

## The Little Heat Engine: Heat Transfer in Solids, Liquids and Gases

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In this work, an introductory exposition of the laws of thermodynamics and radiative heat transfer is presented while exploring the concepts of the ideal solid, the lattice, and the vibrational, translational, and rotational degrees of freedom. Analysis of heat transfer in this manner helps scientists to recognize that the laws of thermal radiation are strictly applicable only to the ideal solid. On the Earth, such a solid is best represented by either graphite or soot. Indeed, certain forms of graphite can approach perfect absorption over a relatively large frequency range. Nonetheless, in dealing with heat, solids will eventually sublime or melt. Similarly, liquids will give way to the gas phase. That thermal conductivity eventually decreases in the solid signals an inability to further dissipate heat and the coming breakdown of Planck's law. Ultimately, this breakdown is reflected in the thermal emission of gases. Interestingly, total gaseous emissivity can decrease with increasing temperature. Consequently, neither solids, liquids, or gases can maintain the behavior predicted by the laws of thermal emission. Since the laws of thermal emission are, in fact, not universal, the extension of these principles to non-solids constitutes a serious overextension of the work of Kirchhoff, Wien, Stefan and Planck.

The question now is wherein the mistake consists and how it can be removed.

*Max Planck, Philosophy of Physics, 1936.*

While it is true that the field of thermodynamics can be complex [1–8] the basic ideas behind the study of heat (or energy) transfer remain simple. Let us begin this study with an ideal solid,  $S_1$ , in an empty universe.  $S_1$  contains atoms arranged in a regular array called a “lattice” (see Figure 1). Bonding electrons may be present. The nuclei of each atom act as weights and the bonding electrons as springs in an oscillator model. Non-bonding electrons may also be present, however in an ideal solid these electrons are not involved in carrying current. By extension,  $S_1$  contains no electronic conduction bands. The non-bonding electrons may be involved in Van der Waals (or contact) interactions between atoms. Given these restraints, it is clear that  $S_1$  is a non-metal.

Ideal solids do not exist. However, graphite provides a close approximation of such an object. Graphite is a black, carbon-containing, solid material. Each carbon atom within graphite is bonded to 3 neighbors. Graphite is black because it very efficiently absorbs light which is incident upon its surface. In the 1800's, scientists studied objects made from graphite plates. Since the graphite plates were black, these objects became known as “blackbodies”. By extension, we will therefore assume that  $S_1$ , being an ideal solid, is also a perfect blackbody. That is to say,  $S_1$  can perfectly absorb any light incident on its surface.

Let us place our ideal solid,  $S_1$ , in an imaginary box. The walls of this box have the property of not permitting any heat to be transferred from inside the box to the outside world and

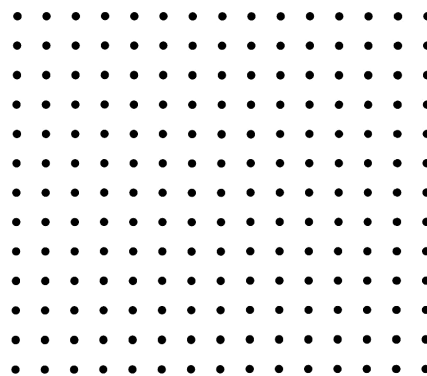


Fig. 1: Schematic representation of the ideal solid,  $S_1$ . The atoms are arranged in a regular array, or “lattice”.

vice versa. When an imaginary partition has the property of not permitting the transfer of heat, mass, and light, we say that the partition is adiabatic. Since,  $S_1$  is alone inside the adiabatic box, no light can strike its surface (sources of light do not exist). Let us assume that  $S_1$  is in the lowest possible energy state. This is the rest energy,  $E_{rest}$ . For our ideal solid, the rest energy is the sum of the relativistic energy,  $E_{rel}$ , and the energy contained in the bonds of the solid,  $E_{bond}$ . The relativistic energy is given by Einstein's equation,  $E = mc^2$ . Other than relativistic and bonding energy,  $S_1$  contains no other energy (or heat). Simplistically speaking, it is near 0 Kelvin, or absolute zero.

That absolute zero exists is expressed in the form of the 3rd law of thermodynamics, the last major law of heat transfer to be formulated. This law is the most appropriate starting point for our discussion. Thus, an ideal solid contain-

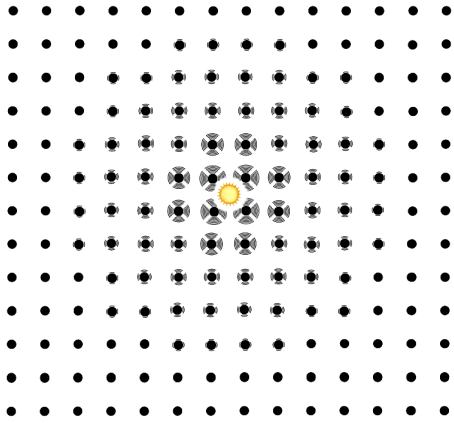


Fig. 2: Depiction of the Little Heat Engine at the center of the lattice. The atoms near this heat source move about their absolute location, such that they experience no net displacement over time. The vibrational degrees of freedom are slowly being filled.

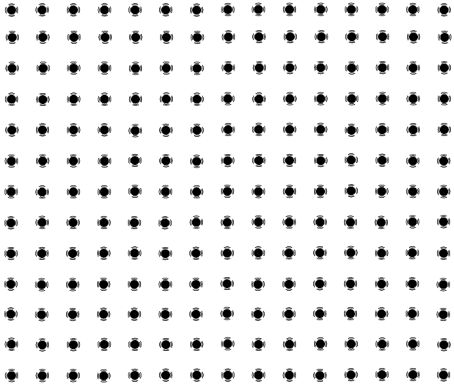


Fig. 3: The Little Heat Engine is turned off and the heat introduced into the lattice begins to equilibrate throughout the solid.

ing no heat energy is close to absolute zero as defined by the 3rd law of thermodynamics. In such a setting, the atoms that make up the solid are perfectly still. Our universe has a total energy ( $E_{total}$ ) equal to the rest mass of the solid:  $E_{total} = E_{solid} = E_{rest} = E_{rel} + E_{bond}$ .

Now, let us imagine that there is a hypothetical little heat engine inside  $S_1$ . We chose an engine rather than a source to reflect the fact that work is being done as we ponder this problem. However, to be strictly correct, a source of heat could have been invoked. For now, we assume that our little heat engine is producing hypothetical work and it is also operating at a single temperature. It is therefore said to be isothermal. As it works, the little heat engine releases heat into its environment.

It is thus possible to turn on this hypothetical little heat engine and to start releasing heat inside our solid. However, where will this heat go? We must introduce some kind of “receptacle” to accept the heat. This receptacle will be referred to as a “degree of freedom”. The first degrees of freedom that we shall introduce are found in the vibration of the atoms

about their absolute location, such that there is no net displacement of the atoms over time. The heat produced by our little heat engine will therefore begin to fill the vibrational degrees of freedom and the atoms in its vicinity will start vibrating. When this happens, the bonds of the solid begin to act as little springs. Let us turn on the heat engine for just a little while and then turn it off again. Now we have introduced a certain quantity of heat (or energy) inside the solid. This heat is in the immediate vicinity of the little heat engine (see Figure 2). As a result, the atoms closest to the heat engine begin to vibrate reflecting the fact that they have been heated. The total amount of energy contained in the vibrational degrees of freedom will be equal to  $E_{vib}$ .

Since the little heat engine has been turned off, the heat produced will now start to equilibrate within the solid (see Figure 3). Thus, the area nearest the little heat engine becomes colder (the atoms nearest the heat engine slow down their vibration) and the areas away from our little engine heat up (they increase their vibration). As this happens,  $S_1$  is moving towards thermal equilibrium. That is, it is becoming isothermal — moving to a single uniform temperature. In this state, all the atoms in  $S_1$  share equally in the energy stored in the vibrational degrees of freedom. The driving force for reaching this thermal equilibrium is contained in the 2nd law of thermodynamics. This law states that heat must always move from hotter to colder regions in an irreversible manner.

That heat flows in an irreversible manner is the central theme of the 2nd law of thermodynamics. Indeed, no matter what mechanism will be invoked to transfer heat in nature, it will always be true that the macroscopic transfer of heat occurs in an irreversible manner.

So far,  $S_1$  is seeking to reach a uniform temperature or thermal equilibrium. For our ideal solid, thermal equilibrium can only be achieved through thermal conduction which in turn is supported by energy contained in the vibrational degrees of freedom. Thermal conduction is the process whereby heat energy is transferred within an object without the absolute displacement of atoms or molecules. If the little heat engine was kept on, then thermal conduction would constantly be trying to bring our solid to thermal equilibrium. If there were no processes other than thermal conduction, and the engine was turned off, eventually one would think that the entire solid would come to a single new temperature and thermal equilibrium would be achieved. At this stage, our universe would have a total energy equal to that contained in the rest energy ( $E_{rel} + E_{bond}$ ) and in the vibrational degrees of freedom ( $E_{total} = E_{solid} = E_{rest} + E_{vib}$ ).

However, even though our little heat engine has been turned off, thermal equilibrium cannot be reached in this scenario. This is because there is another means of dissipating heat available to the solid. Thus, as the solid is heated, it dissipates some of the energy contained in its vibrational degrees of freedom into our universe in an effort to cool down. This is accomplished by converting some of the energy contained

in the vibrational degrees of freedom into light!

The light that objects emit in an attempt to cool down is called thermal radiation. The word thermal comes in because we are dealing with heat. The word radiation comes from the fact that it is light (or radiation) which is being emitted.

This light is emitted at many different frequencies (see Figure 4). We represent the total amount of energy in this emission as  $E_{em}$ . Emission of light provides another means of dealing with heat. Thus, the emission of light joins vibration in providing for our stationary non-metallic solid the only degrees of freedom to which it can ever have access. However, the energy of emission becomes a characteristic of our universe and not of the solid. Thus, the universe now has a total energy given by  $E_{total} = E_{solid} + E_{em}$ . As for the solid, it still has an energy equal only to that stored as rest energy and that contained in the vibrational degrees of freedom,  $E_{solid} = E_{rest} + E_{vib}$ . However, note that since all the heat energy of the solid was initially contained in its vibrational degrees of freedom, the energy of emission ( $E_{em}$ ) must be related to the energy contained in  $E_{vib}$  at the time of emission.

As stated above, light has the property that it cannot cross an adiabatic partition. Consequently, the light produced by heating the solid becomes trapped in our virtual box. If we kept our adiabatic walls close to the solid, eventually thermal equilibrium would be achieved between the solid and the radiation. In this scenario, the solid would be constantly emitting and absorbing radiation. Under a steady state regimen, all of the atoms in the solid would be sharing equally in the energy contained in the vibrational degrees of freedom. However, let us make the box large for now, so that it will take the light many years to reach the walls of the box and be reflected back towards the solid. For all purposes then, the light that the solid emits cannot return and hit the surface of the solid.

Up to this point, by turning on our little heat engine, we have been able to discuss two important processes. The first is thermal conduction. Thermal conduction is that process which tries to bring the internal structure of the solid to thermal equilibrium. In our ideal solid, the vibrations of the atoms are the underlying support for this process. The second process is thermal radiation (also called radiative emission). Through radiative emission, the solid is trying to come to thermal equilibrium with the outside world. There are only two means for an ideal solid to deal with heat. It can strive to achieve internal thermal equilibrium through thermal conduction supported by the vibrations of its atoms and it can dissipate some of the energy contained in its vibrational degrees of freedom to the outside world through thermal radiation.

For an ideal solid, the light emitted in an attempt to reach or maintain thermal equilibrium will contain a continuous range of frequencies (see Figure 4). The intensity of the light at any given frequency will be given by the well known

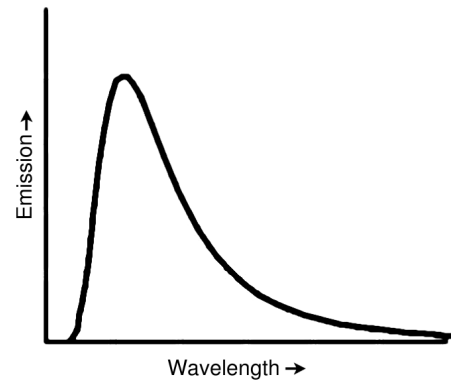


Fig. 4: The light that objects emit in an attempt to cool down is called thermal radiation. Emission of light provides another means of dealing with heat. The emission is continuous over all frequencies for our ideal solid,  $S_1$ .

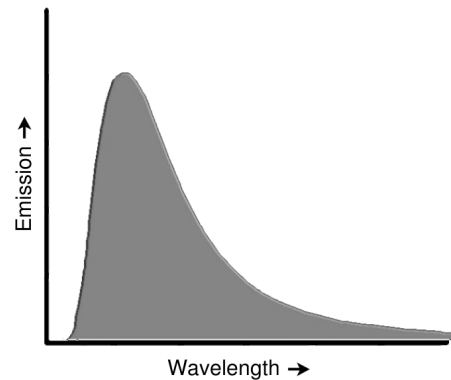


Fig. 5: For the ideal solid,  $S_1$ , the total emission (area under the curve) is proportional to the fourth power of the temperature as dictated by Stefan's law of thermal emission.

Planckian relation [9]

$$B_\nu(T) = \frac{\varepsilon_\nu}{\kappa_\nu} = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}.$$

Planck's equation states that the light produced, at a frequency  $\nu$ , by a blackbody (or an ideal solid),  $B_\nu$ , depends only on two variables: temperature,  $T$ , and the frequency,  $\nu$ . All the other terms in this equation are constants ( $h$  = Planck's constant,  $k$  = Boltzman's constant,  $c$  = speed of light). This equation tells us that the nature of light produced is dependent only on the temperature of the solid and on the frequency of interest. The fact that the light emitted by an ideal solid was dependent only on temperature and frequency was first highlighted by Gustav Robert Kirchhoff in the mid-1800's. Kirchhoff's formulation became known as Kirchhoff's Law of Thermal Radiation [10, 11]

$$B_\nu(T) = \frac{\varepsilon_\nu}{\kappa_\nu}.$$

In this equation,  $\varepsilon_\nu$  represents the ability of the blackbody to emit light (emissivity) and  $\kappa_\nu$  represents its ability

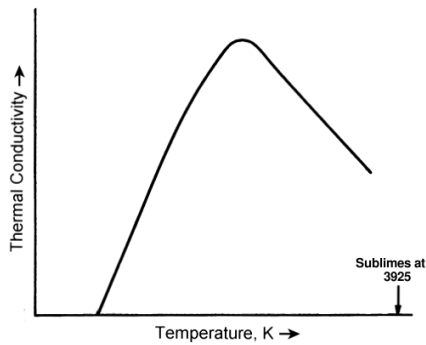


Fig. 6: Thermal conductivity for pyrolytic graphite (parallel to the layer planes) increases to a maximum and then begins to decrease. Eventually, graphite sublimates at 3925 K. Adapted from reference 15, volume 2, *Thermal Conductivity of Nonmetallic Solids*, 1970.

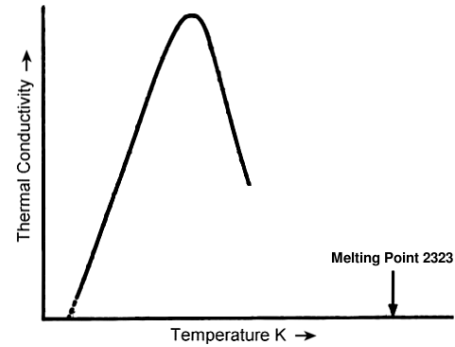


Fig. 7: Thermal conductivity for sapphire ( $\text{Al}_2\text{O}_3$ ) increases to a maximum and then decreases. Eventually, sapphire melts at 2323 K. Adapted from reference 15, volume 2, *Thermal Conductivity of Nonmetallic Solids*, 1970.

to absorb light (opacity) at a given frequency. As mentioned above, an ideal solid is a blackbody, or a perfect absorber of light ( $\kappa_\nu = 1$ ). As such, this equation states that the manner in which a blackbody emits or absorbs light at a given frequency depends exclusively on its temperature. The function,  $f$ , contained in Kirchhoff's Law  $B_\nu = \frac{\epsilon_\nu}{\kappa_\nu} = f(T, \nu)$  was elucidated by Max Planck as shown in the first equation above. It is for this reason that Kirchhoff's equation constitutes the left hand portion of Planck's equation [9]. As a result, any work by Kirchhoff on this topic is critical to our understanding of Planck's work [9, 10, 11].

It has also been observed that the amount of light that our ideal solid will produce, or the total emission (see the area under the curve in Figure 5), is proportional to the fourth power of the solid's temperature. This is known as Stefan's law of emission ( $\epsilon = \sigma T^4$ ), where  $\epsilon$  represents total emission and Stefan's constant,  $\sigma$ , is equal to  $5.67051 \times 10^{-8}$  Watts/(m<sup>2</sup>K<sup>4</sup>) [12]. Note that Stefan's law of emission reveals a pronounced increase in the production of light, with temperature. Thus, as the temperature of the solid increases, thermal radiation can greatly increase to accommodate the increased requirement for heat dissipation. If the solid is at room temperature, this light will be emitted at infrared frequencies, that is, just below the portion of the electromagnetic spectrum that is visible to the human eye. Indeed, this emitted light at room temperatures can be viewed with a thermal or infrared camera of the type used by the military to see at night.

Interestingly for  $S_1$ , the frequency of light at which the maximal emission occurs ( $\nu_{max}$ ) is directly related to the temperature  $\nu_{max}/c = T$ . This is known as Wien's law of displacement [13].

Let us turn on our little heat engine once again. As the little heat engine releases more heat into solid, it becomes apparent that thermal conductivity increases only approximately linearly with temperature. In fact, as temperature is increased for many real solids, thermal conductivity actually may initially increase to a maximum and then suddenly begin to decrease (see Figure 6 for graphite and Figure 7 for sapphire

or  $\text{Al}_2\text{O}_3$ ) [14]. Since the vibrational degrees of freedom are central to both thermal conduction and emission, one can only gather that the vibrational degrees of freedom simply become incapable of dealing with more heat (see Figure 8). Herein lies a problem for maintaining the solid phase. As temperature is increased, there is a greater difficulty of dealing with the internal flow of heat within the solid. The solid must begin to search for a new degree of freedom.

The next available means of dealing with heat lies in breaking bonds that link up the atoms forming the ideal solid. As these bonds begin to break, the atoms (or the molecules) gain the ability to change their average location. New degrees of freedom are born, namely, the translational and rotational degrees of freedom. Interestingly, these new degrees of freedom are associated with both the flow of heat and mass.

With the arrival of the translational and rotational degrees of freedom,  $S_1$  is transformed into one of two possibilities. It can either melt — giving rise to the liquid phase,  $L_1$ ; or, it can sublime — giving rise directly to the gas phase,  $G_1$ . Graphite, perhaps the closest material to an ideal solid, sublimates (see Figure 6) and never melts. Whereas sapphire or  $\text{Al}_2\text{O}_3$  melts (see Figure 7). In any case, as a solid is being converted to a liquid or a gas, the absolute amount of rest energy is changing, because bonds are being broken ( $E_{bond} \rightarrow 0$ ).

Since many solids melt giving rise to  $L_1$ , let us turn our attention first to this situation. We assume that unlike graphite, our ideal solid can in fact melt. Thus, as more heat is pumped into  $S_1$ , the temperature will no longer rise. Rather, the solid  $S_1$  will simply slowly be converted to the liquid  $L_1$ . The melting point has been reached (see Figure 9 and Figure 10) and the liquid created (see Figure 11).

Since  $L_1$  has just been created, let us turn off our little heat engine once again. The liquid  $L_1$  at this stage, much like  $S_1$  of old, is still capable of sustaining thermal conduction as an internal means of trying to reach thermal equilibrium through the vibrational degrees of freedom. However, the absolute level of thermal conduction is often more than 100 times lower than in the solid [8, 15]. The liquid  $L_1$  also



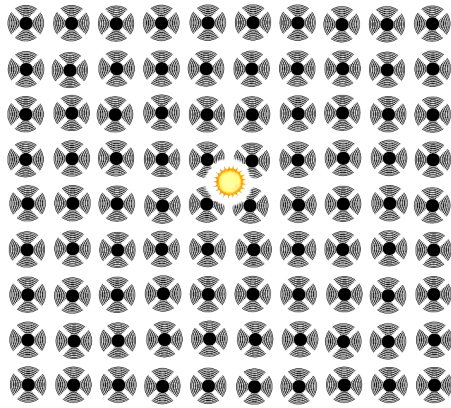


Fig. 8: The Little Heat Engine has introduced so much heat into the lattice that the vibrational degrees of freedom become full. The solid must search for a new way to deal with the continued influx of heat.

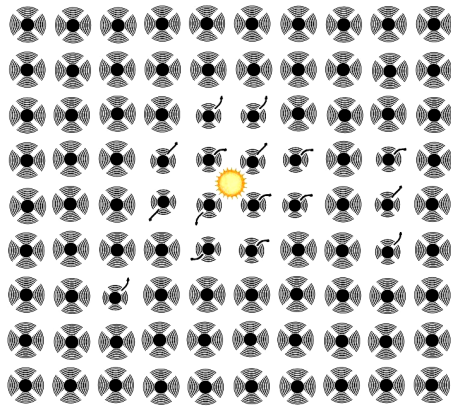


Fig. 9: As The Little Heat Engine continues to heat the lattice, the melting point is eventually reached. The solid,  $S_1$ , begins to melt as the translational and rotational degrees of freedom start to be filled.

has access to thermal radiation as a means of dissipating heat to the outside world.

However, within  $L_1$ , a new reality has taken hold. The requirements placed on conduction and radiative emission for heat dissipation have now been relaxed for the liquid and, mass transfer becomes a key means of dissipating heat within such an object. Indeed, internal convection, the physical displacement (or flow) of atoms or molecules, can now assist thermal conduction in the process of trying to reach internal thermal equilibrium. Convection is a direct result of the arrival of the translational degrees of freedom. The driving force for this process once again is the 2nd law of thermodynamics and the physical phenomenon involved is expressed in kinetic energy of motion. Thus, through internal convection, currents are set up within the liquid, whose sole purpose is an attempt at thermal equilibrium. As convection currents form, the bonds that make up the liquid are constantly in the process of breaking and reforming. Like thermal conduction, the process of internal convection changes approximately linearly with temperature. For its part,  $L_1$  now has three means

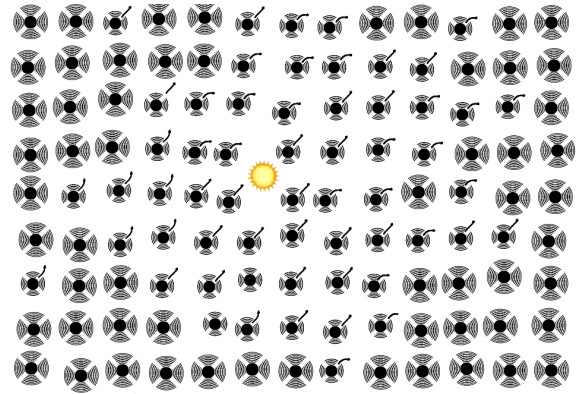


Fig. 10: As The Little Heat Engine continues to heat the lattice, melting continues. The regular array of the solid lattice is being replaced by the fleeting lattice of the liquid.

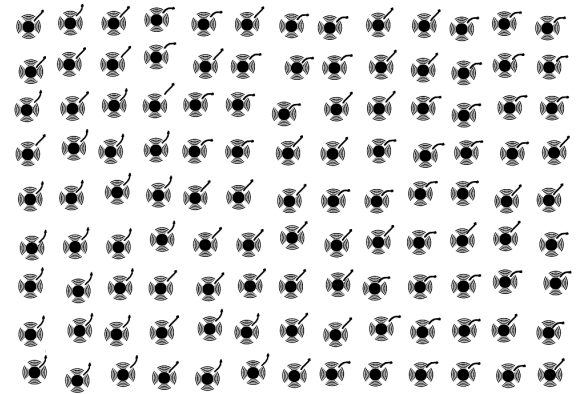


Fig. 11: The Little Heat Engine is turned off and melting of  $S_1$  into  $L_1$  is completed. The regular solid lattice is now completely replaced with the fleeting lattice of the liquid. The individual atoms now experience absolute displacement in position over time.

of dealing with heat transfer: conduction, convection (internal), and thermal radiation (external). The total energy of the universe is now expressed as  $E_{total} = E_{liquid} + E_{emission}$ . The energy within the liquid is divided between the rest energy and the energy flowing through the vibrational, translational, and rotational degrees of freedom,  $E_{liquid} = E_{rest} + E_{vib} + E_{trans} + E_{rot}$ . Thermal conduction and radiative emission remain tied to the energy associated with the vibrational degrees of freedom, while convection becomes associated with the energy within the translational and rotational degrees of freedom. The added heat energy contained within the liquid is now partitioned amongst three separate degrees of freedom:  $E_{vib} + E_{trans} + E_{rot}$ .

At this stage, the little heat engine can be turned on again. Very little is known regarding thermal emission from liquids. However, it appears that when confronted with increased inflow of heat, the liquid responds in a very different way. Indeed, this is seen in its thermal emission. Thus, while thermal emission in the solid increased with the fourth power of the temperature, thermal emissivity in a liquid increases little, if

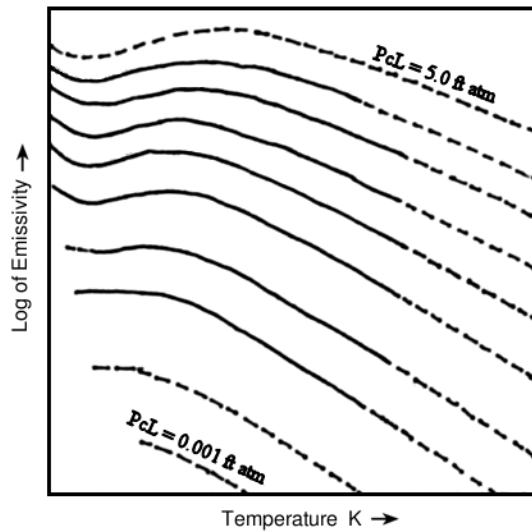


Fig. 12: The total emissivity for  $\text{CO}_2$  at 1 atmosphere for various pressure path lengths. Note that emissivity can actually drop significantly with increasing temperature. Gases are unable to follow Stefan's Law. Adapted from reference 17.

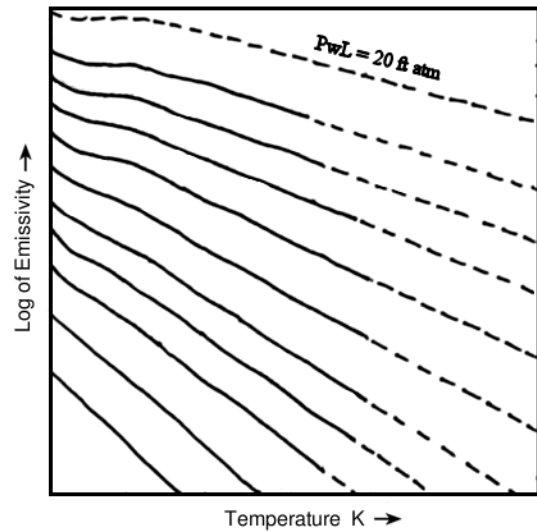


Fig. 13: The total emissivity of water vapor for various pressure path lengths. Note that the total emissivity can actually drop significantly with increasing temperature. Gases are unable to follow Stefan's Law. Adapted from reference 17.

at all, with temperature [8, 15]. Indeed, total thermal emission may actually decrease. Stefan's law does not hold in a liquid. That is because new degrees of freedom, namely the translational and rotational degrees of freedom (and its associated convection), have now been introduced into the problem. Since the vibrational degrees of freedom are no longer exclusively in control of the situation, Stefan's law fails.

It has already been noted that thermal conduction is eventually unable to deal with increased heat in the solid. In liquids, it is often observed that thermal conductivity changes only slightly with temperature and often decreases [8, 14, 15]. At the same time, it is clear that thermal radiation does not increase with temperature in the liquid. One can only surmise that convection rapidly becomes a dominant means of dealing with heat transfer in the liquid phase. This can be seen by examining the viscosity of the liquid. Thus, the viscosity of liquids decreases with temperature and the liquid flows better at higher temperature [14]. This is a direct reflection that an increasing percentage of bonds within the liquid are being broken in order to accommodate the increased flow of heat, or energy, into the translational degrees of freedom.

Let us now return to our little heat engine. Since the little heat engine has been left on, as it continues to heat  $L_1$ , a point will be reached where internal conduction and convection along with thermal radiation can no longer accommodate the increase in heat. At that point, a new process must arise to carry heat away. Thus, with an internal structure weakened by broken bonds, individual atoms or molecules are now free to carry mass and heat directly away from the liquid in the form of kinetic energy of motion. The liquid  $L_1$  enters the gas phase becoming  $G_1$ . This is exactly analogous to what occurred previously for the solid with sublimation. The li-

quid  $L_1$  has now reached the boiling point. While it boils, its temperature will no longer increase. Rather, it is simply being slowly converted from the liquid  $L_1$  to the gas  $G_1$ . According to the kinetic theory of gases, the molecules of the gas are traveling at a particular average velocity related to the temperature of the gas at a given pressure. It is our adiabatic partitions that have ensured that we can speak of pressure. The fact that the gas molecules are moving is a reflection of the convection within the gas which, in turn, is an expression of the translational degrees of freedom. Let us turn off our little heat engine for a moment in order to analyze what has just transpired.

In the gas  $G_1$ , individual molecules are not attached to each other but are free to move about. This is once again a reflection of the translational degrees of freedom.  $G_1$  can have either a molecular nature (it is made up of individual molecules) or an atomic nature (it is made up of individual atoms). For now, let us make the assumption that  $S_1$  was selected such that a diatomic molecular gas,  $G_1$ , is produced. Let us also assume that our diatomic molecular gas will be made up of two different types of atoms. Note that we are deviating slightly from the requirements of an ideal solid in order to deal with molecular gases. Once in the gas phase, the molecular gas can also invoke rotational degrees of freedom. Therefore, the molecular gas  $G_1$  has energy partitioned amongst its available degrees of freedom,  $E_{\text{gas}} = E_{\text{rest}} + E_{\text{vib}} + E_{\text{trans}} + E_{\text{rot}}$ . Note that in the molecular gas the  $E_{\text{rest}}$  term decreases, reflecting the breakdown of  $S_1$  and  $L_1$  into the gas  $G_1$  (less energy is now contained in  $E_{\text{bond}}$ ). From above, we now see that the total energy in the universe is  $E_{\text{total}} = E_{\text{gas}} + E_{\text{em}} = E_{\text{rest}} + E_{\text{vib}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{em}}$ . The molecular gas will still be able to emit ra-

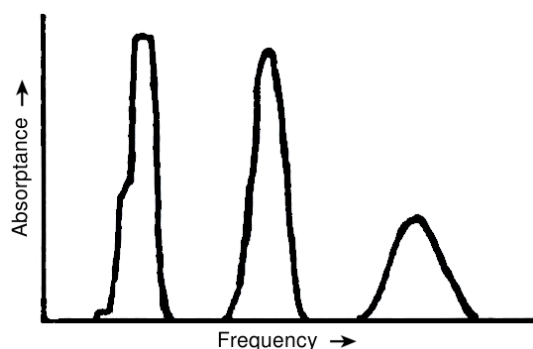


Fig. 14: Schematic representation of the absorbance for  $\text{CO}_2$  at 830 K and 10 atmospheres for a path length of 0.388 meters. The gas absorbs in discrete bands and not in a continuous fashion as previously observed for a solid. Adapted from reference 8.

diation, typically in the microwave or infrared region of the electromagnetic spectrum.

It is now time to turn our little heat engine on again. As more heat is generated, the gas will increase the average kinetic energy of motion of its constituent molecules. Nonetheless, thermal conduction within  $G_1$  is now at least 10 times lower than was the case for the liquid [15]. Most importantly the total radiative emissivity for the molecular gas at constant pressure actually begins to drop dramatically with increased temperature [7, 16]. We can speak of constant pressure when we do not permit the adiabatic walls of our imaginary box to move. If we now move in our adiabatic walls we increase the pressure on the gas and the emissivity will increase, corresponding to a higher apparent temperature.

Nonetheless, it should be noted that the total emissivity for a gas at constant pressure can actually drop significantly with increasing temperature (see Figure 12 and Figure 13). Consequently, we can see that Stefan's law does not hold for gases [7]. In fact, thermal emission for the diatomic gas (like CO and NO) occurs in discrete bands of the electromagnetic spectrum and in a manner not simply related to temperature (see Figure 14, Figure 15 and Figure 16) [8, 16]. The situation becomes even more interesting if the gas is not molecular, but rather monatomic in nature (like Ar or He for instance). In that case, when moving from the liquid to the gas phase,  $G_1$  loses both its rotational, and more importantly, its vibrational, degrees of freedom,  $E_{\text{bond}} = E_{\text{vib}} = E_{\text{rot}} = 0$ . Neglecting electronic emission, which typically occurs in the ultra violet or visible range, a monatomic gas cannot emit significant radiation in the microwave and infrared regions. Indeed, for such a gas, Stefan's law no longer has any real meaning.

It is now clear that relative to  $S_1$  (and even  $L_1$ ), the molecular gas  $G_1$  is unable to dissipate its heat effectively to the outside world in response to increased temperature. Indeed, since thermal emission can drop dramatically with temperature for molecular gases, as temperature is increased, a greater fraction of the heat energy must be dealt with by the transla-

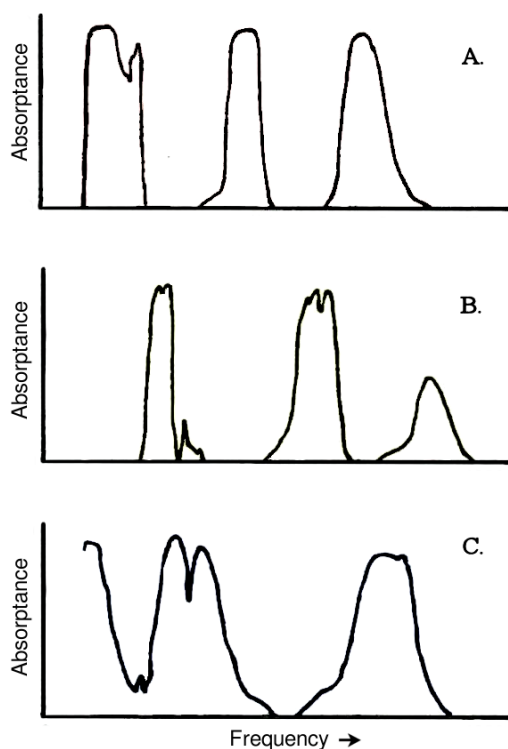


Fig. 15: Schematic representation of the absorbance for carbon dioxide (A:  $\text{CO}_2$  partial pressure path product = 3.9 atm m, temperature = 1389 K, total pressure = 10 atm, partial pressure = 10 atm), water (B:  $\text{H}_2\text{O}$  partial pressure path product = 3.9 atm m, temperature = 1389 K, total pressure = 10 atm, partial pressure = 10 atm), and methane (C:  $\text{CH}_4$  partial pressure path product = 3.9 atm m, temperature = 1389 K, total pressure = 10 atm, partial pressure = 10 atm). Note that for gases absorbance is not continuous and occurs in discrete bands. Adapted from reference 8.

tional and rotational degrees of freedom. If the gas is made up of molecules as is the case for  $G_1$ , then as more heat is pumped into the gas by our little engine, the gas molecules will eventually break apart into their constituent atoms. The gas then adopts the nature of monatomic gases as mentioned above with  $E_{\text{bond}} = E_{\text{vib}} = E_{\text{rot}} = 0$ . As more heat is pumped into the system, electronic transitions within each atom becomes more and more important. If the little heat engine is not stopped, much like what happened in the case of the solid and the liquid, the atomic gas will no longer be able to deal with the increased heat. Eventually, the electrons gain enough energy to start emitting radiation in the visible or ultra-violet range. As the little heat engine continues to generate heat, the electrons will gain enough energy to become free of the nucleus and a final new state is born — the plasma. The discussion of heat flow in plasmas is beyond our scope at this stage. Suffice it to say that if the little heat engine continues to operate, still another process would occur, namely nuclear reactions.

It is now time to finally turn off our little heat engine. We have learned a lot with this little device and so it is somewhat

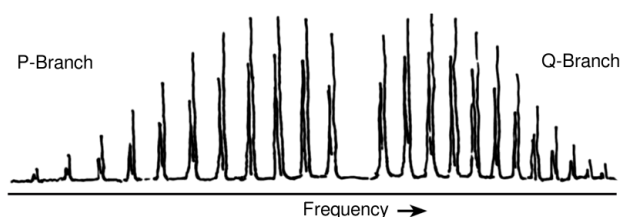


Fig. 16: Vibrational-rotational spectrum of hydrochloric acid at room temperature. The spectrum reveals the presence of the two isotopic form,  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ . Adapted from reference 18.

sad to state that it can live only in our imagination. This is because our little heat engine violates the 1st law of thermodynamics. That law states that there must be conservation of energy. Namely, energy cannot be created or destroyed. However, when Einstein introduced relativity he demonstrated that  $E = mc^2$ . Thus, it is actually possible to convert mass into energy and vice versa. As a result, after Einstein, the 1st law of thermodynamics had to be modified. Consequently, the 1st law of thermodynamics now states that there must be conservation of mass and energy. Theoretically, these two entities could be freely interchanged with one another.

For a moment in closing however, let us return to our initial solid  $S_1$ . Of course, in the real world our solid is not in an isolated universe. Other solids, liquids (like our oceans) and gases (like our atmosphere) also exist. How do these affect our solid? In order to understand this, let us now bring two other solids into our adiabatic box. We will assume that these two solids, denoted " $S_2$ " and " $S_3$ ", are in thermal equilibrium with each other. That is to say that, if " $S_2$ " is placed in direct contact with " $S_3$ " no net heat will flow between these objects. Now, if we now place solid " $S_1$ " in contact with solid " $S_2$ ", we will discover one of two things. Either solid " $S_1$ " is in thermal equilibrium with solid " $S_2$ ", or it is not in equilibrium. If it is in equilibrium with  $S_2$ , then by the 0th law of thermodynamics, it must also be in equilibrium with  $S_3$ . If on the other hand the solid  $S_1$  it is not in equilibrium with  $S_2$ , then  $S_1$ ,  $S_2$  and  $S_3$  will all move to a new thermal equilibrium with each other. If they are not in direct physical contact, this can only occur through thermal emission. However, if they are in direct contact, then they can use the much more efficient means of conduction to reach thermal equilibrium. If in turn we substitute a liquid or a gas for one of the solids, then convection can also be used to reach thermal equilibrium amongst all the objects. This is provided of course that the solids remain in physical contact with the gas or liquid. In the real universe therefore, all of the matter is simultaneously trying to reach thermal equilibrium with all other matter. The 2nd law of thermodynamics is governing this flow of heat. Most importantly, this process on a macroscopic scale is irreversible.

But now what of our little heat engine? Would it not be nice to bring it back? Perhaps we can! That is because, for our solar system, it is our Sun, and its internal energy, which

is the ultimate source of energy. Therefore our Sun becomes for us a local little heat engine. As for the stars, they become other local heat engines, in a universe constantly striving for thermal equilibrium.

#### Author's comment on The Little Heat Engine:

The Little Heat Engine is telling us that the internal processes involved in heat transfer cannot be ignored. However, modern courses in classical thermodynamics often neglect the internal workings of the system. In large part, this is because the fathers of thermodynamics (men like Kirchhoff, Gibbs and Clausius) did not yet have knowledge of the internal workings of the system. As such, they had no choice but to treat the entire system.

In this essay, it becomes apparent that Stefan's Law of thermal emission does not hold for liquids and gases. This is a reflection that these two states of matter have other available degrees of freedom. For instance, if Stefan's Law had held, solids would have no need to melt. They could keep dealing with heat easily, simply by emitting photons in a manner proportional with the fourth power of the temperature. However, the drop in thermal conductivity observed in the solid heralds the breakdown of Stefan's law and the ensuing change in phase. The Little Heat Engine is telling us that statistical thermodynamics must be applied when dealing with thermal emission. The Little Heat Engine is a constant reminder that universality does not exist in thermal radiation. The only materials which approach the blackbody on the Earth are generally made of either graphite or soot. The application, by astrophysics, of the laws of blackbody radiation [9–13] to the Sun [19, 20] and to unknown signals [21] irrespective of the phase of origin constitutes a serious overextension of these laws. Experimental physics has well established that there is no universality and that the laws of thermal radiation are properly restricted to the solid [22, 23].

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