

Lecture 40

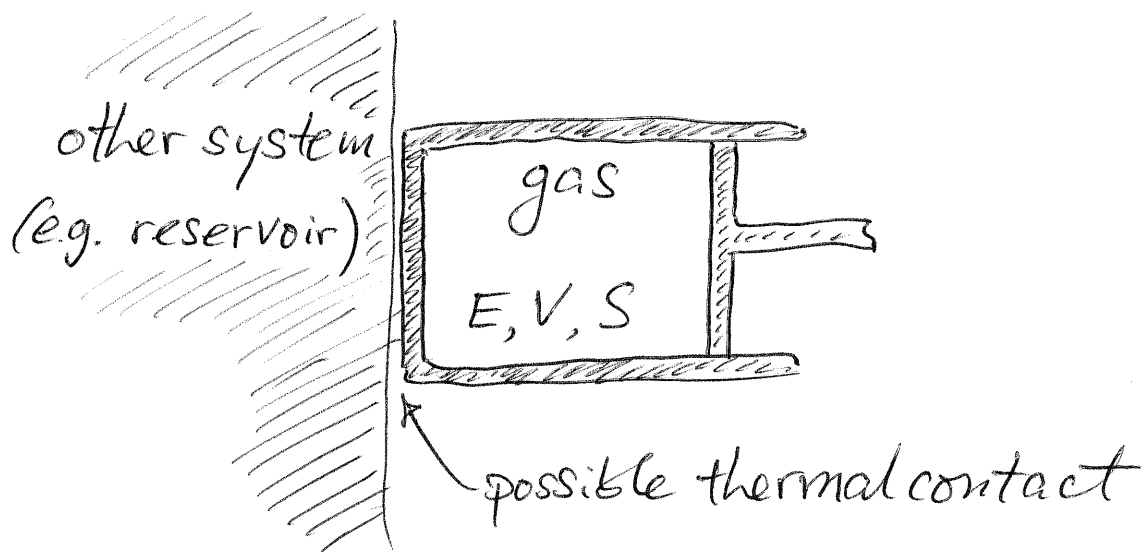
(40.1)

We will derive the ideal gas law

$$pV = k_B NT$$

in a way that brings together many of the key ideas in thermodynamics, in particular, the role played by entropy.

Thermodynamics distinguishes two ways that a system can change its energy. We will illustrate both for the case of a gas:



Two kinds of energy change:

(40.2)

work

- requires change in a macroscopic parameter, e.g. $\Delta V \neq 0$

- mechanical process,

$$W = \Delta E = -p \Delta V$$

- $\Delta S = 0$ "adiabatic"

heat

- macroscopic parameters are fixed, e.g. $\Delta V = 0$

- microscopic process,

$$Q = \Delta E = T \Delta S$$

- $\Delta S \neq 0$

Let's recall some things we worked out for gases, when viewed as

mechanical systems :

(40.3)

mono-atomic : $E(V) \propto V^{2/3}$

$$P(V) = -\frac{dE}{dV} \propto V^{5/3}$$

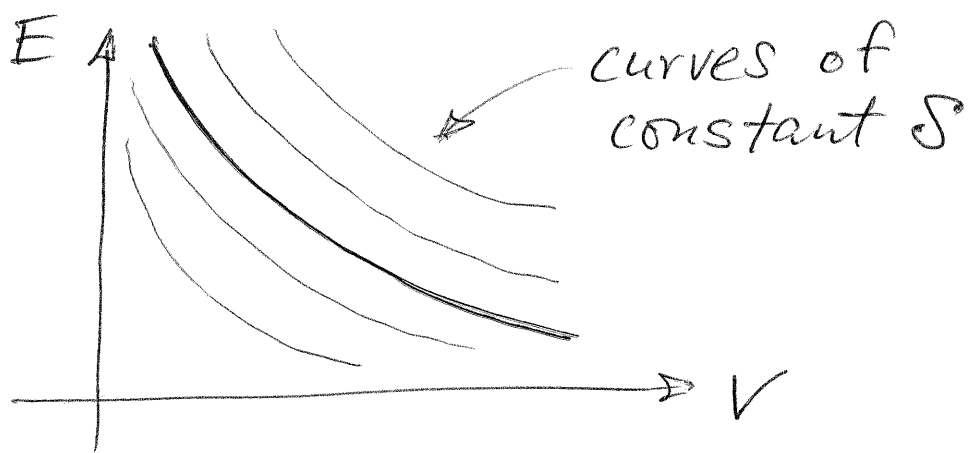
These hold when the volume is changed slowly and there is no other mechanism for transferring energy (thermal contact).

Later we calculated the entropy of the gas :

mono-atomic :

$$S(V, E) = k_B N \log(V E^{3/2}) + S_0$$

The rule $E \propto V^{2/3}$ is equivalent to $S = \text{constant}$.



(40.4)

If we stay on one of the curves of constant S and take the slope, we obtain the (negative) pressure.

In thermodynamics we define pressure always as

$$P = - \left. \frac{\partial E}{\partial V} \right|_S \rightarrow \text{"keep } S = \text{constant"}$$

The same three quantities (E, V, S) but in a different order, were used in our definition of temperature :

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V \rightarrow \text{"keep macroscopic parameters such as } V \text{ constant"}$$

To derive the ideal gas law we also need the bare-minimum definition of its properties. Here is probably the simplest mathematical statement of what it means to be an ideal gas:

$$Q_{ideal}(V, E) \propto V^N f(E)$$

$f(E)$ = an arbitrary function (different for mono-atomic, diatomic, etc.) but importantly, not a function of V

(40.6)

$$S_{\text{ideal}} = k_B \log \Omega_{\text{ideal}}$$

$$= k_B N \log V + k_B \log f(E) + S_0$$

The following derivative does not depend on the function f :

$$\left. \frac{\partial S_{\text{ideal}}}{\partial V} \right|_E = \frac{k_B N}{V}$$

Finally, we need a mathematical identity for partial derivatives that dates back to Euler :

$$\left. \frac{\partial E}{\partial V} \right|_S \cdot \left. \frac{\partial V}{\partial S} \right|_E \cdot \left. \frac{\partial S}{\partial E} \right|_V = -1$$

[Applies whenever one of three variables is a function of the other two.]

(40.7)

$$P = - \left. \frac{\partial E}{\partial V} \right|_S = + \frac{1}{\left. \frac{\partial V}{\partial S} \right|_E \cdot \left. \frac{\partial S}{\partial E} \right|_V}$$

Next, use the elementary calculus identity

$$\left. \frac{\partial V}{\partial S} \right|_E = \frac{1}{\left. \frac{\partial S}{\partial V} \right|_E}$$

to express the pressure as

$$P = \frac{\left. \frac{\partial S}{\partial V} \right|_E}{\left. \frac{\partial S}{\partial E} \right|_V} \xrightarrow{\text{Ideal}} \frac{k_B N}{V} = \frac{1}{\underset{T}{\left. \frac{\partial E}{\partial S} \right|_V}}$$

$$\Rightarrow PV = k_B N T$$