PHYS 301: Wrapping up Thermodynamics
The Third Law and Realistic Engines

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1 The Second Law (Recap)

Last time, we saw that the Second Law of Thermodynamics implies the Clausius inequality:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{1}$$

For an infinitesimal process, this is equivalently written as:

$$dS \geq \frac{\delta Q}{T} \tag{2}$$

- **Equality** holds for *reversible* processes (no entropy is created).
- **Strict Inequality** holds for *irreversible* processes (entropy is created).

The Second Law is fundamentally concerned with entropy *differences* (ΔS). However, to define an absolute entropy for a system, we need a baseline. The Third Law of Thermodynamics provides us with an absolute reference scale for entropy.

2 The Third Law of Thermodynamics

Statement: The entropy of a system approaches a constant value as the temperature approaches absolute zero. For a perfect crystal (or a unique quantum ground state), this constant is zero.

$$\lim_{T \to 0} S(T) = 0 \tag{3}$$

Unlike the other laws, there is no specific function of state associated directly with the Third Law. A more precise statistical mechanics formulation is: *"Ground state entropy should not grow extensively with N"*, where N is the number of particles in the system.

2.1 Microscopic Justification

In statistical mechanics, entropy is defined by the number of accessible microstates Ω:

$$S = k_B \ln \Omega \tag{4}$$

As $T \to 0$, quantum systems settle into their unique, lowest-energy ground state ($\Omega \to 1$).

- **Bosons:** As $T \to 0$, they form a Bose-Einstein Condensate. All particles collapse into the exact same lowest energy state, meaning there is a unique ground state ($\Omega = 1$). Thus, $S = k_B \ln 1 = 0$.
- **Fermions:** As $T \to 0$, they fill all available energy levels from the bottom up to the Fermi energy (forming a degenerate Fermi sea). There is only one way to perfectly pack these states ($\Omega = 1$). Thus, $S = k_B \ln 1 = 0$.

2.2 Consequence for Heat Capacity

A direct consequence of the Third Law is that the heat capacity must vanish as $T \to 0$. Recall the thermodynamic definition of entropy change at constant volume:

$$S(T) - S(0) = \int_0^T \frac{C_V(T')}{T'} dT' \tag{5}$$

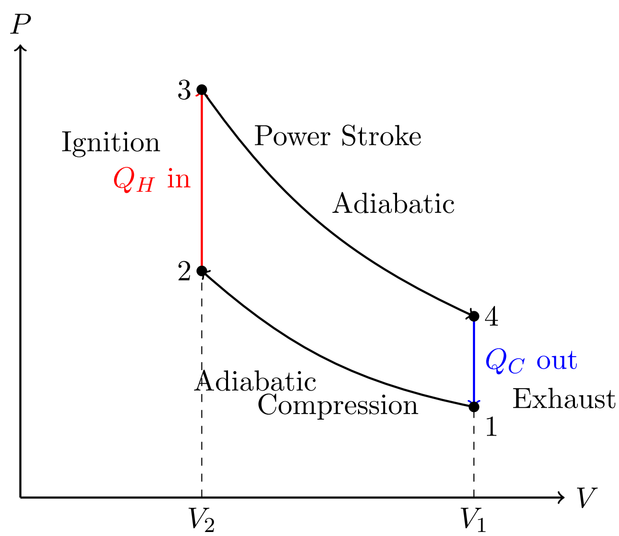
For the entropy $S(T)$ to be finite and approach zero smoothly as $T \to 0$, the integral must converge. This requires that $C_V \to 0$ as $T \to 0$. Specifically, C_V must be proportional to T^n where $n > 0$. For quantum systems in 3 dimensions, we typically have $n \geq 1$, so this bound is always satisfied.

3 Real Engines: The Otto Cycle

The Otto cycle is the idealized thermodynamic cycle that models the operation of a typical spark-ignition internal combustion engine (e.g., a gasoline engine).

We will model the working fluid as a fixed amount of an ideal **diatomic gas** (like atmospheric N_2 or O_2), where the internal energy is:

$$E = \frac{5}{2} N k_B T \tag{6}$$



3.1 Efficiency Derivation

The thermal efficiency η is defined as the net work done divided by the heat absorbed:

$$\eta_{\text{Otto}} \equiv \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \tag{7}$$

Step 1: Adiabatic Compression $(1 \to 2)$
Because the process is adiabatic, $\delta Q = 0$. The First Law gives $dE = -PdV$.

$$\frac{5}{2} N k_B dT = -\frac{N k_B T}{V} dV \tag{8}$$

Rearranging to separate variables:

$$\frac{5}{2} \int_{T_1}^{T_2} \frac{dT}{T} = -\int_{V_1}^{V_2} \frac{dV}{V} \tag{9}$$

$$\frac{5}{2} \ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right) \implies \left(\frac{T_2}{T_1}\right)^{5/2} = \frac{V_1}{V_2} \tag{10}$$

Solving for the temperature ratio, we find:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/5} \tag{11}$$

Note: The exponent $2/5$ *is exactly* $\gamma - 1$ *for a diatomic gas, where* $\gamma = C_P/C_V = 7/5$.

Step 2: Isochoric Heating ($2 \to 3$)

Because volume is constant ($dV = 0$), no work is done. By the First Law, $\Delta E = Q_H$:

$$Q_H = \frac{5}{2} N k_B (T_3 - T_2) \tag{12}$$

Step 3: Adiabatic Expansion ($3 \to 4$)

By identical logic for the power stroke, we find:

$$\frac{T_3}{T_4} = \left(\frac{V_1}{V_2}\right)^{2/5} \tag{13}$$

Therefore, $\frac{T_2}{T_1} = \frac{T_3}{T_4}$, which can be rearranged to $\frac{T_4}{T_1} = \frac{T_3}{T_2}$.

Step 4: Isochoric Cooling ($4 \to 1$)

Similarly, the heat rejected during the exhaust phase is:

$$Q_C = \frac{5}{2} N k_B (T_4 - T_1) \tag{14}$$

Step 5: Final Efficiency

Substitute the heats into the efficiency equation:

$$\eta_{\text{Otto}} = 1 - \frac{\frac{5}{2} N k_B (T_4 - T_1)}{\frac{5}{2} N k_B (T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{15}$$

Factor out T_1 from the numerator and T_2 from the denominator:

$$\eta_{\text{Otto}} = 1 - \frac{T_1 \left(\frac{T_4}{T_1} - 1\right)}{T_2 \left(\frac{T_3}{T_2} - 1\right)} \tag{16}$$

Since $\frac{T_4}{T_1} = \frac{T_3}{T_2}$, the bracketed terms cancel perfectly:

$$\boxed{\eta_{\text{Otto}} = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{V_2}{V_1}\right)^{2/5}} \tag{17}$$

The efficiency of the Otto cycle depends entirely on the geometric compression ratio ($r = V_1/V_2$) and the nature of the gas!