Thermodynamics of a fluid

Entropy equation

We wish to write the entropy equation

$$T\frac{DS}{Dt} = Q$$

in terms of Dp/Dt and $D\rho/Dt$ only. However, the easiest way to do this is to begin with the equation for temperature and pressure changes. If we take the entropy to be a function of temperature and pressure, $S = S(T, p)$, we have

$$T\left(\frac{\partial S}{\partial T}\right)_p \frac{DT}{Dt} + T\left(\frac{\partial S}{\partial p}\right)_T \frac{Dp}{Dt} = Q \tag{1}$$

where the subscripts indicate the quantity held fixed. We need expressions for

$$\left(\frac{\partial S}{\partial T}\right)_p \quad \text{and} \quad \left(\frac{\partial S}{\partial p}\right)_T$$

The first of these quantities can be written in terms of the specific heat at constant pressure c_p:

$$T\left(\frac{\partial S}{\partial T}\right)_p = c_p \tag{2}$$

The heat added at constant pressure, TdS, is equal to c_p times the temperature change dT. The subscript on the specific heat is *not* a derivative.

The second quantity can be rewritten in terms of the equation of state — a relationship between the specific volume, the temperature and the pressure — $\alpha = \alpha(T, p)$ by using a "Maxwell" relationship. From the internal energy equation

$$de = TdS - pd\alpha$$

we have
$$d[e - TS + p\alpha] = TdS - pd\alpha - TdS - SdT + pd\alpha + \alpha dp$$
$$= -SdT + \alpha dp$$

which is the equation for the Gibbs' free energy, $G = e - TS + p\alpha$, we find

$$\alpha = \left(\frac{\partial G}{\partial p}\right)_T, \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_p$$

Cross differentiating these two implies

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial \alpha}{\partial T}\right)_p = -\alpha_T \tag{3}$$

We use subscripts for derivatives of $\alpha(T,p)$ since there is no ambiguity about which quantities are held constant. These derivatives are determined from the equation of state. Thus we have the second required derivative.

Putting (2) and (3) in (1) yields

$$c_p \frac{DT}{Dt} - T\alpha_T \frac{Dp}{Dt} = Q \tag{4}$$

From this, we can readily find the adiabatic ($Q = 0$, implying S is constant) change in temperature with pressure:

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T\alpha_T}{c_p}$$

and, by using the hydrostatic relation,

$$\left(\frac{\partial T}{\partial z}\right)_S = -\frac{gT\alpha_T}{\alpha c_p}$$

For a perfect gas, $T\alpha_T = \alpha$, and the adiabatic temperature gradient is just $-g/c_p$.

We now rewrite (4) in terms of density and pressure as the basic variables. For $\rho = \rho(T,p)$ we have

$$\frac{D\rho}{Dt} = \rho_T \frac{DT}{Dt} + \rho_p \frac{Dp}{Dt}$$
$$= \rho_T \frac{Q}{c_p} + \rho_T \frac{T\alpha_T}{c_p} \frac{Dp}{Dt} + \rho_p \frac{Dp}{Dt}$$
$$= \rho_T \frac{Q}{c_p} + \left(\rho_p - \frac{\rho_T^2 T}{c_p \rho^2}\right) \frac{Dp}{Dt}$$

This is written in terms of the speed of sound

$$\frac{D\rho}{Dt} - \frac{1}{c_s^2} \frac{Dp}{Dt} = \frac{\rho_T Q}{c_p} \tag{5}$$

with the speed of sound being defined by

$$c_s^2 = \left(\frac{\partial p}{\partial \rho}\right)_S = \left(\rho_p - \frac{T\rho_T^2}{\rho^2 c_p}\right)^{-1}$$

We can replace the equation of state by relationships $c_s^2(p,\rho)$, $\rho_T(p,\rho)$ to complete our dynamical equations:

$$\frac{Du}{Dt} - fv = -\frac{1}{\rho} p_x$$
$$\frac{Dv}{Dt} + fu = -\frac{1}{\rho} p_y$$
$$\frac{Dw}{Dt} = -\frac{1}{\rho} p_z - g$$
$$\frac{D\rho}{Dt} + \rho(u_x + v_y + w_z) = 0$$
$$\frac{D\rho}{Dt} - \frac{1}{c_s^2} \frac{Dp}{Dt} = \frac{\rho_T Q}{c_p}$$

2

in the five variables, u, v, w, p, ρ.

Notes

Speed of sound: In the case of a perfect gas, the equation of state $\rho = p/RT$ implies that

$$c_s^2 = \left(\frac{1}{RT} - \frac{Tp^2}{R^2 T^4 \rho^2 c_p} \right)^{-1}$$

$$= \left(\frac{1}{RT} - \frac{1}{T c_p} \right)^{-1}$$

$$= \left(\frac{c_p - R}{c_p RT} \right)^{-1}$$

$$= \frac{c_p}{c_v} RT = \gamma RT$$

In terms of the basic variables, $c_s^2 = \gamma p / \rho$.

General relationship for specific heats: If we combine (4) with an equation for specific volume changes

$$\frac{D\alpha}{Dt} = \alpha_T \frac{DT}{Dt} + \alpha_p \frac{Dp}{Dt}$$

and eliminate the pressure changes term, we find

$$\left(c_p + \frac{T\alpha_T^2}{\alpha_p} \right) \frac{DT}{Dt} - \frac{T\alpha_T}{\alpha_p} \frac{D\alpha}{Dt} = Q$$

Thus, if volume is held fixed, the relationship between temperature changes and heat added implies

$$c_v = c_p + \frac{T\alpha_T^2}{\alpha_p}$$

In the perfect gas case, this gives $c_v = c_p - R$.

Entropy: The existence of an entropy state function is more difficult to demonstrate for a general fluid. See texts on statistical mechanics; e.g. Reif.

Potential Temperature: The potential temperature θ evolves according to

$$\frac{D\theta}{Dt} = \theta_T \frac{DT}{Dt} + \theta_p \frac{Dp}{Dt}$$

But the potential temperature can be defined as the solution to

$$\theta_p = -\frac{T\alpha_T}{c_p} \theta_T$$

subject to the condition $\theta(p_{ref}, T) = T$, so that

$$\frac{D\theta}{Dt} = \frac{\theta_T Q}{c_p}$$

using (4).