MOLECULAR VELOCITIES

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 an imaginary sphere surrounded by the *p-*population.

Definition of Summed Kinetic Velocity: Quantum theory mandates that those *p-*population molecules might or might not have individual molecular motions in any or all of the translational, rotational, vibrational, and librational modes. For any individual gas molecule, its summed translational kinetic velocity along both arms of the *p-*axis is therefore:

$$v_{\pm p}^{\Sigma} = v_{\pm p}^{translation} + v_{\pm p}^{rotation} + v_{\pm p}^{vibration} + v_{\pm p}^{libration} \qquad \text{SPD01}$$

Here, the *v* in each term is the individual molecule's velocity in meters per second in either of the two proximity axis directions. For most atmospheric gas molecules, the last three of these terms have values that are usually zero. For atmospheric liquids and solids all four right-hand terms will often have significant values.

Postulation of Gaseous Proximity Velocity: A few atmospheric gas molecules do have some of these other modes of movement. But, the total proportion of such molecules is so small that these non-translational velocities of movement have no measurable effect on mean proximity velocity values when the conventional scientific single order of magnitude and three significant figures are used (see Translational Equipartition). Consequently, we will postulate:

$$v_{\pm p} = v_{\pm p}^{\Sigma} = v_{\pm p}^{translation} \qquad \text{SPD02}$$

Mean Proximity Velocity: With that clarification, we can go on to define mean molecular proximity velocity as:

$$\bar{v}_{\pm p} = \frac{1}{\bar{n}} \sum_{1}^{\bar{n}} v_{\pm p} = 0 \qquad \text{SPD03}$$

Here, $\bar{n}$ is the mean number of gas molecules per cubic meter, and $v_{\pm p}$ is the individual molecular velocity in meters per second. Since we postulated all or our molecular motions as random, statistical mechanics mandates that velocity distribution must be symmetrical over both the *+p* and the *-p* axial arms. Hence, the mean proximity velocity of the entire *p-*population is zero.

The Standard Deviation of the Molecular Velocity Distribution: Having proceeded this far, we may now obtain the standard deviation of the proximity velocity distribution. Since the mean proximity velocity is zero, the individual velocities are in themselves deviations from the mean, and:

$$\sigma = \left(\frac{1}{\bar{n}} \sum_1^{\bar{n}} v_{\pm p}^2 \right)^{\frac{1}{2}} \qquad \text{SPD04}$$

The standard deviation of a distribution is the square-root of the mean of the squares of the individual deviations. Since our individual deviations are individual velocities, the standard deviation is the square-root of the mean of the squares of the individual velocities. In kinetic gas theory, this concept is termed the root-mean-square velocity (v^{rms}). In statistical mechanics, it is termed the standard deviation (σ). We will use both terms, as well as the denotation term, sigma—which is easier to say and print than either of the other two.

Unlike the mean proximity velocity, which is always zero under conditions of equilibrium, sigma will always have a specific positive value. This is because all negative values are eliminated in the process of squaring.

The Ideal Gas Probability Density Function for Molecular Velocities: Not all molecular velocities are equally probable, however. This leaves us with the question of just how probable a given velocity might be. In *Statistical Physics*, Brown tells us that the distribution of molecular velocities along a single axis of movement in an ideal gas under conditions of equilibrium will be:

$$\Phi\left(v_x\right)dv_x = \left(\frac{m}{2\pi k_B \bar{T}} \right)^{\frac{1}{2}} \exp- \frac{mv_x^2}{2k_B \bar{T}} dv_x \qquad \text{SPD05}$$

Here, $\Phi\left(v_x\right)dv_x$ is the probability that a molecule chosen at random from the system population will have a velocity between v_x and dv_x along the x-axis in meters per second. In addition, m is the system's unique molecular mass in kilograms, k_B is Boltzmann's Constant in joules per Kelvin per molecule, and $\bar{T}$ is the system temperature in Kelvins.

To apply this equation to gaseous atmospheric air, we must substitute $\bar{m}_i$ (the mean molecular impulse mass of the air) for m. We are also going to substitute the *p*-axis for the x-axis.

We shall also do some simple algebraic manipulation to put this equation completely into statistical mechanical terms. The mean molecular kinetic energy of translation ($\bar{u}_i$) is:

$$\bar{u}_i = k_B \bar{T} = \bar{m}_i \sigma^2 \qquad \text{SPD06}$$

This means that:

$$\sigma^2 = \frac{k_B \bar{T}}{\bar{m}_i} \qquad \text{SPD07}$$

Making these changes turns SPD05 into:

$$\Phi\left(v_p\right)dv_p = \frac{1}{\sqrt{2\pi}\sigma} \exp-\frac{v^2}{2\sigma^2}dv_p \qquad \text{SPD08}$$

Putting this probability in terms of the number of molecules in one cubic meter that have velocities along the **p**-axis between v_p and dv_p, we get:

$$\frac{d\bar{n}}{dv_p} = \frac{\bar{n}}{\sqrt{2\pi}\sigma} \exp-\frac{v_p^2}{2\sigma^2} \qquad \text{SPD09}$$

The alert reader will note that when this expression is normalized by making sigma equal to unity, it becomes a form of the standard normal probability curve.

Single Arm Proximity Velocities: It is often useful to know the distribution of molecular velocities for that portions of the **p**-population that are either approaching a surface of interest or leaving it. For the distribution of molecular proximity velocities along a single axial arm, we get:

$$\frac{d\bar{n}_p}{dv_p} = \sqrt{\frac{2}{\pi}}\frac{\bar{n}_p}{\sigma} \exp-\frac{v_p^2}{2\sigma^2} \qquad \text{SPD10}$$

Note that we have multiplied the coefficient in SPD09 by a factor of 2. This is because $\bar{n}_p$ has only one-half the value of $\bar{n}$ and we must maintain the total probability at unity.

The Mean Single Arm Proximity Velocity: To find the mean velocity of SPD11, we multiply SPD11 by v_p, integrate over all possible values of v_p, and divide by $\bar{n}_p$. This gives us:

$$\bar{v}_p = \sqrt{\frac{2}{\pi}}\frac{1}{\sigma}\int_0^\infty v_p \exp-\frac{v_p^2}{2\sigma^2}dv_p \qquad \text{SPD11}$$

The integral has the value:

$$\int_0^\infty v_p \exp-\frac{v_p^2}{2\sigma^2}dv_p = \sigma^2 \qquad \text{SPD12}$$

so that:

$$\bar{v}_p = \sqrt{\tfrac{2}{\pi}}\sigma \qquad\qquad \text{SPD13}$$

Here, $\bar{v}_p$ is the mean molecular proximity velocity under isothermal conditions. That is, it is the mean velocity at which the molecules of our system are approaching our surface of interest. It is, of course, also the mean velocity with which the molecules of our system are moving away from our surface of interest.

If we know the system mean molecular impulse mass and its temperature, we can easily obtain a numerical value for this mean molecular proximity velocity:

$$\bar{v}_p = \sqrt{\dfrac{2\mathbf{k_B}\bar{T}}{\pi\bar{m}_i}} \qquad\qquad \text{SPD14}$$

Parameters of the Impulse Velocity Distribution (dn/dv_i)

We should not assume, however, that because $\bar{v}_p$ is the mean velocity with which the molecules in our population are approaching a surface of interest that is also the velocity with which they interact with that surface. Such is not the case.

A moment's thought will show that a molecule having a velocity of $2v_p$ is twice as likely to impact upon a given surface (or pass through a given plane) as one with a velocity of merely v_p. If we think of the volume of our system as consisting or an infinite series of evenly-spaced planes, we can see that in unit time a molecule of velocity $2v_p$ will pass through exactly twice as many planes as one of velocity v_p. Therefore, the number of such molecules passing through any one plane in unit time is likely to be twice as great.

Thus, the probability of any molecule in our proximity population interacting with a surface having the specific velocity normal to that surface of v_i is proportional both to the probability of that molecule having that velocity in the first place, and is also proportional to the magnitude of that velocity.

The i subscript means that we are dealing with interactions with the surface of interest. This interaction requires a time frame. Let us use the standard time of one second. Molecular Flows tells us that during one second $\bar{f}_i$ interactions will occur over one square meter of area. Moreover,

$$\bar{f}_i = \bar{n}_p\bar{v}_p \qquad\qquad \text{SPD15}$$

By definition,

$$\overline{v}_p = \frac{1}{\overline{n}_p} \sum_{1}^{\overline{n}_p} v_p \qquad \text{SPD16}$$

Therefore, out of $\overline{f}_i$ interactions, each molecule of velocity v_p will interact with the surface exactly as many times as the magnitude of v_p —if the normal distribution is followed. Equation SPD10 tells us that there are dn_p / dv_p molecules of velocity v_p out of a population of n_p molecules. Thus, the probability of a given interaction occurring at velocity v_i is:

$$\phi(v_i) = \frac{dn_p v_p}{dv_p n \overline{v}_p} \qquad \text{SPD17}$$

It follows that—out of $\overline{f}_i$ impacts—the number occurring with impulse velocities between v_i and $v_i + dv_i$ will be:

$$d\overline{f}_i = \frac{\overline{f}_i}{\sigma^2} v_i \exp{-\frac{v_i^2}{\sigma^2}} dv_i \qquad \text{SPD18}$$

The Mean Impulse Velocity ($\overline{v}_i$): To obtain the mean impulse velocity, $\overline{v}_i$, we proceed as before to multiply by v_i, integrate over all possible values of v_i, and divide by $\overline{f}_i$. The mean impulse velocity thus becomes,

$$\overline{v}_i = \frac{1}{\sigma^2} \int_{0}^{\infty} v_i^2 \exp{-\frac{v_i^2}{\sigma^2}} dv_i \qquad \text{SPD19}$$

The integral has the value:

$$\int_{0}^{\infty} v_i^2 \exp{-\frac{v_i^2}{\sigma^2}} dv_i = \sqrt{\frac{\pi}{2}} \sigma^3 \qquad \text{SPD20}$$

thus:

$$\overline{v}_i = \sqrt{\frac{\pi}{2}} \sigma \qquad \text{SPD21}$$

Here, $\overline{v}_i$ is the mean velocity normal to and toward the surface of interest of those molecules interacting with that surface. It is this interaction velocity that determines the rate of transfer of momentum during collisions with a surface (or with another molecule). Hence, it is the mean impulse velocity.

If we know the system mean molecular impulse mass and its temperature, we can easily obtain a numerical value for this mean molecular impulse velocity:

$$\bar{v}_i = \sqrt{\frac{\pi k_B \bar{T}}{2\bar{m}_i}}$$ SPD22

Comparison of Molecular Velocity Parameters: To summarize: Each of our two molecular velocities in proximity space has been defined, been given a distribution function, and has had the means of their velocities evaluated. They may be related to one another by their common relationship to sigma **σ**. Thus,

$$\sigma = \sqrt{\tfrac{\pi}{2}}\,\bar{v}_p = \sqrt{\tfrac{2}{\pi}}\,\bar{v}_i$$ SPD23

This also means that,

$$\sigma^2 = \bar{v}_p \bar{v}_i$$ SPD24

This is an equivalence that we shall find very useful in advanced papers.

Molecular Velocities in the Other Halves of the Populations: The reader will note that the above distributions, derivations, and means refer only to the positive subscripts of the total population of molecules. However, distributions, derivations, and means may be obtained for the negative subscripts of the total population in a similar fashion.

The reader should keep in mind that under non-equilibrium conditions (the usual situation in the free atmosphere) the distributions and resulting means of the two sub-populations of both the general population and the interactive population *will not* be identical. For example, vapor molecules that are evaporating from a surface do not have the same velocity distribution and means as vapor molecules condensing on that same surface. Symmetry is not one of the free atmosphere's endearing characteristics.

Still Air Parameters: The essay Still Air Parameters gives the following values 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.

σ = 293.55 m sec^{-1}
$\underset{\sim}{\sigma}$ = 370.95 m sec^{-1}
$\overset{.}{\sigma}$ = 292.99 m sec^{-1}

$\bar{v}_p$ = 234.22 m sec^{-1}

$\underset{\sim}{\bar{v}}_p$ = 295.98 m sec^{-1}

$\underset{\cdot}{\bar{v}}_p$ = 233.78 m sec^{-1}

$\bar{v}_i$ = 367.91 m sec^{-1}

$\underset{\sim}{\bar{v}}_i$ = 464.92 m sec^{-1}

$\underset{\cdot}{\bar{v}}_i$ = 367.21 m sec^{-1}

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

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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.

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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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