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# Entropy of Spin Systems in Magnetic Resonance Phenomena

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A well-known principal difficulty in statistical thermodynamics of irreversible processes is the correct introduction of the concepts of entropy and temperature [1]. It was shown by the author [2], that for relaxing spin systems under the influence of alternating magnetic fields the "entropy" defined by Wangsness [3, 4] is physically meaningless and that therefore a principle of minimum entropy production for simple or double resonance phenomena (e.g. Overhauser effect) cannot be established without further considerations.

Often the description of a spin state by means of occupation numbers  $N_i$  of energy niveaux is sufficient (one neglects then the nondiagonal elements of the density matrix  $\rho$ , these are proportional to the amplitude of the  $H_1$ -field). In this case the entropy for a system of  $N$  (noninteracting) spins (in Boltzmann statistics) is simply

$$S = -Nk \sum (N_i/N) \ln (N_i/N), \quad (1)$$

and the minimum entropy production principle is to be formulated by use of a master equation for  $\partial N_i/\partial t$  [5] or in terms of spin temperatures [6], the spin temperature being only an occupation number parameter and no longer a thermodynamic temperature.

For spin systems with irreversible processes there is no need to change the v. Neumann equilibrium definition of entropy

$$S = -Nk \text{Tr} (\rho \ln \rho) \quad (2)$$

(compare also [1, 7]). Callen [8] stated in the language of phenomenological thermodynamics of irreversible processes, that in absence of magnetic fields the microscopic density matrix  $\rho$  itself generally minimizes the rate

of entropy production. The author shows [9] for a spin system in a stationary state, that by use of a suitably orientated coordinate system, rotating with the frequency  $\omega$  of the  $H_1$ -field, the following statements are valid:

- 1) the transformed density matrix  $\tilde{\rho}$  is diagonal;
- 2) the correct calculation of the entropy according to (2) amounts to the use of (1). The entropy is the same as in the original coordinate system;
- 3) a spin temperature (as an occupation number parameter) can be defined;
- 4) the principle of minimum entropy production is valid formally.

1. The diagonalization of  $\rho$  is performed with a unitary matrix  $U$ :

$$\tilde{\rho} = U^{-1} \rho U \quad (3)$$

with (in common notation)

$$U = e^{i\varphi I_y} e^{-i(\omega t - \psi) I_z} \quad (4)$$

( $I_y, I_z$ : Pauli spin operators). With the stationary matrix [2, 10] (for  $I = \frac{1}{2}$ )

$$\rho = \frac{1}{Z} \begin{pmatrix} 1 + \frac{1}{2}a_0 + \frac{1}{8}(a_0^2 + a_1 a_1^*) & a_1 e^{i\omega t} \\ a_1^* e^{-i\omega t} & 1 - \frac{1}{2}a_0 + \frac{1}{8}(a_0^2 + a_1 a_1^*) \end{pmatrix} \quad (5)$$

with  $Z = 2 \left\{ 1 + \frac{1}{8}(a_0^2 + a_1 a_1^*) \right\} \approx 2$  (partition function),

$$a_0 = \frac{\gamma \hbar}{kT} \left( H_0 - \frac{\omega \gamma H_1^2 \tau^2}{n} \right) \quad (T: \text{lattice temperature}),$$

$$a_1 = \frac{\gamma \hbar H_1}{kT} \left( 1 - i\omega \tau \frac{1 + i(\gamma H_0 - \omega) \tau}{n} \right),$$

$$n = 1 + (\gamma H_0 - \omega)^2 \tau^2 + \gamma^2 H_1^2 \tau^2,$$

$$a_1 a_1^* = \left( \frac{\gamma \hbar H_1}{kT} \right)^2 \frac{\chi'^2 + \chi''^2}{\chi_0},$$

it follows

$$\tilde{\rho} = \frac{1}{2} \begin{pmatrix} 1 + \frac{1}{Z} \sqrt{a_0^2 + a_1 a_1^*} & \sigma \\ \sigma & 1 - \frac{1}{Z} \sqrt{a_0^2 + a_1 a_1^*} \end{pmatrix}. \quad (6)$$

From (3) ... (6) the angle  $\varphi$  between the new and the old  $z$ -axis can be calculated, and likewise the angle  $\psi = \arctg(\chi''/\chi') = \arctg(v/u)$  ( $v$ : absorption,  $u$ : dispersion). The new coordinate system is inclined to the laboratory system and rotates with  $\omega$  and a phase difference  $\psi$  behind the  $H_1$ -field.

2. The entropy is, using (5) or (6),

$$\begin{aligned} S &= -Nk \text{Tr}(\rho \ln \rho) = -Nk \text{Tr}(\tilde{\rho} \ln \tilde{\rho}) \\ &= -Nk \left\{ \ln 2 - \frac{1}{2Z^2} (a_0^2 + a_1 a_1^*) \right\}. \end{aligned} \quad (7)$$

3. By writing (6) approximatively in exponential form and setting  $Z \approx 2$ , the spin temperature  $T_s$  is defined by

$$\frac{1}{Z} e^{-\tilde{H}/kT} = \frac{1}{Z} e^{-\gamma \hbar \sqrt{H_0^2 + H_1^2}/kT_s} \quad (8)$$

( $\tilde{H}$ : formal Hamiltonian in the transformed coordinate system), or with  $\beta_s = 1/kT_s$  by

$$\beta_s = \frac{1}{\sqrt{H_0^2 + H_1^2}} \sqrt{(H_0 - \omega \gamma H_1^2 \tau^2/n)^2 + H_1^2 (\chi'^2 + \chi''^2)/\chi_0^2}. \quad (9)$$

4. For the discussion of the entropy production see [9].

For spin systems obeying *FD*-statistics, e.g. electron spins in metals, the separation of the system entropy in lattice entropy and spin entropy in density matrix or occupation number formalism is not possible [11]. Our transformation to a rotating coordinate system is purely formal and has only the purpose of diagonalizing the density matrix, in contrary to the work of Redfield, Slichter, and others [12, 13], where an *effective* Hamiltonian is introduced and *physics in the rotating coordinate system* is studied.

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#### DISCUSSION

*M. Kastler.* — Lässt sich die Entropie-Definition auch durchführen bei einer Sachlage, die einer negativen absoluten Temperatur des Spinsystems (Besetzungsumkehr) entspricht?

*M. Vojta.* — Ja in genau der gleichen Weise wie für eine positive absolute Temperatur des Spinsystems.