That the quadratic form is always negative implies that the determinant of the matrix must be positive.

\[
\frac{\partial^2 S}{\partial E^2} \frac{\partial^2 S}{\partial V^2} - \left( \frac{\partial^2 S}{\partial E \partial V} \right)^2 \geq 0
\]

Note: \[
\left( \frac{\partial^2 S}{\partial E^2} \right)_V = \frac{\partial}{\partial E} \left( \frac{1}{T} \right)_V = -\frac{1}{T^2} \left( \frac{\partial T}{\partial E} \right)_V = \frac{1}{T^2 C_V}
\]

So \[
\left( \frac{\partial^2 S}{\partial E^2} \right)_V \leq 0 \Rightarrow C_V \geq 0 \quad \text{specific heat is positive}
\]

Other Potentials

One can use the minimization principles of the other thermodynamic potentials, \( E, A, G, \) etc. to derive other stability criteria.

Energy

\( S \) is maximum \( \Rightarrow E \) is minimum

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

\[\Rightarrow E(S + \Delta S, V + \Delta V, N) + E(S - \Delta S, V - \Delta V, N) \geq 2E(S, V, N)\]

for \( \Delta V = 0 \) \hspace{2cm} \text{for} \ \Delta S = 0

\[
\left( \frac{\partial^2 E}{\partial S^2} \right)_V \left( \frac{\partial^2 E}{\partial V^2} \right)_S \geq 0 \quad \text{and} \quad \left( \frac{\partial^2 E}{\partial V \partial S} \right)_S = -\left( \frac{\partial P}{\partial V} \right)_S \geq 0
\]

and \[
\left( \frac{\partial^2 E}{\partial S^2} \right) \left( \frac{\partial^2 E}{\partial V^2} \right) - \left( \frac{\partial^2 E}{\partial S \partial V} \right)^2 \geq 0
\]

\[
\left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial P}{\partial V} \right)_S - \left( \frac{\partial T}{\partial V} \right)_S \geq 0
\]
\[ \text{using} \quad (\frac{\partial T}{\partial s})_v = \frac{T}{C_v} \quad \Rightarrow \quad (\frac{\partial P}{\partial V})_s = -\frac{1}{V k_s} \quad \Rightarrow \quad (\frac{\partial T}{\partial V})_s \]

we get

\[ \frac{T}{V C_v k_s} \gg (\frac{\partial T}{\partial V})_s \]
Helmholtz free energy

\[ A(T, V, N) = E - TS \]

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

\[ \left( \frac{\partial^2 A}{\partial T^2} \right)_{V, N} = -\left( \frac{\partial S}{\partial T} \right)_{V, N} \quad \left( \frac{\partial^2 E}{\partial S^2} \right)_{V, N} = \left( \frac{\partial T}{\partial S} \right)_{V, N} \]

hence \[ \left( \frac{\partial^2 A}{\partial T^2} \right)_{V, N} = -\frac{1}{\left( \frac{\partial^2 E}{\partial S^2} \right)_{V, N}} \]

Since \[ \left( \frac{\partial^2 E}{\partial S^2} \right)_{V, N} > 0 \Rightarrow \left( \frac{\partial^2 A}{\partial T^2} \right)_{V, N} < 0 \]

\[ E \text{ is convex in } S \Rightarrow A \text{ is concave in } T \]

Consider \[ \left( \frac{\partial^2 A}{\partial T^2} \right)_{V, N} = -\left( \frac{\partial S}{\partial T} \right)_{V, N} = -\frac{\partial V}{T} < 0 \]

\[ \left( \frac{\partial^2 A}{\partial V^2} \right)_{T, N} = -\left( \frac{\partial p}{\partial V} \right)_{T, N} \Rightarrow \frac{\partial V}{T} > 0 \]

regard \( p \) as \( p(S(T, V), V) \) hence \( p = -\frac{\partial E}{\partial S} \frac{1}{N} \)

\[ \Rightarrow \left( \frac{\partial p}{\partial V} \right)_T = \left( \frac{\partial p}{\partial V} \right)_S + \left( \frac{\partial p}{\partial S} \right)_V \left( \frac{\partial S}{\partial V} \right)_T \]

Now \[ \left( \frac{\partial S}{\partial V} \right)_T = -\frac{\partial^2 A}{\partial T^2 V} = \left( \frac{\partial p}{\partial T} \right)_V = \frac{\partial p}{\partial S} \left( \frac{\partial T}{\partial S} \right)_V \]
\[ \frac{\partial p}{\partial V} \bigg|_T = \left( \frac{\partial p}{\partial V} \right) \bigg|_S + \left( \frac{\partial p}{\partial S} \right) \bigg|_V \]

\[ \frac{\partial T}{\partial S} \bigg|_V \]

\[ = - \left( \frac{\partial^2 E}{\partial V^2} \right) \bigg|_S + \left( \frac{\partial E}{\partial S} \right) \bigg|_S \left( \frac{\partial^2 E}{\partial S^2} \right) \bigg|_V \]

So,

\[ \left( \frac{\partial^2 A}{\partial V^2} \right) \bigg|_{T,N} = - \left( \frac{\partial p}{\partial V} \right) \bigg|_{T,N} = \left( \frac{\partial^2 E}{\partial V^2} \right) \bigg|_{T,N} \left( \frac{\partial^2 E}{\partial S^2} \right) \bigg|_V - \left( \frac{\partial E}{\partial S} \right) \bigg|_S \left( \frac{\partial^2 E}{\partial S^2} \right) \bigg|_V \geq 0 \]

\[ \left( \frac{\partial^2 E}{\partial S^2} \right) \bigg|_V \]

\[ \text{since } E \text{ is convex} \]

\[ \Rightarrow \left( \frac{\partial^2 A}{\partial V^2} \right) \bigg|_{T,N} \geq 0 \quad \text{A is convex in } V \]

\[ \text{in general,} \quad \left( \frac{\partial^2 A}{\partial V^2} \right) \bigg|_{T,N} = - \left( \frac{\partial p}{\partial V} \right) \bigg|_{T,N} = \frac{1}{Vk_T} > 0 \Rightarrow k_T > 0 \]

\[ \text{isothermal compressibility must be positive} \]
Gibbs free energy

\[ G(T, p, N) = E - TS + pV \]

Legendre transformed from \( E \) in both \( S \) and \( V \).

\[ \Rightarrow \left( \frac{\partial^2 G}{\partial T^2} \right)_p \leq 0 \quad \text{\( G \) concave in \( T \)} \]

\[ \left( \frac{\partial^2 G}{\partial p^2} \right)_T \leq 0 \quad \text{\( G \) concave in \( p \)} \]

In general, the thermodynamic free energies for constant \( N \) (i.e. \( E \) and its Legendre transforms) are convex in their extensive variables (i.e. \( S, V \)) and concave in their intensive variables (i.e. \( T, p \)).

Le Châtelier's Principle - any inhomogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity - Criterion for stability.
Heat Engines

one of the most important topics that preoccupied early investigations of thermodynamics was the study of heat engines—how to convert thermal energy (i.e., heat) into mechanical work.

A model for a heat engine is sketched below:

\[
\begin{align*}
\text{Th} & \quad \text{Working body} \quad \text{Qc} \\
\text{hot reservoir} & \quad \rightarrow & \quad \text{cold reservoir} \\
\text{W} & \quad \text{work done}
\end{align*}
\]

Two thermal reservoirs, one hot at temperature \( T_h \) and one cold at temperature \( T_c \), interact with a "working body" that will convert heat flowing from hot to cold reservoir into mechanical work.

For example, the hot reservoir might be some sort of furnace burning fuel, the cold reservoir might be the ambient atmosphere, and the working body might be a chamber of gas that can push a piston.

The hot reservoir can be called the "heat source," the cold reservoir can be called the "heat sink."
The working body is assumed to run on a "thermodynamic cycle" — it passes quasi-statically (at every moment in time it is in equilibrium) through a set of thermodynamic parameters, periodically returning to the same initial state in order to repeat the process for another cycle. This assumption of quasi-static behavior is clearly a gross simplification for a real engine, but we make it as a theoretical model.

\[ \eta = \frac{W}{Q_H} = \frac{\text{work out}}{\text{heat in}} \]  

\[ \eta \] measures the fraction of heat pumped into the working body that gets converted into mechanical work. For one cycle, \( \eta = 1 \) is ideal efficiency — all heat converted to work. We will see that this ideal can never be attained.

Since the working body operates quasi-statically, changes in energy are related to changes in the thermodynamic parameters (for a gas, as in an engine):

\[ dE = TdS - pdV = dQ - dW \]  

heat in work out
Since the working body operates in a cycle, returning to its initial state, we can integrate above over one cycle of operation

\[ 0 = \oint dE = \oint TdS - \oint pdV \]

where \( \oint dE = E_{\text{final}} - E_{\text{initial}} = 0 \) since returns to initial state

Now \( \oint pdV = \text{work done in one cycle} \)

\[ \oint TdS = \Delta H - \Delta C = \Delta Q_{\text{total}} \]

\( \Delta Q_{\text{total}} \) transferred to working body in one cycle

Heat pumped in \hspace{1cm} Heat released to

from hot reservoir \hspace{1cm} cold reservoir

\[ \text{Above} \Rightarrow 0 = \Delta H - \Delta C - W \]

\[ W = \Delta H - \Delta C \]

So efficiency can be written as

\[ \eta = \frac{W}{\Delta H} = \frac{\Delta H - \Delta C}{\Delta H} \]

\[ \eta = 1 - \frac{\Delta C}{\Delta H} = 1 - \frac{\text{heat released}}{\text{heat absorbed}} \]
A general engine cycle can be represented as a closed loop in the $T-S$ plane.

As the system goes from $A \rightarrow B$, the heat transferred to the working body is the area under the (top) curve.

$$\Delta Q_{AB} = \int_{A}^{B} T \, dS > 0$$

$\Delta Q > 0 \Rightarrow$ this is heat transferred to the working body from the hot reservoir, i.e. $Q_H = \Delta Q_{AB}$

As the system goes from $B \rightarrow A$, the heat transferred from the working body is the area under the (bottom) curve.

$$\Delta Q = \int_{B}^{A} T \, dS < 0$$

negative since the integral goes from $S_B$ to smaller $S_A$

$\Delta Q < 0 \Rightarrow$ this is the heat released by the working body to the cold reservoir, i.e. $Q_C = -\Delta Q_{BA}$

Total heat transferred $Q^{tot} = Q_H - Q_C$ in the
area bounded by the loop.

To maximize the engine efficiency, we want to maximize area under curve from A to B while minimizing the area under the curve from B to A

$$\varepsilon = 1 - \frac{Q_c}{Q_H} = 1 - \frac{\text{area under } B \rightarrow A}{\text{area under } A \rightarrow B}$$

For an engine operating between two reservoirs of fixed temperatures $T_H$ and $T_C$, the most efficient such cycle is the Carnot cycle given by the T-S diagram below:

![Carnot cycle diagram](image)

For this cycle it is easy to compute the efficiency

$$Q_H = T_H (S_B - S_A) \quad \text{heat absorbed}$$

$$Q_C = T_C (S_B - S_A) \quad \text{heat released}$$

$$\varepsilon = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

Since $T_C$ and $T_H$ must be finite, one always has $\varepsilon < 1$. 
One often sees the Carnot cycle depicted as a loop in the $p$-$V$ plane rather than the $T$-$S$ plane. Here it looks as sketched below.

1) $A' \rightarrow B$ is isothermal expansion of the gas at the temperature $T_H$ of the reservoir. Expanding gas pushes piston and does work. Working body absorbs heat $Q_H = T_H (S_B - S_A)$ from hot reservoir.

2) $B \rightarrow B'$ is adiabatic expansion of the gas. Working body is thermally isolated from the hot reservoir, gas continues to do work as it expands. No heat added to gas as it expands (i.e., $\Delta Q = 0$) $\rightarrow$ temperature of gas decreases until reaches $T_C$, temperature of cold reservoir.

3) $B' \rightarrow A'$ is isothermal compression of gas. Working body is in thermal contact with the cold reservoir, maintaining temperature at $T_C$. Work done on the working body to compress the gas keeping $T_C$ fixed $\rightarrow$ working body releases heat $\Delta Q = Q_C = T_C (S_B - S_A)$ to cold reservoir.
4) A → A' is adiabatic compression of gas.

Wary body is thermally isolated from reservoirs.
No heat flows in or out of working body.
Compressing gas raises its temperature back up to T_0 of the hot reservoir.

Isothermal segments of the cycle are curves in the p-V plane given by

\[
P V = N k B T \Rightarrow P = \frac{N k B T}{V}
\]

with N fixed at T fixed (isothermal)

\[
\Rightarrow p \propto \frac{1}{V}
\]

Adiabatic segments of the cycle are curves in p-V plane given by

\[
p \propto \frac{1}{V^\gamma} \quad \forall > 0
\]

(see problem (1f) of Problem Set #1)
Another common thermodynamic cycle is the "Otto" cycle which consists of two adiabatic and two constant volume "strokes."

\[\begin{align*}
\text{constant volume} \\
\text{adiabatic}
\end{align*}\]

one can show that the efficiency of the Otto cycle is given by

\[E = 1 - \left( \frac{V_B}{V_A} \right) \frac{C_p - C_v}{C_v}\]

where \(C_v\) and \(C_p\) are the specific heats at constant volume and pressure respectively.
Note: The same cycle can be represented as a curve in either T-S plane, p-V plane, S-V plane, or other variable choices, by the following observation.

A particular, let us take $E(s,v)$ as our thermodynamic potential. A given "stroke" of a cycle can therefore be represented as a curve in the S-V plane (as in the Otto cycle diagram) that tells how S must vary as V varies during the stroke of the cycle, i.e $S(V)$.

But we also have
\[-\frac{\partial E}{\partial V}_S = p(5;V)\]

So the stroke can also be represented by the curve $p(S_0(V),V)$ in the p-V plane (as in the 2nd way we drew the Carnot cycle).

Also, we can invert the curve $S_0(V)$ to get $V_0(S)$ and then use
\[-\frac{\partial E}{\partial S}_V = T(S,V)\]

to represent the stroke as the curve $T(S,V_0(S))$ in the T-S plane (as in our 1st way of representing the Carnot cycle).

Hence, we can represent the stroke in many equivalent different but equivalent ways.