

## **Atomic/Molecular Origin and Physics Description of Magnetic Susceptibility: Diamagnetism, Paramagnetism, Ferromagnetism, Superparamagnetism**

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**Introduction** The volume magnetic susceptibility,  $\chi$  is the property which relates the magnetization,  $\mathbf{M}$  induced in a material to the applied magnetic field,  $\mathbf{H}$ , via

$$\mathbf{M} = \chi \mathbf{H}. \quad [1]$$

In linear, isotropic and homogeneous materials,  $\chi$  is a scalar, constant and the magnetization is directly proportional to the applied magnetic field. This is the case for most biological materials at accessible magnetic field strengths. The magnetic induction,  $\mathbf{B}$  is related to  $\mathbf{M}$  and  $\mathbf{H}$ , by

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu_0 (1 + \chi) \mathbf{H}, \quad [2]$$

where  $\mu_0 = 4\pi \times 10^{-7} \text{ m kg s}^{-2} \text{ A}^{-2}$  is the permeability of free space and  $(1 + \chi)$  is equal to the relative permeability,  $\mu_r$ . The NMR frequency,  $\omega$ , is dictated by the magnitude of the magnetic induction via the Larmor equation ( $\omega = \gamma B$ ) and it is important to take account of the effects of magnetic susceptibility when calculating frequency offsets inside real samples.

$\chi$  is negative in *diamagnetic* materials and positive in *paramagnetic* materials. This means that the field and NMR frequency are both typically reduced in diamagnetic materials and enhanced in paramagnetic materials (though in calculating  $\omega$  it is important to take account of the effect of the sample shape and the sphere of Lorentz). Paramagnetic/diamagnetic materials are attracted/repelled by a magnetic.

The magnetic susceptibility of a material can also be described by the mass susceptibility,  $\chi_m$ , and molar susceptibility,  $\chi_M$ , which characterize the susceptibility per unit mass or per Mole of the substance, respectively. These are related to the volume susceptibility by the following equations:

$$\chi_m = \chi/\rho; \quad \chi_M = m \chi/\rho \quad [3]$$

where  $\rho$  is the density and  $m$  is the molar mass.

Volume susceptibility values are still often quoted in cgs units which can cause confusion when reviewing the literature. To convert a cgs volume susceptibility value to an SI value, it is necessary to multiply by  $4\pi$ . By way of example, the volume magnetic susceptibility of water at 293 K is -9.0 ppm in SI units, while the value in cgs units is  $-9.0/4\pi = -0.72$  ppm. The mass susceptibility is  $-9.0 \times 10^{-6}/1000 = -9.0 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$  (SI) and the molar susceptibility is  $-9.0 \times 10^{-9} \times 0.018 = -1.6 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$  (SI). The equivalent values in cgs units are  $\chi_m = -7.2 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1}$  and  $\chi_M = -1.3 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ .

Most biological tissues are diamagnetic with a small negative magnetic susceptibility similar in magnitude to the susceptibility of water. Some bio-molecules, such as de-oxyhaemoglobin are paramagnetic as a result of the presence of paramagnetic iron, and it is the blood oxygenation level dependent (BOLD) variation of the susceptibility of blood that causes the changes in gradient echo signal intensity that are exploited in fMRI experiments. The presence of significant levels of accumulated iron, generally sequestered in ferritin, makes the deep grey matter nuclei more paramagnetic than other brain regions. Some anisotropic materials, including myelin, have an anisotropic susceptibility. This means that the strength of the induced magnetization in white matter depends quite strongly on the orientation of the field with respect to the nerve fibers. In such materials, the susceptibility is described by a symmetric tensor.

In ferromagnetic materials the susceptibility is large and positive, but not simply proportional to the applied magnetic field, and of course ferromagnetic material can exhibit magnetization even in the absence of an applied field. The large induced magnetization means that ferromagnetic materials are strongly attracted to sources of magnetic field. Ferromagnetic objects must consequently be excluded from the region surrounding an MRI scanner, since they may be pulled into the scanner, forming dangerous projectiles.

The following sections provide a brief description of the molecular/atomic origins of the different types of magnetic behavior, which will be expanded upon in the presentation.

**Diamagnetism** arises from the effect of an applied magnetic field on the electron orbits in molecules and atoms. The order of magnitude of the effect can be derived by using the classical Langevin treatment (although a quantum mechanical approach is needed to describe the effect fully). If we consider an atom or ion with  $Z$  electrons in a closed shell configuration (so that the net orbital and spin angular momentum of the electrons is zero), then the torque on an “orbiting” electron due to a magnetic field,  $B$ , applied along the  $z$ -direction, produces a Larmor precession of the orbit at a frequency,  $\omega = eB/2m_e$ . The resulting precession of all of the electrons in the atom generates a current of magnitude  $-Ze \omega/2\pi = -Ze^2B/4\pi m_e$  and this produces a magnetic dipole of magnitude  $-Ze^2B \langle r_{\perp}^2 \rangle /4m_e$ , where  $\langle r_{\perp}^2 \rangle$  is the mean square radius of the orbit in the plane normal to the field (which is  $2/3$  of the mean square radius of the orbit  $\langle r^2 \rangle$ ). In a material containing,  $n$ , atoms per unit volume, the magnetization is then given by

$$M = -nZe^2B \langle r^2 \rangle /6m_e \quad [4]$$

yielding a diamagnetic magnetic susceptibility of  $-\frac{n\mu_0 Z e^2 \langle r^2 \rangle}{6m_e}$ . When  $Z \langle r^2 \rangle \sim 10^{-19} \text{ m}^2$  (corresponding to a neon atom), this yields a molar susceptibility of  $-4 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$  (SI) in agreement with experiment. Calculation of diamagnetic susceptibilities of more complex molecules requires application of perturbation theory to the appropriate Hamiltonian.

**Paramagnetism** is manifested in atoms and molecules containing unpaired electrons, whose total angular momentum,  $\mathbf{J}$ , then gives rise to a net magnetic moment  $-\frac{g\mu_B}{\hbar} \mathbf{J}$ , where  $\mu_B$  is the Bohr magneton and  $g$  is the Landé  $g$ -factor (which depends on the quantum numbers describing the electron’s spin, orbital and total angular momentum). When placed

in a magnetic field the magnetic moments tend to line up with the applied field giving rise to a positive net magnetization, but thermal fluctuations mean that the component of the magnetic moment along the field randomly varies across different atoms/molecules. The net magnetization is consequently described by Boltzmann statistics, and in the case where only the lowest  $2J+1$  energy states are populated, the net magnetization in a material containing  $n$  atoms per unit volume is given by

$$M = \frac{n \sum_{m=-J}^{m=J} m g \mu_B e^{m g \mu_B / k_B T}}{\sum_{m=-J}^{m=J} e^{m g \mu_B / k_B T}} = n g \mu_B B_J(g \mu_B B / k_B T), \quad [5]$$

where  $B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{1}{2J} x$ . The form of Eq. [5] means that the magnetization is not always linear function of the applied magnetic field and will in particular saturate at large values of  $g \mu_B B / k_B T$ . However working at room temperature and at the magnetic field strengths used in MRI, the condition  $g \mu_B B \ll k_B T$  holds for paramagnetic ions and Eq. [5] consequently simplifies to a Curie law form.

$$M = n \frac{(g \mu_B)^2 J(J+1)}{3 k_B T} B \quad . \quad [6]$$

The volume susceptibility is therefore given by  $\chi = n \frac{(g \mu_B)^2 J(J+1)}{3 k_B T}$ . The positive susceptibility values of paramagnetic ions are generally much larger in magnitude than the diamagnetic effects. Considering  $\text{Fe}^{3+}$  ions, for example,  $g \sqrt{J(J+1)} = 5.92$ , yielding a value of  $\chi \sim 0.02$  ppm (SI) for a 1 mM concentration of  $\text{Fe}^{3+}$ .

**Ferromagnetism** results from the strong interactions between paramagnetic atoms or molecules that occur in some materials leading to a coherent alignment of the magnetic dipoles and thus a large magnetization. The interaction between proximal atoms that produces the alignment is generally not magnetic in origin (i.e. not the dipolar interaction), but rather stems from the electrostatic interactions between electronic charges. In fact it results from the Pauli exclusion principle, which broadly means that electrons with similar spin quantum numbers cannot have the same position. Consequently, overlap of the orbitals of electrons on adjacent atoms may be reduced when the electron spins are parallel rather than anti-parallel. The reduced overlap decreases the electrostatic energy and thus means that it is energetically favorable for the spins to align.

In materials in which the energy difference produced by this exchange interaction is large, the magnetic dipoles in the material will spontaneously align producing a large permanent magnetic moment even in the absence of an applied field. Ferromagnetism disappears above a critical temperature,  $T_c$ , as a result of thermal fluctuations, and for temperatures above  $T_c$  the material exhibits paramagnetism with a susceptibility that follows a Curie-Weiss "law" such that  $\chi \propto (T - T_c)^{-1}$ .

Although the critical temperature for iron is greater than 1000 K most iron objects are not permanent magnets. This is because in the absence of a significant applied field, it is energetically favorable for the material to divide up into a series of domains, formed such that the magnetic moments are all aligned in the same direction within one domain, but so that the direction of alignment varies across domains. The total net magnetization of a bulk sample in this state is not large because the contributions from different domains cancel one

another. Domains form because the magnetic dipole interaction is much longer ranged than the exchange interaction: formation of domains causes an increase in the exchange energy in regions where the direction of the magnetic moment changes (in the so-called, domain walls), but this is outweighed by the reduction of magnetic energy throughout the sample that results from the reduction in net magnetic field inside the sample that occurs when domains form. When a magnetic field is externally applied, the domain structure changes producing an increase in net magnetization. These changes are characterized by the material's hysteresis curve.

In solid materials containing different types of magnetic moments, it is possible to have a different type of ordering in which there are interdigitated lattices, upon which the magnetic moments are anti-parallel to one another. If the magnetic moments of the different lattices cancel one another, the material is said to be anti-ferromagnetic, while in a ferrimagnet there is residual magnetization because the magnetic moments of the different lattices do not completely cancel out.

**Superparamagnetism** arises in nanoparticles of ferro- or ferromagnetic material which are smaller than the typical domain size, so that each particle forms a single domain. In an applied magnetic field the total magnetic moment of the particle,  $\mu$ , can be aligned with or against the field and (assuming the easy axis of the particle is aligned with the field) and in a sample containing  $n$  particles per unit volume the net magnetization is again described by Boltzmann statistics, taking the following form (under certain conditions):

$$M = n\mu \tanh \frac{\mu B}{k_B T}. \quad [7]$$

In this equation the magnetic moment of the particle effectively replaces the moment of a single atom used in deriving Eq. [5], so that a large magnetization/susceptibility results. Superparamagnetic iron oxide (SPIO) particles can be used as  $T_2/T_2^*$  contrast agents.

## References

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