

boundary is

$$T_w = C_2 + Cu_y|_{y=0} \tag{7a}$$

The heat flux from the surface is

$$-kT_y|_{y=0} = -kCu_{yy}|_{y=0} = (-kC/\mu)p_x \tag{7b}$$

The problem for which Eq. (7) is the solution is the one in which the heat flux is given by Eq. (7b).

To simplify the problem, let one specialize to flow at zero incidence over a flat plate. Then $p_x = 0$, and the boundary conditions are u and $v = 0$ on the plate. The result is

$$(T - T_0/T_1) = [1 - (T_0/T_1)](u/U_1) + (U_1^2/2C_p T_1)(u/U_1)[1 - (u/U_1)] + (Cu_y/T_1) \tag{8}$$

where T_0 is the constant part of the plate temperature. Consider the quadrant of the x - y plane formed by $x = 0$ and $y = 0$. In this region the solution is specified by appropriate boundary conditions. It is seen that the added term in Eq. (8) alters the problem by changing the (specified) temperature at $x = 0$. The temperature on the plate is given by Eq. (8) as

$$T_p = T_0 + Cu_y|_{y=0} \tag{8a}$$

a function that increases near the leading edge. If the temperature of the plate is held constant at T_0 , then $C = 0$ would be required. But of course the temperature at $x = 0$ would not be given correctly by Eq. (8) in general. It is difficult to say how serious this failure of the Crocco solution is. The heat flux for Eq. (8), using Eq. (2), is

$$-kT_y = [(T_1 - T_0) + (U_1^2/2C_p)](u_y/U_1)|_{y=0} \tag{8b}$$

The heat flux is the same as would be obtained for the corresponding isothermal plate problem. The adiabatic plate problem has the solution

$$T = T_1 + (1/2C_p)(U_1^2 - u^2) + Cu_y \tag{8c}$$

and the temperature on the plate is altered by the added term, showing larger changes near the leading edge.

Perhaps the most interesting consequences are obtained through the use of the similarity solution for the velocity. The familiar Blasius solution² for u is

$$\left. \begin{aligned} u &= \frac{1}{2}U_1(df(z)/dz) \\ z &= (y/2)(U_1/\nu x)^{1/2} \end{aligned} \right\} \tag{9}$$

so that

$$u_y = \frac{1}{4}U_1(U_1/\nu x)^{1/2}[d^2f(z)/dz^2] \tag{10}$$

Substituting in Eq. (8), one sees that the temperature on the plate is

$$T_p = T_0 + (C/4)(U_1^3/\nu x)^{1/2} \cdot f''(0) \tag{11}$$

One has the solution of the problem in which the temperature of the plate increases like $x^{-1/2}$ near the leading edge. Such heating of a leading edge is of some practical interest.

Using the asymptotic properties of the Blasius function,³

$$u = U_1 \left\{ 1 + \alpha \int_{\infty}^z \exp[-(z' - \frac{1}{2}\beta)^2] dz' \right\} \quad z \gg 1 \tag{12}$$

where β and α are constants of order one; one sees that T , given by Eq. (8), is constant, and all of its derivatives are zero as $x \rightarrow 0^+$. One sees that the new part of the solution $[(C/T_1)u_y]$ vanishes as $x \rightarrow 0$. It also vanishes both as $y \rightarrow \infty$ and as $x \rightarrow \infty$, and it has a y derivative, which vanishes on the plate ($y \rightarrow 0$). It is known that there is no solution that satisfies the parabolic differential equation [Eq. (3)] and vanishes in this way. In fact, the solution u_y has a singularity at the leading edge, $x = y = 0$.

By investigating the region of the leading edge, using Eq. (12), one finds that there is a heat flux from the leading edge

caused by u_y in Eq. (8). It is

$$H = (kU_1^2/2\nu)GC \tag{13}$$

where the constant G is given by

$$G = - \int_0^{\infty} \frac{f' - a_2 z}{z^3} \tag{14}$$

and $(a_2/2)$ is the coefficient of the quadratic term in the power series expansion of f . For the usual Blasius flow, there is a quantity of heat generated by the loss of kinetic energy in the stagnation region, when the plate has finite thickness h . This energy appears as heat in this region in the approximate amount (on one side of the plate)

$$H = \frac{1}{4}\rho U_1^3 h \tag{15}$$

so that the solution of the adiabatic plate problem should be, from Eq. (8c),

$$T = T_1 + (1/2C_p)(U_1^2 - u^2) + Cu_y$$

where

$$C = \nu\rho U_1 h/kG \tag{16}$$

Hence the temperature behaves like $x^{-1/2}$ near $x = 0$ and goes to a constant for x large.

References

¹ Crocco, L., "Lo strato limite laminare vei gas," Monograph. Sci. Aeronaut., no. 3 (1946).
² Schlichting, H., *Boundary Layer Theory* (McGraw-Hill Book Co., Inc., New York, 1960), pp. 116, 341.
³ Meksyn, D., *Laminar Boundary-Layer Theory* (Pergamon Press, New York, 1961), p. 180.

Use of Equilibrium Constants in Nonequilibrium Flow Computations

CHONG-WEI CHU*

Northrop Corporation, Hawthorne, Calif.

THE use of equilibrium constants to relate forward and backward reaction-rate constants is a common practice in nonequilibrium flow computations. The forward reaction-rate constant $k(T)$ is usually determined by experiments; the backward reaction-rate constant $k'(T)$ is then derived from the relation

$$K_e(T) = k(T)/k'(T) \tag{1}$$

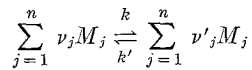
where $K_e(T)$ is the equilibrium constant. Although (1) is valid for most reversible reactions at equilibrium or near it, it is by no means obvious that (1) still holds far away from the chemical equilibrium. Careful investigators usually make an assumption for this relation (see Resler,¹ Marrone,² and Vincenti³). Many merely use (1) without referring to its validity, whereas some have stated that (1) is "usually applied"⁴ or "often made use of."⁵ Although everyone uses the relation, a deductive examination of its validity seems lacking.

In this note, we shall demonstrate that (1) follows necessarily from the postulated structure of the rate equation and shall mention situations in which (1) does not apply.

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* Senior Scientist, Gas Dynamics Branch, Propulsion and Aerballistics Research Group, Norair Division.

Consider the following reversible reaction for species M_j ($j = 1, \dots, n$)



where the ν_j are the stoichiometric coefficients for the reactants as are the ν'_j for the products (ν_j and ν'_j have no common factor). If the species represented by M_i does not occur as a reactant, then $\nu_i = 0$, etc. The reaction-rate constants k and k' are considered to be functions of temperature only. If we suppose that the rate equation

$$\frac{d[M_i]}{dt} = (\nu'_i - \nu_i) \left\{ k(T) \prod_{j=1}^n [M_j]^{\nu_j} - k'(T) \prod_{j=1}^n [M_j]^{\nu'_j} \right\} \quad (2)$$

in which k and k' are functions of temperature only is valid for all processes and for the full range of species concentrations,[†] it then follows that $K_e(T) = k(T)/k'(T)$ where $K_e(T)$ is the equilibrium constant.

To prove this statement, we define $K(T) = k(T)/k'(T)$ and show that $K(T) \equiv K_e(T)$. Let us consider a process in which constant temperature is maintained at $T = T_0$ by heat sources or by sinks, whichever is needed; in the beginning of the process, let the species be either all reactants or all products. Since (2) is valid for all processes and for the full range of species concentrations, the rate of change of species M_i is dictated by (2), and all chemical species will eventually approach their equilibrium values. Throughout the process, the function $K(T)$ remains constant $K(T) = K(T_0)$. At equilibrium, we have $d[M_i]/dt = 0$ or

$$K(T_0) = \frac{k(T_0)}{k'(T_0)} = \frac{\prod_{j=1}^n [M_j^*]^{\nu_j}}{\prod_{j=1}^n [M_j^*]^{\nu'_j}} \quad (3)$$

where $[M_j^*]$ denotes concentrations of M_j at equilibrium. The right-hand side of (3), however, is precisely the equilibrium constant $K_e(T_0)$; hence, we obtain $K(T_0) = K_e(T_0)$. We now let T_0 take every value of temperature in the range of interest and show that $K(T) \equiv K_e(T)$. Note that it suffices to consider the isothermal process to prove (1) deductively. Besides, other processes can be considered to be isothermal in a short time interval, and the rate constants depend only on the temperature, not on the rate of change of temperature. Since in a short time interval any given process cannot be distinguished from an isothermal process so far as the rate constants are concerned, if (1) is valid for the isothermal process, it is valid for all other processes.

Experiments to determine $k(T)$ are often carried out behind a shock wave in a region where dissociation predominates, whereas experiments to determine $k'(T)$ are often carried out behind an expansion wave in a region where recombination predominates. At present, the available experimental data differ rather widely from one another.^{6,7} Suppose that such measurements can be made highly accurate and that (1) is repeatedly disproved by accurate measurements; then the rate equation (2) must be modified since (2) implies (1).

In some cases, the relation (1) is not valid. We may mention the following simple example.⁸ Consider the reaction $A \rightleftharpoons B$ for which two mechanisms are possible: $2A \rightleftharpoons A + B$ and $2A \rightleftharpoons 2B$. If the first mechanism dominated, the backward rate would be $(k/K_e)[A][B]$; however, if the second reaction dominated, the backward rate would be $(k/K_e^2)[B]^2$. From the latter, we find $k/k' = K_e^2$. We may also note that, when the system is not in vibrational equilibrium, the reaction-rate constants depend on some variables besides temperature, and (1) is not valid.⁹ Nevertheless, with the introduction of a coupling factor and a modified-rate equation, the simple relation (1) can still be used when dissociation is coupled to vibrational relaxation.²

In sum, the use of (1) to relate the equilibrium constant to the reaction-rate constants is consistent with the use of (2) to express the rate of change of species, so long as the rate constants depend on temperature only. If the relation (1) is disproved by experiments or, in some cases, when the rate constants also depend on variables characterizing the deviation from equilibrium, the rate equation (2) must be modified.

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A Simple Relationship between the Drag Near Zero Lift and the Initial Normal-Force-Curve Slope Obtained from Newtonian Theory

GARY T. CHAPMAN*

NASA Ames Research Center, Moffett Field, Calif.

FROM the integrals of pressure distribution used for obtaining the forces acting on a body, it can be shown that a simple relationship exists between C_{D0} , the drag coefficient and $C_{N\alpha}$, the initial slope of the normal-force-coefficient curve when the pressures are given by Newtonian impact theory. The analysis to follow is for axially symmetric bodies, although a parallel argument can be made for two-dimensional symmetric bodies. The axial- and normal-force coefficients are given, respectively, by

$$C_x = \frac{1}{A_r} \int_A C_P \sin\theta \, dA \quad (1)$$

and

$$C_N = \frac{1}{A_r} \int_A C_P \cos\theta \cos\Phi \, dA \quad (2)$$

where θ is the angle between the local tangent and the body axis, C_P is the local pressure coefficient, Φ is the angle of revolution about the body axis, A is the surface area, and A_r is a reference area.

From modified Newtonian theory

$$C_P = C_{P_{\max}} \cos^2\beta \quad (3)$$

where $C_{P_{\max}}$ is the stagnation-point (or maximum) pressure

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* Research Scientist. Member AIAA.

[†] This requirement must be met if (2) is to be used for various nonequilibrium flow computations.