

THE EQUIPARTITION CONUNDRUM

The equipartition conundrum has to do with uncertainties in how kinetic energy is transferred between the internal kinetic energies of gas molecules (energies of rotation, vibration, and libration) and their external kinetic energies (the various kinetic energies of translation), and vice versa.

Measurements of heat capacity of various gases show that this energy transfer does take place. These measurements show that enthalpy is divided more or less equally between the various degrees of freedom of a gas. When quantum considerations are taken into account, the experimental allocation of enthalpy to the various degrees of freedom is well explained by the theoretical constraints.

Moreover, when energy is added to the internal motions of atmospheric water vapor by the absorption of photons of solar insolation, this energy appears to be quickly shared both with the external motions of that water vapor and with both the internal and external energies of the other atmospheric gases.

Similarly, when energy is added to the external motions of the atmospheric gases by conduction from the earth's surface, it appears to be just as quickly shared with the internal motions of all of the atmospheric gases.

To explain this, equipartition requires that three separate interchanges of energy must take place:

Internal ↔ Internal
External ↔ External
Internal ↔ External

THE KINETIC ATMOSPHERE

The Equipartition Conundrum

The first exchange is easily explained by radiative transfer of photons. Although each gas has its own unique spectrum of allowable energy levels, there is enough overlap for radiative transfer back and forth to take place. And all matter continually (albeit, at discrete intervals) emits and absorbs photons.

The second exchange is equally easily explained by simple conduction during the billions of intermolecular collisions that each atmospheric gas molecule undergoes each second. Although energies of translation have quantum constraints just as internal energies do, the number of allowable energy states is far, far greater.

The third exchange is the problem. Under the normal range of atmospheric temperatures and pressures, experiments do not detect any significant interchange of kinetic energies between the internal and external kinetic energies during molecular collisions. The impulses and kinetic energies transferred seem to be purely translational.

How then does this third exchange take place? Therein, lies the conundrum.

Definition of Terms

Equipartition – The principle of equipartition requires that the total kinetic energy of a population of molecules must be equally divided among the various available degrees of freedom of molecular movement. This principle does not apply to individual molecules, but only to populations.

Degrees of Freedom – Monatomic molecules (such as argon) are presumed to have three translational degrees of freedom only—one for each axis of a three-dimensional reference system. Diatomic molecules (such as oxygen and nitrogen) are presumed to have five degrees of freedom—three translational and two rotational¹. Polyatomic molecules (such as water vapor and carbon dioxide) can have nine or more degrees of freedom—depending upon their molecular structure.

¹ The third degree of rotational freedom—rotation about the common axis—is presumed not to be in use. The next permissible energy level above the ground state would require temperatures so high that the molecule would disassociate before that temperature could be reached.

THE KINETIC ATMOSPHERE

The Equipartition Conundrum

Allocation of Kinetic Energies – For a population of molecules, each degree of freedom is entitled to $\frac{1}{2}k_B\bar{T}$ joules of kinetic energy per molecule. This means that the more degrees of freedom that a gas has the more heat must be required to raise its temperature by one degree. This is because the heat is being divided up between more degrees of freedom, and temperature only measures one of these degrees of freedom—kinetic energies of translation normal to the sensing surface.

Quantum Restraints – The basic principle of quantum thermodynamics is that energy exists and can be transferred only in whole number multiples of some basic quantum of energy. Intermediate levels of energy are not allowed and do not in fact exist. Each of the three kinetic energy modes (translational, rotational, and vibrational/librational) has its own allowable energy levels.

The allowable energy levels for translational energy are so numerous and so close together that they form a virtual continuum. By contrast, rotational and vibrational kinetic energy levels are far fewer in number and quite separate from one another. Molecules go from one energy level to another without ever being at any intermediate level. The jump is discrete and instantaneous.

Enthalpic Heat Capacities of Air – Atmospheric air is some 98% diatomic, about 1% monatomic, and about 1% polyatomic. An ideal diatomic gas will have a gamma ratio (γ) of 1.400. Air has a gamma ratio of about 1.403 at NTP. At the range of temperatures normally encountered in the troposphere, air thus reacts to heating much as does an ideal gas. Equipartition is obviously in effect.

The Mechanism of Equipartition – Common sense tells us that the transfer of kinetic energy between the translational and rotational and vibrational modes must take place during molecular collisions. It must take place sometime, and transfer during collisions—when the molecules are close together—seems to be more likely than transfer at a distance. Unfortunately, this does not seem to be the case. The impulses and kinetic energies transferred during molecular impacts appear to be purely translational. Thus the mechanism of equipartition remains unclear and obscure.

THE KINETIC ATMOSPHERE

The Equipartition Conundrum

Hypothesis: I should like to suggest a possible solution to this conundrum. This solution is based on certain assumptions.

1. Most Intermolecular Collisions are Non-Contact – When gas molecules “collide” they don’t actually make contact with one another in the vast majority of cases. After all, the intermolecular repulsive forces are greater than the intermolecular attractive forces or the substance would not be a gas. Instead, during “collisions”, molecules get close enough to one another to transfer translational momentum through the various inter-molecular repulsive forces without getting close enough to transfer rotational or vibrational momenta. I should like to suggest that the vast majority of all molecular “collisions” are non-contact.

In only a statistically small number of collisions, are the translational energy levels great enough to overcome the repulsive forces of the molecules. Only these few occasions result in contact and molecular deformation. Only if deformation occurs, can there be a transfer between translational energies and internal energies.

2. Quantum Exclusivity – Since quantum considerations force all kinetic modes (translational, rotational and vibrational) into strictly defined energy levels, in most cases only photons will possess enough energy to move the internal modes from one level to another. Mechanical forces, such as translational kinetic energy, will be excluded unless the energy levels are sufficiently high. At temperatures normally encountered in the free atmosphere, the distribution of kinetic energies of translation is such that only a very, very few molecules will possess the required amounts of translational kinetic energy.

The tremendous range of available energy states in the translational mode makes the transfer of energy from the vibrational and rotational modes to the translational mode a fairly easy occurrence during intermolecular contact when one or both molecules are deformed. Such transfers are quantized, of course. And, obviously, they don’t occur at every collision. Collisions resulting in molecular deformation are rare but occur often enough to meet the first of the obligations of the third equipartition principle—transfer from internal energies to external.

In the opposite direction, the transfer of energy from the translational mode to the rotational and vibrational modes can only occur when the offered

THE KINETIC ATMOSPHERE

The Equipartition Conundrum

translational energy is precisely the value needed for an increase in an internal energy level as prescribed by quantum thermodynamics. The value must be exact. “Close” is not acceptable. Such transfers are also quantized, of course. These external to internal transfers of energy require relatively very large amounts of energy compared to internal to external transfers. Such collisions are rare.

Hence, only a very, very few of the billions of intermolecular collisions each second meet the requirements. These few, however, are sufficient to meet the second obligation of the third equipartition principle—transfer from external energies to internal ones.

It is the scarcity of energy exchanges between the translational and internal modes that makes impulse and energy transfer appear to be solely translational. At the levels of precision normally used in measurements, these transfers simply “fall beneath the radar”; that is, they are too slight to meet the levels of precision (three significant figures) customarily used.

The third exchange is hereby explained and hypothecated. I leave the verification or refutation of this hypothesis to younger souls.

REFERENCES

INTERNAL REFERENCES: These are other papers in this collection that are either cited or linked during the course of the discussion or whose content is especially relevant to the current discussion.

Molecular Impulses – This paper defines the molecular impulse parameter ($\bar{\phi}_i$) and shows how it is derived. The concept of a Universal Impulse Equation is introduced.

Kinetic Energies of Translation – This paper is a fundamental paper in this collection. It defines the various molecular kinetic energies of translation ($\bar{u}, \bar{u}_\sigma, \bar{u}_p, \bar{u}_i, \bar{u}_i'$) and shows how each is derived. It goes on to show the mathematical relationships between the various energies and their relation to the thermal term ($k_B \bar{T}$).

The Nature of Atmospheric Temperatures – This paper develops a universal gas temperature equation $\left(\bar{T} = \bar{u}_i / k_B \right)$ and shows how the ideal gas definition is a special case of the universal equation.

EXTERNAL REFERENCES: These are papers by other authors that contain statements or data that are specifically incorporated into the current discussion.

David Halliday, Robert Resnick; **Fundamentals of Physics**; John Wiley & Sons, New York, 1970.

Dwight E. Gray; **American Institute of Physics Handbook**; Third Edition, McGraw-Hill, New York, 1972.

THE KINETIC ATMOSPHERE
The Equipartition Conundrum

Charles Kittel; **Thermal Physics**; John Wiley & Sons, New York, 1969.

D. Tabor; **Gases, Liquids, and Solids**; Third Edition; Cambridge University Press, 1991.

Enrico Fermi; **Thermodynamics**; Prentice-Hall, New York, 1937. Dover reprint 1956.