PDF file of this section

AGGREGATES OF ATOMS: ORDER AND DISORDER

The objects around us in our everyday life range in size from millimeters to hundreds of meters. But molecules have sizes of less than a billionth of a meter. Things that are ’our size’ therefore contain unimaginably large numbers of atoms (of the order of a million, billion, billion or 10^{24}). How can we understand the behavior of these enormous atom aggregates? Recall that molecules interact - attract and repel each other - even when they do not form chemical bonds. And we also saw how ’molecules’ can extend indefinitely in two or three dimensions - a topic taken up in greater detail in later sections. But are there fundamental guiding principles which allow us to understand how aggregates of atoms and molecules behave?

One of the most profound and important principles which guide our understanding of matter in aggregation is provided by the science of thermodynamics which developed in the Nineteenth Century in response to the engineering and scientific challenges posed by the developing technology of heat engines - in particular the question of the factors which limited their efficiency. And it is one of the most fascinating features of the history of science that this problem in applied science provoked the formulation of one of the most philosophical, profound fields of science. Indeed, considerable mystique has tended to surround the celebrated *’Second Law’* of thermodynamics. However, the basic ideas in thermodynamic theory are simple.

The ’First Law’ has a variety of formulations, but they all correspond to the principle of conservation of energy - the statement that energy is never created or destroyed. Energy is, of course, a key scientific concept which developed along with thermodynamics. It is manifested in numerous forms including motion (kinetic energy),position (potential energy),heat, chemical and electrical energy (as discussed in further detail in the Appendix) which can be interconverted. The usefulness of the concept of energy arises from the principle of conservation which is simply a statement to the effect that with regard to energy, nature operates a "fixed exchange rate" policy: a given amount of electrical energy will, for example, always be converted into the same amount of heat energy and *vice versa.*

The second law is far more subtle and in its most general and useful formulations is one of the most far reaching of scientific concepts. Of the many different ways of stating the law, perhaps the most simple and widely used application is as follows: *’Systems, when considered in their totality, evolve towards a state of increasing entropy.’* Entropy is a precisely definable and measurable quantity which can be interpreted qualitatively in terms of the degree of disorder in the system - a concept that can be underwritten mathematically as we will see shortly. All the other statements of the second law with which the reader may be familiar can be derived from or are equivalent to this formulation. For example, the well known (and correct) statement that "entropy is time’s arrow" merely emphasises that by "evolve" we mean evolve in time.

Thermodynamics is a subject concerned with "macroscopic observables" but it is linked to the microscopic world of atoms and molecules by one of the most important equations of physics:

$$S = k \log_e(W)$$

where S is the entropy of a system, k is a constant (known as the Boltzmann constant after the original formulator of the equation, Ludwig Boltzmann), W is the "probability" of the system in its mathematical sense, that is the number of distinct waysof arranging the atoms or molecules that are consistent with the overall properties of the system. Systems that are ’disordered’ at the atomic level have higher probabilities and hence higher entropies. Boltzmann’s equation therefore gives precision to the interpretation of entropy in terms of disorder; it also unites the macroscopic science of thermodynamics with the microscopic subject of *statistical mechanics* that explores the statistical behavior of matter at the microscopic level.

The second law gives a verifiable and exact expression of one of the most basic features of nature - the drive towards states of increasing disorder. But ordered structures are common in nature. Indeed, we will describe the complex and ordered atomic structures present in crystals; and the science of crystallography is about ordered structures in three dimensions. Living matter is remarkably organised and its high level of organisation is essential for its function. If the relationship between order and entropy means anything, then both crystals and living matter must be low entropy systems. How then do they survive in a universe which is constantly evolving to a state of higher entropy?

The key to this problem which has caused much confusion can be found in our formulation of the second law which we recall referred to systems considered *"in their totality"*. Crystals and living matter are normally only part of a total system; they are surrounded by an environment with which they exchange heat (and possibly matter). The relationship is cleverly formalised in thermodynamics where we focus on the component (the subsystem) of the total system in which we are interested (say our crystal) and consider the rest as a "heat bath" which can supply or withdraw heat and which is characterised by its *temperature.* Next we need to realise that ordered states commonly have low energies - a point to which we return. And on passing from anordered to a disordered state, our ’subsystem’ must absorb energy from itssurroundings. But when we withdrawenergy from the surroundings, they become less disordered; that is, theylose entropy. So what happens depends on the balance between the entropychange in the subsystem and that in its surroundings. Again, the formulation of thermodynamics theory allows us to deal with this complex problem in a straightforward way. The loss of disorder, *i.e.* of entropy, on withdrawing energy from the surroundings decreases with the amount of energy in these surroundings; and the greater the amount of energy in a body, the higher its temperature. So the higher the temperature, the lower the entropy loss. Thermodynamics expresses this intuitively obvious relationship by a precise mathematical relationship: it says that the change in entropy (for which we will use the symbols DS) of any system or subsystem (like our "thermal bath") is related directly to the heat gain or loss (represented by the symbol Q) but scaled by the inverse of the temperature:

$$\Delta S = Q / T$$

which is another of the handful of key equations in science. And temperature in the context of thermodynamics is *defined* so that this equation is true. Moreover, a consequence of this thermodynamic definition of temperature is the concept of "absolute zero" of temperature - a state in which the system has no energy and at which classical physics would lead us to expect completely motionless arrangements of atoms. However, one of the many bizarre consequences of quantum mechanics is the failure of this classical concept. Even when they have no energy, atoms must move, they have *zero point* motion; if they did not, we would know exactly where they were, contradicting the uncertainty principle. ’Absolute zero’ is a hypothetical state; it may never be achieved, although low temperature physicists have got to within a few millionths of a degree of this ideal ’energy less’ state.

But to return to order and disorder, at low temperatures systems tend to adopt an ordered state. As noted above, ordered states are energy efficient. To achieve disorder, a state has to withdraw energy from its surroundings which reduces *their* disorder. As the temperature increases, this loss of disorder from the surroundings becomes less and less, and our system will increasingly pull in energy to achieve greater disorder for itself. One of the most interesting and dramatic of such changes is the process of melting. Crystalline solids are ordered arrangements of atoms; liquids are characterised by disorder at the atomic level. The process of melting - the conversion of the ordered crystalline state into the disordered liquid - invariably requires an input of energy (known as the latent heat of melting) to create the less energy economical disordered state. The crystal melts at the temperature at which the increase in entropy associated with melting outweighs the loss of entropy of the surroundings associated with the system withdrawing the latent heat.

The development of thermodynamic theory and the associated subject of statistical mechanics represent another of the great intellectual achievements of modern science. They allow us to understand the fundamental factors controlling the behavior *in aggregate*of the unbelievable numbers of atoms and molecules present in the objects around us; they bridge the microscopic and macroscopic worlds. And they allow us to understand the balance between order and disorder in the universe. The most ordered of objects are crystals.

Liquids and Glasses