

## Geophysical Fluid Dynamics I 13 ii 2004 P.B. Rhines

NOTES ON THERMODYNAMICS -1 (with corrections, 15 ii 04 and added equation of state notes)

Often we need to work with partial derivatives like  $\left. \frac{\partial T}{\partial p} \right|_{\eta}$  which is the rate of change of temperature with

respect to pressure at constant entropy, How does express such relations in terms of common state variables? It appears in the parcel argument for the buoyancy frequency, worked out in terms of temperature. The thermodynamic state of a 'simple' fluid, one example being a perfect dry gas, is determined by any two of its state variables,  $p, \rho, T, \eta$  .... The 1<sup>st</sup> law of thermodynamics, a microscopic energy equation, can be written in different forms, depending on the choice of variables. The usual form is a relation between internal thermal energy change, heat input and work done (pressure x volume change):

$$\delta E = \delta' q - p \delta v \quad v \equiv 1/\rho$$

where E is internal thermal energy,  $\delta$  is a small change. We would like to write  $DE/Dt = Dq/Dt - pDv/Dt$  using the Lagrangian derivative that follows the fluid parcel. However the 'heat' q is not a state variable but rather  $\delta' q$  is the input or output of heat....the flow of heat into or out of the fluid parcel, so it is not the differential of a state variable.

Clausius and others discovered that by dividing the heat exchange by temperature, they could create a new variable which is uniquely associated with the state of the fluid, and is 'heat-like'. The entropy,  $\eta$ , is a state variable that plays the role of 'heat'. For slowly changing thermal processes, entropy, defined as

$$\delta \eta = \frac{\delta' Q}{T}$$

is conserved, summing over the entire system. It is only for 'non-equilibrium', rapidly changing thermal processes that total entropy is changed (generally, increased). An example of a non-equilibrium process is the mixing together of two volumes of water one at 10C and the other at 90C. Thus "heat" is not a noun, a property of a fluid but it is a verb or an adjective. Thermal energy E is what most people mean when they use "heat" as a noun.

Because of the close connection of entropy and heat exchange we often think of ideal fluid motions in which the entropy of a fluid parcel is constant, even as it is compressed or expanded. This suggests writing an equation of state for pressure p in terms of  $\rho$  and  $\eta$  instead of the usual  $p(\rho, T)$ . For a perfect gas this equation is

$$p = \exp(\eta/C_v) \rho^\gamma$$

where  $\gamma = C_p/C_v$  ( $= 7/5 = 1.4$  for diatomic gases) is the ratio of specific heat capacities at constant pressure and volume, respectively. Derivation is left to the reader. Thus we see that an isentropic movement of a fluid parcel has the density change more rapidly ( $p$  proportional to  $\rho^\gamma$ ) than would an isothermal movement ( $p$  proportional to  $\rho$ )

Now it is still true that

$$p = \rho RT$$

so we can make many useful connections for the ideal gas case.

Using the definition of entropy, the 1<sup>st</sup> Law becomes

$$\delta E = T \delta \eta - p \delta v$$

which now can be written all in terms of D/Dt operators.

Now, to work out an expression for  $\left. \frac{\partial T}{\partial p} \right|_{\eta}$  we would like to have a relationship between T, p and  $\eta$ ... an equation of the form

$$\delta T = \left. \frac{\partial T}{\partial p} \right|_{\eta} \delta p + \left. \frac{\partial T}{\partial \eta} \right|_p \delta \eta$$

which includes that term. The first law above is not very helpful. However by changing to other state variables, it will be.

For a perfect gas,  $E = C_v T$ , the internal energy is equal to the temperature multiplied by the specific heat capacity at constant volume. This is virtually a result of the definition of  $C_v$ . If volume,  $v$ , is held constant,  $\delta E = \delta' q$ , and  $C_v$  is defined as the heat gain per degree of temperature increase,  $\delta' q / \delta T$ .

Now the 1<sup>st</sup> Law is now

$$C_v \delta T = T \delta \eta - p \delta v$$

involving the differentials of T,  $\eta$  and  $v$ . But we need an expression using differentials of T,  $\eta$  and  $p$ . So write (using the equation of state for a perfect gas,  $p = \rho RT = RT/v$ )

$$\begin{aligned} C_v \delta T &= T \delta \eta - \delta(pv) + v \delta p \\ &= T \delta \eta - R \delta T + v \delta p \end{aligned}$$

$$(C_v + R) \delta T = T \delta \eta + v \delta p$$

$$C_p \delta T = T \delta \eta + v \delta p$$

Divide through by  $C_p$  and we have

$$\delta T = \frac{T}{C_p} \delta \eta + \frac{v}{C_p} \delta p$$

where we have used  $R = C_p - C_v$ . Now we know that in general

$$\delta T = \left. \frac{\partial T}{\partial p} \right|_{\eta} \delta p + \left. \frac{\partial T}{\partial \eta} \right|_p \delta \eta$$

so comparing the last two equations we have

$$\left. \frac{\partial T}{\partial p} \right|_{\eta} = \frac{v}{C_p} \equiv \frac{1}{\rho C_p}$$

which is what we were seeking. This gives a useful expression for the formula for buoyancy frequency in terms of temperature, and the thermal expansion coefficient  $\alpha \equiv \frac{-1}{\rho} \frac{\partial \rho}{\partial T}$ :

$$\begin{aligned} N^2 &= -g \alpha (T_{parcel} - T_{surrounding fluid}) / \delta z \\ &= +g \alpha \left( \frac{dT_0}{dz} - \left. \frac{\partial T}{\partial p} \right|_{\eta} \frac{dp}{dz} \right) \\ &= +g \left( \frac{1}{T} \frac{dT_0}{dz} + \frac{g}{C_p T} \right) \end{aligned}$$

where we have used  $p_z = -g\rho$  and  $\alpha = 1/T$  for a perfect gas. We see that the *adiabatic lapse rate*, the vertical temperature gradient that has no buoyancy gradient, is

$$\left. \frac{dT}{dz} \right|_{adiabatic} = \frac{-g}{C_p}$$

which is about  $10^{\circ}\text{C}$  per km. The lower atmosphere is often close to ‘neutral’ (no buoyancy gradient), hence this is close to the cooling that one feels in climbing a mountain.

Note that the adiabatic lapse rate is *negative* so that often we have temperature decreasing with height. At first sight this would seem to imply that the density increases with height, but it is not, because pressure decreases with height and ‘wins’ (in the  $p = \rho RT$  equation).

See Gill sections 3.2-36 for more; and be aware that some expressions are more general than others (for example Gill’s parcel calculation for  $\delta\rho$ , equation 3.6.7 is valid for seawater as well as air).