

Thermodynamics of spin systems in paramagnetic crystals

Marcello Colozzo

Abstract

We propose a theoretical model of non-normal thermodynamic system (i.e. at negative absolute temperature), through the application (and consequent instantaneous inversion) of a magnetic field to a crystal.

1 Two energy level system

1.1 Positive absolute temperature

Let us consider a system Σ of N particelle in cui l'energia di singola particella può assumere solo due valori distinti: particles in which the energy of a single particle can assume only two distinct values: $\varepsilon = 0, E > 0$.

We denote with n_j ($j = 0, 1$) the occupation number of the j -th level. The number of particles present there follows:

$$n'_j = g_j n_j$$

being g_j the degree of degeneracy. Without loss of generality, assume $g_j = 1$ (absence of degeneracy). The internal energy of the system is

$$U = n_1 E \quad (1)$$

while the occupation numbers are constrained by the relationship

$$n_0 + n_1 = N \quad (2)$$

If W is the thermodynamic weight, the entropy is

$$S = k_B \ln W, \quad k_B = \text{Boltzmann constant} \quad (3)$$

Recall that W is the number of ways in which we can distribute the N particles in the two levels $\varepsilon = 0, E$.

$$W = \frac{N!}{n_0! n_1!} \quad (4)$$

By defining:

$$n = n_1 - n_0 \quad (5)$$

the (4) is written:

$$\ln W = \frac{N!}{\left(\ln \frac{N-n}{2}\right)! \left(\ln \frac{N+n}{2}\right)!} \quad (6)$$

We recall Stirling's formula:

$$k \gg 1 \implies k! \simeq k^k e^{-k} \sqrt{2\pi k} \left(1 + \frac{1}{12k} + \dots\right)$$

for which

$$\begin{aligned} N \gg 1 \implies \ln(N!) &\simeq \ln \left[N^N e^{-N} \sqrt{2\pi N} \left(1 + \frac{1}{12N} + \dots\right) \right] \\ &= N \ln N - N \\ \implies \ln \left[\left(\frac{N \pm n}{2}\right)! \right] &\simeq \frac{N \pm n}{2} \ln \left(\frac{N \pm n}{2}\right) - \frac{N \pm n}{2} \end{aligned}$$

So the (6) becomes:

$$\ln W \simeq N \ln N - \frac{N-n}{2} \ln \frac{N-n}{2} - \frac{N+n}{2} \ln \frac{N+n}{2}$$

In that order of approximation, the entropy is

$$S = k_B \left(N \ln N - \frac{N-n}{2} \ln \frac{N-n}{2} - \frac{N+n}{2} \ln \frac{N+n}{2} \right) \quad (7)$$

At thermodynamic equilibrium

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial n} \frac{\partial n}{\partial U} \quad (8)$$

Turns out

$$U = n_1 E = (n + n_0) E \implies n(U) = \frac{U}{E} - n_0 \implies \frac{\partial n}{\partial U} = \frac{1}{E}$$

which replaced in the (8):

$$\frac{1}{T} = \frac{1}{E} \frac{\partial S}{\partial n} \quad (9)$$

From (7):

$$\frac{\partial S}{\partial n} = \frac{k_B}{2} \ln \left(\frac{n_0}{n_1} \right)$$

Finally, replacing the latter in (9):

$$\frac{1}{T} = \frac{k_B}{2E} \ln \left(\frac{n_0}{n_1} \right) \quad (10)$$

It follows

$$T > 0 \implies \ln \left(\frac{n_0}{n_1} \right) > 0 \implies n_0 > n_1 \quad (11)$$

That is, for any thermodynamic equilibrium temperature T , the ground level is more populated than the excited level. This is because absolute temperature is always non-negative. This conclusion is generalized to a multi-level (even infinite) system.

We discuss the behavior of the various quantities as a function of temperature. From (10):

$$n_0 = n_1 e^{\frac{2E}{k_B T}} \xrightarrow{n_0+n_1=N} n_1 e^{\frac{2E}{k_B T}} + n_1 = N$$

from which

$$n_1(T) = N \frac{e^{-\frac{E}{k_B T}}}{e^{\frac{E}{k_B T}} + e^{-\frac{E}{k_B T}}} \quad (12)$$

$$n_0(T) = N - n_1(T) = N \frac{e^{\frac{E}{k_B T}}}{e^{\frac{E}{k_B T}} + e^{-\frac{E}{k_B T}}}$$

$$n(T) = n_1(T) - n_0(T) = -N \tanh \left(\frac{E}{k_B T} \right)$$

$$U(T) = n_1(T) E = NE \frac{e^{-\frac{E}{k_B T}}}{e^{\frac{E}{k_B T}} + e^{-\frac{E}{k_B T}}}$$

It follows

$$\begin{aligned} \lim_{T \rightarrow 0^+} U(T) &= 0, & \lim_{T \rightarrow +\infty} U(T) &= \frac{NE}{2} \\ \lim_{T \rightarrow 0^+} n_1(T) &= \lim_{T \rightarrow 0^+} \frac{U(T)}{E} = 0, & \lim_{T \rightarrow +\infty} n_1(T) &= \lim_{T \rightarrow +\infty} \frac{U(T)}{E} = \frac{N}{2} \end{aligned}$$

For $T = 0$ the internal energy is zero, and only the fundamental level is populated. In the opposite limit ($T \rightarrow +\infty$), the two levels are equally populated:

$$\lim_{T \rightarrow +\infty} n_0(T) = N - \lim_{T \rightarrow +\infty} n_1(T) = \frac{N}{2} \quad (13)$$

This can be seen directly from (10):

$$\frac{1}{T} = \frac{k_B}{2E} \ln \left(\frac{n_0}{n_1} \right) \implies n_0 = n_1 \iff T \rightarrow +\infty$$

In fig. 1 the trend of individual populations.

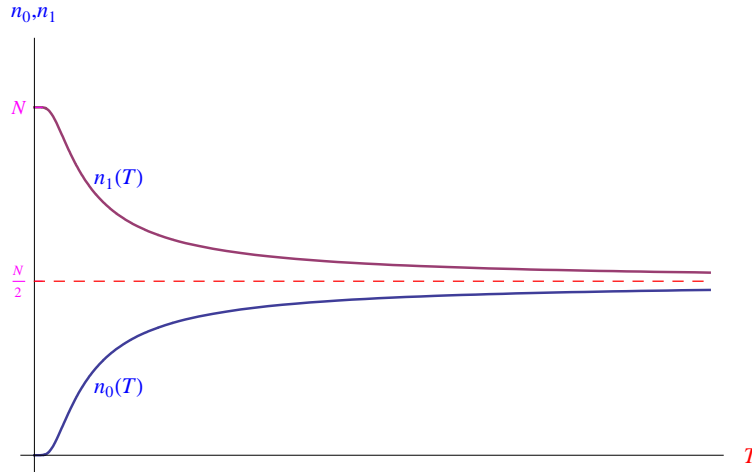


Figure 1: Trend of $n_0(T)$, $n_1(T)$.

We study the behavior of entropy. From the (7):

$$\lim_{T \rightarrow +\infty} S(T) = \lim_{T \rightarrow +\infty} k_B \left[N \ln N - \frac{N - n(T)}{2} \ln \frac{N - n(T)}{2} - \frac{N + n(T)}{2} \ln \frac{N + n(T)}{2} \right]$$

But $\lim_{T \rightarrow +\infty} n(T) = -N \lim_{T \rightarrow +\infty} \tanh \left(\frac{E}{k_B T} \right) = 0$

$$\lim_{T \rightarrow +\infty} S(T) = k_B N \ln 2 \quad (14)$$

in the opposite limit $\lim_{T \rightarrow 0^+} n(T) = -N \lim_{T \rightarrow 0^+} \tanh \left(\frac{E}{k_B T} \right) = -N$

$$\lim_{T \rightarrow 0^+} S(T) = 0 \quad (15)$$

in accordance with the Nernst theorem (third law of thermodynamics). In fig. 2 we report the graph of this quantity.

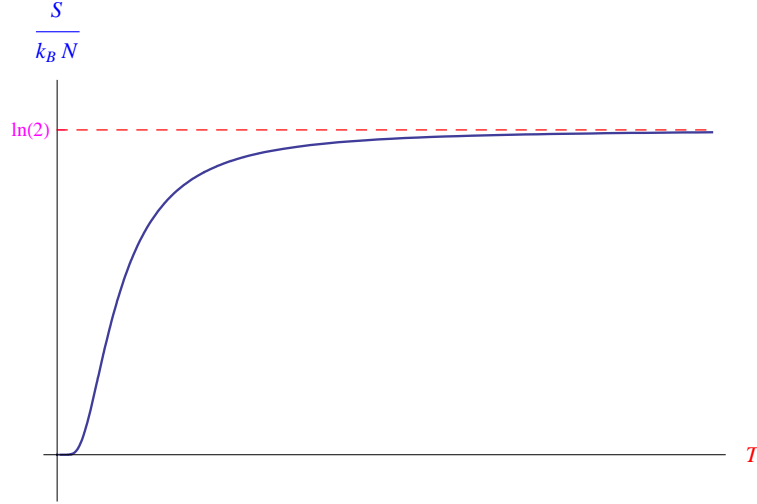


Figure 2: Trend of the dimensionless entropy normalized on the number of particles.

1.2 Negative absolute temperature

Formally, nothing prevents us from considering $T < 0$. From the(10):

$$T < 0 \iff n_1 > n_0 \quad (16)$$

In other words, the excited level is more populated than the fundamental level if and only if the absolute temperature of “thermodynamic equilibrium” is negative. The quotation marks suggest caution, since we should first prove the existence of thermodynamic states of equilibrium with $T < 0$. However, the following exists

Definition 1 *The inequality $n_1 > n_0$ expresses a **population inversion**.*

Definition 2 *A thermodynamic system at $T < 0$ is said to be **non-normal**.*

Concerning the existence of thermodynamic states of equilibrium at $T < 0$, we begin by observing that making a thermodynamic system non-normal means «bringing» a macroscopic number of particles into the excited level $\varepsilon = E$. Operationally this has an energy cost. The corresponding thermodynamic state is metastable: the system tends to repopulate the fundamental level with the consequent emission of energy (partly thermal energy which is transferred to the environment or to any body in non-normal thermal contact with the system). So the body at $T > 0$ in contact with the one at $T < 0$ heats up. It follows that a body at $T < 0$ is “hotter” than a body at $T > 0$.

To mathematically verify what has just been asserted, let us study the behavior of the internal energy function $U(T)$ for $T \in (-\infty, +\infty)$. After executing the change of variable $x = \frac{E}{k_B T}$, we define the dimensionless quantity:

$$f(x) = \frac{U(T)}{NE} = \frac{e^{-x}}{e^x + e^{-x}}, \quad \forall x \in (-\infty, +\infty) \quad (17)$$

It turns out:

$$\begin{aligned} \lim_{x \rightarrow +\infty} f(x) = 0^+ &\implies \lim_{T \rightarrow 0^+} \frac{U(T)}{NE} = 0^+ \implies U(0^+) = 0^+ \\ \lim_{x \rightarrow -\infty} f(x) = 1 &\implies \lim_{T \rightarrow 0^-} \frac{U(T)}{NE} = 1 \implies U(0^-) = 1 \end{aligned}$$

for which $T = 0$ is a discontinuity point of the first kind for $U(T)$. The discontinuity jump is -1 . Furthermore

$$f(0) = \frac{1}{2} \implies \lim_{T \rightarrow \pm\infty} \frac{U(T)}{NE} = \frac{1}{2}$$

In fig. 3 we report the complete graph. In fig. 4 we report the entropy graph.

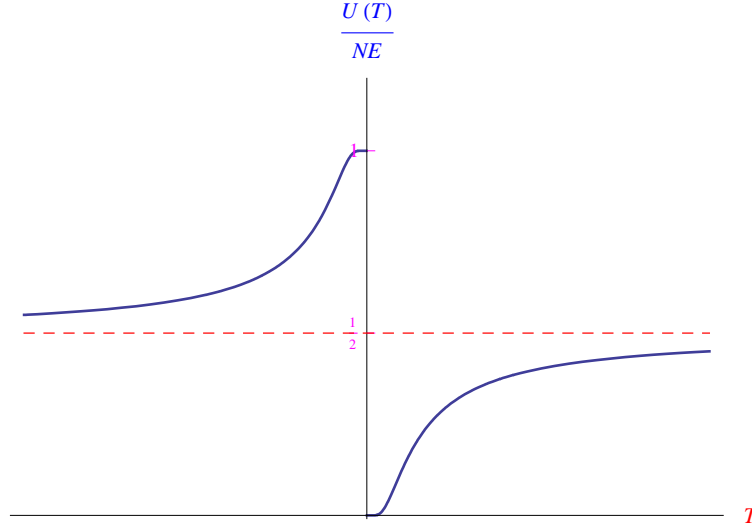


Figure 3: Trend of the dimensionless energy normalized on the number of particles.

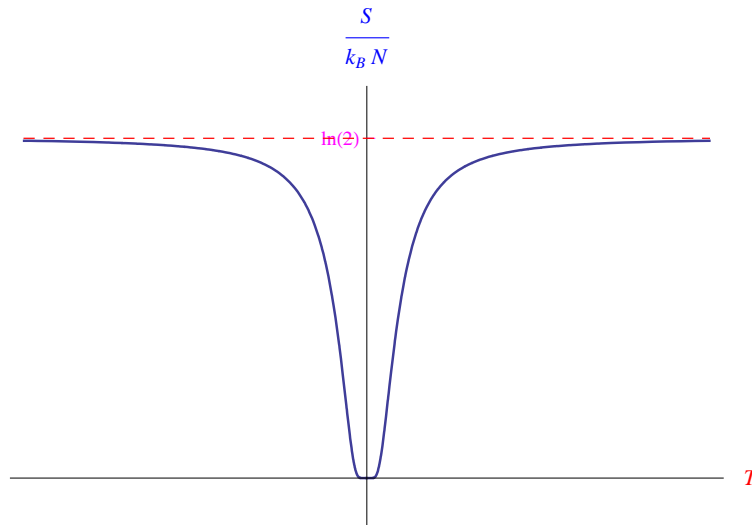


Figure 4: Trend of the dimensionless entropy normalized on the number of particles, extended to negative temperatures.

From this it follows that while the internal energy $U(T)$ is monotonically increasing in $(-\infty, 0) \cup (0, +\infty)$, the entropy $S(T)$ is monotonically decreasing in $(-\infty, 0)$ and monotonically increasing in $(0, +\infty)$. Note that for energy we have excluded the temperature $T = 0$ since there the function is not defined. The physically interesting aspect is that the thermodynamic states at $T < 0$ are characterized by a higher energy and this corroborates the previous arguments. Entropy, on the other hand, is invariant under the transformation $T \rightarrow -T$. What changes is the monotonicity: for $T < 0$ as T increases, the entropy decreases instead of increasing. Furthermore, since the states at $T < 0$ have a greater internal energy, the region of negative temperatures is found «above» the

temperature $T = +\infty$. In other words, we cannot represent the states at $T < 0$ in a line graph. From the asymptotic behavior of the functions $U(T), S(T)$ we see that the temperatures $T = -\infty$ and $T = +\infty$ are thermodynamically identical. In symbols:

$$T = 0^+, \dots, +\infty \equiv -\infty, \dots, 0^-$$

Consider two identical systems Σ, Σ^* with N particles and two levels. S is at temperature $T_1 > 0$, while Σ^* is at temperature $-T_1$. At the instant $t_0 = 0$ they are brought into thermal contact. The two systems will reach an equilibrium state with temperature $T_2 > T_1$.

2 Magnetic moment of an electric charge. Magnetomechanical parallelism

2.1 Orbital angular momentum and magnetic moment

The interaction potential energy of a dipole magnetic moment $\boldsymbol{\mu}$ subjected to an induction magnetic field \mathbf{B} , is:

$$V = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (18)$$

The magnetic moment is expressed through the magnetization $\mathbf{M}(\mathbf{x})$ (magnetic moment density) [1]:

$$\boldsymbol{\mu} = \int_{\mathbb{R}^3} \mathbf{M}(\mathbf{x}) d^3x$$

As a special case, consider a point charge q moving in a uniform and constant magnetic field \mathbf{B}_0 :

$$\mathbf{B}_0 = \text{rot}\mathbf{A}$$

where $\mathbf{A}(\mathbf{x})$ is the vector potential. It turns out:

$$\mathbf{A} = \frac{1}{2}\mathbf{B}_0 \wedge \mathbf{x} \quad (19)$$

If $\mathbf{v}(t)$ is the velocity of the charge located at $r(t)$, the current density is (CGS units of Gauss):

$$\mathbf{j}(\mathbf{x}) = q\frac{\mathbf{v}}{c}\delta^{(3)}(\mathbf{x} - \mathbf{r})$$

where $\delta^{(3)}(\mathbf{x} - \mathbf{r})$ is the three-dimensional Dirac delta. The interaction potential energy is

$$\begin{aligned} V &= - \int_{\mathbb{R}^3} \mathbf{j}(\mathbf{x}) \cdot \mathbf{A}(\mathbf{x}) d^3x = -\frac{q}{2c} \int_{\mathbb{R}^3} \mathbf{v} \cdot (\mathbf{H}_0 \wedge \mathbf{x}) \delta^{(3)}(\mathbf{x} - \mathbf{r}) d^3x \\ &= -\frac{q}{2c} \mathbf{v} \cdot (\mathbf{H}_0 \wedge \mathbf{r}) \end{aligned}$$

For the invariance of the mixed product under cyclic permutation:

$$V = -\frac{q}{2mc} \mathbf{L} \cdot \mathbf{B}_0 \quad (20)$$

being $\mathbf{L} = m\mathbf{r} \wedge \mathbf{v}$ the angular momentum of the charge q of mass m . From the (18):

$$\boldsymbol{\mu} = \frac{q}{2mc} \mathbf{L} \quad (21)$$

So any charged particle that follows a curvilinear trajectory (i.e. $\mathbf{L} \neq \mathbf{0}$) has a magnetic dipole moment. It follows that the vectors $\boldsymbol{\mu}, \mathbf{L}$ are proportional, and the proportionality factor does not depend on the characteristics of the motion. In particular, if $q > 0$ the vectors $\boldsymbol{\mu}, \mathbf{L}$ are parallel and in agreement. If $q < 0$, they are parallel and discordant (or antiparallel). The proportionality between the aforementioned vectors expresses the *magneto-mechanical parallelism* [2].

2.2 Electron spin and magnetic moment

Let us ask ourselves: does (21) retain its validity for the spin angular momentum of subatomic particles? The answer is affirmative provided that the proportionality factor is modified. In the case of the electron ($q = -e$):

$$\boldsymbol{\mu} = -g_s \frac{e}{2m_e c} \mathbf{S} \quad (22)$$

where: S is the spin angular momentum of the electron; g_s is a dimensionless term known as the *Landè factor*. The classic analogy suggests $g_s = 1$. Experimentally, however, is $g_s \simeq 2.0023$. In Dirac's quantum-relativistic framework, is $g_s = 2$ (spin is a typical quantum-relativistic effect). The difference between the theoretical value 2 and the experimental one can be explained through the interaction of the electronic charge with the radiation field emitted by the electron itself (in the framework of quantum electrodynamics). Assuming $g_s = 2$:

$$\boldsymbol{\mu} = -\frac{e}{m_e c} \mathbf{S} \quad (23)$$

As is known, the electron has spin 1/2 and recalling the known commutation relation of the corresponding Hermitian operators [4]:

$$\left[\hat{S}^2, \hat{S}_z \right] = 0 \quad (24)$$

for which these observables have in common a set of simultaneous eigenstates:

$$\begin{aligned} \hat{S}^2 |s, m_s\rangle &= \hbar^2 s(s+1) |s, m_s\rangle \\ \hat{S}_z |s, m_s\rangle &= \hbar m_s |s, m_s\rangle, \quad m_s = -s, -s+1, \dots, s-2, s \end{aligned}$$

For what has been said it is $s = 1/2$, therefore in compact notation as regards the component S_z

$$\begin{aligned} \hat{S}_z |\uparrow\rangle &= \frac{\hbar}{2} |\uparrow\rangle \\ \hat{S}_z |\downarrow\rangle &= -\frac{\hbar}{2} |\downarrow\rangle \end{aligned}$$

where

$$\begin{aligned} |\uparrow\rangle &\equiv \left| s = \frac{1}{2}, m_s = \frac{1}{2} \right\rangle \quad \text{spin up} \\ |\downarrow\rangle &\equiv \left| s = \frac{1}{2}, m_s = -\frac{1}{2} \right\rangle \quad \text{spin down} \end{aligned} \quad (25)$$

From (23) $\hat{\mu}_z = -\frac{e}{m_e c} \hat{S}_z$, for which spin up/down are eigenstates of μ_z with eigenvalues

$$\begin{aligned} -\frac{e\hbar}{m_e c}, \quad |\uparrow\rangle \\ \frac{e\hbar}{m_e c}, \quad |\downarrow\rangle \end{aligned} \quad (26)$$

We define the *Bohr magneton*

$$\mu_B = \frac{e\hbar}{2m_e c} \quad (27)$$

which identifies the eigenvalues of μ_z . It follows that if the electron is in the spin up state, the magnetic moment is $-\mu_B$ and vice versa. Stated another way, the Bohr magneton expresses the quantization of the magnetic moment due to the spin. The (23) is rewritten:

$$\boldsymbol{\mu} = -g_s \frac{\mu_B}{\hbar} \mathbf{S} \quad (28)$$

2.3 Spin and magnetic moment of atomic nuclei

The spin angular momentum of a nucleus is denoted by \mathbf{I} . The corresponding Hermitian operator obeys the usual commutation relations:

$$\left[\hat{I}^2, \hat{I}_z \right] = 0 \quad (29)$$

So

$$\begin{aligned} \hat{I}^2 |I, I_z\rangle &= \hbar^2 I(I+1) |I, I_z\rangle \\ \hat{I}_z |s, I_z\rangle &= \hbar I_z |I, I_z\rangle, \quad I_z = -I, -I+1, \dots, I-2, I \end{aligned} \quad (30)$$

The simplest nucleus is that of the hydrogen atom, which is made up of a single proton, therefore $I = 1/2$. The magnetic dipole moment follows:

$$\boldsymbol{\mu} = g_I \frac{2}{2m_p c} \mathbf{I} \quad (31)$$

being g_I the Landè factor for the proton. This factor can only be calculated experimentally: $g_I \simeq 5.58$. Thus, the eigenvalues of the magnetic moment correspond to the up/down nuclear spin states

$$\begin{aligned} g_I \frac{e\hbar}{4m_e c}, \quad |\uparrow\rangle \\ -g_I \frac{e\hbar}{4m_e c}, \quad |\downarrow\rangle \end{aligned} \quad (32)$$

We define the *nuclear magneton*:

$$\mu_N = \frac{e\hbar}{2m_p c} \simeq \frac{\mu_B}{1836} \quad (33)$$

which identifies the eigenvalues of μ_z . It follows that if the proton is in the spin up state, the magnetic moment is $+\mu_N$ and vice versa. With this position, the magnetic moment of the proton is written:

$$\boldsymbol{\mu} = g_I \frac{\mu_N}{\hbar} \mathbf{I} \quad (34)$$

Let us now consider a generic spin 1/2 nucleus. The magnetic moment is again expressed with the (34) obviously with a different value of g_I . We apply a static and uniform magnetic field \mathbf{B}_0 in the direction of the z -axis: $\mathbf{B}_0 = (0, 0, B_0)$. Assuming the nucleus at rest, its Hamiltonian reduces to the potential energy term describing the dipole-magnetic field interaction:

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\mu_z B_0 \quad (35)$$

Taking into account the (34) the corresponding Hamiltonian operator is written:

$$\hat{H} = -\omega_0 \hat{I}_z \quad (36)$$

having introduced the pulsation

$$\omega_0 = g_I \frac{\mu_N}{\hbar} B_0 \quad (37)$$

From (36) $[\hat{H}, \hat{I}_z] = 0$ so the spin up/down states are energy eigenstates:

$$\begin{aligned} \hat{H} |\uparrow\rangle &= -\frac{\hbar\omega_0}{2} |\uparrow\rangle \\ \hat{H} |\downarrow\rangle &= +\frac{\hbar\omega_0}{2} |\downarrow\rangle \end{aligned} \quad (38)$$

Classically the vector $\boldsymbol{\mu}$ is parallel and agrees to the vector $(0, 0, I_z)$; so the corresponding quantum state is the fundamental level $-\frac{\hbar\omega_0}{2}$. Since we are dealing with potential energy, we are free to choose its zero. Placing it in the fundamental level, we obtain the two-level diagram of fig. 5.

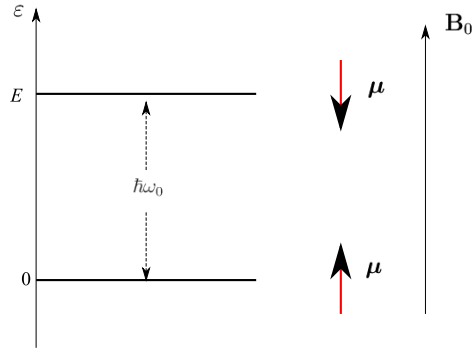


Figure 5: Energy levels of a single nuclear spin.

3 Paramagnetic system of nuclear spins of a crystal

Consider the ions/nuclei of a crystal lattice. In the Born-Oppenheimer approximation, the nuclei are assumed to be stationary at the nodes of the lattice. In the particular case of spin 1/2 nuclei, we have a system of $N \gg 1$ spin 1/2 of those examined in the previous number, which in turn can be represented by the system studied in section 1. In the case under examination, the inversion of population is achieved by «instantaneously» rotating the magnet that generates the field B_0 [5]. In the new magnetic field configuration, the fundamental level becomes the first excited level, which is more populated, and as established in § 1.2 results in $T < 0$. Being a metastable state, the system tends to return to temperatures $T > 0$. This will release a certain amount of heat to the grating.

References

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