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Necessity of spin temperature

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It is well known that the concept of spin temperature may not be used to describe a statistical ensemble if the off-diagonal elements of the density matrix are not zero. This concept does not provide a valid description of masers, lasers, or conventional NMR or electron-spin resonance (ESR). It may be used to characterize transient behavior in a spin system "prepared" by sudden reversal of the magnetic field or a saturating pulse. Spin temperature, in such cases, is well defined after a time T_2. In nuclear-spin systems this is generally much shorter than the time T_1 required to reach thermal equilibrium with the lattice. The thermodynamics of irreversible processes provides an alternate and more comprehensive theoretical model for the description of spin systems. Examples are given where it may be used when the off-diagonal elements of the density matrix are not zero. The advantages and limitations of the spin-temperature formalism have been experimentally studied, primarily by means of the techniques of NMR. It is suggested that the predictions of irreversible thermodynamics be tested by observing the steady-state heat capacity of a maser at low temperature or the rate of evaporation of liquid helium in a transient experiment on a nuclear-spin system in which heat is being delivered irreversibly to the bath.

INTRODUCTION

The concept of spin temperature, which links nuclear magnetism and thermodynamics, has been used to provide a theoretical description of systems not in thermostatic equilibrium for about 30 years.[1] In some instances such a description is rigorously justifiable on theoretical grounds, and it has been successful in the interpretation of a variety of experiments. In other cases, the concept is introduced only as a convenience and is not a valid thermodynamic coordinate.

The development of the thermodynamics of irreversible processes antedates the spin-temperature concept by about 15 years.[2] It has been used to extend the ideas of thermodynamics from the description of a closed system in which all macroscopic quantities remain time invariant to an open system in which there is a steady-state flux from the environment. The thermodynamics of irreversible processes has been applied primarily[3] to the thermoelectric effect, molecular diffusion, chemical reactions, and similar processes. However, a few papers have been written about systems which have also been described using spin temperature.[4]

It is the purpose of this paper to treat several examples of spin systems in which both approaches are used to predict or interpret the physical behavior. We will consider thermostatic prototypes which are limiting cases of steady state and transient systems. In each example treated, we will derive the thermodynamic properties in both the spin-temperature and irreversible-thermodynamics language. We will not derive the underlying formalism used, but rather use the results of general arguments from the literature to critique the discussion. We will relate some of the results to actual experimental situations and suggest observational tests of the theory.

CASE 1. SPIN-$\frac{1}{2}$ SYSTEM

Consider N identical particles of spin $\frac{1}{2}\hbar$ and magnetic moment in a static magnetic field H_0 which may or may not be in thermostatic equilibrium with a heat reservoir at temperature T_L. The system could be protons each of magnetic moment $\mu = 2.79e\hbar/2Mc = 1.41\times10^{-23}$ erg G^{-1} or a nondegenerate electron gas each with magnetic moment $\mu = e\hbar/2mc = 9.27\times10^{-21}$ erg G^{-1}.

Let us imagine that the spin system is isolated from its environment and is characterized by its own temperature T_S. This spin temperature is defined by means of the fundamental thermodynamic relationship

$$T_S dS = dE + M dH \, , \tag{1}$$

with

$$\frac{1}{T_S} \equiv \left[\frac{dS}{dE} \right]_H \, . \tag{2}$$

In general

$$S = -Nk \, \mathrm{Tr} \hat{\rho} \ln \hat{\rho} \, , \tag{3}$$

where $\hat{\rho}$ is the spin-density matrix. Let us assume the off-diagonal elements of $\hat{\rho}$ are zero, without which no meaningful definition of temperature exists.[5] It is easy to construct the diagonal values of $\hat{\rho}$ in the energy representation. They are just the relative population numbers of the eigenstates of the Hamiltonian

$$\mathscr{H}_0 = -\vec{\mu} \cdot \vec{\mathrm{H}}_0 \, , \tag{4}$$

whose eigenvalues are

$$\epsilon_1 = -|\mu| H_0 \, ,$$

$$\epsilon_2 = |\mu| H_0 \, . \tag{5}$$

That is $\rho_i \equiv n_i / N$ $i = 1,2$, where the n_i are the occupation numbers of the two states such that

$$\sum_{i=1}^{2} n_i = N \, . \tag{6}$$

See Fig. 1. The energy of the system

$$E = \sum_i n_i \epsilon_i \, . \tag{7}$$

Hence

$$\rho_1 = \frac{N|\mu|H_0 - E}{2N|\mu|H_0}$$

and

$$\rho_2 = \frac{N|\mu|H_0 + E}{2N|\mu|H_0} \, . \tag{8}$$

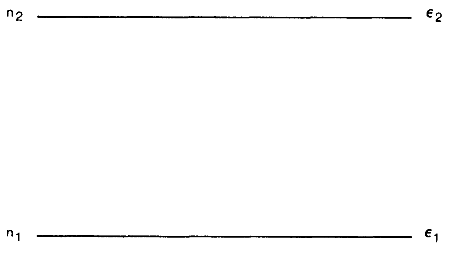

FIG. 1. Energy level diagram for spin-$\frac{1}{2}$ system.

The entropy may now be written explicitly as a function of E and H,

$$\begin{aligned} S &= -Nk \sum_i \rho_i \ln \rho_i \\ &= -k \left[\frac{N|\mu|H_0 - E}{2|\mu|H_0} \ln \frac{N|\mu|H_0 - E}{2N|\mu|H_0} \right. \\ &\quad \left. + \frac{N|\mu|H_0 + E}{2|\mu|H_0} \ln \frac{N|\mu|H_0 + E}{2N|\mu|H_0} \right] . \end{aligned} \tag{9}$$

Using the definition of spin temperature (2), we have

$$T_S = \frac{2|\mu|H_0}{k \ln \rho_1 / \rho_2} \, . \tag{10}$$

Equivalently, the ratio of the occupation numbers

$$\frac{n_1}{n_2} = \exp \frac{2|\mu|H_0}{kT_S} \, . \tag{11}$$

It is clear from (8) and (10) that the spin temperature ranges from 0 to $\pm\infty$ to -0 depending on E. If $E = -N|\mu|H_0$, $\rho_1 = 1$, $\rho_2 = 0$, and $T_S = 0$. If E is negative, but $|E| < N|\mu|H_0$, $\rho_1 > \rho_2$, and $T_S > 0$. If $E = 0$, $\rho_1 = \rho_2$ and $T_S = \pm\infty$. If $0 < E < N|\mu|H_0$, $\rho_1 < \rho_2$ and $T_S < 0$. Finally if $E = N|\mu|H_0$, $\rho_2 = 1$, $\rho_1 = 0$, and $T_S = -0$.

In the vast majority of thermodynamic systems, the temperature is positive. This is because the energy involves the particle kinetic energy, for which, in principle, there is no upper limit. The corresponding entropy increases monotonically with energy, guaranteeing a positive slope for dS/dE for which $T > 0$. In the spin system on the other hand, the energy is bounded below and above. The entropy starts at zero, goes through a maximum at $E = 0$ and returns to zero as E approaches its upper limit.

In the thermodynamics of irreversible processes, one basic assumption is that the Gibbs relation

$$T_L dS = dE + M dH - \sum_i \mu_i dn_i \tag{12}$$

is valid when the system is not in thermostatic equilibrium. We use T_L here to denote the temperature of the heat reservoir or lattice, in which the spin system is embedded. The chemical potentials

$$\mu_i \equiv -T_L \left[\frac{dS}{dn_i} \right]_{E,H,n_j \neq n_i} \tag{13}$$

are the key parameters in this formulation of the problem. We construct the entropy as a function of E, H (or the ϵ_i and the n_i). Rewriting (9),

$$S=-Nk\sum_i \rho_i \ln\rho_i$$

$$=Nk\ln N-k\sum_i n_i\ln n_i-\frac{1}{T_L}\sum_i n_i\epsilon_i+\frac{E}{T_L}\ . \tag{14}$$

From (13) and (14)

$$\mu_i=kT_L(1+\ln n_i)+\epsilon_i\ . \tag{15}$$

Now the ratio of occupation numbers is

$$\frac{n_1}{n_2}=\exp\left[\frac{(\mu_1-\mu_2)+2\,|\mu\,|H_0}{kT_L}\right]\ . \tag{16}$$

By comparing (11) and (16) we have a formal link between the spin temperature and the lattice temperature,

$$T_S=\frac{T_L}{1+(\mu_1-\mu_2)/2\,|\mu\,|H_0}\ . \tag{17}$$

If $\mu_1=\mu_2$, the system is in thermostatic equilibrium: $T_S=T_L=T$. If $\mu_1>\mu_2$, the spin system is colder than the lattice $0<T_S<T_L$. If $\mu_2-\mu_1=2\,|\mu\,|H_0$, $n_1=n_2$, or $T_s=\pm\infty$. If $\mu_2-\mu_1>2\,|\mu\,|H_0$, there is population inversion, $n_2>n_1$ or $T_s<0$.

We now outline the thermostatic properties of this system. They will be useful in the discussion of more complex physical situations. Starting with (16) or (11), with $\mu_1=\mu_2$, $T_S=T_L=T$ the relative occupation numbers are

$$\rho_1=\frac{e^x}{e^x+e^{-x}},\quad \rho_2=\frac{e^{-x}}{e^x+e^{-x}}\ . \tag{18}$$

The partition function of the canonical distribution is

$$Z=e^x+e^{-x}\ ,$$

with (19)

$$x\equiv\beta\,|\mu\,|H_0,\quad \beta\equiv(kT)^{-1}\ .$$

The energy E, magnetization M, entropy S, and heat capacity C_H may now be found from Z:

$$E=-N\frac{\partial}{\partial\beta}\ln Z=-N\,|\mu\,|H_0\tanh\frac{|\mu\,|H_0}{kT}\ , \tag{20}$$

$$M=\frac{N}{\beta}\frac{\partial}{\partial H}\ln Z=N\,|\mu\,|\,\tanh\frac{|\mu\,|H_0}{kT}\ , \tag{21}$$

$$S=Nk(\ln Z+\beta\bar{\epsilon})$$

$$=Nk[\ln(e^x+e^{-x})-x\tanh x]\ , \tag{22}$$

and

$$C_H=T\left[\frac{dS}{dT}\right]_H=\left[\frac{dE}{dT}\right]_H=Nkx^2\,\mathrm{sech}^2x\ . \tag{23}$$

It is clear that $\lim C_H=0$ as $T\to 0$ or as $T\to\infty$. C_H is finite and positive for all other values of T. It is easy to show that C_H is a maximum at $x=1.20$, for which

$$(C_H)_{\max}=0.439Nk\ . \tag{24}$$

It is well known[6] that this heat capacity is very large indeed compared to the lattice heat capacity. If we take a moderate magnetic field $H_0=3000$ gauss,

$$T_{\max}=\begin{cases}1.68\times10^{-1}\ \mathrm{K} & \text{for electrons}\ ,\\ 2.55\times10^{-3}\ \mathrm{K} & \text{for protons}\ ,\end{cases} \tag{25}$$

The low-temperature lattice heat capacity corresponding to the Debye model is

$$C_V=\frac{12\pi^4}{5}Nk\left[\frac{T}{\Theta_D}\right]^3\ ,$$

with

$$\Theta_D\approx 250\ \mathrm{K}\ . \tag{26}$$

Comparing C_H and C_V at $T_{\max}$, we find

$$\frac{C_H}{C_V}=\begin{cases}6.19\times10^{6} & \text{for electrons}\ ,\\ 1.76\times10^{15} & \text{for protons}\ .\end{cases} \tag{27}$$

Roughly 1 g of an electron paramagnetic salt or 3 μ of a nuclear paramagnetic solid has the heat capacity of 6 tons of diamagnetic material. At these low temperatures, an appropriate spin system, rather than the lattice, must be taken as the heat reservoir.

CASE 2. SPIN-$\frac{1}{2}$ SYSTEM

Transient behavior

The spin-$\frac{1}{2}$ system described in case 1 is allowed to come to thermostatic equilibrium in a static magnetic field so that

$$\frac{N_1}{N_2} = \exp\frac{\gamma_n \hbar H_0}{kT_L} \ . \tag{28}$$

Here T_L is the lattice temperature, $\gamma_n = \mu_n / \frac{1}{2}\hbar$ is a positive nuclear gyromagnetic ratio. We use capital N_i to denote equilibrium occupation numbers and lower case n_i for the transient values.

In a time $\Delta t << T_1$, the spin lattice relaxation time, we reverse the direction of the magnetic field.[7] In this process no transitions are induced and the population of the energy levels remains unchanged. It is an adiabatic transformation in the Ehrenfest sense.[8] The rate equation describing the chemical reaction

$$n_{1/2} \rightleftarrows n_{1/2} \tag{29}$$

is

$$\frac{dn_1}{dt} = -n_1\omega_{12} + n_2\omega_{21} = -\frac{dn_2}{dt} \ , \tag{30}$$

where $n_1 + n_2 = N$. In thermostatic equilibrium, the rate equation is zero and

$$\frac{n_1}{n_2} = \frac{N_1}{N_2} = \frac{\omega_{21}}{\omega_{12}} = \exp\frac{\gamma_n \hbar H_0}{kT} \ . \tag{31}$$

We assume that the ratio of the thermal relaxation rates remains constant for all values of the n_i. The equilibrium states of the n_i's occur after a time interval $\Delta t >> T_1$. The ω_{ij} and the relaxation time T_1 are related,

$$T_1^{-1} = \frac{\omega_{12} + \omega_{21}}{2} \ . \tag{32}$$

At $t = 0$, immediately after reversal, $n_1 = N_2$, $n_2 = N_1$. We solve (30) for n_1 and n_2:

$$n_1 = N\left[\frac{e^x}{e^x + e^{-x}} - e^{-2t/T_1}\tanh x\right] \ ,$$

and

$$n_2 = N\left[\frac{e^{-x}}{e^x + e^{-x}} + e^{-2t/T_1}\tanh x\right] \ , \tag{33}$$

with x defined by (19). This solution satisfies the boundary conditions at $t = 0$ and $t = \infty$.

The limiting case $T = 0$ is of interest. At this temperature $x \rightarrow \infty$ and

$$n_1 = N(1 - e^{-2t/T_1})$$

and

$$n_2 = Ne^{-2t/T_1} \ . \tag{34}$$

At $t = 0$, $n_1 = 0$, $n_2 = N$. As $t \rightarrow \infty$, $n_1 = N$, $n_2 = 0$. Equating $n_1 = n_2$ in (34), we find that $t = (T_1/2)\ln 2$ is the time lapse for the two populations to become equal to $N/2$.

Given the occupation numbers, the other transient thermodynamic quantities, E, M, S, and C_H, are readily found:

$$E = -N\mu H_0 \tanh x[1 - 2e^{-2t/T_1}] \ . \tag{35}$$

At $t \rightarrow \infty$ and $t = 0$

$$E = -N\mu H_0 \tanh x \quad \text{and} \quad +N\mu H_0 \tanh x \ , \tag{36}$$

respectively.

$$M = (n_1 - n_2)\mu = N\mu \tanh x[1 - 2e^{-2t/T_1}] \ . \tag{37}$$

At $t \rightarrow \infty$ and $t = 0$

$$M - N\mu \tanh x \quad \text{and} \quad -N\mu \tanh x \ ,$$

respectively.

$$\begin{aligned} S = Nk\Bigg[\ln N &- \left[\frac{e^x}{e^x + e^{-x}} - e^{-2t/T_1}\tanh x\right]\ln N\left[\frac{e^x}{e^x + e^{-x}} - e^{-2t/T_1}\tanh x\right] \\ &- \left[\frac{e^{-x}}{e^x + e^{-x}} + e^{-2t/T_1}\tanh x\right]\ln N\left[\frac{e^{-x}}{e^x + e^{-x}} + e^{-2t/T_1}\tanh x\right]\Bigg] \ . \end{aligned} \tag{38}$$

At $t = 0$ and $t \rightarrow \infty$, the entropy has the same value,

$$S = Nk\left[\ln N - \left[\frac{e^x}{e^x + e^{-x}}\ln\frac{Ne^x}{e^x + e^{-x}}\right] - \left[\frac{e^{-x}}{e^x + e^{-x}}\ln\frac{Ne^{-x}}{e^x + e^{-x}}\right]\right] \ . \tag{39}$$

At both limiting times, as $T \to 0$, $S \to 0$. At $t = \frac{1}{2}T_1 \ln 2$. $S = Nk \ln 2$. S also has this maximum value when either $T \to \infty$ or $H = 0$ for which $x = 0$:

$$C_H = T\left[\frac{dS}{dT}\right]_H = \frac{Nkx}{2}\operatorname{sech}^2 x \ln\frac{n_1}{n_2}[1-2e^{-2t/T_1}] , \tag{40}$$

with $n_1(t)$ and $n_2(t)$ given by (33). At $t \to \infty$ and at $t = 0$,

$$C_H = Nkx^2 \operatorname{sech}^2 x . \tag{41}$$

At $T \to 0$, $x = 0$, $n_1 = N(1-e^{-2t/T_1})$, $n_2 = Ne^{-2t/T_1}$. In this limit

$$C_H = 0 . \tag{42}$$

This holds for all values of t, which is a remarkable confirmation of the third law of thermodynamics. Equation (40) is valid for T_1 independent of T.[9]

From the expressions derived, especially those for the transient values of n_i, we may now examine the "spin temperature" and irreversible thermodynamic descriptions of this system.

Using (10),

$$T_S = \frac{2|\mu|H_0}{k\left[\ln\left[\frac{e^x}{e^x+e^{-x}} - e^{-2t/T_1}\tanh x\right] - \ln\left[\frac{e^{-x}}{e^x+e^{-x}} - e^{-2t/T_1}\tanh x\right]\right]} . \tag{43}$$

At $t = \infty$, $T_S = T_L$. At $t = 0$, $T_S = -T_L$. At $T_L = 0$, $T_S = \pm 0$. These limiting results are expected. The decay of T_S to the lattice temperature T_L does not have a simple functional dependence. We may write

$$E = -N|\mu|H_0 \tanh\frac{|\mu|H}{kT_S} \tag{44}$$

and equate this to (35). There the factor $1-2e^{-2t/T_1}$ is not part of the argument of the hyperbolic tangent. If we take both $\mu H/kT_L$ and $\mu H/kT_S \ll 1$, then by equating (35) and (44) we have

$$T_S = \frac{T}{1-2e^{-2t/T_1}} . \tag{45}$$

This describes a simple exponential approach of T_S to T through negative values as t progresses from 0 to several spin lattice relaxation times.

We construct the chemical potentials from (15) and (33),

$$\mu_1 = \epsilon_1 + kT + kT\ln N\left[\frac{e^x}{e^x+e^{-x}} - e^{-2t/T_1}\tanh x\right]$$

and

$$\mu_2 = \epsilon_2 + kT + kT\ln N\left[\frac{e^{-x}}{e^x+e^{-x}} + e^{-2t/T_1}\tanh x\right] . \tag{46}$$

These expressions are consistent with (16) and with (40), where we note that the heat capacity may also be found from

$$C_H = \left[\frac{dE}{dT}\right]_H - \sum_i \mu_i\left[\frac{dn_i}{dT}\right]_H . \tag{47}$$

The advantage of the approach used by irreversible thermodynamics is that it gives the same results as the spin-temperature description at any instant of time. In addition it provides a temporal description of the way the system approaches thermostatic equilibrium, most graphically by means of the rate of internal entropy production.

In this system, the irreversible process $n_{-1/2} \rightleftarrows n_{1/2}$ describes the nuclear spin flips in which energy is taken from or delivered to the lattice.

The internal entropy production[10] is d_iS/dT,

$$T_L\frac{d_iS}{dt} = A\frac{d\xi}{dt} , \tag{48}$$

where the chemical affinity

$$A \equiv \mu_2 - \mu_1 = 2\mu H - kT_L \ln\frac{n_1}{n_2} , \tag{49}$$

and the degree of advancement per unit time $d\xi/dt$ is

$$\frac{dn_1}{dt}=-n_1\omega_{12}+n_2\omega_{21}=e^{-2t/T_1}\frac{2N}{T_1}\tanh x\ . \tag{50}$$

Thus

$$T_L\frac{d_iS}{dt}$$
$$=e^{-2t/T_1}\left[\frac{2N}{T_1}\tanh\frac{\mu H_0}{kT_L}\right]\left[2\mu H_0-kT_L\ln\frac{n_1}{n_2}\right]\ . \tag{51}$$

At $t=0$, $n_1=Ne^{-x}/e^x+e^{-x}$, $n_2=Ne^x/e^x+e^{-x}$, $\ln n_1/n_2=-2\mu H_0/kT_L$, and

$$T_L\frac{d_iS}{dt}=\left[\frac{8N\mu H_0}{T_1}\tanh\frac{\mu H_0}{kT_H}\right]e^{-2t/T_1}\ . \tag{52}$$

As t increases, the entropy production decreases. At $t=\frac{1}{2}T_1\ln 2$, $n_1=n_2=N/2$, and

$$T_L\frac{d_iS}{dt}=\left[\frac{4N\mu H_0}{T_1}\tanh\frac{\mu H_0}{kT_L}\right]e^{-2t/T_1}\ . \tag{53}$$

And at $t=\infty$,

$$n_1=\frac{Ne^x}{e^x+e^{-x}},\quad n_2=\frac{Ne^{-x}}{e^x+e^{-x}}\ ,$$
$$\ln\frac{n_1}{n_2}=\frac{2\mu H_0}{kT_L}\ .$$

Thus

$$T_L\frac{d_iS}{dt}=0\ . \tag{54}$$

This is the thermostatic equilibrium condition.

It is constructive to evaluate the total heat delivered to the "lattice,"

$$Q_i=\int_{t=0}^{\infty}T_L\frac{d_iS}{dT}dt\ . \tag{55}$$

In the high-temperature limit, where $\mu H_0/kT=x<<1$,

$$n_1=N\left[\frac{1+x-xe^{-2t/T_1}}{2}\right]\ ,$$

and (56)

$$n_2=N\left[\frac{1-x+xe^{-2t/T_1}}{2}\right]\ ,$$

then

$$T_L\frac{d_iS}{dt}\approx\frac{4N\mu^2H^2}{T_1kT_L}e^{-4t/T_1} \tag{57}$$

and

$$Q_i\cong\frac{N\mu^2H^2}{kT_L} \tag{58}$$

is the total heat delivered to the lattice as the spin system returns to thermostatic equilibrium by the irreversible relaxation process.

CASE 3. SPIN-$\frac{3}{2}$ SYSTEM

Consider N molecules of NaCl in a single crystal[11] placed in a static magnetic field H_0 at a lattice temperature T. The two abundant isotopes ^{23}Na and ^{35}Cl have a spin $I=\frac{3}{2}$. We take $\gamma_n\hbar H_0/kT_L<<1$ and consider three different physical situations: (a) thermostatic equilibrium, (b) transient behavior just when the system is irradiated with an ultrasonic wave at a frequency $\omega=2\gamma_nH_0$, (c) the steady-state behavior while the ultrasonic saturating "pump" is still on.

In thermostatic equilibrium

$$\frac{n_i}{n_{i+1}}=e^{\delta}\ ,$$

where (59)

$$\delta=\frac{\epsilon}{kT}=\frac{\gamma_n\hbar H_0}{kT},\quad i=1,2,3\ .$$

Here the spin temperature and the lattice temperature coincide. Inasmuch as

$$\sum_{i=1}^{4}n_i=N\ , \tag{60}$$

it is very easy to construct the equilibrium n_i for $\delta<<1$:

$$n_i=\frac{N}{4}(1+m_i\delta)\ . \tag{61}$$

See Fig. 2. The energy E and magnetization M are

$$E=-\frac{5N}{4}\frac{(\gamma_n\hbar H_0)^2}{kT} \tag{62}$$

and

$$M=\frac{5N}{4}\frac{\gamma_n^2\hbar^2H_0}{kT}\ . \tag{63}$$

The power absorbed in a nuclear magnetic reso-

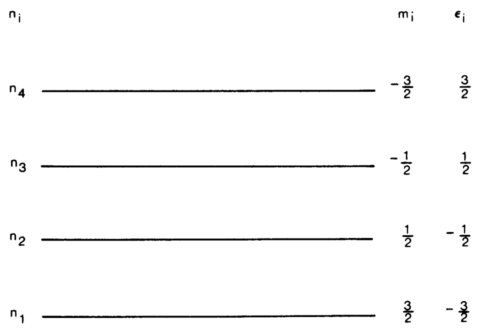

FIG. 2. Energy level diagram for spin-$\frac{3}{2}$ system. $\epsilon \equiv \gamma_n \hbar H_0$, $\epsilon_i \equiv -m_i \epsilon$.

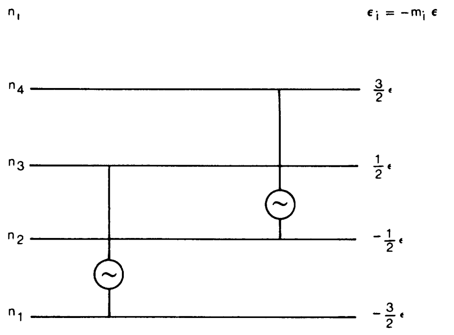

FIG. 3. Energy level diagram for spin-$\frac{3}{2}$ system showing saturating acoustic pumps: $n_1 = n_3$, $n_2 = n_4$.

nance experiment is

$$P = \sum_{i=1}^{3} (n_i - n_{i+1}) \hbar\omega W_N = \frac{3N}{4} \frac{(\gamma_n \hbar H_0)^2}{kT} W_N , \tag{64}$$

where W_N is the radiative induced transition probability for a conventional NMR signal and $\omega = \gamma_n H_0$ is the nuclear Larmor frequency.

The entropy can be readily calculated from

$$S = -Nk \sum_{i=1}^{4} \rho_i \ln \rho_i , \tag{65}$$

where the ρ_i are given by

$$\rho_i = \frac{n_i}{N} = \tfrac{1}{4}(1 + m_i \delta) . \tag{66}$$

Then

$$S = Nk \left[\ln 4 - \frac{5}{4} \left[\frac{\gamma_n \hbar H_0}{kT} \right]^2 \right] , \tag{67}$$

and the heat capacity

$$C_H = \tfrac{5}{2} Nk \left[\frac{\gamma_n \hbar H_0}{kT} \right]^2 . \tag{68}$$

This result is not consistent with the third law of thermodynamics because it is obtained for the high-temperature limit. Nuclei of spin $I > \frac{1}{2}$ have nuclear quadrupole moments. If these spins are in a crystalline environment with an electric field, they can respond to acoustic signals inducing transitions $\Delta m = \pm 2$. In NaCl the internal stark field does not appreciably disturb the equality of the Zeeman splitting.

We consider the system shown in Fig. 3 shortly after the acoustic signals have been switched on. More precisely we are interested in the system's behavior for $T_2 << t << T_1$, where T_2 is the nuclear-spin-spin relaxation time and T_1 the nuclear-spin-lattice relaxation time.

In nuclear-spin systems in solids T_2 may be of the order of 10's of microseconds and T_1 of the order of minutes. The nuclear dipole-dipole interaction is much stronger than the nuclear-spin-lattice relaxation time.

The dipole-dipole interaction includes energy conserving reactions of the form

$$n_m + n_{m'-1} \rightleftarrows n_{m-1} + n_{m'} . \tag{69}$$

It is precisely this mechanism[12] which rearranges the population distribution corresponding to the most probable distribution of populations among the levels consistent with conservation of the initial energy E. This is the Boltzmann population distribution with temperature T_S,

$$\frac{n_i}{n_{i+1}} = \exp \frac{\gamma_n \hbar H_0}{kT_S} . \tag{70}$$

From (70) $n_1/n_2 = n_2/n_3 = n_3/n_4$ and from the acoustic saturation $n_1 = n_3$, $n_2 = n_4$. Hence

$$n_1 = n_2 = n_3 = n_4 = \frac{N}{4} \text{ and } T_S = \infty .$$

Given the transient (tr) occupation numbers it is easy to see that

$$E_{\text{tr}} = 0 ,$$
$$M_{\text{tr}} = 0 . \tag{71}$$

No power will be absorbed in an NMR experiment:

$$P_{\text{tr}} = 0 . \tag{72}$$

The entropy reaches its expected maximum

$$S_{\rm tr}=Nk\ln 4\,, \tag{73}$$

and the heat capacity

$$C_H=\lim_{T_S\to\infty}\tfrac{5}{4}Nk\left[\frac{\gamma_n\hbar H_0}{kT_S}\right]^2=0\,. \tag{74}$$

Note that C_H is calculated from $(dE/dT_S)_H$ because T_S is the only temperature defined in the spin-temperature formalism.

If we look at the transient behavior from the chemical potential point of view, we write

$$\frac{n_i}{n_{i+1}}=\exp\left[\frac{\mu_i-\mu_{i+2}+2\epsilon}{kT_L}\right]$$

and (75)

$$\frac{n_i}{n_{i+1}}=\exp\left[\frac{\mu_i-\mu_{i+1}+\epsilon}{kT_L}\right].$$

Since $n_1=n_3$ and $n_2=n_4$ by virtue of the acoustic pumps

$$\mu_1-\mu_3=\mu_2-\mu_4=-2\epsilon\,. \tag{76}$$

The reversible reaction induced by the flip-flop dipole-dipole interaction comes to equilibrium in a time $T_2<t<<T_1$. This means that

$$\mu_1-\mu_2=\mu_2-\mu_3=\mu_3-\mu_4\,. \tag{77}$$

If we combine the constraint (76) with the equilibrium reaction equations (77), we find that

$$\mu_i-\mu_{i+1}=-\epsilon,\ \ i=1,2,3\,. \tag{78}$$

When this is inserted into (75), we have

$$n_1=n_2=n_3=n_4=\frac{N}{4}\,. \tag{79}$$

Now we find that the transient values of the energy, magnetization, and NMR power absorbed are all zero as in the spin-temperature description. The entropy has the same maximum value. The heat capacity C_H is again zero, but for a different reason,

$$C_H\equiv T_L\frac{dS}{dT_L}=0\,. \tag{80}$$

Now S is independent of the lattice temperature and T_L is finite.

The steady state comes about after a time $t\geq T_1$ when the reactions

$$n_{3/2}\rightleftarrows n_{1/2} \tag{81}$$

and $n_{-1/2}\rightleftarrows n_{3/2}$ come to equilibrium. Then

$$\mu_4=\mu_3$$

and (82)

$$\mu_2=\mu_1\,.$$

The occupation numbers are now

$$\frac{n_1}{n_2}=\exp\frac{\gamma_n\hbar H_0}{kT_L}\,,$$

(83)

$$\frac{n_3}{n_4}=\exp\frac{\gamma_n\hbar H_0}{kT_L}\,,$$

and

$$n_1=n_3,\ \ n_2=n_4\,.$$

See Fig. 3.

The spin-temperature point of view is no longer valid. If it were used there would be two such temperatures. The temperature characterizing the ratio n_1/n_3 and n_2/n_4 would be by $T_S=\infty$ as in the transient case. The spin temperature characterizing the ratio n_1/n_2 and n_3/n_4 would be $T_S'=T_L$. It is well recognized in spin temperature theory[13] that

$$\frac{n_m}{n_{m-1}}=\exp\left[\frac{\epsilon_{m-1}-\epsilon_m}{kT_S}\right] \tag{84}$$

with a single value of T_S for all m. This criterion is met only for those times t such that $T_2<<t<<T_1$, i.e., the transient case.

The energy, magnetization, entropy, NMR power absorbed, and heat capacity for the steady state may be readily found from the occupation numbers, which we write in the high T limit,

$$n_1=\frac{N}{4}\left[1+\frac{\delta}{2}\right]=n_3$$

and (85)

$$n_3=\frac{N}{4}\left[1-\frac{\delta}{2}\right]=n_4\,.$$

Thus

$$E_{\rm SS}=-\frac{NkT_L}{8}\left[\frac{\gamma_n\hbar H_0}{kT_L}\right]^2, \tag{86}$$

$$M_{\rm SS}=\frac{N}{8}\frac{(\gamma_n\hbar)^2}{kT_L}H_0\,, \tag{87}$$

$$S_{\rm SS}=Nk\left[\ln 4-\frac{1}{4}\left[\frac{\gamma_n\hbar H_0}{kT_L}\right]^2\right], \tag{88}$$

$$P_{\mathrm{SS}}=\frac{N}{4}\frac{(\gamma_n\hbar H_0)^2}{kT_L}W\,, \tag{89}$$

and

$$C_H=T_L\left[\frac{dS}{dT_L}\right]_H=\frac{Nk}{2}\left[\frac{\gamma_n\hbar_0 H_0}{kT_L}\right]^2 . \tag{90}$$

We note that $(dE/dT_L)_H=(Nk/8)(\gamma_n\hbar H_0/kT_L)^2$ is not C_H because there is a contribution from $-\sum_i \mu_i dn_i$ in the Gibbs relation.

The connecting link between the transient and the steady-state behavior is provided by solving the rate equations and by studying the internal entropy production,

$$\frac{dn_1}{dt}=-n_1\omega_{12}+n_2\omega_{21} \tag{91}$$

and

$$\frac{dn_3}{dt}=-n_3\omega_{34}+n_4\omega_{43}\,. \tag{92}$$

At $t=0$, $n_1=n_2=n_3=n_4=N/4$. At $t=\infty$, $n_1=n_3=(N/4)(1+\delta/2)$ and $n_2=n_4=(N/4)\times(1-\delta/2)$. The solution is

$$n_1=\frac{N}{4}\left[1+\frac{\delta}{2}-\frac{\delta}{2}e^{-2t/T_1}\right]=n_3$$

and (93)

$$n_2=\frac{N}{4}\left[1-\frac{\delta}{2}+\frac{\delta}{2}e^{-2t/T_1}\right]=n_4\,.$$

The internal entropy production

$$\frac{d_iS}{dT_L}=T_L^{-1}\sum_j A_j\frac{dn_i}{dt}\,, \tag{94}$$

where j denotes the two irreversible chemical reactions. The chemical affinities and the degrees of enhancement for the two reactions are equal:

$$T_L\frac{d_iS}{dt}=2A\frac{dn_1}{dt}\,, \tag{95}$$

where

$$A=\mu_2-\mu_1=\mu_3-\mu_4=\gamma_n\hbar H_0-kT\ln\frac{n_1}{n_2}\,. \tag{96}$$

From

$$\frac{dn_1}{dt}=\frac{N\gamma_n\hbar H_0}{4kT_L}\frac{e^{-2t_1/T_1}}{T_1}\,,$$

(97)

$$A=\gamma_n\hbar H_0 e^{-2t/T_1}\,.$$

Hence

$$\frac{d_iS}{dt}=\frac{Nk}{2}\left[\frac{\gamma_n\hbar H_0}{kT_L}\right]^2\frac{e^{-4t/T_1}}{T_1}\,.$$

At $t=0$, (98)

$$\frac{d_iS}{dt}=\frac{Nk}{2T_1}\left[\frac{\gamma_n\hbar H_0}{kT_L}\right]^2$$

is a maximum. As $t\to\infty$ $d_iS/dt\to 0$, as it should for the steady state. The total amount of heat delivered to the lattice as the system proceeds from the transient to the steady state is

$$Q_i=NkT_L\left[\frac{\gamma_n\hbar H_0}{kT_L}\right]^2 . \tag{99}$$

CASE 4. THE THREE-LEVEL MASER OR LASER STEADY STATE

In this example we consider a quantum-mechanical amplifier or oscillator operating CW (in the steady state) with a pump and compare this behavior with the system when quiescent (in thermostatic equilibrium). See Fig. 4.

A typical maser is one in which the signal wave length $\lambda=21$ cm. It is operated cold to minimize the noise: $T\cong 4$ K. The level spacing is not equal because of competition between the internal electric field and the external magnetic field. It is the

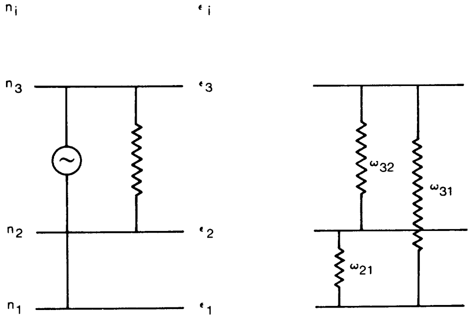

FIG. 4. Energy level diagram for a three-level maser or laser with and without a pump.

mixing of Zeeman and Stark wave functions which makes it possible to pump between levels 1 and 3. For this maser $h\nu/kT=1.71\times10^{-2}$. Thus we can linearize this Boltzmann factor.

A typical laser might have an operating wave length $\lambda=500$ mμ. If we take the temperature at 300 K, then $h\nu/kT=96$. Here we need to use the exact Boltzmann factor.

In thermostatic equilibrium, the occupation numbers are

$$n_1=N\left[\frac{1}{1+e^{-\delta}+e^{-\Delta-\delta}}\right]\simeq\frac{N}{3}\left[1+\frac{2\delta+\Delta}{3}\right],$$

$$n_2=N\left[\frac{e^{-\delta}}{1+e^{-\delta}+e^{-\Delta-\delta}}\right]\simeq\frac{N}{3}\left[1-\frac{\delta}{3}+\frac{\Delta}{3}\right],\tag{100}$$

and

$$n_3=N\left[\frac{e^{-\Delta-\delta}}{1+e^{-\delta}+e^{-\Delta-\delta}}\right]\simeq\frac{N}{3}\left[1-\frac{2\Delta}{3}-\frac{\delta}{3}\right].$$

Here

$$\delta=\frac{h\nu_{21}}{kT_L},\quad \Delta=\frac{h\nu_{32}}{kT_L}.\tag{101}$$

In the steady state when the pump is on, $n_1=n_3$. We can immediately write the steady-state occupation numbers by recognizing that the pump acts as a constraint so that

$$\mu_1-\mu_3=-kT_L(\delta+\Delta)=-h\nu_{31}.\tag{102}$$

This follows from

$$\frac{n_1}{n_3}=\exp\frac{(\mu_1-\mu_3)+h\nu_{31}}{kT_L}=1.\tag{103}$$

At the same time we see that the relaxation process connecting levels 3 and 2 comes to equilibrium, such that $\mu_3=\mu_2$. Hence

$$\frac{n_2}{n_3}=\exp\frac{(\mu_2-\mu_3)+h\nu_{32}}{kT_L}=e^{\Delta}.\tag{104}$$

Using the normalization condition $\sum_{i=1}^{3}n_i=N$, we have

$$n_1=n_3=\frac{N}{2+e^{\Delta}}\simeq\frac{N}{3}\left[1-\frac{\Delta}{3}\right]$$

and

$$n_2=\frac{Ne^{\Delta}}{2+e^{\Delta}}\simeq\left[1+\frac{2\Delta}{3}\right].\tag{105}$$

This system should not be described by spin temperature; although it has become customary,[14] as a matter of convenience, to refer to the 2-1 levels by means of a negative spin temperature,

$$\frac{n_1}{n_2}=e^{-h\nu_{32}/kT_S}.\tag{106}$$

In thermostatic equilibrium

$$\frac{n_1}{n_2}=e^{h\nu_{21}/kT_L}.\tag{107}$$

Thus

$$T_S=-\frac{\nu_{32}}{\nu_{21}}T_L.\tag{108}$$

Logically, the three-level system has two additional spin temperatures. Between levels 3 and 1, there is an infinite spin temperature. Between levels 3 and 2, the spin temperature is the lattice temperature. It is ludicrous to have

$$T_S(21)=-\frac{\nu_{32}}{\nu_{21}}T_L,$$

$$T_S(31)=\infty,\tag{109}$$

and

$$T_S(32)=T_L.$$

Here temperature loses its thermodynamic meaning. It is well known that this description is not rigorous. The physical reasons are significant. In a three-level system, where the spacing is unequal, there is generally no fast spin-spin, energy conserving process which can bring the system to internal equilibrium as in the case of NaCl.

Ruby (Cr^{3+} doped Al_2O_3) has been used both as a maser and as a laser.[15] In this system, as in other paramagnetic systems where the paramagnetism is electronic (not nuclear) $T_2\approx T_1$. In the NaCl case, the nuclear $T_2<<T_1$.

Furthermore in the CW laser or maser, it is clear that the off-diagonal elements of the density matrix are not zero.[16] Spin temperature is not well defined[17] unless $\rho_{ij}\approx0$, $i\neq j$.

From the point of view of irreversible thermodynamics we can describe the steady state properties (SS) and compare them with the equilibrium (eq) properties of this three-level system:

$$E_{\mathrm{SS}}=\frac{Nh}{2+e^{\Delta}}(\nu_{13}+e^{\Delta}\nu_{12})$$

$$\simeq\frac{Nh}{3}\left[\nu_{13}+\nu_{12}-\frac{\nu_{13}\Delta}{3}+\frac{2\nu_{12}\Delta}{3}\right]\tag{110}$$

and

$$E_{\mathrm{eq}}=\frac{Nh}{1+e^{-\delta}+e^{-\Delta}}(\nu_{13}e^{-\Delta-\delta}+\nu_{12}e^{-\delta})$$

$$\simeq\frac{Nh}{3}\left[\nu_{13}+\nu_{12}-\frac{\Delta}{3}(2\nu_{13}-\nu_{12})\right.$$

$$\left.-\frac{\delta}{3}(\nu_{13}+\nu_{12})\right]\;; \qquad (111)$$

at $T\to 0$, $\Delta\to\infty$, $\delta\to\infty$,

$$E_{\mathrm{SS}}=Nh\nu_{12} \text{ and } E_{\mathrm{eq}}=0\;;$$

at $T\to\infty$, $\Delta\to 0$, $\delta\to 0$,

$$E_{\mathrm{SS}}=E_{\mathrm{eq}}=\frac{Nh}{3}(\nu_{13}+\nu_{12})\;.$$

At all intermediate temperatures it is clear that $E_{\mathrm{SS}}>E_{\mathrm{eq}}$. At those T_L values for which Δ and δ are small compared to one,

$$E_{\mathrm{SS}}-E_{\mathrm{eq}}=\frac{Nh}{9}[\Delta(\nu_{13}+3\nu_{12})+\delta(\nu_{13}+\nu_{12})]\;. \qquad (112)$$

The entropy $S=-Nk\sum_i \rho_i \ln\rho_i$. In the steady state

$$S_{\mathrm{SS}}=Nk\left[\ln(e^{\Delta}+2)-\frac{\Delta e^{\Delta}}{e^{\Delta}+2}\right] \qquad (113)$$

and

$$S_{\mathrm{eq}}=Nk\left[\ln(1+e^{-\delta}+e^{-\delta-\Delta})\right.$$

$$\left.+\frac{\delta e^{-\delta}+(\Delta+\delta)e^{-\delta-\Delta}}{1+e^{-\delta}+e^{-\Delta-\delta}}\right]\;. \qquad (114)$$

At $T_L\to 0$, both S_{SS} and $S_{\mathrm{eq}}\to 0$. As $T_L\to\infty$, $S_{\mathrm{SS}}=S_{\mathrm{eq}}=Nk\ln 3$. At all intermediate values of T_L, $S_{\mathrm{SS}}<S_{\mathrm{eq}}$. In the case of the maser when $\delta,\Delta<<1$, $S_{\mathrm{eq}}-S_{\mathrm{SS}}$ is second order in $h\nu/kT_L$.

To find C_H, we must use $T(dS/dT_L)_H$ for $(C_H)_{\mathrm{SS}}$ but we may use $(dE/dT_L)_H$ for $(C_H)_{\mathrm{eq}}$. The reason is that the $-\sum_i \mu_i dn_i$ term makes a contribution in the steady state. However, in thermostatic equilibrium $\mu_1=\mu_2=\mu_3=\mu$. Thus $-\sum_i \mu_i dn_i=-\mu N$ which is temperature independent:

$$(C_H)_{\mathrm{SS}}=\frac{2Nk\Delta^2 e^{\Delta}}{(2+e^{\Delta})^2} \qquad (113')$$

and

$$(C_H)_{\mathrm{eq}}=\frac{Nk}{(1+e^{-\delta}+e^{-\Delta})^2}\left\{\begin{matrix}(1+e^{-\delta}+e^{-\Delta})(\delta^2 e^{-\Delta})\\ -e^{-\delta}\delta\end{matrix}\right\} \qquad (114')$$

As $T_L\to\infty$, all levels are equally occupied and both values of $C_H\to 0$. At $T_L=0$, in the equilibrium state $n_i\to N$. But in this limit $n_2\to N$ in the steady state. These are both states of perfect order for which we have found $S\to 0$. The heat capacities also go to zero, as they should, to be in keeping with the third law of thermodynamics. The heat capacity for the steady state has one Schottky peak,[18] but the heat capacity for the quiescent state has two Schottky peaks. At $0<T_L<\infty$, we expect $(C_H)_{\mathrm{SS}}$ and $(C_H)_{\mathrm{eq}}$ to cross twice. We note that both heat capacities remain positive for $T_L>0$.

The steady-state three-level maser has some striking similarities with the three-level degenerate system whose splitting is due to the interaction of the nuclear quadrupole moment with the internal Stark field. We note that $n_1=(2+e^{\Delta})^{-1}$, $n_2=e^{\Delta}/2+e^{\Delta}$, and $n_3=(2+e^{\Delta})^{-1}$ in both cases. The maser is steady state, the nuclear spin $I=1$ is in thermostatic equilibrium. As a result the two entropy expressions and the two heat capacity expressions are identical. However, we note that

$$E_{\mathrm{maser}}=\frac{Nk}{2+e^{\Delta}}(\nu_{13}+\nu_{12}e^{\Delta})\;, \qquad (115)$$

whereas

$$E_{\mathrm{stark}}=\frac{2Nk\nu_{12}}{2+e^{\Delta}}\;. \qquad (116)$$

CASE 5. NUCLEAR CALORIMETRY

Single crystals of LiF of high purity make ideal samples for the study of nuclear calorimetry. Fluorine has a spin $I'=\frac{1}{2}$ and a magnetic moment $\mu'=2.6273e\hbar/2Mc$. Lithium has a spin $I''=\frac{3}{2}$ and a magnetic moment $\mu''=3.256e\hbar/2Mc$. Both spin systems[18] have a $T_2\simeq 5\,\mu\mathrm{s}$ and a $T_1\simeq 2-5$ min. These values are just right for the establishment of spin temperatures T_S' and T_S''.

We have already studied the thermostatic properties of spin $I=\frac{1}{2}$ and $I=\frac{3}{2}$ systems. In the spin-temperature formalism, all we need do is replace the lattice T_L by T_S. We take the Boltzmann factor to be small compared to unity.

Thus

$$M' = \frac{N'}{4}\frac{(\gamma_n'\hbar)^2 H_0}{kT_S'}\,,\quad M'' = \frac{5N''}{4}\frac{(\gamma_n''\hbar)^2 H_0}{kT_S''}\,, \tag{117}$$

$$E' = -M'H_0,\quad E'' = -M''H_0\,, \tag{118}$$

$$C_H' = \frac{N'k}{4}\left[\frac{\gamma_n'\hbar H_0}{kT_S'}\right]^2,\quad C_H'' = \frac{5N''k}{4}\left[\frac{\gamma_n''\hbar H_0}{kT_S''}\right]^2. \tag{119}$$

The number of ^{7}Li nuclei is less than the number of ^{19}F nuclei because the isotopic abundance of the former is 92.57% and of the latter is 100%. We ignore ^{6}Li in this discussion.

The magnetization may be thought of as a thermostatic property. A positive magnetization corresponds to $T_S > 0$, a zero magnetization implies that $T_S = \infty$, and a negative magnetization is a measure of a negative T_S.

In our study of $M < 0$ in case 2, the negative magnetization was achieved by a sudden reversal of the magnetic field H_0. In nuclear calorimetry we wish the spin species in the sample to have different initial temperatures. A field reversal would give Li and F the same negative T_S. The experimental technique of preparing the two species is well known.[19] A positive T_S is obtained by allowing the species in question to rest several relaxation times in a strong field. An infinite T_S is obtained by modulating the field over the resonance value, thereby saturating the species in question. A negative T_S is obtained by fast passage. The two spin systems which are prepared to have different T_S values are isolated from one another by the different spacing of their energy levels in the same strong field.

Mixing of the two spin systems is achieved by lowering the field until the Zeeman spacings overlap. This occurs at about 75 gauss for LiF. The spin systems exchange heat and come to a common equilibrium temperature T_S after a time T_2. Measurement of M' and M'' after mixing provides an observational test of this formalism.

The thermal equilibrium temperature may be calculated by equating the heat exchange in the system to zero:

$$\int_{T_i'}^{T_S} C_H'\,dT + \int_{T_i''}^{T_S} C_H''\,dT = 0\,. \tag{120}$$

Therefore,

$$\frac{N'\gamma_n'^2}{T_i'} + \frac{5N''\gamma_n''^2}{T_i''} = \frac{1}{T_S}[N'\gamma_n'^2 + 5N''\gamma_n''^2] \tag{121}$$

and

$$\frac{1}{T_S} = \left[\frac{1}{T_i'} + \frac{\mu}{T_i''}\right](1+\mu)^{-1}\,, \tag{122}$$

where

$$\mu = \frac{N''\gamma''^2 I''(I''+1)}{N'\gamma'^2 I'(I'+1)} = 0.7898\,. \tag{123}$$

In Table I, we list the results of eight nuclear calorimetry experiments performed[19] with LiF. The magnetization and temperatures are given before mixing. The theoretical temperature and magnetization values after mixing are listed next to the observed magnetization values.

The theoretical and experimental results disagree by as much as 30% in some cases. This is due, as

TABLE I. Magnetization and spin temperatures of fluorine and lithium nuclei before and after mixing.

	Before mixing		*After mixing*: Theory	*Observation*	
	Fluorine	Lithium	Fluorine and Lithium		
Expt.	M', T_i'	M'', T_i''	T_s, M	Fluorine	Lithium
(a)	M_0, 300	M_0, 300	300, M_0	$0.95M_0$	$0.95M_0$
(b)	M_0, 300	0, 00	537, $0.56M_0$	$0.42M_0$	$0.51M_0$
(c)	0, 00	M_0, 300	680, $0.44M_0$	$0.42M_0$	$0.43M_0$
(d)	M_0, 300	$-M_0$, 300	2554, $0.12M_0$	$0.27M_0$	$0.20M_0$
(e)	$-M_0$, -300	M_0, 300	-2554, $-0.12M_0$	$0.05M_0$	$0.00M_0$
(f)	0, 00	$-M_0$, -300	-680, $-44M_0$	$-0.16M_0$	$-0.17M_0$
(g)	$-M_0$, -300	0, 00	-537, $-0.56M_0$	$-0.29M_0$	$-0.34M_0$
(h)	$-M_0$, -300	$-M_0$, -300	-300, $-M_0$	$-0.71M_0$	$-0.72M_0$

Abragam[20] points out, to the finite relaxation time T_1 of both ^{19}F and ^{7}Li and to the ratio of the mixing time τ to t_1 at the various field strengths in which mixing takes place.

In any case this experiment in nuclear calorimetry is impressive. This experiment (and the ultrasonic experiment on NaCl) were characterized by Abragam and Proctor as *explainable only by utilizing the concept of spin temperature.*[21]

I disagree. The thermodynamics of irreversible processes, employing chemical potentials, provides an alternate and more inclusive explanation.

The basic relationship we use to start this discussion is the ratio of occupation numbers in adjacent Zeeman levels,

$$\frac{n_i}{n_{i+1}}=\exp\left[\frac{\mu_i-\mu_{i+1}+\gamma_n\hbar H_0}{kT_L}\right]. \tag{124}$$

Here $\mu_1=\mu_{i+1}$ only when the spin system is in equilibrium with the lattice. If we use the linear approximation to the Boltzmann factor,

$$\frac{n_i}{n_{i+1}}\simeq 1+\alpha\ ,$$

where (125)

$$\alpha=\frac{\mu_i-\mu_{i+1}+\gamma_n\hbar H_0}{kT_L}\ ,$$

Now we write the magnetization and energy for fluorine and lithium nuclei.

$$M'=\frac{N'}{4}\gamma'_n\hbar\left[\frac{\gamma'_n\hbar H_0+(\mu_1-\mu_2)'}{kT_L}\right], \tag{126}$$

$$M''=\frac{5N''}{4}\gamma_n''\hbar\left[\frac{\gamma_n''\hbar H_0+(\mu_i-\mu_{i+1})''}{kT_L}\right], \tag{127}$$

and

$$E'=-M'H_0,\ \ E''\equiv -M''H_0\ ,$$

When the two spin systems are mixed, there is no heat exchange by virtue of a difference in temperature. The process is isothermal. Rather there is a chemical reaction which takes place by virtue of the spin-spin interaction. The chemical affinities $(\mu_i-\mu_{i+1})$ for F and Li become equal. This brings about a change in the occupation numbers. We can find the equilibrium chemical affinity by setting the total change in energy equal to zero:

$$E_i'-E_f'+E_i''-E_f''=0\ . \tag{128}$$

Using (127)

$$\begin{aligned}\frac{N'}{4}\gamma'_n\hbar H_0\left[\frac{(\mu_i-\mu_{i+1})+\gamma'_n\hbar H_0}{kT_L}\right]+\frac{5N''}{4}\gamma_n''\hbar H_0\left[\frac{(\mu_i-\mu_{i+1})+\gamma_n''\hbar H_0}{kT_L}\right]\\ =\frac{N'}{4}\gamma'_n\hbar H_0\left[\frac{(\mu_i-\mu_{i+1})'+\gamma'_n\hbar H_0}{kT_L}\right]+\frac{5N''}{4}\gamma_n''\hbar H_0\left[\frac{(\mu_i-\mu_{i+1})''+\gamma_n''\hbar H_0}{kT_L}\right].\end{aligned} \tag{129}$$

TABLE II. Chemical affinities of fluorine and lithium nuclei before and after mixing.

	Before mixing		*After mixing*
Expt.	Fluorine	Lithium	Fluorine and Lithium
	$(\mu_i-\mu_{i+1})'$	$(\mu_i-\mu_{i+1})''$	$\gamma_n\hbar H_0$
(a)	0	0	0
(b)	0	$-\gamma_n''\hbar H_0$	-0.44
(c)	$-\gamma'_n\hbar H_0$	0	-0.56
(d)	0	$-2\gamma_n''\hbar H_0$	-0.88
(e)	$-2\gamma'_n\hbar H_0$	0	-1.12
(f)	$-\gamma'_n\hbar H_0$	$-2\gamma_n''\hbar H_0$	-1.44
(g)	$-2\gamma'_n\hbar H_0$	$-\gamma_n''\hbar H_0$	-1.56
(h)	$-2\gamma'_n\hbar H_0$	$-2\gamma_n''\hbar H_0$	-2.00

This expression is seen to be precisely (121) if we make the formal substitution

$$T_S=T_L\left[1+\frac{\mu_i-\mu_{i+1}}{\gamma_n\hbar H_0}\right]^{-1}.$$

This is essentially (17). This establishes the equivalence between the two theories. They both say the same thing about the initial and final magnetization. They differ in the thermodynamic parameter used to describe these initial and final states.

In the accompanying Table, we write the initial and final chemical affinities corresponding to the various experiments given above.

The predictions using chemical potentials agree with those using spin temperature. Agreement with observation could be improved by means of a transient treatment incorporating T_1 into the formulation. The procedure for doing this is worked out in case 2.

CASE 6. STEADY STATE MAGNETIC RESONANCE FOR A SYSTEM OF SPIN $=\frac{1}{2}$

Consider N nuclei or electrons of spin $\frac{1}{2}$ in a magnetic field: $\vec{\mathrm{H}}=H_0\hat{k}+\vec{\mathrm{H}}_{rf}$ where the sinusoidal field is at right angles to the static field. It is convenient for this discussion to take the angular frequency of the time varying field at resonance, i.e., $\omega_0=\gamma H_0$. The steady state solution to this problem is very well known.[22] Bloch's phenomenological theory will be used here as a point of departure.

The macroscopic magnetization M satisfies the equation

$$\frac{d\vec{\mathrm{M}}}{dt}=\gamma\vec{\mathrm{M}}\times\vec{\mathrm{H}}-\frac{M_x\hat{i}+M_y\hat{j}}{T_2}-\frac{M_z-M_0}{T_1}\hat{k}\ , \tag{130}$$

where T_2 and T_1 are the transverse and longitudinal relaxation times and $\hat{i}$, $\hat{j}$, $\hat{k}$ are the unit vectors in the laboratory frame of reference.

The steady-state solutions for M_z and $M_x \pm iM_y$ are

$$M_z=\frac{M_0}{1+\gamma^2T_1T_2H_1^2}\ , \tag{131}$$

$$M_x \pm iM_y=\pm i\gamma M_0T_2H_1\exp(\mp i\omega_0 t)\ . \tag{132}$$

In the absence of a time varying field

$$M_z=M_0=\frac{N\gamma^2\hbar^2H_0}{4kT}\ . \tag{133}$$

Here the separation between spin levels $\gamma\hbar H_0$ is to be taken small compared to kT.

The elements of the density matrix

$$\hat{\rho}=\begin{vmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{vmatrix}$$

may not be explicitly constructed. In this formalism the predicted value of any observable $\mathscr{O}$ of a statistical ensemble of N identical systems of spin I is given by the equation.[23]

$$\langle\mathscr{O}\rangle=\mathrm{Tr}(\hat{\rho}\mathscr{O})\ . \tag{134}$$

Thus

$$\langle M_z\rangle=\tfrac{1}{2}\gamma\hbar N\langle\sigma_z\rangle=\tfrac{1}{2}\gamma\hbar N(\rho_{11}-\rho_{22})\ . \tag{135}$$

The quantities ρ_{11} and ρ_{22} are the relative populations of levels 1 and 2, normalized such that $\rho_{11}+\rho_{22}=1$. It follows from (131) and (135) that

$$\rho_{11}=\frac{1}{2}+\frac{\hbar\omega_0}{4kT}\left[\frac{1}{1+\gamma^2T_1T_2H_1^2}\right]\ , \tag{136}$$

$$\rho_{22}=\frac{1}{2}-\frac{\hbar\omega_0}{4kT}\left[\frac{1}{1+\gamma^2T_1T_2H_1^2}\right]\ , \tag{137}$$

$$M_+=M_x+iM_y=\frac{\gamma\hbar N}{2}\langle\sigma_+\rangle=\frac{\gamma\hbar N}{2}\rho_{21}\ , \tag{138}$$

and

$$M_-=M_x-iM_y=\frac{\gamma\hbar N}{2}\langle\sigma_-\rangle=\frac{\gamma\hbar N}{2}\rho_{12}\ . \tag{139}$$

The off-diagonal elements of the density matrix can be obtained from (132) and (138) and (139). They are

$$\rho_{21}=ie^{-i\omega_0 t}\gamma H_1T_2\frac{\hbar\omega_0}{2kT}\ , \tag{140}$$

$$\rho_{12}=-ie^{i\omega_0 t}\gamma H_1T_2\frac{\hbar\omega_0}{2kT}=\rho_{21}'\ . \tag{141}$$

In principle, since ρ_{21} and ρ_{12} are not zero, a spin temperature may not be used to describe this system. If T_2 is very small compared to T_1, ρ_{21} and ρ_{12} are almost zero. In this case a spin temperature may be used as a thermodynamic parameter. This means that internal equilibrium in the spin system is established long before the system comes into equilibrium with the lattice. Such a temperature is appropriate for nuclear spin systems but is not for the conduction electrons in a metal where $T_2\approx T_1$.

The concept of spin temperature may once again be entirely avoided by using the thermodynamics of irreversible processes.

We start with the Gibbs relation (12) and the expression for the chemical potential of the ith energy level (15)

$$\mu_i=kT(1+\ln n_i)+\epsilon_i,\quad i=1,2 \tag{142}$$

where

$$\epsilon_i=-\tfrac{1}{2}\hbar\omega_0,\quad \epsilon_2=\tfrac{1}{2}\hbar\omega_0\ .$$

A nucleus or an electron of spin $\frac{1}{2}$ may flip from the state $m_1=\pm\frac{1}{2}$ to the state $m_2=\mp\frac{1}{2}$ by the radiative induced reversible reaction

$$\langle \tfrac{1}{2} \rangle + \hbar\omega_0 \rightleftarrows \langle -\tfrac{1}{2} \rangle ,$$

at the rate

$$W = \frac{\pi\gamma^2 H_1^2}{2} g(\omega_0) , \tag{143}$$

with

$$\frac{d\zeta_R}{dt} = (-n_1 + n_2)W ,$$

or by the irreversible process

$$\langle \tfrac{1}{2} \rangle \rightleftarrows \langle -\tfrac{1}{2} \rangle , \tag{144}$$

in which thermal energy is exchanged with the lattice at the rate T_1^{-1}. By this process

$$\frac{d\zeta_{\mathrm{IR}}}{dt} = -n_1\omega_{12} + n_2\omega_{21} . \tag{145}$$

The ω_{ij} are the spin lattice relaxation rates [see (31) and (32)]. The chemical affinity

$$A = \mu_2 - \mu_1 = kT \ln\frac{n_2}{n_1} + \hbar\omega_0 . \tag{146}$$

The energy lost due to internal entropy production by the relaxation process (144) is

$$T\frac{d_iS}{dt} = (\mu_2 - \mu_1)(n_2\omega_{21} - n_1\omega_{12}) . \tag{147}$$

In the steady state this is just balanced by the isothermal rate of increase of internal energy by radiation $-A d\zeta_R/dt$.

Equating these contributions leads to the familiar rate equation

$$-n_1\omega_{12} + n_2\omega_{21} + (n_2 - n_1)W = 0 . \tag{148}$$

From (148) and the normalization condition $n_1 + n_2 = N$, the steady-state occupation numbers may be found. These are functions of N, H_0, T, and the rates T_1^{-1} and W. If we take the absorption line shape at resonance to be $g(\omega_0) = T_2/\pi$, we may readily calculate the z component of magnetization and the power absorbed

$$M_z = \frac{\gamma\hbar}{2}(n_1 - n_2) , \tag{149}$$

and

$$P = (n_1 - n_2)\hbar\omega_0 W = 2\omega_0 \chi'' H_1^2 .$$

Here χ'' is the imaginary part of the complex susceptibility. The real part of the complex susceptibility χ' may be obtained by means of the Kramers-Kronig relations, but for $\omega = \omega_0$ it is zero. The expressions for M_+ and M_- immediately follow.

This example shows that the thermodynamics of irreversible processes may readily be used in conjunction with quantum mechanical perturbation theory and the Kramers-Kronig relations to obtain the familiar Bloch equations for NMR and ESR.[24] However, the spin-temperature formalism does not possess this versatility. The conditions under which it may be used are not generally satisfied in this case.

EXPERIMENTAL APPROACHES

This paper is devoted primarily to the theoretical models which are used to describe spin systems. It is quite natural that the techniques of magnetic resonance,[25] both steady state and transient, are more frequently used in experimental investigations. These have demonstrated the validity and the limitations of the spin-temperature concept.

Measurements of a different type might be considered to study the range of validity of the thermodynamics of irreversible processes as applied to spin systems. In particular it would be interesting to study the steady-state heat capacity and magnetic susceptibility. In addition transient properties could be studied for those cases where the experimental measurement time is small compared to the spin lattice relaxation time. The theory of irreversible processes does predict that heat will be delivered to the lattice at a certain rate. This could be observed at low temperatures by monitoring the increased rate at which liquid helium is vaporized in a transient or steady-state experiment as compared to the quiescent rate.

CONCLUSION

The concept of spin temperatures may be used to describe a temperature different from the lattice temperature if the off-diagonal elements of the density matrix are zero. This precludes such a description for a steady state NMR or ESR experiment or for a maser or laser. However, an rf field may be used to "prepare" a spin system and the spin-temperature concept may be used to describe its behavior several T_2's after the field is turned off. This concept is certainly useful in describing nuclear spin calorimetry.

The thermodynamics of irreversible processes appears, for the examples considered, to offer a theoretical picture of nuclear and electron spin systems which is more comprehensive than the spin temperature formalism. In all the cases where spin temperature is strictly forbidden, irreversible thermodynamics may be used. Where spin temperature may be used, irreversible thermodynamics provides an alternate theoretical framework.

The principal conclusion of this paper is that spin temperature is a useful concept, but that its use is a matter of convenience. None of the examples cited show that spin temperature is an indispensable concept. In each case irreversible thermodynamics makes available a more inclusive description.

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[1] F. Bloch, Phys. Rev. 70, 460 (1946); E. M. Purcell and R. V. Pound, Phys. Rev. 81, 279 (1951); R. V. Pound, Phys. Rev. 81, 156 (1951); A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961), Chap. 5; M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon, Oxford, 1970).

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[3] See S. R. de Groot and P. Mazur, Ref. 2, Chaps. 10–13.

[4] W. A. Barker and E. A. Desloge, Phys. Rev. 108, 924 (1957); 36, 872 (1964); W. A. Barker, M. L. Narchal, S. Misra, A. Bevolo, F. Haas, C. Birkbeck, B. Kuehne, and J. Witte, Rev. Mod. Phys. 36, 872 (1964); W. A. Barker and M. McGuire, J. Chem. Phys. 49, 4114 (1968).

[5] A. Abragam, Ref. 1, p. 134.

[6] See for example, Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1953), p. 138.

[7] This type of experiment was performed on LiF by E. M. Purcell and R. V. Pound, Phys. Rev. 86, 279 (1951). A more sophisticated method for achieving negative magnetization is by fast passage. See A. Abragam, ref. 1, p. 547.

[8] Adiabatic in the quantum mechanical or Ehrenfest sense refers to the evolution of a statistical ensemble when an external parameter such as H_0 is changed in such a way that the populations of the various levels remain unchanged and no transitions are induced. See A. Abragam, Ref. 1, p. 135.

[9] It is easy to extend the theory to include T_1, a function of T.

[10] See, for example, I. Prigogine, Ref. 2, Chap. 3.

[11] W. G. Proctor and W. W. Robinson, Phys. Rev. 104, 1344 (1956). See also A. Abragam, Ref. 1, p. 139 and M. Goldman, Ref. 1, p. 9.

[12] See M. Goldman, Ref. 1, p. 9.

[13] See M. Goldman, Ref. 1, p. 8.

[14] See, for example, J. R. Singer, *Masers* (Wiley, New York, 1959), pp. 18 and 112.

[15] See, for example, G. R. Fowles, *Introduction to Modern Optics* (Holt, Rinehart and Winston, New York, 1975), 2nd edition, p. 285.

[16] A. A. Vuylsteke, *Elements of Maser Theory* (van Nostrand, New York, 1960), Chap. 7.

[17] A. Abragam, Ref. 1, p. 134.

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[23] A. Abragam, Ref. 1, p. 26.

[24] Mary Duns Scotus Breitbart and W. A. Barker, Am. J. Phys. 36, 152 (1968).

[25] See, for example, A. Abragam, Ref. 1.