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# THE SIZE AND SHAPE OF MOLECULES

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IN the study of the size and shape of atoms and molecules, modern physics and chemistry make use of the same methods and rely upon the same principles of mechanics that are employed in modern engineering practice. It is not at all far-fetched to speak of the "civil engineering" or the "mechanical engineering" or the "electrical engineering" of the atoms and molecules. In fact it was one of the greatest electrical engineers that ever lived, Lord Kelvin, who first gave us a definite conception of the size of molecules.

Molecules, as everyone knows, even if he has never studied chemistry, are the smallest particles of compounds which can exist as such. Atoms are the smallest particles of elements. There are probably just 92 elements in our universe, of which 90 have now been discovered, examined, and named. Atoms of two or more different elements combine with one another to form molecules, which as we have just said, are the ultimate particles of compounds. Vast numbers of different compounds are known, perhaps as many as 500,000. Many of these have been found in nature, but the larger part have been made synthetically, "created" in the chemist's laboratory.

Let us now stop for a moment to ask and answer the question: How do we know that molecules exist at all? Not even the most enthusiastic chemist or physicist can claim that he has ever actually seen a molecule. Molecules are much too small to be seen even under the most powerful microscope, and the magnifying power of the microscope has already been developed to the fullest possible extent. We cannot see molecules, and we shall certainly never be able to see them, simply because they are very much smaller than the shortest wave-length of light to which the retina of our eye is sensitive. If we are foolish enough to decide to adopt as our guide in this matter the test that "seeing is believing," we naturally would never be able to believe in the existence of molecules. There are, however, many extremely good reasons for believing in the actual objective existence of these invisible molecules.

For example, if a moth-ball, which consists of the chemical substance naphthalene, is placed on a table in a large room of quiescent air, free from convection currents which might waft the vapors of the naphthalene into all parts of the room, not much time will elapse until naphthalene can really be smelled in every corner of the room. It would be exceeding difficult, if not impossible, to explain satisfactorily how this spread or diffusion of the volatile substance could occur on any other basis than that it is simply a case of the escape of molecules (that is tiny particles) of naphthalene, and a spreading of these molecules in all directions through the air. Such an argument of course does not prove the existence of naphthalene molecules, but it goes a long way toward proving it.

Again, let us take another illustration. Everyone who has looked into the jewelers' shop windows on High Street has seen the little radiometers which spin around in sunlight. The explanation of this effect takes us back to an experiment performed by Benjamin Franklin. One morning after a new-fallen snow, when the warm sunlight was beginning to melt the snow, Franklin went into his back yard and spread out two pieces of cloth, one black and the other white. He observed that the snow melted much more rapidly under the black cloth and concluded that a black surface absorbs sunlight more readily than a similar white surface. Exactly the same principle is involved in our choice of white or light-colored clothes for wear in hot summer weather, rather than black or dark clothes. The same principle enters also into our consideration of this radiometer. The radiometer consists of a small spindle which carries 4 vanes, placed 90° apart, and mounted so that the whole will spin (like a top) in a glass bulb from which most of the air has been pumped out. Each vane is highly polished on one side and blackened with a lamp-black on the other. When sunlight or any strong light shines on the vanes, the black sides become warmer than the polished sides, and the air molecules which are moving about quite freely in the partially evacuated glass bulb, when they strike the warmer side of the
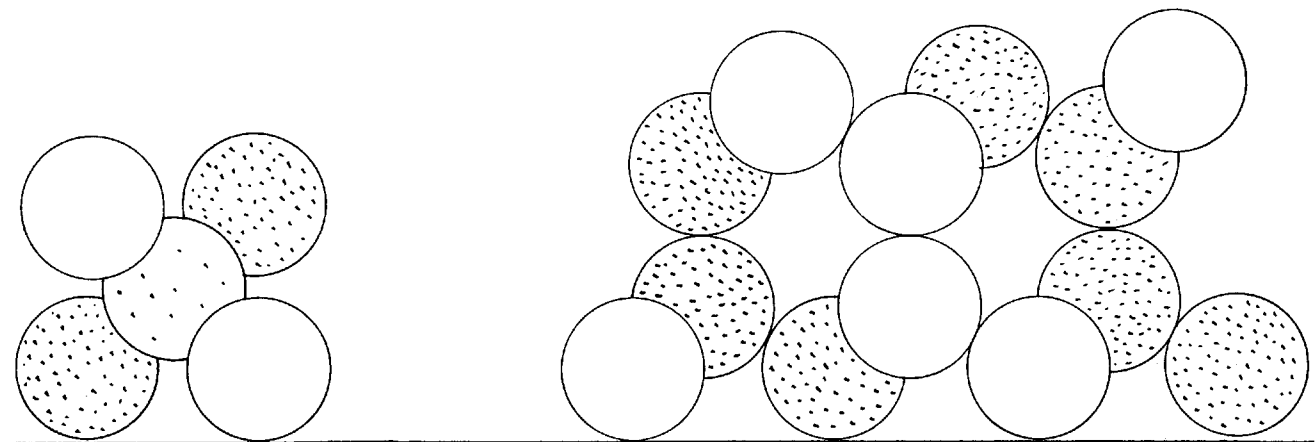


Figure 1



Figure 2

vane acquire a greater velocity of motion and jump away more violently than they do from the polished side, because of this temperature difference. The recoil is sufficient to make the spindle turn. Here, also, it would be very difficult to imagine how this spinning of the radiometer could be set up, if we did not have such things as air molecules.

There are many other even more convincing arguments for the existence of particles of matter, which cannot however be given in detail here, such as the evidence of the spinthariscope, of the Brownian movement, and of the experiment of Onnes with the copper wire in liquid helium.

In Lord Kelvin's time, very little if anything was known about the shapes of molecules, and chemists and physicists for the sake of simplicity assumed that molecules were spherical, and in the text books of that day we note that the molecules were frequently referred to as tiny "billiard balls." Today we have more definite information about shapes of molecules and we may now consider the nature of the evidence.

## X-RAYS

While it is impossible to see the molecules with our eyes, a method has been developed for examining the size and arrangement of atoms and and molecules in crystals by directing a beam of X-rays on a crystal-face in such a way that it will be reflected and registered on a photographic film. X-rays are roughly about a 1000 times shorter than visible light and are of about the same size as atoms and molecules. In this arrangement that we have just described, the photographic film plays the part of a substitute for the retina. When the X-rays strike the crystal face, they are not reflected entirely at the outer surface but they penetrate rather deeply into the crystal. Since crystals all have definite forms, we are certainly justified in supposing that the atoms or molecules, as the case may be, of which the crystalline substance is composed, are all arranged in some perfectly definite pattern, or lattice-structure, layer upon layer. It is the nature of this arrangement which determines what the shape of the crystal shall be. Now, when the X-rays (referred to above) penetrate down into the substance of the crystal they are reflected to some extent from each successive layer of molecules, and from the nature of the photographic effect produced on the film by these reflected X-rays, it is possible to calculate the distance between the successive layers of molecules in the crystal, and, also to arrive at a very definite idea about the arrangement of the atoms or molecules in the crystal.

In this way a very careful study has been made of the structure of the common metals, and a great deal of very valuable information has been accumulated which is of remarkable assistance to us in accounting for the properties of the various metals. For example, it has been recently shown that practically all of the ductile and malleable metals have a certain crystalline lattice structure, and those metals which are brittle and non-plastic have their atoms arranged in some other different pattern.

An especially interesting crystal is the diamond. X-ray examination has shown that the carbon atoms, of which a diamond is composed, as every-



A    Figure 4    B
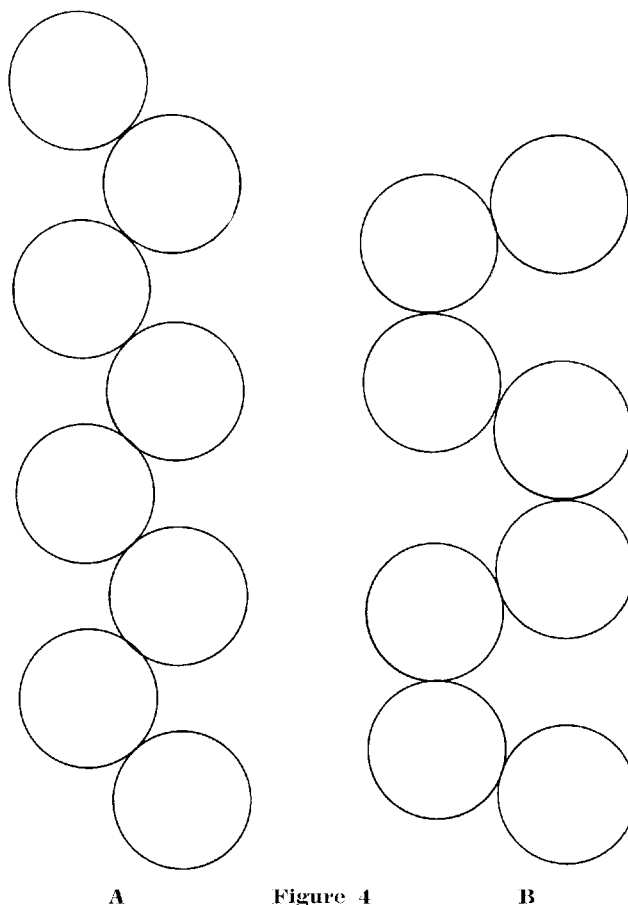
one knows, are arranged in such a way that every carbon atom is surrounded by four other carbon atoms. This is made clear by Figure 1. This arrangement simply amounts to placing a carbon atom at each one of the four corners of a regular tetrahedron, and another carbon atom at the center of the tetrahedron, and repeating this arrangement over and over again in all directions in space. (Figure 2). In graphite, which also is a crystalline substance, the carbon atoms are arranged differently. If the crystal is viewed from the same position as shown in Fig. 2 for diamond, the upper crinkled layer is raised up a considerable distance from the lower layer, and because of this greater distance separating the successive planes in a graphite crystal the layers can slip and slide over one another. This is why graphite is such a fine lubricant. In diamond, on the other hand, the atoms are bound together by equally strong forces in every direction, and it is not easy for the planes to glide or slip.

One of the most important substances in which chemists are interested is the compound benzol, found in coal-tar. The molecule of benzol contains six atoms of carbon and six atoms of hydrogen so that chemists represent this substance by the formula $C_6H_6$. Chemists have supposed for now nearly seventy years that these six carbon atoms with the attached hydrogen atoms are arranged like a closed ring something like a hexagon,
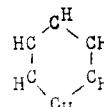
But the exact manner of this arrangement has long been disputed. If the reader will look at Fig.

2 he will notice that there are six-membered carbon rings in the diamond lattice. Recently an English physical chemist, Sir William H. Bragg, has suggested that this is the benzol ring. Naphthalene, which the chemists write like this,
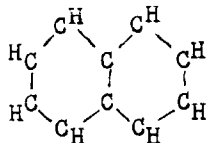


would then be simply two of the diamond rings joined together as shown in Fig. 2. Of course, hydrogen atoms must be attached to the carbon atoms, and if we wished we might represent the hydrogen atoms by little spheres. The distance between centers of adjacent carbon atoms in diamond is about 1.5 angstrom units (an angstrom unit is 1/100,000,000 cm.). This is equivalent to saying that the diameter of a carbon atom is 1.5 angstrom units if we will agree to think of the carbon atom as a sphere, and if we will agree that the carbon atoms are all packed so closely together that they touch one another as shown in Fig. 2. The most recent examination of crystals of benzol and of naphthalene by X-rays supports very strongly the idea that they are indeed made up of carbon rings of the same size and shape as those found in the diamond lattice.

## OIL FILMS

Let us now turn to another type of evidence. Every engineer is familiar with the fact that if gasoline or kerosene or paraffin oil, or any other mineral oil is placed on a water surface it will spread fairly readily to give a pool or lens of oil on the surface. If, however, a vegetable or animal oil such as castor oil, peanut oil, cotton seed oil, sperm oil, or lard oil is dropped onto a clean surface of water, a film of an entirely different sort is produced. For one thing this oil film spreads much more rapidly than the mineral oil. In the second place the film is not thick in the middle and tapering out at the edges as in the case of a mineral oil lens, but it is of uniform thickness throughout and if not confined too much it will spread out to give an extremely thin film. This difference in behavior of the two sorts of oil is due to a difference in the nature of their molecules. The molecule of a mineral oil consists of a long chain of carbon atoms with hydrogen atoms attached to each carbon atom in this way,

```
  H  H  H  H  H  H
  |  |  |  |  |  |
HC-C-C-C-C-C-H
  |  |  |  |  |  |
  H  H  H  H  H  H
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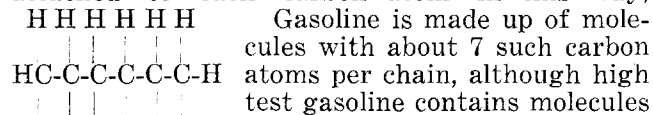
Gasoline is made up of molecules with about 7 such carbon atoms per chain, although high test gasoline contains molecules with only 5 or 6 carbon atoms. As a matter of fact, gasoline is a mixture of a number of different-sized molecules. The average kerosene molecules are much longer, of about 10 or 12 carbon atoms, vaseline still longer, paraffin even longer. None of these materials is soluble in water, and so when such an oil is poured on water, we would expect the oil molecules to be piled together in a haphazard way on the surface like so many sticks of wood. But the vegetable and animal oils have molecules which differ from mineral oil molecules in one important respect. They, too, consist of long carbon chains, but attached to one end of the chain are some oxygen atoms as shown in the following formula,

```
H  H  H  H  H  H  H  H  H  H
HC-C-C-C-C-C-C-C-C-C-COOH
H  H  H  H  H  H  H  H  H  H
```
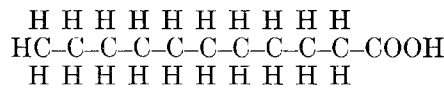
These oxygen atoms are soluble in water, and they confer solubility on one end of the molecule but the rest of the carbon-chain molecule remains just as insoluble as ever. As a consequence of this, when vast numbers of these molecules are placed on a water surface, the molecules all stick one end into the water and the rest of the molecule into the air so that they are all standing up on end or are oriented, as we say (Fig. 3).
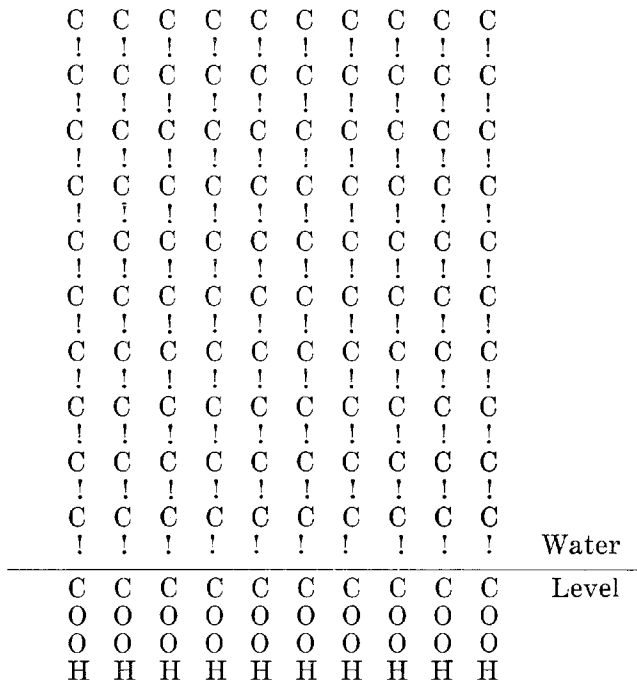


Fig. 3.

If this picture really represents the true situation we can easily understand why the film should spread out into a very thin uniform layer just one molecule deep. Various considerations show that this is probably exactly what happens.

If now we measure the area occupied by such a film and divide the area into the volume of the oil which was originally dropped onto the surface, the quotient of course would represent the thickness of the film, which is the same thing as the length of the molecule chain. Chemical analysis of the oil tells us the number of carbon atoms in the molecule. If we then divide the length of the chain by the number of carbon atoms present in the chain we get the length or diameter of each carbon atom. A great deal of careful work along this line with various vegetable and animal oils by Dr. Langmuir of the General Electric Company has shown that the average length contributed to the chain by each carbon atom is about 1.2 angstrom units. This result seems very peculiar because one would naturally suppose that in soft buttery materials like these oils the carbon atoms would not be packed together more closely than they are in the very dense and extremely hard diamond. But, as a matter of fact this distance in the diamond, as has already been pointed out, is 1.5 angstrom units. In order to reconcile these

apparently inconsistent results Dr. Langmuir suggested the idea that the carbon atoms in a hydro-carbon oil chain are arranged in a zig-zag fashion as shown in Fig. 4-A and 4-B. With a chain of this structure the actual distance from center to center of the carbon atoms can be 1.5 anstrom units and the vertical distance from center to center, which after all is the thing which is measured in the oil the film experiment, turns out to be almost exactly 1.2 angstrom units if the angles at which the carbon atoms are connected with one another are tetrahedral angles, that is, angles just like those at which the carbon atoms are joined together in diamond. Within the last two or three years X-ray measurements on these same substances in the laboratory of Sir William H. Bragg in London have confirmed Dr. Langmuir's idea about this zig-zag structure, and it has even been possible to show that certain types of oil molecules probably have a different zig-zag structure, like that shown in Fig. 4-B.

## EMULSIONS

As we have already stated, kerosene is insoluble in water. If a quantity of kerosene and water are shaken up violently together in a bottle there is formed what we call an emulsion of kerosene in water. Such an emulsion, however, is not stable. The droplets of kerosene soon coalesce and separate from the water into a layer. But if a small bit of soap is present in the bottle while the shaking is going on, the emulsion becomes quite permanent. Now this stability which the emulsion acquires with the soap's assistance may be explained quite convincingly in terms of the same sort of orientation of molecules which we have just employed to account for the spreading of animal and vegetable oils. A molecule of soap is exactly like the molecules of Fig. 3, except that the hydrogen atom in the COOH group at one end
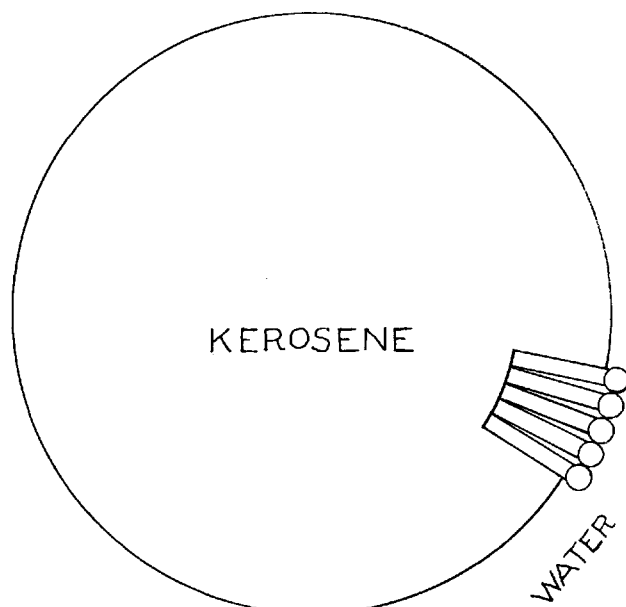


Figure 5

of the molecule has been replaced by the atom of some metal, for example sodium or potassium. Thus we may have a soap of any metal, such as a sodium soap, a zinc soap, a calcium soap, an aluminum soap, etc. Now, when soap molecules, let us

say of sodium, are mixed with the kerosene and water emulsion the carbon chain part of the soap molecules will stick through the surface of the kerosene droplets, since it is quite a general rule that "like dissolves like." But the COONa (where Na stands for a sodium atom) is soluble in water and is not soluble in kerosene, so that we would expect to have the convex surfaces of all the little kerosene droplets coated with molecules of sodium soap very much like pins sticking into a pin cushion. (Fig. 5.) Naturally then, since the whole outer surface of the droplet is plastered over with soluble groups we are not surprised to find that the whole droplet has become soluble in water and will remain suspended indefinitely with no tendency to coalesce with other droplets and form a kerosene layer.

If this pretty theory, which is also a product of Dr. Langmuir's brain, amounts to anything, it may be tested in a very striking manner. Suppose, instead of using a sodium soap we use a potassium soap. An atom of potassium is much larger than an atom of sodium and this would mean that the pin-head part of the soap molecule would be much larger in the potassium soap than in the sodium soap and would also mean that the curvature of the kerosene surface stabilized by the soap molecules would be much greater, that is, the droplet would be much smaller for the soap of potassium than for that of sodium. Such experiments have been carried out and microscopic observation of the droplet sizes in the case of these two soaps and many other soaps, seem to bear out fully the whole theory.

It is very interesting to note that the detergent action of soap is probably due to exactly this effect we have just described. When we attempt to cleanse our skin, for example, by washing with water alone, the difficulty lies not in washing off "the dirt." but in removing the oil and grease exuded through the pores of the skin or collected on the skin by outside contamination. These oils and greases do not dissolve in water, even in hot water and it is the function of the soap to emulsify these substances and render them soluble in just exactly the same way as in the case of kerosene.

There are many other lines of evidence bearing on the shape of molecules, but now in bringing this short review to a close, we will mention only one other method. Let us go back several pages to the illustration which we gave of naphthalene vapor spreading out through the air of a room. These naphthalene molecules which are diffusing through the air travel with a velocity which depends on a number of factors, among which are the mass of the molecule, the temperature at which diffusion occurs, and the pressure of the air. Another very important factor is the size of the naphthalene molecule, that is, the average cross-sectional area which it presents to bombardment and collision by the air molecules through which it is picking its way. In other words, the "wind resistance" of a molecule seems to determine to some extent the velocity with which it diffuses. By measuring the velocity of diffusion it is possible to calculate the average cross-sectional area of the molecule. For benzol this turns out to be 21.7 square angstrom units,

## THE SIZE AND SHAPE OF MOLECULES

and for naphthalene 32.4. When the average cross-sectional areas for the benzol and naphthalene molecules proposed by Bragg (Fig. 2) are estimated by some projection method, the agreement between their values and those determined by the diffusion method, is extremely good.

Thus it is possible by inference and by indirect methods to obtain some clear ideas about the sizes and shapes of the invisible molecules. Unquestionably the chemical and physical properties of substances depend very largely on the size and shapes of their molecules; and undoubtedly, as our knowledge along these lines increases, we shall be in a much better position to understand various chemical and physical effects which today still seem very mysterious.

# Ship Ahoy!

# ALL ENGINEERS ON DECK

The good ship "ENGINEERS' DAY" has been sighted off the starboard bow.

She will make this harbor
## FRIDAY, MAY 21st

Captain Kidd says that any Prof. who holds classes that afternoon will walk the plank.

Furthermore---All Land-lubbers out on the campus deck for a big Engineers Pee-rade.

# SWAB THOSE GUNS