Az egyensúly felé törekvés és a valószínűség interpretációja

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When two gases mix their temperatures equalize.

Kinetic energy of a particle: $\frac{mv^2}{2}$.
Total kinetic energy of a gas: $K = \sum_{i=1}^{N} \frac{m_i v_i^2}{2}$.

Kinetic theory of gases: temperature of a gas is proportional to the mean kinetic energy of its particles.

$$T \approx \frac{1}{N} K = \frac{1}{N} \sum_{i=1}^{N} \frac{m_i v_i^2}{2} = \overline{\frac{mv^2}{2}}.$$

Temperatures equalize $\leftrightarrow$ mean kinetic energies equalize.

First attempt at a mechanical explanation of equalization of temperatures based on the kinetic theory: Proposition VI of Maxwell (1860): "Illustrations of the Dynamical Theory of Gases."

It seems amazing to me that Maxwell should have thought he was proving a tendency toward equalization of kinetic energies by this argument, or that any of his contemporaries who bothered to examine the argument in detail would have accepted it. (Brush 1976, p. 344)

... a rather lame argument. (Uffink 2007, p. 951)

Suppose that a box contains red and blue particles; for simplicity we assume that similarly colored particles have the same mass.

Let the total kinetic energy (and hence the temperature) of the red particles be higher than those of the blue: $K > K$.

We need to show that this difference diminishes over time, that is $K^t - K^t \to 0$.

We will assume that all collisions are pairwise and perfectly elastic, and hence the combined kinetic energy of two particles do not change during a collision. We also assume that in time interval Δt many pairwise collisions occur, but no particles collide with more than one other particle.

K_{nc}: total kinetic energy of red particles (before collisions) that do not collide during Δt,
K_r: total kinetic energy of red particles (before collisions) that collide with red particles during Δt,
K_b: total kinetic energy of red particles (before collisions) that collide with blue particles during Δt.

Then

$$K - K = (K_{nc} + K_r + K_b) - (K_{nc} + K_b + K_r) .$$

K_{nc}, K_r, K_{nc}, K_b does not change during Δt.

K_b and K_r may change during Δt, so any change in $K - K$ during collision is due to a change in $K_b - K_r$.

The following proof attempts to show that after the collisions $K'_b - K'_r \approx 0$, and hence $K' - K' < K - K$ (if $K_b - K_r > 0$).

Then after many Δt collision periods $K^t - K^t \to 0$, and hence the temperatures of the red and blue gas equalizes.

(Remark: The assumption that $K_b - K_r > 0$ is *very "probable"*, but not necessary! Allowing for the second law to have only statistical validity is another very neat feature of the proof.)

How does the proof work?

(i) First analyze pairwise collisions.

(ii) Aggregate the result of many collisions by making a probabilistic independence / frequency assumption about many collisions.

$\mathbf{v}_h, \mathbf{V}_c$: incoming velocities of particle h with mass m and particle c with mass M.

$\mathbf{v}'_h, \mathbf{V}'_c$: velocities of particles h and c after rebound.

Velocity of center of mass: $\mathbf{v}_{CM} = \frac{1}{m+M}(m\mathbf{v}_h + M\mathbf{V}_c)$.

$\mathbf{v}_h = \mathbf{r}_h + \mathbf{v}_{CM}$,

where $\mathbf{r}_h$: incoming velocity of particle h relative to the velocity of center of mass.

$\mathbf{v}'_h = \mathbf{r}'_h + \mathbf{v}'_{CM}$.

Due to conservation of momentum the collision does not change the velocity of the center of mass: $\mathbf{v}'_{CM} = \mathbf{v}_{CM}$.

Maxwell (in Proposition I–III) shows that the collision keeps the magnitude of velocity relative to the center of mass intact:

$$r'_h = |\mathbf{r}'_h| = |\mathbf{r}_h| = r_h,$$

however the collision alters the direction of rebound, i.e. the direction $\hat{\mathbf{r}}'_h = \frac{1}{r'_h}\mathbf{r}'_h$ of the velocity relative to the center of mass.

In sum the velocity after rebound can be expressed as

$$\mathbf{v}'_h = \mathbf{v}_{CM} + r_h\, \hat{\mathbf{r}}'_h.$$

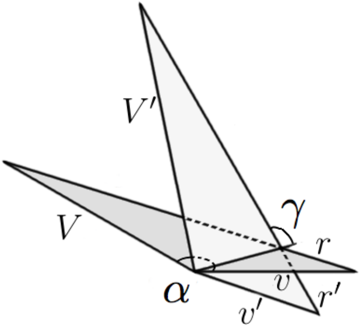


Figure: $\mathbf{v}, \mathbf{V}$: incoming velocities; $\alpha = \angle(\mathbf{v}, \mathbf{V})$: angle between incoming velocities; $\mathbf{r} = \mathbf{v} - \mathbf{v}_{CM}$: incoming velocity of particle h relative to the center of mass; $\mathbf{r}'$: velocity of particle h after rebound relative to center of mass; $\mathbf{v}', \mathbf{V}'$: velocities after rebound ($\mathbf{v}' = \mathbf{v}_{CM} + \mathbf{r}'$); $\gamma = \angle(\mathbf{v}_{CM}, \mathbf{r}') = \angle(\mathbf{v}_{CM}, \hat{\mathbf{r}}')$.

First let's assume that $m = M = m$. The following can be thought of as a *charitable* reconstruction of the proof of Maxwell's Proposition VI (more on this later).

Brief calculation shows that the difference between kinetic energies after a pairwise collision takes the form:

$$\left(\frac{m{v'_h}^2}{2} - \frac{m{V'_c}^2}{2}\right) = 2m\, r_h\, \mathbf{v}_{CM} \cdot \hat{\mathbf{r}}'_h. \tag{1}$$

Consider many pairwise collisions that happen between red and blue particles that share the same center of mass frame.

Key assumption: all directions of rebound occur with roughly equal frequency.

Let us write $(h, c) \in I^{\Delta t}_{\mathbf{v},\mathbf{V}}$ whenever

- particles h and c collide during Δt,
- h is a red particle with incoming velocity $\mathbf{v}$,
- c is a blue particle with incoming velocity $\mathbf{V}$.

We assume that Δt is long enough for $|I^{\Delta t}_{\mathbf{v},\mathbf{V}}|$ to be "large," but short enough to allow for at most one collision for each particles.

Let's add up the equation (1) for all colliding particle pairs whose incoming velocities are $\mathbf{v}$ and $\mathbf{V}$. We get

$$\sum_{(h,c)\in I^{\Delta t}_{\mathbf{v},\mathbf{V}}} \left(\frac{m{v'_h}^2}{2} - \frac{m{V'_c}^2}{2} \right) \approx 0 \qquad (2)$$

since for fixed $\mathbf{v}, \mathbf{V}$ (and hence fixed r_h and $\mathbf{v}_{CM}$) the right hand side terms in the added up equations (1) cancel for opposite $\hat{\mathbf{r}}'_h$ directions of rebound!

Now add further up for all different possible $\mathbf{v}$ and $\mathbf{V}$:

$$\sum_{\mathbf{v},\mathbf{V}} \sum_{(h,c)\in I^{\Delta t}_{\mathbf{v},\mathbf{V}}} \left(\frac{m{v'_h}^2}{2} - \frac{m{V'_c}^2}{2} \right) \approx 0, \tag{3}$$

which, since we accounted for all colliding red and blue particles exactly once, after normalization yields

$$\overline{\frac{mv'^2}{2}} - \overline{\frac{mV'^2}{2}} \approx 0, \tag{4}$$

meaning that

$$K'_b - K'_r \approx 0,$$

which is what we intended to prove.

When the two colliding particles have different masses instead of (1) we get:

$$\left(\frac{m{v'_h}^2}{2} - \frac{M{V'_c}^2}{2}\right) = \left(\frac{m-M}{m+M}\right)^2 \left(\frac{mv_h^2}{2} - \frac{MV_c^2}{2}\right) \tag{5}$$

$$+2\frac{mM(m-M)}{(m+M)^2}\,\mathbf{v}_h \cdot \mathbf{V}_c \tag{6}$$

$$+2m\,r_h\,\mathbf{v}_{CM} \cdot \hat{\mathbf{r}}'_h. \tag{7}$$

- Cancellation of the third term: hold the incoming velocities **v** and **V** fixed.
- Cancellation of the second term: assume further that all directions of incoming velocities for colliding particle pairs occur with roughly equal frequency. (Return later to the issue of physical reasonableness!)

Result of summing up for all collisions:

$$\overline{\frac{mv'^2}{2}} - \overline{\frac{MV'^2}{2}} \approx \left(\frac{m-M}{m+M}\right)^2 \left(\overline{\frac{mv^2}{2}} - \overline{\frac{MV^2}{2}}\right), \qquad (8)$$

meaning that the difference between the mean kinetic energies of the colliding particles decrease after the collisions.

It seems amazing to me that Maxwell should have thought he was proving a tendency toward equalization of kinetic energies by this argument, or that any of his contemporaries who bothered to examine the argument in detail would have accepted it. All Maxwell has done is to pick out one very special kind of collision for which the kinetic energies become more nearly equal and then claim that the same result will follow for all *collisions. This is an instance of a very common fallacy in statistical reasoning [...] (Brush 1976, p. 344)*

Reminder:

$$\left(\frac{m{v'_h}^2}{2} - \frac{M{V'_c}^2}{2}\right) = \left(\frac{m-M}{m+M}\right)^2 \left(\frac{mv_h^2}{2} - \frac{MV_c^2}{2}\right) + 2\frac{mM(m-M)}{(m+M)^2}\,\mathbf{v}_h \cdot \mathbf{V}_c + 2m\, r_h\, \mathbf{v}_{CM} \cdot \hat{\mathbf{r}}'_h.$$

(Note: this formula does not show up in Maxwell's proof.)

On the surface reading, Maxwell seems to have considered a collision between particles with the following choices:

(a1) $\angle(\mathbf{v}_{CM}, \hat{\mathbf{r}}'_h) = 90^o$.

Substituting (a1) the third term cancels and we get:

$$\left(\frac{m{v'_h}^2}{2} - \frac{M{V'_c}^2}{2}\right) = \left(\frac{m-M}{m+M}\right)^2\left(\frac{mv_h^2}{2} - \frac{MV_c^2}{2}\right) + 2\frac{mM(m-M)}{(m+M)^2}\,\mathbf{v}_h\cdot\mathbf{V}_c.$$

Maxwell also assumes:

(a3) $v_h = \overline{v}$, $V_c = \overline{V}$,

(a4) $|\mathbf{v}_h - \mathbf{V}_c| = |\overline{\mathbf{v} - \mathbf{V}}|$,

which, due to his Proposition V, entails

(a2) $\angle(\mathbf{v}_h, \mathbf{V}_c) = 90^o$.

Applying these assumptions Maxwell's derivation would have established

$$\frac{m\overline{v}'^2}{2} - \frac{M\overline{V}'^2}{2} = \left(\frac{m-M}{m+M}\right)^2 \cdot \left(\frac{m\overline{v}^2}{2} - \frac{M\overline{V}^2}{2}\right), \qquad (9)$$

but he interprets the formula he derives as if he obtained the previously seen

$$\overline{\frac{mv'^2}{2}} - \overline{\frac{MV'^2}{2}} \approx \left(\frac{m-M}{m+M}\right)^2 \left(\overline{\frac{mv^2}{2}} - \overline{\frac{MV^2}{2}}\right). \qquad (10)$$

This is an instance of a very common fallacy in statistical reasoning: to assume that if a certain member of a population is just average with respect to property A, then any other property B, computed for that one member, will be equal to the average value of B for the entire population. In other words, one can interchange the operation of averaging with any other analytical operation. This type of shortcut is expecially [sic!] tempting when, as in gas theory, one has to deal with an effectively infinite population, and one knows that the distributions of some properties, at least, are very sharply peaked around the average value. (Brush 1976, p. 344)

Have Maxwell committed this statistical fallacy, or was his proof instead being too terse?

In Propositions I–III of his paper Maxwell tries to establish the **Key Assumption** of the proof by analyzing particle collisions with the aim to argue that particle collisions form a sort of process that brings about a stationary distribution of kinetic energies:

> *If a great many equal spherical particles were in motion in a perfectly elastic vessel, collisions would take place among the particles, and their velocities would be altered at every collision; so that after a certain time the* vis viva *will be divided among the particles according to some regular law, the average number of particles whose velocity lies between certain limits being ascertainable, though the velocity of each particle changes at every collision.* (Maxwell 1860, p. 289.)

General structure of the first six Propositions of the 1860 paper:

Prop. I–III: analysis of perfectly elastic collisions.

Prop. IV: velocity distribution law.

Prop. V: distribution of relative velocities.

Prop. VI: equalization of mean kinetic energies.

The direction or rebound $\hat{\mathbf{r}}'$ is a vector of unit length that can be parametrized by a so-called impact parameter ρ.

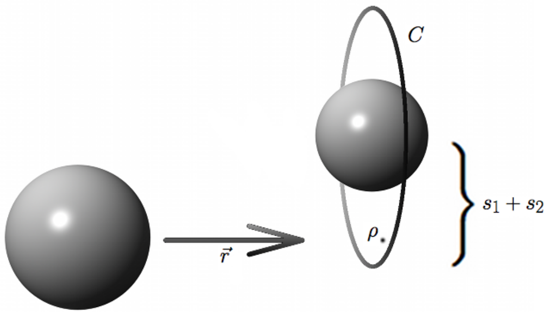


Figure: **r**: incoming velocity of particle 1 relative to the center of mass. C: circle of radii $s = s_1 + s_2$ centered on the second particle in the plane perpendicular to **r**. ρ: point where the line of motion of the first particle intersects circle C.

Maxwell's Proposition II shows that if the assumption that

Condition M the impact parameter ρ is distributed uniformly within the circle C

holds then

Condition A the $\hat{\mathbf{r}}'(\rho)$ directions of rebound are distributed uniformly on the surface of the unit sphere.

When we consider collisions between many particles Condition A implies our **Key Assumption**.

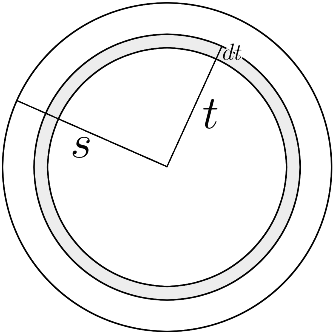


Figure: Ratio of the shaded area between circles of radii t and $t + dt$ to the area of the whole circle C (of radii s): $\frac{(t+dt)^2 - t^2)\pi}{s^2\pi} = \frac{2tdt+dt^2}{s^2} \approx \frac{2tdt}{s^2}$.

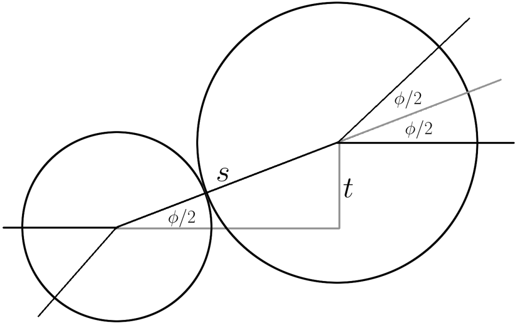


Figure: $t = s\sin\left(\frac{1}{2}\phi\right)$; $dt = s\cos\left(\frac{1}{2}\phi\right)\frac{1}{2}d\phi$; hence the area $\frac{2tdt}{s^2} = \frac{2\sin\left(\frac{1}{2}\phi\right)\cdot s\frac{1}{2}\cos\left(\frac{1}{2}\phi\right)d\phi}{s^2} = \frac{1}{2}\sin(\phi)d\phi$.

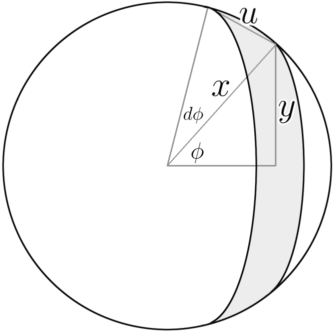
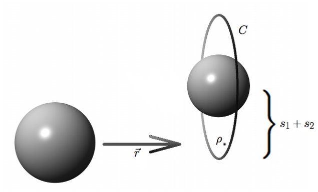


Figure: $y = x\sin(\phi)$; $u = 2x\sin\left(\frac{1}{2}d\phi\right) \approx x \cdot d\phi$. Shaded area on the surface: $\approx u \cdot 2y\pi = x \cdot d\phi \cdot x\sin(\phi)\pi = 4\pi x^2 \cdot \frac{1}{2}\sin(\phi)d\phi = \frac{1}{2}\sin(\phi)d\phi$ after substituting $x = \frac{1}{\sqrt{4\pi}}$ which is the radius of a sphere with unit surface area.

Justification of Condition M?



Condition M the impact parameter ρ is distributed uniformly within the circle C.

How can Condition M be physically justified?

Justification of Condition M?

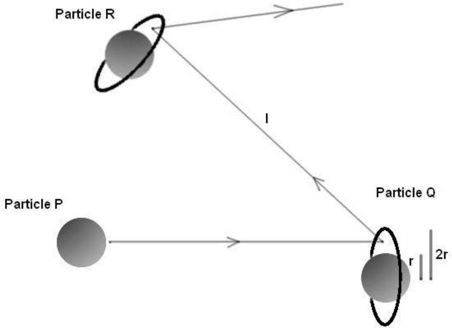


Figure: For an ideal gas the (mean) free path *l* is much larger than the radii of the particles.

- Note however: Condition M is assumed to hold in the center of mass frame of the colliding pairs!

Further problems with Condition M:

- Needs to hold for all successive periods.
- There is no justification of it in terms of the underlying dynamics. (Research question: what sort of dynamics satisfies the condition approximately?)
- Loschmidt reversibility objection!
- "No matter what the other particles are doing" – a form of probabilistic independence.

Maxwell's Proposition IV

What is the relationship between Condition M and Maxwell's assumption of independence of velocity components that is the key behind his proof of his famous Proposition IV (the velocity distribution law)?

> *Prop. IV. To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of equal particles.*

Maxwell's proof relies on that the only solution of

$$f^2(0) \cdot f(|\mathbf{v}|) = f(v_x) \cdot f(v_y) \cdot f(v_z) \tag{11}$$

is the Gaussian

$$f(v_i) = C \cdot e^{A \cdot v_i^2}. \tag{12}$$

Equation (11) arises from three assumptions: that

(A1) a stationary velocity distribution exists;

(A2) the components of velocity in an orthogonal coordinate system are independent: $\mathbf{f}(\mathbf{v}) = \mathbf{f}_x(v_x)\mathbf{f}_y(v_y)\mathbf{f}_z(v_z)$;

(A3) the velocity distribution only depends on the magnitude of the velocity: there exists a function g for which $\mathbf{f}(\mathbf{v}) = g(|\mathbf{v}|)$.

Let N be the whole number of particles. Let v_x, v_y, v_z be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which v_x lies between v_x and $v_x + dv_x$, be $Nf(v_x)dv_x$, where $f(v_x)$ is a function of v_x to be determined.
The number of particles for which v_y lies between v_y and $v_y + dv_y$ will be $Nf(v_y)dv_y$; and the number for which v_z lies between v_z and $v_z + dv_z$ will be $Nf(v_z)dv_z$, where f always stands for the same function.
Now the existence of the velocity v_x does not in any way affect that of the velocities v_y or v_z, since these are all at right angles to each other and independent, *[...]*

[...] so that the number of particles whose velocity lies between v_x and $v_x + dv_x$, and also between v_y and $v_y + dv_y$, and also between v_z and $v_z + dv_z$, is

$$Nf(v_x)f(v_y)f(v_z)dv_x dv_y dv_z.$$

If we suppose the N particles to start from the origin at the same instant, then this will be the number in the element of volume $(dv_x dv_y dv_z)$ after unit of time, and the number referred to unit of volume will be

$$Nf(v_x)f(v_y)f(v_z).$$

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(v_x)f(v_y)f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2).$$

Solving this functional equation, we find

$$f(v_x) = Ce^{Av_x^2}, \quad \phi(v^2) = C^3 e^{Av^2}.$$

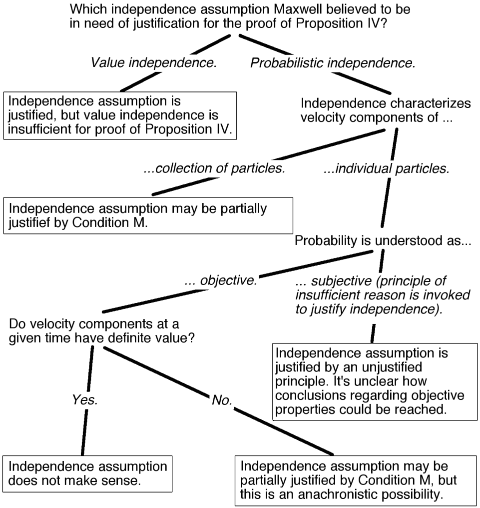
By applying the fact that the total number of particles is finite and fixing the constants, $f(v_x)$ turns out to be the normal distribution, $\frac{1}{a\sqrt{\pi}}e^{-\frac{v_x^2}{a^2}}$. Thus, Maxwell concludes, the number of particles whose velocity in a given direction lies between v_x and $v_x + dv_x$ is

$$dN_{v_x}^{v_x+dv_x} = N\frac{1}{a\sqrt{\pi}}e^{-\frac{v_x^2}{a^2}}dv_x \tag{13}$$

and the number whose speed lies between v and $v + dv$ is

$$dN_v^{v+dv} = N\frac{4}{a^3\sqrt{\pi}}v^2e^{-\frac{v^2}{a^2}}dv. \tag{14}$$

Condition M and Proposition IV



Conclusion

If we charitably assume that Maxwell's arrangement choices stood in as geometrically intuitive shortcuts for a cancellation argument which (as we showed) can be based on his own prior analysis of particle collisions, Proposition VI becomes a terse but convincing demonstration of an irreversible tendency towards equilibrium that lives up to the standards of its time. If so then Maxwell's 1860 proof preceded Boltzmann's first attempt at a mechanical explanation of tendency towards equilibrium with at least 6 years.