Chapter 2
Magnetism

2.1 Origin of Magnetism

Undoubtedly, everybody knows what magnetic materials do but few think how a magnet works. To realize this phenomenon, one should first understand the inextricable connection between electricity and magnetism.

A simple electromagnet can be induced by a simple design of copper wire wrapped into the form of a coil and connecting the wire to a battery. A magnetic field is formed in the coil but its sustention is only stable once the electricity passes through the wire. An ordinary bar magnet does not have an obvious connection to the electricity, thus how does it work? The field created by the magnet is attributed to the electron motion and their interactions. Indeed, as shown in Fig. 2.1, the motion of electrons produces two kinds of magnetic moments: (1) Orbital magnetic moment (μ_{orb}), which is caused from the electrons motion around the nucleus of atom and (2) spin magnetic moment (μ_{s}), which is induced from the motion of the electron around its own axis. The combination of these two generates an atomic magnetic moment, which is strongly material dependent. In certain magnetic materials the magnetic moments of a large proportion of the electrons align, creating a unified magnetic field.

In fact, the spin magnetic moment is an intrinsic behavior of an electron and it is associated with the spin angular moment (S) by the Eq. (2.1) as follows [1]:

$$\mu_{\mathrm{s}} = \frac{e}{m} S \tag{2.1}$$

where m and e refer to the mass and charge of electron, respectively. The S is quantized and can only be $\pm 1/2$. Since only the z component of S is measurable, hence, the z component of μ_{s} can be estimated from the Eq. (2.2) [1];

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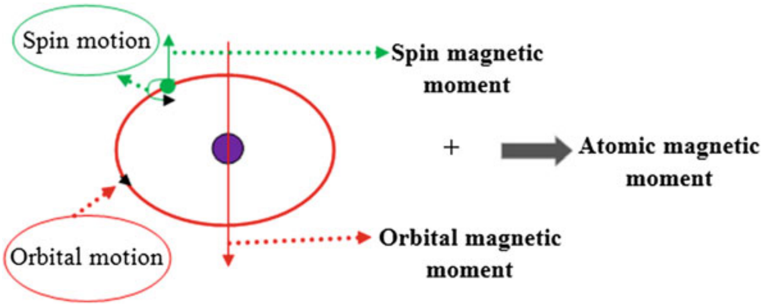


Fig. 2.1 Electron circulation around itself and the nucleus of an atom

$$\mu_{s,z} = \pm \frac{eh}{4\pi m} \tag{2.2}$$

where h is Plank's Constant. The positive value of this equation is equal to 9.27×10^{-24} J T^{-1} and is known as Bohr magneton (μ_b). The μ_b is the most basic unit of magnetic moment in magnetism and magnetic materials are explained based on this quantity. The combination of spin magnetic moment and orbital magnetic moment influences the type of magnetism which is present for each element.

Magnetization is a behavior that explains the extent to which a magnetic material is influenced by a magnetic field. Materials are, hence, categorized in terms of their response to an externally applied field. Description of the magnetic moments orientations in materials spans various magnetism forms existing in nature. Thus, when electrons are paired together, their opposite direction of spins results in the cancelation of their magnetic moments by each other. Consequently, no net magnetic moment is present. Conversely, a net magnetic moment will exist in materials with some unpaired electrons and will react to an externally applied field. Six fundamental kinds of magnetism can be classified: diamagnetism, paramagnetism,

Table 2.1 Presented units and quantities employed in magnetism

Quantity	Symbol	Gaussian units	Conversion factor	SI units
Magnetic flux density, magnetic induction	B	Gauss (G)	10^{-4}	Tesla (T)
Magnetic flux	Φ	Maxwell (Mx)	10^{-8}	Weber (Wb)
Magnetic field strength	H	Oersted (Oe)	$10^3/4\pi$	Ampere/meter (A/m)
Volume magnetization	4πM	G	$10^3/4\pi$	A/m
Mass magnetization	σ, M	emu/g	1	Am^2/kg
Magnetic moment	M	Mu	10^{-3}	Am^2
Magnetic dipole moment	J	emu	$4\pi \times 10^{-10}$	Wbm
Volume susceptibility	χ	Dimensionless	4π	Dimensionless
Mass susceptibility	χ_p	cm^3/g	$4\pi \times 10^{-3}$	m^3/kg

ferromagnetism, antiferromagnetism, ferrimagnetism, and superparamagnetism. As a prelude to the description of magnetic materials, a table introducing the units and quantities employed in magnetism is presented in Table 2.1.

2.2 Types of Magnetism in Materials

2.2.1 Diamagnetism

Diamagnetism is the behavior of the diamagnetic materials in which the atoms do not have magnetic moment when there is no external applied field. Thus, by applying an externally magnetic field, they would tend to generate a magnetic field in an opposite direction of the applied field, resulting in a repulsive effect. In fact, applying external field alters the electrons' orbital velocity around their nuclei and leads to the variation of magnetic dipole moment in an opposite direction of the applied field [2]. As the diamagnetism property is very weak, thereby any other form of magnetic behavior that a material may involves typically overpowers this effect. Based on the electronic configuration of materials, this state of magnetism occurred in those materials with filled electronic sub-shells in which the magnetic moments are paired and overall cancel out each other.

2.2.2 Paramagnetism

Paramagnetism is the behavior of those materials that exhibit a permanent magnetic dipole moment. They also include an unpaired electron shell usually in the 3*d* or 4*f* shells [2, 3]. Various theories of paramagnetism are presented which are true for certain kinds of materials. For example, the Langevin model, which is valid for those materials with noninteracting concentrated electrons, asserts that the magnetic moments of each atom orientate in a random state as a consequence of thermal agitation. Applying an external magnetic field gives rise to the small alignment of these magnetic moments and, accordingly, results in the creation of low magnetization in the applied field direction.

For paramagnetism, both the orbital angular moment and the electron spin contribute to the magnetization which results in positive susceptibility between 10^{-2} and 10^{-4} at room temperature. At a lower applied field the magnetization, M, is proportional to the applied field H, but it deviates from proportionality at a higher applied field where saturation magnetization starts to occur.

The reason of the occurrence of slight alignment is described by the inverse correlation of susceptibility (χ) with temperature (T). This manner is known as Curie's Law and is presented by the equation of $\chi = C/T$. According to this equation, at a higher applied field the temperature increases and causes an enhancement of thermal agitation. Consequently, it is difficult for the magnetic moments to be aligned. Curie's Law also describes the positive susceptibility and more generally is stated as Eq. (2.3);

$$\chi = \frac{C\mu_0 NM^2}{KT} \tag{2.3}$$

where C, N, μ_0, T and K designate a constant, the number of magnetic dipoles (m) per unit volume, the permeability of vacuum, the absolute temperature, and Boltzmann's Constant, respectively [4]. Except for very low temperatures, usually less than 5 K, some paramagnetic materials follow from this equation at most temperatures. However, a majority of paramagnetic materials obey the Curie–Weiss Law;

$$\chi = \frac{C}{T - \theta_C} \tag{2.4}$$

where C is the Curie constant and θ_c is the critical temperature.

2.2.3 Ferromagnetism

Ferromagnetism is the principal mechanism by which special types of materials like Fe produce permanent magnets or/and present powerful interactions with magnets. This behavior occurs only by the arrangement of atoms in the lattice structure and the atomic magnetic moment interacts to align to each other. The atomic moments in ferromagnetism materials present gigantic strength interactions which are formed by electronic exchange force and cause a parallel alignment of atomic moments. A huge exchange force is equivalent to a field of about 1000T. Moreover, because of the relative spins orientation of two electrons, the exchange force is a quantum mechanical phenomenon.

Parallel alignment of the net moments in ferromagnetic materials causes a tremendous net magnetization even though there is no external applied field. Therefore, these materials have two main traits: (1) spontaneous magnetization, which is the net magnetization that can be presented inside of an even magnetized microscopic volume, and (2) the presence of magnetic ordering temperature.

The susceptibility of ferromagnetic material is often large and positive in value. Moreover, it depends on the microstructure.

2.2.4 Antiferromagnetism

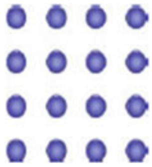
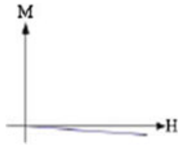
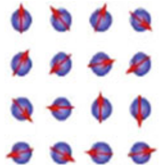
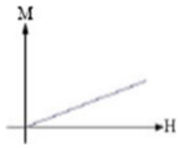
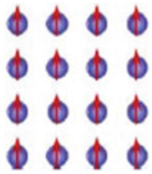
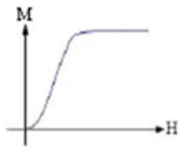
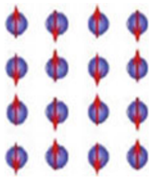
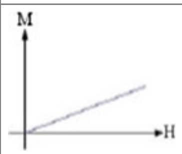
Antiferromagnetism behavior occurs when the two sub-lattices are equally stated in an opposite direction resulting in zero net moment. Antiferromagnetic materials such as transition metal oxides are similar to ferromagnetic materials but the exchange interaction between the adjacent atoms results in the antiparallel alignment of the atomic magnetic moments. Thus, the magnetic moments cancel out and the material would prefer to act like low magnetization materials. Susceptibility behavior above a critical temperature, known as Neel temperature (T_N) is the clue to explain antiferromagnetism properties. Above T_N, a sufficient thermal energy causes equal and oppositionally aligned atomic magnetic moments to cancel out. Therefore, the randomly fluctuation alignment results in the vanishing of their long-range order. In this condition the materials would prefer to present a paramagnetic manner. In fact, above T_N the Curie–Weiss law paramagnet is favorable for susceptibility but a negative intercept implying negative exchange interactions. Below T_N, spontaneous magnetization occurs in antiferromagnetic materials, resulting in antiparallel alignment of magnetic dipole moments of the sub-lattices to each other [3].

2.2.5 Ferrimagnetism

Ferrimagnetism is a behavior displayed by ionic compounds including more complex crystal structures whose ions or atoms tend to assume a magnetic ordering but nonparallel alignment in zero applied field. The ferrimagnetic materials retain a spontaneous magnetization below the T_N and exhibit no magnetic order (paramagnetic materials behavior) above the T_N [4]. Normally, within a magnetic domain, a net magnetic moment is induced from the antiparallel arrangement of adjacent nonequivalent sub-lattices. Therefore, the macroscopic behavior of ferrimagnetism is effectively a ferromagnetism behavior. In ferrimagnetic materials, the magnetic dipole moments fall into sub-lattices and are organized as a subset of antiferromagnetic materials. Each sub-lattice can be conducted as a ferromagnetic materials behavior and the existence of discrepancy between the magnetic dipole moments for them leads to the net magnetization for the ferrimagnetic material [4].

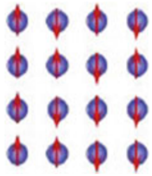
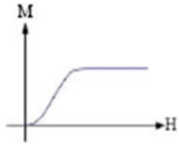
The continuous interaction of the net magnetic moments of the lattice occurs all over the rest of the crystal in such a way that ferrimagnetism can be conducted as a certain type of ferromagnetism and hence domains can produce in a similar manner. Magnetic materials that fall in this category include ferrites such as $CoFe_2O_4$ and transition metal oxides such as Fe_3O_4. Table 2.2 exhibits the summary of various types of magnetic properties in magnetic materials.

Table 2.2 Summary of various kinds of magnetic behavior

Type	Example	Atomic/magnetic behavior		
Diamagnetism	Insert gases; many e.g. Au, Cu, Hg; non-metallic elements e.g. B, Si, P, S; many ions e.g. Na^+, Cl and their salts; diatomic molecules e.g. H_2, N_2; H_2O; most organic compounds	Atoms have no magnetic movement Susceptibility is small and negative, -10^{-6} to 10^{-5}		
Paramagnetism	Some metals, e.g. Al; some diatomic gases, e.g. O_2, NO; ions of transition metals and rare earth metals, and their salts; rare earth oxides	Atoms have randomly oriented magnetic moments Susceptibility is small and positive, $+10^{-5}$ to $+10^{-3}$		
Ferromagnetism	Transition metals Fe, H. Co, Ni, rare earths with $64 \leq Z \leq 69$; alloys of ferromagnetic elements; some alloys of Mn, e.g. MnBi, Cu_2MnAI	Atoms have parallel aligned magnetic moments Susceptibility is large (below T_c)		
Antiferromagnetism	Transition metals Mn, Cr and many of their compound, e.g. MnO, CoO, NiO. Cr_2O_3, MnS, MnSe, CuC_{12}	Atoms have anti-parallel aligned magnetic moments Susceptibility is small and positive, $+10^{-5}$ to $+10^{-3}$		

(continued)

Table 2.2 (continued)

Type	Example	Atomic/magnetic behavior		
Ferrimagnetism	Fe_3O_4 (magnetite); γ-Fe_2O_3 (maghemite); mixed oxides of iron and other elements such as Sr ferrite	Atoms have mixed parallel and anti-parallel aligned magnetic moments Susceptibility is large (below T_c)		

2.2.6 Superparamagnetism

Particle size reduction in nano magnetic materials leads to the production of single-domain particles as well as giving rise to the superparamagnetism phenomenon. In magnetic materials, a single-domain state occurs with their traits similar to the ferromagnetic materials below the transition temperature, θ_C. The reason is that they are saturated in moderate applied magnetic fields, and exhibit hysteresis, i.e., coercivity and remanence and also involve relatively large susceptibility (Fig. 2.2). Above θ_C, superparamagnetic materials, traits are similar to the paramagnetic materials as they do not exhibit magnetic coercivity and remanence [4–6]. Uniform magnetization occurs in superparamagnetic particles along an easy axis. The thermal energy leads the magnetization to switch between equivalent easy axes through an anisotropy obstacle. This switching occurs so quickly that the time average magnetic remanence is zero.

Two mechanisms are introduced for a description of the alignment of superparamagnetic particles with an applied magnetic field. They include Brownian rotation and Neel rotation [7]. The Brownian rotation only takes place when particles are in a fluid and induced from the physical revolving of a particle toward the

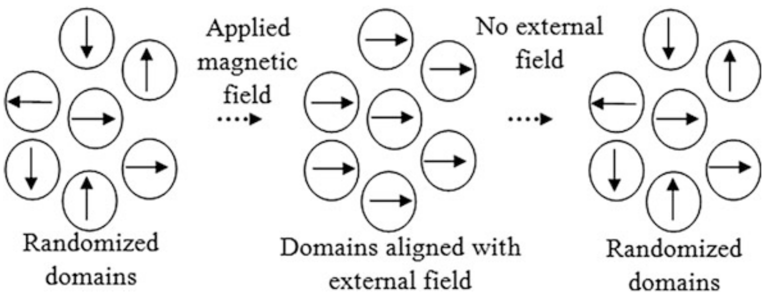


Fig. 2.2 Superparamagnetic particles behavior at the presence and without external applied magnetic field

applied field direction. Neel rotation happens when they are in a solid state or fluid and induces from the revolving a stationary particle magnetic moment [7].

Superparamagnetism in nanomaterials normally happens once the particle size is in the range of 1–10 nm. In this circumstance, even when the temperature is below Θ_C and T_N, as the particle sizes get smaller as the thermal energy is able to overcome the coupling force between adjacent atoms, enough to modify the magnetization direction through the whole crystallite. This occurrence leads the magnetic moment to average to zero. Therefore, the materials' traits are like paramagnetism behavior and the magnetic moment of the whole crystallite would prefer to align with the magnetic field.

Now by understanding this concept, one is interested into know about the magnetic materials that are added to carrier fluids in an MR fluid.

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