5.8: Adiabatic Compressibility

In Chapter 4, we learned about the isothermal compressibility, κ_T, which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

κ_T is a very useful quantity, as it can be measured for many different substances and tabulated. Also, as we will see in the next chapter, it can be used to evaluate several different partial derivatives involving thermodynamic variables.

In his seminal work, *Philosophiae Naturalis Principia Mathematica* (Newton, 1723), Isaac Newton (1643 - 1727) (Doc) calculated the speed of sound through air, assuming that sound was carried by isothermal compression waves. His calculated value of 949 m/s was about 15% smaller than experimental determinations. He accounted for the difference by pointing to "non-ideal effects". But it turns out that his error, albeit an understandable one (since sound waves do not appear to change bulk air temperatures) was that the compression waves are adiabatic, rather than isothermal. As such, there are small temperature oscillations that occur due to the adiabatic compression followed by expansion of the gas carrying the sound waves. The oversight was correct by Pierre-Simon Laplace (1749 – 1827) (O'Connor & Robertson, Pierre-Simon Laplace, 1999).

LaPlace modeled the compression waves using the **adiabatic compressibility**, κ_S defined by

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

Since the entropy is defined by

$$dS = \frac{dq_{rev}}{T}$$

it follows that any adiabatic pathway ($dq = 0$) is also **isentropic** ($dS = 0$), or proceeds at constant entropy.

> *Adiabatic pathways are also isentropic.*

A couple of interesting conclusions can be reached by following the derivation of an expression for the speed of sound where the sound waves are modeled as adiabatic compression waves. We can begin by expanding the description of κ_S by using Partial Derivative Transformation Type II. Applying this, the adiabatic compressibility can be expressed

$$\kappa_S = \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_V$$

or by using transformation type I

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_p}$$

Using a simple chain rule, the partial derivatives can be expanded to get something a little easier to evaluate:

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p} \tag{5.8.1}$$

The utility here is that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{5.8.2}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{5.8.3}$$

This means that Equation 5.8.1 simplifies to

$$\kappa_S = \frac{C_V}{C_p}\left(\frac{1}{V}\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p}\right)$$

Simplifying what is in the parenthesis yields

$$\kappa_S = \frac{C_V}{C_p}\left(\frac{1}{V}\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\right)$$

$$\kappa_S = \frac{C_V}{C_p}\left(-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right)$$

$$\kappa_S = \frac{C_V}{C_p}\kappa_T$$

As will be shown in the next chapter, C_p is always bigger than C_V, so κ_S is always smaller than κ_T.

But there is more! We can use this methodology to revisit how pressure affects volume along an adiabat. In order to do this, we would like to evaluate the partial derivative

$$\left(\frac{\partial V}{\partial p}\right)_S$$

This can be expanded in the same way as above

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial S}\right)_V}$$

And further expand

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial S}\right)_V} \tag{5.8.4}$$

And as before, noting that the relationships in Equations 5.8.2 and 5.8.3, Equation 5.8.4 can be simplified to

$$\begin{aligned}\left(\frac{\partial V}{\partial p}\right)_S &= -\frac{C_V}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V \\ &= \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_T \end{aligned} \tag{5.8.5}$$

Or defining $\gamma = C_p/C_V$, Equation 5.8.5 can be easily rearranged to

$$\gamma\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T$$

The right-hand derivative is easy to evaluate if we assume a specific equation of state. For an ideal gas,

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2} = -\frac{V}{p}$$

Substitution yields

$$\gamma\left(\frac{\partial V}{\partial p}\right)_S = -\frac{V}{p}$$

which is now looking like a form that can be integrated. Separation of variables yields

$$\gamma\frac{dV}{V} = \frac{dP}{p}$$

And integration (assuming that g is independent of volume) yields

$$\gamma\int_{V_1}^{V_2}\frac{dV}{V} = \int_{p_1}^{p_2}\frac{dP}{p}$$

or

$$\gamma\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{p_2}{p_1}\right)$$

which is easily manipulated to show that

$$p_1V_1^{\gamma} = p_2V_2^{\gamma}$$

or

$$pV^{\gamma} = \text{constant}$$

which is what we previously determined for the behavior of an ideal gas along an adiabat.

Finally, it should be noted that the correct expression for the speed of sound is given by

$$v_{sound} = \sqrt{\frac{1}{\rho\,\kappa_S}}$$

where ρ is the density of the medium. For an ideal gas, this expression becomes

$$v_{sound} = \sqrt{\frac{\gamma RT}{M}}$$

where M is the molar mass of the gas. Isaac Newton's derivation, based on the idea that sound waves involved isothermal compressions, would produce a result which is missing the factor of γ, accounting for the systematic deviation from experiment which he observed.

Contributors

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