Kinetic Theory: Flatlining of Polyatomic Gases

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By redefining a gas' kinetic energy as translational plus rotational, an alternative kinetic theory was disclosed by this author that was a superior fit with empirical findings than the accepted kinetic theory. This alternative kinetic theory's fit for monatomic, diatomic and triatomic gases is exceptional, however the same cannot be said of large polyatomic gases. Accordingly, a new consideration called "*flatlining*" is proposed in order to explain the discrepancy between theory and the known empirical finding for heat capacities of large polyatomic gases.

1 Introduction

Traditionally accepted kinetic theory is based upon equipartition and degrees of freedom [1,2,3]. Mathematically speaking equipartition uses the concept that a gaseous molecule with n'' atoms has $3n''$ degrees of freedom (f), [4,5] i.e.:

$$f = 3n''. \tag{1}$$

This leads to the isometric molar heat capacity (C_v) for large polyatomic gases being

$$C_v = \frac{3}{2} n'' R \tag{2}$$

where *n"* signifies the *polyatomic number* i.e. the number of atoms in each gas molecule. Numerous explanations for traditional kinetic theory's failure in properly describing empirically determined heat capacities, have been proposed [1,6-10]. Interestingly, Einstein thought that such failures in explaining empirical findings demonstrated the need for quantum theory [11-12].

This author proposed a new alternative kinetic theory [1]. The basis of this alternative theory was that the surrounding walls molecule's mean vibrational energy, as defined by (kT), is continually pumped onto the gaseous molecules that they surround. Where (k) is Boltzmann's constant and (T) is the absolute temperature.

After numerous impacts between the gaseous molecules and walls, the above pumping results in the total kinetic energy ($E_{kT(t,r)}$) of an N-molecule monatomic gas being defined by [1]:

$$E_{kT(t,r)} = \frac{3}{2} NkT. \tag{3}$$

Traditional kinetic theory considers that the kinetic energy as defined by eqn (3) represents purely translational energy.

In terms of this author's alternative kinetic theory, the above stated total kinetic energy consists of the gas' translational plus its rotational energy [1]. Interestingly, this author's theory is a superior fit with various heat capacities studies for gases [1,13-18], when compared to accepted theory.

In order to better understand, consider that you hit a tennis ball with a suitable racquet. If the ball impacts the racquet's face at a 90 degree angle then the ball will have significant translational energy in comparison to any rotational energy.

Conversely, if the ball impacts the racquet at an acute angle, although the same force is imparted onto that ball, the ball's rotational energy can be significant in comparison to its translational energy. The point becomes, that both the translational and rotational energy, are due to the same impact [1].

Now apply the above macroscopic considerations to the microscopic world. When vibrating wall molecules pump their mean vibrational energy onto the gas molecules that they surround it, it only makes sense that this results in both translational and rotational energy of the gas [1].

This author also pointed out that all kinetic theory only holds for sufficiently dilute gases because the predominate energy exchange is due to gas-wall molecule collisions, where wall molecules that act as massive energy pumps, i.e. gas molecules tend to take on the wall's energy with every gas-wall collision [1]. However this would not necessarily be the case for gases that are not sufficiently dilute i.e. gases where inter-gas molecular collisions are the dominate interaction [1].

This author has further asserted [1,19,20] that inter-gas molecular collisions tend to obey conservation of momentum, rather than adhere to kinetic theory. And, when inter-gas collisions dominate over gas-wall collisions then kinetic theory, the ideal gas law, Avogadro's hypothesis, Maxwell's distributions/velocities etc. all start to lose their validity [1].

For a system of diatomic gas molecules, the wall molecules still pass the same mean kinetic energy onto the diatomic gas molecule's center of mass with each collision. Therefore the diatomic gas' kinetic energy is still defined by eqn (3) [1].

The diatomic gas molecule's vibrational energy would be related to the absorption and/or emission of its surrounding blackbody/thermal radiation at temperature (T). The vibrational energy (E_v) of an N-molecule diatomic gas in a closed system becomes [1]

$$E_v = NkT. \tag{4}$$

And the total energy (E_{tot}) for an N molecule diatomic gas becomes [1]

$$E_{tot} = E_{kT(t,r)} + E_v = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT. \tag{5}$$

Similarly, for N molecules of n''-polyatomic gas, the total vibrational energy is [1]

$$E_v = (n'' - 1)NkT. \tag{6}$$

And, the total energy (E_{tot}) for the polyatomic gas molecule becomes [1]:

$$E_{tot} = E_{kT(t,r)} + E_v = \frac{3}{2}NkT + (n'' - 1)NkT. \tag{7}$$

Hence,

$$E_{tot} = \left(n'' + \frac{1}{2}\right)NkT. \tag{8}$$

Dividing both sides by temperature and rewriting in terms of per mole: (N=6.022×10^{23}), equation (8) becomes [1]:

$$\frac{E_{tot}}{T} = Nk\left(n'' + \frac{1}{2}\right) = R\left(n'' + \frac{1}{2}\right). \tag{9}$$

For most temperature regimes, the heat capacity of gases remains fairly constant, hence equation (9) can be rewritten in terms of the isometric molar heat capacity (C_v) [1], i.e.

$$C_v = R\left(n'' + \frac{1}{2}\right). \tag{10}$$

The difference between molar isobaric heat capacity (C_p) and molar isometric heat capacity (C_v) for gases is the ideal gas constant (R). Therefore, a gas's isobaric heat capacity C_p becomes

$$C_p = R\left(n'' + \frac{1}{2}\right). \tag{11}$$

Interestingly this author realized that the above difference between molar heat capacities allows for a relationship between the ideal gas constant (R) and the ability of a mole of gas molecules to do work against a gravitational field [1, 20-21], as a function of temperature.

Based upon equations (10) and (11) the gas's molar specific heats were plotted against its polyatomic number (n'') as is shown by Fig. 1 and compared to the traditional accepted values for large polyatomic gases as given by eqn (2). Note the empirical data used in plotting Fig. 1 can be found in the Tables (1) and (2) provided in this author's previous paper [1] concerning kinetic theory.

Moreover, there was a discrepancy, between our model and empirical findings for relatively large polyatomic gases. It becomes a goal of this paper to provide a plausible explanation for the moderate discrepancy between this author's plots based upon equations (10) and (11) and the accepted empirical findings for large polyatomic molecules i.e. those whose polyatomic number is greater than four (n''> 4).

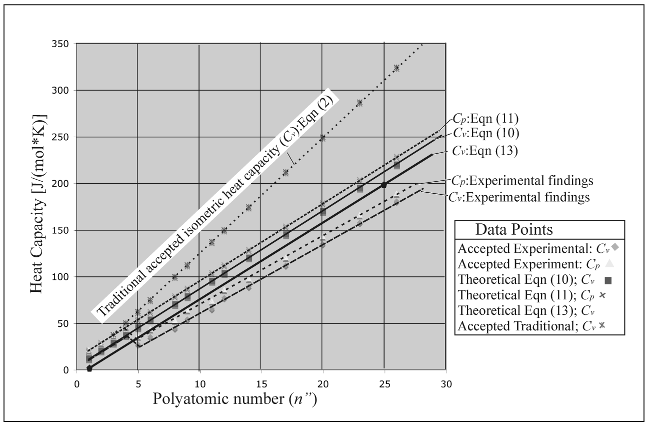

Fig. 1: Empirical versus theoretical heat capacities.

2 Flatlining

Why does the discrepancy exist for n''> 4? Let us consider that the gas molecule's size influences the exchange of kinetic energy (translational plus rotational) with the wall molecule's vibrational energy. How do we model this?

Consider the small monatomic gas molecule hitting the wall at location C, in Fig 2. Here the wall molecule is moving outward from the wall thus instantly imparting momentum, hence pumping its kinetic energy onto the gas molecule during the collision.

Next consider the gas molecule hitting the wall at location B. The wall molecule and gas molecule are initially moving in the same direction, i.e. both into the wall. However, since the wall molecule is vibrating at a very high frequency then within a fraction of a nanosecond, the wall molecule will start moving in the opposite direction. At this point the wall molecule imparts its momentum hence imposes kinetic energy (translational plus rotational) onto the impacting gas molecule.

Understandably, small gas molecules will tend to interact cleanly with the wall molecules, i.e. the significantly larger vibrating wall molecules cleanly pumps/imposes their mean vibrational energy directly onto the much smaller gas molecules. Seemingly, this is not the case for larger mole-cules. Perhaps vibrating wall molecules simply cannot clean-ly pump kinetic energy onto the larger gas molecules.

It can be envisioned that elongated linear gas molecules and/or large gas molecules tend to "*flatline*" against the wall, as is illustrated in Fig 2 at location A. The implication being that such large and/or elongated gas molecules tend to strike two or more (several) vibrating wall molecules at an instant, when some wall molecules are moving inwards, while their neighboring wall molecules are moving outwards, with respect to the wall as a whole. Note: The motions of the molecules are indicated by the arrows in Fig. 2.

Clearly the above should alter the dynamics of any kine-

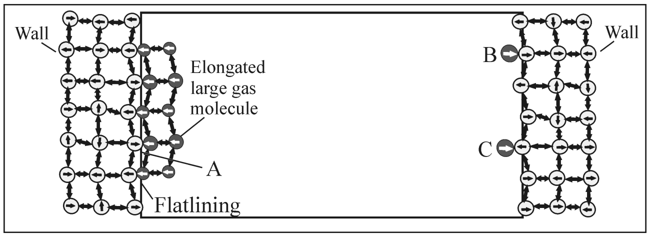

Fig. 2: Shows an elongated linear gas molecule flatlining against a wall at location A and the relative motions of the wall's molecules or atoms plus the relative motions of the gas' atoms. Also shown are smaller gas molecules hitting the wall at locations B and C.

matic energy exchange! The expectation is that a large polyatomic gas molecule's mean kinetic energy would no longer be simply defined in terms of the vibrating wall molecule's mean energy! Furthermore, the expectation is that polyatomic gases still interact with any surrounding blackbody/thermal radiation, thus continually striving for thermal equilibrium.

Consider that the primary energy exchange is between large polyatomic gases and their surroundings is with their surrounding blackbody/thermal radiation. The total energy (E_{tot}) imparted onto the gas molecule becomes the purely vibrational energy as defined by eqn (6). Accordingly:

$$\frac{E_{tot}}{T} = (n'' - 1)Nk. \tag{12}$$

Based upon eqn (12), the expected isometric molar heat capacity becomes:

$$C_v = (n'' - 1)R. \tag{13}$$

The graph for eqn. (13) is shown on Fig. 1; based upon $C_v = 0$ when $n''=1$, and $C_v = 19 \times 8.314 = 158.00$ when $n''=20$. The fit for the isometric molar heat capacity (C_v) based upon eqn. (10) was very good, if not exceptional, for monatomic through triatomic gases ($n'' <$ *or* $= 4$) but not so much larger polyatomic gases i.e. $n'' > 4$. Certainly eqn (13) is a better fit for the larger polyatomic gases than eqn. (10) was but the fit is only fairly good at best!

Reconsider what all might be happening. As previously stated, flatlining implies that large polyatomic gas' kinetic energy is no longer defined/controlled by the pumping of the wall molecule's vibrational energy onto the them. Remember by kinetic energy herein we mean the gas' translational plus rotational energy. In such a situation it becomes cumbersome to infer any net direction of energy flow being exchanged during collisions.

As previously stated, this author [1] understands that a limitation for the isometric molar heat capacity being defined by eqn (10) was the gas being *sufficiently dilute*, i.e. dilute enough that gas-wall molecule collisions are dominate in comparision to inter-gas molecule collisions. Part of the reasoning being that inter gas molecule collisions will obey conservation of momentum but not necessarily conservation of energy [1] i.e. inter-gas collisions tend to be inelastic. With further modelling this may help explain what is witnessed.

This author's insight that inter-gas collisions may generally be inelastic requires that radiation is given off during such collisions thus enabling inelastic collisions to adhere to conservation of energy [1]. Such collision induced radiation, whether it be considered as part of the system's blackbody and/or thermal energy, becomes part of the system being in thermal equilibrium i.e. the walls adsorb as much radiation energy as they emit.

The above is not to say that the walls and/or polyatomic gases necessarily emit the identical spectrum that they adsorb! It is, however to say that the total rate of energy of emission approximates that of the adsorption! Note; the total energy associated with radiation, whether it is blackbody, thermal or otherwise, can often be considered as insignificant, when compared to the energy associated with kinematics of matter. This is not saying that it can simply be ignored as is too often traditionally done in thermodynamics!

It should also be stated that large polyatomic gases will have large cross-sectional areas hence the concept of being sufficiently dilute may require higher mean molecular volumes in the gaseous state i.e. relatively low pressures.

Can we now claim that large polyatomic gas molecules tend to attain their kinetic energy from inter-gas collisions that obey conservation of momentum? No we cannot! However our expectation becomes that large polyatomic gases will not have the specified kinetic energies that smaller gases possess.

To further emphasize; the conceptualization of small gases having their kinetic energy pumped into to them by surrounding vibrating wall molecules, does not necessitate that gas-wall molecules collisions are elastic. On the contrary, it just implies that the gas' mean kinetic energy is driven into them via numerous collisions with wall molecules.

3 Addressing traditional dogma

As previously stated traditional kinetic theory is based upon equipartition and degrees of freedom arguments. We can go back further and acknowledge that for most of us, our learning started with considering a gas molecule's momentum and that momentum is conserved in elastic wall-gas molecule collisions.

The main problem with the above approach being that elastic collisions are a rarity i.e. it is rare to have a collision where both momentum and kinetic energy are conserved. The one simple exception being the case of two balls of equal mass colliding, with the second ball being stationary before the collision and that second ball then attains all the kinetic energy from the first ball, after the collision, i.e. first ball is stationary after the collision.

Rather than address the elephant in the room, traditional kinetic theory simply considered that all collisions are elastic, as well as, the gas molecule leaves the wall with the same magnitude of momentum as it has prior to hitting the wall. Realizing that walls impose their energetics onto the dilute gas implies that traditional teaching may have put the cart ahead of the horse!

Certainly considering all collisions as being elastic avoids having to contemplate the various frequencies of radiation that would be associated with inelastic collisions. And when in equilibrium; since the mean kinetic energy of the gas molecules is constant then yes the mean magnitude of momentum remains constant but this is no longer a requirement for an elastic gas-wall collision!

The situation is no more complicated if it is considered that a dilute gas in thermal equilibrium requires that all of the following three states remain related to the same temperature (T). Basically, as previously stated by this author [1]:

1. The walls are in thermal equilibrium with the enclosed radiation i.e. blackbody, thermal or otherwise.
2. The gas' translational plus rotational energy is pumped into the gas by the more massive vibrating wall molecules.
3. The gas' vibrational energies are in thermal equilibrium with the enclosed radiation i.e. blackbody, thermal or otherwise.

Remember: Part of this radiation surrounding the gas molecules will now be a result of the various inelastic intermolecular collisions.

4 Atmospheric gases

At first glance considering that walls impose/pump their vibrational energy onto relatively small gases' kinetic energy, may feel counter-intuitive in part because gases are routinely put into, and/or removed from containers without any real noticeable temperature changes. However, if we realize that the above does not necessarily hold for enclosed larger polyatomic gases and that such gases generally obtain their vibrational energy from the surrounding blackbody/thermal radiation, then the mean energetics of such gases will not change significantly by placing them into, nor removing them from enclosures.

Certainly small gas molecules in our atmosphere will hit the Earth's rough surface and have a certain amount of their kinetic energy pumped/imposed upon them in various inelastic collisions with Earth's surface. Even so, for atmospheric gases inter-gas collisions still should dominate.

Next consider the collision of a small gas molecule with a larger polyatomic gas. The expectation becomes that the larger gas molecule will behave as a massive wall molecule does, i.e. the large polyatomic gas molecule will use its vibrational energies to pump/impose some fairly well-defined mean kinetic energy (translational plus rotational) onto the colliding small gas molecules.

5 Other proofs for inelastic collisions

There is more proof to inelastic intermolecular collisions than just the awkwardness of the mathematical justification for elastic intermolecular collisions. Some examples being:

1. Viscous dissipation i.e. heat being generated by gases squeezed through a valve.
2. Natural *P-T* relationships i.e. temperature increases with increasing pressure.
3. Joule's weight experiment i.e. Although designed to demonstrate a correlation between work and energy, what it really shows is that imposed increases to a liquid's flow (due to the paddles attached to weights) resulted in increased intermolecular friction, which generated heat.

All of the above is readily explained in terms of inelastic intermolecular collisions, but all are not so readily explainable in terms of traditional understandings.

6 Conclusions

This author's previous conclusion [1]; kinetic theory needs to be redrafted based upon the previous understanding that a gas' kinetic energy has both translational and rotational components that are pumped/imposed onto them due to the same wall molecule's vibrational energy. Moreover, it seemingly holds for most small gaseous molecules i.e. gas' whose polyatomic number is 4 or less.

For larger polyatomic gases, *flatlining* helps explain what is witnessed. Specifically flatlining means that larger polyatomic gases tend to strike two or more vibrating wall molecules at some instant. Therefore any kinetic energy transfer between impacting gas molecule and vibrating wall molecule, is not clean. Moreover it becomes awkward to even determine what direction the net flow of energy exchange actually goes, assuming that there is any actual a net energy exchange!

This certainly improves the fit between accepted empirical findings for large polyatomic gases and the kinetic theory as previously proposed [1], combined with what is currently described herein, by this author.

Interestingly, it can be contemplated that atmospheric gases will tend to follow similar dynamics where large polyatomic gases adsorb surrounding radiation (blackbody and/or thermal) thus increasing their vibrational energy. This vibrational energy is then pumped/imposed onto any small gas molecules that collide with the larger polyatomic gases.

Furthermore, we asserted that most inter-molecular collisons probably are inelastic. In which case radiation (thermal, blackbody or otherwise) will be a byproduct of such collisions, and as such must be considered as part of a system's state, whether or not, that system is in thermal equilibrium. And this does alter our consideration of thermal equlibrium!

The overall implication being that traditional theorists unwittingly put the cart ahead of the horse by beginning the teaching of kinetic theory in terms of gas molecule's momentum and elastic collisions. This ignores the fact that elastic collisions are rare hence may be an unnecessary, illogical, unrealistic, conceptualization when applied to kinetic theory!

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