A New Perspective for Kinetic Theory and Heat Capacity

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The currently accepted kinetic theory considers that a gas' kinetic energy is purely translational and then applies equipartition/degrees of freedom. In order for accepted theory to match known empirical finding, numerous exceptions have been proposed. By redefining the gas' kinetic energy as translational plus rotational, an alternative explanation for kinetic theory is obtained, resulting in a theory that is a better fit with empirical findings. Moreover, exceptions are no longer required to explain known heat capacities. Other plausible implications are discussed.

1 Introduction

The conceptualization of a gaseous system's kinematics originated in the writings of the 19th century greats. In 1875, Maxwell [1] expressed surprise at the ratio of energies (translational, rotational and/or vibrational) all being equal. Boltzmann's work on statistical ensembles reinforced the current acceptance of law of equipartition with a gas's energy being equally distributed among all of its degrees of freedom [2–3]. The net result being that the accepted mean energy for each independent quadratic term being $kT/2$.

The accepted empirically verified value for the energy of a /textitN molecule monatomic gas is $kT/2$ with its isometric molar heat capacity (C_v) being ($3R/2$). An implication is that a monatomic gas only possesses translational energy [4–5]. The reasoning for this exception is that the radius of a monatomic gas is so small that its rotational energy remains negligible, hence its energy contribution is simply ignored.

Mathematically speaking equipartition based kinetic theory states that a molecule with n'' atoms has $3n''$ degrees of freedom (f) [5–6] i.e.:

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

This leads to the isometric molar heat capacity (C_v) for large polyatomic molecules:

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

Interestingly, the theoretical expected heat capacity for N diatomic molecules is $7NkT/2$. This is the summation of the following three energies a) three translational degrees, i.e. $3NkT/2$. b) three rotational degrees of freedom, however since the moment of inertia about the internuclear axis is vanishing small w.r.t. other moments, then it is excluded, i.e. NkT. c) Vibrational energy, i.e. NkT. This implies a molar heat capacity $C_v = 7NkT/2 = 29.3$ J/(mol*K). However, empirical findings indicate that the isometric molar heat capacity for a diatomic gas is actually 20.8 J/(mol*K), which equates to $5RT/2$ [6]. This discrepancy for diatomic gases certainly allows one to question the precise validity of accepted kinetic theory! In 1875 Maxwell noted that since atoms have internal parts then this discrepancy maybe worse than we believe [7].

Various explanations for equipartition's failure in describing heat capacities have been proposed. Boltzmann suggested that the gases might not be in thermal equilibrium [8]. Planck [9] followed by Einstein and Stern [10] argued the possibility of zero-point harmonic oscillator. More recently Dahl [11] has shown that a zero point oscillator to be illusionary. Lord Kelvin [12–13] realized that equipartition maybe wrongly derived. The debate was somewhat ended by Einstein claiming that equipartition's failure demonstrated the need for quantum theory [14–15]. Heat capacities of gases have been studied throughout the 20th century [16–19] with significantly more complex models being developed [20–21].

It becomes a goal of this paper to clearly show that an alternative kinetic theory/model exists. A simple theory that correlates better with empirical findings without relying on exceptions while correlating with quantum theory.

2 Kinetic theory and heat capacity simplified

Consider wall molecules 1 through 8, in Fig. 1. The total mean energy along the x-axis of a vibrating wall molecule is

$$\overline{E}_x = kT. \tag{3}$$

Half of a wall molecule's mean energy would be kinetic energy, and half would be potential energy. Thus, the mean kinetic energy along the x-axis, remains

$$\overline{E}_x = \frac{kT}{2}. \tag{4}$$

In equilibrium, the mean kinetic energy of a wall molecule, as defined by equation (4) equals the mean kinetic energy of the gas molecule along the same x-axis. Herein, the wall in the y-z plane acts as a massive pump, pumping its mean kinetic energy along the x-axis onto the much smaller gas molecules.

In equilibrium each gas molecule will have received a component of kinetic energy along each orthogonal axis. Although there are six possible directions, at any given instant, a gas molecule can only have components of motion along three directions, i.e. it cannot be moving along both the positive and negative x-axis at the same time. Therefore, the total kinetic energy of the N molecule gas is defined by

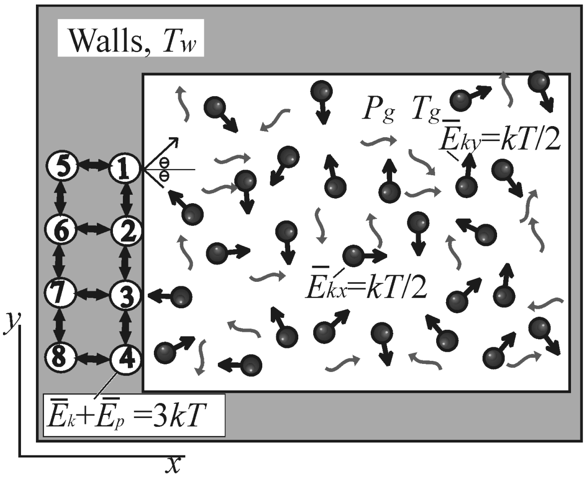

Fig. 1: Ideal monoatomic gas at pressure P_g and temperature T_g sourrounded by walls at temperature $T_w = T_g$. Gas molecules have no vibrational energy.

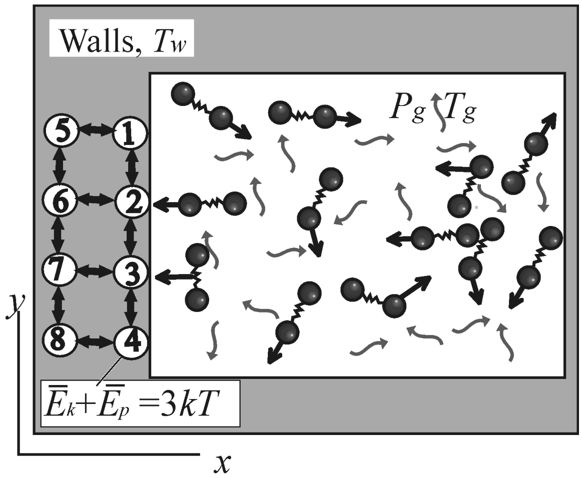

Fig. 2: Ideal diatomic gas at pressure P_g and temperature T_g sourrounded by walls at temperature $T_w = T_g$. Gas molecules have vibrational energy.

equation (4) i.e. $3NkT/2$. Up to this point we remain in agreement with accepted theory.

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 being, in real life both the translational and rotational energy, are due to the same impact.

Now reconsider kinetic theory. Understandably, momentum transfer between both the wall's and gas' molecules result in energy exchanges between the massive wall and small gas molecules. Moreover, the exact nature of the impact will vary, even though the exchanged mean energy is constant.

Case 1: Imagine that a monatomic gas molecule collides head on with a wall molecule, e.g. the gas molecule hitting wall molecule no. 3 in Fig. 1. Herein, the gas molecule might only exchange translational energy with the wall, resulting in the gas molecule's mean kinetic energy being purely translational, and defined by equation (4).

Case 2: Imagine that a monatomic gas molecule strikes wall molecule no. 1 at an acute angle. The gas molecule would obtain both rotational and translational energy from the impact such that the total resultant mean energy of the gas molecule would be the same as it was in Case 1, i.e. defined by equation (4).

Case 3: Imagine a rotating and translating monatomic gas molecule striking the wall. Both the rotational and translational energies will be passed onto the wall molecule. Since the wall molecule is bound to its neighbors, it cannot rotate hence both energies can only result in vibrational energy of the wall molecules along its three orthogonal axis.

After numerous wall impacts, our model predicts that an N molecule monatomic gas will have a total kinetic energy (translational plus rotational) defined by

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

Fig. 2 illustrates a system of diatomic gas molecules in a container. 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 defined by equation (5). The diatomic gas molecule's vibrational energy would be related to the absorption and emission of its surrounding blackbody/thermal radiation. Therefore, the mean x-axis vibrational energy within a diatomic gas molecule remains defined by equation (3) and the total mean energy for a diatomic gas molecule becomes defined by

$$\overline{E}_{tot} = \overline{E}_{kT(t,r)} + \overline{E}_v = \frac{3}{2} kT + kT = \frac{5}{2} kT. \tag{6}$$

Therefore the total energy for an N molecule diatomic gas becomes

$$E_{tot} = E_{kT(t,r)} + E_v = \frac{3}{2} NkT + NkT = \frac{5}{2} NkT. \tag{7}$$

For an N molecule triatomic gas:

$$E_{tot} = E_{kT(t,r)} + E_v = \frac{3}{2} NkT + 2NkT = \frac{7}{2} NkT, \tag{8}$$

n'' signifies the polyatomic number. Therefore for N molecules of n''-polyatomic gas, the vibrational energy is

$$E_v = (n'' - 1)NkT. \tag{9}$$

Therefore, the total energy for a polyatomic gas molecule is:

$$\begin{aligned} E_{tot} = E_{kT(t,r)} + E_v = & \ \frac{3}{2} NkT + (n'' - 1) NkT \\ = & \left(n'' + \frac{1}{2}\right) NkT. \end{aligned} \tag{10}$$

Dividing both sides by temperature and rewriting in terms of per mole (N=6.02 × 10^{23}) then equation (10) becomes:

$$\frac{E_{tot}}{T} = nk\left(n'' + \frac{1}{2}\right) = R\left(n'' + \frac{1}{2}\right). \tag{11}$$

For most temperature regimes, the heat capacity of gases remains fairly constant, hence equation (11) can be rewritten in terms of the isometric molar heat capacity (C_v), i.e.

$$C_v = R\left(n'' + \frac{1}{2}\right). \tag{12}$$

The difference between molar isobaric heat capacity (C_p) and molar isometric heat capacity (C_v) for gases is the ideal gas constant (R) [see equation (15)]. Therefore, a gas's isobaric heat capacity C_p becomes

$$C_p = R\left(n'' + \frac{1}{2}\right) + R = R\left(n'' + \frac{3}{2}\right). \tag{13}$$

The adiabatic index is the ratio of heat capacities, i.e. dividing equation (13) by equation (12) gives the adiabatic index

$$\gamma = \frac{C_p}{C_v} = \frac{\left(n'' + \frac{3}{2}\right)}{\left(n'' + \frac{1}{2}\right)}. \tag{14}$$

Table 1 shows the accepted isometric and isobaric molar heat capacities for various substances for $0 > n'' > 27$. These values were calculated using data (specific heats) from an engineering table (Rolle [22]) that is shown in Table 2. Note: Engineer's use specific heats (per mass), physicists and chemists prefer heat capacity (per mole).

In Fig. 3, both our theoretical molar isometric and isobaric [equations (12) and (13)] heat capacities are plotted against the number of atoms (n'') in each molecule. The accepted empirically determined values for heat capacities versus n'' (from Table 1) are also plotted. The traditional theoretical values for molar heat capacities [eq. (2)] are also plotted.

The theory/model proposed herein remains a better fit to empirical findings for all polyatomic molecules. Importantly, it does not rely upon the exceptions that plague the traditionally accepted degrees of freedom based kinetic theory.

Interestingly, there is a discrepancy, between our model and empirical known values for $4 < n'' < 9$. Moreover, the slope of our theoretical values visually remains close to the slope of empirically determined values for $n'' > 8$. Furthermore, hydrogen peroxide (H_2O_2, C_v= 37.8, $n'' = 4$) and acetylene (C_2H_2, $n'' = 4$, C_v= 35.7) are linear bent molecules and good fit, while pyramidal ammonia (NH_3, $n'' = 4$, C_v = 27.34) is not. Could the gas molecule's shape influence how it absorbs surrounding thermal radiation, hence its vibrational energy?

Table 2 shows the accepted adiabatic index versus our theoretical adiabatic index for most of the same substances shown in Table 1. Our theoretical adiabatic index compares rather well with the accepted empirical based values, especially for low $n'' < 4$ and high $n'' > 11$, as is clearly seen in Fig. 4. Although not 100% perfect, this new theory/model certainly warrants due consideration by others.

3 Kinetic theory and thermal equilibrium

Kinetic theory holds because the walls act as massive energy pumps, i.e. gas molecules take on the wall's energy with every gas-wall collision. For sufficiently dilute gases, this remains the dominant method of energy exchange. Mayhew [23–24] has asserted that inter-gas molecular collisions tend to obey conservation of momentum, rather than adhere to kinetic theory. Therefore, when inter-gas collisions dominate over gas-wall collisions, then kinetic theory, the ideal gas law, Avogadro's hypothesis, Maxwell's velocities etc. all can start to lose their precise validity.

It is accepted that there are changes to heat capacity in and around dissociation temperatures. Firstly, at such high temperatures, the pressure tends to be high; hence the inter-gas collisions may dominate. This author believes that this actually helps explain why kinetic theory falters in polytropic stars, wherein high-density gases collide in a condensed matter fashion hence one must use polytropic solutions. Secondly, at high temperatures a system's thermal energy density is no longer proportional to temperature, i.e. a blast furnace's thermal energy density is proportional to T^4 [22].

Blackbody radiation describes the radiation within an enclosure. For an open system and/or none blackbody, the thermal radiation surrounding the gas molecules may be better to considered. Herein thermal radiation means radiation that is readily absorbed and radiated by condensed matter and/or polyatomic gases, resulting in both intramolecular and intermolecular vibrations.

For a system of dilute polyatomic gas e.g. Fig. 2, thermal equilibrium requires that all of the following three states remain related to the same temperature (T):

1. The walls are in thermal equilibrium with the enclosed blackbody/thermal radiation.
2. The gas' translational plus rotational energy is in mechanical equilibrium with the molecular vibrations of the walls.
3. The gas' vibrational energies are in thermal equilibrium with the enclosed blackbody/thermal radiation.

Imagine that a system of dilute polyatomic gas is taken to remote outer space, and that the walls are magically re-

Table 1: Accepted isometric and isobaric heat capacities versus theoretical i.e. empirical findings versus Eqn. (12), Eqn. (13), as well as Eqn. (2). Note: Accepted heat capacities were calculated from the engineer's specific heats in Table 2 (Rolle [22]), exception being H_2O_2 which was taken from Giguere [19].

Substance		n''	Accepted C_v [J/mol*K]	Eqn. (12) C_v [J/mol*K]	Accepted C_p [J/mol*K]	Eqn. (13) C_p [J/mol*K]	Eqn. (2) C_v [J/mol*K]
Helium	He	1	12.48	12.47	20.80	20.78	
Neon	Ne	1	12.47	12.47	20.79	20.78	
Argon	Ar	1	12.46	12.47	20.81	20.78	
Xenon	Xe	1	12.47	12.47	20.58	20.78	
Hydrogen	H_2	2	20.52	20.78	28.83	29.09	
Nitrogen	N_2	2	20.82	20.78	29.14	29.09	
Oxygen	O_2	2	21.02	20.78	29.34	29.09	
Nitric oxide	NO	2	21.55	20.78	29.86	29.09	
Water vapor	H_2O	3	25.26	29.09	33.58	37.40	37.40
Carbon dioxide	CO_2	3	28.83	29.09	37.14	37.40	37.40
Sulfur dioxide	SO_2	3	31.46	29.09	39.78	37.40	37.40
Hydrogen peroxide	H_2O_2	4	37.4	37.73	46.05	45.71	49.86
Ammonia	NH_3	4	27.37	37.40	35.70	45.71	49.86
Methane	CH_4	5	27.4	45.71	35.72	54.0	62.33
Ethylene	C_2H_4	6	35.24	54.02	43.54	62.33	74.79
Ethane	C_2H_6	8	44.35	70.64	52.65	78.95	99.72
Propylene	C_3H_6	9	53.82	78.95	63.92	87.26	112.19
Propane	C_3H_8	11	65.18	95.57	73.51	103.88	137.12
Benzene	C_6H_6	12	73.50	103.88	81.63	112.19	149.58
Isobutene	C_4H_8	12	77.09	103.88	85.68	112.19	149.58
n-Butane	C_4H_{10}	14	89.10	120.50	97.42	128.81	174.51
Isobutane	C_4H_{10}	14	88.52	120.50	96.84	128.81	174.51
n-Pentane	C_5H_{12}	17	111.91	145.43	120.20	153.74	211.91
Isopentane	C_5H_{12}	17	111.69	145.43	119.99	153.74	211.91
n-Hexane	C_6H_{14}	20	134.78	170.36	143.06	178.67	249.30
n-Heptane	C_7H_{16}	23	157.62	195.29	165.94	203.60	286.70
Octane	C_8H_{18}	26	180.60	220.22	188.83	228.53	324.09

moved and the gas disperses. Spreading at the speed of light the blackbody/thermal radiation density decreases faster than the density of slower moving gas molecules. As the radiation density decreases, the rate at which polyatomic gaseous molecules absorbs blackbody/thermal radiation decreases in time. Hence their vibrational energy decreases although their mean velocity remains constant. Now place a thermometer in the expanding wall-less gas, what will it read? Traditional kinetic theory claims that the temperature will be the same because the gas molecule's velocity remains constant i.e. temperature is only associated with the system's kinematics [2–3]. However, without walls the blackbody/thermal radiation decouples from thermal equilibrium i.e. the mean velocity of the gas molecules are associated with one temperature, but the radiation density is no longer associated with that temperature. This bodes the question: What is the real temperature? Of course this means accepting that the thermometer not only exchanges kinetic energy with the gas molecules, but it also exchanges blackbody/thermal radiation with its surroundings.

The above is another reason that this author hypothesizes that kinetic theory can falter in systems without walls. The

Table 2: Engineer's accepted adiabatic index compared to theoretical: Eqn. (14). Note: Data in first six columns after Rolle [22]. Rolle's reference: J.F. Masi, Trans. ASME, 76:1067 (October, 1954): National Source of Standards (U.S.) Circ. 500, Feb. 1952; Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas, A&M University, College Station, Texas.

Substance		n''	Molar mass [g/mol]	Engineer's R [J/kg*K)]	Engineer's C_p [kJ/mol*K)]	Engineer's C_v [kJ/mol*K)]	Accepted adiabatic index(γ)	Theoretical index (γ) Eqn. (14)
Helium	He	1	4.00	2079	5.196	3.117	1.67	1.67
Neon	Ne	1	20.18	412	1.030	0.618	1.67	1.67
Argon	Ar	1	39.94	208	0.521	0.312	1.67	1.67
Xenon	Xe	1	131.30	63	0.1568	0.095	1.67	1.67
Hydrogen	H_2	2	2.02	4124	14.302	10.178	1.41	1.4
Nitrogen	N_2	2	28.02	297	1.040	0.743	1.4	1.4
Oxygen	O_2	2	32.00	260	0.917	0.657	1.4	1.4
Nitric oxide	NO	2	30.01	277	0.995	0.718	1.39	1.4
Water vapor	H_2O	3	18.02	462	1.864	1.402	1.33	1.29
Carbon dioxide	CO_2	3	44.01	189	0.844	0.655	1.29	1.29
Sulfur dioxide	SO_2	3	64.07	130	0.621	0.491	1.26	1.29
Ammonia	NH_3	4	17.03	488	2.096	1.607	1.30	1.22
Methane	CH_4	5	16.04	519	2.227	1.708	1.30	1.18
Ethylene	C_2H_4	6	28.05	297	1.552	1.256	1.24	1.15
Ethane	C_2H_6	8	30.07	277	1.751	1.475	1.19	1.12
Propylene	C_3H_6	9	42.08	198	1.519	1.279	1.19	1.11
Propane	C_3H_8	11	44.10	189	1.667	1.478	1.13	1.09
Benzene	C_6H_6	12	78.11	106	1.045	0.939	1.11	1.08
Isobutene	C_4H_8	12	56.11	148	1.527	1.374	1.11	1.08
n-Butane	C_4H_{10}	14	58.12	143	1.676	1.533	1.09	1.07
Isobutane	C_4H_{10}	14	58.12	143	1.666	1.523	1.09	1.07
n-Pentane	C_5H_{12}	17	72.15	115	1.666	1.551	1.07	1.06
Isopentane	C_5H_{12}	17	72.15	115	1.663	1.548	1.07	1.06
n-Hexane	C_6H_{14}	20	86.18	96	1.660	1.564	1.06	1.05
n-Heptane	C_7H_{16}	23	100.20	83	1.656	1.573	1.05	1.04
Octane	C_8H_{18}	26	114.23	73	1.653	1.581	1.05	1.04

other reason kinetic theory may falter without walls is that wall-gas interactions no longer exist, hence kinetic theory's complete virtues may be limited to systems with walls [24–25] i.e. experimental systems.

4 Discussion of other implications

This author [24–25] has hypothesized that blackbody/thermal radiation within a system has a temperature associated with it. So although the total energy associated with radiation often is infinitesimally small in comparison to the total energy associated with the kinematics of matter, the idea that blackbody radiation has a temperature associated with it, should no longer be ignored. In other words, even a vacuum can have a temperature, although it has no matter and comparatively speaking only contains a minute amount of energy.

Pressure is traditionally envisioned as being solely due to change in translational energy i.e. "every molecule that impinges and rebounds exerts an impulse equal to the difference in its momenta before and after impact" [pg. 32, 20]. Interestingly, the analysis given herein does alter such explanations just because the rotational energy plus the translational energy of the gas molecules now combine to exert pressure. Moreover, consider the tennis ball impacting a wall. Ask

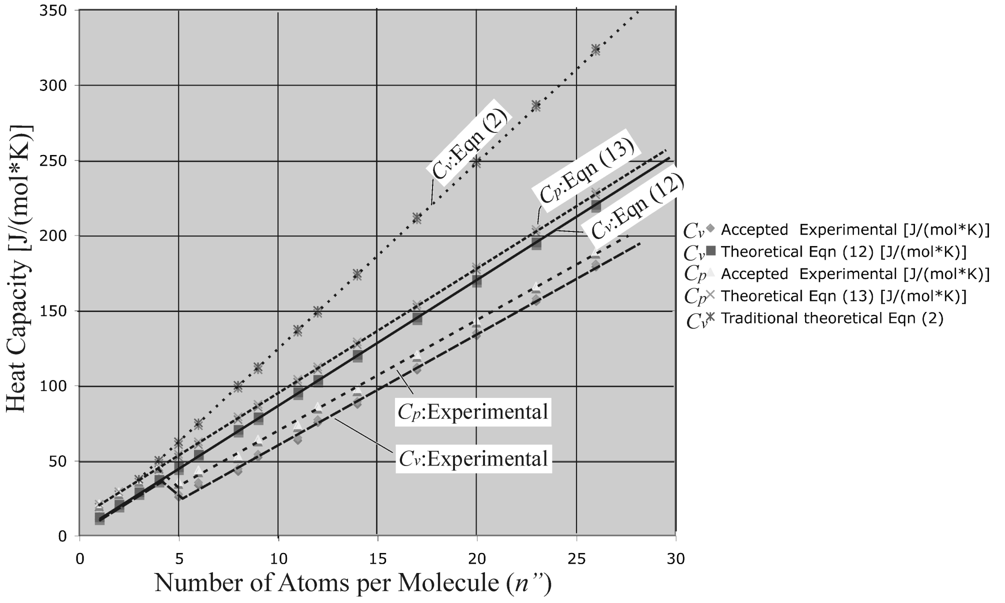

Fig. 3: Theoretical molar heat capacity based on our theoretical equations (12) and (13) versus empirical values, plus the traditional theoretical isometric molar heat capacity plot [based upon degrees of freedom, equation (2)].

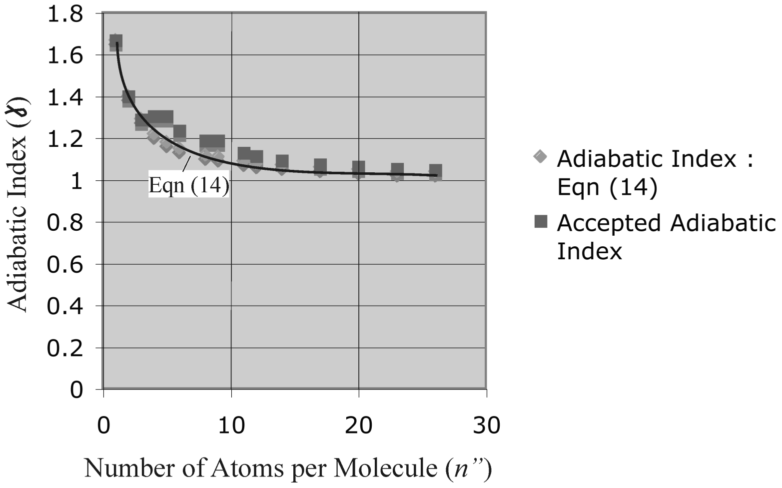

Fig. 4: Theoretical adiabatic index [eq. (14)] versus number of atoms (solid line). Adiabatic index data points based upon engineering table for gases.

yourself: Are not both the rotational and translational energy of that ball exchanged with the wall. So why would a gas molecule behave any differently? Just because wall molecules are bound i.e. cannot rotate, does not mean that they don’t exchange rotational energy/momentum with an impacting gas! The gas’ mean translational velocity ($mv^2/2$) can no longer be simply equated in terms of Boltzmann’s constant ($kT/2$). This has consequences to fundaments such as Maxwell’s velocity distributions for gases. In our analysis, the magnitude of translational energy compared to rotational energy is not defined beyond that they add up to and equal, the summation of the walls molecule’s kinetic energies! Since the gas’ total kinetic energy remains the same, then most of what is known in quantum theorem still applies with the change being how a gas’ kinetic energy is expressed.

Consider the hypothesis that rotational energy of a gas is frozen out at low temperatures [26]. This is like claiming that gas molecules never impact a wall at acute angles, when in a cold environment. This author thinks in terms of thermal energy being energy that results in both intermolecular and intramolecular vibrations within condensed matter. Just consider the blackbody radiation curve for 3 K, whose peak is located at wavelength of 1 mm. Compare this to 300 K, where the radiation curves’ peak occurs in the infrared spectrum, wavelength equals 10 micrometers. Accepting that the majority of thermal energy is in the infrared then this author also believes that somewhere between 3 K and 300 K, a system's thermal energy density will no longer proportional to temperature i.e. probably aroound 100 K. Perhaps it is the gas' vibrational energy that is frozen out? Understandably, at low temperatures the blackbody/thermal radiation within the system may be such that it does not provide enough thermal energy (infrared) for measurable gas vibration. However, this should equally apply to the system's walls, unless the walls have more thermal energy relative to the gas i.e. apparatus considerations? This is conjecture, as remains the current notion that rotational energies are frozen out.

For gases the accepted difference between molar isobaric heat capacity and molar isometric heat capacity is the ideal gas constant (R). Accordingly [2–3]:

$$C_p - C_v = R. \tag{15}$$

The difference in heat capacities is obviously independent of the type of gas. This implies that the difference depends upon the system's surroundings and not the experimental system, nor its contents. This fits this author's assertion that "the ideal gas constant is the molar ability of a gas to do work per degree Kelvin" [27]. This is based upon the realization that work is required by expanding systems to upwardly displace our atmosphere's weight, i.e. an expanding system does such work, which becomes irreversibly lost into the surrounding Earth's atmosphere. The lost work being [24, 28–29]

$$W_{lost} = P_{atm}\, dV. \tag{16}$$

This does not mean that the atmosphere is always upwardly displaced, rather that the energy lost by an expanding system is defined by equation (17). This lost energy can be associated with a potential energy increase of the atmosphere, or a regional pressure increase. Note: A regional pressure increase will result in either a volume increase, or viscous dissipation i.e. heat created = lost work. This requires the acceptance that the atmosphere has mass and resides in a gravitational field. It is no different than realizing that an expanding system at the bottom of an ocean, i.e. a nucleating bubble, must displace the weight of the ocean plus atmosphere. Accordingly, any expanding system here on Earth's surface must expend energy/work to displace our atmosphere's weight and such lost work, is immediately or eventually lost into the surrounding atmosphere. Accepting this then allows one to question our understanding of entropy [24, 29].

5 Conclusions

Kinetic theory has been reconstructed with the understanding that a gas' kinetic energy has both translational and rotational components that are obtained from the wall molecule's kinetic energy. Therefore, the gas' translational plus rotational energies along each of the x, y and z-axis, are added and equated to the wall molecules' kinetic energy along the identical three axes. No knowledge pertaining to the magnitudes of the gas' rotational energy versus translational energy is claimed. This is then added to the gas' internal energy e.g. vibrational energy, in order to determine the gas' total energy.

The empirically known heat capacity and adiabatic index for all gases are clearly a better fit to this new theory/model, when compared to accepted theory. The fit for monatomic through triatomic gases is exceptional, without any reliance upon traditionally accepted exceptions! Moreover, our model treats all polyatomic molecules in the same manner as condensed matter.

Seemingly, Lord Kelvin's assertion that equipartition was wrongly derived, may have been right after all. Accepting that the traditional degrees of freedom in equipartition theory may be mathematical conjecture rather than constructive reasoning will cause some displeasure. Certainly, one could argue that what is said herein is really just an adjustment to our understanding. Even so, it will alter how pressure is perceived that being due to the gas molecules' momenta from both rotation and translation, which is imparted onto a surface. Ditto for the consideration of a gas' energy in quantum theory.

The consequence of a polyatomic gas' thermal vibrations being related to its surrounding thermal radiation may alter our conceptualization of temperature, i.e. a vacuum now has a temperature. The notion that rotation in cold gases is frozen out was also questioned. Perhaps it is a case that the thermal energy density does not remain proportional to temperature, as T approaches 0, which also is the case for very high temperature gases.

The difference between isobaric and isometric heat capacity is gas independent. This fits well with this author's assertion that lost work represents the energy lost by an expanding system into the surrounding atmosphere. Interestingly, for a mole of gas molecules this lost work can be related to the ideal gas constant.

To some, the combining of a gas' rotational and translational energy may seem like a minor alteration, however the significance to the various realms of science maybe shattering. Not only may this help put to rest more than a century of speculations, it also may alter the way that thermodynamics is envisioned. If accepted it actually opens the door for a simpler new thermodynamics vested in constructive logic, rather than mathematical conjecture.

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6 Example calculations

1. Table 1 for $n'' = 3$; our theoretical values: [equation (12)]: I.e. $C_v = \frac{7}{2}R = \frac{7}{2}\ 8.31$ J/(mol*K) = 29.09 J/(mol*K).

[eq. (13)]: I.e. $C_p = \frac{9}{2}R = \frac{9}{2}$ 8.31 J/(mol*K) = 37.40 J/(mol*K).

For n''=3, traditional accepted theoretical value is equation (2): I.e. $C_v = \frac{9}{2}R = \frac{9}{2}$ 8.31 J/(mol*K) = 37.40 J/(mol*K).

2. Table 2, for $n'' = 3$. Accepted adiabatic index (γ) for carbon dioxide ($n'' = 3$) based upon engineering data [22] is $\gamma = 0.844/0.655 = 1.29$. Our theoretical adiabatic index (γ) is equation (14): I.e.

$$\gamma = \frac{\frac{9}{2}}{\frac{7}{2}} = 1.29.$$

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