EQUIVALENCE OF PHASE TEMPERATURES

A Thought Problem

Let us postulate three closed but contiguous systems. The first contains natural water vapor at a temperature of 0°C and a vapor pressure that is the equilibrium vapor pressure for that temperature. The second system contains liquid natural water at the same temperature. The third system contains natural water ice at that same temperature.

All three systems also contain well-calibrated contact thermometers. The three systems all border one another, but are separated by three interfaces that prohibit the transfer of mass. These interfaces, however, allow the passage of both photons and kinetic impulses (conduction) without diminution.

We may justifiably conclude that, whatever the form or forms of energy that the three thermometers are measuring, the sum total of those energy forms transferred to the thermometers is the same per unit area of sensing surface in each of the three systems.

Moreover, since the three systems are separated by interfaces that readily allow the transfer of both radiative and conductive thermal energy and these systems are remaining in thermal equilibrium, we may safely assume that the total thermal energy transmitted through the three interfaces is the same per unit area of interface in both directions.

Next, we separate the three systems temporarily by a vacuum through which the kinetic impulses impacting upon the interfaces are unable to transfer. Now, the transfer of thermal energy between the three systems is by radiation only. Since the three systems are all at the same temperature, the thermodynamic definition of heat prohibits the transfer of heat between the systems. The logical conclusion is that the radiative transfer of thermal energy is the same between any two of the three systems, and is exactly the same in each of the six directions of transfer.

That being the case, simple logic requires us to conclude that the transfer of kinetic impulses between any two systems is also the same in each of the six directions of transfer.

Conclusion: Each of the three phases of water both radiates the same amount of thermal energy per unit of contact area and conducts the same amount of thermal energy per unit of contact area.

Modes of Transfer of Thermal Energy: There are three known ways in which thermal energy (heat, in engineering terms and everyday usage) may be transferred across an interface between two phases: mass transfer, radiation, and conduction.

Mass transfer involves the actual movement of matter across the phase interface. As the mass moves, so do all modes of energy associated with that mass. These energies are primarily kinetic energies of various kinds and the electronic energies that produce photons and ionic forces. Examples of mass transfer of thermal energy (heat) include advection, convection, diffusion, evaporation, and condensation.

Radiation involves the transfer of electromagnetic energy across the phase interface. In these papers, we are treating this energy as consisting of photons—massless particles that travel at the speed of light. Each photon has a singular *energy level* that (for our purposes) does not ever vary. That energy, however, alternates rhythmically between electromagnetic and electrostatic forms. The number of such cycles in one second is termed the *frequency* of that radiation. The distance that a photon travels while undergoing one cycle is termed the *wavelength* of that radiation.

Conduction involves the transfer of the kinetic energy of molecular and atomic motions across the phase interface. These motions are of four possible kinetic modes: translation, rotation, vibration, and libration. All four modes are constrained by quantum considerations. However, the number of possible energy levels association with the kinetic energy of translation is so large and the levels are so close together that the distribution may be treated as continuous without incurring significant error.

The various quantum physical theories that deal with solids, liquids, and gases do not assume that all four kinetic modes are equally possible for each phase.

Ice, for instance, is assumed to have no significant kinetic energies of translation or rotation at all. Its kinetic energies are solely vibrational and librational. Yet our ice most definitely does possess a temperature.

Liquid water is assumed to possess all four modes, but the proportion of energy in each mode varies with both the temperature and (to a small degree) the isotopic nature of the water.

Water vapor possesses all four modes of kinetic energy as well, but—at temperature normally found within the atmosphere—only a few of the molecules will have their vibrational or librational modes excited.

Yet, all three of these water phases have measurable temperatures. The only logical conclusion is that the total kinetic energy remains constant for any given temperature, while the amount of energy each mode contributes to the temperature varies with the nature of the material and with its temperature. This conclusion holds true for all three phases of water—water vapor, liquid water, and solid ice.

$$\bar{u}_i^{\Sigma} = \bar{u}_i^{translation} + \bar{u}_i^{rotation} + \bar{u}_i^{vibration} + \bar{u}_i^{libration} \qquad \text{EPT01}$$

Here, $\bar{u}_i$ is the mean of the distribution of values over the molecular population having that particular mode of kinetic energy. The i subscript indicates that the distribution is along the single axis of movement that is normal to and toward the sensing surface or interface. Furthermore,

$$\bar{u}_i^{\Sigma vapor} = \bar{u}_i^{\Sigma water} = \bar{u}_i^{\Sigma ice} \qquad \text{EPT02}$$

<u>Equivalence of Kinetic Energy Transfer</u>: Regardless of the kinetic energy mode, transfer across the phase interface is always and without exception the transfer of a distribution of impulses along an axis that is normal to the interface (the $\boldsymbol{i}$ axis, in these papers). These impulses travel through their respective phase mediums at the speed of sound (the mode of the impulse speed distribution) in that medium at that temperature until they reach the phase interface. At that point, the speed of the impulses changes, but the total amount of kinetic energy remains the same and is measured in Joules.

The Nature of Gas Temperatures: In *The Nature of Gas Temperatures* we defined the gas temperature as:

$$\bar{T} = \frac{\bar{u}_i}{\mathrm{k_B}} \qquad \text{EPT03}$$

Here, $\bar{T}$ is the mean gas temperature in Kelvins, $\bar{u}_i$ is the mean kinetic energy of translation in Joules per molecule measured normal to and toward the sensing surface, and $\mathrm{k_B}$ is Boltzmann's Constant in Joules per molecule per Kelvin.

Generalized Definition of Temperature: We may generalize this definition of gas temperatures to include all phases of matter. The equation now becomes:

$$\bar{T} = \frac{\bar{u}_i^{\Sigma}}{\mathrm{k_B}} = \frac{\bar{u}_i^{translation} + \bar{u}_i^{rotation} + \bar{u}_i^{vibration} + \bar{u}_i^{libration}}{\mathrm{k_B}} \qquad \text{EPT04}$$

Thus, temperature measures the mean total kinetic energies transmitted to the sensing surface of the thermometer by the impulses of a substance's molecules with that surface. The impulse energies may be translational, rotational, vibrational, librational or any combination of the various modes. Boltzmann's Constant plays the role of the constant of proportionality relating temperature to this total kinetic energy.

We may then reasonably argue that—at the same temperature—the mean impulse exerted against a surface molecule of liquid water by the "nudging" of molecules beneath it is the same as the mean impulse of a vapor molecule impacting upon a surface and the same as the mean impulse exerted against the bonds holding an ice molecule in place on the surface of an ice crystal.

The Equipartition Conundrum: Why doesn't the temperature of a gas appear to measure rotational and vibrational modes of kinetic energy as well as translational? *The Equipartition Conundrum* answers this question by showing how quantum considerations limit the contribution of the internal energies to gas temperatures. It appears that the number of molecular collisions that involve sufficient kinetic energy to move rotational or vibrational energies to their next available quantum level is a very small portion of the kinetic energies involved at the normal range of atmospheric temperatures. Hence, when measurements are made to three significant figures of precision, the contributions of rotational and vibrational energy exchanges are too small to show up.

In any case, experiment and observation both confirm that gas temperatures appear to measure only the translational kinetic energies of gases within the range of temperatures normally encountered in the free atmosphere.

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 ($\bar{\varphi}_i$) 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 ($\bar{\boldsymbol{u}}, \bar{\boldsymbol{u}}_\sigma, \bar{\boldsymbol{u}}_p, \bar{\boldsymbol{u}}_i, \bar{\boldsymbol{u}}_{i'}$) 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. Possible mechanisms for the transfer of internal energies to external energies and from external energies to internal energies are explored.

The Speed of Sound – This paper discusses the Gamma Function and its relation to the speed of sound in gases. The Gamma Function is shown to be a function of the root-mean-square speed ($\boldsymbol{\sigma}$). The speed of sound is shown to be the modal velocity of the impulse velocity distribution curve.

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

GENERAL REFERENCES: These are works by other authors that contain general treatments of kinetic gas theory, statistical mechanics and thermodynamics, atmospheric physics, and other scientific fields that are used in the current paper. They primarily contribute conceptual frameworks; but offer specific scientific data on occasion.

Walter Benenson, John W. Harris, Horst Stocker, Holger Lutz, editors; **Handbook of Physics**; Springer, New York, 2006.

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