

Physics 415 - Lecture 11: Ideal Gas Applications

February 14, 2025

Summary

- Equilibrium macro system: $dE = TdS - pdV$, with $E = E(S, V)$.
- First Law of Thermo: $dE = dQ - dW$.
- For quasi-static process: $dW = pdV$ and $dQ = TdS$.
- Heat Capacity: $dQ|_x = C_x dT$. C_x = heat capacity at constant x .
- $C_x = T \left(\frac{\partial S}{\partial T} \right)_x$. Allows finding entropy change at fixed x :

$$\Delta S = S(x, T_2) - S(x, T_1) = \int_{T_1}^{T_2} dT \frac{C_x(T)}{T}$$

(Measuring $C_x(T)$ determines changes in S).

Ideal Gas

Definition: A gas in which interactions between particles are so weak they can be neglected.

- Usually achieved in the limit of dilute gases, where particles are almost always far apart, so interaction forces are small.

Ideal gas equation of state:

$$pV = NT$$

(where T is in energy units). Alternatively, using T in Kelvin (degrees):

$$pV = Nk_B T$$

We can also write this in terms of moles: $N = \nu N_A$, where $\nu = \#$ moles and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ (Avogadro's number).

$$pV = \nu(N_A k_B) T$$

Let $R = N_A k_B \approx 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ be the ideal gas constant.

$$pV = \nu RT$$

We previously derived the equation of state $pV = NT$ from the microscopic calculation $\Omega(E, V) \propto V^N E^{3N/2}$ for a classical monatomic ideal gas.

Energy of Ideal Gas

Earlier, we showed from microscopic considerations that $E = \frac{3}{2}NT$ (monatomic). As a first application of macroscopic thermodynamics, let's re-derive the result that E depends only on T , i.e., $E = E(T)$, independent of V , using only the equation of state $pV = NT$ and general thermodynamic relations.

Take (T, V) as independent variables, so $E = E(T, V)$ in general.

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

Also, from the fundamental relation $dE = TdS - pdV$, we can write $dS = \frac{1}{T}dE + \frac{p}{T}dV$. Considering $S = S(T, V)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Substitute dE into the expression for dS :

$$dS = \frac{1}{T} \left[\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \right] + \frac{p}{T}dV$$

$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_T + \frac{p}{T} \right] dV$$

Comparing the coefficients of dT and dV with the expression for dS in terms of T, V :

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_T + \frac{p}{T}$$

Now use the equality of mixed second partial derivatives: $\frac{\partial}{\partial V} \left[\left(\frac{\partial S}{\partial T}\right)_V \right]_T = \frac{\partial}{\partial T} \left[\left(\frac{\partial S}{\partial V}\right)_T \right]_V$.

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial S}{\partial T}\right)_V \right]_T = \frac{\partial}{\partial T} \left[\left(\frac{\partial S}{\partial V}\right)_T \right]_V$$

$$\frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V \right]_T = \frac{\partial}{\partial T} \left[\frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_T + \frac{p}{T} \right]_V$$

The derivative $\partial/\partial V$ acts on $(\partial E/\partial T)_V$. The derivative $\partial/\partial T$ acts on $1/T$, $(\partial E/\partial V)_T$, and p/T .

$$\frac{1}{T} \frac{\partial}{\partial V} \left[\left(\frac{\partial E}{\partial T}\right)_V \right]_T = -\frac{1}{T^2} \left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T} \frac{\partial}{\partial T} \left[\left(\frac{\partial E}{\partial V}\right)_T \right]_V + \frac{\partial}{\partial T} \left(\frac{p}{T} \right)_V$$

Since mixed partials of E are equal, the terms with $\partial^2 E$ cancel:

$$0 = -\frac{1}{T^2} \left(\frac{\partial E}{\partial V}\right)_T + \frac{\partial}{\partial T} \left(\frac{p}{T} \right)_V$$

$$\implies \left(\frac{\partial E}{\partial V}\right)_T = T^2 \frac{\partial}{\partial T} \left(\frac{p}{T} \right)_V$$

This is a general thermodynamic result. Now, apply it to an ideal gas. From $pV = NT$, we have $p/T = N/V$.

$$\frac{\partial}{\partial T} \left(\frac{p}{T} \right)_V = \frac{\partial}{\partial T} \left(\frac{N}{V} \right)_V = 0$$

(since N/V is independent of T at constant V).

$$\implies \left(\frac{\partial E}{\partial V} \right)_T = 0$$

This proves from macroscopic thermodynamics (using the ideal gas law) that the internal energy E of an ideal gas is independent of volume V ; it depends only on temperature T .

$$E = E(T) \quad (\text{Ideal Gas})$$

Heat Capacity / Specific Heat of Ideal Gas

Define molar specific heat $c_x = C_x/\nu$ (heat capacity per mole). C_x is extensive, c_x is intensive.

Constant Volume: $dQ|_V = C_V dT = \nu c_v dT$. From First Law, $dQ|_V = dE|_V + dW|_V$. Since $dV = 0$, $dW|_V = 0$. $dQ|_V = dE|_V$. Since $E = E(T, V)$ generally, $dE = (\partial E/\partial T)_V dT + (\partial E/\partial V)_T dV$. $dE|_V = (\partial E/\partial T)_V dT$. $\implies \nu c_v dT = (\partial E/\partial T)_V dT$.

$$c_v = \frac{1}{\nu} \left(\frac{\partial E}{\partial T} \right)_V \quad (\text{General result})$$

Note: Since stability requires T to increase with E (usually), $\partial E/\partial T > 0$, so $c_v > 0$.

For an ideal gas, $E = E(T)$ only. $\implies (\partial E/\partial T)_V = dE/dT$.

$$dE = \nu c_v dT \quad (\text{Ideal Gas})$$

This means for an ideal gas, the change in energy depends only on the temperature change, regardless of the process.

Constant Pressure: $dQ|_p = C_p dT = \nu c_p dT$. First Law: $dQ|_p = dE|_p + dW|_p = dE|_p + p dV|_p$. For an ideal gas, $dE = \nu c_v dT$. From $pV = \nu RT$, at constant p : $p dV|_p = \nu R dT|_p$. Substitute these into the First Law expression for $dQ|_p$:

$$\nu c_p dT = (\nu c_v dT) + (\nu R dT)$$

$$\implies c_p = c_v + R \quad (\text{Ideal Gas})$$

Note: $C_p = C_V + \nu R$. Since $R > 0$, we have $c_p > c_v$. This is because at constant pressure, some added heat goes into doing expansion work ($p dV$), whereas at constant volume all added heat goes into increasing internal energy E .

Microscopic View (Monatomic Ideal Gas)

This is as much as we can say from macro theory alone (plus ideal gas law). We also know $c_v = c_v(T)$ since $E = E(T)$. To say more, we need microscopic input.

Recall: For classical monatomic ideal gas, $E = \frac{3}{2}NT = \frac{3}{2}\nu RT$. (Using T in Kelvin now for R). Using $c_v = \frac{1}{\nu}(\partial E/\partial T)_V = \frac{1}{\nu}(dE/dT)$:

$$c_v = \frac{1}{\nu} \frac{d}{dT} \left(\frac{3}{2} \nu RT \right) = \frac{3}{2} R$$

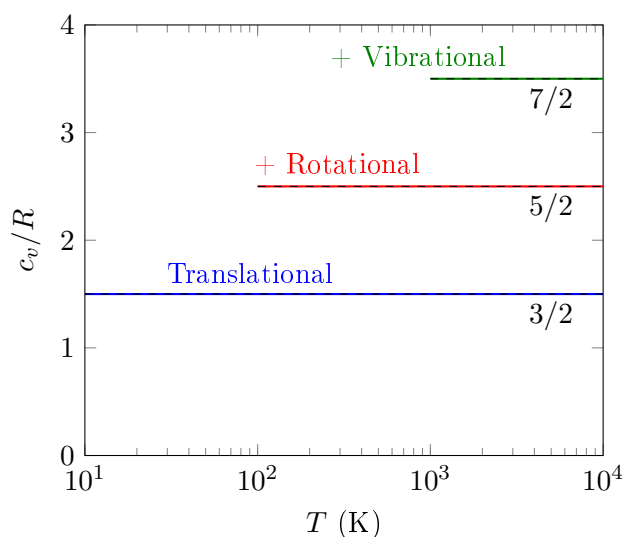
This is a constant, independent of T . Then $c_p = c_v + R = \frac{3}{2}R + R = \frac{5}{2}R$. The ratio of specific heats (adiabatic index) is:

$$\gamma \equiv \frac{c_p}{c_v} = \frac{5/2R}{3/2R} = \frac{5}{3}$$

(γ can be measured from the speed of sound in the gas).

For polyatomic gases, c_v is generally larger (due to rotational, vibrational DOF) and can depend on T as different DOFs become active. This dependence involves QM effects.

Molar Specific Heat c_v (Schematic for Diatomic Gas like H_2)



However, treating c_v (and hence γ) as constant is often a good approximation over broad ranges of T .

Processes in Ideal Gas

Investigate ideal gas subject to various processes.

Isothermal Expansion

Quasi-static process at constant T . From $pV = \nu RT = \text{const}$, we have $pV = \text{constant}$, or $p \propto 1/V$.

Adiabatic Expansion

Quasi-static process with no heat transfer ($dQ = 0$). Gas will change energy (\implies change T) by doing work. What is the relationship between p and V for such a process?

First Law: $dQ = dE + dW \implies 0 = dE + pdV$. For ideal gas, $dE = \nu c_v dT$. So, $\nu c_v dT + pdV = 0$.

We need to relate dT to p, V . Use equation of state $pV = \nu RT$. Differentiate: $pdV + Vdp = \nu R dT$. Solve for dT : $dT = \frac{pdV + Vdp}{\nu R}$. Substitute into the First Law equation:

$$\nu c_v \left(\frac{pdV + Vdp}{\nu R} \right) + pdV = 0$$

$$\frac{c_v}{R} (pdV + Vdp) + pdV = 0$$

$$\left(\frac{c_v}{R} + 1 \right) pdV + \frac{c_v}{R} Vdp = 0$$

Use $c_p = c_v + R \implies c_p/R = c_v/R + 1$.

$$\left(\frac{c_p}{R} \right) pdV + \left(\frac{c_v}{R} \right) Vdp = 0$$

Multiply by R :

$$c_p pdV + c_v Vdp = 0$$

Divide by $c_v p V$ (assuming $p, V, c_v \neq 0$):

$$\frac{c_p}{c_v} \frac{dV}{V} + \frac{dp}{p} = 0$$

Let $\gamma = c_p/c_v$.

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \quad (*)$$

Assuming γ is constant (which is true for monatomic ideal gas, and approx true for others over ranges of T), we can integrate (*):

$$\gamma \int \frac{dV}{V} + \int \frac{dp}{p} = \text{constant}$$

$$\gamma \ln V + \ln p = \text{constant}$$

$$\ln(pV^\gamma) = \text{constant}$$

$$\implies pV^\gamma = \text{constant} \quad (\text{Adiabatic process for Ideal Gas})$$

This relates p and V during a quasi-static adiabatic process. Using $pV = NT$, we can also write $TV^{\gamma-1} = \text{constant}$.

In an adiabatic process, $p \propto V^{-\gamma}$. Since $\gamma = c_p/c_v > 1$, pressure varies more rapidly with V than for an isothermal process where $p \propto V^{-1}$.