The definition of pressure above agrees with the mechanical notion that pressure is force per unit area. Consider a gas confined in the chamber of a piston.

If the chamber is thermally insulating so no heat is added or taken out, and the gas is allowed to expand by moving the piston wall a distance $\Delta x$, then the work done by the gas on the wall is $F_{\text{total}} \Delta x = \phi A \Delta x = p \Delta V$ where $\Delta V = A \Delta x$ is the change in volume.

Since the gas is not heated (chamber thermally insulating) and it does mechanical work, the energy of the gas must decrease by the work done.

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

$$\Rightarrow \ \left( \frac{\partial E}{\partial V} \right)_{S,N} = -p \text{ as defined above}$$

\[ \uparrow \text{constant S means no heat is exchanged with gas and outside world.} \]
when \( dN = 0 \), as is the case for a gas confined to a box,

\[
dE = TdS - pdV
\]

Since we just showed that \( pdV \) is the mechanical work done by the gas, then

\[ TdS = dQ \] is the heat absorbed by the gas

heat absorbed \( \Rightarrow \) entropy increases

---

From

\[
dE = TdS - pdV + \mu dN
\]

we have

\[
TdS = dE + pdV - \mu dN
\]

\[ \Rightarrow \]

\[
ds = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN
\]

from which we have

\[
\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T}
\]

\[
\left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{p}{T}
\]

\[
\left( \frac{\partial S}{\partial N} \right)_{E,V} = \frac{-\mu}{T}
\]
Thermal Equilibrium

\[ E = E_1 + E_2 \]
\[ S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \]

immoveable, impenetrable, insulating wall

thermally insulating wall is often called an "adiabatic" wall — no heat can flow across it.
(A "diathermal" wall is a wall that can conduct heat.)

As long as the wall is in place, the two subsystems cannot exchange energy, volume, or particles.

1) Suppose now that the wall is changed to a thermally conducting one, so the systems can exchange energy? What will be the new \( E_1 \) and \( E_2 \) after the system equilibrates?

\[ E = E_1 + E_2 \] is a fixed constant by conservation of energy

But \( E_1 \) and \( E_2 = E - E_1 \) can change,
\( E = E_1 + E_2 \) \quad \text{fixed} \quad \Rightarrow \quad \text{d}E = \text{d}E_1 + \text{d}E_2 = 0

So \( \text{d}E_2 = -\text{d}E_1 \)

Change in entropy \( S = S_1 + S_2 \) as system equilibrates is then

\[
\text{d}s = \left( \frac{\partial S_1}{\partial E_1} \right)_{V,N_1} \text{d}E_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{V,N_2} \text{d}E_2
\]

\[
= \frac{1}{T_1} \text{d}E_1 + \frac{1}{T_2} \text{d}E_2
\]

\[
= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{d}E_1 \quad \text{as} \quad \text{d}E_2 = -\text{d}E_1
\]

Equilibrium is when \( S \) becomes maximum.

At the maximum, \( \text{d}S = 0 \), i.e., \( S \) will not change for small changes in \( E \).

\[
\text{d}S = 0 \quad \Rightarrow \quad \frac{T_1}{T_2}
\]

System is in equilibrium when the two sub-systems have the same temperature.

Note: \( \text{d}S = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{d}E_1 \) \Rightarrow If \( T_1 > T_2 \) then since system evolves so that \( \text{d}S > 0 \) always (entropy increases as one approaches equilibrium) \( \Rightarrow \text{d}E_1 < 0 \). So energy flows from \( 1 \) to \( 2 \) \& from higher \( T_1 \) to lower \( T_2 \). Agrees with our intuition about temperature that heat flows from hot to cold.
Mechanical Equilibrium

2) Now suppose the wall is thermally conducting AND it is allowed to slide so that volumes $V_1$ and $V_2$ can change.

Still the total volume $V = V_1 + V_2$ is fixed so $V_2 = V - V_1$ and $dV_2 = -dV_1$

We have

$E = E_1 + E_2$ fixed $\Rightarrow dE_2 = -dE_1$

$V = V_1 + V_2$ fixed $\Rightarrow dV_2 = -dV_1$

We will also assume that the wall moves slowly so that no energy is dissipated in friction of the moving wall
as system equilibrates the change in entropy is
\[ \dot{S} = \left( \frac{\partial S_1}{\partial E_1} \right)_{E_2 N_1} dE_1 + \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1 N_1} dV_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{E_2 N_2} dE_2 + \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2 N_2} dV_2 \]

\[ = \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 \]

\[ = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_2 \]

\[ \dot{S} = 0 \text{ at equilib } \Rightarrow T_1 = T_2 \]
\[ p_1 = p_2 \]

When volume can change, equilib is reached when pressure of separate subsystems are equal.

Chemical Equilibria

3) Now suppose wall becomes conducting, can slide, and is permeable to particles?

\[ E = E_1 + E_2 \Rightarrow \dot{E}_1 = -\dot{E}_2 \]
\[ V = V_1 + V_2 \Rightarrow \dot{V}_1 = -\dot{V}_2 \]
\[ N = N_1 + N_2 \Rightarrow \dot{N}_1 = -\dot{N}_2 \]

\[ \text{At number N fixed, but } N_1 \text{ and } N_2 = N - N_1 \text{ vary} \]

\[ \dot{S} = \left( \frac{\partial S_1}{\partial E_1} \right)_{E_2 N_1} dE_1 + \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1 N_1} dV_1 + \left( \frac{\partial S_1}{\partial N_1} \right)_{E_1 V_1} dN_1 \]

\[ + \left( \frac{\partial S_2}{\partial E_2} \right)_{E_2 N_2} dE_2 + \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2 N_2} dV_2 + \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2 V_2} dN_2 \]
\[
= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dN_1 - \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1
\]

\[ds = 0 \Rightarrow T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2\]

When particles can be exchanged, equilibrium is reached when the subsystems have equal chemical potentials.

The role of statistical mechanics is to calculate the entropy from the microscopic details of the system. Once the entropy is known, all thermodynamic properties follow.

**Convexity of the Entropy**

From postulate II we know \( S \) will be maximized whenever a constraint is removed. We can use this to show that \( S \) is a convex function of its variables. Consider a system that we conceptually split in half (no physical wall)

\[
\begin{array}{c|c|c|c|c|c}
\varepsilon + \Delta \varepsilon & \varepsilon - \Delta \varepsilon \\ \hline
N/2 & N/2 & N/2 & N/2
\end{array}
\]

in equal \( \Delta E = 0 \), as the two halves must have equal energy. But consider how the entropy changes if \( \Delta E \) is allowed to vary.
Return to a previous problem
another way to look at the problem of thermal + mechanical equilibrium

\[ N_1, N_2 \text{ fixed so we ignore them} \]

Initially wall is adiabatic and immoveable - subsystems are in equilibrium with energies and volumes \( E_1, V_1 \) on left, \( E_2, V_2 \) on right

Now wall is allowed to move ad to conduct heat

\[ E = E_1 + E_2 \text{ stays fixed } \Rightarrow E_2 = E - E_1 \]
\[ V = V_1 + V_2 \text{ stays fixed } \Rightarrow V_2 = V - V_1 \]

Total entropy is

\[ S = S_1(E_1,V_1) + S_2(E-E_1,V-V_1) \]

is maximized when system reaches equilibrium

\[ \Rightarrow \text{ equilibrium is when} \]

\[ 0 = \left( \frac{\partial S}{\partial E} \right)_{V_1} = \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1} + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2} \frac{\partial E_2}{\partial E_1} = \frac{1}{T_1} - \frac{1}{T_2} \]

\[ 0 = \left( \frac{\partial S}{\partial V} \right)_{E_1} = \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1} + \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2} \frac{\partial V_2}{\partial V_1} = \frac{p_1}{T_1} - \frac{p_2}{T_2} \]

\[ \Rightarrow T_1 = T_2 \text{ and } p_1 = p_2 \]
or more specifically, since $T$ and $p$ are functions of $E$ and $V$,

\[
\begin{align*}
T_1(E_1, V_1) &= T_2(E-E_1, V-V_1) \\
p_1(E, V) &= p_2(E-E_1, V-V_1)
\end{align*}
\]

above is two equations for the two unknowns $E_1$ and $V_1$. In principle, one can therefore solve them to find $E_1$ and $V_1$ (and hence $E_2 = E - E_1$, $V_2 = V - V_1$) of the new equilibrium state.

However, consider the same initial situation, but now the wall is made moveable but stays adiabatic, i.e., still no heat can be transported across the wall between the two subsystems. Since $dQ = TdS = 0$ (no heat flows through wall)

\[\Rightarrow \quad dS_1 = dS_2 = 0 \quad \text{total entropy of system cannot change}\]

\[
dS_1 = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_E dV_1 = 0
\]

\[
= \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 = 0
\]

\[\Rightarrow \quad dE_1 = -p_1 dV_1 \]

Similarly

\[dE_2 = -p_2 dV_2\]

Energy of each side can change only due to mechanical work done in moving the wall.
Total Energy is still conserved $\Rightarrow E = E_1 + E_2 = \text{fixed}$
$\Rightarrow \Delta E_2 = -\Delta E_1$

Total Volume is fixed $\Rightarrow V = V_1 + V_2 = \text{fixed}$
$\Rightarrow \Delta V_2 = -\Delta V_1$

$\begin{align*}
\Delta E_1 &= -p_1 \Delta V_1 \\
\Delta E_2 &= -p_2 \Delta V_2 \\
\Rightarrow -\Delta E_1 &= p_2 \Delta V_1 \\
\end{align*}$

$\therefore p_1(E_1, V_1) = p_2(E - E_1, V - V_1)$

In equilibrium, the pressures of the two subsystems must be equal so net force on the wall is zero.

But above is just one equation for two unknowns $E_1$ and $V_1$. Thermodynamics alone does not give us enough information to determine the new equilibrium state. I postulate of maximizing the entropy does not help here since total entropy does not change $\Delta S = \Delta S_1 + \Delta S_2 = 0$ when the wall is adiabatic.

The new equilibrium state will depend on details such as the viscosity of the gases in each subsystem. Viscosity is the mechanism by which the energy added to one subsystem via the mechanical work done by the wall goes into increasing the temperature of that gas. If the gases had no viscosity, the wall would just oscillate in single harmonic motion, and no equilibrium would ever be reached.
**Concavity of the Entropy**

Consider a container of gas conceptually divided into two equal halves (no physical wall).

If \( N \) and \( V \) are fixed to be the same on both sides, we expect the energy will be equal on both sides:

\[
S_{\text{total}} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N)
\]

Consider how \( S \) depends on \( E \). If \( S \) were not convex, a convex function of \( E \) (i.e., if \( \frac{d^2S}{dE^2} > 0 \)) then the system would be unstable as follows:

\[
\frac{1}{2} [S(E_0 + \Delta E) + S(E_0 - \Delta E)]
\]

If \( S(E) \) is not convex, then we have from above:

\[
S_{\text{total}} = 2S(E_0) < S(E_0 + \Delta E) + S(E_0 - \Delta E)
\]

Therefore, the total system would increase its entropy by sharing the LHS with \( E_0 - \Delta E \), and the RHS with \( E_0 + \Delta E \) — the system would not be stable with equal energies on both sides!
Since, by Postulate II, the system acts so as to maximize its entropy, we see that the system will be unstable if \( S(E) \) is not concave.

If \( S(E) \) is concave, i.e. \( \frac{d^2S}{dE^2} < 0 \), this does not happen.

\[
S(E_0) \rightarrow \frac{1}{2} [S(E_0 + \Delta E) + S(E_0 - \Delta E)]
\]

Now \( 2S(E_0) > S(E_0 + \Delta E) + S(E_0 - \Delta E) \)

The maximum total entropy state will be when both halves have equal energy \( E \).

\( \Rightarrow S(E) \) is concave.

By similar argument, \( S \) must be a concave function of all its variables.

\( d^2S < 0 \) concave concave.
Further consequences of $S$ being a 1st order homogeneous function:

$$S(E, V, N) = S(\lambda E, \lambda V, \lambda N)$$

$$\Rightarrow \frac{\partial E}{\partial S} (S, V, N) = E(\lambda S, \lambda V, \lambda N)$$

$E$ is also a 1st order homogeneous function. Differentiate with respect to $S$.

$$\Rightarrow \frac{\partial}{\partial S} \left( \frac{\partial E(S, V, N)}{\partial S} \right)_{\lambda, N} = \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda S)}_{\lambda V, \lambda N} \left( \frac{\partial (\lambda S)}{\partial S} \right)$$

$$\Rightarrow \lambda T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \lambda$$

$$T(S, V, N) = T(\lambda S, \lambda V, \lambda N)$$

Similarly, from $P = -\frac{\partial E}{\partial V} S, V$ and $\mu = \frac{\partial E}{\partial N} S, V$

we conclude

$$T(S, V, N) = T(\lambda S, \lambda V, \lambda N)$$

$$P(S, V, N) = P(\lambda S, \lambda V, \lambda N)$$

$$\mu(S, V, N) = \mu(\lambda S, \lambda V, \lambda N)$$

$T, P, \mu$ are homogeneous functions of 2nd order.

Let $\lambda = \frac{1}{\lambda}$, then

$$T(S, V, N) = T\left( \frac{S}{\lambda}, \frac{V}{\lambda}, 1 \right) = T(x, v)$$

$\{"equations of state"$}

$$P(S, V, N) = P\left( \frac{S}{\lambda}, \frac{V}{\lambda}, 1 \right) = P(x, v)$$

$$\mu(S, V, N) = \mu(\frac{S}{\lambda}, \frac{V}{\lambda}, 1) = \mu(x, v)$$