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**Thermodynamics**  
 (revised)  
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Sir Isaac Newton spoke of forces as the "active agents of nature." He said that, in a forceless universe, nothing would really be happening, even though there might be a vast number of particles all moving along their straight inertial paths at constant speed. Collisions could not occur because force is required to change either the speed or direction of a particle motion. Indeed, it is the action of forces of attraction that lead to the formation of objects (e.g., galaxies, stars, humans, atoms, nuclei). It is the action of forces of repulsion that almost always balances with forces of attraction in order to prevent matter from coming together and 'densifying' without limit. It is the action of forces that pump our blood, move our muscles, and send our nerve signals.

It is a very large leap from the action of two atoms attracting each other to form a molecule or that of two colliding atoms or molecules rebounding from each other, to the actions of individual humans and their interactions in small and large social groupings. The leap must be made in stages. At this point, suffice it to say that it is the action of biological and social 'forces' that move people to act, behave, vote, and feel the way they do.

While not as obvious to the non-physicist, it is already a large leap from the interaction between two atoms or simple molecules to the behavior of a macroscopically large number

of interacting atoms or molecules as in a gas. In this essay, we describe:

- a) the basic **physics of interaction** between two simple 'particles',
- b) the strategy of describing the **macroscopic properties** of a large number of such particles, and
- c) the **relation** between the macroscopic description and the microscopic physics of particle-particle interaction.

Thermodynamics (from the Greek *therme*, meaning "heat" and *dynamis*, meaning "power") is the study of processes that involve changes in temperature, transformation of energy, the relationship between heat and work. It studies heat energy and its relation to macroscopic variables such as temperature, pressure, and volume. Thermodynamics is the macrophysics within and between organized levels. It will be our tool for studying societies and for developing a social physics.

### **Physics of Interaction - the Micro Level**

Imagine a large number of simple particles, atoms, or molecules moving around in some space. To consider the simplest case, we assume that the forces of attraction between these particles are negligible. If we then follow the motion of any individual particle, we will see it undergoing a zigzag motion consisting of straight flights separated by rapid changes of direction. Each straight flight is the 'free flight' motion that takes place when no force is acting on the particle. By *Newton's first law of motion*, this takes place at

constant velocity. The rapid changes of direction and of speed occur when the particle collides with another particle. The repulsive force between the colliding particles changes the speeds and directions of both particles. Think of billiard ball collisions as a well-known macroscopic example.

According to *Newton's second law of motion*, a force on a particle causes its velocity to change at a rate given by the strength of the force divided by the mass of the particle. This rate is called the *acceleration*. The change in the velocity takes place in the direction of the force. A consequence of this law is the following: If we define the *momentum* of a particle as the product of its velocity and its mass, then the action of a force acting for a time is to change the momentum of the particle by an amount given by the product of the force and the time. This product is called the *impulse*.

But, according to *Newton's third law of motion*, forces between particles are always mutual and equal in strength and opposite in direction. It follows that two colliding particles repel each other with forces of equal strength and in opposite directions, and therefore change each other's momentum by equal amounts in opposite directions. Since momentum is a directional quantity (a so-called vector quantity), the sum of the momenta of the particles is the same after the collision as before. Total momentum is said to be '*conserved*'.

The total energy is also conserved. That is, the sum of the energies of the particles is the same after the collision as before. The energy of a stationary particle is called its *internal energy* -- this is the energy of any and all actions taking place

inside the 'particle'. The energy of its motion through space is called its *kinetic energy*, and it is equal to one half its mass times the square of its velocity. The energy of a moving particle is the sum of its internal energy and kinetic energy. The amount of energy transferred from one of the colliding particles to the other is given by the product of the force times the distance over which the force acts. If the collision is not intense enough to cause changes inside the particles, their internal energies are not altered, and then the sum of the kinetic energies of the particles is the same after the collision as before.

If we also assume that collisions are not intense enough to destroy the particles (by breaking them into parts, for example), then the number of particles is always a conserved quantity. Collisions are then characterized by:

- conservation of matter content - particle number or total mass
- conservation of momentum, and
- conservation of energy.

If there are different types of particles (as in air), we give the number of each type in, say, a cubic inch of space. Alternatively, we can give the total mass of each type in a cubic inch. Either of these equivalent descriptions may be termed the *matter content*.

$$\text{Force} = \text{mass} \times \text{acceleration}$$

$$\text{Momentum} = \text{mass} \times \text{velocity}$$

$$\text{Impulse} = \text{force} \times \text{time}$$

$$\text{Energy} = \frac{1}{2} \text{mass} \times \text{velocity}^2$$

### The Macro Level is Unaffected by the Micro Level

Let us now leap from the micro to the macro -- from the physics of the micro level as a succession of particle free flights and collisions, to the macro level description of a gas consisting of a great many interacting particles.

We point out that in one cubic inch of normal air there are about four hundred billion billion ( $4 \times 10^{20}$ ) molecules undergoing stereotypic actions - free flights of length on the order of a hundred thousandth ( $10^{-5}$ ) of an inch at speeds on the order of ten thousand ( $10^4$ ) inches per second (about 700 miles per hour). The duration of each free flight is then about a billionth of a second (or one nanosecond,  $10^{-9}$ ). Each molecule makes about a billion collisions each second. In a gas, the collision duration is a small fraction of the free flight time.

However, to quote Shakespeare, it is ‘much ado about nothing.’ Because, in spite of all the activity taking place in each small time interval in the cubic inch -- all the collisions, all the changes in velocity of the individual particles, and all the changes in their energies -- the values of the conserved quantities are unaffected by the interactions occurring inside the cubic inch. The content of the matter is unchanged, the total momentum is unchanged, the total energy is unchanged. What happens is that the total momentum is distributed by the collisions among all the particles in the cubic inch in some characteristic manner. Similarly, the total energy is distributed among the kinetic energies of all the particles, and among the internal energies that are excited in collisions.

It should be noted that the same physical description of air would hold if one reduced the number of such molecules to a sparse collection of only a few handfuls in a cubic inch container, or in a very small container. The conclusions are valid for all sized boxes as long as each side is significantly longer than the free flight length of  $10^{-5}$  inch in normal air. It is that character of physics which will permit us to extend its scope to discussing more complex systems, such as living things, in which there are a great number of internal actions.

### Equilibrium at the Macro Level

The key idea may now be stated: conditions inside the cubic inch are characterized and determined by the values of the conserved quantities. Two different cubic inches are macroscopically identical if they:

- contain the same matter content (defined as the number of molecules of each molecular type),
- the same momentum, and
- the same energy,

even though one is here now and the other was half way round the globe a century ago. The reason is that the molecular players have the same properties in both cases:

- they interact the same way in both cases, and
- the large number of these stereotypic interactions (e.g., collisions) among the players results in standard distributions of each conserved quantity among the individual players, the distributions being the same in both cubic inches.

These standard distributions are called *equilibrium distributions*, and a small piece of the gas in which the equilibrium distribution is present is said to be in *local thermodynamic equilibrium*. Any deviation from the equilibrium distribution in a small piece is reduced very rapidly to zero by the stereotypical interactions inside the piece which act to share the conserved quantities among the players according to the equilibrium distribution. It is precisely this rapid drive toward local equilibrium that underlies the success and power of thermodynamics. Thermodynamics is the macrophysics within and between organized levels.

When the total momentum of a small piece (such as our cubic inch) is zero, the piece is macroscopically at rest. When the total momentum is not zero, the piece is macroscopically in motion. The macroscopic velocity of the piece is equal to its momentum divided by its mass. Every small piece of still air is macroscopically at rest. Each small piece of windy air is in macroscopic motion, with different pieces generally moving with different velocities. What we have here is a *macroscopic flow field*.

The motional aspects of the situation illuminate the relation between the micro and macro levels of activity. The macroscopic velocity of a small piece is simply the directional (vector) average value of the velocities of all the microscopic players in the piece, each velocity being weighted by the mass of each player. Microscopically, there is a great deal of motion and action going on all the time even in a piece that is macroscopically at rest. The velocities of the individual players

in such a piece have the standard equilibrium distribution. In a piece that is in macroscopic motion, the same equilibrium distribution of microscopic velocities is present, but in addition there is also the common macroscopic velocity. If such a piece is observed by an observer moving along with it, it appears identical to a piece that is macroscopically at rest.

### The Macroscopic Equation of State

The stereotypical interactions in a piece in local thermodynamic equilibrium give rise to a state of mechanical *stress* inside the piece. This stress is a mechanical measure of the intensity and frequency of the collisions taking place (the interactions that share the momentum among the players). The stress in a gas is called the *pressure*. It measures the average pressing force exerted (through collisions) by the players on one side of a square inch of area on the players on the other side of the same square inch. The pressure in a gas confined by a container is also the force exerted on each square inch of the container material (by collisions of the gas particles with the container walls).

Because the interactions share energy as well as momentum, there are also energy measures for the intensity of the local interactions. The direct measure is simply the energy per unit mass, or the energy per unit volume. A very important indirect, but more universal, measure is the *temperature*. Although temperature and the direct energy measure are closely related, the quantitative relation between them is different for different types of matter. Consider a macroscopically stationary piece of matter. When it is at its

lowest possible temperature -- absolute zero -- it is at its lowest possible energy level, and its energy is called the *zero-point energy*. The energy of the piece increases as the temperature is raised. The excess of the energy above the zero-point energy is called the *thermal excitation energy*, or more simply, the *heat energy*. It is the heat energy that is distributed among the microscopic players according to the equilibrium distribution.

The temperature measure determines which way heat energy flows when two pieces of matter are placed in contact. Heat energy flows from higher to lower temperature. (When a finger at normal temperature contacts a hot stove, there is a flow of heat energy from stove to finger, causing it to get hotter and its owner to pull away).

The quantities that describe the macroscopic properties of a small macroscopic piece of a gas that is in local thermodynamic equilibrium are then:

- its matter content,
- its energy content,
- its temperature, and
- its pressure.

The matter content may be given by the *mass density* (mass per unit volume) and the *chemical composition* (the fractions of each of the chemical species making up the matter content). The energy content may similarly be given by the energy density. The macroscopic describers are sometimes called the *thermodynamic coordinates*.

Because the equilibrium distribution of momentum and energy among the players is completely determined by the matter content and energy content (by the actual physical account of local thermodynamic equilibrium), these two describers determine the values of the temperature and pressure. As a result, there is a functional relationship among the matter content, energy content, and temperature. This relation is called the *energy function*. There is also a functional relationship among the matter content, energy content, and pressure. Eliminating the energy content from these two functional relationships provides the function relating the matter content, temperature, and pressure. This relation may be called the *thermomechanical equation of state*.

Although the stereotypical motions of the individual players is different in detail for liquids as compared to gases, the main thermodynamic (macroscopic) conclusions are basically the same. In liquids, the individual molecules are very close to each other, just about touching, the distance determined by a near balance between the (long range) forces of attraction and the (short range) forces of repulsion. In fact, condensed matter - liquids and solids - form because of the forces of attraction.

One aspect of the stereotypical motion of the individual molecules in a liquid may be described as follows: Each molecule is confined by a 'cage' of surrounding molecules, all of them in thermal fluctuational motion. The caged molecule bounces back and forth with its cage for many cycles, until a fluctuation occurs which opens up a 'hole' in the surrounding

cage, allowing the caged molecule to make a 'hop' to an adjoining location and a new cage. In a gas, the molecules make long flights separated by short quick changes in velocity. In a liquid, they make relatively short hops separated by many shorter back and forth bounces within their cage.

The end results are much the same, with the same set of macroscopic descriptors. The difference shows up in the details of the functional relations, the thermomechanical equation of state, and the energy function. (As an example, liquids are much more difficult to compress than gases).

### Different Types of Global Equilibria and Flow Motions

A complete macroscopic description of a flow field may be made by:

- 1) dividing the entire space into small elements of volume, and then
- 2) giving the thermodynamic coordinates and the macroscopic velocity of each small volume.

Such a description may be called a '*hydrodynamical description*'.

Consider a large body of fluid that is macroscopically at rest. If the net force on each of its volume elements is zero, then each volume element remains macroscopically at rest, and the fluid is said to be in *global mechanical equilibrium*. If the forces that act on the volume elements are not in balance, then the net force on each volume element sets it into motion. Friction

between adjacent layers of fluid that slip past each other acts to stop the slipping and to bring the fluid back to rest in a new equilibrium state in which the forces are restored to balance.

If the temperature is uniform throughout, the fluid is said to be in *global thermal equilibrium*. In this state, there is no flow of heat energy between adjacent volume elements. If the temperature is not uniform, heat energy flows through the fluid directed from high temperature places toward low temperature places. The flow is said to be 'down the temperature gradient', the path of greatest change with distance. The heat flow acts to equalize the regional temperatures, to drive the whole system toward global thermal equilibrium.

If the matter content is uniform in all volume elements, with uniform concentrations of each molecular species throughout the fluid, then there is no diffusional flow of any molecular species from element to element, and the fluid is said to be in *global chemical transport equilibrium*. If a concentration of any molecular species is not uniform, there is a *diffusional flow* of that species down the concentration gradient from high to low concentration places. This diffusional flow acts to equalize the concentrations, to drive the system toward global chemical transport equilibrium. (This brief discussion of chemical equilibrium neglects the effect of forces that act differently on different molecular species. Such forces can act to produce equilibrium situations in which some species are more concentrated in one location, and other species in other locations. This can occur by the action of electric forces on ionic species, and even by the gravity force which acts to

concentrate denser species in locations of lower altitude. Also not considered as yet is the possibility of chemical transformations by chemical reactions, which introduces the idea of reaction equilibrium).

### The Drive toward Global Thermodynamic Equilibrium

We have just examined the kinds of motion of flow that takes place in flow fields, and the three kinds of drives - mechanical, thermal, chemical - that are always acting to move the system toward global thermodynamic equilibrium. The state of global thermodynamic equilibrium is characterized by:

- 1) a balance of forces on every volume element and no macroscopic motion of matter,
- 2) uniform temperature throughout and no flow of heat energy,
- 3) uniform concentration of each chemical species (or a balance of special species forces) and no diffusional flow of any particular species.

The macroscopic motion induced by net forces is convective momentum flow. It is more simply called convective motion or **convection**. The momentum (and the associated macroscopic kinetic energy) is carried or conveyed by the moving fluid.

The heat energy flowing down the temperature gradient is a flow of heat energy through the fluid; the process is called **heat conduction**. Similarly, the diffusional flow of a particular chemical species is also a flow through the fluid. Diffusional flow generally refers to relative motion of different chemical

species within a volume element of a fluid. Two different chemical species can be diffusing in opposite directions. Finally, the friction force between adjacent layers of fluid that are slipping past each other is accomplished by a non-convective momentum flow through the fluid, flowing from the higher speed fluid to the lower speed fluid. This process is called **viscosity**, more properly viscous diffusion.

To reiterate, macroscopic motion induced by net forces is called convection. In addition, there are three non-convective flows or transports that take place throughout the fluid:

- 1) heat conduction, or the transport of heat energy down temperature gradients,
- 2) diffusion flow, or the transport of particular chemical species down concentration gradients, and
- 3) viscosity, or the viscous momentum flow down slip-velocity gradients

These three non-convective flows are the mechanisms of the drive toward global thermodynamic equilibrium. In an isolated system -- one closed by fixed walls that prevent the exchange of matter and of energy between the system and outside -- these mechanisms invariably and inexorably drive the system toward global equilibrium. The time scale for the approach to global equilibrium depends on the size of the system; but it is, in any case, a macroscopic time as compared to the short time scale for achieving the local equilibrium distributions within any small volume element.

### Commonality of the Global Equilibrium Mechanisms

Although at first sight, the mechanisms of heat conduction, diffusion of chemical species, and viscosity appear to be different and independent, they all spring from the same process: the stereotypical fluctuational motion of the molecular players in the local equilibrium distribution.

To see this, focus attention on any imagined area inside a fluid. The molecules on each side of this area will, by virtue of their stereotypical fluctuational motions, do some crossing over to the other side of the area. This kind of 'diffusion mixing' across the common boundaries of adjacent volume elements acts to share and equalize the properties of the volume elements. If the fluid is hotter on one side of the area than the other, the diffusional mixing carries more energetic molecules into the hotter element, resulting in a transport of heat energy. Similarly, if a particular chemical species is more concentrated on one side of the area than the other, the diffusional mixing accomplished by the fluctuational motions of these molecules results in a diffusion transport. Finally, if the macroscopic velocity is larger on one side of the area than the other, the diffusional mixing carries molecules with larger macroscopic velocity into the region of smaller macroscopic velocity, and carries molecules with smaller macroscopic velocity into the region of larger macroscopic velocity, resulting in a momentum transport down the velocity gradient.

The mechanisms of heat conduction, diffusional flow, and viscous momentum flow -- the three one-way drives toward global thermodynamic equilibrium -- all arise from the

combined action of a macroscopic gradient (of temperature, concentration, or slip velocity) and the diffusional mixing generated by the local stereotypical fluctuation of the molecular players.

### Examples of Macroscopic Action

Let us take a moment to look at the rich variety of processes that can occur in macroscopic flow fields. Firstly, consider some of the ways that forces are exerted on volume elements of the field matter. Forces may be exerted by external agents such as:

- the gravitational field of the Earth (this force is the weight of the volume element),
- an external electric or magnetic field (when the matter has appropriate electrical or magnetic properties),
- a variety of other agents such as fan blades or paddles.

Forces may also be exerted by a pressure gradient within the fluid itself, in which case a larger force is exerted on one side of a volume element than on the other side. The net pressure force on a volume element is directed down the pressure gradient, from high to lower pressure.

For a simple example, take a horizontal cylinder containing water confined between the closed end of the cylinder and a piston which is pushed against the water, thus pressurizing the water to a pressure that is higher than that of the surrounding atmosphere, 14.7 pounds per square inch, or psi.

If a small hole is made in the closed end of the cylinder, the water will squirt out at high speed because the pressure exerted on each piece of water at the position of the hole is greater on the side facing the high pressure water than on the side facing the lower pressure air.

An example that involves two kinds of force is that of the atmosphere. Although the atmosphere is never macroscopically at rest, it is almost always fairly close to a balance of force on each of its volume elements. Small net forces result in large weather patterns. We may ask why the pressure at sea level is always fairly close to the value 14.7 psi. We may also ask why a piece of air that is located some distance above the ground or the ocean does not fall down. After all, Earth attracts all matter with a gravity force. The answer to the first question is that a vertical column erected on one square inch of the Earth's surface and extending all the way up to extremely high altitudes, contains an amount of air that weighs 14.7 pounds. The atmosphere is pressurized by its own weight, by gravity force. The answer to the second question follows from the answer to the first. The pressure at each altitude is simply the weight of the air sitting above one square inch at that altitude, and consequently is greatest at sea level and decreases to zero at higher and higher altitudes. There is then a net upward pressure force exerted on each piece of air, called the *buoyant force*. The buoyant force is the excess of the upward directed pressure force exerted on its bottom face over the downward directed pressure force exerted on its top face. The upward buoyant force due to the pressure gradient balances the gravity force.

As a third example, consider an ordinary candle staying lit by the combustion of wax and oxygen at the tip of its wick. By its own action, the candle generates a steady supply of fresh oxygen-containing air (and a fresh supply of wax) at the wick tip. The heat generated by the chemical combustion process raises the temperature of the air in the flame cone. As a result, the air there expands, becomes less dense, and rises by buoyancy. As this air leaves by rising, the pressure is lowered causing surrounding air to be forced inward toward the burning place. The local heating leads to a continued flow of air inward from the surroundings and upward above the burning place. By its own action, the candle generates this convection flow that ensures a steady supply of fresh air. (At the same time, the heat of the flame melts the top of the candle, and molten wax climbs the wick - by capillary action - to the burning place. That capillary action represents the action of another force system which will not be explained here at this time. In any, case, again by its own action, the candle ensures a continued supply of wax at the burning place).

The candle process occurs in many forms in many places in nature. It initiates atmospheric motion on the Earth. Solar energy is absorbed mostly at sea level (ground level), resulting in heating of the air at sea level. This leads to convective rising and roiling motions in the atmosphere. Convective roiling in the Earth's mantle is initiated by the heat in the Earth's core and the radioactive heat produced in the mantle, and is responsible for the motion of the Earth's plates. The heat energy, generated in the core of the Sun by (slow) nuclear fusion processes, is transported towards the

surface first by heat conduction occurring via photons of light energy; but in the Sun's outer half, the heat is carried to the surface by convective roiling where it is radiated out as sunshine.

Adding to the Earth processes already mentioned - gravity, solar heating from without and the roiling within - the spinning of the Earth (which affects the motion of the atmosphere, the oceans, and the fluid parts of the Earth's interior), the process of phase change (evaporation, condensation, cloud formation, rain, snow, glaciation, melting and freezing), capillary action, and the process of chemical transformation via chemical reaction, leads to the rich geophysical/geochemical/ bio-chemical evolutionary history of planet Earth.

Study of flow field processes demonstrates that the diversity of macroscopic action at all scales of activity is always enhanced by diversity of structure (heterogeneity) at all scales, and by diversity of forces and energy supplies. (Even though the basic physical forces in nature are few, the diversification of their effects by the various ways they combine is rather enormous).

This is illustrated by a final simple example, that of a coffee percolator in which a repeated 'chug' cycle occurs because of the central tube of the percolator. When a pot of water without a central tube is heated from below, the heat is transferred to the entire body of water by convective roiling, resulting in boiling throughout the water (phase change from water to steam within the water). In a coffee percolator, the central tube (with its flanged bottom) is too narrow to allow roiling inside it. As a result, the water at the bottom of the tube remains in

place and is heated steadily to the boiling point at which time it quickly boils into steam and erupts upward in a geyser of hot water and steam -- a chug. This eruption shakes the central tube causing it to lose contact with the bottom of the pot, and cooler water from outside the tube enters to be heated again to the boiling point leading to the next chug cycle.

### **Summary**

Thermodynamics is used to study the interactions between large ensembles of objects. Three types of drives -- mechanical, thermal, and chemical -- are always acting to move a system towards global thermodynamic equilibrium. This state is characterized by a balance of forces, uniform temperature, and uniform concentration of each chemical species. The mechanisms that drive a system toward global thermodynamic equilibrium are three non-convective flows: heat conduction, diffusion flow, and viscous momentum flow. All three spring from the stereotypical fluctuational motion of particles in the local equilibrium distribution. An ordinary candle uses convection flow to ensure a steady supply of fresh air to fuel the fire, using the change in air temperature and pressure to create a flow field. This same process is seen in atmospheric motion and roiling in the Earth's mantle. The study of flow field processes demonstrates that the diversity of macroscopic action at all scales of activity is always enhanced by diversity of structure, forces, and energy supplies.