Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, IV

To: Group 63 Staff

From: Arthur L. Loeb and Norman Menyuk

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Curie first noticed the linear variation of the susceptibility of paramagnetic materials with the inverse of temperature, arriving empirically at the equation

$$\chi_m = \frac{C_M}{T}$$

This was first explained by Langevin on the basis of classical concepts. He considered a paramagnetic gas in which each particle has a magnetic moment $\vec{M}$. In a magnetic field there is a tendency for each particle to be set with its magnetic axis parallel with the field. However, thermal agitations will tend to prevent this alignment and increase the entropy of the system. The entropy expresses the randomness of the system, which is decreased by a lining up of magnetic axes. The result will be a statistical type of equilibrium between the forces tending to increase the entropy of the system and those trying to decrease the energy.

Consider the energy of one independent pole making an angle Θ with the magnetic field $\vec{H}$. (Figure 4)

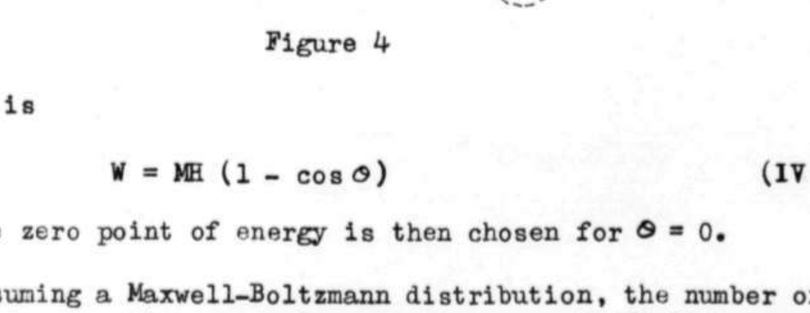

Figure 4

Its energy W is

$$W = MH\,(1 - \cos\Theta) \qquad \text{(IV - 1)}$$

The zero point of energy is then chosen for $\Theta = 0$.

Assuming a Maxwell-Boltzmann distribution, the number of particles with magnetic axes making an angle with the magnetic field between Θ and $\Theta + d\Theta$ (or solid angle $d\omega$ - see Figure 4) will be:

$$dN = A' e^{-\frac{W}{kT}} d\omega = A' e^{\frac{MH \cos\Theta}{kT}} e^{-\frac{MH}{kT}} d\omega$$

$$= A e^{\frac{MH \cos\Theta}{kT}} d\omega \qquad \text{(IV - 2)}$$

where $A = A' e^{-\frac{MH}{kT}}$

and since $\omega = 2\pi (1 - \cos\Theta)$

$$d\omega = 2\pi \sin\Theta d\Theta = -2\pi d(\cos\Theta)$$

Therefore,

$$N_o = \int_{\Theta=0}^{\pi} dN = A \int_0^{4\pi} e^{\frac{MH \cos\Theta}{kT}} d\omega$$

$$= -2\pi A \int_{+1}^{-1} e^{\frac{MH \cos\Theta}{kT}} d(\cos\Theta)$$

$$= -\frac{2\pi kT}{MH} A \left. e^{\frac{MH \cos\Theta}{kT}} \right]_{+1}^{-1}$$

$$= -\frac{2\pi kTA}{MH} \left(e^{-\frac{MH}{kT}} - e^{\frac{MH}{kT}} \right)$$

$$N_o = \frac{4\pi kTA}{MH} \operatorname{Sinh} \frac{MH}{kT} \qquad \text{(IV - 3)}$$

and

$$A = \frac{N_o MH}{4\pi kT} \operatorname{Cosech} \frac{MH}{kT} \qquad \text{(IV - 4)}$$

The average value of the component of magnetic moment in the direction of the field, $M \cos\Theta$, is

$$\bar{M}_H = \frac{\int M \cos\Theta \, dN}{N_o} = \frac{A \int_0^{4\pi} M \cos\Theta \, e^{\frac{MH \cos\Theta}{kT}} d\omega}{\frac{4\pi kTA}{MH} \operatorname{Sinh} \frac{MH}{kT}}$$

$$\bar{M}_H = \frac{MH \int_{+1}^{-1} M \cos\theta \, e^{\frac{MH\cos\theta}{kT}} \left[-2\pi d(\cos\theta)\right]}{4\pi kT \, \text{Sinh}\, \frac{MH}{kT}}$$

$$= -\frac{MH \int_{+1}^{-1} M\cos\theta \, e^{\frac{MH\cos\theta}{kT}} \, d(\cos\theta)}{2kT \, \text{Sinh}\, \frac{MH}{kT}}$$

$$= -\frac{\int_{+MH}^{-MH} MH\cos\theta \; e^{\frac{MH\cos\theta}{kT}} \, d\,(MH\cos\theta)}{2kTH \, \text{Sinh}\, \frac{MH}{kT}}$$

This integral is now in the form $\frac{1}{K}\int x e^{ax} dx$, which has the solution

$$\frac{e^{ax}}{Ka^2}(ax - 1)$$

Therefore

$$\bar{M}_H = \left[-\frac{e^{\frac{MH\cos\theta}{kT}} \; k^2T^2}{2kTH \; \text{Sinh}\frac{MH}{kT}} \left(\frac{MH\cos\theta}{kT} - 1\right)\right]_{+MH}^{-MH}$$

$$\bar{M}_H = -\frac{kT}{2H \; \text{Sinh}\frac{MH}{kT}} \left\{ e^{-\frac{MH}{kT}}\left(-\frac{MH}{kT} - 1\right) - e^{\frac{MH}{kT}}\left(\frac{MH}{kT} - 1\right)\right\}$$

$$= \frac{kT}{2H \; \text{Sinh}\frac{MH}{kT}} \left\{ \frac{MH}{kT}\left(e^{\frac{MH}{kT}} + e^{-\frac{MH}{kT}}\right) - \left(e^{\frac{MH}{kT}} - e^{-\frac{MH}{kT}}\right)\right\}$$

$$= \frac{kT}{H \; \text{Sinh}\frac{MH}{kT}} \left\{ \frac{MH}{kT} \; \text{Cosh}\frac{MH}{kT} - \text{Sinh}\frac{MH}{kT} \right\}$$

$$\therefore \bar{M} = M \; \text{Coth}\frac{MH}{kT} - \frac{kT}{H}$$

Therefore

$$\frac{\bar{M}}{M} = \text{Coth}\,\frac{MH}{kT} - \frac{kT}{MH} \qquad (IV - 5)$$

since, in general

$$\text{Coth}\,x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \frac{7x^5}{2160} \ldots\ldots\ldots$$

For the special case wherein $kT \gg MH$ (corresponding to weak fields and high temperatures)

$$\frac{\bar{M}}{M} = \frac{kT}{MH} + \frac{MH}{3kT} - \frac{1}{45}\left(\frac{MH}{kT}\right)^3 + \ldots\ldots\ldots - \frac{kT}{MH}$$

$$\doteq \frac{MH}{3kT} - \frac{1}{45}\left(\frac{MH}{kT}\right)^3 + \ldots$$

$$\approx \frac{MH}{3kT}$$

Molar Susceptibility

$$\chi_M = \frac{N\bar{M}}{H} = \frac{NM^2}{3kT} = \frac{N^2M^2}{3RT} = \frac{C_M}{T}$$

Therefore

$$C_M = \text{Curie Constant}$$

$$= \frac{NM^2}{3k} = \frac{N^2M^2}{3R} \qquad (IV - 6)$$

when

$$MH \gg kT$$

$$\frac{M}{M} = \text{Coth}\,\frac{MH}{kT} - \frac{kT}{MH} = \frac{\text{Cosh}\,\frac{MH}{kT}}{\text{Sinh}\,\frac{MH}{kT}} - \frac{kT}{MH}$$

$$= \frac{e^{\frac{MH}{kT}} + e^{-\frac{MH}{kT}}}{e^{\frac{MH}{kT}} - e^{-\frac{MH}{kT}}} - \frac{kT}{MH} = \frac{1 + e^{-\frac{2MH}{kT}}}{1 - e^{-\frac{2MH}{kT}}} - \frac{kT}{MH}$$

$$= 1 + 2e^{-\frac{2MH}{kT}} + 2e^{-\frac{4MH}{kT}} + \ldots\ldots\ldots - \frac{kT}{MH}$$

As mentioned previously, Langevin's results are in disagreement with Miss Van Leeuwen's proof that the classical application of Boltzmann statistics to a dynamic system must result in a zero susceptibility.

The reason for this is that Langevin's paramagnetic theory assumes a priori a permanent molecular magnetic moment which is the same for all similar molecules. Since magnetic moment is proportional to angular momentum, this assumes one definite value for the electronic angular momentum. This, of course, is not permissible with pure classical statistics, as there must be a continuous range of all permissible values of angular momentum.

Similarly in the diamagnetic case, the radius of a given orbit can have a continuous range of values rather than the one particular size assumed in the Langevin theory.

Thus, from a purely classical standpoint, Langevin's arguments break down and we are left with a solution which contradicts established experimental facts. How can this be explained?

The answer is that it cannot be explained by classical physics, and so we must turn to a new tool to adequately describe this phenomenon, as well as many others. The basic difficulty arises from the assumption of a continuous set of values for various quantities. This difficulty has since been successfully overcome by the advent of the quantum mechanics.

However, prior to the general theory of Schrödinger and Heisenberg, many problems were solved on the basis of two postulates by Bohr. They were arbitrarily stated with no proofs presented, but they represented a powerful tool enabling scientists to solve a large number of problems which had been incapable of solution by classical methods. The postulates are:

1. Of the infinite number of classically possible electron orbits about a nucleus, only certain discrete orbits are permissible. Furthermore, the electron in one of these discrete orbits emits no electromagnetic waves despite its accelerated motion.

2. Energy is emitted or absorbed by an electron only when the electron jumps from one permissible orbit to another.

It should be noted that Bohr's postulates were not only new, but that they are in complete contradiction to classical electromagnetic theory. Since an electron with orbital motion is accelerating, it would be expected to radiate energy continuously. This would lead to a reduction of the electron energy and an ever decreasing orbital radius until the electron finally collapses into the nucleus.

Signed Arthur L. Loeb
Arthur L. Loeb

Norman Menyuk
Norman Menyuk

Approved DRB
David R. Brown

ALL/NM:jk
Group 62 (15)
L. Gold