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V. Montelatici: STATISTICAL APPROACH TO THE SPIN
REFRIGERATOR. -

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INTRODUCTION. -

A new method for polarizing a spin system was proposed at the same time on 1963 by C. D. Jeffries⁽¹⁾ and by A. Abragam⁽²⁾, and successfully applied by Jeffries⁽³⁾ recently. This method, in the version given by Jeffries⁽⁴⁾, has been given the denomination "proton spin refrigerator". It has a close relation with the earlier "spin engine" of Bloembergen⁽⁵⁾.

Let us consider a substance which can be thought as composed by a crystal lattice and by two systems of magnetic moments, the system (S) and (I). The substance is immersed in an externally magnetic field sufficiently high, and it is in thermal contact with a heat bath at temperature T_0 .

We suppose the system (S) as having a strong anisotropic Landè g factor, with effective spin $S = 1/2$, but with one value equal to that of the system (I); for example: $g_S(\theta_1) = 2$, $g_S(\theta_2) = 10^{-3} = g_I = \text{constant}$, where θ is the angle between the crystal axis and the direction of the magnetic field. In the crystal position θ_2 we suppose there is an interaction capable of exchanging energy only between the system (S) and (I). Moreover we suppose the spin lattice relaxation time of system

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(S) to increase from position θ_1 to θ_2 , whereas the relaxation time of the system (I) is assumed always very long.

If a rotation of the crystal from position θ_1 to θ_2 is performed in a time shorter than the relaxation time, then the (S) system cools; in such time interval the system cannot exchange energy with the heat bath. But the system (S) has, now in position θ_2 , the same energy splitting of system (I), so that the two systems are in thermal contact among them. Rapidly an intermediate temperature is reached, depending on the thermal capacities of the two systems. Since, in the position θ_2 , the spin lattice relaxation times are supposed long the two systems are isolated from the heat bath. It is then possible to determine the common temperature reached after a characteristic time which depends on the interaction between the systems.

The final temperature, T_x , has been calculated by A. Abragam^(6, 7):

$$\frac{1}{T_x} = \frac{\frac{H^2+h_S^2}{3KT_S} N_S \gamma_S^2 \hbar^2 S(S+1) + \frac{H^2+h_I^2}{3KT_I} N_I \gamma_I^2 \hbar^2 I(I+1)}{\frac{H^2+h_S^2}{3K} N_S \gamma_S^2 \hbar^2 S(S+1) + \frac{H^2+h_I^2}{3K} N_I \gamma_I^2 \hbar^2 I(I+1)}$$

where h_S and h_I are the local fields of the (S) and (I) systems; $\gamma = g\beta/h$ with β and g the Bohr magneton and Landè g factor; N_S and N_I the total number of spins at the initial temperatures T_S and T_I ; S and I the quantum spin numbers.

It is immediately seen that for $N_S/N_I = 10^{-3}$, $T_S/T_I = 10^{-3}$, $g_S/g_I = 1$, $H \gg h_S, h_I$, $S = I = 1/2$ the final temperature is $T_x = 1/2 T_I$.

The assumed conditions for the spin lattice relaxation times and for the energy splitting of the two systems subsist in some diamagnetic crystals with paramagnetic impurities.

The spin systems are most suitable to be studied by using the statistical mechanics especially in cases where their spin lattice relaxation times are long compared with the times necessary to perform experiments. The details of the mechanism in which various systems come into statistical equilibrium can be followed by defining a spin temperature for each system. Many experimental effects have been interpreted by the use of a spin temperature, for example: the cross relaxation between two spin systems^(6, 8, 9, 10, 11); the direct cooling of a spin system which has finite width of the resonance line^(12, 13); the adiabatic demagnetization of a spin system^(14, 15); the mixing of two spin systems at different temperatures both of which taking positive, negative or infinite values^(6, 8); the measurements of nuclear rela

xation times in low fields for the superconducting state where the magnetic field does not penetrate inside superconductor^(16, 17). The hypotheses on the relaxation times and on the energy splittings of the two systems are required in the spin refrigerator, in which the final aim is the cooling of the system (I) to a temperature lower than the temperature T_0 of the heat bath. By introducing the chemical potentials, as parameters determining the occupation numbers of the two systems, it is possible to derive the conditions to which the relaxation times and the energy splitting must satisfy when various equilibrium conditions are required.

The thermodynamical equilibrium conditions between the two spin systems become simple relations between the chemical potentials, which in turn are related to the relaxation times of the two systems.

Since for each equilibrium conditions the ratio of the chemical potentials is determined, the relaxation times are determined as well.

SPIN TEMPERATURE AND CHEMICAL POTENTIALS. -

A system of spin magnetic moments with quantum number $1/2$, immersed in a constant magnetic field H_0 and in thermal contact with a heat bath at temperature T_0 , has the occupation numbers, n_+ and n_- corresponding to two energy levels: $E_+(m = +1/2)$ and $E_-(m = -1/2)$ respectively. From Boltzman relation one has :

$$(1) \quad \frac{n_+}{n_-} = \exp\left(\frac{-\Delta E}{KT_0}\right) \equiv \exp\left(\frac{-\hbar\gamma H_0}{KT_0}\right)$$

where $\Delta E = E_+ - E_-$.

Experimentally since the field H_0 is constant, in order to change the ratio (1), one must change the temperature, for example by means of an electromagnetic field of frequency $\nu = \Delta E/h$. This means that the spin temperature rises to a value T_* ; the relation (1) becoming:

$$(2) \quad \left(\frac{n_+}{n_-}\right)_* = \exp\left(\frac{-\Delta E}{KT_*}\right)$$

The possibility of defining these temperatures requires an interaction^(18, 19) mechanism which conserves the energy among the spins (i. e. as a result of this interaction among the spins the number of transitions per unite time in one direction equals that in the reverse direction). These temperatures are reached in a characteristic time depending on the spin-spin interaction.

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Another view point is possible⁽²⁰⁾: the spin system is divided into groups according to the spin energy state in which they are (x). To each group a chemical potential is assigned, which becomes the parameter describing the population distribution. In this case the temperature is fixed by the initial conditions satisfied by the chemical potentials in absence of the electromagnetic field.

The heat bath fixes the lattice and spin temperature in the initial state. The ratio (2) becomes :

$$(3) \quad \left(\frac{n_+}{n_-} \right)_* = \exp \left(\frac{\Delta\mu - \Delta E}{KT_o} \right)$$

where $\Delta\mu = \mu_+(m=+1/2) - \mu_-(m=-1/2)$ is the chemical potentials difference.

Equation (3) is derived from relationship⁽²²⁾ :

$$(4) \quad E_i - KT_o \log n_i = \mu_i \equiv \frac{\partial F_i}{\partial n_i}$$

with $i = 1, 2$, where the index i represent the state with quantum number $m_1 = +1/2$ and $m_2 = -1/2$,

$$F_i = KT_o \log Z_i = KT_o n_i \log n_i + KT_o n_i + n_i E_i$$

in the free energy of the i^{th} energy level, and

$$Z_i = \frac{1}{n_i!} \exp \left(\frac{-E_i}{KT_o} \right)^{n_i}$$

is its partition function.

Clearly, these two view points must lead to the same population ratio for the various possible equilibrium states when an electromagnetic field is applied to the system. That is the distribution may be represented by spin temperatures, or by chemical potentials; therefore from (2) and (3) one has the relation :

$$(5) \quad \Delta\mu = \Delta E \left(1 - \frac{T_o}{T_*} \right) .$$

(x) - Subdivision of spin system into groups is implicit in the article by P. Brovotto⁽²¹⁾.

Fig. 1 gives the behaviour of the spin temperature, T_{\star} , as a function of the energy Δ/μ . The temperature T_{\star} is related⁽²³⁾ to the

electromagnetic field power $P_{e. m.} \propto H_1^2$ by :

$$T_{\star} = T_0(1 + 2VT_1)$$

where T_1 is the spin lattice relaxation time and $V \propto P_{e. m.}$ is the induced transition probability due to the alternating field of frequency ν and amplitude H_1 . Therefore the difference Δ/μ takes the meaning of an energy given to spin system through the relation :

$$\Delta/\mu = \Delta E \left(1 + \frac{1}{2VT_1}\right)^{-1}$$

In this case Δ/μ takes all the values from $\Delta/\mu = 0$ to $\Delta/\mu = \Delta E$ as for as H_1 changes from $H_1 = 0$ to $H_1 = \infty$. By making a formal extension of Δ/μ for all real values one can give a physical significance to the spin temperature, as follows.

By considering the negative values of Δ/μ as representing energies taken off the system, from the relation $\frac{dS(T_{\star})}{dT_{\star}} = \frac{1}{T_{\star}}$ where $\mathcal{E} \equiv \Delta/\mu$ and $S(T_{\star})$ is the entropy, one has :

$$(5') \quad S(T_{\star}) = K n \log 2 - \frac{\Delta E}{2T_0} \left(\frac{T_0}{T_{\star}}\right)^2$$

where $n = \sum n_i$. The integration can be performed by considering that for infinite temperature the spin system has an equal distribution probability.

Fig. 2 gives the behaviour of the positive values of $S(T_{\star})$ and shows that the temperatures $T_{\star} = -\infty$ and $T_{\star} = +\infty$ are equivalent and represent the same physical state of the system, whereas the temperatures $T_{\star} = \pm \left(\frac{\Delta E T_0}{2K n \log 2}\right)^{1/2}$ represent two different physical states, in which $\Delta/\mu = \Delta E \mp (\Delta E T_0 2 n K \log 2)^{1/2}$. The maximum, $\Delta/\mu > 0$,

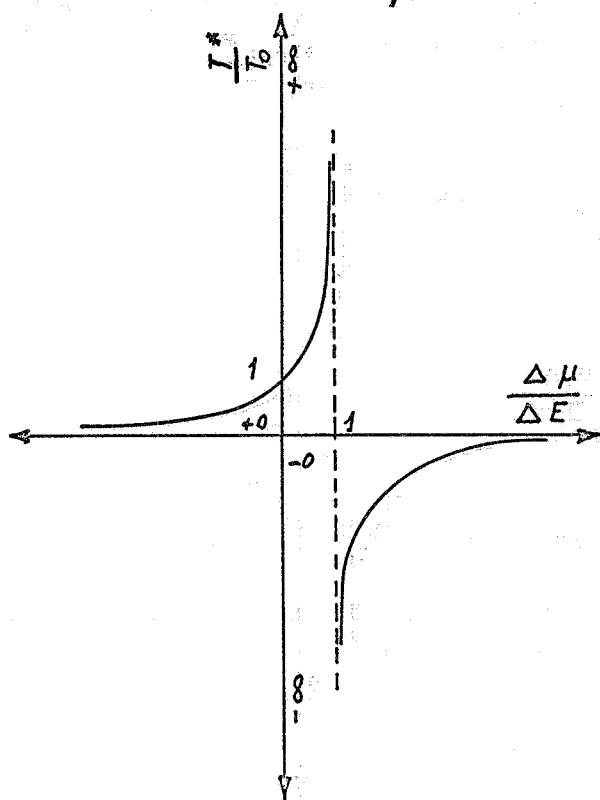


FIG. 1 - Schematic dependence of T_{\star}/T_0 vs. $\Delta/\mu/\Delta E$.

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corresponds to the case when all the spins are in the higher energy level, while the minimum, $\Delta/\mu_{\text{MIN}} < 0$, corresponds to the case when all the spin are in the lower energy level. The former case corresponds to a temperature $T_{\star} = -0$, the latter one to a temperature $T_{\star} = +0$. The

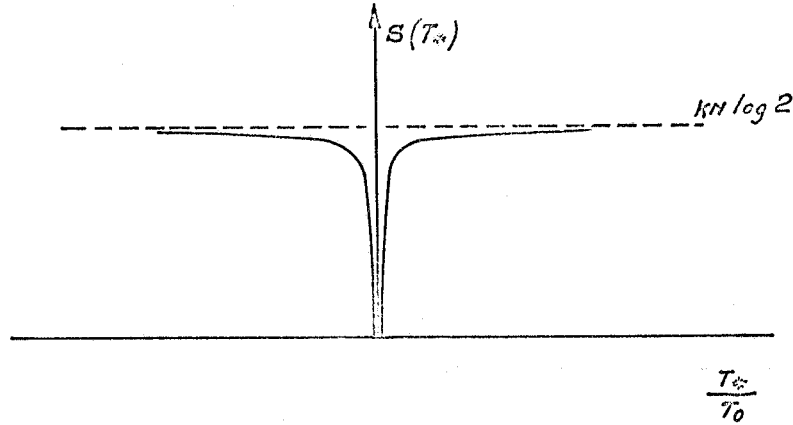


FIG. 2 - Schematic dependence of $S(T_{\star})$ vs. T_{\star}/T_0 .

population inversion, that is the possibility to "prepare" a spin system at negative temperatures (hotter than all the positive temperatures) requires the following conditions :

- 1) the system must be thermally isolated ;
- 2) the elements of the spin system must be in thermodynamic equilibrium among them so that the system is described by a unique temperature ;
- 3) an upper limit must exist for the energy states permitted to spins.

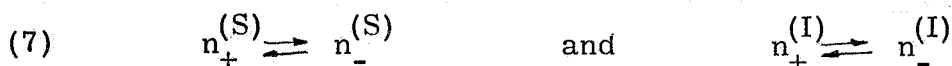
These conditions exist for many spin systems, and E. M. Purcell and R. N. Pound⁽²⁴⁾ were able to prepare a spin system at positive, negative and infinite temperatures.

THERMAL MIXING OF TWO INTERACTING SPIN SYSTEMS. -

For two spin systems at different temperatures T_S and T_I two similar relationships, relating the chemical potentials and the temperatures, can be obtained. By denoting with (S) and (I) the two systems one has :

$$(6) \quad \begin{aligned} \Delta \mu^{(S)} &= \Delta E^{(S)} \left(1 - \frac{T_0}{T_S}\right) \\ \Delta \mu^{(I)} &= \Delta E^{(I)} \left(1 - \frac{T_0}{T_I}\right) . \end{aligned}$$

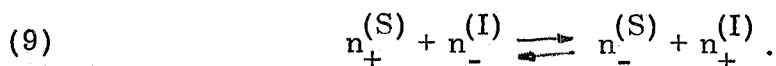
In the case $T_S = T_I = T_0$ one has the relations $\Delta\mu^{(S)} = 0$ and $\Delta\mu^{(I)} = 0$, which give the thermal equilibrium⁽²⁵⁾ conditions of the chemical reactions:



If $\Delta E^{(S)} \neq \Delta E^{(I)}$, the two reactions are independent, and represent two distinct systems in thermal equilibrium with the heat bath at temperature T_0 . In the case $T_x = T_S = T_I \neq T_0$ from (6) one has:

$$(8) \quad \frac{\Delta\mu^{(S)}}{\Delta\mu^{(I)}} = \frac{\Delta E^{(S)}}{\Delta E^{(I)}}.$$

If $\Delta E^{(S)} = \Delta E^{(I)}$ then $\Delta\mu^{(S)} = \Delta\mu^{(I)}$ which gives the equilibrium condition at temperature $T_x \neq T_0$ in the chemical reaction:



On the other hand, the relation of Van't Hoff applied to (9) gives:

$$\frac{d\mathcal{K}}{dT_x} = -\frac{\Delta\mathcal{H}}{KT_x}$$

where $\mathcal{K} = (n_+^{(S)} n_-^{(I)}) / (n_-^{(S)} n_+^{(I)})$ and $\Delta\mathcal{H} = n^{(I)}\Delta E^{(I)} - n^{(S)}\Delta E^{(S)}$ is the reaction heat. By integrating, under the condition $\mathcal{K} = 1$ for $T_x \rightarrow \infty$, one has:

$$(9') \quad \mathcal{K} = \exp \frac{-n^{(I)}\Delta E^{(I)} - n^{(S)}\Delta E^{(S)}}{KT_x}$$

The (9') under the condition $n^{(I)}\Delta E^{(I)} = n^{(S)}\Delta E^{(S)}$ gives:

$$(9'') \quad \frac{n_+^{(S)}}{n_-^{(S)}} = \frac{n_+^{(I)}}{n_-^{(I)}}$$

when the two systems have an equal number of spins ($n^{(S)} = n^{(I)}$), one has $\Delta E^{(S)} = \Delta E^{(I)}$, and from (8) $\Delta\mu^{(S)} = \Delta\mu^{(I)}$.

When for the two systems $n^{(S)} \neq n^{(I)}$ (if $n^{(S)}\Delta E^{(S)}$ and $n^{(I)}\Delta E^{(I)}$ are substituted to $\Delta E^{(S)}$ and $\Delta E^{(I)}$ respectively in (8)) again one can have equal energy splitting, and therefore $\Delta\mu^{(S)}/\Delta\mu^{(I)} = n^{(S)}/n^{(I)}$. In this latter case the system with less number of spins performs more transitions in unit time than the system with more spins.

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Clearly this fact implies a mixing relaxation time shorter for the system with less number of spins. Also it can happen that the energy splittings are not equal, but that $\Delta E^{(S)}$ and $\Delta E^{(I)}$ are commensurable in the ratio different from 1 : 1. In this case the system with less number of spins has a larger energy splitting; so that it is energetically favorable for $n^{(S)}$ spins to flip $n^{(I)}$ spins since $n^{(S)}\Delta E^{(S)} = n^{(I)}\Delta E^{(I)}$.

It can be noted that the systems (S) and (I) in the reaction (9) change their state simultaneously in such a way to verify the selection rule $\Delta m^{(S)} = -\Delta m^{(I)} = \pm 1$ where Δm is the variation of the magnetic quantum number.

The equilibrium state is reached with a time evolution given by the solution of the coupled differential equations :

$$(9''') \quad \begin{aligned} \dot{P} &= -n^{(I)} W_x (P - p) \\ \dot{p} &= n^{(S)} W_x (P - p) \end{aligned}$$

where $n^{(S)}P = n_+^{(S)} - n_-^{(S)}$ and $n^{(I)}p = n_+^{(I)} - n_-^{(I)}$, and W_x is a cross relaxation probability, the minus sign, in the first of (9'''), has been introduced because of the initial temperatures conditions are supposed to be $T_S < T_I$.

The interaction between system (S) and (I) plays a fundamental role in the simultaneous transitions in the chemical reaction (9). We consider each element of the two systems under the action of an effective field which is the sum of the external field and a fictitious field^(26, 27). The fictitious field represents the interaction among the spins of the two systems in the i^{th} energy level, it gives a potential energy \mathcal{F}_i which can be determined by a self-consistent method.

However for our purpose it suffices to state that the total energy of the i^{th} level is :

$$E_i^{\text{tot}} = E_i(\text{Zeeman}) + \mathcal{F}_i(\text{potential energy});$$

obviously enough at high field \mathcal{F}_i is neglected. In the preceding expressions one must write $\Delta E^{\text{tot}} = \Delta E^Z + \Delta \mathcal{F}$ p. e. .

The condition on energy splittings, to satisfy the equilibrium condition at the mixing temperature, becomes :

$$(10) \quad \Delta E^{(S)}(Z) - \Delta E^{(I)}(Z) = \mathcal{F}$$

The relation (10) means that the interaction energy balances the Zee-

man energy difference of the two systems. On the other hand the reaction (9) occurs only if a mechanism exists which changes the states of the spins in such a way to satisfy the selection rule $\Delta m^{(S)} = -\Delta m^{(I)} = \pm 1$.

Such a mechanism is due to the magnetic dipolar interaction among the spins :

$$\mathcal{H}_d = - \frac{g_S g_I}{r_{ij}^3} \beta^2 \left[\bar{I}_j \cdot \bar{S}_i - \frac{3(\bar{I} \cdot \bar{r}_{ij})(\bar{S}_i \cdot \bar{r}_{ij})}{r_{ij}^2} \right]$$

For instance, there may be an I^+S^- term in the Hamiltonian which reduce $n_-^{(I)}$, $n_+^{(S)}$ by one and which simultaneously raises $n_+^{(I)}$, $n_-^{(S)}$ by one.

CONDITIONS ON THE SPIN LATTICE RELAXATION TIMES TO OBTAIN NEGATIVE AND POSITIVE SPIN TEMPERATURES. -

We consider now two systems of spin magnetic moments in a constant magnetic field at the temperature T_0 of the heat bath. They are labelled by the symbols (S) and (I). The angular momentum associated to the spins are $S=I=1/2$, and their Landè factors are g_S and g_I . Their magnetic moments are :

$$\bar{m}_S = g_S \beta \bar{S}, \quad \bar{m}_I = g_I \beta \bar{I}$$

We assume that the dipolar magnetic interaction between the systems (S) and (I) can be neglected with respect to the Zeeman energies. We can apply to these systems the Gibbs relation^(22, 28):

$$T dS = dU + dW - \sum_i \mu_i dn_i^*$$

where $dW = MdH$ is zero ($M =$ magnetization) since the magnetic field is constant; dU is the energy; $\sum_i \mu_i dn_i^*$ is the energy production⁽²⁹⁾ due to the transitions among the $(2S+1)(2I+1)$ energy levels which represent the system composed by (S) and (I). In the equilibrium state at temperature T_0 one has :

$$(11) \quad \left(\frac{dS}{dt} \right)_{int} = - \frac{1}{T_0} \sum_i \mu_i \frac{dn_i^*}{dt} = 0$$

The energy of the i^{th} level is :

$$E_i = E^{(S)}(m_S) + E^{(I)}(m_I)$$

and to this level the chemical potential

$$\mu_i = \mu^{(S)}(m_S) + \mu^{(I)}(m_I)$$

is associated.

By denoting with N_{m_S} and n_{m_I} the occupation numbers of systems (S) and (I) in the state of quantum number m_S and m_I , one can use the statistical relations :

$$\mu^{(S)}(m_S) = E^{(S)}(m_S) + KT_0 \log N_{m_S}$$

$$\mu^{(I)}(m_I) = E^{(I)}(m_I) + KT_0 \log n_{m_I}.$$

Therefore :

$$(12) \quad \mu_i = E_i + KT_0 \log n_i^*$$

with $n_i^* = N_{m_S} n_{m_I}$ (30), see Fig. 3 and foot note(x), the full lines re-

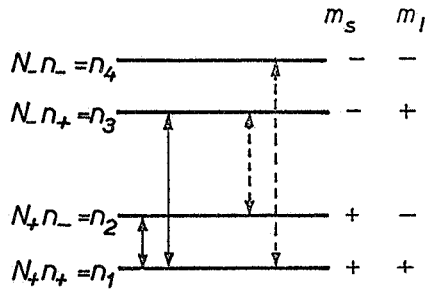


FIG. 3 - Skecth of the unperturbated energy levels of the composed systems, m_S and m_I magnetic quantum numbers.

(x) - The values of n_i^* , which are the product of the occupation numbers of the systems (S) and (I) could be obtained from the use of the particular partition function :

$$Z_i = \frac{1}{n_i^* !} \left[\exp\left(-\frac{E_i}{KT}\right) \right]^{n_i^*}$$

in which n_i^* should be all the possible pairs of a spin (S) and a spin (I), each belonging to the energy level $E_i(m_S, m_I)$. In this way one should take account the cases in which a spin (S) induces relaxation of more than one spin (I).

present the Zeeman transitions with selection rules $\Delta m_S = \pm 1$, $\Delta m_I = 0$ and $\Delta m_I = \pm 1$, $\Delta m_S = 0$; the dotted lines represent the transitions allowed by the dipolar interaction for which $\Delta m_S = -\Delta m_I = \pm 1$ and $\Delta m_S = \Delta m_I = \pm 1$.

Now the relations must be found between the relaxation times for the systems (S) and (I) when one of the following two relations applies :

$$(13) \quad 1) \quad n_4^* = n_1^* \quad , \quad 2) \quad n_3^* = n_2^*$$

Also the temperatures of the two systems at the equilibrium must be obtained.

We apply (11) to the composed system keeping in mind (13). The times rate of n_i^* are given by the expressions :

$$(14) \quad \frac{dn_i^*}{dt} = \sum_j (n_j^* w_{ji} - n_i^* w_{ij})$$

where w_{ij} are the probability transitions given by the relationships :

$$w_{ji} \exp\left(-\frac{E_j}{KT_0}\right) = w_{ij} \exp\left(-\frac{E_i}{KT_0}\right)$$

These relations show that the systems follow the Boltzman distribution, and they relax to the heat bath. That is, we disregard the lattice oscillations which are supposed at temperature T_0 of the heat bath.

From (11), by using (14), one has :

$$(15) \quad \left(\frac{dS}{dt}\right)_{int} = -\frac{1}{T_0} \left\{ (\mu_2 - \mu_1) \left[(n_1^* + n_3^*) w_{12} - (n_2^* + n_4^*) w_{21} \right] + \right. \\ \left. + (\mu_3 - \mu_1) \left[(n_1^* + n_2^*) w_{13} - (n_3^* + n_4^*) w_{31} \right] + \right. \\ \left. + (\mu_4 - \mu_1) \left[n_1^* w_{14} - n_4^* w_{41} \right] + (\mu_3 - \mu_2) \left[n_2^* w_{23} - n_3^* w_{32} \right] \right\}$$

By keeping in mind that the differences of chemical potentials are not independent, but they on the contrary obey (12) which gives :

$$\mu_4 - \mu_2 = \mu_3 - \mu_1$$

one obtains :

12.

$$(16) \quad \left(\frac{dS}{dt}\right)_{\text{int}} = -\frac{1}{T_0} \left\{ (\mu_3 - \mu_1)(P - P_0) \cosh \Delta \left[w_S^{+(1-pp_0)} w_S \cosh \delta \right] + \right. \\ \left. + (\mu_2 - \mu_1)(p - p_0) \cosh \delta \left[w_I^{+(1-PP_0)} \cosh \Delta \cdot \alpha w_S \right] \right\} N n$$

where :

$$\delta = \frac{g_I \beta H_0}{2KT_0}, \quad \Delta = \frac{g_S \beta H_0}{2KT_0}$$

$NP = N_+ - N_-$ and $np = n_+ - n_-$, $P_0 = \tanh \Delta$ and $p_0 = \tanh \delta$, w_I is the transition probability between levels (1 ÷ 2) and (3 ÷ 4), w_S is the transition probability between levels (1 ÷ 3) and (2 ÷ 4), while the transition probability between levels (2 ÷ 3) and (1 ÷ 4) is $w = \alpha w_S$.

A perturbative calculation shows that

$$\alpha = \frac{g_S^2 \beta^2}{H_0^2 r_{ij}^6} \approx 10^{-4} \quad \text{for } H_0 = 10^3 \text{ gauss and}$$

r_{ij} (distance between spin S_i and spin I_j) $\approx 10 \text{ \AA}$ and for $g_S = 2$ (as in the case of electrons and protons). Therefore one can write :

$$(16') \quad T_S^{-1} = \left[1 + (1 - pp_0) \alpha \cosh \delta \right] w_S \cosh \Delta \approx (1 + \alpha) w_S \cosh \Delta \\ T_I^{-1} = \left[w_I^{+(1-PP_0)} \alpha w_S \cosh \Delta \right] \cosh \delta \approx \\ \approx w_I + (1 - P_0^2) \alpha w_S \cosh \Delta$$

The equilibrium state, by imposing the relations (13, 1) or (13, 2) gives :

$$(17) \quad (\mu_2 - \mu_1) = \frac{+}{-} (\mu_3 - \mu_1) \frac{1 + \alpha}{\frac{w_I}{w_S \cosh \Delta} + (1 - P_0^2)} = \\ = \frac{+}{-} (\mu_3 - \mu_1) \frac{T_I}{T_S}$$

where the upper sign must be taken when (13, 1) applies and the lower one when (13, 2) applies. On the other hand from (12) by using (13) one has :

$$(18) \quad (\nu_4 - \nu_1) \equiv (\nu_3 - \nu_1) + (\nu_2 - \nu_1) = E_4 - E_1 = h(\nu_S + \nu_I)$$

$$(\nu_3 - \nu_2) = (\nu_3 - \nu_1) - (\nu_2 - \nu_1) = E_3 - E_2 = h(\nu_S - \nu_I)$$

From (17) and (18) one obtains :

$$(19) \quad (\nu_3 - \nu_1) = \frac{h(\nu_S \pm \nu_I)}{1 + (T_S/T_I)^{-1}} \xrightarrow{(T_S/T_I) \rightarrow 0} 0$$

$$(\nu_2 - \nu_1) = \frac{\pm h(\nu_S \pm \nu_I)}{1 + (T_S/T_I)} \xrightarrow{(T_S/T_I) \rightarrow 0} \pm h(\nu_S \pm \nu_I)$$

The explicit form of the spin lattice relaxation times ratio is :

$$(20) \quad \frac{T_S}{T_I} = \frac{\frac{w_I}{w_S \cosh \Delta} + \alpha (1 - P_o^2)}{1 + \alpha} \approx \frac{(1 - P_o^2)}{1 + \alpha} \xrightarrow{\alpha \rightarrow 0, P_o \rightarrow 1} 0$$

in which $w_I \ll w_S$ (31).

By substituting the values (19) in (12) one has :

$$(21) \quad \frac{n_3^*}{n_1^*} = \frac{N_-}{N_+} = \exp\left(-\frac{h\nu_S}{KT_o}\right) = \exp\left(-\frac{h\nu_S}{KT_*}\right)$$

$$\frac{n_2^*}{n_1^*} = \frac{n_-}{n_+} = \exp\left(\frac{\pm h(\nu_S \pm \nu_I) - h\nu_I}{KT_o}\right) \equiv \exp\left(\frac{-h\nu_I}{KT_{**}}\right)$$

One can conclude that, if the ratio between relaxation times is given by (20) and one of the relations (13) is satisfied the system (S) remains at temperature T_o of heat bath, while the system (I) takes one of the new temperatures, $T_{**} = \pm T_o (g_I/g_S)$ as far as (13, 2) (upper sign) or (13, 1) (lower sign) is satisfied.

AN EXPERIMENT TO DETECT POSITIVE, NEGATIVE AND INFINITE SPIN TEMPERATURES. -

The conditions (13) can be experimentally realized by means of the solid effect⁽³²⁾ in which a pumping power of frequency ($\nu_S \pm \nu_I$) induces a saturation between energy levels $E_4 \div E_1$ or $E_3 \div E_2$.

In order to obtain the population given in (21) by the solid effect, the system (S) must be in thermal contact with the heat bath while the system (I) is isolated from it. In the solid effect performed in the diamagnetic crystal $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ doped with Nd^{3+} ion this requirement is well satisfied; indeed at a temperature of about 2°K for heat bath, $T_I \approx 10^3$ sec, $T_S \approx 10^{-2}$ sec (when $n/N \approx 10^3$) and $H_0 \approx 6000$ gauss.

In this case it is easy to observe the magnetization signals at positive, negative and infinite spin temperatures.

From (19) one can consider two cases :

$$1) \quad \frac{\Delta \mu^{(I)}}{\Delta E^{(I)}} = \frac{\nu_S + \nu_I}{\nu_I} > 1$$

$$2) \quad \frac{\Delta \mu^{(I)}}{\Delta E^{(I)}} = - \frac{\nu_S - \nu_I}{\nu_I} < 0$$

which correspond to two different physical situations of system (I). In the case 1) energy is given to system (I) (through the mechanism of dipolar interaction) taken from system (S), and the temperature of system (I) rises beyond infinite values, so that an emission magnetization signal can be observed. In the case 2) (through a similar mechanism due to dipolar interaction) energy is taken from the system (I) and released to the heat bath through system (S), so that an absorption signal can be observed.

By the use of the solid effect^(33, 34, 35) one can study both these two different situations. Photograph in Fig. 4 shows the emission of energy from system (I) superimposed to the energy of a resonant LC circuit at frequency ν_I ; spins (I) populate the upper level more than the lower one and when relaxing to the heat bath, release the observed energy. Photograph of Fig. 5 shows a situation where the spin (I) at temperature lower than the temperature of the heat bath.

The situation $\Delta \mu^{(I)} = \Delta E^{(I)}$, in which the system (I) does not release or gain energy is shown photographs of Fig. 6. The magnetization signals of system (I) is "prepared" pumping power at constants frequency and magnetic field :

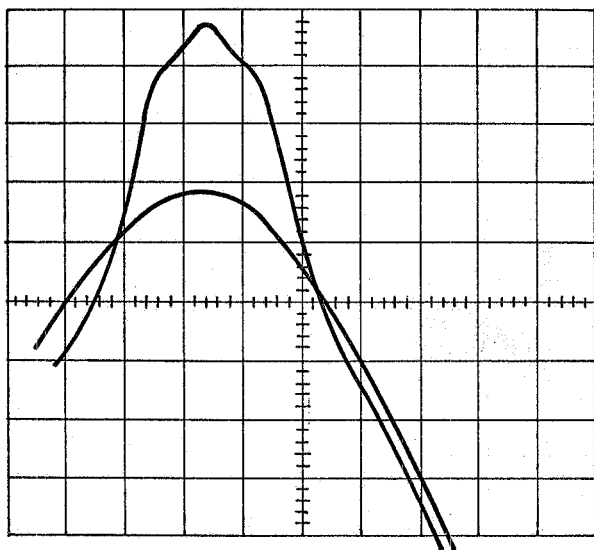


FIG. 4 - Magnetization signal photograph of protons at $H_0 = 6200$ gauss with a spin temperature :

$$T_x = -T_0 \frac{g_I}{g_S} \zeta \approx -7 \times 10^{-3} \text{ oK} \quad \text{and} \quad T_0 = 2 \text{ oK}$$

The parabolic curve is the response of the resonant LC circuit at frequency of 27379 Kc/s, trace about 800 Kc/s.

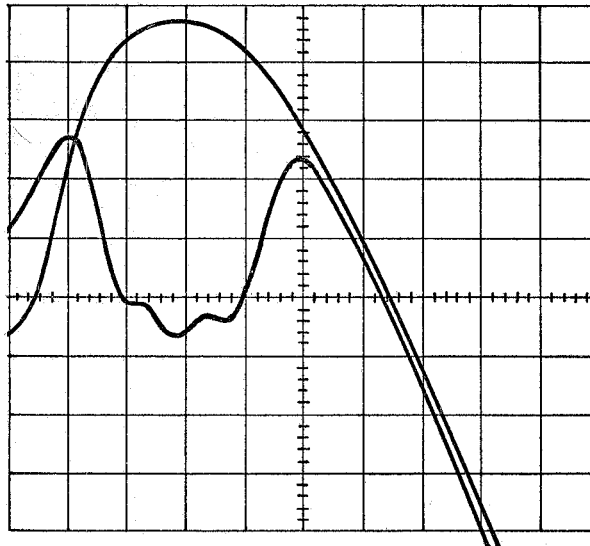
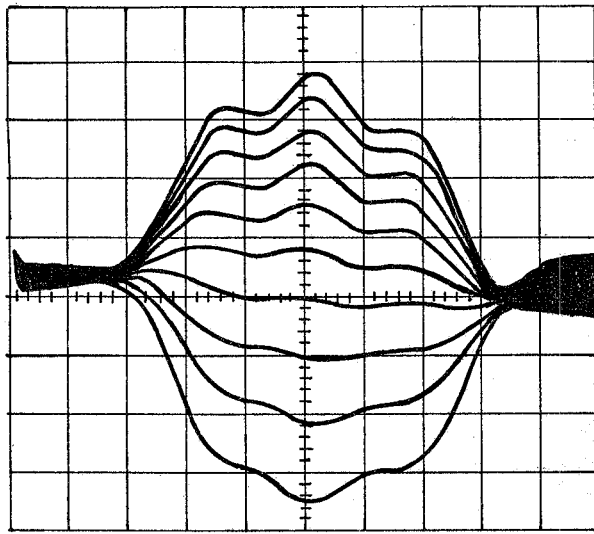


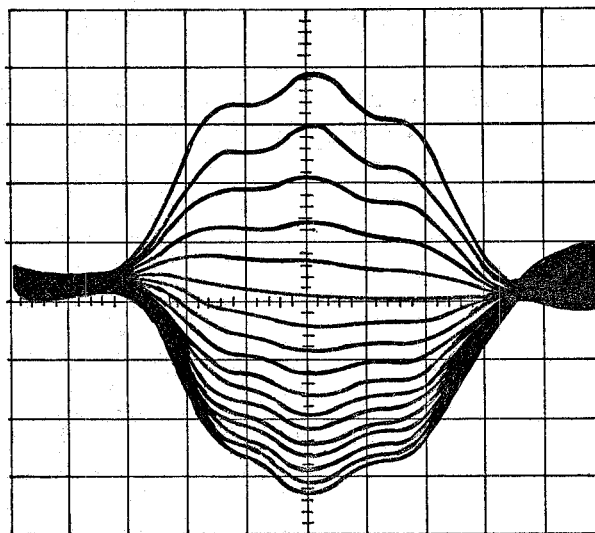
FIG. 5 - The same signal but at spin temperature

$$T_x = +T_0 \frac{g_I}{g_S} \zeta \approx +7 \times 10^{-3} \text{ oK.}$$

Note : ζ is a factor depending on the physical property of the sample and on the pumping power; it rises spin temperature above the ideal value $T_0(g_I/g_S) \approx T_0 \cdot 10^{-3}$.



a)



b)

FIG. 6 - Photographs a) and b) show the passage through zero magnetization signal ($T_x = \pm \infty$): b) initial signal at temperature $T_x < 0$, a) initial signal at temperature $T_x > 0$. Trace (about 160 Kc/s \pm 38 gauss) is obtained superimposing to the LC response a similar inverted signal, so that an approximately rectilinear base line is obtained on which the magnetization signals are detected. Each magnetization signals is 20 seconds apart in time for photograph a) and 10 seconds for photograph b).

$$\nu = \left[g_{\perp} \sin \theta_1 + g_{\parallel} \right] \frac{\beta H_0}{h} \equiv (g_S + g_I) \frac{\beta H_0}{h}$$

A rotation of the direction of magnetic field with respect to the crystal axis reduces θ_1 to such a value for which the pumping power is at the frequency

$$\nu = \left[g_{\perp} \sin \theta_2 + g_{\parallel} \right] \frac{\beta H_0}{h} = (g_S - g_I) \frac{\beta H_0}{h}$$

The rotation is performed in a time (about 2 sec) much shorter than the spin lattice relaxation time of the system (I). Now, in the position θ_2 , the magnetization is forced to invert by the pumping power; and a reversed signal can be observed. The magnetization signal passes, through $T = \pm \infty$, from $T > 0$ to $T < 0$.

CONDITION ON THE CROSS RELAXATION TIME AT THE TEMPERATURE OF MIXING. -

The condition (13, 2) must be satisfied in the spin refrigerator, in order the system (I) assumes the temperature $T_{**} = +T_0(g_I/g_S)$, while system (S) remains at the temperature T_0 . In other words system (I) gains the polarization of system (S). If the system (I), initially at temperature T_0 , is put in thermal contact with another system S^{**} at temperature T_{**} having a population ratio equal to that of system (S) at temperature T_0 , then the condition $n_3^* = n_2^*$ is verified.

To perform thermal contact between the two systems is necessary to satisfy (10). The system S^{**} can be realized by use of the fact that the Landé g factor is anisotropic, and that the spin lattice relaxation time is dependent on θ .

A concrete example can be found in some diamagnetic crystals doped with paramagnetic impurity for which one has^(36, 37) :

$$g(\theta) = \left[g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \right]^{1/2}$$

with $g_{\parallel} \approx 3$ and $g_{\perp} \approx 3 \times 10^{-3}$, and :

$$T_S(\theta)^{-1} \approx A H^4 \sin^2 \theta \cdot \cos^2 \theta \cdot T + B(T).$$

Therefore an adiabatic transformation,

$$S \left[T_0, g\left(\frac{\pi}{4}\right), T_S\left(\frac{\pi}{4}\right) \right] \rightarrow S^{**} \left[T^{**}, g\left(\frac{\pi}{2}\right), T_S\left(\frac{\pi}{2}\right) \right]$$

is possible leaving the population ratio unchanged as far as it is performed in a time shorter than the spin lattice relaxation time. The adiabatic transformation occurs for a rotation of the crystal, for example, from $\theta_1 \approx \pi/4$ to $\theta_2 \approx \pi/2$; the thermal mixing, in position $\theta_2 = \pi/2$, should be realized between system (S^{**}) and system (I); indeed system (S^{**}) is now at temperature $T_{**} = T_0(3 \times 10^{-3})/3$ and $g_{S^{**}} \equiv g_{\perp} = g_I$.

The dipolar magnetic interaction induces the transitions of the reaction (9) with a transition probability W_x , and the difference of Zeeman energies balances the interaction energy.

We wish to derive the condition which must be satisfied by the transition probability W_x when $n_3^* = n_2^*$. Again (11) is applied, by keeping in mind the rules $\Delta m_{S^{**}} = -\Delta m_I = \pm 1$, see Fig. 7.

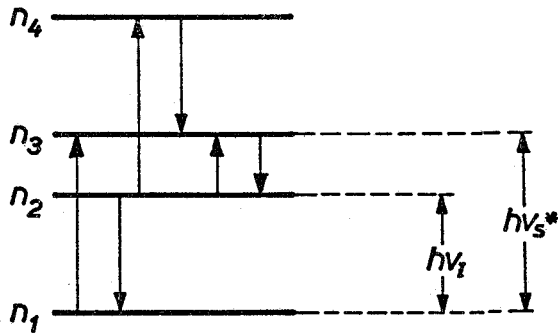


FIG. 7 - Sketch of the unperturbed energy levels for

$$\Delta E(S^{**}) \approx \Delta E(I)$$

The cross relaxation terms must be added to the thermal relaxation terms in (11), which becomes :

$$(22) \quad \left(\frac{dS}{dt}\right)_{\text{int}} = -\frac{1}{T_x} \sum_{i=1}^4 \mu_i \left(\frac{dn_i^*}{dt}\right)_{\text{th. relax.}} + \sum_{i=1}^4 \mu_i \left(\frac{dn_i^*}{dt}\right)_{\text{cr. relax.}}$$

with

$$\left(\frac{dn_i^*}{dt}\right)_{\text{cr. relax.}} = \frac{W_x}{\sum_j n_j^*} \sum_{j,k} (n_j^* n_k^* - n_i^* n_l^*)$$

where the indexes of number n^* are those of the energy levels for which $E_j - E_i \approx E_k - E_l$, and $W_x = (Nn)^{-1} \sum w_{ij}$, w_{ij} is the transition probability between spin S_i^{**} and I_j .

From (22), after rearrangement, one obtains :

$$(22') \quad \left(\frac{dS}{dt} \right)_{\text{int}} = - \frac{Nn}{T_x} \left\{ (\mu_3 - \mu_1)(P - P_0) T_{S^{**}}^{-1} + (\mu_2 - \mu_1)(p - p_0) T_I^{-1} + \right. \\ \left. + \frac{n}{2} (\mu_3 - \mu_1) W_x (P - p) - \frac{N}{2} (\mu_2 - \mu_1) W_x (P - p) \right\}$$

where we introduce the total number n and N to conserve the energy in the cross relaxation.

From the equilibrium condition one obtains :

$$(23) \quad \frac{\mu_3 - \mu_1}{\mu_2 - \mu_1} = - \frac{(p - p_0) \frac{\tau_I}{T_I} - \frac{1}{2} (P - p) \frac{N}{n}}{(P - P_0) \frac{\tau_{S^{**}}}{T_{S^{**}}} + \frac{1}{2} (P - p) \frac{N}{n}}$$

$$\text{where: } W_x = \frac{\tau_x^{-1}}{N + n}, \quad \tau_I = \frac{N + n}{N} \tau_x, \quad \tau_{S^{**}} = \frac{N + n}{N} \tau_x.$$

(23) satisfies to equilibrium condition :

$$n \Delta \mu^{(S^{**})} = N \Delta \mu^{(I)} \quad \text{for } \frac{\tau_I}{T_I} \longrightarrow 0 \quad \text{and} \quad \frac{\tau_{S^{**}}}{T_{S^{**}}} \longrightarrow 0$$

It is to be noted that $\tau_{S^{**}}/\tau_I = N/n$: two systems with different numbers of spins cross-relaxes with different cross relaxation times, the system with less number of spins having a shorter cross relaxation time.

RATE EQUATION. -

In order to determine the differential equation, whose solution gives the evolution of $p(t)$ and $P(t)$ for $\theta = \pi/2$, we consider now the reactions:



they are equivalent to count two times the reaction $N_- \rightleftharpoons N_+$ of the system (S) they give the entropy production of the system (S) :

$$\begin{aligned} \left(\frac{dS}{dt}\right)_{S, \text{int.}} &= -\frac{1}{T_x} \left[(\mu_3 - \mu_1) \left(\frac{dn_3^*}{dt} - \frac{dn_1^*}{dt} \right) + (\mu_4 - \mu_2) \left(\frac{dn_4^*}{dt} - \frac{dn_2^*}{dt} \right) \right] \frac{1}{2} = \\ &= -\frac{1}{2T_x} (\mu_3 - \mu_1) \frac{d}{dt} (n_1^* + n_2^* - n_3^* - n_4^*) = (\mu_3 - \mu_1) \frac{Nn}{2T_x} \frac{dP}{dt} \end{aligned}$$

In the same way if we consider the reactions :



we obtain for the entropy of the system (I) :

$$\left(\frac{dS}{dt}\right)_{I, \text{int.}} = (\mu_2 - \mu_1) \frac{Nn}{2T_x} \frac{dp}{dt}$$

The expression (22) is :

$$(24) \quad \left(\frac{dS}{dt}\right)_{\text{int.}} = \frac{1}{T_x} \frac{Nn}{2} (\mu_3 - \mu_1) \dot{P}(t) + (\mu_2 - \mu_1) \dot{p}(t)$$

By comparison of (24) and (22') one obtains the coupled differential equations :

$$\begin{aligned} \dot{P}(t) &= -(P - P_0) T_{S^{**}}^{-1} - \frac{n}{N+n} \zeta_x^{-1} (P - p) \\ (25) \quad \dot{p}(t) &= -(p - p_0) T_I^{-1} + \frac{N}{N+n} \zeta_x^{-1} (P - p) \end{aligned}$$

Now one has :

$$\begin{aligned} T_{S^{**}}^{-1} &\simeq 2(1 + \alpha) w_{S^{**}} \cosh \Delta^{**} \\ T_I^{-1} &\simeq 2w_I + 2w_{S^{**}} \alpha (1 - P_0^2) \cosh \Delta^{**} \end{aligned}$$

In the position $\theta_1 = \pi/4$ the two systems obey the same form of equations with $W_x = 0$ and $T_{S^{**}}$ substituted by T_S . $\times \pi$

QUALITATIVE DISCUSSION OF THE SPIN REFRIGERATOR. -

The preceding results apply to the proton spin refrigerator. The system (S) is constituted by paramagnetic Ytterbium ions, Yb, which are diluted (some percent) in the single crystal of Yttrium ethyl sulfate, $Y(C_2H_5SO_4) \cdot 9H_2O$.

This doped diamagnetic crystal has a strong axial anisotropic Landè g factor⁽³⁸⁾

$$g(\theta) = [g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta]^{1/2}$$

with

$$g_{\parallel} \approx 3.3 \quad \text{and} \quad g_{\perp} \approx 3 \times 10^{-3}$$

The spin-lattice relaxation time has the angular dependence given by :

$$(26) \quad T_S(\theta)^{-1} \approx AH^4 \sin^2 \theta \cos^2 \theta T + B(T).$$

The proton of hydration water constitute the system (I), which has a very long spin lattice relaxation time at temperatures T_0 , say 2°K, of the heat bath.

When the direction of the magnetic field is at an angle $\theta = (2K+1)\pi/4$ (K integer) with crystal axis, the condition $T_S/T_I \approx 0$ is satisfied, while for $\theta = (2K+1)\pi/2$ the condition $\mathcal{C}_{Sxx}/T_{Sxx} \approx 0$ and $\mathcal{C}_I/T_I \approx 0$ is satisfied.

If Δt is the time interval between two subsequent times of cross relaxation, we assume now $\Delta t = t_1 + t_2$, where t_2 is of the same order of \mathcal{C}_x and $t_1 \gg t_2$.

The system $S[\theta = (2K+1)\pi/2]$ and I have a time evolution given by the solution of coupled equations (25) during the time interval t_2 ; while, in the time interval t_1 , one has :

$$(27) \quad \begin{aligned} \dot{P}(t) &= -[P(t) - P_0(t)] T_S^{-1}(t) \\ \dot{p}(t) &= -[p(t) - p_0] T_I^{-1} \end{aligned}$$

The solution of (25) and (27) have been studied theoretically and verified experimentally, the behaviour of $p(t)$ and $P(t)$ is represented schematically in Fig. 8 for two cycles, under the condition $T_S[(2K+1)\pi/4] \ll t_1 \ll T_I$.

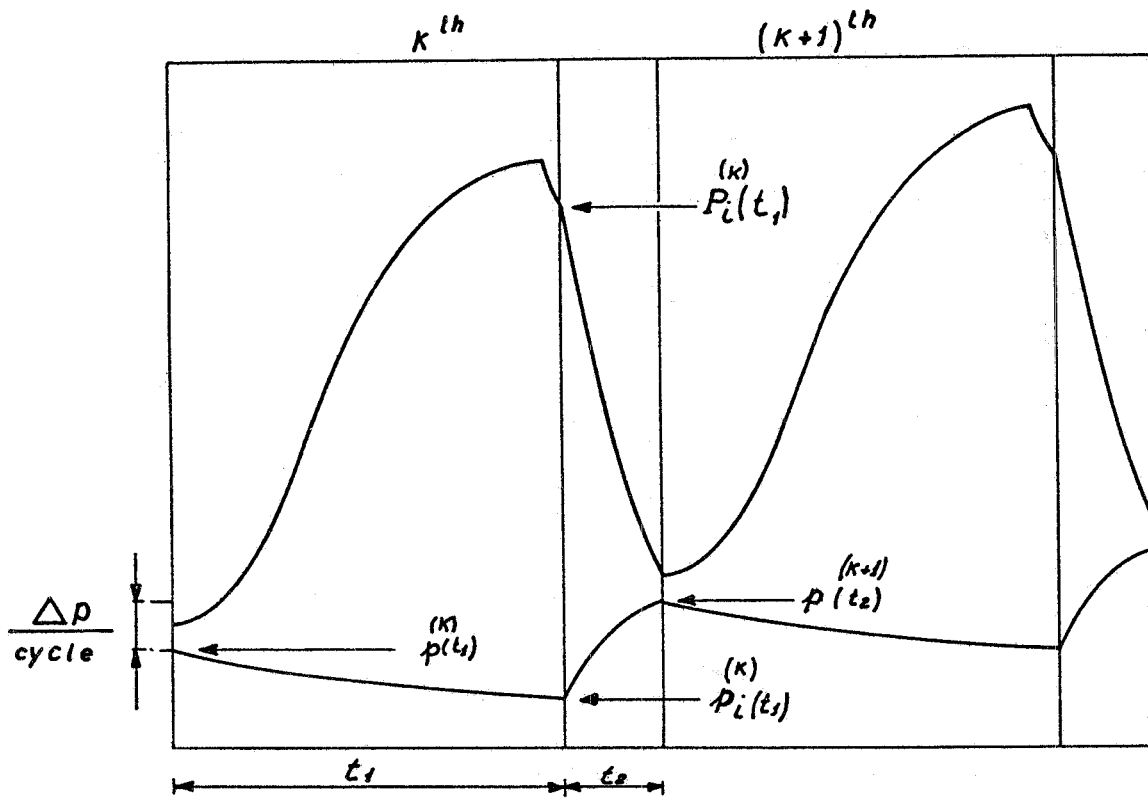


FIG. 8 - Sckecth of polarization $P(t)$ and $p(t)$ of the spin refrige_rator for two cycles.

In such a way the system (S) takes maximum polarization for $\theta = \text{odd integers of } \pi/4$ and at the same time there is not appreciable decay of the polarization of system (I). The net gain of polarization is:

$$p_{\text{final:f}}^{(K)} - p_{\text{initial:i}}^{(K)} = \Delta p$$

Since, after a time t , a number of cycles $K = t/(t_1+t_2)$ have been per_ormed one can write the approximate differential equation:

$$\frac{dp_i}{dt} = p_i - f\gamma(p_i - P_i) - \frac{p_i - p_0 \frac{t_1}{T_I}}{1 - \frac{t_1}{T_I}}$$

where $\gamma \equiv N(N+n)^{-1}$, $f \equiv 1 - \exp(-\frac{t_2}{T_x})$.

Its approximate solution is :

$$p_i \approx \frac{P_i}{1 + \frac{1}{f\gamma} \frac{t_1}{T_I}} \left\{ 1 - \exp \left[- \left(f\gamma + \frac{t_1}{T_I} \right) K \right] \right\}$$

where $P_i[\theta(t)] \xrightarrow{K \rightarrow \infty} P_S$, with P_S given by stationary solution of (27).

When Δt is greater than every $T(\theta)$, P_S assumes the value $P(\theta)$ which is the equilibrium value with the heat bath for each value of θ ; in this case the adiabatic transformation is not performed. When Δt decrease, but still $t_1 > T_S[(2K+1)\pi/4]$, the adiabatic transformation is more and more efficient: P_S rises with the rotation frequency, $f_r = 1/(2\Delta t)$, reaching a limit depending on the relaxation time which is a function of the magnetic field given by (26).

When, at constant field and for $\Delta t < T_S(\pi/4)$, system (S) does not reach the equilibrium value with the heat bath; consequently P_S is low. Now the adiabatic transformation is efficient, and in this case an higher value of the magnetic field rises P_S , making $\Delta t > T_S(\pi/4)$.

The value of P_S rises with magnetic field when the rotation frequency is constant, it reaches a value for which efficient equilibrium temperature with heat bath is obtained and the adiabatic transformation is obtained. Further increase of the field decreases P_S until the equilibrium temperature of the heat bath is reached for all values of θ , in this condition there is lack in the adiabacity.

CONCLUSIONS. -

The limiting values of the spin lattice relaxation times of two spin systems, required for the best efficiency of the spin refrigerator, are derived from thermodynamical considerations under the condition (N_+/N_-) Boltzman at $T_0 = n_+/n_-$. From the limiting value

$$\frac{T_S[(2K+1)\pi/4]}{T_I} \longrightarrow 0$$

one obtain that the system (S) must be in thermal contact with the heat bath and that the system (I) isolated from it. Furthermore from relation (20) it is obtained that the coefficient $\propto \propto \text{const.}/H_0^2 r_{ij}^6$ goes to zero with high field and low ion concentration.

Use of high fields are preferable with respect to the use of low concentrations, since, in this latter case, there is not efficient action of the spin S_i on the spin I_j to perform the transition (9), induced by dipolar magnetic interaction when $\theta = (2K+1)\pi/2$. On the other hand it is to be noted that the cross relaxation probability

$$W_x \propto w_{ij} \propto \frac{1}{r_{ij}^6} \quad \text{must go to infinity.}$$

24.

This fact would suggest to prefer high concentrations of ions. However, such high ion concentrations must be avoided either because high concentrations shorten the spin lattice relaxation time of system (I) (from (16') one has :

$$T_I \approx T_S (1 - P_o^2)^{-1} \frac{r_{ij}^6 H^2}{g_S^2 \beta^2}),$$

and because, as said above, the coefficient α must goes to zero.

Experiments, performed on the proton spin refrigerator by Jeffries and coworkers, have been obtained polarization as high as 35% on protons of hydration water in Ittium ethyl sulfate doped with Itterbium.

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