Teacher notes
Topic B

Internal energy

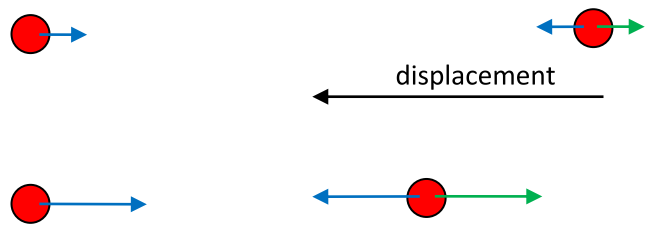
The internal energy, U, of a substance is defined as the total *random* kinetic energy of the molecules plus the total intermolecular potential energy of the molecules. It is important to stress the word random. Thus, a block of copper at temperature T and an identical block at the same temperature will have the same internal energy even if the second block is made to move at high speed (by putting it on a plane say). This is because the high speed of the plane does not contribute to any random motion of the molecules.

Intermolecular potential energy is also an obscure concept for students. Potential energy, in general, is the work that needs to be done by an external agent to bring a system into a given state. Examples include:

Lifting a book from the ground and placing it on a table a height h from the ground. The work done is mgh and this is the potential energy of the book on the table.

Stretching a spring by a distance x over the natural length of the spring. The work done is $\frac{1}{2}kx^2$ and this is the potential energy of the spring when extended.

What about the intermolecular potential energy? There are forces between molecules which are mainly attractive. So to increase the separation of two molecules an external agent will have to do work. That work is the intermolecular potential energy of the two molecules. Adding up the intermolecular potential energy of all pairs of molecules gives the intermolecular potential energy of the substance. Now, increasing the separation of two molecules by a very large distance (formally infinite) should result in a state with zero potential energy because the molecules are so far apart, they exert zero forces on each other and are not aware of each other. This means that when the molecules are a finite distance apart, their intermolecular potential energy must be negative. We can think of this differently as follows. The state when the two molecules are infinitely apart is the state of zero potential energy. An external agent will now move one molecule slowly and bring it to a finite distance from the other molecule. The work done by this external agent will be the potential energy of the pair of molecules. But the work done must be negative: the molecules attract (blue arrows) so the external agent must apply a force (green arrows) to keep the molecules from running into each other.

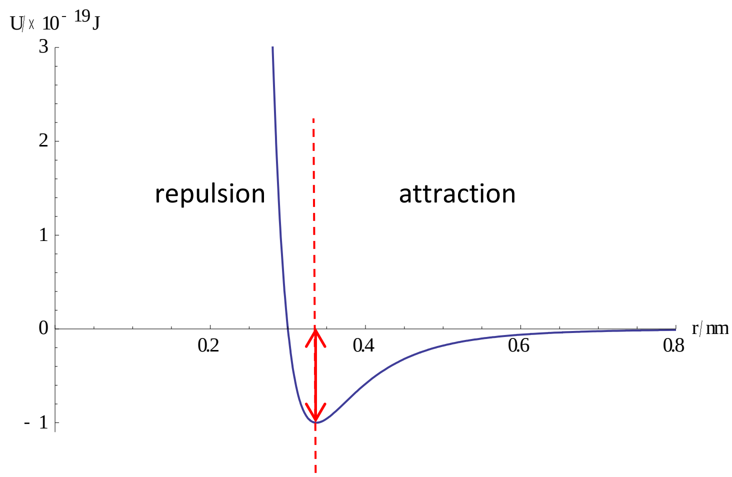


But the displacement is in the opposite direction to that of the force and so the work done is negative.

The potential energy is a function of the separation *r*. The negative gradient of the graph of potential energy versus separation gives the force between the pair of molecules. A positive force implies repulsion and a negative force attraction.

A simple and widely studied model for the potential energy of two molecules separated by a distance *r* is the Lennard-Jones model (named after John Lennard-Jones, an English chemist). It is given by

$U(r)=\frac{A}{r^{12}}-\frac{B}{r^{6}}$ where *A* and *B* are constants. This is plotted below.



The model assumes interactions between pairs of molecules only. We see from the graph that the gradient is positive (and hence the force is attractive) for $r > 0.34$ nm. At $r = 0.34$ nm the force is zero and so this represents the equilibrium separation of the pair of molecules. The potential energy of the pair is negative for $r > 0.3$ nm. As the separation increases the potential energy *increases* and approaches zero. This is why we say that an ideal gas (with no forces between the molecules) has greater internal energy than a liquid at the same temperature. This is consistent with the fact that a liquid at its boiling temperature must be provided with energy (the latent heat of vaporization) to turn it into vapor at the same temperature. Providing the latent heat of vaporization increases the intermolecular potential energy but not the random kinetic energy of the molecules and thus increases the internal energy. The intermolecular potential energy *increases* from some negative value to zero.