year 1968. He studied nuclear physics on the Faculty of Mathematics and Physics of the Charles University and graduated in 1957. Then he started to work as assistant in the Faculty of Technical and Nuclear Physics of the Charles University, and was three years later promoted to the rank assistant professor. In 1961 he left for seven years to work in JINR Dubna, where he defended his PhD thesis entitled “Neutron scattering on protons at energy of 630 MeV” in 1966.

The grandfather of Franz Lehar was the composer and conductor of same name, who developed his career in Vienna in the first half of the 20th century. Dramatically, while driving to the Rochester Conference of Vienna on 21 August 1968, Lehar and his wife learned of the invasion of Prague by the USSR-led troops of Warsaw Pact. In Vienna they decided to look for political asylum in France, which was awarded in 1972. Three months later they were sentenced to prison in Prague and their property was confiscated.

Franz and Lilian Lehar obtained French citizenship in 1974. Appointed by CNRS, Lehar had worked since 1968 with Ludwig Van Rossum in several experiments at CERN and in CEA Saclay, before embarking in the Nucleon-Nucleon collaboration in Saturne II where he played a leading role.

The acceleration of polarized protons and deuterons at the 3 GeV Saturne II synchrotron was highly successful, with polarized proton and deuteron beam intensities and qualities close to those of the unpolarized ones after the completion of the MIMAS booster. Lehar and the NN collaboration worked throughout the whole life of Saturne II, for nearly two decades, measuring $pp$ and $pn$ cross sections, analysing powers, spin correlations, and spin transfers, until the machine was shut down in December 1997. For this programme the collaboration needed a frozen spin polarized target with large acceptance. The design promoted by Franz Lehar consisted of a vertical dilution refrigerator with a movable 2.5 T superconducting (SC) magnet with the vertical field quality required by high DNP, supplemented by large vertical and horizontal orthogonal SC coils for holding the target spin polarization vector in any direction required by the parameter under study [5,6]. The target material was initially butanol-water doped with with EHBA-Cr(V), and in the later part of the programme irradiated $^6$LiD and $^6$LiH were used.

An example of the perfection of Lehar’s work is the publication “Proton-proton Data Measured by the Saclay Nucleon-Nucleon Collaboration at Saturne II” in CTU Reports series [7]. This paper summarizes the 6112 independent data points obtained at Saturne II using the polarized beam and/or polarized proton target, for 13 to 15 independent observables in polarized $pp$ scattering.

A great advantage of the Saclay NN collaboration was that they had access to a quasi-monochromatic neutron beam up to $\approx 1.15$ GeV produced by the breakup of the primary deuteron beam. A particular feature of the frozen spin target was then to match the rather large beam size. The target was therefore a cylinder of 5 cm height and of 5 cm diameter, requiring a high cooling power from the dilution refrigerator. Altogether 1757 data points were measured.
thus for the $pn$ interaction. At higher energies the collaboration used quasi-free scattering of a polarized proton on the polarized neutron in the deuteron, yielding 157 $pn$ data points above 1.1 GeV kinetic energy.

In the $pp$ and $pn$ scattering experiments 2 or 3 spins were measured, and complete reconstruction of the scattering amplitudes based on this wealth of experimental data was published in a series of papers listed in ref. [7].

An obituary of Franz Lehar was published [8] by Czech Technical University (CTU) on their web site, and biographical information is also available in an article of Scintillations (CEA France) [9]. The article is based on a talk of Bernard Peyaud delivered on 23 April 1996 in Prague on the occasion of awarding Lehar the rank and rights of honorary Doctor of Physical and Mathematical Sciences of CTU. Previously, in 1990, Franz and his wife had already got back their Czech citizenships, and their prison sentences and confiscation of property of 1972 had been annulled by Vaclav Havel.

2. DNP in solids at low temperature: dynamic cooling of the spin systems

The physics of solid polarized targets is that of spins bound in solid matter, under conditions favourable for high polarization: high magnetic field and low temperature. While the high field allows one to use some simplifications in theoretical modeling, the low temperature and high polarization lead to complications that were not well mastered until the 1960s. Moreover, the high densities of nuclear and electronic spins, also required in polarized targets, lead to additional difficulties due to the strength of the dipolar interactions. The description of magnetic resonance saturation then needs quantum statistics (QS) to model the dynamic behavior of large arrays of spins. The first theoretical work was made by Provotorov in 1961, who described the correct RF field dependence of the resonance lineshape in his well-known paper [10]. This explained the experimental findings of Redfield [11] and enabled further extensions of the technique to cross relaxation and spin-lattice relaxation.

The QS treatment of saturation is based on writing the correct spin density matrix that rigorously describes the spin system in a high static field superimposed by a transverse oscillating field. For those unfamiliar with statistical physics and spin system dynamics, we note that the spin density matrix has nothing to do with the spin-dependent scattering matrix [12], but describes a spin system in a mixed state, which is a statistical ensemble of many quantum states. The density matrix is the quantum-mechanical analogue to the probability distribution of position and momentum in classical statistical mechanics. It is a matrix representation of the density operator that is the sum of the products $\hat{\rho} = \sum_i p_i |\psi_i\rangle \langle \psi_i|$, where $p_i$ is the probability of finding the quantum system in a state with state vector labeled by $i$. The matrix elements are evaluated in a basis that does not need to be orthogonal. The choice of the basis is often the key to solving practical problems.

It follows directly from the definition of the elements of the density matrix that the expectation value of an operator $Q$ can be obtained for a given density matrix by

$$\langle Q \rangle = \text{Tr} \left\{ \rho Q \right\}.$$  (1)
For a spin system, the operator can be, for example, the energy (spin Hamiltonian), magnetization parallel or transverse to the static field, entropy, or other thermodynamic entities. The problems that can be handled range from spin-lattice relaxation to cross relaxation, evaluation of thermodynamic and transport properties with and without resonant fields, and behavior of spin systems in transient states.

For example, the Maxwell-Boltzmann distribution is obtained by maximizing the entropy

$$ S = -k_B \text{Tr} \{ \rho \ln \rho \} $$

at constant energy $E = \text{Tr} \{ \rho \mathcal{H} \}$. This yields the density matrix in the practical form

$$ \rho = Z^{-1} \exp \left( -\frac{\mathcal{H}}{kT} \right), $$

where $Z$, the partition function, normalizes the trace to 1:

$$ Z = \text{Tr} \left\{ \exp \left( -\frac{\mathcal{H}}{kT} \right) \right\}. $$

In the high-temperature approximation the density matrix (2) is expanded in a Taylor series truncated after the linear term. At low temperatures the series expansion describes very poorly the exponential, even after adding more terms. The evaluation of the expectation values of the operators therefore calls for the algebra of exponential operators.

The solutions of many problems also involve transforming the Hamiltonian to the rotating frame, where its main part becomes time-independent.

The time evolution of the density matrix $\rho$ obeys the von Neumann-Liouville equation

$$ i\hbar \frac{d\rho(t)}{dt} = \mathcal{H} \rho(t), $$

and the time evolution and steady state value of an operator $Q$ is obtained from

$$ \frac{d}{dt} \langle Q \rangle = \left\langle \frac{i}{\hbar} [\mathcal{H}, Q] + \frac{\partial Q}{\partial t} \right\rangle. $$

Using this powerful formulation, Provotorov derived his time-evolution and steady-state equations [10] for the complex components of the magnetic resonance signal in the high-temperature approximation. The novelties of his treatment are that it is applicable to spins in solid materials, and that it correctly describes the response of the spin system to strong transverse RF fields. Borghini [2] extended this to low temperatures and for the case where the electron spin resonance line is broadened substantially by the anisotropy of hyperfine interactions and of the g-tensor, which dominate the dipolar broadening in glassy materials doped by paramagnetic molecules. He wrote the Hamiltonian in the rotating frame, where its main part becomes time-independent, in the form

$$ \hbar \mathcal{H}^r = \sum_i \hbar (\omega_i - \omega) \hat{S}_i \cdot \hat{\omega}_i + \sum_{ij} \hbar (\hat{\omega}_i \cdot \mathbf{A}_{ij} \cdot \hat{K}_j) \hat{S}_i \cdot \hat{\omega}_j $$

(6)
where $\hbar \omega_l = |g_l \beta \cdot \vec{H}_0|$, $\rho_0 = Z^{-1} \exp(-\alpha_0 \mathcal{H})$ before applying RF field, and after turning it on it becomes $\rho^* = Z^{-1} \exp(-\alpha \mathcal{H}^*)$; $g_l$ and $\mathbf{A}_j$ are the anisotropic $g$- and hyperfine tensors of spin $S_l$. The steady state inverse spin temperature $\alpha$ is then obtained from

$$\text{Tr} \rho^* \mathcal{H}^* = \text{Tr} \rho_0 \mathcal{H}^*, \quad (7)$$

if the various parts of the Hamiltonian have the same relaxation towards lattice.

The idea that all electron spins of the inhomogeneously broadened line then share a common spin temperature is an assumption that is supported by the strength of dipolar interactions yielding fast dipolar relaxation in the rotating frame. This and the fast relaxation of the Zeeman temperature in the rotating frame were proven by experiments at low lattice temperature, with low microwave power [3]. A relatively high electron spin density is clearly required, although this has not been theoretically quantified. More theoretical and experimental work would be desirable to clarify this point. Furthermore, it would be interesting to quantify theoretically the role of electron spin-lattice relaxation in the heat transfer from nuclear spins to the lattice; at present this is well understood only qualitatively.

Before focusing on his model of DNP, Borghini had explored a broad range of potential polarized target materials; his compilation [13] is still excellent reading for the experts in the field. He and various other authors calculated the ultimate spin temperatures and polarizations for several paramagnetic molecules embedded in hydrogen rich target matrices. Figure 1 shows an example of the results in deuterated propanediol doped by PD-Cr(V) [14]. The numeric calculations neglected leakage relaxation, weak hyperfine lines, and dipolar interactions, because line broadening is dominated by the $g$-factor anisotropy that gives the main features of the EPR line in PD-Cr(V).

The results shown in Figure 1 have several interesting features that cannot be understood by simple extrapolation of the high-temperature formulas to low temperatures:

![Figure 1: Ultimate DNP in deuterated propanediol doped with PD-Cr(V) [14]. Left – Optimum inverse deuteron spin temperatures as a function of lattice temperature in 2.5 T field; Right – optimum microwave frequencies as a function of lattice temperature. No leakage relaxation is assumed.](image)
• The enhancements of optimum inverse spin temperatures increase down to 0.6 K, and below 0.4 K the maxima of inverse temperatures become suddenly flat.

• The optimum frequency for positive polarization is deep in the resonance line at 1.4 K lattice temperature, and shifts with lowered lattice temperature towards the line edge that it almost touches at 0.6 K. It then shifts slightly back towards the line centre.

• The optimum frequency for negative polarization is practically constant. Above 0.6 K it is just outside the line edge, and shifts slightly into the main line below 0.6 K.

• The leveling in the curves of inverse spin temperature depends on \( \Delta g \) but not on \( B \). At constant lattice temperature below 0.4 K one may therefore reach higher polarization by increasing the static field \( B \). In practice this might not be very effective, because higher field may require higher microwave power, if the spin-lattice relaxation time is due to the direct process and becomes too short. The higher power dissipation then prevents working at constant lattice temperature.

• Theoretically the best way to obtain lower spin temperatures is to reduce the EPR linewidth, by choosing a paramagnetic centre with smaller anisotropy of the g-factor and with low or negligible hyperfine splittings. This idea was already promoted by Borghini [13]. However, as the low \( \Delta g \) leads to slow spin-lattice relaxation, the slow DNP would probably have to be compensated by a higher static field, which increases the relaxation rate.

• The inverse spin temperature has narrower peaks (not shown in Fig. 1) when the lattice temperature is lower. This narrowing calls for better inhomogeneity of the static field [14]. In the case of Figure 1, one should have the field uniform to \( 10^{-5} \) or better below 0.6 K lattice temperature.

The large polarized deuterated target [15] of the Spin Muon Collaboration (SMC) at CERN was built keeping the above considerations in mind. The material was deuterated butanol doped with EDBA-Cr(V), which is a pure material and therefore likely to contain little Cr(III) that is known to cause leakage relaxation. With low microwave power, the lower lattice temperature enabled to reach over 60% deuteron polarization in a 2.5 T field, the homogeneity of which was close to \( 10^{-5} \). The modulation of the microwave frequency helped in speeding up the DNP, while the reduction of the saturation of the deuteron NMR signal allowed to reach around 60% polarizations. This was achieved by periodically turning off the RF power to the NMR Q-meters.

Yet higher deuteron polarizations have been reached in materials doped by new trityl free radicals [16], in irradiated deuterated butanol [16,17], and in irradiated deuterated ammonia [18]. Common to these and to irradiated \(^6\)LiD is their narrow ESR line, that allows to reach a low deuteron spin temperature by dynamic cooling of the spin-spin interactions of the unpaired electrons.

3. NMR measurement of nuclear spin polarization

The series-tuned Q-meter has been adopted by most PT specialists, and various circuit-theoretical simulations have shown its merits in comparison with other circuits. These simulations also demonstrate the limits of the technique: the non-linear distortions yield substantial errors in proton polarization measurement, forcing to reduce the filling factor and to make corrections based on simulation. In the case of deuteron polarization measurement, the smaller signal is less susceptible to errors due to non-linearity, but linear distortions tend to mix in the dispersion signal that makes it awkward to fit the baseline under the absorption signal.
In view of these limitations, it has been suggested to improve the series-tuned Q-meter circuit by replacing the ordinary mixer (the phase sensitive detector) by a quadrature mixer that detects both the real and the imaginary parts of the RF signal after pre-amplification [19].

The saturation of the NMR signal not only reduces the polarization that can achieved, but it also worsens the accuracy of polarization measurement, because the saturation is strongest where the sampling is most sensitive, i.e. close to the coil wire. The frequently-used Liverpool Q-meter circuit delivers about 0.3 mA current to the probe coil [20], and leads to a saturation time constant of about 3 h for deuterons in continuous scanning mode. As the DNP time constant above 50% deuteron polarization was more than 10 h in the SMC target, the RF source feeding the Q-meters was turned off during most of the time, in order not to introduce large error in the polarization measurement [15]. For future designs of the Q-meter, it is therefore advisable to reduce the probe coil current to the range 0.03 mA to 0.1 mA.

At high nuclear polarization the NMR signal suffers also from distortions that are due to the fact that the density matrix of Eq. (2) cannot be truncated after the linear term of its Taylor expansion, because the spin temperature is too low, even in the high static field. Numeric simulations of this yield practical formulas, reported in Ref. [21]. Although this does not cause non-linearity in the integral of the absorption signal, it may lead to problems of fitting the wings. Furthermore, distortion due to saturation becomes more pronounced. These facts strengthen the conclusion that the probe coil current should be reduced, and that both parts of the complex NMR signal should be measured so as to extract the true absorption part. From these the true absorption and dispersion parts of the transverse susceptibility can be solved directly.

4. Cooling of the lattice and refrigeration

4.1 Heat transfer from target to coolant

For the handling and cooling of polarized targets, the material is composed of round glassy beads in the case of glassy hydrocarbons, or fragments of crushed crystals in the case of ammonia, lithium hydrides and other crystalline substances.

The heat generated by microwave power absorption in the target material is transported to the surface of the beads or fragments by phonons. The phonon conductivity is limited by scattering on impurities and defects. A part of the phonons is reflected back from the interface; this generates the Kapitza resistance. Because of its steep temperature dependence, the Kapitza resistance tends to dominate below 1 K, when the bead diameter is 2 mm or smaller.

In the liquid phase of evaporation refrigerators, the phonons are either absorbed by liquid-vapour phase transition, characterized by nucleate boiling heat transfer, or, in the case of higher heat flux, by boiling heat resistance in 2-phase flow. The latter happens in particular when the liquid-gas mixture enters below the target. This heat transfer coefficient is very large for superfluid $^4$He, which makes the $^4$He refrigerator the best choice for targets in intense beams. A particular feature in boiling of superfluid $^4$He at low pressure is that the heat flux increases quadratically with $\Delta T$, unlike for $^3$He and normal $^4$He, which show a linear behavior. Moreover, the burnout heat flux is very high for the superfluid 2-phase flow boiling.
Cooling by evaporation of $^3$He has been gradually replaced by dilution refrigeration, because substantially higher polarization can be achieved, and because the frozen spin technique enables more freedom in the choice of magnetic field in some experiments. In dilution refrigerators the phonon transport across the solid-liquid interface is limited by the Kapitza resistance of same order of magnitude as in the case of fluids of pure He isotopes, but the heat transport in the fluid happens by convection of the dilute phase. Owing to the low viscosity of the dilute solution above 20 mK, the convection heat transfer is very effective, and reaches a maximum around 100 mK. Dilution refrigeration is therefore effective also for large targets; in SMC polarized target it was estimated that at 0.2 K coolant temperature the maximum temperature difference in the fluid filling the target volume was less than 10 mK, which is substantially less than that due to the Kapitza resistance.

4.2 Refrigeration using quantum fluids

Pure and mixed liquid helium isotopes are called quantum fluids, because their thermodynamic and transport characteristics cannot be understood by classical statistical physics. Among their peculiar features are that they remain liquid under their vapour pressure down to absolute zero temperature, that their liquid density is low, and that the specific heat and the heat transport capability are very high. These are the key factors that enable DNP in solid targets down to 0.1 K and perhaps below in suitable substances.

As was stated above, two refrigeration principles dominate presently: evaporation of $^4$He in an open cycle, and dilution of $^3$He by $^4$He in a closed cycle. Many evaporation cryostats were fabricated using the original horizontal design of P. Roubeau [22], which works even better in the vertical geometry [23] and with superconducting rather than iron magnets.

Dilution refrigerators were introduced to the polarized targets in the 1970s, with horizontal [4, 24] and vertical [5] designs. The dogleg design of the SMC the double-cell target [25] allows to fit large targets better in the experiment.

References

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[8] Frantisek Lehar passed away


