INTERMOLECULAR COLLISIONS

The System of Study: Let us postulate a system of study consisting of a *p-*population of gaseous atmospheric molecules in random motion in proximity space. The surface of interest is the intangible surface of one of the molecules of the *p-*population.

Definition of an Intermolecular Collision: A molecule may be said to undergo an intermolecular collision if its interaction with another molecule results in a change in either molecule's path or speed. A forceful contact with another molecule is obviously a collision. A "near miss" is also a collision if the forces of intermolecular repulsion have the same result. The clear majority of intermolecular collisions do not result from actual molecule-to-molecule contact.

Intermolecular Collision Frequency: Molecular flows tells us that the number of molecules impacting upon one square meter of surface in one second is,

$$\bar{f}_i = \bar{n}_p \bar{v}_p \qquad\qquad\qquad \text{MCS01}$$

Obviously, the surface of an atmospheric gas molecule is a great deal smaller than one square meter. To ascertain how many intermolecular collisions the average atmospheric gas molecule undergoes in one second, then, we must know the mean surface area of an atmospheric gas molecule. That quest starts with an estimation of the mean molecular radius.

Effective Molecular Radius: Textbooks often use packing density to define a molecule's radius. That definition may be useful for liquids and solids, but is less useful for gases. Gas molecules do not need to be "touching" to influence one another. For a gas, the intermolecular repulsive forces are greater than the intermolecular attractive forces. Otherwise, we wouldn't have a gas, we would have a liquid or a solid.

Logically then, we should define the effective radius to be that radial distance at which the passage of another molecule causes any change in molecular speed or direction. Unfortunately, we don't have useful values for those distances.

Consequently, we must default to using packing density to define the molecule's radius, in the absence of better measures. For dry air, this has been set at 1.90×10^{-10} meters. For water vapor, we use 1.55×10^{-10} meters. Because this use of packing values eliminates the many "near-miss" collisions, these values significantly underestimate the actual frequency of collisions. Unfortunately, we must use the information available at the time of writing. Future scholars may be more accurate.

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Approximations for Humid Air: Since water vapor is the most significant variable in the atmospheres' composition, a useful ***approximation*** of the mean effective molecular radius for humid air is:

$$\bar{r} \approx \frac{1}{n}\left(\overline{\underset{\sim}{n}\underset{\sim}{r}} + \overline{\underset{.}{n}\underset{.}{r}}\right) \qquad\qquad\qquad \text{MCS02}$$

Here, the ***tilde*** under the term indicates that it applies to water vapor and the dot under the term indicates that it applies to dry air. The absence of either indicates that the parameter applies to humid air. As is customary, the bar over each term indicates that that term is the mean value of a population of values.

Molecular Shapes: The molecules of the atmosphere are not spherical. They have a variety of shapes and many of those shapes change with time as the molecules and their constituent atomic components rotate, vibrate, and librate.

However, we can consider them as spherical if we consider that as these molecules undergo these movements, they effectively "clear out" a space that is more or less spherical. We will proceed to consider the molecules of the atmosphere as spherical for the purposes of estimating intermolecular collision frequencies.

Intermolecular Collisions with a Stationary Molecule: Let us start our discussion of molecular collisions by assuming a perfectly stationary molecule. Because each molecule has a mean effective radius $\bar{r}$, the approach of any other molecule to a distance between molecular centers of $2\bar{r}$ will result in a collision.

The stationary molecule may thus be considered as having an effective target area ($\otimes$) of $\mathbf{16\pi\bar{r}^{2\,2}}$ (the surface area of a sphere of radius $2\bar{r}$) and being struck by mass points. That is,

$$\otimes \approx \mathbf{16\pi\bar{r}^{2}} \qquad\qquad\qquad \text{MCS03}$$

Using the mean molecular radii given above, this formula produces effective molecular target areas of 1.82 x 10^{-18} square meters for the mean dry air molecule and 1.21 x 10^{-18} square meters for the mean vapor molecule.

Equation MCS03 shows that the frequency of collision is directly related to the square of the effective molecular radii ($\bar{r}^{2}$). The molecules of the air have a wide variety of effective molecular radii. To calculate the frequency of collision of a molecule of specific radius with the rest of the atmospheric molecules, we must substitute the value of $(r_{s} + \bar{r})$ for the radius $\mathbf{2\bar{r}}$ in our calculations.

Since the number of molecules impacting upon unit area in unit time is given by MCS01 as $\bar{f}_i$, the number $\bar{f}_\otimes$ colliding with our stationary target molecule in unit time from all directions is:

$$\bar{f}_\otimes \approx \otimes \bar{f}_i \approx 16\pi\bar{r}^2\bar{n}_p\bar{v}_p \qquad\qquad \text{MCS04}$$

That is also the frequency of collision undergone by a moving molecule.

Inter-Molecular Impacts with a Moving Molecule: The number of molecular impacts upon another molecule remains the same as shown in MCS04 whether the other molecule is moving or not. This may seem counter-intuitive, but nevertheless it is true. This topic is well covered in Molecular Interactions.

Intermolecular Collisions in Moving Air: When the wind blows, the values of many atmospheric parameters change significantly. These changes will be functions of the wind speed and the wind direction relative to the surface of interest. Phenomena related to fluid flows are discussed in advanced papers in this collection.

Frequency of Collisions in the Free Atmosphere: If we assume calm air, then the frequency of molecular collisions in the free atmosphere is essentially a function of the ambient temperature, the ambient pressure, and the ambient humidity. Temperature and pressure control the number density, temperature and humidity control the mean proximity velocity, and humidity controls the effective molecular radius.

Still Air Parameters: The essay Still Air Parameters gives the following value for still air with no net evaporation or condensation.   The system temperature is 25° C, and the system pressure is 1,000 hectopascals.   The system vapor pressure is 10 hectopascals.

$\bar{f}_{\bar{\otimes}} \approx$ 5.11 x 10^9 intermolecular collisions per humid air molecule per second

$\bar{f}_{\bar{\otimes}}^{\Sigma} \approx$ 1.24 x 10^{35} intermolecular collisions per cubic meter per second

REFERENCES

Internal References: References to other essays in this collection are linked in the essay text by hyperlinks. You may follow these hyperlinks or ignore them, as you choose.

External References: These are papers by other authors that contain statements or data that are specifically incorporated into this essay. This paper has no external references.

General References: These are works that I have read carefully and whose views have helped to shape the views presented in this collection. None of these authors are have any responsibility for my many unconventional views and opinions.

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