3.7: Non-fluid Systems

All the results of the previous section relied on the underlying assumption that the system was a pure fluid and thus could be described by specifying, for example, the temperature T, the volume V, and the particle number N. Recall that the latter two were simply examples of many possible mechanical parameters that could be listed, such as the molecular mass, the molecular moment of inertia, or pair interaction parameters such as the hard-sphere radius or the Lennard-Jones parameters.

But of course nature presents us with many materials that are not pure fluids! One obvious example is a fluid mixture, the specification of which requires the number of molecules of each constituent. Another example is a crystal of a layered material such as graphite. To find the energy, for example, it is not sufficient to specify only the volume. You must know the area of the layers and the height to which these layers are stacked.

In this book we will focus instead on a third example, namely magnets. The fundamental thermodynamic relation for magnetic systems is

$$dE = TdS - MdH, \tag{3.7.1}$$

where H, the applied magnetic field, is an intensive mechanical parameter and M, the magnetization (total magnetic dipole moment of the sample), is extensive. Just as the thermodynamic equations for fluids presented in the previous section implicitly assume that the magnetic properties of the sample can be ignored (either because the substance is non-magnetic or because the magnetic field does not change), so the equation above implicitly assumes that the volume and number specification of the sample can be ignored.

In another course, you may have learned a mnemonic for remembering the thermodynamic differentials and Maxwell relations of a pure fluid systems with a constant particle number. Such mnemonics encourage the very worst problem solving strategy, namely "poke around until you discover an equation that fits". Anyone who uses this strategy finds it impossible to investigate mixtures, crystals, magnets, or any other member of the rich array of materials that nature has so generously spread before us. Instead of memorizing equations and hoping that the right one will present itself, you should think about what sort of equation you will need to solve a problem and then derive it. Appendix J will remind you of the strategy of the thermodynamic dance and will help you keep your signs straight.

3.28 Magnetic systems

Show that for magnetic systems (see equation (3.100)),

$$\frac{\partial M}{\partial T})_H = \frac{\partial S}{\partial H})_T \tag{3.7.2}$$

and

$$\frac{\partial H}{\partial T})_M = -\frac{\partial S}{\partial M})_T. \tag{3.7.3}$$