A New Definition of Pressure Based on Kinetic Theory Derivations

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Abstract

Typical derivations of kinetic theory equations often exchange the contact time of the particle on a wall with the period of the particle's motion between walls. In this paper we redefine pressure as time-dependent in order to solve this issue and show that this definition makes much more intuitive and theoretical sense than our old definition of pressure.

1 Introduction

In typical introductory physics, teachers often combine Newtonian mechanics and the ideal gas law,

$$PV = NkT$$

to prove that

$$\overline{K} = \frac{3}{2}kT$$

where $\overline{K}$ is the average kinetic energy of the ideal gas, k is Boltzmann's constant, and T is the temperature of the gas.

About a year ago, I decided to revisit this derivation. I began by considering a single particle bouncing off the wall of a rectangular prism and applying Newton's second law as anyone might, but I hit a road block when trying to derive the contact time of the particle with the wall. Online research showed that physicists typically solve this problem by simply plugging in the period of the particle's journey to and from the wall. This clearly does not equal the contact time and results in a totally different impulse applied to the wall, but nevertheless the derivation gives correct results. It turns out that the problem does not lie in Newton's equations (heaven forbid), but rather in our definition of pressure.

As we shall see,

$$P = \frac{F}{A} \tag{1.0.1}$$

does not suffice as a definition of pressure. Instead, we must include time dependence, giving us a new definition of

$$P_n = \lim_{\tau \to \infty} \frac{1}{\tau A} \int_0^{\tau} F_n(t)dt \tag{1.0.2}$$

where P_n represents the pressure exerted by particle n on one wall, A represents the area of said wall, τ represents an arbitrary period of time, and $F_n(t)$ represents the function of the force the particle applies to the wall over time.

David Thompson goes over this fact in *The Physics Teacher* [Tho97], but he does not give the full derivation nor does he give an explicit mathematical definition of pressure as we do here.

In addition, Semat and Katz [SK58] show a clever method to get around the pressure problem by calculating the impulse for a large portion of particles first and then canceling the Δt's afterwards. However, this still does not address pressure's time-dependent nature, which we will discuss here.

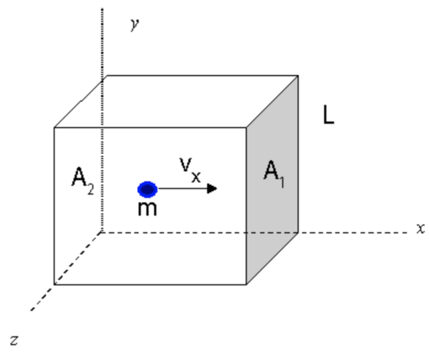

Figure 1: Particle n approaches wall of area A with velocity v_x.

2 The Problem

2.1 The Original Derivation

We begin our derivation with Newton's second law on the x axis,

$$F = m\frac{\Delta v_x}{\Delta t} \tag{2.1.1}$$

where Δt is the particle's contact time with the wall. Assuming a perfectly elastic collision with the wall for an ideal gas, the total change in velocity will equal $2v_x$ (we invert the x axis here to get rid of the negative sign), giving us

$$F = \frac{2mv_x}{\Delta t}. \tag{2.1.2}$$

Now we must find an expression for Δt to plug in; unfortunately, we have no way to derive this information. Newton only tells us what the impulse should be, not the time over which it occurs. Instead, most derivations input the period of the particle's back-and-forth motion in the box, which I will label as τ. We have

$$\tau = \frac{2L_x}{v_x} \tag{2.1.3}$$

where L_x is the length of our box in the x direction (see Figure 1). Plugging this into Newton's equation gives us

$$F = \frac{mv_x^2}{L_x} \tag{2.1.4}$$

which works nicely with the old definition of pressure, $P = \frac{F}{A}$ and spits out

$$P = \frac{mv_x^2}{L_x A}. \tag{2.1.5}$$

If we assume this particle has a square velocity equal to the average square velocity of all particles in the box, we can simply multiply the RHS by the total number of particles, N, to get the total pressure on our single wall. According to the ideal gas law, $P = \frac{NkT}{V}$, so we have

$$\frac{Nm\overline{v_x^2}}{L_x A} = \frac{NkT}{V} \tag{2.1.6}$$

where V represents the volume of the box, or $L_x A$. Thus we can cancel the N terms and volume terms on both sides, leaving us with

$$m\overline{v_x^2} = kT. \tag{2.1.7}$$

Statistically, since every set of axes and reference frame gives the same results, this equation applies to the y and z axes as well. If we use the Pythagorean theorem to find the total velocity in terms of component velocities and take the equation's average, we also find

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}. \tag{2.1.8}$$

Combining these two facts, we find that $\overline{v^2} = 3\overline{v_x^2}$. Equation 2.1.7 therefore generalizes to three dimensions and becomes,

$$m\overline{v^2} = 3kT. \tag{2.1.9}$$

Dividing by 2, we find that the LHS becomes the equation for average kinetic energy, giving us our final result of

$$\overline{K} = \frac{3}{2}kT. \tag{2.1.10}$$

2.2 Old Issues

Not only does our old definition of pressure fail to properly derive the above equation using Newtonian mechanics; it also fails to intuitively describe single-particle systems.

Consider, for instance, a cubic box with a single particle in it at temperature T. Empirical evidence confirms the equation we just derived, so we know for a fact that this temperature determines the velocity of our single particle in the box. This velocity in turn sets the impact force of our particle on the wall. Now, if we double the length of our box along an isotherm, the ideal gas equation tells us that the pressure must halve as the volume doubles and NkT stays constant.

However, this constant temperature implies a constant particle velocity and therefore the same impact force. The wall's area hasn't changed either, so we see that $P = \frac{F}{A}$ stays constant, violating the ideal gas law.

In addition, consider an infinite wall sitting in open space with a single particle moving towards it. The particle hits the wall once, rebounds, and proceeds in the opposite direction, never to return. According to our old definition of pressure, the particle exerts a small force on this wall because it came in contact with it. However, we can call this wall a box of infinite length, area, and volume; as such the pressure must be zero according to the ideal gas law.

We must resolve these discrepancies in some way. But how?

3 Our New Definition

3.1 What Changes?

Something must change in the previous examples to result in a different pressure. However, we can rule out area, temperature, force, velocity, volume, and so on; we have already accounted for these quantities in the equations themselves.

Instead, the *frequency of impact* changes. The particle impacts the wall half as often in the first example and, for all practical purposes, never in the second example, so we must define a new, time-dependent version of the old pressure equation.

3.2 Time Dependence

In order to keep the proper units of pressure, we can assume that our new definition of pressure will include the average value of force over time as opposed to force itself:

$$P_n = \frac{1}{\tau A}\int_0^\tau F_n(t)dt \tag{3.2.1}$$

However, we have no way to determine this arbitrary time interval, τ. Since pressure is an emergent, macroscopic property, we can extend the time interval to infinity to encompass all possible microstates and reach a proper value:

$$P_n = \lim_{\tau\to\infty} \frac{1}{\tau A}\int_0^\tau F_n(t)dt \tag{3.2.2}$$

Thus, we have a new definition of pressure for individual particles. In the first example above, the doubled length of the container would halve the frequency at which the particle impacted the wall, therefore halving the average and halving the pressure, just as the ideal gas law says.

In the second example, the time-dependent force function has one small blip when t is small and nothing else; thus, its average goes to zero as τ goes to zero. The pressure becomes zero, just as we expected.

Figure 2: $F_n(t)$ resembles a square wave of period τ with "blips" of height F and duration Δt.

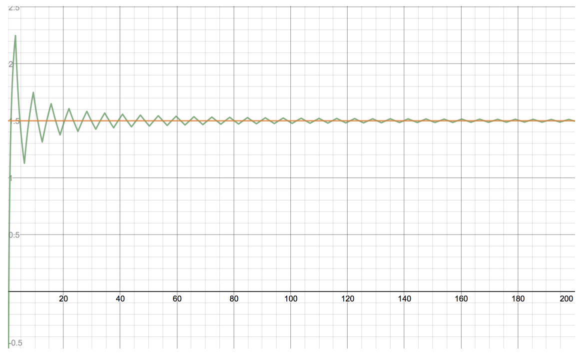

Figure 3: The average value of a square wave tends towards the average over one period as the interval goes to infinity.

Now that we have shown how the new definition fares against our two theoretical examples, let's go through the derivation from the beginning of this paper once more. We'll find that Newton's laws stay intact this time.

3.3 The New Derivation

Let's start the new derivation by examining how the force on our one wall changes over time. For the purpose of simplicity we'll assume that the force is constant for the entire interaction, growing to some value immediately and falling back to zero after impact. We can therefore represent our force function as a sort of square wave (see Figure 2). Each "blip" represents the particle hitting the wall with force F and duration Δt, and each event repeats after a period of τ.

The average over this periodic function as the interval goes to infinity turns out to be the same as the average over one period (see Figure 3). This is the reason we used τ for both our arbitrary time interval and our period. As such, our original definition shrinks down to

$$P_n = \frac{1}{\tau A}\int_0^\tau F_n(t)dt. \tag{3.3.1}$$

The area over a single period is just the area under a single "blip," or $F\Delta t$, making our equation

$$P_n = \frac{F\Delta t}{\tau A}. \tag{3.3.2}$$

However, we already know the value of F; we calculated it in Equation 2.1.2. Combining these equations gives us

$$P_n = \frac{2mv_x\Delta t}{\tau A\Delta t} = \frac{2mv_x}{\tau A}. \tag{3.3.3}$$

If we plug in our expression for τ from Equation 2.1.3, our equation finally turns into Equation 2.1.5:

$$P_n = \frac{mv_x^2}{L_x A}. \tag{3.3.4}$$

The rest of the derivation follows normally.

3.4 Macroscopic View

We have one last test for our new definition of pressure: on large scales, it must tend towards the regular definition of pressure, $P = \frac{F}{A}$, similar to Bohr's correspondence principle in quantum mechanics. If we imagine a total force function $F(t)$ for a large number of particles, this is clearly the case; statistically speaking, this graph would be approximately flat, since particles constantly and randomly hit all walls of the box. Thus, the average value of the function over time would equal the value of the flat function itself; P would really equal $\frac{F}{A}$.

4 Conclusions

Our new definition of pressure represents little more than a curiosity; it leads to the same macroscopic predictions and laws and assumes a classical universe. This new definition may help modern physics in laying the framework for quantum thermodynamics and operator counterparts, but it mainly serves to clear up confusion for those first working through the derivation and learning kinetic theory.

5 Acknowledgements

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References

[SK58] Henry Semat and Robert Katz. Physics, chapter 16: Kinetic theory of gases. *Robert Katz Publications*, 166:301–306, 1958.

[Tho97] David Thompson. Derivation of the ideal gas law from kinetic theory. *The Physics Teacher*, 35:238, 1997.