NANO MATERIALS - AN EQUATION OF STATE – B.Viswanathan

In an earlier presentation in this site, the question regarding the equation of state for nano materials was raised and it has been left out without answering. It is generally known that the question of state has to connect the fundamental thermodynamic variables of pressure, volume and temperature and it has to do with the energy content of the system in some form. In continuum mechanics, an equation of state suitable for modeling solids is naturally rather different from the ideal gas law. A solid has a certain equilibrium volume V_0, and the energy increases quadratic ally as volume is increased or decreased a small amount from that value. The simplest plausible dependence of energy on volume would be some constant value of energy E_0 and also the variation with volume somehow related to the bulk modulus which is the derivative of pressure with volume. Since the solids are nearly incompressible the equation of state predicts not much of variation.

The possible available equations of state for solids go with the names of Murnaghan equation of state and also that of Birch–Murnaghan equation of state. As is the case with gases there can be a number of equations of state with a variety of power series. In all these available equations of state it is generally felt that the variation of volume or pressure with respect to the energy of the system is small and hence the thermodynamic variables may not have considerable influence in the behaviour of these systems under normal variations of these parameters.

However in the case of nanomaterials, these parameters have quite a different significance. For example it is known that the nanomateials have very low melting point (this can be as low as room temperature depending on the size of the nano particles) and hence volume variation with either temperature or pressure should be different from that of the bulk solid. These moduli can have significant influence on the behaviour of these solid state (so called) materials.

One has to also consider the fact that the energy contents of these systems and their variation with the thermodynamic variables can be expected to be totally different from that of the bulk solids. The support for this proposition comes from the fact that these nano state materials can manifest all the forms of electronic behaviour, namely metallic, semi-conducting and insulating type. Another factor is that the mobility of the charge carriers in these systems can be totally of different magnitude and hence their temperature (other thermodynamic variables) dependence can be different from the known types of variation.

The another parameter of significance is the derivative of pressure versus volume (the so called surface or bulk modulus) or dependence of energy with respect to pressure or even volume since in nano state the system is in a dilatory condition and hence the energy per unit volume can be different from that of the bulk solids.

Hence it is clear that the correct form of equation of state may account for many of the properties associated with this type of materials. We do hope we will continue on this discussion.