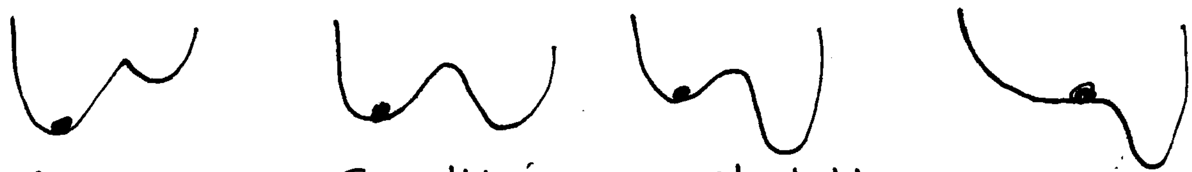
Metastability



Stable   Equilibrium   metastable   unstable (limit of stab.)

[1-D mechanical analog]

- metastable states can exist for long (macroscopic) times — see movies in class
- "quasi equilibrium" properties can be measured
- superheated liquids (→ need "nucleation stones" in orgo labs)
- supersaturated vapors (e.g. contrails condensing water droplets / ice crystals on nucleation sites)

There are <u>limits of stability</u> beyond which systems can no longer exist in a metastable state. There is potential for catastrophic failure, e.g. in LNG tanks.

Starting point: E is min @ const. S, V, N_i

$\Delta E > 0$ for any perturbation away from equil.

Taylor-expand $\quad \delta E + \frac{1}{2!}\delta E^2 + \frac{1}{3!}\delta^3 E + \cdots > 0$

For equilibrium, $\quad \delta E = 0$

For stability, $\quad \delta^2 E > 0 \quad$ (if $=0$, look @ higher order)

$$\delta E^2 = \delta^2 y^{(0)} = \sum_{i=1}^{n+2} \sum_{j=1}^{n+2} y_{ij}^{(0)} \underbrace{\delta x_i \delta x_j}_{\text{variations in variables } i, j \text{ to 1st order}} > 0 \quad [1]$$

2nd derivatives: $y_{ij}^{(0)} = \left(\frac{\partial E}{\partial x_i \partial x_j} \right)$

n: number of components

All δx_i, δx_j are independent, so $y_{ii}^{(0)} > 0$

– this is necessary, but <u>not</u> sufficient for stability

Eq. [1] on previous page can be recast into a quadratic form:

$$\delta^2 E = \delta^2 y^{(0)} = \sum_{k=1}^{n+1} y_{kk}^{(k-1)} (\delta z_k)^2 \qquad [2]$$

where $y_{kk}^{(k-1)}$ are the k,k second derivatives of the k-1 Legendre Transform of $y^{(0)}$

$$\delta z_k = \delta x_k + \sum_{j=k+1}^{n+2} y_{kj}^{(k)} \delta x_j \qquad k = 1, 2, \ldots n+1$$

Proof is given in $\underbrace{\text{Model + Reid}}_{M+R}$, "Thermodynamics + Its applications"

Eq. [2] suggests that a necessary + sufficient condition for stability involves all n+1 derivatives

$$y_{11}^{(0)},\ y_{22}^{(1)},\ y_{33}^{(2)}, \ldots\ y_{n+1,n+1}^{(n)} > 0$$

Note that the next one, $y_{n+2,n+2}^{(n+1)} = 0$

[e.g. $n=1$ $\frac{\partial^2 y^{(2)}}{\partial x_3^2}$ from $y^{(0)} = E(S,V,N)$ is $\left.\frac{\partial^2 G}{\partial N^2}\right)_{T,P} = \left.\frac{\partial \mu}{\partial N}\right)_{T,P} = 0$ since $\mu = \mu(T,P)$ only]

For example, for $n=1$ $y^{(0)} = E(S,V,N)$ we have

$$y_{11}^{(0)} = \left.\frac{\partial^2 E}{\partial S^2}\right)_{V,N} = \left.\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{C_V} > 0 \qquad y_{22}^{(1)} = \left.\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left.\frac{\partial P}{\partial V}\right)_{T,N} > 0$$

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Note that if the variables in $y^{(0)}$ are ordered in a different way, apparently different stability conditions result:

$$y^{(0)} = E(V,S,N) \Rightarrow y^{(1)}_{22} = \left.\frac{\partial^2 H}{\partial S^2}\right)_{P,N} = \left.\frac{\partial T}{\partial S}\right)_{P,N} = \frac{T}{C_P} > 0$$

$$y^{(0)} = E(S,N,V) \Rightarrow y^{(1)}_{22} = \left.\frac{\partial^2 A}{\partial N^2}\right)_{T,V} = \left.\frac{\partial \mu}{\partial N}\right)_{T,V} > 0$$

However: ALL of these "different-looking" derivatives of Legendre transforms of the same order $^{(n)}$ go to zero at the same point, identified as the stability limit.
(see M+R for proof)

Moreover $y^{(n)}_{n+1,n+1}$ goes to zero before the other derivatives when starting from a stable system.

Proof:
$$y^{(k-1)}_{kk} = y^{(k-2)}_{kk} - \frac{\left[y^{(k-2)}_{k,k-1}\right]^2}{y^{(k-2)}_{k-1,k-1}}$$
general "step-down" relationship

If stable system: $y^{(k-2)}_{kk} > 0$, $y^{(k-2)}_{k-1,k-1} > 0$

If $y^{(k-2)}_{k-1,k-1}$ were to $\to 0$ at a limit of stability, the second term would go to $-\infty$, making $y^{(k-1)}_{kk}$ negative; this is a contradiction.

$\therefore$ key stability condition is $\boxed{y^{(n)}_{n+1,n+1} > 0}$

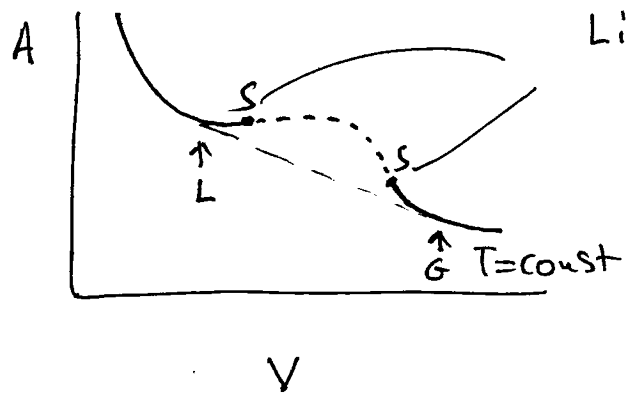
E.g. $n=2$ $y^{(0)} = E(S,V,N_1,N_2) \Rightarrow y^{(2)}_{33} = \left.\frac{\partial^2 G}{\partial N_1^2}\right)_{T,P,N_2} = \left.\frac{\partial \mu_1}{\partial N_1}\right)_{T,P,N_2} > 0$

On page 211, Shell gives 6 equivalent stability conditions for $n=1$. All are $y^{(1)}_{22}$ (w diff. order):

$$\left.\frac{\partial T}{\partial S}\right)_{V,\mu} > 0 \quad \left[\text{from } y^{(0)} = E(N,S,V)\right] \cdot \quad \left.\frac{\partial P}{\partial V}\right)_{S,\mu} < 0 \quad \left.\frac{\partial \mu}{\partial N}\right)_{S,P} > 0$$

Common Tangent

As already seen, for $n=1$ the key derivative is $y^{(1)}_{22}$. For $E(S,V,N)$ $y^{(1)}$ is $A(T,V,N)$.



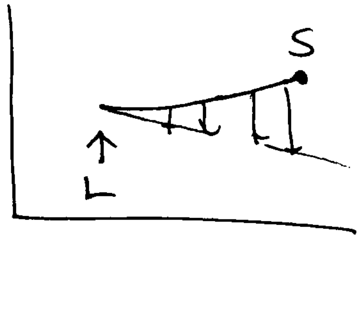
Limits of stability where

$$\left.\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = 0$$

------ is an unstable (unphysical) region that cannot be seen in a real system

Since $\left.\frac{\partial A}{\partial V}\right)_{T,N} = -P$, the long-dashed line and arrows mark the equilibrium path between phases of densities "L" and "G"

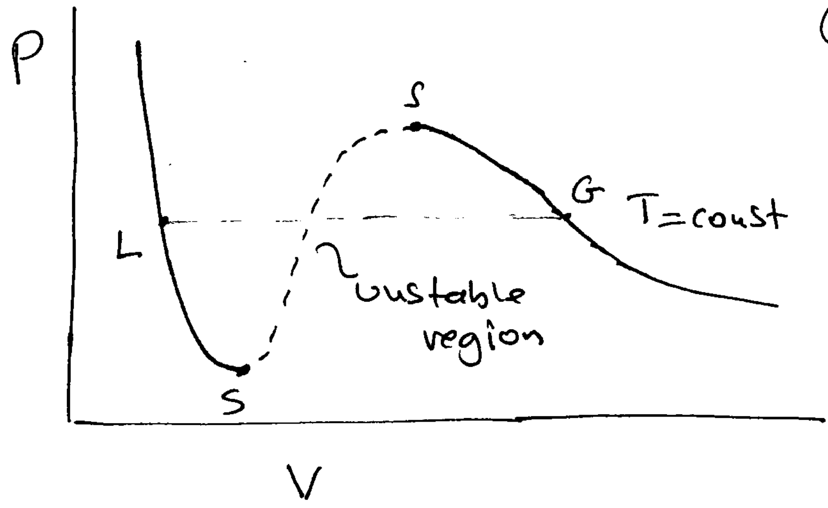
Detail



Beyond point L, the system can lower its Helmoltz free energy A by splitting into two phases

[Recall A is min @ equil. at const T, V, N]

The same information on the (P,V) plane: $(T < T_c)$



The two points for the limit of stability of the liquid and gas define the spinodal curve