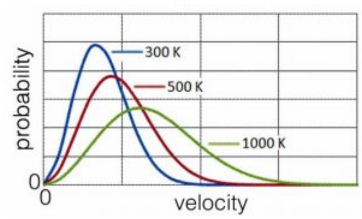
5.2: Thinking About Populations of Molecules

Within a population of atoms and molecules, the many collisions that occur per second lead to a range of speeds and directions (that is, velocities) of the atoms/molecules. When large numbers of particles are involved in a phenomenon, their individual actions are not important, for example when measuring temperature or pressure (although they are when individual molecules collide, that is, take part in chemical reactions). We treat large numbers of molecules as a population. A population is characterized by the distribution of the number or probability of molecules moving with various velocities.[5] This makes it possible to use statistical methods to characterize the behavior of the population. Although any particular molecule behaves differently from one moment to the next, depending upon whether it collides with other molecules or not, the behavior of the population is quite predictable.[6]

From this population perspective, it is the distribution of kinetic energies of atoms or molecules that depends upon the temperature of the system. We will not concern ourselves with deriving the equations that describe these relationships, but rather focus on a general description of the behavior of the motions of atoms and molecules in various states of matter.



Let us think about a population of molecules at a particular temperature in the gas phase. Because of their constant collisions with one another, the population of molecules has a distribution of speeds. We can calculate the probability of a particular molecule moving at a particular speed. This relationship is known as the Maxwell–Boltzmann distribution, shown in the graph. Its shape is a function of the temperature of the system; typically it rises fairly steeply from zero (all of the curves begin at zero – why is that do you think?) to a maximum, which then decreases and tails off at higher velocities (which correspond to higher kinetic energies). Because we are plotting probability versus kinetic energy (or rms velocity or speed) we can set the area under the curve to be equal to one (or any other constant). As the temperature changes, the area under the curve stays constant. Why? Because we are completely certain that each particle has some defined amount of kinetic energy (or velocity or speed), even if it is zero and even if we could not possibly know it (remember the uncertainty principle). As the temperature is increased, the relative number of particles that are moving at higher speeds and with more kinetic energy increases. The shape of the curve flattens out and becomes broader. There are still molecules moving very slowly, but there are relatively fewer of them. The most probable speed (the peak of the curve) and the average speed (which is a little higher since the curve is not symmetrical) increase as the temperature increases.

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Questions to Answer

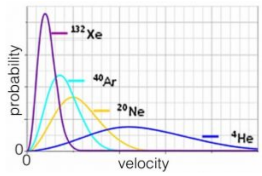
- What happens to the average speed of molecules as temperature increases?
- When molecules collide, why don't they stick together?
- What do you think happens to the average speed as molecular weight increases (assuming the temperature stays the same)?
- Imagine a system composed of two different types of molecules, one much heavier than the other. At a particular temperature, how do their average kinetic energies compare? Which, on average, is moving faster?

Questions to Ponder

- How large does a system have to be to have a temperature, 10 molecules or $10,000,000$?
- If one considers the uncertainty principle, what is the slowest velocity at which a molecule can move?
- If you place a thermometer into a solution, why does it take time for the reading on the thermometer to correspond to the temperature of the solution?

Temperature, Kinetic Energy and Gases

Now here is an unexpected fact: the average kinetic energies of molecules of any gas at the same temperature are equal (since $\mathrm{KE} = \frac{3}{2}k\mathrm{T}$, the identity of the gas does not matter). Let us think about how that could be true and what it implies about gases. Under most circumstances the molecules in a gas do not significantly interact with each other; all they do is collide with one another like billiard balls. So when two gases are at the same temperature, their molecules have the same average kinetic energy. However, an even more unexpected fact is that the mass of the molecules of one gas is different from the mass of the molecules of the other gas. Therefore, given that the average kinetic energies are the same, but the molecular masses are different, the average velocities of molecules in the two gases must be different. For example, let us compare molecular hydrogen (H_2) gas (molecular weight $= 2\ g/mol$) with molecular oxygen (O_2) gas (molecular weight $= 32\ g/mol$), at the same temperature. Since they are at the same temperature the average kinetic energy of H_2 must be equal to the average kinetic energy of O_2, then the H_2 molecules must be moving, on average, faster than the O_2 molecules.[7]



So the average speed at which an atom or molecule moves depends on its mass. Heavier particles move more slowly, on average, which makes perfect sense. Consider a plot of the behavior of the noble (monoatomic) gases, all at the same temperature. On average helium atoms move much faster than xenon atoms, which are over 30 times heavier. As a side note, gas molecules tend to move very fast. At $0°C$ the average H_2 molecule is moving at about $2000\ m/s$, which is more than a mile per second and the average O_2 molecule is moving at approximately $500\ m/s$. This explains why smells travel relatively fast: if someone spills perfume on one side of a room, you can smell it almost instantaneously. It also explains why you can't smell something unless it is a gas. We will return to this idea later.

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Questions to Answer

- Why don't all gas particles move with the same speed at a given temperature?
- Where would krypton appear on the plot above? Why?
- Consider air, a gas composed primarily of N_2, O_2, and CO_2. At a particular temperature, how do the average kinetic energies of these molecules compare to one another?
- What would a plot of kinetic energy versus probability look like for the same gas at different temperatures?
- What would a plot of kinetic energy (rather than speed) versus probability look like for different gases (e.g., the noble gases) at the same temperature?

Questions to Ponder

- If gas molecules are moving so fast (around $500\ m/s$), why do most smells travel at significantly less than that?
- Why does it not matter much if we use speed, velocity, or kinetic energy to present the distribution of motion of particles in a system (assuming the particles are all the same)?