Derivation of Maxwell's Mechanical Formula of Heat Capacity Ratio

Hejie Lin[1] and Tsung-Wu Lin[2]

[1]*Department of Mechanical Engineering,*
Oakland University, Rochester Hills, Michigan, USA

[2]*Department of Civil Engineering,*
National Taiwan University, Taipei, Taiwan

Abstract

The ratio of heat capacity is an absolute necessity for expressing physical properties in various fields including chemistry, physics, thermal dynamics, fluid dynamics, and acoustics. The ratio of heat capacity is defined as the heat capacity at constant pressure (Cp) divided by the heat capacity at constant volume (Cv). James Clerk Maxwell derived a formula for heat capacity ratio in terms of translational and rotational kinetic energies in his paper "On the Dynamical Theory of Gases" published in 1867. A similar derivation of the formula of heat capacity ratio is presented in this note.

Keywords: ratio of heat capacity, heat capacity ratio, ratio of specific heat, specific heat ratio, heat capacity at constant pressure, heat capacity at constant volume, kinetic theory of gases, kinetic energy, collision simulation of particles, James Clerk Maxwell.

Introduction

The ratio of heat capacity is defined as the heat capacity at constant pressure (Cp) divided by the heat capacity at constant volume (Cv). Based on the equipartition theorem, the ratio of heat capacity (γ) of an ideal gas is related to the number (f) of translational degrees of freedom (DOF) of the colliding motion of gases as following.

$$\gamma = \frac{f+2}{f} \tag{1}$$

where, for a monatomic gas, the number (f) of degrees of freedom (DOF) is 3 and the ratio of heat capacity (γ) is $\frac{5}{3}$. And, for a diatomic gas, the number (f) of degrees of freedom (DOF) is 5 and the ratio of heat capacity (γ) is $\frac{7}{5}$.

James Clerk Maxwell derived a formula for the ratio of heat capacity in terms of the translational and rotational kinetic energies in "On the Dynamical Theory of Gases" [1] in 1867 as (where α is denoted as β in Eq. 114 of Maxwell's paper)

$$\gamma = \frac{3\alpha+2}{3\alpha} \tag{2}$$

where α is defined as the ratio of total kinetic energy to the translational kinetic energy as

$$\alpha \equiv \frac{E_t+E_r}{E_t} \tag{3}$$

Where E_t is the translational kinetic energy, E_r is the rotational kinetic energy. For monatomic gases with a negligible rotational kinetic energy, $E_r = 0$, $\alpha = 1$, and $\gamma = \frac{5}{3}$. For diatomic gases with $E_r = \frac{2}{3}E_t$, $\alpha = \frac{5}{3}$, and $\gamma = \frac{7}{5}$. A similar derivation of the same mechanical formula of heat capacity ratio is presented in this note.

The derivation is based on the definition of the ratio of the heat capacity as
$$\gamma \equiv \frac{C_P}{C_V} \tag{4}$$
Where C_P is the heat capacity at constant pressure, C_V is the heat capacity at constant volume. The formulas shown below for the heat capacity at constant pressure (C_P) and the heat capacity at constant volume (C_V) will be derived.
$$C_V = \frac{3}{2}\alpha nR \tag{5}$$
$$C_P = \frac{3}{2}\alpha nR + nR \tag{6}$$
where, n is the number of moles and R is the ideal gas constant. Note that Maxwell used β instead α with the same meaning in his formulation.

Setup for the Derivation

The three equations below (Eqs.7-9) will be used to derive the formulas for the ratio of heat capacity (Eq.2), the heat capacity at constant volume (Eq.5), and the heat capacity at constant pressure (Eq.6). The following three equations are the foundation of the kinetic theory of gases.
$$E_t = \frac{1}{2}nN_A mv^2 \tag{7}$$
$$E_r = \frac{1}{2}nN_A I\omega^2 \tag{8}$$
$$PV = \frac{1}{3}nN_A mv^2 \tag{9}$$

where E_t is the translational kinetic energy, E_r is the rotational (spin) kinetic energy, n is the number of moles, N_A is Avogadro's number, m is the mass of one molecule, I is the mass moment of inertia of one molecule, v is the translational RMS velocity, ω is the angular RMS velocity, P is the pressure, V is the volume. Combining Eq.7 and Eq.9, the translational kinetic energy (E_t) can be related to the pressure (P) as
$$E_t = \frac{3}{2}PV \tag{10}$$
The definition of the heat capacity at constant volume (C_V) and the heat capacity at constant pressure (C_P) are defined as the heat input (ΔQ) per unit temperature increase (ΔT) at constant volume and at constant pressure respectively as
$$C_V \equiv \left.\frac{\Delta Q}{\Delta T}\right|_V \tag{11}$$
$$C_P \equiv \left.\frac{\Delta Q}{\Delta T}\right|_P \tag{12}$$
Temperature (T) is not presented in the formula (Eqs. 4-6) of heat capacity ratio, but it is used for the definition of heat capacity at constant volume (C_V) and the heat capacity at constant pressure (C_P) as in the two equations above. To bring temperature (T) into the derivation, the general gas equation is used to relate temperature to pressure as
$$PV = nRT \tag{13}$$
where T is temperature, n is number of moles, R is the ideal gas constant.

A new variable α is introduced as the ratio of total kinetic energy $(E_t + E_r)$ to the translational kinetic energy (E_t) as

$$\alpha \equiv \frac{E_t + E_r}{E_t} \tag{14}$$

This new variable α will be used to represent total kinetic energy $(E_t + E_r)$ with the translational kinetic energy (E_t) as: $E_t + E_r = \alpha E_t$.

Derivation of the Ratio of Heat Capacity

The ratio of heat capacity (γ) is derived from its definition as C_p divided by C_v as shown in Eq.4.
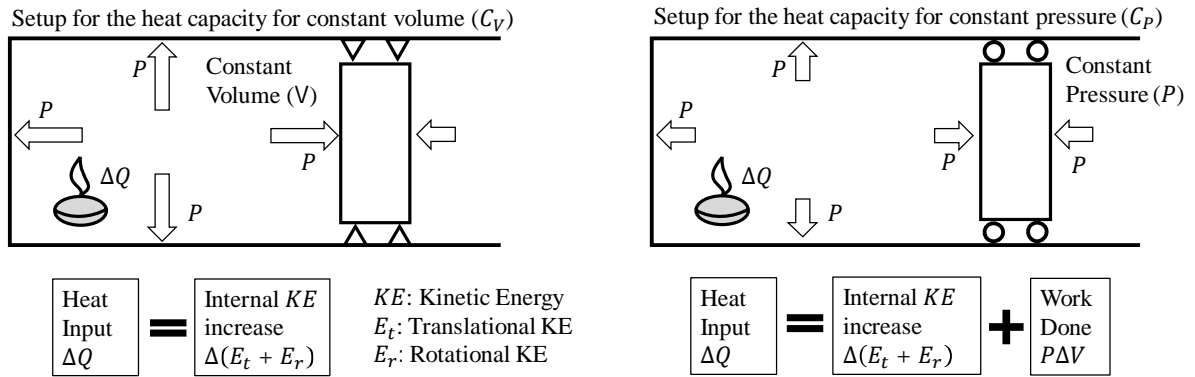

Figure 1. Setup for the Heat Capacities

For the heat capacity at constant volume (C_V) in an adiabatic process, all heat input (ΔQ) transfers to the total kinetic energy increment, $\Delta(E_t + E_r)$ which is a combination of the translational kinetic energy increment ΔE_t and the rotational kinetic energy increment ΔE_r as

$$\Delta Q = \Delta(E_t + E_r) \tag{15}$$

Substituting the equation above (Eq.15) into the definition of heat capacity at constant volume (Eq.11) gives

$$C_V \equiv \left.\frac{\Delta Q}{\Delta T}\right|_V = \frac{\Delta(E_t + E_r)}{\Delta T} \tag{16}$$

For the heat capacity at constant pressure (C_P) in an adiabatic process, the heat input (ΔQ) transfers to the total kinetic energy increment, $\Delta(E_t + E_r)$ and the work done $(P\Delta V)$ in the system. Note that, since P is constant, $P\Delta V$ can be replaced by $\Delta(PV)$.

$$\Delta Q = \Delta(E_t + E_r) + P\Delta V = \Delta(E_t + E_r) + \Delta(PV) \tag{17}$$

Substituting the equation above (Eq.17) into the definition of heat capacity at constant pressure (Eq.12) gives

$$C_P \equiv \left.\frac{\Delta Q}{\Delta T}\right|_P = \frac{\Delta(E_t + E_r) + \Delta(PV)}{\Delta T} \tag{18}$$

With the new variable (α), the total kinetic energy $(E_t + E_r)$ can be replaced by the translational kinetic energy (αE_t). Following this approach, substituting Eq.14 into Eq.16 and Eq.18 gives

$$C_V \equiv \left.\frac{\Delta Q}{\Delta T}\right|_V = \frac{\Delta(E_t + E_r)}{\Delta T} = \frac{\Delta(\alpha E_t)}{\Delta T} \tag{19}$$

$$C_P \equiv \left.\frac{\Delta Q}{\Delta T}\right|_P = \frac{\Delta(E_t + E_r) + \Delta(PV)}{\Delta T} = \frac{\Delta(\alpha E_t) + \Delta(PV)}{\Delta T} \tag{20}$$

3

Substituting C_V and C_P (Eq.19 and Eq.20 respectively) into the definition of the ratio of heat capacity (Eq.4) and canceling out temperature (ΔT) yields

$$\gamma \equiv \frac{C_P}{C_V} = \frac{\frac{\Delta(\alpha E_t)+\Delta(PV)}{\Delta T}}{\frac{\Delta(\alpha E_t)}{\Delta T}} = \frac{\Delta(\alpha E_t)+\Delta(PV)}{\Delta(\alpha E_t)} \tag{21}$$

Next, replacing the translational kinetic energy (E_t) with $\frac{3}{2}PV$ by substituting Eq.10 into Eq.21 gives the formula of the ratio of heat capacity as

$$\gamma \equiv \frac{C_P}{C_V} = \frac{\Delta(\alpha E_t)+\Delta(PV)}{\Delta(\alpha E_t)} = \frac{\Delta\left(\alpha\frac{3}{2}PV\right)+\Delta(PV)}{\Delta\left(\alpha\frac{3}{2}PV\right)} = \frac{\alpha\frac{3}{2}\Delta(PV)+\Delta(PV)}{\alpha\frac{3}{2}\Delta(PV)} = \frac{3\alpha+2}{3\alpha} \tag{22}$$

Note that α, as defined in Eq. 3, is the ratio of "total kinetic energy" to "translational kinetic energy" and should be a constant assuming that this ratio is not affected by pressure or volume change. For monatomic gases with a negligible rotational kinetic energy, $E_r = 0$, $\alpha = 1$, and $\gamma = \frac{5}{3}$. For diatomic gases with $E_r = \frac{2}{3}E_t$, $\alpha = \frac{5}{3}$, and $\gamma = \frac{7}{5}$. The ratio of heat capacity calculated with the proposed formula match the conventional values for both monatomic and diatomic gases. This simple formula is more comprehensible than the conventional formula (Eq.1) because this formula provides information about the kinetic properties of gases and allows us to better model the dynamic behavior of molecules.
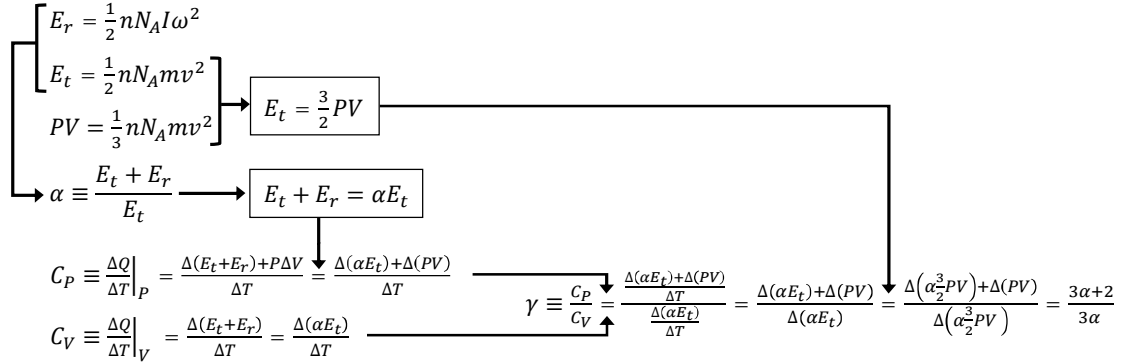

Figure 2. Derivation of the Ratio of Heat Capacity

In addition, heat capacity at constant volume (C_V) can be formulated by replacing translational kinetic energy (E_t) with ($\frac{3}{2}nRT$) by substituting Eqs.10 and 13 into Eq.19 to get

$$C_V \equiv \left.\frac{\Delta Q}{\Delta T}\right|_V = \frac{\Delta(E_t+E_r)}{\Delta T} = \frac{\Delta(\alpha E_t)}{\Delta T} = \frac{\Delta\left(\alpha\frac{3}{2}nRT\right)}{\Delta T} = \frac{\alpha\frac{3}{2}nR\Delta(T)}{\Delta T} = \frac{3\alpha}{2}nR \tag{23}$$

Also, heat capacity at constant pressure (C_P) can be formulated by replacing translational kinetic energy (E_t) with ($\frac{3}{2}nRT$) by substituting Eqs.10 and 13 into Eq.20 and then replacing PV with nRT (Eq.13) to get

$$C_P \equiv \left.\frac{\Delta Q}{\Delta T}\right|_P = \frac{\Delta(E_t+E_r)+\Delta(PV)}{\Delta T} = \frac{\Delta(\alpha E_t)+\Delta(PV)}{\Delta T} = \frac{\Delta\left(\alpha\frac{3}{2}nRT\right)+\Delta(nRT)}{\Delta T} = \frac{3\alpha+2}{2}nR \tag{24}$$

Note that both heat capacity at constant volume (C_V) and heat capacity at constant pressure (C_P) are functions of the new variable α which was defined in Eq.3. For monatomic gases with a negligible rotational kinetic energy, $E_r = 0$, $\alpha = 1$, $C_V = \frac{3}{2}nR$, and $C_P = \frac{5}{2}nR$. For diatomic gases with $E_r =$

$\frac{2}{3}E_t$, $\alpha = \frac{5}{3}$, and $C_V = \frac{5}{2}nR$, and $C_P = \frac{7}{2}nR$. The values of both C_V and C_P calculated with the proposed formulas match the conventional values for monatomic and diatomic gases.

$$
\begin{aligned}
&\begin{cases}
E_r = \frac{1}{2}nN_A I\omega^2 \\
\begin{cases}
E_t = \frac{1}{2}nN_A mv^2 \\
PV = \frac{1}{3}nN_A mv^2 \\
PV = nRT
\end{cases}
\rightarrow \boxed{E_t = \frac{3}{2}PV = \frac{3}{2}nRT}
\end{cases}\\
&\alpha \equiv \frac{E_t + E_r}{E_t} \longrightarrow \boxed{E_t + E_r = \alpha E_t}\\
&C_P \equiv \left.\frac{\Delta Q}{\Delta T}\right|_P = \frac{\Delta(E_t+E_r)+P\Delta V}{\Delta T} = \frac{\Delta(\alpha E_t)+\Delta(PV)}{\Delta T} = \frac{\Delta\left(\alpha\frac{3}{2}nRT\right)+\Delta(nRT)}{\Delta T} = \frac{3\alpha+2}{2}nR\\
&C_V \equiv \left.\frac{\Delta Q}{\Delta T}\right|_V = \frac{\Delta(E_t+E_r)}{\Delta T} = \frac{\Delta(\alpha E_t)}{\Delta T} = \frac{\Delta\left(\alpha\frac{3}{2}nRT\right)}{\Delta T} = \frac{3\alpha}{2}nR
\end{aligned}
$$

Figure 3. The Derivation of Heat Capacities

It is worth noting that the new formula (Eq.2) remains valid even when the elastic strain energy (E_s) caused by internal relative vibrations between atoms is considered. It can be shown that the derivation, Eqs.14-22, remains valid even after the total kinetic energy ($E_t + E_r$) in Eq.15 is replaced by a combination of the total kinetic energy and the elastic strain energy ($E_t + E_r + E_s$). Also note that for low temperatures, vibrational energies are negligible when comparing to kinetic energies.

Conclusion

James Clerk Maxwell derived the mechanical formula of heat capacity ratio as a function of the translational and rotational kinetic energies in his paper "On the Dynamical Theory of Gases" published in 1867 [1]. A similar derivation of a Maxwell's mechanical formula for the ratio of heat capacity is presented in this note. The small internal vibrational energy between atoms is neglected in the formula. This mechanical formula not only provides a comprehensive explanation of how the kinetic energy affect the ratio of the heat capacity but also allows for the determination of the ratio of heat capacity from the mechanic analysis such as the numerical collision simulation of particles.

Reference

1. Maxwell, J.C., (1867), "On the Dynamical Theory of Gases", *Philosophical Transactions of the Royal Society of London*, Vol. 157, pp.49-88.