COURSE ON ACOUSTICS

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1. Appendix - Some thermodynamics for acoustics - Maxwell's relations

In the lectures we defined the following thermodynamic response functions: The isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T, \tag{1}$$

and the isobaric coefficient of thermal expansion

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P. \tag{2}$$

Now, we will derive the thermodynamic relations used in the lectures

1.1. **The conservation of energy.** The conservation of energy (the first law of thermodynamics) states that the change of the internal energy density u is the sum of the heat energy $dq = Tds$ and the work done $Pd(1/\rho)$.

$$du = Tds - Pd(1/\rho) \tag{3}$$

This is more familiar if we use extensive quantities

$$dU = TdS - PDV \tag{4}$$

Hence,

$$T = \left(\frac{\partial U}{\partial S}\right)_V \tag{5}$$

and

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \tag{6}$$

As we can change the order of the derivations, we get one of the Maxwell's relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial^2 U}{\partial V \partial S}\right) = -\left(\frac{\partial P}{\partial S}\right)_V \tag{7}$$

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The entropy is not an easy state variable to measure. We can change the set of variables that are considered independent using a Legendre transformation. Let the Helmoholtz free energy be

$$F = U - TS \tag{8}$$

Differentiating this from both sides gives

$$dF = dU - TdS - SdT = TdS - PdV - TdS - SdT = -SdT - PdV \tag{9}$$

This gives another Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial^2 F}{\partial V \partial T}\right) = \left(\frac{\partial P}{\partial T}\right)_V \tag{10}$$

Let us derive a third relation. Use the law of energy conservation (4) in a form that has temperature T and volume V as independent state variables.

(11)
$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T dV + \frac{P}{T}dV = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial T}\right)_T\right] dV$$

Now, use the old had trick and take the double partial derivatives for

$$\frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right] = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(P + \left(\frac{\partial U}{\partial T}\right)_T\right)\right] \tag{12}$$

That is

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

or

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

1.2. **The relations of partial derivatives.** Let x, y, and z be quantities (state variables) with one constraint equation (equation of state) $z = z(x, y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{15}$$

Setting $dy = 0$, we get

$$dx = \left[\left(\frac{\partial z}{\partial x}\right)_y\right]^{-1} dz \tag{16}$$

or

(17) $$\left(\frac{\partial x}{\partial z}\right)_y = \left[\left(\frac{\partial z}{\partial x}\right)_y\right]^{-1}.$$

Similarly, setting $dz = 0$, we get

(18) $$dx = -\left[\left(\frac{\partial z}{\partial x}\right)_y\right]^{-1}\left(\frac{\partial z}{\partial y}\right)_x dy$$

This gives

(19) $$\left(\frac{\partial x}{\partial y}\right)_z = -\left[\left(\frac{\partial z}{\partial x}\right)_y\right]^{-1}\left(\frac{\partial z}{\partial y}\right)_x,$$

which is equivalent, after using the relation for the inverses (16), to

(20) $$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$$

This can be used to relate the thermodynamic response functions to measurable response functions, for example,

(21) $$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T = -1$$

1.3. **The heat capacities and partial derivatives of temperature with respect to pressure.** After this brief side step to methodics we will consider heat capacities. The amount of heat (energy) Q, transferred $đQ$ (inexact differential) is given by the exact differential TdS

(22) $$đQ = TdS = dU + PdV$$

At constant volume $dV = 0$ (density) the change of heat with a change of temperature is the heat capacity C_V

(23) $$C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V.$$

The heat capacity at constant pressure, the independent variables should be temperature and pressure: $S = S(T, V(T, P))$. The change of heat becomes, when pressure is kept constant

(24) $$đQ = TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP.$$

Therefore the heat capacity at constant pressure is

$$C_P = \left(\frac{đQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{25}$$

We can continue by keeping in mind that $S = S(T, V(T, P))$ in taking the derivatives

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \tag{26}$$

From this equation we see that the difference of constant volume and constant pressure heat capacity is

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \tag{27}$$

Let's play with the partial derivatives in this equation, this is equal to

$$C_P - C_V = T\left[\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P\right]\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P, \tag{28}$$

because by the rule (16) the value of the expression in the square brackets is equal to one. Using the definition for the heat capacity at constant pressure (25), we can substitute it back in

$$C_P - C_V = C_P\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = C_P\left[\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P\right]\left(\frac{\partial S}{\partial V}\right)_T \tag{29}$$

where we can use chain rule

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial S}\right)_P, \tag{30}$$

to replace the derivatives in the square bracket to give

$$C_P - C_V = C_P\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial V}\right)_T \tag{31}$$

Let us insert more multiplying ones inside (two this time!)

$$C_P - C_V = C_P\left[\left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial S}\right)_V\right]\left[\left(\frac{\partial P}{\partial V}\right)_S\left(\frac{\partial V}{\partial P}\right)_S\right]\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial V}\right)_T \tag{32}$$

This can be reordered to

$$C_P - C_V = C_P\left[\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_S\right]\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial V}{\partial P}\right)_S\left(\frac{\partial S}{\partial V}\right)_T \tag{33}$$

This time the point is that the term in the square brackets equals to -1 (for a change). Hence,

$$C_P - C_V = -C_P \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial S}{\partial V}\right)_T . \tag{34}$$

Some additional ones again

$$C_P - C_V = -C_P \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial S}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S\right] \left[\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V ,\right] \tag{35}$$

and reorderging for a -1 inside the bracket

$$C_P - C_V = -C_P \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left[\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial S}\right)_V\right] \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V \tag{36}$$

We get

$$C_P - C_V = C_P \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V = C_P \left[\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V\right] \left[\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial P}\right)_S ,\right] \tag{37}$$

where the last reordering unveils two chain rules that finally give

$$C_P - C_V = C_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_S , \tag{38}$$

This was the aim of this exercise - find a formula for the changes of temperature in adiabatic (entropy is constant - like in acoustics it usually is) compression:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{C_P - C_V}{C_P} \left(\frac{\partial T}{\partial P}\right)_V \tag{39}$$

This equation is used in the lectures to derive the temperature fluctuations incurring in sound as it propagates in the gas.

1.4. **Heat capacities and their connection to compressibilities and thermal expansion.** Let the volume be a function of temperature and pressure $V = V(T, P)$

$$đQ = TdS = dU + PdV = dU + P\left(\frac{\partial V}{\partial T}\right)_P dT + P\left(\frac{\partial V}{\partial P}\right)_T dP \tag{40}$$

Equivalently for the internal energy $U = U(T, V(T, P))$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP \tag{41}$$

Combining these provides

(42)
$$đQ = \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP$$
Heat capacity at constant pressure C_P is thus,

(43)
$$C_P = \left(\frac{đQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$
We derived a helpful relation in the first section (14) that we can use for the term in the bracket

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \tag{44}$$

that we can use now:

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{45}$$

Because,

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1, \tag{46}$$

we can give the heat capacities with response functions

$$C_P = C_V - T\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = C_V + TV\frac{\frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P^2}{\frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = C_V + TV\frac{\beta^2}{\kappa_T} \tag{47}$$

which is

$$C_P - C_V = TV\frac{\beta^2}{\kappa_T} \tag{48}$$

1.5. **The compressibilities with heat capacities.** As last relations, let us derive the compressibilities in terms of heat capacities

$$V(\kappa_T - \kappa_S) = \left(\frac{\partial V}{\partial P}\right)_S - \left(\frac{\partial V}{\partial P}\right)_T \tag{49}$$

We will again introduces ones

(50)
$$\left(\frac{\partial V}{\partial P}\right)_S \left[\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial S}\right)_P\right] \left[\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial P}\right)_V\right] - \left(\frac{\partial V}{\partial P}\right)_T \left[\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P\right] \left[\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V\right]$$
and reorder for emerging minus ones

(51)
$$\left[\left(\frac{\partial V}{\partial P}\right)_S\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_P\right]\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_V-\left[\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\right]\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V$$
that leaves

$$V(\kappa_T-\kappa_S)=\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V-\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_V \tag{52}$$

Rather boringly we add again a set of new ones

(53)
$$V(\kappa_T-\kappa_S)=\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left[\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial T}\right)_P\right]-\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_V\left[\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial T}\right)_V\right],$$
and combine derivatives to get

$$V(\kappa_T-\kappa_S)=\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial S}{\partial T}\right)_P-\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V \tag{54}$$

that is in a form that we can factorize it

$$V(\kappa_T-\kappa_S)=\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left[\left(\frac{\partial S}{\partial T}\right)_P-\left(\frac{\partial S}{\partial T}\right)_V\right]. \tag{55}$$

Now, the square bracket term can be given in many forms (28) and (31),

$$\left(\frac{\partial S}{\partial T}\right)_P-\left(\frac{\partial S}{\partial T}\right)_V=\frac{C_P}{T}-\frac{C_V}{T}=\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P=\frac{C_P}{T}\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial V}\right)_T \tag{56}$$

Hence,

$$V(\kappa_T-\kappa_S)=\left(\frac{\partial V}{\partial S}\right)_P\left[\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial S}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{57}$$

The term in the square brackets is one, since it is one of the Maxwell's relations (10)we derived

$$\left(\frac{\partial P}{\partial T}\right)_V=\left(\frac{\partial S}{\partial V}\right)_T. \tag{58}$$

Therefore, with on additional use of chain rule

$$V(\kappa_T-\kappa_S)=\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial V}{\partial T}\right)_P=\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial V}{\partial T}\right)_P \tag{59}$$

All terms in this are nice response functions

(60) $$V(\kappa_T - \kappa_S) = \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial T}{\partial S}\right)_P = \frac{TV^2\beta^2}{C_P},$$

and we get

(61) $$C_P(\kappa_T - \kappa_S) = TV\beta^2.$$

Dividing this result with the relation (48) on both sides

(62) $$C_P - C_V = TV\frac{\beta^2}{\kappa_T}$$

we get

(63) $$\frac{C_P(\kappa_T - \kappa_S)}{C_P - C_V} = \kappa_T \Leftrightarrow \gamma \equiv \frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S},$$

which is the relation used in lectures to get the speed of sound. The ratio of heat capacities γ is the same as the ratio of isothermal and adiabatic compressibility.

1.5.1. *General relations for small variables.* Finally, let us look a general chain rule relation on how small changes in density δ and entropy $\sigma$are related to small changes of temperature τ and pressure p.

(64) $$\begin{cases} \delta = & \left(\frac{\partial\rho}{\partial P}\right)_T p + \left(\frac{\partial\rho}{\partial T}\right)_P \tau \\ \sigma = & \left(\frac{\partial S}{\partial P}\right)_T p + \left(\frac{\partial S}{\partial T}\right)_P \tau \end{cases}$$

Most of the partial derivatives are already done. By definitions (1) and (2)

(65) $$\left(\frac{\partial\rho}{\partial P}\right)_T = \rho\kappa_T,$$

and

(66) $$\left(\frac{\partial\rho}{\partial T}\right)_P = -\rho\beta$$

Also, by (25)

(67) $$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}.$$

The last partial derivative requires a little more work. Since

(68) $$\left[\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial S}\right)_P\right] = -1.$$

Therefore,

(69) $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial T}{\partial P}\right)_S \frac{C_p}{T}.$$

From relation (39)

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{C_p - C_V}{C_p}\left(\frac{\partial T}{\partial P}\right)_V = \frac{C_p - C_V}{C_p}\left[\frac{\frac{1}{V}\left(\frac{\partial T}{\partial P}\right)_V}{-\frac{1}{V}\left(\frac{\partial T}{\partial P}\right)_V}\right] = \frac{C_p - C_V}{C_p}\frac{\kappa_T}{\beta}, \tag{70}$$

which means that

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\gamma - 1}{\gamma}\frac{\kappa_T}{\beta}. \tag{71}$$

Thus, the last partial derivative is

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\gamma - 1}{\gamma}\frac{\kappa_T C_p}{\beta T} \tag{72}$$

Replacing these to the (64) we get the general relations:

$$\begin{cases} \delta = & \rho\kappa_T p - \rho\beta\tau \\ \sigma = & -\frac{\gamma-1}{\gamma}\frac{\kappa_T C_p}{\beta T}p + \frac{C_p}{T}\tau \end{cases} \tag{73}$$