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Although the new term on the right-hand side is identically zero *only* for constant pressure conditions (that is, the material is a solid or it is stationary so that $Dp/Dt \equiv 0$), we shall see that it is frequently small compared with other terms in (2–50).

We have seen that the energy conservation principle, applied to a material control volume of fluid, is equivalent to the first law of thermodynamics. A natural question, then, is whether any additional useful information can be obtained from the *second law of thermodynamics*. In its usual differential form the second law states

$$dS \geq \frac{dQ}{\theta},$$

where dS is the entropy change for the thermodynamic system of interest, dQ is the change in its total heat content due to heat exchange with the surroundings, and θ is its temperature. When applied to a material control volume of fluid, this principle can be expressed in the form

$$\boxed{\frac{D}{Dt}\int_{V_m(t)} (\rho s)\, dV + \int_{S_m(t)} \frac{\mathbf{n}\cdot\mathbf{q}}{\theta}\, dS \geq 0,} \tag{2–51}$$

where s is the entropy per unit mass of the fluid. The only mechanism for heat transfer from the surrounding fluid is molecular transport represented by the heat flux vector $\mathbf{q}$. The sign in front of the second term is a consequence of the fact that $\mathbf{n}$ is the outer unit normal. A differential form of the inequality (2–51) is obtained easily by applying the Reynolds transport theorem to the first term and the divergence theorem to the second term to show

$$\int_{V_m(t)} \left[\rho \frac{Ds}{Dt} + \nabla\cdot\left(\frac{\mathbf{q}}{\theta}\right)\right] dV \geq 0.$$

This inequality can be satisfied for an arbitrary material control volume $V_m(t)$ only if

$$\boxed{\rho \frac{Ds}{Dt} + \nabla\cdot\left(\frac{\mathbf{q}}{\theta}\right) \geq 0.} \tag{2–52}$$

An inequality that is equivalent to (2–52) can be obtained using thermodynamics to express Ds/Dt in the form

$$\theta\rho\frac{Ds}{Dt} = \rho\frac{De}{Dt} - \frac{p}{\rho}\frac{D\rho}{Dt}$$

and then substituting for De/Dt from the energy conservation (2–45). The result for Ds/Dt is

$$\boxed{\rho\frac{Ds}{Dt} = \frac{1}{\theta}\left[\mathbf{T}{:}\mathbf{E} + p(\nabla\cdot\mathbf{u}) - \nabla\cdot\mathbf{q}\right].} \tag{2–53}$$

Then, since

$$\nabla\cdot\left(\frac{\mathbf{q}}{\theta}\right) = \frac{1}{\theta}\nabla\cdot\mathbf{q} - \frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta,$$

the inequality (2–52) can be combined with (2–53) to obtain

$$\boxed{\frac{1}{\theta}(\mathbf{T}:\mathbf{E}+p(\nabla\cdot\mathbf{u}))-\frac{\mathbf{q}\cdot\nabla\theta}{\theta^2}\geq 0.} \tag{2–54}$$

Although there is no immediately useful information that we can glean from (2–54), we shall see that it provides a constraint on allowable constitutive relationships for **T** and **q**. In this sense, it plays a similar role to the angular momentum principle which led to the constraint (2–39) that **T** be symmetric in the absence of body couples. In solving fluid mechanics problems, assuming that the fluid is isothermal, we will use the equation of continuity, (2–5) or (2–19), and the Cauchy equation of motion (2–30), to determine the velocity field, but angular momentum conservation and the second law of thermodynamics will appear only indirectly as constraints on allowable constitutive forms for **T**. Similarly, for nonisothermal conditions, we will use (2–5) or (2–19), (2–30), and either (2–49) or (2–50) to determine the velocity and temperature distributions, but neither angular momentum conservation nor the second law of thermodynamics will appear directly. However, we are getting ahead of our story.

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So far, we have seen that the basic conservation principles of continuum mechanics lead to a set of five scalar differential equations—sometimes called the field equations of continuum mechanics—namely, (2–5) or (2–19), (2–30), and (2–49) or (2–50). On the other hand, we have identified many more unknown variables, **u**, **T**, θ, p, and **q**, plus various fluid or material properties such as ρ, c_v, (or c_p), $(\partial p/\partial\theta)_p$, or $(\partial\rho/\partial\theta)_p$, which generally require additional equations of state to be determined from p and θ if the latter are adopted as the thermodynamic state variables. Let us focus just on the independent variables **u**, **T**, θ, p, and **q**. Taking account of the symmetry of **T**, these comprise 14 unknown scalar variables for which we have so far obtained only the five independent "field" equations that were listed above. It is evident that we require additional equations relating the various unknown variables if we are to achieve a well-posed problem from a mathematical point of view. Where are these equations to come from? Why is it that the fundamental conservation principles of continuum physics do not, in themselves, lead to a complete, well-posed mathematical problem?

E. Constitutive Equations

We have seen that the basic field equations of continuum mechanics are not sufficient in number to provide a well-posed mathematical problem from which to determine solutions for the independent field variables **u**, **T**, θ, p, and **q**. It is apparent that additional relationships must be found, hopefully without introducing more independent variables. In the next several sections, we discuss the origin and form of the so-called constitutive equations that provide the necessary additional relationships.

We begin with some general observations. In the first place, the idea that additional equations are necessary has so far been based on the purely mathematical statement that the field equations by themselves do not lend to a well-posed problem. While this argument is powerful and certainly persuasive, it is also instructive to think about