

Chapter 2: Thermal Energy and Kinetic theory

Thermodynamics concerns the interactions of thermal energy and matter, or if you prefer, how systems of matter behave as a function of temperature. Herein will be discussed the fundamentals of thermal energy and kinetic theory. It should be stated that traditional kinetic theory does not match empirical findings for heat capacity particularly well. This will be discussed, as well an improved kinetic theory will be presented, a theory that better matches known empirical findings as envisioned by this author and published in Journal "Progress in Physics" in July 2017, followed by April 2018.

Thermal Energy

As was discussed in Chapter 1, thermal energy resides in condensed matter as both *intermolecular vibrations* are between molecules, and *intramolecular vibrations* are between the various atoms, all of which can be consider as vibrations between bonds whose packets of energy are considered as *phonons*. Accordingly, the photons associated with the thermal radiation from our Sun are fundamental to any consideration of the temperatures that is witnessed here on Earth. Certainly other sources of thermal energy contribute, such as heat associated with pressure, heat from irreversible processes etc etc.

Liquids and amorphous solids lack the crystalline structure to which phonons are mathematically related. Even so, it is accepted that the thermal energy contained within such substances can be considered as phonons (packets of energy) that are treated in the same manner. Liquid molecules also have freedom of movement (e.g. convection), and accordingly they possess both translational and rotational energies. However, both of these energies are generally considered to be minor in comparison to vibrational energy. Therefore, most of the thermal energy within all condensed matter can be attributed to vibrational energy within that matter.

It is understood that condensed matter adsorb thermal energy by the absorption of thermal photons, turning them into phonons. Conversely condensed matter release thermal radiation by emitting photons. Importantly from a perspective of volume, all matter tends to concentrate thermal energy i.e. increase the thermal energy density within a given volume. As complicated as explanations could become, all that is needed is the understanding that thermal energy is somehow held within condensed matter! This leads the question: what is thermal energy?

Simply defined thermal energy is heat. A better definition is that thermal energy consists of a spectrum of thermal photons and/or phonons, i.e. those whose wavelengths are sufficiently long that they are readily absorbed by condensed matter, becoming either intramolecular or intermolecular vibrations. For the most part thermal energy consists of a spectrum of infrared wavelengths. However, depending upon the substance and temperature, the spectrum of thermal energy may also include microwave and/or visible & UV light.

Energetics within Condensed Matter

When dealing with the energy of molecules in condensed matter there are two energy terms. The first term represents the energy associated with the momentum of the molecule i.e. the molecule's kinetic energy. The second term represents the potential energy, which depends upon the location of the molecule and/or its elements. This is similar to a harmonic oscillator, e.g. two masses attached via a spring, wherein we associate both a kinetic and a potential energy (See Appendix B.5). If x = position coordinate along the x -axis, \vec{p}_x is the momentum along the x -axis and α = spring constant, then the energy of a one-dimensional harmonic oscillator can be written as^{1,2}:

$$\bar{E} = |\vec{p}_x|^2 / 2m + \alpha x^2 / 2 \quad 2.1$$

When applied to the energy within condensed matter, both the terms on the R.H.S. of eqn 2.1 are quadratics, thus the equipartition theorem gives^{1,2}:

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$$\text{Mean kinetic energy} = \bar{E}_k = |\bar{p}_x|^2 / 2m = kT/2 \quad 2.2$$

$$\text{Mean potential energy} = \bar{E}_p = \alpha x^2 / 2 = kT/2 \quad 2.3$$

The total mean vibrational energy (\bar{E}_v) of a one-dimensional harmonic oscillator is the summation of the kinetic and potential energies, that being^{1,2}:

$$\bar{E}_v = \bar{E}_k + \bar{E}_p = kT/2 + kT/2 = kT \quad 2.4$$

For a crystalline solid, each molecule is considered as a simple harmonic oscillator about its lattice site with the molecular motions being along all three orthogonal axes (x,y,z). Moreover, the mean energy along each axis is taken to be equivalent, with a mean magnitude defined by eqn 2.4. Accordingly, for N molecules the total thermal energy (E_T) along the three axes is:

$$E_T = 3NkT \quad 2.5$$

For a mole of molecules ($N = 6.02 \times 10^{23}$ molecules) $Nk = R$, where: R is the universal gas constant = 8.31 J/mol/K. Then eqn 2.5 becomes:

$$E_T = 3RT \quad 2.6$$

Note that eqn 2.5 and eqn 2.6 consider the total thermal energy as being purely vibrational, therefore for condensed matter: $E_T = E_v$.

Note: Those familiar with traditional thermodynamics will realize that eqn 2.5 and 2.6 are what one would obtain based upon traditional analysis using equipartition and degree of freedom arguments e.g. each molecule has 3 degrees of freedom with each degree of freedom having a mean energy defined by kT . In so much as the results for condensed matter agree with empirical findings we do not agree with the implications to gases, hence herein the merits of such arguments are diminished, beyond the fact that it is a mathematical construct rather than a logic based result. Basically condensed matter adsorbs thermal radiation, and then equally distributes it in all directions throughout that matter via molecular vibrations.

Equipartition & Crystalline Solids

In order to calculate the thermal energy (dQ) that can be extracted from a crystalline system resulting in a temperature change (dT), eqn 1.2.5 is used: $dQ = C_v dT$. The subscript "v" indicates that the molar heat capacity is taken at a constant volume⁷:

$$C_v = dQ / dT = 3R = 6 \text{ cal/mole/K} = 25.10 \text{ joules/mole/K} \quad 2.7$$

Eqn 2.7 has been empirically shown to apply to most condensed crystalline matter and is known as the *Law of Dulong and Petit*. Fig. 2.1 shows the molar heat capacity as a function of temperature for three substances, namely: lead, copper, and diamond.

For most crystalline substances, the law of Dulong and Petit is not valid when at extremely low temperatures. Moreover, the heat capacity of solids tends to zero, as the temperature tends toward absolute zero, at which point the Debye's theory must be used (See Appendix B.4).

For most crystalline substances room temperature (395 K) is sufficiently high that the molar heat capacity can be equated to $3R$. Rather than on a molar basis, eqn 2.7 can be rewritten in terms of its N molecules, for most crystalline substances i.e.:

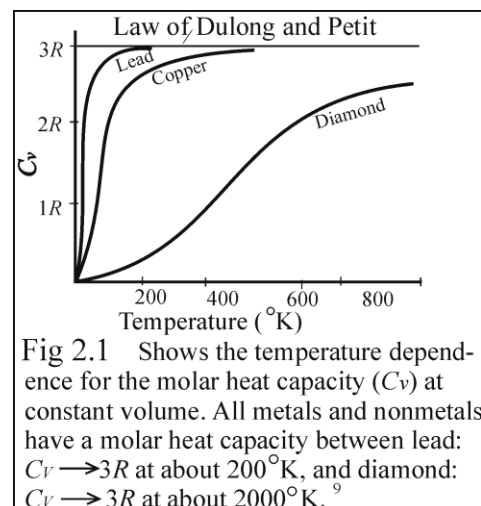


Fig 2.1 Shows the temperature dependence for the molar heat capacity (C_v) at constant volume. All metals and nonmetals have a molar heat capacity between lead: $C_v \rightarrow 3R$ at about $200^{\circ}K$, and diamond: $C_v \rightarrow 3R$ at about $2000^{\circ}K$.⁹

$$C_v = dQ/dT = 3Nk \quad 2.8$$

Eqn 2.8 states that the thermal energy stored per degree Kelvin (or Celsius) is $3Nk$, for most crystalline matter, i.e. the total thermal energy (E_T) stored in an N molecule crystalline substance, at temp T , can be approximated by eqn 2.5: $E_T = E_v = 3NkT$.

As seen in Fig 2.1, diamond is an exception to the above in that its molar heat capacity does not approach $3R$ until its temperature reaches 2000 K. As explained to this author by an acquaintance: Diamond has a perfect infinite tetrahedral lattice thus there are no/few intermolecular vibrations in diamond. In fact a one-carat diamond is a one-carat molecule making diamond the largest solitary molecule on Earth!

System of Gas

Consider a gaseous system. There are four types of energy associated with a volume of gas:

- 1) Rotational energy
- 2) The translational energy
- 3) Vibrational energy within any polyatomic gas molecules.
- 4) Radiation energy residing in freespace, i.e. thermal radiation.

Monatomic gases have no vibrational energy, while polyatomic gases will possess vibrational energies between the molecule's atoms along their atomic bonds, i.e. they absorb and emit thermal photons.

Generally, the energy associated with the thermal radiation³ is infinitesimally small in comparison to the energies of motion of the molecules. Therefore, when calculating a system's total energy, the thermal radiation can often be omitted. Even so, it is prudent to keep the radiation energy as part of our logic.

A New Perspective for Kinetic Theory

The interaction of gases with condensed matter is the basis of kinetic theory. The theory has its origins in the 18th century with Bernoulli; however the current traditionally accepted understanding is more based upon 19th century conceptualizations by the likes of Maxwell, Clausius and Boltzmann. That being a combination of the law of equipartition (theory) and the degrees of freedom argument, which may be more a mathematical conjecture than some logically, construed theory. Interestingly the following is Maxwell describing some attributes of the theory in his 1875 paper.⁴

"The kinetic energy of the molecule may be regarded as made up of two parts--that of the mass of the molecule supposed to be concentrated at its centre of mass, and that of the motions of the parts relative to the centre of mass. The first is called the energy of translation, the second that of rotation and vibration. The sum of these is the whole energy of motion of the molecule.

The pressure of the gas depends, as we have seen, on the energy of translation alone. The specific heat depends on the rate at which the whole energy, kinetic and potential, increases as the temperature rises.

Clausius had long ago pointed out that the ratio of the increment of the whole energy to that of the energy of translation may be determined if we know by experiment the ratio of the specific heat at constant pressure to that at constant volume.

He did not, however, attempt to determine à priori the ratio of the two parts of the energy, though he suggested, as an extremely probable hypothesis, that the average values of the two parts of the energy in a given substance always adjust themselves to the same ratio. He left the numerical value of this ratio to be determined by experiment.

In 1860 I investigated the ratio of the two parts of the energy on the hypothesis that the molecules are elastic bodies of invariable form. I found, to my great surprise, that whatever be the shape of the molecules, provided they are not perfectly smooth and spherical, the ratio of the two parts of the energy

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must be always the same, the two parts being in fact equal. This result is confirmed by the researches of Boltzmann, who has worked out the general case of a molecule having n variables."

It is interesting to note Maxwell's surprise at the ratio of energies (the translational motion the rotational and vibrational) being equal, as not even he expected this result! This, and the ensuing work of Boltzmann and the conceptualization of statistical ensembles, led to the 20th century understanding of the determination of molecular energy using statistical analysis, the law of equipartition and degrees of freedom based argument. The basics of equipartition theory and degrees of freedom are discussed in Appendix B.3 of this text. For those interested in more encompassing analysis, other texts do give a more thorough discussion e.g. Reif¹, Carey⁵.

Problematic traditional kinetic theory

Due to inconsistencies between theory and empirical findings for heat capacities of gases, traditionally accepted kinetic theory often makes various exceptions. In literature you may find any combination of the following exceptions:

- 1) Monatomic gases have no rotational energy.
- 2) Diatomic gases have no vibrational energy or that they too have no rotational energy.

Amazingly the above exceptions are blindly accepted so that the purely mathematical based equipartition theory better matches known empirical data. Limiting monatomic and/or diatomic gases to translational energy is like saying a curve ball in baseball has no rotational energy!

The accepted argument being that small radius mean small to no angular momentum. This is ridiculous because given the same impulse/force passing on a certain angular momentum, simply means that the smaller the radius the higher the angular velocity will be. In other words the expectation is that for a given collision, the smaller the radius, the larger the angular velocity will be. Accordingly smaller radius molecules can/will have the same angular momentum, as larger radii molecules.

Furthermore it is irrational to then think that triatomic molecules all of a sudden have full rotational energy ($kT/2$ per degree of freedom), while both monatomic and/or diatomic molecules have none. And any contention that diatomic gases have no vibrational energy, is like saying the bonds are different for diatomic gases than triatomic and/or polyatomic gases!

It must also be said that Einstein⁸ stated that reason quantum theory was developed, was in part to explain why traditional kinetic theory and known empirical finding for gas's heat capacities do not match more closely than they did. The completeness of what is said will become more apparent when heat capacities are discussed in later chapters of this book. As a side-point this authors wonders to what extend quantum theory would have been fully embraced if the great minds of over a century ago had adhered to kinetic theory as presented herein.

Our new perspective

Herein an alternate perspective than the traditionally accepted theory, will be taken. By applying some of the conscripts of equipartition to condensed matter and then making other logical deductions for the kinetic theory of gases, this author's theory will be presented, a previously peer-reviewed published interpretation that better explains known empirical findings^{6,7}. This is simply not a case of arbitrarily choosing some aspects of traditional/statistical thermodynamics over other ones; rather it is a consequence of logical deduction, backed by empirical data. The irrefutable evidence confirming our new understanding will be given in Chapter 5 and then other aspects will be discussed in Chapters 6 & 7.

Visualizing the Translational, Rotational Energies of a Monatomic Gas

In Fig.2.2, a sufficiently dilute monatomic gas is illustrated where the collisions are primarily between the gas molecules and their surrounding walls.

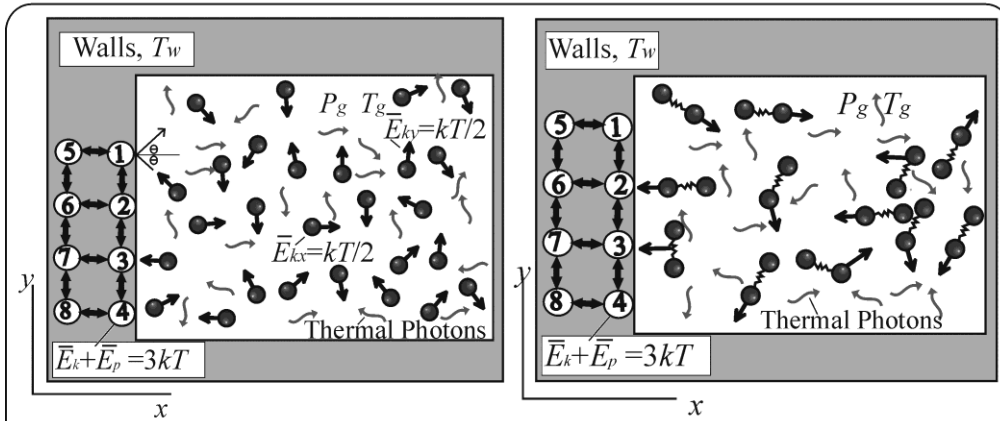


Fig. 2.2 Shows an ideal monatomic gas, at pressure: P_g and temperature: T_g , surrounded by walls at temperature T_w . The gas molecules have no vibrational energy.

Fig. 2.3 Shows an ideal diatomic gas, at pressure: P_g and temperature: T_g , surrounded by walls at temperature T_w . The gas molecules all have vibrational energy.

Traditional equipartition and degrees of freedom: The mean kinetic energy per gas molecule along the x -axis is: $\bar{E}_{kx} = kT/2$. Similarly along the y and z -axis, the mean kinetic energies respectively are: $\bar{E}_{ky} = kT/2$, and $\bar{E}_{kz} = kT/2$. The energy of a wall molecule along the x -axis is due to both kinetic and potential energy: $\bar{E}_{kx} + \bar{E}_{px} = kT$. And similarly for the y and z axis: $\bar{E}_{ky} + \bar{E}_{py} = kT$ and $\bar{E}_{kz} + \bar{E}_{pz} = kT$. The mean total energy of each wall molecule is: $\bar{E}_k + \bar{E}_p = 3kT$

Our new perspective has the gas's mean translational kinetic energy along the three axis plus its mean rotational energy equal to the above described wall molecule's kinetic energy.

Note: Both the gases are in thermal equilibrium when the wall's temperature equals the gas's temperature: i.e. $T_w = T_g$, which also equals the temperature associated with the surrounding radiation (blackbody/thermal).

Case 1): Start by imagining that a monatomic gas molecule collides dead on with a wall molecule, e.g. the gas molecule hitting wall molecule #3 in Fig 2.2. Herein, the gas molecule should only obtain translational energy from the vibrating wall molecule. Accordingly, the gas molecule's resulting mean kinetic energy (\bar{E}_k) (due to impact) would be purely translational. It is like hitting a golf ball square on and having the majority of the golf ball's energy being purely translational, thus attaining a long distance down towards the golf green.

Case 2): Imagine that the monatomic gas molecule hits the wall molecule at some angle other than $\theta = 90^\circ$. As expected, the gas molecule would obtain both rotational and translational energy from the vibrating wall molecule such that the total mean resultant energy (due to impact) of the gas molecule would be the same as it was in Case 1). It is like hitting a golf ball with the same force/impulse of impact but slicing the ball, hence giving the ball a significant amount rotational energy in comparison to its translational energy, thus watching your golf ball plummet into the woods, shortly after contact.

Case 3): Imagine a rotating and translating monatomic gas molecule striking the wall transferring both its rotational and translational energies onto the wall molecule. The wall molecule cannot rotate therefore both energies will only result in the wall molecule attaining vibrational energies from the impact, where the wall molecule's vibrational energy is along some combination of its three orthogonal axes.

Note in the above: The total mean energy of a wall molecule is still $3kT$, of which kT is directed along the x -axis with kT including both the potential and kinetic energy of the wall molecule, with the mean kinetic energy of the wall molecule along the x -axis being $kT/2$. This energy along positive x -axis is then passed onto any gas molecules that collide with the wall molecule, resulting in both translational and

rotational energy of that gas molecule. This is different than traditional accepted theory, which is based upon the mathematical degree of freedom argument and $kT/2$ along each degree as claimed by equipartition, hence the gas molecule's translational energy along the x -axis is $kT/2$.

Mathematics for the Translational, Rotational Energies of a Monatomic Gas

Now what is going on has been visualized, the proper equations can be determined. For the group of wall molecules 1 through 8 shown in Fig 2.2, the total mean thermal energy associated with a vibrating wall molecule, along the x -axis, is defined by:

$$\bar{E}_x = kT \quad 2.9$$

As was previously discussed half of a wall molecule's mean thermal energy would be kinetic energy, and half would be potential energy, Accordingly, the mean kinetic energy (\bar{E}_{kx}) of a wall molecule along the x -axis, is based upon eqn 2.2 that being:

$$\bar{E}_{kx} = kT/2 \quad 2.10$$

Due to the massive size of the wall in comparison to gas molecules, the wall's continuous vibrations, and the continuous collisions, the gas molecule's mean energy along the x -axis is defined by 2.10. This equally applies to gas molecule-wall collisions along both the y and z -axis.

This all can be viewed another way; the wall behaves like a massive machine pumping its kinetic energy onto the smaller gaseous molecules, along all three axes. Since each orthogonal wall will impart the same mean kinetic energy onto each gas molecule, then the mean translational plus rotational energy of the gas molecule [$\bar{E}_{k(t,r)}$] equals three times the wall's mean kinetic energy along any one axis, i.e.:

$$\bar{E}_{k(t,r)} = 3kT/2 \quad 2.11$$

For N gaseous molecules, the total kinetic energy (translational plus rotational energy) [$E_{Tk(t,r)}$] becomes⁶:

$$E_{Tk(t,r)} = 3NkT/2 \quad 2.12$$

The magnitude for total energy as defined by eqn 2.12 equals what is traditionally accepted for the translational energy. However our analysis and nomenclature for the energy of gas molecule emphasizes that it is both translational and rotational energy of the gas that is obtained from the wall molecule's kinetic energy. It should be emphasized that eqn 2.12 is only valid for systems wherein gas-wall collisions dominate when compared to gas-gas collisions.

Translational, Rotational, Vibrational Energies of a Polyatomic Gas

Fig 2.3 illustrates a system of dilute diatomic gas molecules in a container. The vibrating wall molecules still pass the same amount of kinetic energy onto the diatomic gas molecule's center of mass with each collision, as was the case for the monatomic gas. It really does not matter how the diatomic molecule strikes the wall molecule, e.g. the same principles apply whether it be a diatomic gas molecule that is striking wall molecule #2, or the one striking wall molecule #3 in Fig 2.3. Note: For a more enlightened analysis of diatomic collisions, see Appendix B.5.

So as was the case for the monatomic gas, the diatomic gas molecule's total translational plus rotational energy remains defined by eqn 2.11. What about the vibration energy of the diatomic gas molecules? As is the case for condensed matter, this is related to the absorption and emission of the blackbody/thermal radiation surrounding the diatomic gas molecules. Therefore the mean vibrational energy within a diatomic gas molecule is also defined by eqn 2.4: $\bar{E}_v = kT$.

Accordingly, the mean total energy (\bar{E}_{tot}) for the sufficiently dilute diatomic gas molecule must be the

addition of its mean translational energy and rotational energy plus its mean vibrational energy. That being:

$$\bar{E}_{tot} = \bar{E}_{T(t,r)} + \bar{E}_v = 3kT/2 + kT = 5kT/2 \quad 2.13$$

Now consider a triatomic gas molecule. The mean vibrational energy should be twice that of a diatomic, therefore for a triatomic gas molecule the mean vibrational energy (\bar{E}_v) is:

$$\bar{E}_v = kT + kT = 2kT \quad 2.14$$

Similarly, the total mean energy of the triatomic gas molecule must be the addition of its mean kinetic (translational and rotational) energy, plus its mean vibrational energy, that being:

$$\bar{E}_{tot} = \bar{E}_{Tk(t,r)} + \bar{E}_v = 7kT/2 \quad 2.15$$

If the polyatomic gas molecule absorbs/emits thermal photons in a manner similar to diatomic molecules, then an n'' -molecule polyatomic gas molecule should have a mean vibrational energy of⁶:

$$\bar{E}_v \cong (n''-1)kT \quad 2.16$$

where n'' signifies the number of atoms in each gas molecule, which shall be called *polyatomic number*. The mean total energy (\bar{E}_{tot}) for a polyatomic gas molecule becomes the addition of its mean kinetic energy plus its mean vibrational energy. In other words equations 2.12 and 2.16 are added together, thus obtaining for the mean total energy (\bar{E}_{tot}):

$$\bar{E}_{tot} \cong (n''-1)kT + 3kT/2 \quad 2.17$$

Collecting the terms, gives:

$$\bar{E}_{tot} \cong (n''+1/2)kT \quad 2.18$$

The total energy [E_T] for N gas molecules, becomes⁶:

$$E_T \cong NkT(n''+1/2) \quad 2.19$$

Consider n moles of gas then eqn 2.19 becomes⁶:

$$E_T \cong nRT(n''+1/2) \quad 2.20$$

Eqn 2.19 is a theoretical approximation, which matches exceptionally well with empirical findings for heat capacities of gases for all values of the number of atoms in each gas molecule, where $n'' < 4$. At $n'' = 4$, there is a marked change between empirical findings and this theory however there is a small marked decrease in heat capacity for the empirical findings, when compared to theoretical. Importantly the difference between the two never changes i.e. the difference between empirical findings and this theory remains constant for $4 < n'' < 20$. It must be emphasized that the fit of this theory with empirical finding is far superior when compared to the fit with the traditional kinetic theory.

At first this author thought that the difference was perhaps due to variations in the molecule's shape and how they may interact with the surrounding thermal radiation. Having second thoughts this author then realized that it was long linear gaseous molecules whose empirical findings did not match theory. At which point this author started to think it was because of *flatlining*.

Flatlining

Imagine linear molecule where $n'' \geq 4$ that flatline's against a wall as illustrated in Fig 2.4. Obviously, when one wall molecule is moving outward from the wall, then its neighbor is likely moving inward into the wall.

So the long flatlining molecule still bounces off of the wall but not as cleanly as a smaller molecule would. Accordingly, the wall molecules mean kinetic energy is not cleanly pumped onto any flatlining molecules. There may be other explanations but this one certainly fits and will be discussed again in more detail in Chapter 5.

A new perspective for thermal equilibrium & the role of walls

Consider that both a given volume of dilute gas and surrounding walls are in thermal equilibrium at temperature T , as is illustrated in Fig. 2.3. This means⁶:

- 1) The walls are in thermal equilibrium with the enclosed blackbody radiation e.g. both are related to the same temperature (T).
- 2) The gas molecule's translational plus rotational energy is energy equilibrium with the molecular vibrations of the wall molecules at T .
- 3) The gas molecule's vibrational energies are in thermal equilibrium with the enclosed blackbody radiation e.g. both are related to the same temperature (T).

The combination of these three states of equilibrium causes the energies of the gas molecules and wall molecules to correspond with each other as well as their surrounding thermal radiation, i.e. if isothermal walls did not surround the gas then true equilibrium between the gas molecules and the surrounding thermal radiation may not exist. A fact overlooked by traditional analysis, one that will be revisited in Chapters 5 thru 7. Note for radiation equilibrium does not mean that same is spectrum is emitted as adsorbed rather it means that the energy flux (rate) is the same for absorption as emission.

Gas's Kinetic Energy

The kinetic energy of the walls from three orthogonal axes is passed/pumped/imposed onto an enclosed gas molecule, resulting in both the gas's kinetic and rotational energies. However in the future chapters of this book when discussing issues like work, the gas's kinetic energy means both the translational and rotational energy because it is both of those energies from the gas that is passed on, enabling systems to perform work. Also, this is because most often work done simply results in a kinetic and/or potential energy increase of something external to the system i.e. surroundings.

Also herein it was never determined to what degree such kinetic energy would be rotational versus translational. The implication being that the translational velocities of gases may actually be lower than Maxwell's velocity distribution implies, although the energy of the gas as implied by the distribution functions should remain approximately correct especially for smaller (i.e. monatomic, diatomic, triatomic) sufficiently dilute gases, expectation remains for small molecules translational > rotational energy . Another case of the sciences getting answers right for the wrong reasons. To what exact extend a sufficiently dilute gas's energy is rotational vs translational is now up for debate.

Traditional: Loschmidt's Paradox (1876)

It is of interest that that Loschmidt paradox (A.K.A. irreversibility paradox) which puts the time reversal of fundamental processes at odds with the second law that was used to describes macroscopic systems. Namely that Joseph Loschmidt's challenged Boltzmann's H-theorem, which used traditional

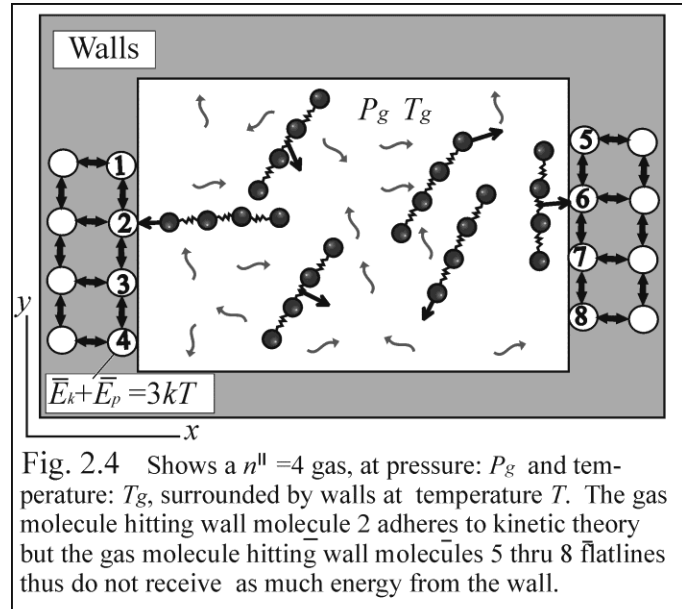


Fig. 2.4 Shows a $n^u = 4$ gas, at pressure: P_g and temperature: T_g , surrounded by walls at temperature T . The gas molecule hitting wall molecule 2 adheres to kinetic theory but the gas molecule hitting wall molecules 5 thru 8 flatlines thus do not receive as much energy from the wall.

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kinetic theory to explain the entropy increase of a non-equilibrium state ideal gas, when the gas molecules are allowed to collide. Specifics are left to others, but our new understanding does impose challenges to such accepted doctrine.

Closing Remarks

We discussed the kinematics of matter, presenting a simple explanation as to how the energy of a system relates to Boltzmann's constant (k). Basically the orthogonal walls of a closed system act as massive pumps, pumping/imparting/imposing a mean energy of $kT/2$ onto each of the significantly smaller gas molecules. The important revelations being:

1) That the kinetic energy of the wall molecules equals the dilute gas' translational plus rotational energy. This says nothing about the relative values of rotational and translational energies of a gas, except that they are to be added and equated to the summation of the wall molecule's mean kinetic energies along all three axes.

2) The total energy of the dilute gas being equated to the translational plus rotational energy, plus any vibrational energy. In Chapter 5 it will be shown that this insight better explains the accepted empirical findings for the heat capacity of gases, than the traditional understanding.

3) The thermal radiation of the blackbody radiation that exists in interior volumes of freespace is what allows for thermal equilibrium to exist in many systems.

4) The above stated thermal radiation is responsible for the vibrational energies of the dilute polyatomic gases within a system i.e. polyatomic gases and condensed matter are to be treated equally.

5) The energy associated with the above stated radiation are generally infinitesimally small when compared to the kinematic energies associated with matter. Exceptions being vacuums and extremely high temperature systems e.g. blast furnaces.

At first glance the above defies the traditionally accepted mathematically based equipartition theory. However, one might consider this as a more logical altered equipartition wherein the rotational plus translational energy of sufficiently dilute gases are part of (equated to) one and the same degree of freedom. Of course degree of freedom is a mathematical consequence whose definition may require change.

It should be further stated that most empirical data is obtained using closed systems contained within walls. The ramifications of such walls will become readily apparent in Chapters 5 through 7, as to will the proof be given concerning what was discussed herein. Note: See Graph 5.1, where empirically obtained heat capacities of gases clearly prove that our new perspective concerning kinetic theory is superior to the traditionally accepted theory.

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