30 May 1969, Volume 164, Number 3883

SCIENCE

Nuclear Spin Thermodynamics in the Rotating Frame

Spins in solids interact weakly and behave irreversibly, yet retain vestiges of isolated-spin dynamics.

Alfred G. Redfield

The interactions of nuclear spins with each other and with externally applied magnetic fields are precisely known. At laboratory temperatures nuclear spin systems in solids are like dilute ideal gases in the simplicity and universality of their thermodynamics. But if a spin system is subjected to a strong radio-frequency field it has unexpected properties (1, 2). For example, whereas electromagnetic radiation generally heats up a system irreversibly with constantly increasing entropy, a nuclear spin system can be induced to change its energy reversibly and isentropically, under the influence of suitable variations of the applied radio-frequency field. And by application of a steady radio-frequency field, steady temperatures less than 1°K can be produced, in a certain sense, within the nuclear spin system in a solid at room temperature.

The unique behavior of spins results mainly from three properties: (i) in a large steady magnetic field they precess at nearly the same frequency, only slightly modified by interspin interactions; (ii) their energy has an upper bound (when all the spin moments are pointed exactly opposite to the magnetic field) as well as a lower bound; and (iii) strong, completely monochromatic radio-frequency fields can easily be applied to them.

The energy of interaction between spins, although small compared to their interaction energy with the typically large applied field, can nevertheless serve as an important thermodynamic reservoir for energy and entropy, as well as a mechanism for thermal contact between spins. It is helpful-and frequently essential-to recognize the thermodynamic importance of the spinspin interaction in the analysis of techniques for sensitivity enhancement in nuclear resonance, for dynamic polarization of spins in nuclear physics targets, and in any other experiment involving strong radio- or microwave fields in resonance with spins.

The rotating-frame transformation for spins is somewhat like the rotatingcoordinate transformation familiar in mechanics, which simplifies calculations of kinetic theory. However, in the spin system, the characteristic energies of the system are changed importantly, and with them the dynamics of spin motion are changed. The spin system tends toward a state of quasi-equilibrium in the rotating frame, which is far from any equilibrium state in the fixed frame.

I will develop the ideas used to analyze rotating-coordinate physics by analogy with certain experiments performed in the absence of a radio-frequency field, and will start with a description of the spin system and a review of these fixed-frame experiments.

General Description

An isolated nuclear spin placed in a steady magnetic field \mathbf{H}_0 will precess about it at an angular frequency ω_0 $= \gamma H_0$, where γ is the nuclear magnetic moment μ , divided by the spin angular momentum. In a 10-kilogauss field, the resonance frequency $\omega_0/2\pi$ is roughly 10 megahertz for many isotopes, and is 42.8 megahertz at most, for protons.

I discuss here the properties of a solid like ice or aluminum which contains only one isotope (¹H or ²⁷Al, respectively), at a temperature well below the melting point, so that atomic diffusion and thermal motion of the lattice are negligible for our purposes. The nuclear spins in such a system can be regarded as forming a thermodynamic system because they exchange energy with one another more rapidly than with nonspin degrees of freedom.

The *i*th spin moment y_i obeys the precession equation

$d\boldsymbol{\mathfrak{y}}_i/dt = \gamma \boldsymbol{\mathfrak{y}}_i \times (\mathbf{H} + \mathbf{h}_i) \qquad (1)$

where t is time, **H** is the externally applied magnetic field including a radiofrequency field, and \mathbf{h}_i is the "local field" of a few gauss which spin *i* feels, because of its neighboring nuclear magnetic moments (3). Later I will discuss what happens when **H** includes radiofrequency fields; for the moment let us assume that **H** is a steady field \mathbf{H}_0 in the z direction. If \mathbf{h}_i were zero, Eq. 1 would predict steady precession at frequency γH_0 radians per second. We ignore for the moment fields produced by nonspin degrees of freedom.

Because of variations in \mathbf{h}_i , different spins precess at slightly different rates even if \mathbf{H}_0 is uniform. More important, \mathbf{h}_i contains a high frequency part owing to the high-frequency precession of the neighboring spins. This high frequency is nearly in resonance with the spin and can therefore make it change its angle of precession with respect to \mathbf{H}_0 , and thereby its magnetic energy $\mathbf{\mu}_i \cdot \mathbf{H}_0$. Such a process is usually called a "spin flip," though there is no reason to regard it as an abrupt process as suggested by the word "flip." Since overall energy must be conserved, such a flip

The author is a physicist at the IBM Watson Laboratory, Columbia University, New York 10025.

is accompanied by a reverse "flop" of the neighbors. So the spin precesses nearly uniformly about \mathbf{H}_0 , changing its angle with respect to \mathbf{H}_0 , and its precession phase relative to a uniform precession at frequency γH_0 , over a time scale of the order of a precession period in the *local* field, that is, over tens of microseconds. Thus, if \mathbf{H}_0 is much larger than the local field \mathbf{h}_i , the uniform precession of a spin is only slightly modified by \mathbf{h}_i .

If \mathbf{H}_0 is comparable to \mathbf{h}_i , then the precession of a moment about \mathbf{H}_0 becomes almost obscured by the spin-spin interaction field, and if H_0 is zero the spins precess chaotically about a local field which itself changes direction chaotically over an interval of tens of microseconds.

For all attainable temperatures T and fields H_0 , the maximum variation in spin energy ($\sim \mu_i H_0$) is much less than kT, where k is Boltzmann's constant; this is why the spins are nearly random in direction. The experimenter studies small departures from the completely random, infinite temperature state by measuring the magnetization

$$\mathbf{M} = \sum_{i} \mathbf{u}_{i} \tag{2}$$

which is always much less than its maximum possible value N_{μ} , where N is the number of spins and μ is the magnitude of the vector \mathbf{u}_i which is assumed the same for all spins. The theorist's task is simplified by the need to describe only small departures from the random state. The field \mathbf{h}_i can be regarded as due to only rather near neighbors of *i* because the sum of the contributions from more distant neighbors will tend to approach zero, so that cooperative phenomena (spin waves, ferromagnetism) are absent.

The local field \mathbf{h}_i is the sum of the classical fields from the neighboring magnetic dipoles

$$\mathbf{h}_{i} = -\sum_{j} \left(\frac{\mathbf{y}_{j}}{\mathbf{r}_{ij}^{3}} - \frac{3\mathbf{r}_{ij}}{\mathbf{r}_{ij}^{5}} \mathbf{y}_{j} \cdot \mathbf{r}_{ij} \right) \quad (3)$$

where $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$; and \mathbf{r}_i and \mathbf{r}_j are the positions of spins *i*, *j*. The details of Eq. 3 are unimportant; what matters is that it contains time-invariant factors, involving the \mathbf{r}_{ij} , multiplying the vectors \mathbf{y}_j , which are precessing about their own fields.

The root-mean-square magnitude of the local field \mathbf{h}_i will be denoted by $H_{\rm L}$; more precisely, $H_{\rm L}^2$ is defined as $\frac{1}{2} h_i^2$, first averaged over all orientations of the \mathbf{y}_j , as appropriate in the high-temperature approximation, and



Fig. 1. Relative variation of spin temperature, magnetization, and spin-spin interaction energy as the applied magnetic field H_o is varied in an isentropic demagnetization. The negative entropies corresponding to M and E_s/H_L are proportional to the squares of these quantities.

then averaged over all spin sites *i*. Since only near neighbors contribute appreciably to the sum of Eq. 3, $H_{\rm L}$ is a few times μ divided by the cube of the lattice spacing, usually a few gauss, roughly the same as the ordinary nuclear resonance linewidth.

Besides **H** and h_i , each spin "feels" a small interaction field because of nonspin degrees of freedom of the solid; these are lumped under the general name "lattice," even though lattice vibrations may not be the most important of them, and the interaction is called the spin-lattice interaction. The spin-lattice interaction forces the spin system to approach thermal equilibrium with the lattice at a rate more or less proportional to the departure of the spin system energy (not its temperature) from equilibrium. The time constant for this equilibration is called the spin-lattice relaxation time. It can range from microseconds to hours; for the most part we will assume it to be rather long, at least 1 second. Magnetic impurities in insulators, and conduction electrons in metals, are important in spin-lattice relaxation, but detailed understanding of the process is unnecessary here.

Energy and Entropy of Ordering

Inasmuch as the spin system is always close to the infinite-temperature, completely disordered state, it is convenient to define the energy and entropy of this state to be zero. Thus entropy will always be negative or zero, but energy can be positive or negative. A positive temperature leads to negative energy, but we will see that negative temperatures are also possible, and lead to positive energy. Both energy and entropy are analytic functions of T^{-1} , not T.

Assume that \mathbf{H}_0 has been applied for a long enough time so that spinlattice relaxation has produced equilibrium. The departures of the system from the completely disordered state are manifested by a nonzero nuclear magnetization \mathbf{M}_0 which is expected to be proportional to the spin energy μH_0 divided by the thermal energy kT. Thus

$$\mathbf{M} = C\mathbf{H}_0/T_{\mathbf{s}} \tag{4}$$

This is known as Curie's law, and C (Curie's constant) is, classically, $N\mu^2/3k$. The temperature is denoted by T_s , on the grounds that the spins can have a "spin temperature" (4-6) very different from the lattice temperature T.

The energy of the system (7) is mainly its interaction with the external field

$$\mathbf{E}_{\mathrm{p}} = -\mathbf{M} \cdot \mathbf{H}_{0} \tag{5}$$

This is Zeeman, or polarization, energy; therefore the subscript p.

The entropy is expected to be an analytic function of the state variable **M** having a maximum of zero when $\mathbf{M} = 0$, that is, when the spins are completely disordered. Thus it is likely that entropy is a negative constant times M^2 , for small **M**. Calculation by standard configuration counting, with the spins being considered independent, confirms this and shows that the polarization entropy is

$$S_{\rm p} \equiv -M^2/2C \tag{6}$$

Curie's law (Eq. 4) follows from minimization of free energy $E_{\rm p} = T_{\rm s}S_{\rm p}$ with *H* and $T_{\rm s}$ constant (7). Solving Eqs. 4 to 6 yields

$$S_{\rm p} = E_{\rm p}/2T_{\rm s} \tag{7}$$

as expected dimensionally, and

$$E_{\rm p} = - C H_0^2 / T_{\rm s}$$
 (8)

It is easy to produce a negative spin temperature $T_{\rm s}$, in which **M** and \mathbf{H}_0 are oppositely pointing, by suddenly reversing \mathbf{H}_0 in a time so short that **M** cannot change, or by applying suitable radio-frequency pulses. In that case, Eqs. 4 to 8 still apply (6). Negative temperatures are possible only for a system whose energy has an upper bound, because otherwise Boltzmann factors $\exp(-\varepsilon/kT)$ diverge.

Next, suppose that the system is in equilibrium in zero external field (\mathbf{H}_0

SCIENCE, VOL. 164

= 0). Then M = 0, and at first sight the spin system is disordered. In fact, there is a small negative energy and entropy associated with the spin-spin interaction which produces a slight ordering of the spin moments with respect to their local field. A snapshot of the spins, giving their directions \mathbf{u}_i at some instant of time, would not show this ordering in an obvious way: the spins would appear random. But if h; were calculated with the use of Eq. 3, each spin *i* would be more likely to be pointed along its local field \mathbf{h}_i than against it. The total energy associated with this ordering is therefore nonzero. It is (8)

$$E_{\rm s} = - \frac{1}{2} \sum_i \boldsymbol{\mu}_i \cdot \mathbf{h}_i \qquad (9)$$

The factor $\frac{1}{2}$ merely avoids double counting of this energy between pairs *i,j* of spins. In thermal equilibrium the energy E_s is given by an expression analogous to Eq. 8

$$E_{\rm s} = - C H_{\rm L}^2 / T_{\rm s} \qquad (10)$$

where $H_{\rm L}$ is the root-mean-square local field defined after Eq. 3. The formal proof (9, 10) of Eq. 10 is more complicated than that of Eq. 8 but the physics is the same.

The entropy associated with the spinspin ordering is

$$S_{\rm s} = + E_{\rm s}/2T_{\rm s} = - CH_{\rm L}^2/2T_{\rm s}^2$$
 (11)

in analogy with Eq. 7, or by trivial thermodynamics (11) from the energy (Eq. 10).

Although Eq. 11 involves energy, S_s is really a measure of the disorder of the spins, not their energy. To see this, recall that C is $N\mu^2/3k$, so that Eq. 11 can be written

$$S_{\rm s} = -\frac{1}{6}Nk(\mu H_{\rm L}/kT)^2$$

The ratio $\mu H_{\rm L}/kT$ gives the degree of internal polarization of the spins, that is, it is roughly the difference between the fraction of spins pointing generally along their local field and the fraction oppositely pointing. Thus $S_{\rm s}$ gives the

magnitude of this internal polarization. Individual spins will change their own energy $-\underline{u}_i \cdot \mathbf{h}_i$ as time passes; but the sum, Eq. 9, will be essentially constant.

The spin-spin ordering will be present even if H_0 is nonzero, and is still described by Eqs. 10 and 11 in the high-temperature approximation. The total energy and entropy are given by the sums of the polarization and spinspin parts. It may seem inconsistent to talk about spins which are ordered both with respect to external and to local fields-and would be so if the ordering were complete as in an antiferromagnet—but there is no problem when the ordering is slight so that the h_i are nearly randomly oriented relative to \mathbf{H}_{0} . The contributions E_{s} and S_{s} were ignored in Eqs. 6 to 8, for in thermal equilibrium $E_{\rm s}$ is $H_{\rm L}^2/H_0^2$ times $E_{\rm p}$, therefore negligible if $H_0 > 100$ gauss. When $H_0 \simeq H_L$, and later in the rotating frame, they will be important.

Isentropic Cooling

It is frequently possible to find a temperature range where the spinlattice relaxation time is several minutes or more, and then it is easy to perform experiments in which the spin system is prepared by "soaking" the solid in a large (several kilogauss) field for many spin-lattice relaxation times to build up equilibrium nuclear magnetization, and subsequently to manipulate the spin system in a time short compared to the relaxation time. When I talk about experiments done on an isolated spin system, I refer to such experiments; of course, it is impossible to remove the thermal contact between the spins and the lattice. In practice, one generally repeats many times the sequence of soaking and manipulating, either to average out noise, where it is a problem, or to vary parameters in the "isolated" experiment. The experiments on negative temperature mentioned earlier are of this kind.

Isentropic cooling (or nuclear adiabatic demagnetization) is an even simpler experiment of this kind, and can produce spin temperatures less than 1°K with only a commonplace laboratory magnet (4). In many pure salts (such as CaF_2) the nuclear spin-lattice relaxation time is many seconds. If CaF_2 is inserted in a 1-kilogauss field, the ¹⁹F nuclear magnetization will build up to equilibrium, eventually given by Eq. 4 with T_s equal to the room temperature. The solid can then be removed from the field in a second or less, and doing so immediately reduces the nuclear magnetization to zero, without waiting for spin-lattice relaxation. If the sample is again placed in the field, the magnetization immediately returns to its full equilibrium value. The spin system is completely demagnetized when in zero field, and we will see that it is then at roughly 1°K spin temperature. However, this is an isentropic demagnetization, reversible by putting the sample back in the field. Unfortunately it is difficult to verify directly that the spin temperature is 1°K because the heat capacity of the nuclear spin system is minute, but many indirect experiments have confirmed the temperature variation and reversibility (12).

Isentropic cooling of a spin system is not much different in principle from the adiabatic cooling of a gas as its volume is slowly increased. There the cooling is easier to measure unambiguously, even though it is not practical to get such large temperature ratios.

In isentropic cooling, the constant entropy is the sum of the polarization entropy S_p and the spin-spin entropy S_s

$$S = \text{constant} S_{\rm p} + S_{\rm s} = -\frac{1}{2}C(H_0^2 + H_{\rm L}^2)/T_{\rm s}^2$$
(12)

from Eqs. 7, 8, and 11. Thus, when $H_0 \gg H_{\rm L}$, constant S implies that $T_{\rm s}$ decreases in proportion to H_0 (see Fig. 1). When H_0 approaches $H_{\rm L}$, $T_{\rm s}$ stops decreasing and levels off at a value lower



30 MAY 1969

Fig. 2. Oscillogram of voltage induced in a surrounding coil by precessing ²⁵³Na spins which have been cooled isentropically from 2 millidegrees Kelvin at 30 kilogauss to 20 microdegrees Kelvin at 5.5 gauss. The temperature is inferred by measuring the magnetization and invoking Curie's law. This oscillogram was obtained after the spins were cooled, by application of a 0.1-millisecond pulse of magnetic field perpendicular to H_0 . This pulse turned M away from H_0 by a small angle. The subsequent precession of M about H_0 at 6 kilohertz produced the oscillatory signal shown, but the precession is damped within a few cycles by the differing local fields on different spins which dephase their initially coherent precessions. [After Walstedt *et al.* (14)]

than the lattice temperature T by the ratio of $H_{\rm L}$ (a few gauss) to the initial value of H_0 (several kilogauss). The magnetization still obeys Curie's law $\mathbf{M}=C\mathbf{H}_0/T_{\rm s}$. The lowest temperatures ever attained (a few millionths of a degree) have been achieved in this way (13, 14) (see Fig. 2).

Microscopically, as the field is decreased, a spin goes smoothly from a state of precession about—and polarization along—the external field, to a state of chaotic precession about—and polarization along—its chaotically varying internal field which is of order $H_{\rm L}$. The physically important change occurs when $H_0 \simeq H_{\rm L}$ and entropy is transferred from polarization to spin-spin ordering; here entropy is more important than temperature as a variable.

If the field H_0 is reapplied slowly, before spin-lattice relaxation saps away the entropy of spin-spin ordering, the magnetization reversibly reappears along H_0 , from Eqs. 4 and 12. As with any reversible process, the variations in external variables must be slow compared to internal equilibrium times; in this case H_0 must pass through the regime from several times $H_{\rm L}$ to zero, where S_p and S_s change, in a time long compared to the internal equilibration time $(\gamma H_{\rm L})^{-1}$. The entire variation of H_0 must also take place in a time short compared to the spin-lattice relaxation time, or else corrections for lattice relaxation are necessary. For isentropic expansion of a gas, the corresponding conditions are that the piston velocity be less than the velocity of sound, but great enough so that thermal conduction out of the gas be negligible.

Rotating Frame of Reference

When the applied field **H** in Eq. 1 includes a radio-frequency field, the spin motion changes in a fairly complicated way. Much of the complication is removed, if \mathbf{H}_0 is much larger than the radio-frequency and local fields, by viewing the system from a rotating frame of reference (15). It is then easy to apply, in the rotating frame, many of the notions we outlined above for the rest frame with no radiofrequency field.

As a first approximation, if $H_0 \gg H_L$, all the spins tend to precess about H_0 in the same sense at frequency γH_0 . Therefore, it is useful to decompose the applied linearly polarized radiofrequency field into a circularly polarized component perpendicular to H_0 , rotating in the sense of the spin precession; and an equal component oppositely rotating. The first component stays nearly in step with a precessing spin and will be important later; the second, counterrotating, component can be neglected if its magnitude is much less than H_0 because it is "out of step" with the spins. The magnitude of each component is denoted by H_1 , and their sum, the applied radio-frequency field, is thus $2H_1$ at its peak.

For the moment, consider the motion of an isolated spin \boldsymbol{u} obeying the precession equation

$$d\boldsymbol{\mu}/dt = \gamma \boldsymbol{\mu} \times \mathbf{H}$$
(13)

where **H** now is the sum of \mathbf{H}_0 and the circularly polarized radio-frequency field component.

Now view the motion of a spin from a coordinate system rotating about \mathbf{H}_0 at the radio frequency ω (near but not in general equal to $\omega_0 = \gamma H_0$, the natural precession frequency), and with the same sense of rotation as the natural precession. In this frame, the circularly polarized radio-frequency field becomes stationary, and is in some arbitrary fixed direction in the rotating frame, perpendicular to H_0 . This direction is arbitrarily defined as the x-direction, and thus the radio-frequency field becomes a vector of magnitude H_1 in the x-direction in the rotating frame. Less obviously, and most importantly, the field \mathbf{H}_0 is replaced by a field in the same (z) direction, of magnitude $H_0 - (\omega/\gamma)$. In other words, viewed from the rotating frame the applied magnetic field transforms like any vector but an extra field $-\omega/\gamma$ must be added along the axis of rotation, analogous to the centrifugal and especially the Coriolis forces which appear in the rotating frame in mechanics.

Viewed from this frame, the spin \boldsymbol{u} moves as if it were in a relatively small field called the *effective field* \mathbf{H}_{e} , given by

 $\mathbf{H}_{\mathrm{e}} = H_{1}\mathbf{u} + [H_{0} - (\omega/\gamma)]\mathbf{w} \quad (14)$

where **u** and **w** are unit vectors in the rotating-frame x and z directions, respectively. If no local field is present, the spin would precess uniformly about \mathbf{H}_{e} at a frequency γH_{e} —of order γH_{1} or $\omega - \omega_{0}$, whichever is larger; typically this is a frequency of 100 kilohertz or less.

Back in the fixed frame, the simple precession of the spin y becomes a nutation: roughly, the spin still precesses at $\omega_0 \approx \omega$, many megahertz, but its angle with respect to \mathbf{H}_0 , and its phase relative to a uniform precession at ω vary periodically with kilohertz frequency γH_{e^*}

Truncation of the Spin-Spin Interaction

Now let us see how the spin-spin interaction can also be simplified, following Van Vleck (8, 15). To a first approximation, viewed from the fixed frame, a spin *i* feels a magnetic field (Eq. 3) from spins j which are precessing uniformly at a frequency of roughly ω_0 . If $H_0 \ge H_L$, then certain parts of this field can be neglected; for example, there is a component of \mathbf{h}_i which is rotating in the x-y plane opposite to the precession sense of spin i. This component is presumably negligible by the reasoning of the previous section. Neglect of this, and other similarly ineffective parts of \mathbf{h}_i , leaves a truncated local field given by

$$\mathbf{h}_{ir} = \frac{1}{2} \sum_{j} \frac{1 - 3\cos^2 \theta_{ij}}{\mathbf{r}_{ij}^3} (3\mu_{jz} \mathbf{w} - \mathbf{y}_j) (3a)$$

where θ_{ij} is the angle between the zdirection and \mathbf{r}_{ij} . Note that if the \mathbf{y}_j are all uniformly precessing about the z-direction at frequency ω_0 , then \mathbf{h}_{ir} is likewise precessing. Corresponding to the truncation of \mathbf{h}_i , the spin-spin energy E_s can be replaced by a truncated spin-spin energy

$$E_{\rm sr} = - \frac{1}{2} \sum_i \mu_i \cdot \mathbf{h}_{ir}$$

or

$$E_{\rm sr} = -\frac{1}{4} \sum_{ij} \frac{1 - 3\cos^2\theta_{ij}}{r_{ij}^3} \times (15)$$
$$(3\mu_{iz}\mu_{jz} - \mu_i \cdot \mu_j)$$

 $E_{\rm sr}$ is the only part of $E_{\rm s}$ which need be considered when $H_0 \gg H_{\rm L}$; for example, the truncated equations of motion (Eq. 1 with ${\bf h}_{i\rm r}$ substituted for ${\bf h}_i$) follow from Eq. 15 and standard analytical dynamics. The assumption that $E_{\rm s}$ can be replaced by $E_{\rm sr}$ is essential to what follows, and is generally excellent when $H_0 \gtrsim 10 H_{\rm L}$.

Next, we note that the truncated interaction $E_{\rm sr}$ appears unchanged viewed from the rotating coordinate system. Since the coordinate system rotates about the z-axis, the components μ_{iz} and μ_{jz} are unaffected; therefore the product $\mu_{iz}\mu_{jz}$ in $E_{\rm sr}$ is unchanged. Likewise, $\mu_i \cdot \mu_j$ is invariant because

SCIENCE, VOL. 164



Fig. 3. Transition from rest-frame equilibrium to rotating-frame quasi-equilibrium. In sequence (b), the applied radio frequency is greater than the resonance frequency γH_{o} , and the final rotating-frame temperature is negative even though the starting rest-frame temperature is positive. The dotted line shows the transient decay. The pictures are appropriate for $H_1 \approx \frac{1}{2} H_{Lr}$.

it is just $\mu_i \mu_j$ multiplied by the angle between \mathbf{u}_i and \mathbf{u}_j , and this angle, as well as the magnitudes \mathbf{u}_i and \mathbf{u}_j , are unchanged when viewed from the rotating frame (16).

Thus, the truncated spin-spin interaction has the important property of being the same when the spins are viewed from the rotating frame; this is no accident (9), since the neglected parts of E_s were thrown away, on the basis of an argument which paralleled the argument used to throw out parts of the radio-frequency field which are time varying after being transformed to the rotating frame (17, 18). Likewise, the equations of motion in the rotating frame are similar to Eq. 1 in the fixed frame, the field $\mathbf{H} + \mathbf{h}_i$ being replaced by $\mathbf{H}_e + \mathbf{h}_{ir}$.

In the rotating frame, then, the spin motion is described by two interactions: an interaction with an effective field (Eq. 14) which is constant if H_0 , H_1 , and the radio frequency ω are constant; and a spin-spin interaction (Eq. 15) which is time-invariant even though it describes interaction fields \mathbf{h}_i which can be thought of as fluctuating. This is true only in a solid well below the melting point, for which the r_{ij} and θ_{ij} are constant. Besides these there is, of course, a spin-lattice interaction which makes the system tend to move slowly toward rest-frame equilibrium.

Effective Energy

We have just seen that when H_0 is large, the system obeys equations of motion in the rotating frame which are similar to those in the fixed frame, for H_0 large or small. Thus we can 30 MAY 1969 carry over ideas from the rest to the rotating frame.

If no time-varying radio-frequency field is applied, the rest-frame spin energy $E_{\rm p} + E_{\rm s}$ is conserved if H_0 is constant, no matter how small H_0 is. Analogously, in the rotating frame, for large H_0 , if the amplitude and frequency, H_1 and ω , of the applied radiofrequency field are constant, there is conservation of the apparent energy in the rotating frame given by

$$E_{\rm e} = E_{\rm sr} - \mathbf{M}_{\rm r} \cdot \mathbf{H}_{\rm e} \qquad (16)$$

Here \mathbf{M}_{v} is the magnetization \mathbf{M} viewed from the rotating frame, so that $\mathbf{M}_{r} \cdot \mathbf{H}_{e}$ is the Zeeman energy with respect to the effective field. The combination $E_{\rm e}$ is called effective energy. Because a radio-frequency field is applied, the energy of the spins in the fixed frame is not constant, because the rest-frame equations of motion are time-dependent, containing the explicitly time-varying radio-frequency field. If the radio-frequency field is monochromatic, then "energy in the rotating frame" E_e is conserved, in place of the true energy of the spin system in the fixed frame.

Conservation of effective energy has not been based on the presence of the radio-frequency field, although motivated thereby. If no radio-frequency field is applied, and spin-lattice relaxation is negligible, then energy in the fixed frame is conserved as well as effective energy in the rotating frame. Thus if no radio-frequency field is applied there are two conservation laws: In a frame rotating at exact resonance $(\omega = \gamma H_0)$, H_e is zero if H_1 is zero, so $E_e = E_{sr}$; and E_{sr} is conserved since E_e is. In the fixed frame, on the other hand, the dominant energy is $-\mathbf{M} \cdot \mathbf{H}_0 = -M_z H_0$; since H_0 is constant, conservation of fixed-frame energy leads to conservation of M_z (19).

Thus, in summary, when no radiofrequency field is applied, the truncated spin-spin interaction $E_{\rm sr}$ and z-component of magnetization M_z are conserved separately. If a steady radiofrequency field is applied at ω , effective energy as a whole is conserved but not $E_{\rm sr}$ or M_z or $-\mathbf{M}_r \cdot \mathbf{H}_e$ separately. These conservation laws apply only if spin-lattice relaxation is negligible and $H_0 \gg H_{\rm L}$.

Spin Temperature

The idea of spin temperature in the rotating frame may seem trivial now, after this long preparation. It is a straightforward application of standard statistical mechanics to the system viewed from the rotating frame: the system tends to be in, or move toward, the state of maximum entropy consistent with the conservation law (or laws) just delineated. When a radiofrequency field is present, this is a state described by a rotating-frame spin temperature which may be positive or negative, and is typically much smaller in magnitude than the lattice temperature.

This hypothesis has nothing to do with spin-lattice relaxation, except insofar as the lattice temperature may determine the starting conditions. We are talking about nonequilibrium states, and the spins never actually reach the state described by a temperature in the rotating frame; but they can come very close to it if thermal contact with the



(b) Adiabatic demagnetization in the rotating frame

Fig. 4. Magnetization and effective field variation during the course of isentropic processes in the rotating frame. In the upper sequence (a) the magnetization M_r decreases reversibly by about 50 percent near resonance. It also decreases very slightly, irreversibly, between the first two pictures because H_e is not much greater than H_{Lr} . In the text of this article, the term adiabatic has been avoided because of several meanings of this word; the processes depicted here are labeled with names established in the literature, and adiabatic means here both slow and thermally isolated, therefore isentropic.

lattice is low. The spin-temperature state is described by a single parameter (temperature) which determines all the other observables. The quasi-equilibrium spin temperature can frequently be calculated rather simply by (effective) energy conservation.

An experiment diagramed in Fig. 3 will illustrate the transition from spinlattice equilibrium in the fixed frame to internal equilibrium in the rotating frame. Start with equilibrium in large H_0 ; M_z (in both frames) is CH_0/T , and spin-spin ordering is negligible. Now instantly apply strong off-resonant radio frequency, with H_1 and also the distance from resonance $H_0 = (\omega/\gamma)$ both of order of magnitude $H_{\rm L}$ (center pictures of Fig. 3). Fixed-frame energy is no longer conserved, but effective energy is, so we ensconce ourselves comfortably in the rotating frame, and observe the behavior of magnetization, M_r, from there. The instant after radio frequency is applied, \mathbf{M}_{r} is the same as before (that is, CH_0/T in the z-direction) because the equation of motion, Eq. 1, does not permit instantaneous variation of the μ_i (thus $\mathbf{M}_{\mathbf{r}}$) as long as H and h; are finite. In the rotating frame, after H_1 is applied, M_r tends to precess around \mathbf{H}_{e} , but in a short time decays in a complicated way toward a final rotating-frame equilibrium state -far from rest-frame equilibriumwhich is easily predictable from the spin-temperature hypothesis. The time scale and other details of this decay can be only partially predicated (20, 21), but it is expected that the final state is a thermal state from all the standard (ergodic hypothesis) arguments of equilibrium statistical mechanics carried over to the rotating frame.

This hypothesis immediately leads to the prediction that $\mathbf{M}_{\rm r}$ is finally along $\mathbf{H}_{\rm e}$, just as \mathbf{M} was along $\mathbf{H}_{\rm 0}$ in restframe equilibrium. This prediction has been experimentally verified (20, 22).

Back in the fixed frame, after the initial transient, **M** precesses in phase with the radio-frequency field, and the spins therefore absorb no energy from the radio-frequency field. That is absolutely necessary for consistency—otherwise the rest-frame energy of the spins would increase constantly, inconsistent with the assumption of time-independence of the spin state in the rotating frame. $\mathbf{M}_{\rm r}$ is given by Curie's law, Eq. 4, with \mathbf{H}_0 replaced by $\mathbf{H}_{\rm e}$ and $T_{\rm s}$ replaced by $T_{\rm sr}$, the spin temperature in the rotating frame.

Just after radio frequency is applied, then, there is a transient process in which both M_z and also the projection of \mathbf{M}_r on \mathbf{H}_e change. This process lasts tens of microseconds, and during it the system cannot be described by any temperature in any frame of reference, just as a gas cannot be described by a temperature just after an explosive chemical reaction. During the transient process, rest-frame energy increases, by absorption from the radio-frequency field, but effective energy is conserved. Afterward, both energies and also M_z are constant. This state would persist forever if it were not disturbed by lattice relaxation.

The final temperature $T_{\rm sr}$ in the rotating frame is predicted by equating the initial effective energy, just after H_1 is applied, to the final effective energy (Eq. 16) reexpressed in terms of $T_{\rm sr}$. Initially, $E_{\rm sr}$ is negligibly small, since in rest-frame equilibrium spin-spin order is negligible. Thus, initially $E_{\rm e}$ is $-\mathbf{M}_{\rm r} \cdot \mathbf{H}_{\rm e}$ which is $-(CH_0/T)[H_0 - (\omega/\gamma)]$ since $\mathbf{M}_{\rm r}$ is CH_0/T in magnitude, and is in the z-direction.

After the decay to a state described by a spin temperature $T_{\rm sr}$ in the rotating frame, the truncated spin-spin energy $E_{\rm sr}$ is given by the analog of Eq. 10

$$E_{\rm sr} = -CH_{\rm Lr}^2/T_{\rm sr} \qquad (10a)$$

The parameter $H_{\rm Lr}$ is the "local field in the rotating frame" and is calculated from the truncated spin-spin interaction in the same way that $H_{\rm L}$ is calculated from the full spin-spin interaction. The truncated local field $H_{\rm Lr}$ is about half as large as $H_{\rm L}$, thus also a few gauss.

The relation between effective energy $E_{\rm e}$ and $T_{\rm sr}$ is obtained by substituting Eq. 10a and Curie's law into Eq. 16

$$E_{\rm e} = -C(H_{\rm Lr}^2 + H_{\rm e}^2)/T_{\rm sr}$$
 (16a)

The spin temperature describing the equilibrium state is obtained by equating this expression with the initial effective energy deduced above, $-CH_0[H_0 - (\omega/\gamma)]/T$.

If, for example, both H_1 and the distance from resonance $|H_0^{-}(\omega/\gamma)|$ are picked equal to $H_{\rm Lr}$, then the final $T_{\rm sr}$ is thus deduced to be $3H_{\rm L}/H_0$ times the lattice temperature T in magnitude, and will be negative if $H_0^{-}(\omega/\gamma)$ is negative. In the equilibrium state, the spins are ordered along \mathbf{H}_{e} and also along their truncated internal fields -the latter ordering being typically much larger than spin-spin ordering at rest-frame equilibrium at H_0 . The rotating-frame state is analogous to the fixed-frame state obtained if H_0 is suddenly reduced to a value equal to $H_{\rm T}$ except that in the latter case spins are polarized along their full local field, and also the degree of polarization may be greater or less depending on whether H_0 is lowered slowly or rapidly compared to $(\gamma H_{\rm L})^{-1}$. Experiments (2022) have verified these predictions in detail.

A much easier experiment leading to rotating temperature is called nuclear resonance "saturation." It is performed by making H_0 , ω , and H_1 fixed over a time long compared to the spin-lattice relaxation time. The spin system reaches a steady state predictable by rate equations for the flow of energy in the fixed and rotating frames. The theory is not difficult (9, 23) and, for sufficiently large H_1 , predicts a rotatingframe spin temperature often not very different from that predicted above for the end state of an isolated process for the same ω , H_1 and H_0 . Thus, the steady-state rotating temperature is much smaller than the lattice temperature, and is negative when $H_0 - (\omega/\gamma)$ is negative. The precessing magnetization is comparable to the equilibrium magnetization, but is nearly in phase with the radio-frequency field, resulting in small absorption. An understanding of saturation is useful because by tuning a conventional nuclear magnetic resonance spectrometer to optimize sensitivity for this signal, a large increase in signal-to-noise ratio is easily achievable in solids (9, 24).

Isentropic Passage

It is easy to produce isentropic changes of state in a spin system by applying radio-frequency power while varying H_0 slowly (9, 25). Normally electromagnetic radiation heats a system irreversibly, as required by considerations of the second law of thermodynamics. That is true for spins also, if the radio-frequency field is not monochromatic, and contains two or more frequencies near ω_0 . But for a steady monochromatic radio-frequency field we have seen that effective energy is conserved; we now consider the effect of slow changes of \mathbf{H}_{e} by analogy with the rest-frame experiments on isentropic cooling.

The general principle is that, if the effective field is varied sufficiently slowly, then even though effective energy is no longer conserved, the entropy will remain constant and the system will always be described by a rotating-frame spin temperature which will vary slowly as H_1 , ω , or H_0 are slowly varied. If H_e becomes comparable to H_L , then M will decrease, but reversibly, just as in the case of isentropic cooling in the fixed frame; and

the decrease will be governed by the rotating-frame analog of Eq. 12.

Consider a system prepared in restframe equilibrium, having initial M along the z-direction, negligible spinspin ordering, and therefore entropy $-M^2/2C$, by Eq. 3. This is the state depicted by the first (left-hand) diagram of the sequence in Fig. 4a. Slowly apply a radio-frequency field of eventual amplitude $H_1 \approx H_L$, whose frequency is far from resonance in the sense that $(\omega_0 - \omega) \ge \gamma H_{\rm L}$. In the rotating frame the effective field (Eq. 15) changes unimportantly from being in the + z-direction of magnitude $H_0 - (\omega/\gamma)$, to being slightly tilted away from the z-axis as H_1 is applied, having nearly the same magnitude as when $H_1 = 0$, since $H_1 \ll H_e$ (second diagram, Fig. 4a). The magnetization \mathbf{M}_{r} follows this tilt unchanged in magnitude as long as H_1 is applied slowly. [A spin precessing about a slowly varying field always maintains a constant precession angle between its magnetic moment and the field. This can be proven from Eq. 13 by transforming to a coordinate system moving with H (H_e in this case), or by the adiabatic theorem of quantum mechanics (15).]

Fig. 5. Rapid passage signals from metallic ²⁷Al at 1.5°K. Steady radio-frequency power of about 1 gauss at 6 megahertz is applied while H_{o} is swept sinusoidally and symmetrically through resonance and the spectrometer is tuned to measure the component of M_r perpendicular to H_0 . The phase-detected signal from this component is the vertical deflection in this picture. The period and amplitude of the H_0 sweep ranges from 5 seconds and ± 100 gauss in the top picture to $\frac{1}{2}$ second and roughly \pm 10 gauss at the bottom. The sweep frequency is applied to the horizontal amplifier of the oscilloscope (but, except in the top trace, is phase-shifted relative to the field sweep). Each sweep through resonance inverts M and gives a signal which is proportional to M_r , thus to M_z just before resonance. In the top sweep, the time between inversions is long compared to the spin-lattice relaxation time, and the spins fully equilibrate with the lattice between sweeps when the radio frequency is far from resonance. The direction of vertical deflection of the signal gives the sign of the rotating-frame spin temperature during the sweep. This temperature is positive when H_o is swept downward, and negative when H_o is swept back upward. In the bottom picture, the time between sweeps is less than the relaxation time and, therefore, the magnetization does not recover to rest-frame equilibrium between sweeps so that the signals are reduced; in this way the spin-lattice relaxation time can be accurately estimated (38). The increase from the top to the bottom picture, in the breadth of the signal, results solely from a decreasing ratio of magnetic field (gauss) to distance (centimeters) as the sweep amplitude decreases from top to bottom.



Now slowly decrease H_0 toward and through the resonance condition, so that ω_0 approaches ω , keeping H_1 constant (Fig. 4a). The z-component of H_e now goes through zero, but the xcomponent is constant (H_1) , so \mathbf{H}_{e} turns toward the x-axis, being in the xdirection when exact resonance is reached ($\omega_0 = \omega$) and toward the negative z-direction beyond resonance. As resonance is neared, we have $H_{\rm e} \gtrsim$ $H_1 \approx H_{\rm L}$. The magnetization will follow \mathbf{H}_{e} isentropically, and when H_{e} approaches $H_{\rm L}$ it will decrease reversibly, some of the polarization entropy being repartitioned into spin-spin ordering in complete analogy with isentropic cooling in the fixed frame.

The variation of $\mathbf{M}_{\rm r}$ throughout the process is governed by Eq. 12 with H_0 and $H_{\rm L}$ replaced by $H_{\rm e}$ and $H_{\rm Lr}$. The only differences between isentropic cooling and isentropic passage are that in the rotating frame $\mathbf{H}_{\rm e}$ is itself slowly changing direction as well as magnitude —which makes no real difference—and also that the shortest permissible time for $H_{\rm e}$ to pass through the regime where $H_{\rm e} \sim H_{\rm Lr}$ is greater than the corresponding time in the fixed frame.

If the slow decrease of H_0 is stopped when H_0 is well below resonance $[(\omega/\gamma) - H_0 \gg H_L]$ then \mathbf{M}_r will have returned to its full initial value and be pointed along \mathbf{H}_e which is now roughly opposite to H_0 , though slightly tilted away from it. If H_1 is now slowly removed, then H_e and M will approach the negative z-direction, and the spin system will be, finally, in a negative temperature in the rest system with Mopposite H_0 . This process is known as adiabatic rapid passage—rapid because it must be performed in a time short compared to the spin-lattice relaxation time, and adiabatic meaning isentropic.

In the process described above, the spin temperature in the rotating frame is positive and much lower than the starting fixed-frame temperature. The rotating-frame temperature can decrease to as low as $H_{\rm Lr}/H_0$ times the starting temperature-easily 1°K starting from room temperature in practical cases. If one started with H_0 increasing from below resonance instead of decreasing from above resonance, the process would be similar, but the rotating-frame spin temperature would be negative throughout. Adiabatic rapid passage is an especially simple and convenient method for measuring long spin-lattice relaxation times (Fig. 5).

The slow sweep of H_0 can be stopped anywhere near resonance, and H_1 can be turned off slowly, resulting in any desired partitioning of entropy between polarization and spin-spin. If, for example, passage is stopped exactly at resonance and H_1 is turned off slowly,



Fig. 6. Resonances of spins which are near neighbors of potassium and bromine impurities in reagent-grade NaCl powder, observed by a variant of the Hartmann-Hahn double-resonance technique. These resonances are pure quadrupole resonances obtained by switching H_o to zero during irradiation of the rare species at a frequency $\Omega/2\pi$. The abundant species is that group of ²⁰Na spins which are far from impurities, and the ordinate is the signal from these spins after a large field is reapplied. The dips A to F occur at frequencies connecting levels split by the interaction of the nuclear electric quadrupole moment with electric field gradients near the impurities. The assignment of these resonances to particular impurities was verified in other experiments in which K and Br were added intentionally. In some cases individual resonances can be identified with particular sites near an impurity. [After Slusher and Hahn (29)]

then $\mathbf{M}_{\rm r}$ will demagnetize to zero because $\mathbf{H}_{\rm e}$ will approach zero (Fig. 4b). All the initial polarization ordering is transferred to spin-spin ordering. This is known as adiabatic demagnetization in the rotating frame (25).

The degree of spin-spin ordering can be measured by reversing the isentropic demagnetization in the rotating frame and measuring the remagnetization; or by suddenly applying a suitable pulsed or steady radio-frequency field near resonance (22).

Near resonance during isentropic passage the radio-frequency field "locks" the magnetization along \mathbf{H}_{e} , and energy and entropy considerations prevent its irreversible decay. By contrast, if H_1 is turned off suddenly at resonance, the magnetization will decay irreversibly, in microseconds, to zero, with an increase in entropy and with no change in either rest-frame or effective energy.

Double Resonance

Rotating-frame thermodynamics has been used by Hartmann and Hahn (26) to analyze their ingenious method for increasing the sensitivity of nuclear resonance detection of low-abundance isotopes. The method is applicable when the solid also contains an abundant isotope having a strong resonance. In its simplest form, the abundant isotope is continuously resonated with a strong radio-frequency field (slightly off-resonance, to produce a finite rotating spin temperature). The rare-spin resonance is sought with a second radio-frequency field of slowly varying frequency; when this second field is in resonance with the rare spins, the abundant-spin resonance signal might be expected to change. This experiment can be analyzed by viewing the abundant spins from a frame rotating with their nearly resonant radio-frequency field, and the rare spins from a frame rotating at the second frequency (9, 26, 27). Straightforward extension of the truncation procedure and thermodynamic reasoning shows that the rare spins have an effect on the abundant spins roughly proportional to their number, therefore generally negligible. However, Hartmann and Hahn showed that the effect of resonating the rare spins could be greatly increased by violating one of the caveats I emphasized above-that the radio-frequency fields must be monochromatic. The second (swept) field was amplitude-modulated

SCIENCE, VOL. 164

at a few kilohertz. In the rotating frame this becomes a corresponding kilohertz variation of the H_1 for the rare spins. As a result, effective energy in the rotating frame is no longer conserved, and the time-varying effective field on the rare spins makes the spin temperature in the rotating frame increase steadily, and the spin-spin ordering decrease. This decrease is detected through abundant-spin resonance, and occurs only when the second radio-frequency field is reasonably close to the rare-spin resonance. In this way resonances of spins with abundance as low as 10⁻⁷ can conceivably be detected, and the Hartmann-Hahn technique is being developed by several laboratories mainly as a tool for the study of imperfections in solids (28, 29). An example is shown in Fig. 6.

Other Applications

These ideas have not been applied much to electron paramagnetic resonance because the interspin-coupling is typically small in relation to hyperfine, crystal-field, and other broadening energies, so that the state described by a single rotating-frame temperature is seldom approached. However, certain experiments on the dynamic polarization of nuclei by electrons irradiated by strong radio-frequency fields appear to be best described in these terms (30). In these experiments nuclei can act as a thermometer in the rest frame to sense the spin temperature in the electron's rotating frame, which supports the idea that the rotating-frame temperature is not just a theoretical artifice. Experiments on a model system (31) show that it is possible in principle to achieve a greater percentage of polarization of the nuclei than the electrons would have at equilibrium with the lattice.

From the strong analogy between the rest and rotating frames, it is obvious that many rest-frame experiments besides isentropic and sudden variation of the applied field can be performed equally well in the rotating frame with a strong radio-frequency field or in the rest frame with small H_0 and no radiofrequency field. These include ordinary and longitudinal (32) nuclear resonance, spin echoes (33), the lattice relaxation of spin-spin ordering (34), ultraslow diffusion (35), cross relaxation (36), and spin diffusion (1, 2, 37).

Conclusion

By applying standard statistical mechanical arguments in the rotating frame, the qualitative features of spin dynamics can be predicted under most circumstances. Continuing development of applications to sensitivity enhancement and high resolution in nuclear resonance, studies of spin-lattice interactions, and dynamic polarization is likely. There has been no application of these ideas outside of magnetic resonance, either as an obvious extension to higher frequency spectroscopy, or as a theoretical model for completely different kinds of problems.

References and Notes

- 1. Advanced reviews with more complete references have been given in articles by J. Jeener (2); by L. C. Hebel, in Solid State Phys. 15, 409 (1963); in M. Goldman, Spin Tem-perature and Nuclear Magnetic Resonance in Solids (Oxford Univ. Press, London, in press); and in A. Abragam, The Principles of Nuclear Magnetism (Oxford Univ. Press, London, 1961), chap. 12. These reviews London, 1961), chap. 12. These reviews cover related rest-frame experiments more adequately than this article does. J. Jeener, Advan. Magnetic Resonance 3, 206
- 2. (1968)
- 3. For simplicity I avoid a quantum description of the spins, in favor of the semiclassical Eq. 1; in this model the spins are non-classical only in that they have permanent moments and angular momenta. The semiresults provided electric quadrupole inter-actions are negligible. I assume that there are no such interactions and also that there are no unpaired electron spins present except
- are no unparted electron spins present except perhaps as impurities.
 A. Abragam and W. G. Proctor, *Phys. Rev.* 106, 160 (1957); *ibid.* 109, 1441 (1958).
 E. M. Purcell and R. V. Pound, *ibid.* 81, 279 (1951).
- N. F. Ramsey, ibid. 103, 20 (1956). 7. The conventions used in magnetic thermo-dynamics are excruciatingly complicated. Here I am using the convention in which magnetic work is MdH. Under the more frequent convention where magnetic work is -HdM, the energy E would be equal to E_s, and the sum E_s $-M \cdot H$ is a kind of enthalpy. See F. Reif, Fundamentals of Statistical and Thermal Physics (McGraw-Hill, New York, 1965), chap. 11; and N. F. Ramsey (6).
 J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
 A. G. Redfield, *ibid.* 98, 1787 (1955); 128, 2551 (1962).
- 10. J. H. Van Vleck, J. Chem. Phys. 5, 320
- For *H* and *M* equal to 0, $T_s dS_s = dE_s = (+CH_L^2/T_s^2) dT_s = T_s d(E_s/2T_s)$. Since S_s and E_s are both zero, by definition, when $T_s = \infty$, 11. For Eq. 11 follows.
- Eq. 11 follows. The concept of a spin system thermo-dynamically distinct from the lattice, de-scribed by a time-varying spin temperature, was introduced by H. G. B. Casimir and F. K. du Pre, *Physica* 5, 507 (1938). See also C. J. Gorter, *Paramagnetic Relaxation* (Elsevier, Amsterdam, 1947). N. Kurti, *Advan. Cryog. Eng.* 8, 1 (1963). R. E. Walstedt, E. L. Hahn, C. Froidevaux, E. Geissler, *Proc. Roy. Soc. London Ser.* A 248, 499 (1965). See, for example, C. P. Slichter, *Principles* 12.

- A 248, 499 (1965).
 15. See, for example, C. P. Slichter, Principles of Magnetic Resonance (Harper and Row, New York, 1963).
 16. The term (1-3cos² θ_{ij})/r_{ij³} is also invariant, but that is of no importance since the rotating-frame transformation is viewed as one which operates only on the dipoles **y** and not on space coordinates of nuclei or other degrees of freedom.

- If H_e is large enough, further truncation in the rotating frame is reasonable, with interesting consequences. See M. Lee and W. I. Goldberg, Phys. Rev. 140, A1261 (1965); U. Haeberlen and J. S. Waugh, *ibid.* 175, 453 (1968); and D. Tse and S. R. Hartmann, Phys. Rev. Lett. 21, 511 (1968). Actual rotation of the solid also leads to further truncation and narrowing, as reviewed by E. R. Andrew in (18).
 R. Blinc, Ed., Magnetic Resonance and Relaxation (XIV Colloque Ampere) (NorthHolland, Amsterdam, 1967).
 Stated technically, M_z commutes with Ee when H₁ is zero, therefore is conserved.
 For a review of work on transient processes and pulse experiments by Provotorov, Goldburg, Norberg, Lowe, Strombotne, and 17. If H_e is large enough, further truncation in
- and pulse experiments by Provotorov, Goldburg, Norberg, Lowe, Strombotne, and others, see J. Jeener (2). Also see J. R. Franz and C. P. Slichter, *Phys. Rev.* **148**, 287 (1966); H. Einbeinder and S. R. Hartmann, Phys. Rev. Lett. 17, 518 (1966); and A. G. Anderson and S. R. Hartmann, (21).
- A. G. Anderson and S. R. Hartmann, Phys. Rev. 128, 2023 (1962). 21.
- 22. The component of M transverse to H_0 induces a voltage in a coil which surrounds the sample; the phase of this voltage relative to the voltage induced by the radio-frequency field H_1 gives the direction of the component in the rotating frame relative to the radio-frequency field. Usually M_z is measured by turning off H_1 , waiting roughly a milli-second for M to decay to the z-axis, then turning the remaining magnetization 90° to the z-axis with a short radio-frequency pulse, the z-axis with a short radio-frequency pulse, and measuring the voltage induced by this magnetization just after the pulse. Finally, the spin-spin energy E_{sr} can also be measured by observing the signal some microseconds after a suitable pulse (20, 21).
 23. B. N. Provotorov, Zh. Eksp. Teor. Fiz. 45, 730 (1963) [English translation: Sov. Phys. JETP 4, 2155 (1962)].
 24. L. Solomon and L. Erzatty, Phys. Rev. 127.
- 24. I. Solomon and J. Ezratty, Phys. Rev. 127, (1962)
- 25. C. P. Slichter and W. C. Holton, *ibid.* 122, 1701 (1961).
- 26. S Hartmann and E. L. Hahn, ibid. 128, . R. 2023 (1962)
- See N. Bloembergen and P. P. Sorokin [*ibid.* 110, 865 (1958)] for an interesting two-species 27. xperiment
- experiment.
 28. G. T. Mallick, Jr., and R. T. Schumacher, *ibid.* 166, 350 (1968); A. G. Redfield, *ibid.* 130, 589 (1963); E. P. Jones and S. R. Hartmann, *Phys. Rev. Lett.* 22, 867 (1969); E. L. Hahn in (18).
 29. R. E. Slusher and E. L. Hahn, *Phys. Rev.* 166, 350 (1968).
- 30.
- The spin-temperature-in-the-rotating-frame description of dynamic polarization is only a use-ful embellishment for most cases; see A. Abragam and M. Borghini, in *Progr. Low Temp. Phys.* 4, 384 (1964). It appears to be Temp. Phys. 4, 384 (1964). It appears to be more essential in explanations of some recent experiments; see M. Borghini, Phys. Rev. Lett.
 20, 419 (1968); C. Hwang and D. A. Hill, Phys. Rev. Lett. 19, 1011 (1967); V. A. Atsarkin, A. E. Medfed, M. I. Rodak, Zh. Eksp. Teor. Fiz. Pisma Red. 6, 942 (1967) [English translation: JETP Lett. 6, 359 (1967)]; G. M. Van den Heuvel, C. T. C. Heyning, T. J. B. Swanenberg, N. J. Poulis, Phys. Lett. 27A, 38 (1968).
 31. M. Goldman and A. Landesman, Phys. Rev. 132, 610 (1963).
 32. A. G. Anderson, *ibid.* 25, 1517 (1962).
 33. I. Solomon, Phys. Rev. Lett. 2, 301 (1954).

- A. G. Anderson, *ibid.* 25, 1517 (1962).
 I. Solomon, *Phys. Rev. Lett.* 2, 301 (1954).
 J. Poitrenaud and J. M. Winter, *J. Phys. Chem. Solids* 25, 123 (1964); ______, *ibid.* 27, 169 (1967); A. G. Anderson and A. G. Redfield, *Phys. Rev.* 116, 583 (1959).
 D. Ailion and C. P. Slichter, *Phys. Rev.* 135, A1099 (1964); _____, *ibid.* 137, A235 (1965); D. W. McCall, D. C. Douglass, D. R. Facone, *J. Phys. Chem.* 71, 998 (1967); H. A. Resing, N. T. Corke, J. N. Sherwood, *Phys. Rev. Lett.* 20, 1227 (1968). 20, 1227 (1968).
- An astounding early experiment by W. Goldberg [*Phys. Rev.* 115, 48 (1959)] was explained by J. Jeener (2).
 A. G. Redfield and W. Yu, *Phys. Rev.* 169, 443 (1968).
- 38. A. G. Redfield, *ibid.* 101, 67 (1956). 39. I thank many colleagues for help with this
- paper, particularly P. J. Price.