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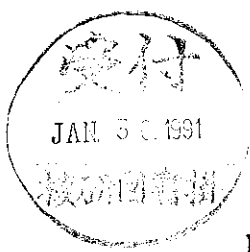

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III. SPIN 1/2 PARAMAGNETS

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1990 MIRAMARE-TRIESTE

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NONEQUILIBRIUM ENSEMBLES III. SPIN $\frac{1}{2}$ PARAMAGNETS *

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ABSTRACT

The thermodynamic state of a paramagnetic substance in which the spin vectors precess coherently is investigated. The state is a time dependent one. The corresponding density matrix and the thermodynamics emerging from it is worked out. A laboratory preparation of such a system is discussed.

MIRAMARE – TRIESTE
July 1990

* Submitted for publication.
Contribution No.22, Biruni Observatory.

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1 INTRODUCTON

This paper supplements number II in the series devoted to a variational formulation of nonequilibrium ensemble theories. In papers I and II maximum entropy distribution functions were obtained as $\rho = Z^{-1}exp(-\chi/kT)$, where χ, in general, was a time dependent solution of either Liouville's equation, for classical systems[1], or of vonNeumann's equation, for quantum mechanical systems[2]. Here we give an example to elucidate the notions developed so far. The example is an ensemble of spin $\frac{1}{2}$ paramagnets, initially not in thermodynamic equilibrium. The density matrix describing the time evolution of such a state is obtained in section 2. The ensuing thermodynamic functions are discussed in section 3. The laboratory preparation of the ensemble is elaborated on in section 4. References to equation numbers of papers I and II are preceeded by the same roman numerals.

2 DESCRIPTION OF THE SYSTEM

An electron in a magnetic field B in z-direction has the hamiltonian $H = -\frac{1}{2}\hbar\omega\sigma_z$, where ω is Larmor's frequency and σ's here and below are Pauli matrices. In the notation of paper II the four eigensolutions of vonNeumann's equations,

$$i\hbar\dot{\chi} = [H, \chi], \tag{1}$$

are

$$\chi(11) = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} = \frac{1}{2}(1 + \sigma_z), \tag{2a}$$

$$\chi(12) = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} exp(i\omega t) = \frac{1}{2}\sigma_+ exp(i\omega t), \tag{2b}$$

$$\chi(21) = \chi^\dagger(12) = \frac{1}{2}\sigma_- exp(-i\omega t), \tag{2c}$$

$$\chi(22) = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} = \frac{1}{2}(1 - \sigma_z), \tag{2d}$$

where I is the unit 2×2 matrix. Out of this complete set of solutions we construct the following positive definite and hermitian matrix

$$\rho = Z^{-1}exp(-\chi/kT), \tag{3a}$$

where the exponent matrix, χ, is the linear combination of the eigenmatrices of Eqs. (2),

$$\chi = -\frac{1}{2}\hbar\omega\{\beta\sigma_z - \frac{1}{2}[\alpha\sigma_+ exp(i\omega t) + \alpha^*\sigma_- exp(-i\omega t)]\}. \tag{3b}$$

The combination $\chi(11) - \chi(22) = \sigma_z$ is used in Eq. (3b). The other combination $\chi(11) + \chi(22) = I$, trace-orthogonal to σ_z, contributes a constant factor to ρ and is absorbed in the partion function Z. The factor $\frac{1}{2}\hbar\omega$ is included to give χ and kT the dimensions of energy in concordance with the conventions of thermodynamics. The eigenvalues of χ are $\pm\frac{1}{2}\hbar\omega\lambda$, $\lambda = (\beta^2 + \alpha^*\alpha)^{\frac{1}{2}}$. For the partition function one obtains

$$Z = exp(\hbar\omega\lambda/2kT) + exp(-\hbar\omega\lambda/2kT) = 2cosh(\hbar\omega\lambda/2kT). \quad (3c)$$

Equations (3a, b, c) complete our description of the most general density matrix for a nonequilibrium ensemble of spin $\frac{1}{2}$ paramagnets. The physical significance of the constants β, α and α^* and their determination from the constraints imposed on the system will become clear when we discuss the thermodynamic variables. Let us only point out that $\beta = 1$ and $\alpha = \alpha^* = 0$ gives the familiar canonical density matrix of equilibrium ensembles.

3 THERMODYNAMIC FUNCTIONS

3.1 Invariants of the system

The foremost of these invariants is the partition function. From this we define Helmholtz' potential

$$F = -kTlnZ = -kTlncoshx, \quad (4a)$$

$$x = \hbar\omega\lambda/2kT, \ \lambda = (\beta^2 + \alpha^*\alpha)^{\frac{1}{2}}. \quad (4b)$$

By Eq. (II. 27) the entropy is

$$S = -\partial F/\partial T = -F/T - kxtghx. \quad (5a)$$

An increase in either β or $\alpha\alpha^*$ results in a decrease in the entropy,

$$\partial S/\partial\beta^2 = \partial S/\partial(\alpha^*\alpha) = \lambda^{-1}\partial S/\partial\lambda = -kx^2/cosh^2x < 0. \quad (5b)$$

We shall see shortly that higher values of these parameters do indeed imply more orderly systems. By Eq. (II.28) the average $< \chi >$ is

$$X = kT^2\partial lnZ/\partial T = TS + F. \quad (6)$$

By Eq. (II.30), the internal energy is

$$U = -kT\partial lnZ/\partial\beta = \beta\lambda^{-2}(TS + F). \quad (7)$$

These thermodynamic relations are identical to those of equilibrium cases except for the presence of λ and β. More invariants can be constructed as various functions of Z.

3.2 Magnetization

The z-component of the magnetization vector, $\mathbf{M} = \frac{1}{2}\mu_b < \sigma >, \mu_b =$ Bohr magneton, is invariant,

$$M_z = \frac{1}{2}\mu_b < \sigma_z > = -(\mu_b/\hbar\omega)(\beta/\lambda^2)(TS + F). \quad (8)$$

To find the transverse components we use Eqs. (II.34).

$$M_+ = \frac{1}{2}\mu_b < \sigma_+ > = -(2kT\mu_b/\hbar\omega)\partial lnZ/\partial\alpha exp(-i\omega t)$$

$$= (\mu_b/\hbar\omega)(\alpha^*/\lambda^2)(TS + F)exp(-i\omega t), \quad (9a)$$

$$M_- = (\mu_b/\hbar\omega)(\alpha/\lambda^2)(TS+F)exp(i\omega t). \quad (9b)$$

Adding and subtracting Eqs. (9) gives

$$M_x = (\mu_b/\hbar\omega)\lambda^{-2}(TS+F)(\alpha_r cos\omega t + \alpha_i sin\omega t), \quad (10a)$$

$$M_y = (\mu_b/\hbar\omega)\lambda^{-2}(TS+F)(\alpha_r sin\omega t - \alpha_i cos\omega t), \quad (10b)$$

where α_r and α_i are the real and imaginary parts of α, respectively. Time variations in Eqs. (9) and (10) are the major new features of the present ensembles and are worthy of a comment. A spin vector **S**, in a magnetic field precesses about the field in a sense independent of the sign of S_z. In a collection of spins the phases of the precessions are, in general distributed randomly and lead to vanishing transverse components of the magnetization vector. This corresponds to $\alpha = \alpha^* = 0$, which is the case of equilibrium thermodynamics. If, however, there is a partial coherence among the phases of precession of individual spins, the transverse components of **M** will be nonzero. The projection of **M** in the xy - plane will describe a circle. The larger the $|\alpha|$, the higher the degree of phase coherence and the larger the magnitude of M-transverse. This additional knowledge on **M** implies a more orderly system and therefore a lesser entropy. Equation (5b) is a mathematical expression of this feature.

4 LABORATORY PREPARATION OF A COHERANT PARAMAGNET

We assume an almost ideal system with very weak interactions among the individual spins, therefore with very long relaxation times. We place the substance in a magnetic field in x-direction, say, and wait long enough to attain thermodynamic equilibrium. Next we rotate the field to bring it into the z-direction. Dynamics of the problem shows that, for time intervals shorter than the relaxation time, the substance will be in a state described by a time dependent density matrix of Eqs. (3). First we calculate the evolution matrix, $U(t)$, which transforms an initial density matrix, ρ_0, or an initial quantum state vector, v_0 to $\rho(t)$ or to $v(t)$. Let the magnetic field be in the $xz-$plane and rotate about the $y-$axis with the angular frequency Ω. Thus, $B = B(cos\Omega t, 0, sin\Omega t)$, and the hamiltonian, $H = -\frac{1}{2}\hbar\omega\{\hat{\mathbf{B}}.\sigma\}$, where, $\hat{\mathbf{B}}$ is the unit vector in the field direction. Schrödinger's equation becomes

$$i\dot{v} = -\frac{1}{2}\omega(\sigma_x cos\Omega t + \sigma_z sin\Omega t)v. \quad (11)$$

From a frame rotating with the field, the hamiltonian will appear time independent. This is achieved by transforming Eq. (11) by the unitary matrix

$$Y = exp(\frac{1}{2}i\Omega t\sigma_y) = Icos\frac{1}{2}\Omega t + i\sigma_y sin\Omega t. \quad (12)$$

Thus, let $v = Yv'$ and $H = YH'Y^\dagger$. Equation (11) gives

$$i\dot{v}' = \frac{1}{2}(\Omega\sigma_y - \omega\sigma_z)v' = \frac{1}{2}\mathbf{an}.\sigma v', \quad (13)$$

where $a^2 = \Omega^2 + \omega^2$ and $\mathbf{n} = (-\omega/a = cos\theta, \Omega/a = sin\theta, 0)$ is a unit vector in the xy-plane. The solution of Eq.(13) is

$$v'(t) = exp(-\frac{1}{2}iat\mathbf{n}.\sigma)v_0 = Icos\frac{1}{2}at - i\mathbf{n}.\sigma sin\frac{1}{2}at)v_0, \qquad (14)$$

where $v_0 = v'_0 = v(t = 0)$ is an initial value. For this technique of solving Schrödinger's equation one may consult the literature on nuclear magnetism or electron paramagnetic resonance, e.g. Abragam[3]. Transforming Eq.(14) back to the nonrotating frame gives

$$v(t) = U(t)v_0 = exp(\frac{1}{2}i\Omega t\sigma_y)exp(-\frac{1}{2}iat\mathbf{n}.\sigma)v_0. \qquad (15)$$

The unitary matrix operating on v_0 is the evolution matrix. At $\Omega t = \frac{1}{2}\pi$ we stop the rotation. The field will then be in z-direction and one will have $\frac{1}{2}at = (1 + \omega^2/\Omega^2)^{1/2}\pi/4$. To economize in writing we further assume $\omega^2/\Omega^2 = 3$. This corresponds to $\frac{1}{2}at = \frac{1}{2}\pi$ and $\theta = 4\pi/3$. The latter is the angle between $\mathbf{n}$ and the x-axis. Substituting these values in Eqs. (15) gives

$$U = -2^{-\frac{1}{2}}i(I + i\sigma_y)\mathbf{n}.\sigma = -2^{-\frac{1}{2}}i\begin{bmatrix} exp(i\theta) & exp(-i\theta) \\ exp(i\theta) & -exp(-i\theta) \end{bmatrix}. \qquad (16)$$

We are now ready to go back to our paramagnet. Let us assume that at $t = 0$, where $\mathbf{B}$ is in x-direction and the hamiltonian is $-\frac{1}{2}\hbar\omega\sigma_x$, the paramagnet has reached a thermodynamic equilibrium at temperature T . The density matrix will be

$$\rho_0 = Z^{-1}exp(-x\sigma_x),\ Z = 2coshx,\ x = \hbar\omega/2kT. \qquad (17)$$

at $\Omega t = \frac{1}{2}\pi$, this density will evolve into

$$\rho(\frac{1}{2}\pi) = U\rho_0 U^\dagger = Z^{-1}exp(-xU\sigma_x U^\dagger). \qquad (18a)$$

Substituting for U from Eq. (16) gives

$$U\sigma_x U^\dagger = \begin{bmatrix} cos2\theta & -isin2\theta \\ isin2\theta & -cos2\theta \end{bmatrix} = \sigma_z cos2\theta + \sigma_y sin2\theta. \qquad (18b)$$

After this moment, however, the magnetic field is fixed in the z-direction and the evolution will take place through

$$U_z(t) = exp(\frac{1}{2}i\omega t\sigma_z) = Icos\frac{1}{2}\omega t + i\sigma_z sin\frac{1}{2}\omega t. \qquad (19)$$

Considering Eq. (18a) as an initial density matrix for $U_z(t)$ gives

$$\rho(t) = U_z\rho(\frac{1}{2}\pi)U_z{}^\dagger = Z^{-1}exp(-xU_z U\sigma_x U^\dagger U_z{}^\dagger), \qquad (20a)$$

Substituting for U_z from Eq. (19) gives

$$U_z U\sigma_x U^\dagger U_z{}^\dagger = \sigma_z cos2\theta - \frac{1}{2}isin2\theta[\sigma_+ exp(i\omega t) - \sigma_- exp(-i\omega t)]. \qquad (20b)$$

The density matrix of Eqs. (20) is of the form of Eqs. (3). We only identify $\beta = cos2\theta$ and $\alpha = isin2\theta$.

The procedure outlined above for the preparation of a coherent paramagnet was picked out primarily for its conceptual and computational simplicity. For practical purposes one may borrow techniques from NMR spectroscopy, by applying radio frequency pulses of controlled duration instead or rotating the field or the specimen. Due to various perturbing factors the time dependent states will persist for times shorter than the relaxation time. Any measurement of a thermodynamic variable should be carried out in these short time intervals. The act of measurement should be expected to destroy the state under consideration, and repeated preparations of the state may be required. A feasible measurement showing time dependency is that of the transverse magnetization as discussed in Section 3.2

ACKNOWLEDGMENTS

The authors would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

References

1. Y. Sobouti, Physica A, in press (1990), paper I
2. Y. Sobouti, Physica A, submitted to (1990), paper II
3. A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press, Oxford, 1967)

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