Unit 11

Thermodynamics of an Ideal Gas

11.1 First law of thermodynamics

- Here we consider quasistatic changes to the state of a nondegenerate gas to understand its thermodynamic properties. Thermodynamics are "responses" of a gas to perturbations.
- As already stated, the internal energy per unit volume of an ideal gas is

$$u = \frac{3}{2} n k_{\mathrm{B}} T = \frac{3}{2} \frac{\rho k_{\mathrm{B}} T}{\mu m_p} = \frac{3}{2} P. \tag{11.1}$$

- Therefore the average energy per particle is $3/2 k_{\mathrm{B}} T$. Example problem 6.1 arrived at this in a slightly different way.
- We define the specific volume V as the volume corresponding to unit mass, $V = \text{volume/mass} = 1/\rho$. The specific internal energy is the internal energy per unit mass $U = u/\rho$:

$$U = \frac{3}{2} \frac{k_{\mathrm{B}} T}{\mu m_u}. \tag{11.2}$$

- Remember that the first law of thermodynamics tells us that we can (slowly) change the internal energy of gas by adding heat or doing work:

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W, \tag{11.3}$$

where U is the specific internal energy of the matter, V is the specific volume it occupies, and $\mathrm{d}Q$ is some amount of heat added to it.

- The work done is to contract or expand it, so $\mathrm{d}W = -P\mathrm{d}V$.
- The more proper form for our use is

$$\mathrm{d}Q = \mathrm{d}U + P\mathrm{d}V. \tag{11.4}$$

This heat partly changes the internal energy of the matter and also potentially changes the volume.

- Keeping the volume constant the first law of thermodynamics becomes

$$c_V = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_V = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{3}{2} \frac{k_B}{\mu m_u} = \frac{3}{2} \frac{R}{\mu}. \tag{11.5}$$

This is the specific heat at constant volume.

- Now consider how to arrive at an expression for constant pressure. Rewrite the first law

$$\mathrm{d}Q = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - V\mathrm{d}P = \mathrm{d}U - V\mathrm{d}P + \mathrm{d}(PV), \tag{11.6}$$

$$\mathrm{d}(PV) = \mathrm{d}(Nk_\mathrm{B}T) = \frac{k_\mathrm{B}}{\mu m_u}\mathrm{d}T, \tag{11.7}$$

remembering that $N = nV = n/\rho = \rho/(\mu m_u \rho) = 1/\mu m_u$.

- Then

$$\mathrm{d}Q = \mathrm{d}U - V\mathrm{d}P + \frac{k_\mathrm{B}}{\mu m_p}\mathrm{d}T = \frac{5}{2}\frac{k_\mathrm{B}}{\mu m_u}\mathrm{d}T - V\mathrm{d}P, \tag{11.8}$$

by using Equation (11.2).

- Therefore the specific heat at constant pressure is

$$c_P = \frac{5}{2}\frac{k_\mathrm{B}}{\mu m_u} = \frac{5}{2}\frac{R}{\mu}.. \tag{11.9}$$

Note that $c_P - c_V = R/\mu$.

- Note also the ratio of specific heats, $\gamma = c_P/c_V$, which for an ideal gas $\gamma = 5/3$ since the specific heats are constants.

11.2 Adiabatic process

- An **adiabatic process** is one in which no heat is added to the gas ($\mathrm{d}Q = 0$).
- In this special case, we can find expressions relating changes in P and V. Using the above expressions we can show

$$c_V\left(\frac{\mathrm{d}P}{P} + \frac{\mathrm{d}V}{V}\right) = -\frac{k_\mathrm{B}}{\mu m_p}\frac{\mathrm{d}V}{V} = (c_V - c_P)\frac{\mathrm{d}V}{V}. \tag{11.10}$$

- Finally we see that

$$\frac{\mathrm{d}P}{P} = -\gamma\frac{\mathrm{d}V}{V} = \gamma\frac{\mathrm{d}\rho}{\rho} = -\frac{\gamma}{1-\gamma}\frac{\mathrm{d}T}{T}. \tag{11.11}$$

- Since γ is constant in this case, such equations can be readily integrated to yield relations such as $PV^\gamma = \mathrm{const}$.
- Using the ideal gas law we can also write (just in terms of P, T, and V):

$$\left(\frac{\partial \ln P}{\partial \ln V}\right)_s = -\gamma \equiv -\Gamma_1 \tag{11.12}$$

$$\left(\frac{\partial \ln P}{\partial \ln \rho}\right)_s = \gamma \equiv \Gamma_1 \tag{11.13}$$

$$\left(\frac{\partial \ln P}{\partial \ln T}\right)_s = \frac{\gamma}{\gamma - 1} \equiv \frac{\Gamma_2}{\Gamma_2 - 1} \tag{11.14}$$

$$\left(\frac{\partial \ln T}{\partial \ln V}\right)_s = 1 - \gamma \equiv 1 - \Gamma_3. \tag{11.15}$$

$$\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_s = \gamma - 1 \equiv \Gamma_3 - 1. \tag{11.16}$$

- The s means adiabatic, or at constant entropy, where $\mathrm{d}Q = T\mathrm{d}S$.
- The connection between Eq. (11.12) and (11.13) is clear from the specific volume definition. Similarly for Eq. (11.15) and (11.16).

EXAMPLE PROBLEM 11.1: Derive the 2 equations (11.10) and (11.11).

Answer: Begin with Equation (11.7) rewritten here:

$$P\mathrm{d}V + V\mathrm{d}P = \frac{k_\mathrm{B}}{\mu m_p}\mathrm{d}T.$$

For adiabatic processes, the first law gives us that

$$c_V\mathrm{d}T = -P\mathrm{d}V,$$

so that we have

$$P\mathrm{d}V + V\mathrm{d}P = -\frac{k_\mathrm{B}}{\mu m_p}\frac{1}{c_V}P\mathrm{d}V.$$

Now divide through by PV and recall the relationship between the 2 specific heats to find

$$c_V\left(\frac{\mathrm{d}V}{V} + \frac{\mathrm{d}P}{P}\right) = (c_V - c_P)\frac{\mathrm{d}V}{V}.$$

Collecting terms gives

$$\frac{\mathrm{d}P}{P} = -\gamma\frac{\mathrm{d}V}{V} = \gamma\frac{\mathrm{d}\rho}{\rho}.$$

The term with the log is just a different way of rewriting the above equation, such as

$$\frac{\mathrm{d}\ln P}{\mathrm{d}\ln \rho} = \gamma.$$

To get the term with P and T, remember that with the ideal gas law, $P \sim \rho T$ (forget the constants n or k; they'll drop out in the end). So using the product rule,

$$\mathrm{d}P = T\mathrm{d}\rho + \rho\mathrm{d}T,$$

and then divide by P, multiply by γ, and use the ideal gas law. We find

$$\gamma\frac{\mathrm{d}\rho}{\rho} = \gamma\left(\frac{\mathrm{d}P}{P} - \frac{\mathrm{d}T}{T}\right),$$

and collecting terms can then give you Equation (11.14). Using the ideal gas law again with T and ρ will give you Equation (11.15).