Intermolecular Forces: the Lennard-Jones Curve
or, how a little can explain a lot

In the 1920s, John Lennard-Jones proposed a simple mathematical model to explain many simple observed facts about solids. Others have since found more accurate models, but its simplicity and relative power make it still relevant today in mathematical modelling of solid behaviour. This document will lead you through the ideas behind it, and shows how it can explain why solids expand when they get hot, why soap bubbles are spherical and why many solids obey Hooke's Law.

In simple terms, Lennard-Jones started with the very obvious fact that most solids are fairly difficult to squash or stretch. Since solids are made of atoms, these atoms must have strong **attractive** forces between them (or they wouldn't resist tension), yet also exert strong **repulsive** forces on each other when pushed together (otherwise they wouldn't resist compression). For a solid left to its own devices, these attractive and repulsive forces must **balance** each other, leaving the particles in equilibrium with each other. If you can find mathematical expressions for these two sets of forces, simply adding the two expressions would give you a function you could plot on a graph.

Attractive Forces
These are caused by the interatomic forces that atoms experience when placed closely enough together: ionic/covalent/van der Waals *etc*, depending on the type of atoms. Lennard-Jones used a $1/_{r^7}$ function to model these forces (*i.e.* as the distance between the atoms (r) doubles, the attractive PE goes down by $2^7 = 128$ times)[*].

Repulsive Forces
Although atoms in a solid attract each other, they obviously must repel each other as they get closer (*Why? What would happen if they didn't?*). In simple terms, as two atoms are pushed together the electron clouds of the atoms eventually start to overlap each other and repel, simply because like charges repel[†]. Lennard-Jones used a $1/_{r^{13}}$ function to model the Potential Energy change caused by these forces (*i.e.* as the distance between the atoms (r) halves, the repulsive PE goes up by $2^{13} = 8192$ times). The actual function is much more complicated than this, but using the more accurate function does not lead to a noticeably more accurate model for many purposes.

Questions
1) **What would happen if we lived in a Universe where atoms didn't repel each other at all as they got very close to each other?**

2) **Which are stronger: the attractive or the repulsive forces between atoms?**
   (*Careful: this is not a simple either/or question*)

3) **You have probably been taught (more than once) that particles in solids behave as if they are connected together by tiny springs. Explain in what way(s) Lennard-Jones's model is similar to a spring, and in what way(s) it is different.**

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[*] In fact, Lennard-Jones modelled the *Potential* function between the two atoms. Potential is very closely related to Potential Energy: it's the PE per unit charge (in this case) of the two atoms. You'll learn more about Potential, and its relationship with Force, in the A2 course.

[†] A more correct explanation is that it's the electrons' *orbitals* which overlap each other. The Pauli exclusion principle (from Quantum Mechanics: look it up) forbids two electrons to be in the same energy state at the same time and place, giving rise to a very strongly repulsive force if you try to make this happen by squashing two atoms together.

The most helpful way to see what these functions show about solids is to plot a graph to show how the Forces between the particles change as the particles get closer together or further apart.

The First Graph: Forces

Look carefully at the graph of the Forces between a pair of Na$^+$ and a Cl$^-$ ions, <u>which is typical of nearly all simply-bonded substances</u>.

4)   **a)**   **Read off the distance at which the total Force between the atoms is zero.**
  b)   **What is the significance of this distance?**
  c)   **Around this area of the graph, the total force follows a fairly straight line. How does this explain why many solids obey Hooke's Law?**
  d)   **How would this region of the graph be different for a solid with a much <u>lower</u> Young's Modulus?**

5)   **Shade the half of the graph where the total Force is attractive in one colour and the other half (where the total Force is repulsive) another colour.**

Building on the idea in question 3, we can model the attractive forces between the particles as spring-like and calculate the effective spring constant ($k = \frac{F}{x}$) in Nm^{-1} for the bond and relate it to the Young Modulus of the substance. A simple derivation[‡] can show that $k = r_0 E$, where r_0 is the equilibrium separation of the particles and E is the Young Modulus of the substance.

6)   **The Young Modulus of salt is around 40 GPa. Calculate the effective spring constant of the (imaginary) springs holding the Na$^+$ and a Cl$^-$ ions together.**

7)   **For steel, $E \approx 2 \times 10^{11}$ Pa, and the Iron atoms behave as if connected by springs with $k \approx 60$ Nm^{-1}. Show that the equilibrium separation of the Iron atoms is just less than half a nanometre.**

Surface Tension is the weak force between molecules on the surface of a liquid which makes:

a) water droplets 'bunch up' on a window,

b) liquids form a meniscus inside containers, and

c) makes raindrops and soap bubbles spherical)

The existence of surface tension forces can be explained using the graph.

8)   **Inside a liquid, the molecules are more or less at their equilibrium separation. However, the outermost particles on the surface of a liquid can sit slightly <u>further</u> away from each other. Use the graph to explain why they therefore attract each other slightly <u>more</u> strongly than particles inside the body of the liquid.**

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‡ *e.g.* in **Nuffield Teachers' Guide 1** (1985), p44

The Second Graph: Energy

You can also plot how the PE of the particles changes as their separation changes. Look carefully at the example for a pair of Na$^+$ and a Cl$^-$ ions.

9) **At first, the Energy graph looks almost identical to the Force graph. Compare the two carefully and play Spot the Difference (not counting tediously pedantically obvious things like titles, axis labels, numbers *etc.*).**

10) **Without using the key under the graph's title, how can you see that the attractive Energy (the red dotted line) follows a $1/r^6$ function, but the repulsive Energy (green dashed line) follows a $1/r^{12}$ function?**

11) **Mark the equilibrium separation of the ions (*i.e.* the distance you found in q4a) on the graph. Explain why the graph does what it does at this point.**

12) **Shade the half of the graph where the total Energy is attractive in one colour and the other half (where the total Energy is repulsive) another colour.**

Practically all solids **expand when heated**. This can also be explained using the graph.

13) **As a substance is heated, its particles vibrate about a fixed position. Show on the graph how the particles' PE would change as they vibrated.**

14) **Now show on the graph what would change as the substance is heated more strongly (*i.e.* as the particles vibrate more violently).**

15) **If you have answered the last two questions correctly, looking carefully at the graph should make it clear why solids expand when heated. Write a short note on the graph explaining why this happens.**

Melting
The Total Attractive Energy (ε) of a pair of particles is equal to the depth of the curve below the *x*-axis[§].

16) **Measure ε for Salt from the graph, and convert it to Joules.**

17) **Salt is ionically bonded. Would you expect ε to be much bigger or much smaller for a substance which is held together by van der Waals' bonds?**

Taking the ideas from q13-15, if a solid is heated enough, the particle vibrations eventually become so violent that some bonds are broken and the solid liquefies. This tends to happen when the particles' energies starts to exceed about $\frac{\varepsilon}{10}$.

18) **Mark the region on the graph above the curve where Salt exists as a solid and where it exists as a liquid.**

19) **In which region of the graph would the substance exist as a gas?**

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§ See **Essential Principles of Physics** (Whelan and Hodgson, 1978), p120