

By Kent Mayhew

Appendix B.7: Explaining 66.67% for Work vs Energy

The following analysis concerning the number of gaseous molecules striking a surface is based upon an analysis found in Reif (pg 271) ("Fundamentals of Statistical and Thermal Physics", F. Reif, McGraw-Hill, New York,).

The total molecular "flux" is the number of molecules that strike a unit surface area per unit time. When discussing kinetic theory in Section 1.4, we used a crude analysis arriving at the flux along any one axis in a given direction is:

$$\Phi_0 = n\bar{v}_x/6 \quad 1.4.5$$

More exacting analysis of Flux

Draw an elemental area dA of some system's wall in the x, y plane with the z -axis being perpendicular to said wall, i.e. Fig B.7.1.

Consider the molecules in the immediate vicinity of the wall's elemental area (dA) whose velocities lay between: $v+d v$. ; its direction specified by its polar angle θ with respect to z -axis and its azimuthal angle ϕ is such that these angles lie between $\theta+d\theta$ and $\phi+d\phi$ respectively.

Over a time interval dt the above molecules experience a displacement of vdt . Therefore all the molecules that lay in a infinitesimal cylinder whose cross sectional area dA and have a length of vdt making an angle θ with the z -axis will strike the wall, The infinitesimal cylinder's volume is:

$$dA v dt \cos\theta \quad B.7.1$$

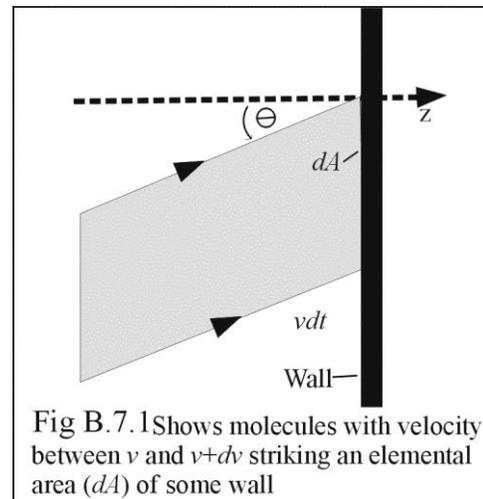
While the number of molecules is:

$$f(v) d^3v \quad B.7.2$$

Therefore the number of molecules that strike the walls surface area dA over a time period of dt becomes the multiplication of eqn B.1.7.1 and B.1.7.2, i.e.:

$$[f(v) d^3v](dA dt \cos\theta) \quad B.7.3$$

Let $\Phi(v) d^3v$ be the number of molecules with velocity between v and $v+d v$ which strike elemental area dA over time frame dt . Dividing eqn B.7.3 by elemental surface area (dA) and elemental time interval (dt) gives:



$$\Phi(v)d^3v = d^3vf(v)v\cos\theta \quad \text{B.7.4}$$

Let Φ_0 represent the total number of molecules that strike dA over time dt . This would be obtained by summing over:

- a) all possible speeds: $0 < v < \infty$
- b) all possible azimuth angles: $0 < \varphi < 2\pi$
- c) all possible angles: $0 < \theta < \pi/2$

Note: Molecules where $\pi/2 < \theta < \pi$ are directed away from the wall's elemental area dA .

Therefore:

$$\Phi_0 = \int_{v(z)>0} d^3vf(v)v\cos\theta \quad \text{B.7.5}$$

However:

$$d^3v = v^2dv(\sin\theta d\theta d\varphi) = v^2dv d\Omega \quad \text{B.7.6}$$

Note: eqn B.7.6 is based upon the elemental solid angle being: $d\Omega = \sin\theta d\theta d\varphi$.

Therefore eqn B.7.5 becomes:

$$\Phi_0 = \int_{v(z)>0} d^2dv \sin\theta d\theta d\varphi f(v)v\cos\theta \quad \text{B.7.7}$$

Which becomes:

$$\Phi_0 = \int_0^\infty f(v)v^3dv \int_0^{\pi/2} \sin\theta \cos\theta d\theta \int_0^{2\pi} d\varphi \quad \text{B.7.8}$$

Since the integration over the azimuth angle (φ) gives 2π , while the integration over all possible angles (θ) gives $1/2$, thus:

$$\Phi_0 = \pi \int_0^\infty f(v)v^3dv \quad \text{B.7.9}$$

The mean speed (which is intrinsically positive) is given by:

$$\bar{v} = (1/n) \iiint f(v)v d^3v \quad \text{B.7.10}$$

Thus

$$\bar{v} = (1/n) \int d^3v f(v) v \quad \text{B.7.11}$$

Hence:

$$\bar{v} = (1/n) \int_0^\infty \int_0^\pi \int_0^{2\pi} (v^2 dv \sin \theta d\theta d\varphi) f(v) v \quad \text{B.7.12}$$

Or:

$$\bar{v} = (4\pi/n) \int_0^\infty f(v) v^3 dv \quad \text{B.7.13}$$

Since the integration over the angles (θ) and azimuth angles (φ) is just the total solid angle about a point a point. Hence eqn B.7.9 can be rewritten as:

$$\Phi_0 = (1/4)n\bar{v} \quad \text{B.7.14}$$

We can see that this exact result differs from the simple initial assumption that the flux along a given axis is 1/6 of the total flux. So our initial rudimentary thought was based upon eqn 1.4.5: $\Phi_0 = (1/6)n\bar{v}$. Hence our rudimentary conceptualization (used in kinetic theory) was 2/3 e.g. 66.667% of the actual result.

What really concerns us is this. The energy of a gas enclosed by a box is due to the contribution of energy from along 3 orthogonal axis thus six directions, as was discussed in Section 1.5 on kinetic theory, and this was really based upon energy contributions from all directions (an offshoot of $\Phi_0 = (1/6)n\bar{v}$ if you prefer). In kinetic theory the total translational plus rotational energy of a monatomic gas was due to energy being pumped/exchanged into the gas along all three orthogonal axis, with that energy being determined to be: $3NkT/2$. (Note our analysis differs with the traditionally accepted theory wherein the energy of a monatomic gas is only translational)

But the actual energy of this gas that can be used as work i.e. being passed onto a given wall, so that it can move in a given direction e.g. along one axis in one direction, is based upon eqn B.7.14: $\Phi_0 = (1/4)n\bar{v}$. Accordingly, only 2/3 e.g. $(1/4)n\bar{v}/(1/6)n\bar{v} = 2/3$, of a monatomic gas's total energy can be used for work, that being: NkT . Remember gas molecules passes both their translational and rotational energy onto a wall, as part of its kinetic energy exchange with the wall molecules.

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Taken from an Appendix in his book (revised edition)