



## Nanocomposites: A New Paradigm in Materials

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### Materials

We learn from books that matter exists in three states, solid, liquid and gas. However, in our daily lives we know that this is not always true. For example, we never see something like 'liquid stone' or 'wood vapor'! On careful observation we find that our first statement is strictly true for only some types of matter that are composed of the same atoms or molecules everywhere. These are what called *substances*. Substances have fixed compositions and structure and so they have fixed properties. The most important of these properties is precisely the occurrence of well-marked regions of temperatures and pressures within which the atomic or molecular structure of the substance remains unchanged, such as in solid, liquid and gas, as well as structural variants in the solid state, where these structures are called *phases*, and they change from one to the other at fixed temperatures and pressures. Some of the common substances are elements and compounds, such as gold, iron, water, and common salt, etc.

The other type of matter does not have a fixed composition. These are the materials. Materials include substances as a special category but, in general, they are *homogeneous* or *heterogeneous* mixtures of substances. In the former the substances mixed together, or the *components*, are in the same ratio everywhere in the mixture though this ratio may vary from mixture to mixture. Examples are air, saline water, and bronze. Since the composition of a homogeneous mixture is same throughout the mixture, we can mark out phases of such mixtures. However, since we can vary this composition, the composition also becomes a 'field parameter' like temperature and pressure that can be varied to get new phases. We shall call such systems *mixtures* in general. As is clear, the number of mixture phases is much larger than the number of phases of a substance.

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A convenient way to present the behavior of a material over the possible range of external or field parameters for which the material is chemically stable is to plot the values of these parameters at which transitions from one phase to another take place. The resulting curves segregate the entire parameter space into the possible phases of the material. This plot is known as the *phase diagram* of the material and the parameter space on which the phases are shown is the *phase space*. For substances, the phase space is two-dimensional and is in most cases a pressure-temperature ( $p$ - $T$ ) space. For mixtures, the phase space is  $(n+1)$ -dimensional, where  $n$  is the number of components in the mixture, and the field parameters are  $p$ ,  $T$ ,  $\rho_1$ , ...,  $\rho_{n-1}$ ,  $\rho$  being the density or concentration of a component.

### Composites

Materials may also have spatially variable compositions, structures, and properties when they are heterogeneous mixtures. Wood, stone, and milk are some common examples. Since these mixtures have different compositions at different regions, a convenient first step to analyze them is to break them up mentally into domains within which the composition is constant. If in this process, we end up with finite sized domains then we call the mixture a *composite*. By this criterion, membranes, multilayers, inclusion alloys, and most of the multi-structured materials, natural or artificial, can be termed composites. However, the composition may also vary continuously, as in some mixtures of viscous liquids and some glasses, as well as in igneous rocks. In those cases, the domains become infinitesimal in size.

The crucial new feature that emerges in composites is the presence of *interfaces* between the domains. The interfacial region separating domains A and B will not be entirely like either of them. In general, it will be a mixture of these domains but unlike a homogeneous mixture in three dimensions, the interfacial region can be considered as a uniform mixture along the boundary interface but with a continuous gradient of composition along the local normal to this interface. Thus the free energy distribution along and normal to the interface are quite different and as a consequence all properties show this asymmetry.

The region normal to the interface is almost infinitesimal relative to the interface area and a consequence of this asymmetry is that any stress developed normal to the interface is easily absorbed along the interface. This gives composites a huge enhancement in mechanical stability over substances or uniform mixtures. Similarly, as domains of different substances try to change in phase, e.g., melt, the adjacent domains of other compositions may remain away from their specific transition point and absorb the transition enthalpy from the former domains, thus preventing them from making the transition. That is the reason we see wood burning but not melting and stones showing almost no phase transition except in such extreme conditions as in volcanic eruptions.

Due to the almost infinite ways these domains can vary in shape, size, and distribution they pose a serious problem to the materials scientist since it is impossible to reproduce a composite material faithfully. All we can hope for is that even under identical growth conditions the composite products can only be described within an average composition and likewise only their average properties can be relied upon. In fact, due to this uncontrollable and huge fluctuations it is not really correct to assign 'phases' to these materials although they are definitely in equilibrium.

### Nanocomposites

When one or more components of a composite material is present in domains that are of nanometers in one or more dimensions then the composite is a *nanocomposite*. The nanocomposite may have the components in question as nanometer-thick layers or ribbons, or nanometer-sized particle, as examples of domains that are nano-dimensional in one, two, or three dimensions, respectively. Another way of achieving a nanocomposite is to have the components in larger domains but located in the matrix with mutual separations in the range of nanometers. Ancient examples of the former are colored glasses and ceramics having nanodomains of metals and metal oxides imparting the specific colors, while a natural example of the latter is mother-of-pearl

where microcrystalline domains of  $\text{CaCO}_3$  in the aragonite form stack up with fixed orientations within a protein matrix. These orientational super-domains are large enough to scatter light within a particular band in a specific direction but they are randomly oriented themselves and also have a size distribution to finally scatter differently colored light in different directions, giving rise to the familiar iridescence.

Nanocomposites differ in two important aspects from composites. First, due to their size the interfacial zone spreads inside the nanodomain, in fact, dominates it. Hence, in a binary nanocomposite of B in A the composition and structure of the nanodomains of B will be very different from B in bulk. How much this difference will be is determined by the shape and, most crucially, the size of the nanodomain. It would also be very much controlled by average separation between any pair of nanodomains, which in turn decides interdomain forces. Hence the structure and properties of these domains and thus of the nanocomposite itself can be tuned by the domain size and separation. We should note that the nanodomains have a very large surface-to-volume ratio. Thus a nanocomposite has an enormous effective surface giving rise to high enhancement of surface-related properties like adsorption, catalysis, giant magnetoresistance, electromagnetic dispersion that leads to refractive index tuning and metamaterials, mechanical and thermal shock absorption, elasticity and tensile strength, to name just a few.

However, the other fundamental difference between a nanocomposite and a composite lies in the ease of growing nanodomains of fixed composition, size, and shape. For most substances these can be kept well within 10% fluctuation and hence the nanocomposites containing these domains are reproducible enough for consistent and rigorous structural and dynamical studies. These studies can be used to assign 'phases' to the material, which will obviously be endowed with a very rich phase-space. The nanodomains may form ordered 'lattices' giving rise to different 'super-crystalline' phases, 'glassy' phases, and even very dilute phases having correlation length and continuous translational and rotational symmetries resembling 'fluids'. All these phases may have specific transitional behavior, study of which can enrich our understanding of materials and expand our ability to manufacture new materials.

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