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Diffusion in Tight Mazes

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Diffusion is transportation by random motion to reduce spatial differences among regions. The objects that undergo diffusion can be bodies such as molecules, particles, virus and bacteria, plants and animals; the objects can also be ideas such as inventions and innovations, and social habits. Perhaps the grandest feat of diffusion in human history is the diaspora of *homo sapiens* from East Africa to occupy all corners of the globe. Diffusion leads to more equality among the regions, which can be quantified by the familiar entropy in thermodynamics and information theory, and by the Gini Coefficient in economics.

The scientific description and analysis of diffusion has a long history, from Lucretius in 60 BC in observing air particles dancing in sunbeam, and Robert Brown in 1827 of pollen grains in water. Albert Einstein in 1905 formulated the theory of Brownian motion. The paradigm of classical diffusion equations were formulated to have scalar or tensor diffusivity, but nature and industry often produce multi-phase materials that do not follow these equations. According to Thomas Kuhn, we continue to use the wrong diffusion equations even when they do not work, as we do not have something better.

Diffusion is used in nature and in the chemical industry to accomplish tasks of making things more uniform, such as adding salt to a beef stew and stirring. Convection is responsible for larger scale mixing, and diffusion does the smaller scale equalization. When there is more than one diffusing objects, diffusion is often used to do separation, or to increase inequality. The kidney separates urine from blood, as the diffusivity is higher for water and urea than for plasma and cells.

Zeolites are micro-porous solids with molecular size windows, and used in Industrial processes to separate molecules A and B. Sometimes the windows are circular or elliptical, but they can also be bizarre like a cloverleaf. The simplest form of Size Selectivity is to assume that helium and argon are rigid spheres with different diameters, and the right zeolite would have a circular window to admit helium but not argon. For a molecule that is an ellipsoid, the ease of going through a window depends on the rotational orientation, and the relevant parameter is the "foot print" as the smallest shadow cast. The footprints of argon and xenon would be circles, and the footprints of normal paraffins and benzene would be approximately ellipses with major and minor diameters. The more sophisticated form of Shape Selectivity is used to separate similar isomers, such as the slim normal paraffins from the wide branched paraffins, and the slim para-xylene from the wide ortho- and meta-xylenes. However this model of rigid molecules and rigid windows often fail to describe reality, as a molecule can squeeze through a window that is too small, especially at higher temperatures.

Each molecule has many degrees of flexibilities: bond lengths, bond angles, and torsion angles can all be modified at the cost of an increase of energy. The fraction of molecules that have sufficient energy to distort to a smaller footprint depends on the temperature and the strain energy involved. Strain Selectivity is the more sophisticated form of separation, based on the comparative strain energies involved in distorting molecules A and B to enter a window. The degree of selectivity is dependent on the temperature, which should be warm enough to allow the slim A, but not warm enough for the wide B.

There are many methods to modify catalysts to increase the ability to separate. The traditional methods are pore modifications such as blockage by coke and polymer deposition, and structure modifications by exchange of H^+ for Ca^{++} ions with different ionic radius. Recent innovations include two-phase catalysts: modifying a micro-porous zeolite with catalytic activity but low diffusivity, by growing within meso-porous crystal with no catalytic activity but high diffusivity. To paraphrase Richard Feynman, "There is Plenty of Room in Tight Mazes".