STRUCTURAL PROPERTIES OF MICROEMULSION-DERIVED

Fe$_2$O$_3$ MICROPARTICLES

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We propose to take an applications-oriented view of microemulsions (ME); that is, we will not study the ME system per se, but use it to produce something else; then, by looking at the end product, we will try to deduce something about the precursor ME. In particular, we have applied the ME technique to synthesize microcrystals (or microparticles, since they may sometimes be amorphous) of Fe$_2$O$_3$.

What is so Interesting about Microcrystals?

We can adopt the following two (not completely equivalent) approaches for studying microcrystals (MC):

a. One can gradually build up a solid starting from a single atom or molecule and try to determine how many atomic units are necessary for it to actually start showing bulk-like solid state properties. Such an approach has been taken, for example, by Sattler's group[1] who have built up metallic clusters (2-500 atoms) by inert gas condensation of metallic vapours.

b. Alternatively one can attempt to synthesize smaller and smaller microparticles and observe just how the long-range cooperative properties (like ferromagnetism, ferroelectricity and superconductivity) get affected by decreasing the particle-size. We have adopted the second approach and have been studying mainly oxidic ferromagnets and ferroelectrics.

How Small is Small Enough?

This really depends on the particular property that we wish to study. For tightly bound electrons and many types of atomic oscillations, short-range potentials are most significant. In such cases a MC of as small as 10 lattice units across would presumably show "bulk" behavior.

However, for the properties determined predominantly by long-range Coulomb interactions or other collective excitations, a crystallite as large as 1000 Å may show significantly different properties when compared with the bulk solid.
Which are the Solid State Properties Affected?

1. Due to the significantly larger number of atoms lying on or close to the surface, various surface effects become predominant in MC. Since the surface in some sense forms an extended defect, this would also affect the core.

2. Due to the relatively smaller number of available electrons, the electronic energy level distribution may become discrete.

3. The phonon spectrum too shows significant changes on going over from bulk to MC due to: a) broken bonds at the surface, b) surface modes, c) change in magnitude of the long-range Coulomb forces and d) a low-frequency cut-off arising from the absence of phonons with a wavelength > D, the crystallite dimension.

4. The MC may be seen as a poor man's pressure apparatus. It can be predicted (qualitatively) from a first-principles theory using Lennard-Jones potentials, that the surface free energy term would lead to a lattice expansion (Negative Equivalent Pressure) in covalent MC, and a lattice contraction (PEP) in ionic MC. This has been experimentally verified in a few materials, e.g. a NEP = 180 kbars has been found in 50 Å Fe₂O₃ MC[2].

How does one make Microcrystals?

1. Precipitation: a finely precipitated material may be dried and heated at low temperatures. The resulting particle size (PS) distribution is rather broad.

2. Hydrosol: preparing a colloidal dispersion in water. This is mainly suitable for metallic MC of some types.

3. Vacuum Evaporation: may be used for some metals and simple compounds. Deposition is on a cooled substrate. Reproducibility is difficult to achieve.

4. High-area Silicates: Many types of MC may be produced by impregnating high-area silicates with a suitable solution and calcining at low temperatures. The PS is reproducible and controllable.

5. Sol-gel: a suspension of metallic oxides/hydroxides (sol) is converted to a semi-rigid mass (gel) by a dehydrating agent, which is heated in vacuum to get the MC.

And the latest technique...

Microcrystals via Microemulsions

Metallic MC have been recently produced by a similar method[3]. We have modified the method for metallic oxides as well. The process consists of:

a) Preparing a thermodynamically stable, optically isotropic three component system consisting of water, hydrocarbon and surfactant. The aqueous phase contains a soluble salt of the metal concerned. The essential constituents are:

- aqueous phase → ferric nitrate solution
- oil/hydrocarbon phase → 2-ethyl hexanol
- surfactant phase → sorbitol mono-oleate