Assignment 3: Lay Article

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Introduction

Whether you heard it on the news or read it in some popular science magazine or learned about it in school, most people know that atoms exist. But how do we know that they exist? We cannot see them or feel them. What evidence is there that atoms are real and that all matter is composed of them? It was not until 1905, 2300 years after the first proposal to the existence of atoms, that Albert Einstein ended the debate with his paper entitled, “On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat”. In this paper Einstein was the first person to assume that gases were composed of atoms. As a result a quantitative explanation for a phenomenon known as Brownian motion was developed. Brownian motion is the random walk of suspended bodies in a liquid, and Robert Brown first discovered this motion in 1827, while observing pollen grains suspended in water under a microscope (see Figure 1(a)). The phenomenon of Brownian motion, coupled with Einstein’s explanation of this motion in terms of collisions of molecules in the liquid with the suspended body, **gave the first indisputable evidence for the existence of atoms** (see Figure 1(b))!

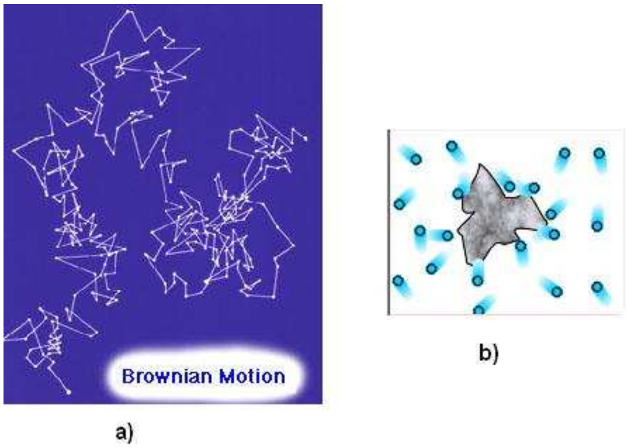

Figure 1: This depicts the motion of the suspended body as seen by Robert Brown under the microscope (a), as well as Einstein’s explanation of this random motion in terms of collisions between the liquid molecules and the suspended body (b). [1, 2]

Osmotic pressure of suspended bodies

Einstein began his paper by considering the amount of osmotic pressure exerted by dissolved particles and suspended bodies. **Osmotic pressure** is the pressure related to the flow of a solvent, like water, through a membrane or a barrier (See Figure 2). It should also be noted that the water will always flow in such a way as to travel from higher concentration of water molecules to the lower concentration.

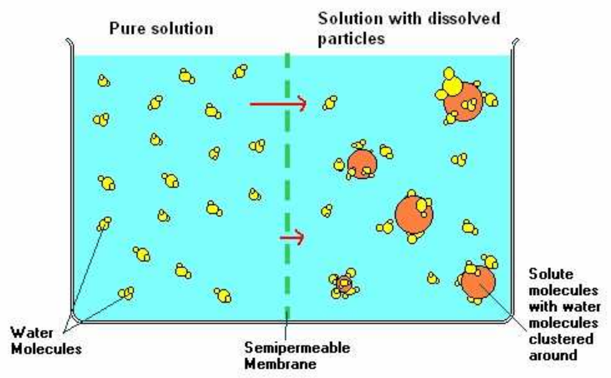

Figure 2: This demonstrates the type of system Einstein was considering. In this case the free water molecules are allowed to travel across the membrane and will move from the left side to the right side. The force that causes this is the osmotic pressure. [6]

Einstein started by assuming that a certain amount of molecules was dissolved into a liquid (Figure 3(a)). The dissolved molecules are referred to as the solute and the dissolving substance is the solvent. Furthermore, the solution mixture containing the solvent and the solute was separated from the pure liquid by a barrier, which only the solvent could pass through. Assuming that we have a dilute solution, the osmotic pressure of the solvent can be described by the ideal gas law. This law simply relates the osmotic pressure to the volume, temperature and mass of the solution. This relationship incorporates the laws of Boyle, Gay-Lussac, Charles, and Avogadro that were determined experimentally over a period of two hundred years.

Einstein next determined the effect of “small suspended bodies” contained in part of the volume of the liquid instead of dissolved molecules (Figure 3(b)). Again these suspended bodies could not pass through the barrier separating the solution with the suspended bodies from the pure liquid. Einstein examined the pressure created by these suspended bodies using two different theories of thermodynamics in place at the time, and obtained two contradicting results!

According to the **classical theory of thermodynamics**, which deals with the macroscopic properties of a system, Einstein discovered that the suspended particles should not exert any pressure on the walls.

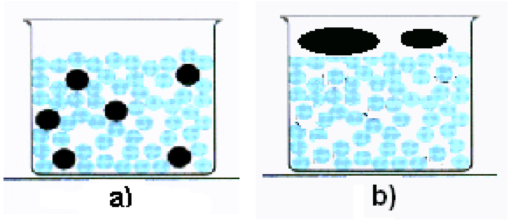

Figure 3: (a) depicts particles dissolved in a liquid, (b) shows bodies suspended in a liquid. [3]

Einstein's second approach to this problem was through the **molecular kinetic theory of heat**. This theory is based on the assumption that atoms exist and that there are a large number of atoms in a macroscopic volume. When this theory refers to a "large" number of atoms or molecules it means on the order of 10^{23} atoms, or one hundred million million billion! To get an appreciation of how large this number is consider having this much money, you could spend over a trillion dollars a second for ten thousand years! According to this theory the only difference between a dissolved molecule in the solution and a suspended body in the solution is the size. With this in mind it is clear that suspended bodies should also produce an osmotic pressure equal to the pressure produced by the same amount of dissolved molecules! Clearly the two models yield two contradicting answers.

Einstein argued in favor of suspended bodies exerting an osmotic pressure and found a formula for this pressure through a series of logical arguments following a single assumption. Einstein assumed "that the suspended bodies perform an irregular, albeit very slow, motion in the liquid due to the liquid's molecular motion." (Einstein 1905) This irregular motion of the suspended body is a result of the constant bombardment of molecules in the liquid at random directions (See Figure 1). This motion is similar to you and bunch of your friends surrounding a basketball and each of you throwing tennis balls at it to get it to move. Obviously the motion of the basketball will be slow and random since not all your friends have the same strength. The only difference is that in the liquid you have 10^{23} friends throwing tennis balls at the basketball. Just like the collisions between the liquid molecules and the suspended body, the liquid molecules would also collide with the barrier creating a pressure. Similarly, the suspended particle may also collide with the barrier exerting a further pressure.

By considering a certain number of suspended bodies in the solution and applying the ideal gas law to the suspended particles, one can determine the osmotic pressure corresponding to the suspended bodies. After some algebraic manipulation this pressure can be expressed as

$$p = \frac{R\,T\,\nu}{N},$$

where p is the osmotic pressure, R is a universal constant, T is the temperature, N is the actual number of molecules per gram-molecule, and ν is the number of suspended particles in the volume V of the solution.

In the next section of his paper Einstein shows how this equation can be derived from the molecular kinetic theory of heat.

Osmotic pressure from the standpoint of the molecular kinetic theory of heat

In this section a certain amount of mathematical formulism and physics jargon is used to eloquently derive the above expression. It is the goal for this section to outline the key concepts of this derivation while foregoing the use of complicated equations.

Einstein began his derivation by completely describing the physical system of interest. The best way to visualize the description of a system in general, is to think of a car driving along the road (See Figure 4). In order to completely describe the motion or state of the car at any point in time, one needs to know where the car is located and how it is moving at that location. For example, if the car was parked in the driveway, one would simply need to tell someone the address of the house where the car is located and that person would know exactly where the car is and how it is moving. Similarly, if the car was driving down the street and had a global position system installed, an outside observer could describe the motion of the car at any point in time. This could be achieved by looking at the GPS coordinates for the car's position and then be told at what direction and at what speed the car was traveling at that moment. In general, to describe this motion mathematically one states the car's position in terms of three spatial coordinates (i.e. the x, y and z position). In addition, one also states the car's velocity in terms of x, y and z coordinates (i.e. the direction of the car's motion and how fast it is going in that direction).

Figure 4: In this situation the car's position in terms of x, y, and z, the spatial coordinates, and car's is moving east at 50 km/h. [4]

Einstein applied the exact same concepts as described above; the only difference was that instead of tracking a single car, he was tracking the position and velocity of all the atoms in the system! This means that each atom requires six numbers to completely determine its motion, so N atoms would require 6N numbers to describe their motion or their physical state.

Once Einstein had assigned these values in terms of variables to each of the atoms in the system, he knew exactly how the system behaved at every instant and from this he computed the entropy of the state. **Entropy** is a thermodynamic quantity and can most easily be explained as disorder. Entropy is simply a measure of the disorder or randomness of a system. The important concept to note about entropy is that it always increases. The easiest way to visual this is by picturing a "just cleaned" child's room. As everyone knows at no point in time is the room going to get any cleaner, soon there will be clothes on the floor, the bed will be unmade, and paper's will clutter the desk. The randomness or entropy of the room has increased. One may also think of increasing entropy from a probabilistic point of view. Figure 5 gives an example of this type of situation.

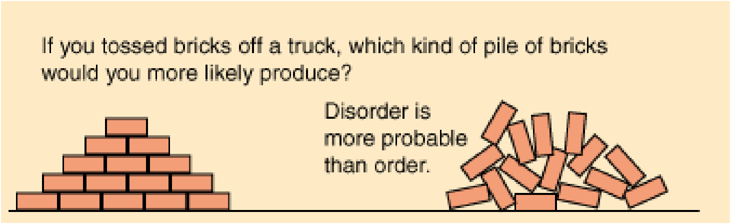

Figure 5: Demonstrates the probabilistic view of entropy. [5]

The entropy of Einstein's system of atoms depended on the temperature of the atoms, the total energy of the system, and the energy of each atom as a function of that atoms position and velocity coordinates. From this expression of entropy coupled with the Helmholtz function, which relates free energy to the internal energy of the system, the entropy and the temperature, Einstein derived the free energy of the system. **Free energy** is simply the energy required to build a system from nothing after all the spontaneous energy transfers have taken place, like entropy.

It turned out that the expression for free energy was too complicated to calculate by hand, and since Einstein did not have a computer he was forced to apply some constraints to the system in order to make this expression more manageable.

Einstein began by considering the position of the center of gravity for each of the suspended bodies or solute molecules. The center of gravity is simply the point inside the atom where one could consider all the mass to be contained. Einstein assigned three spatial coordinates to represent the position of the center of mass for each particle in the system. Einstein further assigned infinitesimally small regions of volume to each of the particles and required that all of these very small volumes lie inside the total volume which contains all the particles. Einstein then required that the center of gravity of each of the particles must lie within the regions of volume assigned to them.

Next Einstein supposed that a second system of infinitesimally small volumes existed, that differed from the original volumes for each particle, only in position and not size. Basically, Einstein was proposing that there was more than one way to confine the position of the center of gravity for each particle in a small volume. Since the sizes of the volumes were the same, by dividing the two expressions Einstein derived a ratio which contained the complicated part in the expression for the free energy.

From previous work on the molecular kinetic theory of heat the value of a similar ratio was known. The physical interpretation of this ratio from this theory is that it represents the probability or likelihood that at any given point in time, the center of gravity of all the particles will be found in their assigned volumes. Provided that the motion of one particle does not affect the motion of the other particles, meaning they are independent, the probability of finding the second system in their respective regions is equal to the probability of finding the first system in its respective region. This allowed Einstein to determine the free energy. With the free energy known Einstein used a well known relationship between pressure and the free energy to determine the osmotic pressure. Thus from the molecular theory of heat the osmotic pressure of the particles is

$$p = \frac{R\,T\,\nu}{N}\;.$$

"This analysis shows that the existence of osmotic pressure can be deduced from the molecular kinetic theory of heat and that at high dilution, according to this theory, equal numbers of solute molecules and suspended particles behave identically as regards to osmotic pressure" (Einstein, 1905).

Conclusions

The first two sections of Einstein's paper dealing with suspended particles showed that **solute molecules and suspended bodies behave the same with regards to osmotic pressure**. This contradicts the classical theory of thermodynamics which predicts osmotic pressure to be produced by the solute molecules but not the suspended particles! As a result, Einstein showed that classical thermodynamics failed in regions defined by a microscope, and in these regions the molecular kinetic theory of heat was required.

Furthermore, Einstein explained Brownian motion in terms of collisions between the liquid molecules and the suspended bodies. These two sections lead into a rather lengthy derivation, via statistics, of the displacement of a suspended particle as a result of the constant bombardment of molecules. The results from further sections provide a direct method for measuring Avogadro's number through a Brownian motion experiment.

References:

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