The Specific Heat at Constant Pressure [Revision : 1.1]

In class (Wed. March 9), I was unable to derive the expression quoted in *Stellar Interiors* (see their eqn. 3.86) for the specific heat at constant pressure, c_P . These notes provide the missing derivation, and discuss some of the assumptions underlying it.

Recall from the class that the specific heat at constant x (where x is some state variable) is defined as

$$c_x \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_x;\tag{1}$$

here, δQ is the amount of heat per unit mass¹ that must be added at constant x to achieve a temperature increase of dT. Note that we write δQ rather than dQ to emphasize that the heat added is not a state variable, and moreover is not an exact differential (more of this later).

Now, the First Law of Thermodynamics for quasi-static changes tells us that

$$\delta Q = \mathrm{d}E + P\mathrm{d}V.\tag{2}$$

From this, we can set dV = 0 and divide through by dT, to trivially find the specific heat at constant volume as

$$c_V \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V.$$
(3)

To find the specific heat at constant pressure, things are a little more involved. We start by expressing a volume change dV in terms of corresponding temperature and pressure changes,

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P. \tag{4}$$

Substituting this into the FLOT gives

$$\delta Q = \mathrm{d}E + P\left[\left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P\right].$$
(5)

Setting dP = 0 and dividing through by dT, we obtain the specific heat at constant pressure, as

$$c_P \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$
(6)

To reproduce the result quoted in *Stellar Interiors*, the internal energy derivative term in the above expression must now be rewritten in terms of c_V . The first step is to use the identity

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = c_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P,\tag{7}$$

which is simply a consequence of the multi-variable chain rule. Substituting this into eqn. (6), we find $\begin{bmatrix} f(0T) \\ 0 \end{bmatrix} = \begin{bmatrix} f(0T) \\ 0 \end{bmatrix}$

$$c_P = c_V + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P.$$
(8)

Now for the tricky bit (i.e., the bit that eluded me in class!). To eliminate the energy derivative from this equation, we must make use of the *Clausius equality*, which is a corollary of the Second Law of Thermodynamics (SLOT) for reversible processes:

$$\oint \frac{\delta Q}{T} = 0. \tag{9}$$

¹The 'per unit mass' should be assumed throughout these notes; I won't mention it again.

This equality essentially tells us that any integral of the quantity $\delta Q/T$ between two fixed points is independent of the path taken between the points, and depends only on the state at the endpoints. Therefore, $\delta Q/T$ must be the differential of a state variable. In fact, this state variable is the specific entropy S, so that

$$\frac{\delta Q}{T} = \mathrm{d}S.\tag{10}$$

With this definition, the FLOT can be written

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V\tag{11}$$

From this, it follows that

$$\left(\frac{\partial S}{\partial T}\right)_{V} = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_{V}, \qquad \left(\frac{\partial S}{\partial V}\right)_{T} = \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_{T} + P \right]. \tag{12}$$

Differentiating the first expression wrt V, and the second wrt T, we then have

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T} \frac{\partial^2 E}{\partial V \partial T}, \qquad \frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{T^2} \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] + \frac{1}{T} \left[\frac{\partial^2 E}{\partial T \partial V} + \left(\frac{\partial P}{\partial T} \right)_V \right]. \tag{13}$$

Because S is a state variable, the left-hand sides of these two expressions must be equal (i.e., differentiation order does not matter). Therefore, it follows (after a little algebra) that

$$\left(\frac{\partial E}{\partial V}\right)_T + P = T \left(\frac{\partial P}{\partial T}\right)_V \tag{14}$$

Substituting the left-hand side back into eqn. (8), we find

$$c_P = c_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P.$$
(15)

Finally, to reproduce the result given in eqn. (3.86) of *Stellar Interiors*, we make use of the triple differential formula

$$\left(\frac{\partial V}{\partial T}\right)_{P} \left(\frac{\partial T}{\partial P}\right)_{V} \left(\frac{\partial P}{\partial V}\right)_{T} = -1 \tag{16}$$

(as with eqn. 7, this is just a consequence of the chain rule). Combining the above expressions, we obtain

$$c_P = c_V - T \left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial P}{\partial V}\right)_T^{-1}.$$
(17)

which is the desired result.

The derivation would have been significantly simpler if we had used the entropy formulation of the FLOT (eqn. 11) right from the start. However, I did things the long way to emphasize that the SLOT is also required to obtain the desired result. So, now you know.