Magnetism of Small Particles

Below a certain critical size, a particle contains only ONE domain.

Why?

Width of domain wall depends on the balance between the Exchange Energy (prefers a wide wall) and the Magnetcrystralline Anisotropy Energy (prefers a narrow wall). Typical domain wall width \( \sim 1000\text{Å} \).

If particle is smaller than \( \sim 1000\text{Å} \), the domain wall can't fit!

More Rigorously:

- Reduction in magnetostatic energy \( \propto \) volume of particle \( (r^3) \)
- Increase in domain wall energy \( \propto \) area of wall \( (r^2) \)

(for more details, see Cullity, Ch.9)
If the domain wall energy is large (e.g., large crystal anisotropy), then forming a wall is unfavorable, and large single-domain particles can form.

If the saturation magnetization is small, then the magnetostatic energy is small, and large single-domain particles can form.
Experimental Evidence for Single Domain Particles


- Showed that large coercivity of small particles is the result of single domains (rather than, e.g., strain, preventing easy domain wall motion).

- Used dilute suspensions of spherical Ni particles in paraffin wax, and measured the field required to saturate the samples.

\[
\text{Particle diameter } 200\text{Å} \quad (< r_c) \\
\text{field required } = 5500\text{e} \\
(\text{only slightly larger than that required to overcome magnetocrystalline anisotropy) } \Rightarrow \text{SINGLE DOMAIN}
\]

\[
\text{Particle diameter } 80,000\text{Å} \quad (> r_c) \\
\text{field required } = 2100\text{e} \\
\therefore \text{different magnetization mechanism! (domain wall motion + rotation).} \\
(\text{cf. demagnetizing field } = \frac{4\pi M_s}{3} = 2020\text{e} \quad \text{for Ni})
\]

- A multi-domain particle can be kept in a saturated state only by a field larger than the demagnetizing field (2020 e in this case).

- A single-domain particle is always saturated, with the spontaneous magnetization in the same direction throughout its volume. Applied field must overcome anisotropy, but not a demagnetizing field.
Mechanism of magnetization

1. Magnetization lies along an easy direction 
   (determined by shape and magnetocrystalline anisotropies).

   ![Easy Axis](image)

2. H field applied in opposite direction
   - Particle can't respond by domain wall motion.
   - Magnetization must rotate through the hard direction

   ![H Field](image)

3. Strong anisotropy forces hold the magnetization in the easy direction; coercivity is large.
Fig. 7-2.6. Similar to Fig. 7-2.5, except that the field is applied along the polar axis ($\theta = 0^\circ$). The jump in the magnetization occurs at $h = 1$. No reversible rotation occurs.

Fig. 7-2.5. The orientation of the magnetization $\mathbf{M}$ of a single-domain ellipsoidal particle as a function of a field applied perpendicular to the particle’s polar axis ($\theta = \pi/2$) is illustrated. In (a) the vectors above the ellipses represent the field, whose magnitude is also indicated in units of $h$. The arrows within the ellipse represent the magnetization. The magnetization curve, plotted in the reduced units of $M_s/M$ versus $h$, is shown at (b). The numbers 1, 2, 3, ..., 16 correspond to successive stages in the application of the field. The hysteresis is zero.

: for recording media, particles must be aligned with their easy axes || the direction in which the write field will be applied.
Inter-Particle Interactions

- When shape anisotropy is dominant, $H_c \downarrow$ as packing density $\uparrow$ because of inter-particle interactions.

> Coercivity (Oe)

![Graph showing coercivity vs packing density for elongated Fe-Co particles]

- Qualitatively:

> \begin{itemize}
>     \item Field from particle A
>     \item Field from A acting on C assists applied field \Rightarrow C reverses its magnetization at a lower applied field.
>     \item Opposite occurs @ B! \} COMPLICATED MANY BODY PROBLEM
> \end{itemize}

\* as packing density $\uparrow$, interactions $\uparrow$ \*

\( \diamond \) for media it is desirable to isolate the particles
Fig. 11.1 Variation of coercivity with particle size for particles deriving their coercivity principally from crystal anisotropy. Luborsky [11.9]

- As size ↓, Hc ↑ as particles change from multi-domain (where magnetization occurs by domain wall motion) to single-domain (where magnetization changes occur by spin rotation).

- Hc reaches a maximum, then Hc ↓ as size ↓ because of THERMAL EFFECTS. The magnetic anisotropy energy which keeps the magnetization stable is reduced as size ↓, so approaches the thermal energy, kT.
Superparamagnetism

\[ H_c \]

\( \text{Single-Domain} \) \( \text{Multi-Domain} \)

Particle diameter

at constant temperature

Superparamagnetic

- Below a certain diameter, the coercivity is zero, because thermal effects are strong enough to demagnetize the particles.

\[ \text{Anisotropy energy (which provides the coercivity)} \]

\[ = KV \]

\( \text{anisotropy constant (ergs/cm}^3\) \)

\( \text{volume of particle (cm}^3\) \)

- as \( V \downarrow \), \( KV \approx kT \)

Thermal energy can overcome the anisotropy force and spontaneously reverse the magnetization of a particle from one easy direction to the other, even in the absence of an applied field.
Magnetic moment of a PARTICLE = $\mu_s V$

- Applied field tends to align particles
- Thermal energy tends to disalign particles

\* LIKE A PARAMAGNET \*

\[ M \text{ (atom)} \approx M_0 \]
\[ M \text{ (50Å particle)} \approx 10,000 M_0 \] \{ SUPERPARA-MAGNETISM \}

If anisotropy = 0 the moment of each particle can point in any direction, so the classical theory of paramagnetism will apply. So the magnetization, magnetic moment per particle

\[ M = N m H z(x) \]

# particles per unit volume \[ \frac{mH}{kT} \]

Because \( M \) is large, \( z \) is large: full magnetization curve, up to saturation, can be observed easily for superparamagnetic particles. (Remember for ordinary paramagnetic materials, very high fields & low temperatures are required).
If anisotropy is finite and particles are aligned with easy axes // each other + the field, then the moment directions are quantized, 

\[ M = Nm \tanh \alpha \]

(The hyperbolic tangent is the special case of the Brillouin function with \( S = \frac{1}{2} \) i.e. only 2 spin orientations are allowed).

General Case non-aligned particles with finite anisotropy – neither of these equations for \( M \) is true. Also, in most samples, all particles are not the same size, + the moment per particle (\( M \)) is not constant.

But in all cases there is no hysteresis (i.e. \( B_r, H_c \) are zero) :: BAD for recording media!

Superparamagnetism can be destroyed by reducing the temperature or increasing the particle size, such that \( KV > kT \).
Magnetization curves of iron particles 44 Å in diameter.

200K, 77K - typical superparamagnetic behavior

4.2K - particles don't have enough thermal energy to come to equilibrium with the field, hysteresis appears (only half the loop is shown).
Magnetoresistance

- The resistance of a material changes when a magnetic field is applied.

\[
\text{MR ratio} = \frac{\text{change in resistance when field is applied}}{\text{resistance at zero field}} = \frac{R_{H} - R_{0}}{R_{0}} = \frac{AR}{R}
\]

Recently, MR has been of great technological interest.

"Magnetoresistance in metals is hardly likely to attract attention except in rather pure materials at low temperatures."

Sir A.B. Pippard, F.R.S., 1989

MR materials are used today in commercially available

- magnetic sensors
- magnetic recording heads
- magnetic memories
CMR Material: \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \)
Colossal Magnetoresistance (CMR) in doped LaMnO$_3$

LaCaMnO film at 77 K

FIG. 1. The phase diagram of \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \), based on the present work. The transition temperatures are taken as the inflection points in \( M(T) \) and \( \rho(T) \), and \( T_N \) for \( x = 0.48 \) and 0.50 is obtained on warming at \( H = 0.1 \) T.

LaMnO₃

all manganese ions are Mn³⁺

with four 3d electrons

↑↑↑↑↑
d electrons align parallel (Hund's rule)

there is one empty orbital.

"Superexchange" \(\Rightarrow\) AFM Mn-Mn ordering

if O²⁻ is between two empty orbitals!

\[\begin{array}{c}
\text{↑} \\
\text{Mn}^{3+} \\
\text{↑} \\
\text{C}^{2-} \\
\text{↓} \\
\text{Mn}^{3+} \\
\end{array}\]

\[\begin{array}{c}
\text{↑} \\
\text{Mn}^{3+} \\
\text{↑} \\
\text{O}^{2-} \\
\text{↓} \\
\text{Mn}^{3+} \\
\end{array}\]

\(\Rightarrow\) FM Mn-Mn ordering

if O²⁻ is between one empty and one filled orbital!
Double Exchange / C. Zener, PR 82, 403 (1951)

\( \text{Mn}^{3+} \): four 3d electrons
\( \text{Mn}^{4+} \): three 3d electrons

Electrical conductivity takes place by an e\(^-\) on \( \text{Mn}^{3+} \) moving to a \( \text{Mn}^{4+} \) via the intervening oxygen ion
\[ \text{Mn}^{3+} - \text{O} - \text{Mn}^{4+} \rightarrow \text{Mn}^{4+} - \text{O} - \text{Mn}^{3+} \]

This is called **double exchange**. The electron transfers from the left \( \text{Mn}^{3+} \) to the oxygen ion simultaneously with the transfer of an electron from the \( \text{O}^{2-} \) ion to the right-hand \( \text{Mn}^{4+} \).

Double exchange can only occur if the spins of the two Mn ions are parallel.

\[ \downarrow \]

FM alignment

(cf. **superexchange** \( \Rightarrow \) AFM alignment)

CMR occurs because there is a phase transition between a PM insulator and a FM metal, induced by an applied magnetic field.