Paramagnetism and Diamagnetism

Here we discuss the magnetic response of systems that do not feature (as opposed to, say, ferromagnets or superconductors) any order relevant to the interaction with the magnetic field. We will confine ourselves to the static response to a homogeneous magnetic field.

Basic definitions

The magnetization $M$ is defined as the magnetic moment per unit volume. In what follows, we will set system volume equal to unity so that the quantities per unit volume and per given volume $V$ will coincide. (It is always straightforward to restore the volume, when necessary). The general statistical mechanical formula for $M$ reads

$$M = -\frac{\partial F(V,N,T,B)}{\partial B},$$

(1)

where $F(V,N,T,B)$ is the free energy as a function of volume, $V$, total number of particles, $N$, temperature, $T$, and the magnetic field, $B$. The magnetic susceptibility $\chi$ is defined as the ratio

$$\chi = \frac{M}{B}.$$  

(2)

The idea behind this definition is that in the limit $B \to 0$ the magnetization $M$ is normally a linear function $B$; in this case, $\chi$ is a $B$-independent coefficient. A system with $\chi > 0$ are called paramagnetic and systems with $\chi < 0$ are called diamagnetic. The response of paramagnetic systems is such that the external magnetic field gets enhanced while the response of diamagnetic systems reduces the external field.

Absence of magnetic response in equilibrium classical statistics

The equilibrium magnetic response is a purely quantum effect. The free energy of classical systems is fundamentally independent of magnetic field. Indeed,

$$F = -T\ln Z,$$

and the partition function for a classical particle\(^1\) is given by

$$Z = \int e^{H[p-(q/c)A(r).r]} d^3p d^3r.$$

\(^1\)The generalization to many particles is trivial.
Here $H$ is the Hamiltonian function, $p$ is the canonical momentum\(^2\) of the particle, $r$ is the coordinate of the particle, $A(r)$ is the vector potential of the magnetic field, $q$ is the electric charge of the particle, and $c$ is the speed of light. The dependence of $H$ on $p$ and $A$ is always through the variable

$$\tilde{p} = p - \left(\frac{q}{c}\right)A(r).$$

This variable can be used as the new integration variable over canonical momentum, because, at any fixed $r$, it is nothing but a shift of the origin of $p$ by the constant $\left(\frac{q}{c}\right)A(r)$, and we get exactly the same expression as at $A = 0$:

$$Z = \int e^{H[\tilde{p}, r]} d^3\tilde{p} d^3r \equiv \int e^{H[p, r]} d^3p d^3r.$$

### Two-level system: Paramagnetic response. Isentropic demagnetization

Consider a macroscopic system formed by $N$ independent two-level systems each of which having the Hamiltonian (written as the diagonal matrix in the representation of the energy eigenstates):

$$H = \begin{pmatrix} \mu_* B & 0 \\ 0 & -\mu_* B \end{pmatrix}, \quad (3)$$

where $\mu_*$ is a certain constant characterizing the strength of the interaction with magnetic field. Without loss of generality, we set $\mu_* > 0$, since changing the sign of $\mu_*$ leads to nothing but re-labeling the eigenvalues, which is irrelevant to the physical properties of the system. The partition function of a single two-level system is

$$Z_0 = e^{-E_-/T} + e^{-E_+/T} = e^x + e^{-x},$$

where $E_\mp = \pm \mu_* B$ and

$$x = \frac{\mu_* B}{T}.$$

The probabilities to find the system in the states ‘−’ and ‘+’ are

$$w_\mp = e^{-E_\mp/T}/Z_0 = \frac{1}{e^{\mp x} + 1}.$$

\(^2\)Not to be confused with mass times velocity, $mv$, which is true only in the absence of magnetic field; the relation between $v$ and $p$ is $mv = p - (q/c)A$.  

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Calculating

\[ M = \frac{-\partial F}{\partial B} = TN \frac{\partial}{\partial B} \ln Z_0 = TN \frac{\partial Z_0}{Z_0}, \]

we find

\[ M = N\mu \tanh x. \]

This formula has a very transparent physical meaning:

\[ M = \mu_\ast (N_- - N_+), \quad N_\mp = N w_\mp. \]

The numbers \( N_- \) and \( N_+ \) are the numbers of two-level systems in the states ‘\(-\)’ and ‘\(+)’, respectively. In the limit of \( B \to 0 \) we have

\[ M \approx \frac{N\mu^2 B}{T} \quad (B \to 0), \]

and

\[ \chi \approx \frac{N\mu^2}{T} \quad (B \to 0). \]

The system demonstrates a paramagnetic response.

Now consider the entropy of the system. By definition, the entropy of a single two-component system is

\[ S_0 = -w_- \ln w_- - w_+ \ln w_+, \]

and the entropy of the whole system is \( S = NS_0 \). Note that \( S \equiv S(x) \), meaning that the dependence of \( S \) on \( B \) and \( T \) is only in terms their ratio. It is straightforward to dramatically reduce \( B \) without changing the probabilities \( w_\pm \), because for the Hamiltonian (3) with time-dependent \( B \) the states ‘\(-\)’ and ‘\(+)’ remain the eigenstates and their probabilities cannot change during the evolution. This means that the state remains an equilibrium state, but with the new temperature that simply follows the evolution of \( B \), preserving the ratio \( B/T \). This process is called isentropic demagnetization. It is one of the standard cryogenic protocols. First one applies a magnetic field to polarize a two-level subsystem (normally, a spin subsystem). Then the magnetic field is quickly reduced to reduce the temperature of the two-level subsystem. The two-level subsystem then equilibrates with the rest of the system. The temperature of the two-level subsystem increases while the temperature of the rest of the system decreases.