# 07. The Wave Theory of Heat

#### Bush (1970)

- <u>Wave Theory</u>: Heat is the vibrations of an ethereal fluid that fills all space and which transmits vibrational motion from one atom to another.
- Two differences from post-1850 conceptions (*kinetic theory*):
  - $\circ$  Role of ether is essential: atomic vibrations alone cannot account for heat.
  - Atoms in a gas do not move freely; rather, they are constrained to vibrate about fixed equilibrium positions.

"It is possible, however, to modify this theory [viz., the vibratory theory], by supposing that heat is produced not merely by the motions of the particles of the heated substance, but by the vibrations or undulations of a very subtile matter existing in all bodies. This will approximate the vibratory theory to that which has been generally considered as its antagonist, will accord well with some recently discovered facts, and will assimilate the vibratory hypothesis of heat to the undulations now so generally received as explanatory of the phenomena of light, to which heat has so intimate a relation... These views lead us to the conclusion that the phenomena of caloric are owing to the movements of a subtile fluid, the particles of which are strongly repellent of each other, and have an affinity for those of all other bodies, different in force according to each kind of matter."

(Traill, T. S. 1856 "Heat", in Encyclopaedia Britannica, 8th Ed.)

#### 1. Steps in the development of 19th century ideas about heat

- 1. <u>Beginning of 19th cent:</u> Heat and light described as particulate fluid substances.
- 2. <u>First half of 19th cent</u>: Experiments of Rumford, Davy and others show that heat lacks weight and can be generated in unlimited quantities by mechanical processes.
- 3. <u>1800-35</u>. Experiments on radiant heat show that it has same properties as light.
- 4. <u>1815-1830</u>. Young-Fresnel wave theory of light replaces Newtonian particle theory.
- 5. Wave theory of heat adopted after 1830.
- 6. <u>1842-1850</u>. Wave theory of heat lends support to development of thermodynamics (cons. of energy, mechanical equivalent of heat, etc).
- 7. <u>1848-70</u>. Revival of kinetic theory of gases displaces central role of ether.
- 8. <u>Latter part of 19th cent</u>: Continued interest in radiant heat keeps wave theory alive. Big Question: "Why doesn't the ether take its share of vibrational energy corresponding to thermal equilibrium with matter?"
- 9. <u>1866-73</u>. Maxwell's electromagnetic theory indicates heat radiation is special type of electromagnetic waves. Reenforces distinction between heat and radiant heat.
- 10. <u>1880's</u>. Boltzmann and Wien show that radiant heat can be treated by combining thermodynamic concepts with Maxwell's electrodynamics.

Two myths:

- (1) The mechanical theory of heat was established by Rumsford and Davy (1800).
- (2) Most scientists accepted the caloric theory unitl it was replaced by thermodynamics (~1849).
- <u>Claim 1</u>: The myths are due to Thomson!
- <u>Claim 2</u>: The establishment of the wave theory of light, and conservation of energy and thermodynamics are not separate events, but rather "...successive and closely related stages of the same transformation of physical theory, in which explanations of phenomena were increasingly based on *motion* rather than on *matter*." (Bush, pg. 148.)





### Young's 2-Slit Experiment (~1800) and the Wave Theory of Light



*Thomas Young* (1773-1829)



Young's 2-Slit Experiment (~1800) and the Wave Theory of Light

• If light consists of corpuscles, should see...



*Thomas Young* (1773-1829)





"It was long an established opinion, that heat consists in vibrations of the particles of bodies, and is capable of being transmitted by undulations through an apparent vacuum (Newt. *Opt.* Qu. I8). This opinion has been of late very much abandoned, Count Rumford, Professor Pictet, and Mr. Davy, are almost the only authors who have appeared to favour it; but it seems to have been rejected without any good grounds, and will probably very soon recover its popularity."

# 2. Radiant Heat and the Decline of the Caloric Theory

- 1825. Height of popularity of the caloric theory.
- <u>In support</u>: Heat can apparently travel through empty space without any accompanying movement of matter; hence it cannot simply be molecular motion.
- 1830-32. Melloni establishes that radiant heat has similar properties as light:
  - $\circ\,$  reflection, refraction, diffraction, polarization, interference



Macedonio Melloni (1798-1854)

• ~1824. Manuscript notes to *Reflexions on the Motive Power of Heat*:



Sadi Carnot

"At present, light is generally regarded as the result of a vibratory movement of the etherial fluid. Light produces heat, or at least accompanies the radiant heat and moves with the same velocity as heat. Radiant heat is therefore a vibratory movement. It would be ridiculous to suppose that it is an emission of matter while the light which accompanies it could only be a movement. Could a motion (that of radiant heat) produce matter (caloric)? Undoubtedly no; it can only produce a motion. Heat is then the result of a motion."

• "Though he had accepted the caloric theory (with some reservations) in his *Reflexions* of 1824, it seems clear from the above passage that Carnot has accepted the wave theory of light shortly afterwards, and by thinking about radiant heat has been led to the mechanical theory of heat." (Bush, pg. 152.)

### 3. Ampère's treatment of the wave theory of heat (1832, 1835).

- "Idées de Mr Ampère sur la chaleur et sur la lumière"; "Note sur la chaleur et sur la lumière considérées comme resultant de mouvement vibratories".
- Initial problem:



André-Marie Ampère (1775-1836)

"instead of a vibratory motion propagated in undulations or waves in such a manner that every wave leaves at rest the fluid which it sets in motion at the instant of its passage, we have a motion propagated gradually in such a manner that the part which originally was the hottest, and consequently the most agitated (explaining the phaenomena of heat by the theory of vibratory motions), although losing heat by degrees, preserves, however, more than the parts to which it is communicating heat."

• "... the problem was to reconcile the propagation of heat by waves (secondorder differential equation in time) in free space, with its propagation as described by Fourier's heat conduction equation (first-order time derivative) in matter." (Bush, pg. 153.)

- Total vis viva of a physical system:  $\sum mv^2 + 2\int \sum \mathbf{F} \cdot \mathbf{dx}$
- Consider atoms vibrating in a fluid enclosed in a container so that total *vis viva* is constant.
- <u>Assume</u>:
  - Rate of flow of *vis viva* between different groups of atoms is proportional to the difference in vis viva between the groups.
  - Difference in *vis viva* between groups is proportional to difference in temps.
- <u>Then</u>: Can derive Fourier's heat conduction equation.



"We find manifestly the same result by considering the subject as we have just enunciated it, according to the system of emission [*i.e.* the material theory] or according to that of vibrations, substituting for the quantity of caloric in the first system, the *vis viva* of the vibratory motions of the molecules in the second. "

• <u>In other words</u>: It makes no difference whether heat is matter or motion, since the same phenomenon can be explained either way.



- <u>In other words</u>: The description of heat as vibrations of atoms transmitted by the ether is easier to comprehend *via* analogy with sound waves.
- <u>And</u>: It might be possible to drop reference to the ether, pending further calculations.

"Now, it is clear that if we admit the phenomena of heat to be produced by vibrations, it is a contradiction to attribute to heat the repulsive force of the atoms requisite to enable them to vibrate."



• <u>In other words</u>: No repulsive forces as in the caloric theory.

## 4. Reception of the wave theory of heat 1831-45.

## • Whewell's *History of the Inductive Sciences* (1837):



William Whewell (1794-1866)

"Till recently, the theory of material heat, and of its propagation by emission, was probably the one most in favour with those who had studied mathematical thermotics... But the recent discovery of the refraction, polarization, and depolarization of heat, has quite altered the theoretical aspect of the subject, and, almost, at a single blow, ruined the emission theory. Since heat is reflected and refracted like light, analogy would lead us to conclude that the mechanism of the processes is the same in the two cases..."

"But here the question occurs, If heat consists in vibrations, whence arises the extraordinary identity of the laws of its propagation with the laws of the flow of matter? How is it that, in conducted heat, this vibration creeps slowly from one part of the body to another, the part first heated remaining hottest; instead of leaving its first place and travelling rapidly to another, as the vibrations of sound and light do? The answer to these questions has been put in a very distinct and plausible form by that distinguished philosopher, M. Ampère..."





"M. Ampère's hypothesis is this; that bodies consist of solid molecules, which may be considered as arranged at intervals in a very rare ether; and that the vibrations of the molecules, causing vibrations of the ether and caused by them, constitute heat."

"The theory at present considered most explanatory... is, as you are probably aware, what is called the *Undulatory*: namely, that which supposes all space and the pores of all bodies to be filled with a medium of extreme tenuity called *Ether*; and that by vibrations or waves propagated through this medium the phenomena are produced. Agreeing as I do in the value and general application of the Undulatory-theory, it has always seemed to me that the assumptions of a specific luminiferous ether, differing from ordinary matter, is gratuitous and difficult of conception." (1842)



William Robert Grove (1811-1896)

• Grove (1842) A lecture on the progress of physical science since the opening of the London Institution.

## 5. Transition from wave theory of heat to thermodynamics

• Kuhn's co-discoverers of energy conservation:

"Energy Conservation as an Example of Simultaneous Discovery" (1959)

- <u>Mayer, Joule, Colding, Helmholtz</u>: Announced a general principle and provided concrete quantitative applications.
- <u>Carnot, Sequin, Holtzmann, Hirn</u>: Affirmed the mechanical equivalent of heat, and computed a value for the conversion coefficient, but did not generalize to other phenomena.
- <u>Mohr, Grove, Faraday, Liebig</u>: Gave general statements about interconvertability of different forms of phenomena in terms of a single "force" that is neither created nor destroyed in such transformations; but no quantitative descriptions.
- <u>Kuhn's contributing factors</u>:
  - $\circ$  A quantitative book-keeping approach in steam-engine technology.
  - $\circ$  Discoveries of conversion processes linking electricity, magnetism, and heat.
  - $\circ$  Speculations of Naturphilosophie suggesting the basic unity of all forces.
- <u>Brush's addition</u>:
  - $\circ$  Investigations of radiant heat and the wave theory of heat.



William Robert Grove

"Heat and light appear to be rather modifications of the same force than distinct forces mutually dependent. The modes of action of radiant heat and of light are so similar, both being subject to the same laws of reflection, refraction, double refraction and polarization, that their difference appears to exist more in the manner in which they affect our senses, than in our mental conception of them." (1843)

• Grove (1843) "On the correlation of physical forces."

"Recently, especially through the complete equality of the laws of heat radiation with those of light, not only the similarity but indeed the identity of both agents has been made probable, and we are thereby led to a wave theory of heat, as to a wave theory of light ... Thus the possibility of a material theory of heat disappears, since the conservation of quantity would be the most necessary consequence of such a theory, and we are forced to consider heat as well as light to be motion." (1845)



Herman von Helmholtz (1821-1894)

• Helmholtz (1845) "Wärme, physiologisch", in Encykolpädisch Hadwörterbuch der medicinischen Wissenschaften.



"From these facts, it follows that the quantity of heat can be absolutely increased by mechanical forces, that therefore calorific phenomena cannot be deduced from the hypothesis of a species of matter, the mere presence of which produces the pheno-mena, but that they are to be referred to changes, to motions, either of a peculiar species of matter, or of the ponderable or imponderable bodies already known, for example of electricity or the luminiferous aether... If it be permitted to make an attempt at rendering the idea of this motion still clearer, the view derived from the hypothesis of Ampère seems best suited to the present state of science." (1847)

• Helmholtz (1847) Ueber die Erhaltung der Kraft.

"We are taught by history that... the most sagacious hypotheses concerning the state and nature of a peculiar 'matter' of heat, concerning a 'thermal aether', whether at rest or in a state of vibration, concerning 'thermal atoms', supposed to exercise their functions in the interstices between the material atoms, or other hypotheses of like nature, have not availed to solve the problem". (1851)



Julius Robert Mayer (1814-1878)

• Mayer (1851) Bemerkungen über das mechanische Aequivalent der Wärme.

"The phenomena of heat have been till now almost exclusively explained in textbooks by the assumption of a heat-substance. The discoveries of Melloni have made this view inapplicable to the phenomena of Radiant Heat; they require the assumption of vibrations similar to those of the Undulatory Theory of Light. The Propagation, Transmission, and Polarization of Radiant Heat have been completely explained by these assumptions; and, with such facts to guide us, it is certainly no mere idle speculation to attempt to extend this view to the phenomena of common or stationary heat... Heat is thus no longer a particular kind of matter, but an oscillatory motion of the smallest parts of bodies." (1876)



Karl Friedrich Mohr (1806-1879)

• Mohr (1876) "Views of the nature of heat", *Phil. Mag. 5, ii.* 



William John Macquorn Rankine (1820-1872)

"...to deduce the laws of elasticity and of heat as connected with elasticity, by means of the principles of mechanics, from a physical supposition consistent with and connected with the theory which deduces the laws of radiant light and heat from the hypothesis of undulations." (1850)

• Rankine (1850) "On the mechanical action of heat, especially in gases and vapours", *Trans. Roy. Soc. Edingburgh, xx.* 

## 6. Disappearance of the wave theory of heat after 1850

- <u>1848-70</u>. Revival of kinetic theory of gases displaces central role of ether.
- "...in order to accept the kinetic theory of gases, it was necessary to assume that molecules can move freely through empty space (except when they collide with each other or with solid objects) so that any kind of energy exchange with an ether has to be ignored." (Brush, pg. 164.)
- "... many books and papers by minor scientists continued to use or refer to the wave theory as if it were still acceptable for several decades after 1850. However, the leading physicists of this period, Joule, Thomson, Clausius, Helmholtz, Maxwell, Boltzmann, etc., seemed to ignore it." (Brush, pg. 165.)
- <u>Why</u>?



• <u>1849</u>. Thomson's "An account of Carnot's theory of the motive power of heat; with numerical results deduced from Regnault's experiments on steam", *Trans. Roy. Soc. Edingburgh, xvi.* 

"Now the ordinarily-received, and almost universally-acknowledged, principles with reference to 'quantities of caloric' and 'latent heat', lead us to conceive that, at the end of a cycle of operations, when a body is left in precisely its primitive physical condition, if it has absorbed any heat during one part of the operations, it must have given out again exactly the same amount during the remainder of the cycle. The truth of this principle is considered as axiomatic by Carnot, who admits it as the foundation of his theory... To deny it would be to overturn the whole theory of heat, in which it is the fundamental principle..."





Since the time when Carnot thus expressed himself, the necessity of a most careful examination of the entire experimental basis of the theory of heat has become more and more urgent. Especially all those assumptions de-pending on the idea that heat is a *substance*, invariable in quantity; not convertible into any other element, and incapable of being *generated* by any physical agency...would require to be tested by a most searching investigation before they ought to be admitted, as they usually have been, by almost every one who has been engaged on the subject, whether in combining the results of experimental research, or in general theoretical investigations."

• Brush (pg. 166): "Thomson's statement about the status of caloric theory in physics in 1849 was simply wrong. (It may have been accurate for engineering.)"

• <u>1851</u>. Thomson's "On the dynamical theory of heat, with numerical results deduced from Mr. Joule's equivalent of a thermal unit, and M. Regnault's observations on steam", *Trans. Roy. Soc. Edingburgh, xx.* 



"The Dynamical Theory of Heat, thus established by Sir Humphry Davy, is extended to radiant heat by the discovery of phenomena, especially those of the polarization of radiant heat, which render it excessively probable that heat propagated through vacant space, or through diathermane substances, consists of waves of transverse vibrations in an all-pervading medium."

• Brush (pg. 167): "Presumably contemporary physicists only bothered to read the later 'correct' paper [1851], and thus learned that the caloric theory had been demolished in 1800; whereas historians went back to the earlier paper [1849] for evidence as to views about the nature of heat just before the adoption of thermodynamics. Both were misled."