THE NATURE OF ATMOSPHERIC TEMPERATURES

<u>Standard Definition of Ideal Gas Temperatures</u>: In kinetic gas theory, the standard definition of the temperature of an ideal gas under conditions of equilibrium takes the form:

$$\bar{T} = \frac{2\bar{u}}{3k_B} \qquad \text{NGT01}$$

Here, $\bar{T}$ is the mean temperature of the ideal gas in Kelvins, $\bar{u}$ is the mean molecular kinetic energy of translation along those molecule's true paths in joules, and k_B is Boltzmann's Constant in joules per molecule per Kelvin.

When it comes to temperature, the molecules of the gases that make up the free atmosphere behave very much as ideal gas molecules for the range of temperatures and pressures normally encountered in the free atmosphere. The problem comes with "conditions of equilibrium". The gases of the free atmosphere are hardly ever—if ever—in a state of equilibrium. The closest we can usually hope for is "quasi-equilibrium"; that is, a departure from the equilibrium state that is too small to show up on our instruments. Moreover, when weather is occurring, we don't even get that.

Nevertheless, in still air with minimal changes in temperature and humidity, Equation NGT01 gives a good approximation.

It is not, however, a very intuitive way of looking at gas temperatures. Our imaginations have a hard time grasping how the molecules of the atmosphere interact in such a way with the sensing surface of a conductive thermometer so as to produce this equation. We have to ask ourselves: What is the phenomenological basis of atmospheric temperatures? Just exactly what is involved in the phenomenon that we call gas temperature from a kinetic gas and statistical mechanics point of view?

Phenomenological Definition of Gas Temperatures: In ***Kinetic Energies of Translation***, we saw that:

$$\bar{T} = \frac{\bar{u}_i}{\mathrm{k_B}} \qquad \text{NGT02}$$

Here, $\bar{u}_i$ is the mean kinetic energy of translation in joules of that sub-population of molecules that actually impact on the temperature sensing surface during some interval of time. This energy is measured normal to the sensing surface at the instant of impact.

This equation is both simple and elegant. It is simple in that it relates a single thermodynamic measurement (temperature) to a single statistical mechanical parameter (mean axial kinetic energy of translation). It is elegant in that it fulfills all three of our ***Three Principles***.

The temperature of a gas is solely a response to those molecules actually interacting with the sensing surface (First Principle). The kinetic energy of that select population of molecules differs from the kinetic energy of the general population (Second Principle). Only the kinetic energy of translation normal to the surface enters into the equation (Third Principle).

The equation is thus satisfying in a philosophical sense, in a phenomenological sense, and in a dimensional sense. It also measures up to common sense. However, let us see if we can derive it in a more conventional way. It turns out that this derivation is exceedingly simple. In ***Kinetic Energies of Translation***, we saw that:

$$\bar{u}_i = \tfrac{2}{3}\bar{u} \qquad \text{NGT03}$$

Substituting NGT03 into NGT01 gives us NGT02. *Quod erat demonstratum*!

Universal Nature of the Gas Temperature Equation: The equation:

$$\bar{T} = \frac{\bar{u}_i}{k_B} \qquad \text{NGT02}$$

is a universal equation. It is valid for ideal gases and for real gases, under conditions of equilibrium and non-equilibrium, for air temperatures sensed by a stationary sensor in still air and a stationary sensor in moving air. It is even valid for the temperatures sensed by a moving sensor in moving air. The reason for this universality is because it is essentially a definition. It is a definition that is immensely satisfying from a phenomenological standpoint.

Non-Intrinsic Nature of Gas Temperatures: In classical thermodynamics, temperature is seen as an intrinsic quality of a substance. In kinetic gas theory, it is not intrinsic to the gas but a function of the relationship between the gas and the sensor. A moment's thought should suffice to show why that is so.

In still air, the mean kinetic energy of translation normal to the sensing surface of a thermometer ($\bar{u}_i$) is solely a function of the air temperature. When the air is moving, however, $\bar{u}_i$ becomes a function of the air temperature, the wind speed, and the angle of incidence that the wind vector makes with the sensing surface. When an object (a raindrop, for instance) is moving through still air, $\bar{u}_i$ becomes a function of the air temperature, the speed of the moving object, and the mean angle of incidence of the air molecules upon the surface of the sensor. Finally, moving objects in moving air give rise to entirely different values of $\bar{u}_i$. Some of these phenomena will be explored in future papers.

The Equipartition Conundrum: You might think that the temperature of a gas should measure rotational and vibrational modes of kinetic energy as well as translational. ***The Equipartition Conundrum*** explains why this is not normally the case for atmospheric gases. In any case, experiment and observation both confirm that temperature generally measures only the translational kinetic energies of gasses within the range of temperatures normally encountered in the free atmosphere.

Individual Molecular Temperatures: Equation NGT02 shows that the temperature of a population of gas molecules is a direct function of the mean kinetic energy of those molecules normal to the thermometer surface at the moment of impact. It does not stretch a point too much to apply this concept to individual molecules. That is,

$$\boldsymbol{T_i = \frac{u_i}{\mathrm{k_B}}} \qquad \text{NGT04}$$

Here, $\boldsymbol{T_i}$ is the temperature of an individual molecule having total kinetic energy $\boldsymbol{u_i}$ normal to the sensing surface at the moment of interaction. This concept has more than a little utility. It is extremely useful in dealing with evaporation and condensation phenomena; and is absolutely essential to understanding the phenomenon of latent heat.

It also enables us to view gas temperatures in a slightly different manner, that is

$$\boldsymbol{\bar{T} = \frac{1}{\bar{f}_i}\sum_{1}^{\bar{f}_i} T_i} \qquad \text{NGT05}$$

Here, all of the terms have their previous definitions.

Radiative Temperature Equilibrium: The emission and absorption of photons by the molecules of a gas is a function of the internal energies of the molecules, and not directly of the energies of translation. These internal phenomena are subject to the constraints of statistical quantum mechanics—a vastly more complex subject than that with which we have been dealing here.

Nevertheless, the Stefan-Boltzmann Equation,

$$\boldsymbol{\varepsilon} = \mathbf{k}\bar{T}^{4} \tag{NGT06}$$

clearly makes the photon emissivity (**ε**) a function of the temperature, hence a function of its mean kinetic energies of translation, and hence of its molecular velocities.

This is probably because an increase in temperature is accompanied by an increase in both the frequency and intensity of the collisions between molecules. As we saw in ***The Equipartition Conundrum***, only a very few of these collisions involve transfers of energy from the translational mode to the internal modes. However, the equipartition principle requires that some transfer must take place.

Consequently, it is at this time (or shortly thereafter) that photons are most likely to be emitted. The question, then, is which of the various translational velocities and kinetic energies is most likely to influence radiative equilibrium.

Let us postulate a volume of space contiguous to the surface of a thermal sensor. The space is so positioned that the emission of a photon from a molecule within that space has a free path to the surface of the sensor, a path that allows the transit without deflection or absorption by any other molecule.

A moment's thought will show that the probability of a given molecule's being within that space in any period of time is a function of its velocity. Faster molecules inhabit more volumes in a given period of time than do slower ones. Since the kinetic energy of translation $\bar{u}_{i'}$ involves higher velocities than the kinetic energy of translation $\bar{u}$, we should expect that the radiative equilibrium exists with the higher kinetic energy.

$$\bar{u}_{i'} = \frac{4}{3}\bar{u} \tag{NGT07}$$

Here $\bar{u}_{i'}$ is the mean total kinetic energy of translation (measured along the true paths) of that subset of molecules interacting with the sensing surface of the thermometer, whereas the mean total kinetic energy of the gas as a whole is $\bar{u}$.

In other words, both conductive and radiative equilibria exist between the thermal sensor and subsets of the general population having higher mean molecular temperatures than the general population ($\bar{T}_i$). The thermometer is not in thermal equilibrium with the mean molecular temperature of the general population ($\bar{T}_p$).

A Thermal Paradox: This situation seems to imply that the thermometer is warmer than the gas it is supposed to be measuring! An interesting paradox!

TABLES

The following tables offer values for the mean impulse velocity ($\bar{v}_i$) and the mean axial impulse kinetic energy of translation ($\bar{u}_i$) for both dry air and water vapor at selected atmospheric temperatures.

In calculating these values, the mean impulse masses ($\bar{m}_i$) have been used. Values for these mean impulse masses may be found in ***Molecular Masses***.

Values for the mean impulse velocities ($\bar{v}_i$) were taken from Table MSV01 in ***Molecular Speeds and Velocities***.

Values for the mean axial impulse kinetic energy of translation ($\bar{u}_i$) were taken from Table KET01 in ***Kinetic Energies of Translation***.

TABLE NGT01A

MEAN MOLECULAR AXIAL ARM VELOCITIES AND KINETIC ENERGIES FOR DRY AIR AT SELECTED TEMPERATURES

CELSIUS TEMP	KELVIN TEMP	MEAN AXIAL ARM IMPULSE VELOCITY	MEAN AXIAL ARM IMPULSE KINETIC ENERGY
°C	K	$\bar{\boldsymbol{v}}_i$	$\bar{\boldsymbol{u}}_i$
		m sec^{-1}	x 10^{-21} J molecule^{-1}
75	348.15	396.82	4.8067
70	343.15	393.96	4.7377
65	338.15	391.08	4.6687
60	333.15	388.17	4.5996
55	328.15	385.25	4.5306
50	323.15	382.30	4.4616
45	318.15	379.33	4.3925
40	313.15	376.34	4.3235
35	308.15	373.32	4.2545
30	303.15	370.28	4.1854
25	298.15	367.22	4.1164
20	293.15	364.12	4.0474
15	288.15	361.01	3.9783
10	283.15	357.86	3.9093
5	278.15	354.69	3.8403
0	273.15	351.48	3.7712

TABLE NGT01B

MEAN MOLECULAR AXIAL ARM VELOCITIES AND KINETIC ENERGIES FOR DRY AIR AT SELECTED TEMPERATURES

CELSIUS TEMP	KELVIN TEMP	MEAN AXIAL ARM IMPULSE VELOCITY	MEAN AXIAL ARM IMPULSE KINETIC ENERGY
°C	K	$\bar{v}_i$	$\bar{u}_i$
		m sec^{-1}	x 10^{-21} J molecule^{-1}
0	273.15	351.48	3.7712
-5	268.15	348.25	3.7022
-10	263.15	344.99	3.6332
-15	258.15	341.70	3.5641
-20	253.15	338.37	3.4951
-25	248.15	335.01	3.4261
-30	243.15	331.62	3.3571
-35	238.15	328.19	3.2880
-40	233.15	324.73	3.2190
-45	228.15	321.23	3.1500
-50	223.15	317.69	3.0809
-55	218.15	314.11	3.0119
-60	213.15	310.49	2.9429
-65	208.15	306.83	2.8738
-70	203.15	303.12	2.8048
-75	198.15	299.37	2.7358

TABLE NGT02A

MEAN MOLECULAR AXIAL ARM VELOCITIES AND KINETIC ENERGIES FOR WATER VAPOR AT SELECTED TEMPERATURES

CELSIUS TEMP	KELVIN TEMP	MEAN AXIAL ARM IMPULSE VELOCITY	MEAN AXIAL ARM IMPULSE KINETIC ENERGY
°C	K	$\underset{\sim}{\bar{v}}_i$	$\underset{\sim}{\bar{u}}_i$
		m sec^{-1}	x 10^{-21} J $molecule^{-1}$
75	348.15	502.39	4.8067
70	343.15	498.77	4.7377
65	338.15	495.13	4.6687
60	333.15	491.45	4.5996
55	328.15	487.75	4.5306
50	323.15	484.02	4.4616
45	318.15	480.26	4.3925
40	313.15	476.47	4.3235
35	308.15	472.65	4.2545
30	303.15	468.80	4.1854
25	298.15	464.92	4.1164
20	293.15	461.01	4.0474
15	288.15	457.06	3.9783
10	283.15	453.07	3.9093
5	278.15	449.06	3.8403
0	273.15	445.00	3.7712

TABLE NGT02B

MEAN MOLECULAR AXIAL ARM VELOCITIES AND KINETIC ENERGIES FOR WATER VAPOR AT SELECTED TEMPERATURES

CELSIUS TEMP	KELVIN TEMP	MEAN AXIAL ARM IMPULSE VELOCITY	MEAN AXIAL ARM IMPULSE KINETIC ENERGY
°C	K	$\underset{\sim}{\bar{v}}_i$	$\underset{\sim}{\bar{u}}_i$
		m sec^{-1}	x 10^{-21} J molecule^{-1}
0	273.15	445.00	3.7712
-5	268.15	440.91	3.7022
-10	263.15	436.78	3.6332
-15	258.15	432.61	3.5641
-20	253.15	428.40	3.4951
-25	248.15	424.15	3.4261
-30	243.15	419.85	3.3571
-35	238.15	415.51	3.2880
-40	233.15	411.13	3.2190
-45	228.15	406.70	3.1500
-50	223.15	402.22	3.0809
-55	218.15	397.68	3.0119
-60	213.15	393.10	2.9429
-65	208.15	388.46	2.8738
-70	203.15	383.77	2.8048
-75	198.15	379.02	2.7358

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 Masses – This paper defines the molecular mass parameters ($\bar{\boldsymbol{m}}, \bar{\boldsymbol{m}}_i$) and shows how their values were calculated.

Molecular Speeds and Velocities – This absolutely essential paper defines the various velocity terms ($\boldsymbol{\sigma}, \bar{\boldsymbol{v}}_p, \bar{\boldsymbol{v}}_i$) used throughout this collection of papers and shows how they are derived and how they relate to one another mathematically.

Kinetic Energies of Translation – This paper is a fundamental paper in this collection. It defines the various molecular kinetic energies of translation ($\bar{\boldsymbol{u}}, \bar{\boldsymbol{u}}_\sigma, \bar{\boldsymbol{u}}_p, \bar{\boldsymbol{u}}_i, \bar{\boldsymbol{u}}_{i'}$) 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 ($\mathrm{k_B}\bar{\boldsymbol{T}}$).

The Equipartition Conundrum – This paper discusses the equipartition conundrum; that is, why molecular collisions appear to transfer only kinetic energies of translation and not kinetic energies of either rotation or vibration.

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

Fundamental Physical Constants: 2006 CODATA – Peter J. Mohr, Barry N. Taylor, and David B. Newell; National Institute of Science and Technology (NIST), ***CODATA Recommended Values of the Fundamental Physical Constants: 2006;*** Gaithersburg, 2007.
http://physics.nist.gov/cuu/Constants/codata.pdf

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Computational System: All calculations were carried out by Microsoft's© Excel Program 2003 (SP3). The reader should be alerted to the fact that this computational system uses sixteen significant figures for all calculations—whether or not such precision is warranted by the accuracy of the data.