

MOLECULAR-KINETICS BASIS FOR THE HEAT-TRANSFER EQUATION

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A hyperbolic heat-transfer equation is derived by the Maxwell method. The correlation between the components of the thermal velocities of the atoms or molecules is taken into account.

The literature reveals a large number of papers devoted to the derivation of a hyperbolic heat-conduction equation [1], apparently motivated by the paradoxical result of an infinite heat-propagation velocity which emerges from the classical theory of heat conduction.

A hyperbolic heat-conduction equation in fact resolves this paradox, but a more accurate analysis of the nonlinear parabolic heat-conduction equation [2] also results in a finite heat-propagation velocity. We are thus confronted with the question of which type of heat-transfer equation corresponds to reality.

A hyperbolic heat-conduction equation was first derived on the basis of molecular-kinetics considerations by an Italian investigator, Cattaneo [3]. He and all subsequent investigators who used the concepts of Maxwell, Boltzmann, and Gibbs found that the coefficient of the hyperbolic term was precisely equal to the relaxation time, which is ordinarily small. This circumstance gave rise to the interpretation that in low-density gases, in which the relaxation time is appreciable, heat is transferred in a wave manner, involving the formation of a front at a uniform temperature. However, experiment shows that the discontinuities in low-density gases fade and disappear, so that heat transfer by a front is ruled out.

Furthermore, as early as 1942 Academician V. V. Shuleikin found experimentally that in the dense gas flows which regulate the changes in the earth's weather the heat is transferred by a front; i.e., the heat flux obeys a wave equation [4]. Much more recently this experimental fact was given a theoretical basis in terms of Riemann manifolds by Predvoditelev [5].

1. Derivation of the Heat-Conduction Equation from the Maxwell Transport Equation. Maxwell offered a method for deriving transfer equations for any quantity; an essential feature of this method is that it absolutely does not involve the calculation of the velocity distribution of the molecules [6].

This method was used to derive the heat-conduction equation by the famous natural scientist Kirchhoff and the Russian physicist Stankevich [7]. Their calculations agree approximately, but in deriving a parabolic heat-conduction equation these investigators used certain assumptions which differ in detail.

Let us consider a monatomic gas in which there is no apparent macroscopic velocity. In this case heat is transferred by conduction alone. Denoting by Q any property of the molecules, we can write the Maxwell transfer equation as

$$N \frac{d\bar{Q}}{dt} = - \left[\frac{\partial}{\partial x} (\overline{N\xi Q}) + \frac{\partial}{\partial y} (\overline{N\eta Q}) + \frac{\partial}{\partial z} (\overline{N\zeta Q}) \right] + \Delta Q; \quad (1.1)$$

here ΔQ is the collision integral. Substituting $Q = m(\xi^2 + \eta^2 + \zeta^2)$ into (1.1) and taking into account the constancy of the kinetic energy during collisions, we find

$$\frac{d}{dt} [\overline{\rho(\xi^2 + \eta^2 + \zeta^2)}] = - \left\{ \frac{\partial}{\partial x} [\overline{\rho\xi(\xi^2 + \eta^2 + \zeta^2)}] + \frac{\partial}{\partial y} [\overline{\rho\eta(\xi^2 + \eta^2 + \zeta^2)}] + \frac{\partial}{\partial z} [\overline{\rho\zeta(\xi^2 + \eta^2 + \zeta^2)}] \right\}. \quad (1.2)$$

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Since the quantity $\overline{(\xi^2 + \eta^2 + \zeta^2)}$ is proportional to the temperature, the product $\rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}$ is proportional to the amount of heat which crosses a unit area yx . We can thus introduce the heat fluxes by means of the equation

$$\begin{aligned} q_x &= \rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}, \\ q_y &= \rho \overline{\eta(\xi^2 + \eta^2 + \zeta^2)}, \\ q_z &= \rho \overline{\zeta(\xi^2 + \eta^2 + \zeta^2)}. \end{aligned} \quad (1.3)$$

Then Eq. (1.2) becomes

$$\frac{d}{dt} [\rho \overline{(\xi^2 + \eta^2 + \zeta^2)}] = -\frac{\partial q_x}{\partial x} - \frac{\partial q_y}{\partial y} - \frac{\partial q_z}{\partial z}. \quad (1.4)$$

The next step is to calculate the heat fluxes q_x , q_y , and q_z . For this purpose we substitute the quantity $m \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}$ into Eq. (1.1), finding

$$\begin{aligned} m \Delta Q [\overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] &= \frac{d}{dt} [\rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] \\ &+ \frac{\partial}{\partial x} [\rho \overline{\xi^2(\xi^2 + \eta^2 + \zeta^2)}] + \frac{\partial}{\partial y} [\rho \overline{\xi \eta(\xi^2 + \eta^2 + \zeta^2)}] + \frac{\partial}{\partial z} [\rho \overline{\xi \zeta(\xi^2 + \eta^2 + \zeta^2)}]. \end{aligned} \quad (1.5)$$

Stankevich subsequently used the assumption that there is no friction, i.e.,

$$\overline{\xi \eta} = \overline{\xi \zeta} = 0,$$

and he used the assumption of a steady-state heat flux; these assumptions lead to

$$\frac{d}{dt} [\rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] = 0. \quad (1.6)$$

Without making assumption (1.6), we rewrite (1.5) as

$$m \Delta Q [\overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] = \frac{d}{dt} [\rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] + \frac{\partial}{\partial x} [\rho \overline{\xi^2(\xi^2 + \eta^2 + \zeta^2)}]. \quad (1.7)$$

Boltzmann [8] calculated the left side of (1.7) for Maxwellized molecules, finding

$$m \Delta Q [\overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] = -2 \sqrt{\frac{k}{2m}} \rho^2 A_2 \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}. \quad (1.8)$$

Using (1.8), we can rewrite (1.7) as

$$\rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)} = -\frac{1}{2A_2 \rho \sqrt{\frac{k}{2m}}} \left\{ \frac{d}{dt} [\rho \overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] + \frac{\partial}{\partial x} [\rho \overline{\xi^2(\xi^2 + \eta^2 + \zeta^2)}] \right\}. \quad (1.9)$$

Using a Maxwell velocity distribution for the molecules, we find

$$\overline{\xi^2(\xi^2 + \eta^2 + \zeta^2)} = \overline{\xi^4} + \overline{\xi^2 \eta^2} + \overline{\xi^2 \zeta^2} = 5 \frac{p^2}{\rho^2},$$

then Eq. (1.9) becomes

$$\overline{\xi(\xi^2 + \eta^2 + \zeta^2)} = -A_1 \frac{d}{dt} [\overline{\xi(\xi^2 + \eta^2 + \zeta^2)}] - 5A_1 \frac{\partial}{\partial x} \left(\frac{p^2}{\rho} \right).$$

If the pressure does not vary from point to point, we find from this latter equation and analogous equations that

$$\begin{aligned} q_x &= -A_1 \frac{dq_x}{dt} - 5A_1 p \frac{\partial}{\partial x} \left(\frac{p}{\rho} \right), \\ q_y &= -A_1 \frac{dq_y}{dt} - 5A_1 p \frac{\partial}{\partial y} \left(\frac{p}{\rho} \right), \\ q_z &= -A_1 \frac{dq_z}{dt} - 5A_1 p \frac{\partial}{\partial z} \left(\frac{p}{\rho} \right). \end{aligned} \quad (1.10)$$

Substituting these equations into Eq. (1.4), we find

$$\begin{aligned} \frac{d}{dt} [\rho (\xi^2 + \eta^2 + \zeta^2)] &= A_1 \frac{\partial}{\partial t} \left[\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} \right] \\ &+ \frac{\partial}{\partial x} \left[5A_1 p \frac{\partial}{\partial x} \left(\frac{p}{\rho} \right) \right] + \frac{\partial}{\partial y} \left[5A_1 p \frac{\partial}{\partial y} \left(\frac{p}{\rho} \right) \right] + \frac{\partial}{\partial z} \left[5A_1 p \frac{\partial}{\partial z} \left(\frac{p}{\rho} \right) \right]. \end{aligned}$$

The first term on the right of this latter equation can be found from Eq. (1.4); then we have

$$\frac{d}{dt} [\rho (\xi^2 + \eta^2 + \zeta^2)] + A_1 \frac{d^2}{dt^2} [\rho (\xi^2 + \eta^2 + \zeta^2)] = \frac{\partial}{\partial x} \left[5A_1 p \frac{\partial}{\partial x} \left(\frac{p}{\rho} \right) \right] + \frac{\partial}{\partial y} \left[5A_1 p \frac{\partial}{\partial y} \left(\frac{p}{\rho} \right) \right] + \frac{\partial}{\partial z} \left[5A_1 p \frac{\partial}{\partial z} \left(\frac{p}{\rho} \right) \right]. \quad (1.11)$$

Here

$$A_1 = \frac{1}{2A_2 \rho \sqrt{\frac{k}{2m}}}. \quad (1.12)$$

According to the concept of Maxwell and Boltzmann the pressure p is defined in terms of the thermal velocities by

$$p = \frac{1}{3} \rho (\xi^2 + \eta^2 + \zeta^2), \quad (1.13)$$

this definition leads to an equation of state in the Clapeyron form

$$p/\rho = RT.$$

Since there is no apparent velocity the continuity equation reduces to

$$\frac{d\rho}{dt} = 0, \quad (1.14)$$

so that we can remove the density ρ from the derivative on the left side of Eq. (1.11).

Multiplying both sides of (1.11) by the specific heat at constant volume, C_v , and using (1.13), we find an equation for the heat transfer:

$$C_v \rho \frac{dT}{dt} + C_v \rho A_1 \frac{d^2 T}{dt^2} = \frac{\partial}{\partial x} \left(\lambda_0 \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda_0 \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\lambda_0 \frac{\partial T}{\partial z} \right). \quad (1.15)$$

Here

$$\lambda_0 = \frac{5}{6} \frac{RC_v T}{A_2 \sqrt{\frac{k}{2m}}} = \frac{5}{2} \mu_0(T) C_v, \quad (1.16)$$

is the thermal conductivity and $\mu_0(T)$ is the viscosity.

This latter equation leads to the establishment of the Maxwell complex

$$\frac{\lambda_0(T)}{C_v \mu_0(T)} = \frac{5}{2} = \text{const.} \quad (1.17)$$

This complex is derived from completely explicit ideas regarding the nature of the thermal motion found in the theory of gases. For more complex thermal motion, involving front motion, we assume that the Maxwell complex is conserved.

If we express the density in Eq. (1.12) in terms of the pressure and temperature, using (1.13), and if we introduce the relaxation time, following Maxwell, we find

$$A_1 = \frac{3}{2} \frac{\mu_0}{\rho} = \frac{3}{2} \tau. \quad (1.18)$$

At atmospheric pressure the relaxation time is on the order of 10^{-10} sec, and we can neglect the hyperbolic term in (1.15) by virtue of the smallness of A_1 ; we then find a heat-conduction equation of the parabolic type. This latter assertion verifies the assumption of Stankevich, in (1.6).

2. Correlating Gas Systems. The concept of a correlating gas system was introduced as a logical generalization of the Maxwell concept by Predvoditelev in works on the equation of state of condensed media [8].

The Maxwell velocity distribution can be thought of as a generalization of the one-dimensional Laplace-Gauss distribution to the case of three statistical characteristics among which there is no correlation. Let us determine the probability for finding the gas system in the phase volume element $d\omega = d\xi d\eta d\zeta$. If $n(\xi, \eta, \zeta)$ is the number of molecules whose velocities lie in the interval $d\omega$, and N is the total number of molecules, then this probability is

$$f(\xi, \eta, \zeta) = \frac{n(\xi, \eta, \zeta)}{N}.$$

We now denote by $f(\xi)$, $f(\eta)$ and $f(\zeta)$ the probabilities for finding molecules in the intervals $d\xi$, $d\eta$ and $d\zeta$, respectively. We assume that these probabilities are independent; then according to the theorem on the multiplication of probabilities we have

$$f(\xi, \eta, \zeta) = f(\xi)f(\eta)f(\zeta). \quad (2.1)$$

Maxwell justified this hypothesis of the independence of probabilities by arguing that the existence of ξ cannot effect the existence of velocities η and ζ in any manner, since they are all right angles to each other and are all independent of each other [9].

We assume that each of these probabilities obeys the Laplace-Gauss equation,

$$f(\xi) = c_1 \exp(-h\xi^2), \quad f(\eta) = c_2 \exp(-h\eta^2), \quad f(\zeta) = c_3 \exp(-h\zeta^2).$$

Then after substituting the latter into (2.1) we find the Maxwell distribution

$$f(\xi, \eta, \zeta) = A \exp[-h(\xi^2 + \eta^2 + \zeta^2)]. \quad (2.2)$$

It is clear from this discussion that the Maxwell velocity distribution has a shaky foundation.

However, further evidence in favor of the universality of this distribution comes from the circumstance that it has been derived as one solution of the Boltzmann integrodifferential equation. However, Boltzmann's hypothesis of a molecularly disordered state of the system is equivalent to the independence of the statistical characteristics, such as the thermal velocities of the atoms or molecules. In other words, Maxwell's concept in (2.1) is implicitly incorporated in the Boltzmann equation.

In his work, Predvoditelev completely avoided spherical symmetry in the statistics of the latent motions and first introduced a distribution function with correlating statistical characteristics; in the case of an isotropic correlation this function is [8]

$$f = A \exp \left[-\frac{R_{33}}{2R\sigma_3^2} (s_1\xi^2 + s_2\eta^2 + s_3\zeta^2) \right], \quad (2.3)$$

where

$$s_1 = \frac{1+3r}{1+r}, \quad s_2 = \frac{1+3r}{1+r}, \quad s_3 = \frac{1-3r}{1+r}.$$

If there is no correlation we have $r = 0$, which leads in turn to $R_{33} = 1$, $R = 1$, $s_1 = s_2 = s_3 = 1$, $\sigma_3 = \sigma$, with distribution function (2.3) converting into (2.2).

Equation (2.3) leads to the following refinement of the Clapeyron equation

$$\frac{p}{\rho} = \Psi(r)RT, \quad (2.4)$$

where

$$\Psi(r) = \frac{(1-r)^{\frac{1}{2}}(1+r)^2(1+2r)^2}{(1+3r)^2(1-3r)^{3/2}}. \quad (2.5)$$

The virial of the internal forces is not taken into account here.

Predvoditelev's Eq. (2.4) accurately describes the experimental data for hydrogen over broad ranges of the temperature and pressure.

Let us adopt a slightly different interpretation in order to solve this problem.

We assume that the heat is transferred by a front. Then at the front there can be either chemical reactions or phase transitions, and the thermal conductivity defined by (1.16) cannot cope with a smoothing of inhomogeneities in the temperature. For such a system we can assume that the pressure, density, and temperature are related by (2.4). In this case this latter equation should be called the "equation of the non-equilibrium process."

If we now use Eq. (2.4) in converting from (1.11) to (1.15), we find

$$C_{vp} \frac{dT}{dt} + C_{vp} A_1 \frac{d^2 T}{dt^2} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\lambda \frac{\partial T}{\partial z} \right), \quad (2.6)$$

where

$$\lambda(T) = \Psi(r) \lambda_0(T). \quad (2.7)$$

Using (2.4), we can rewrite (1.12) as

$$A_1 = \frac{3}{2} \frac{\mu_0}{\rho} \Psi(r) = \frac{3}{2} \tau \Psi(r), \quad (2.8)$$

i.e., the additional processes which occur at the front render A_1 perceptible through a function of the correlation coefficient $\Psi(r)$, and the hyperbolic term must be present in Eq. (2.6).

Since the introduction of a correlating function of the molecular velocity distribution is equivalent to a manifestation of gyroscopic forces, we do not claim to be offering a rigorous solution to this problem. We have simply demonstrated one possible way to solve this problem.

NOTATION

- ξ, η, ζ are the components of the thermal velocity of the atoms or molecules;
 λ_0 is the thermal conductivity determined in accordance with the Maxwell concepts;
 R is the correlation coefficient;
 R_{33} is the minor of the correlation determinant;
 σ_3 is the mean-square deviation along the z axis.

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