2.H.3. Implications of the Stability Requirements for the Free Energies

A function $f(x)$ is convex in the interval $X = (a, b)$ if for any two points x_1 & $x_2 \in X$, the chord joining the points $(x_1, f(x_1))$ & $(x_2, f(x_2))$ always lies above the curve $f(x)$ in a f vs x plot [see Fig.2.9]. If $f(x)$ is twice differentiable, this is equivalent to

$$\frac{d^2 f}{d x^2} > 0 \qquad \forall\ x \in X \tag{2.184a}$$

A function $f(x)$ is concave if $-f(x)$ is convex.

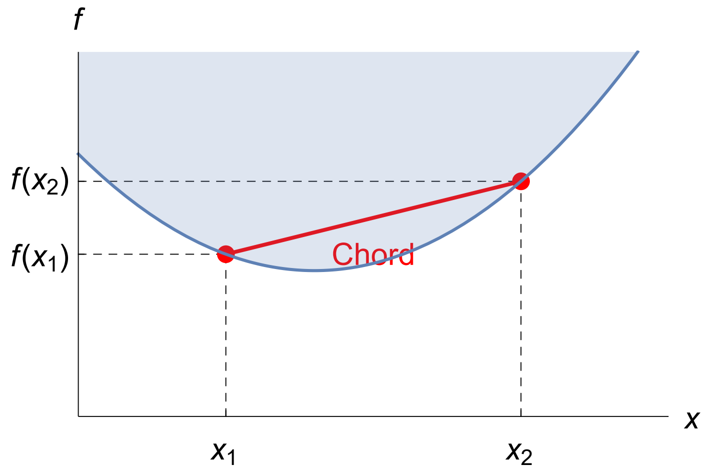

Fig.2.9.

These definitions are easily generalized to the case where the domain of f is an n-D vector space. In which case, the definition in geometrical terms is more intuitive.

As shown in §2.G, response functions are second (partial) derivatives of thermodynamic potentials. The conditions for stability derived in §2.H.2 then translate into the convexity of the potentials.

For example, combining (2.97) with (2.180) gives

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} = -\frac{C_{V,\{N_j\}}}{T} < 0 \tag{2.184}$$

while combining (2.98) with (2.181) gives

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,\{N_j\}} = -\left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} = \frac{1}{V \kappa_{T,\{N_j\}}} > 0 \tag{2.185}$$

Using the shorthand

$$A(T) = A(T, P, \{N_j\})\Big|_{P,\{N_j\}=\text{const}}$$

we see that $A(T)$ is concave while $A(V)$ is convex.

Next, combining (2.109) with (2.180) gives

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{P,\{N_j\}} = -\frac{C_{P,\{N_j\}}}{T} < 0 \tag{2.186}$$

while combining (2.110) with (2.181) gives

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}} = \left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -V\kappa_{T,\{N_j\}} < 0 \qquad (2.187)$$

Hence, both $G(T)$ and $G(P)$ are concave.

We now check on (2.186-7) using known results.

Consider first the ideal gas with [see (2.9) & Ex.2.3]

$$\left(\frac{\partial G}{\partial P}\right)_{T,n} = V = \frac{nRT}{P} \qquad \& \qquad -\left(\frac{\partial G}{\partial T}\right)_{P,n} = S = nR\left\{\frac{5}{2} + \ln\left[\frac{P_0}{P}\left(\frac{T}{T_0}\right)^{5/2}\right]\right\}$$

or

$$V(P) \propto \frac{1}{P} \qquad \& \qquad S(T) \propto \ln T$$

$$\rightarrow \quad G(P) \propto \int \frac{1}{P}\, dP = \ln P \qquad \& \qquad G(T) \propto -\int \ln T\, dT = T - T\ln T$$

The plots of these relations are show in the figure below.

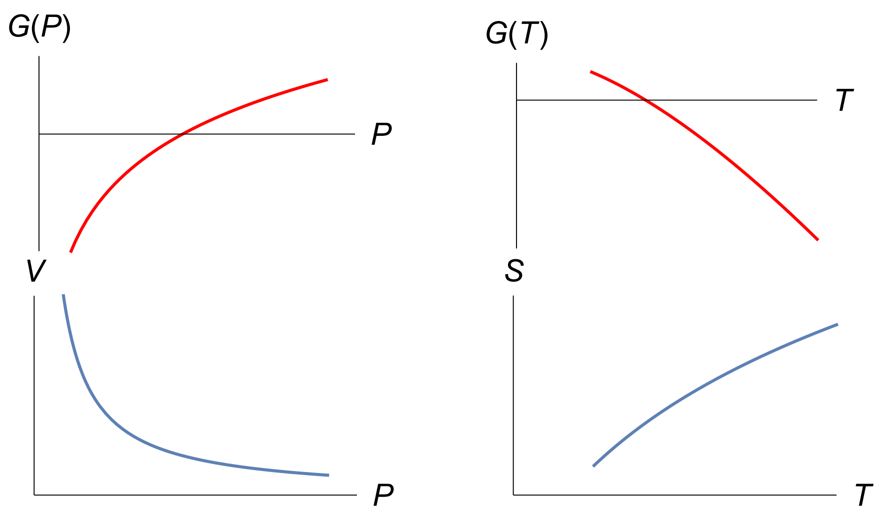

Fig.2.10.

Next, we consider the magnetic system to be described in Ex.7.4, §7.D.2.

From (3) of Ex.7.4, we have, for fixed N,

$$Z \propto T^{3/2}\cosh\frac{B}{T}$$

$$\rightarrow \quad G(T,B) \propto -T\ln Z \propto -T\left(\frac{3}{2}\ln T + \ln\cosh\frac{B}{T}\right)$$

$$\therefore \quad S = -\left(\frac{\partial G}{\partial T}\right)_B \propto \frac{3}{2}\ln T + \ln\cosh\frac{B}{T} + \frac{3}{2} - \frac{B}{T}\tanh\frac{B}{T}$$

$$M = -\left(\frac{\partial G}{\partial B}\right)_T \propto \tanh\frac{B}{T}$$

With the help of the Mathematica code in §(Code: Magnetic System), we get

$$G(T) = -\int S\, dT \propto -\frac{3}{2}T\ln T - T\ln\cosh\frac{B}{T}$$

$$G(B) = -\int M\, dB \propto -T\ln\cosh\frac{B}{T}$$

The plots of these relations are show in the figure below.

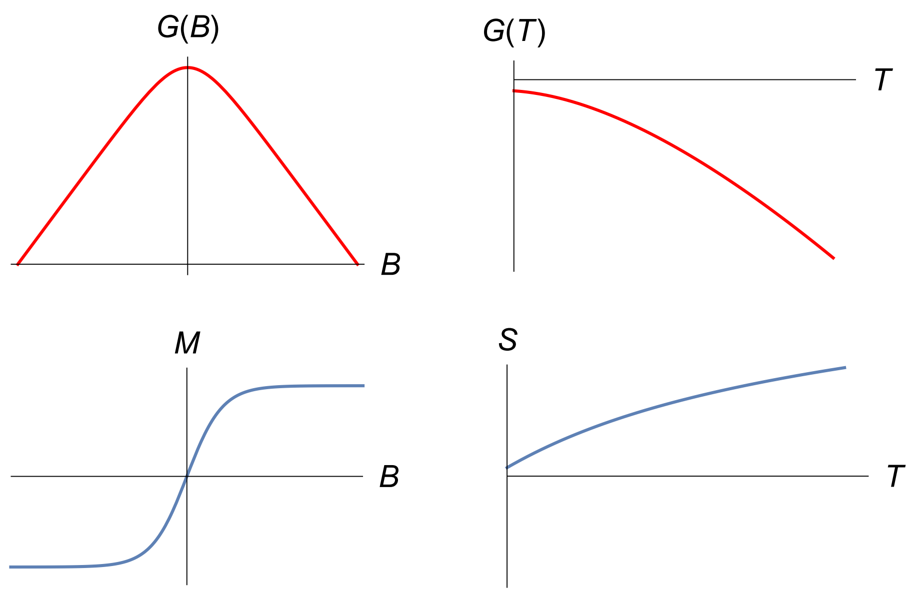

Fig.2.11.

Code: Ideal Gas

```
In[1]:= (* Fig.2.9 *)
f[x_] := .8 + (x - .8)^2
x1 = .5; x2 = 1.5;
Plot[f[x], {x, 0, 2},
    PlotRange → {{0, 2}, {0, 2}},
    AxesLabel → {"x", "f"},
    Ticks → {{{x1, "x1"}, {x2, "x2"}}, {{f[x1], "f(x1) "}, {f[x2], "f(x2) "}}},
    Filling → Top,
    Prolog → {{Dashed, Line[ {{x1, 0}, {x1, f[x1]}}],
                        Line[ {{0, f[x1]}, {x1, f[x1]}}],
                        Line[ {{x2, 0}, {x2, f[x2]}}],
                        Line[ {{0, f[x2]}, {x2, f[x2]}}]},
              Red, Thick, Line[{{x1, f[x1]}, {x2, f[x2]}}],
                  PointSize[.03], Point[{{x1, f[x1]}, {x2, f[x2]}}],
                  Text["Chord", {1/2 (x1 + x2), f[x1]}]
  }
]

In[4]:= (* V(P) *)
Plot[1/P, {P, .1, 2}, PlotRange → {{0, 2.2}, {0, 5}},
        AxesLabel → {"P", "V" }, Ticks → None
]
```

In[5]:=
```
(* G(P) *)
Plot[Log[P], {P, .1, 2}, PlotRange → {{0, 2.2}, {-1.5, 1}},
         AxesLabel → {"P", "G(P)" }, Ticks → None,
         PlotStyle → Red
]
```

In[13]:=
```
(* S(T) *)
Plot[Log[T], {T, 2, 5}, PlotRange → {{1, 5}, {.5, 1.8}},
         AxesLabel → {"T", "S" }, Ticks → None
]
```

In[7]:=

In[8]:=
```
(* G(T) *)
Plot[T - T Log[T], {T, 2, 5}, PlotRange → {{1, 5}, All},
         AxesLabel → {"T", "G(T)" }, Ticks → None,
         PlotStyle → Red
]
```

Code: Magnetic System

In[∘]:= $\{\partial_T \mathrm{Log}[\mathrm{Cosh}[\frac{B}{T}]], \partial_B \mathrm{Log}[\mathrm{Cosh}[\frac{B}{T}]]\}$

Out[∘]= $\{-\frac{B\,\mathrm{Tanh}[\frac{B}{T}]}{T^2}, \frac{\mathrm{Tanh}[\frac{B}{T}]}{T}\}$

In[∘]:= $S = \frac{3}{2}\mathrm{Log}[T] + \mathrm{Log}[\mathrm{Cosh}[\frac{B}{T}]] + \frac{3}{2} - \frac{B}{T}\mathrm{Tanh}[\frac{B}{T}]$

Out[∘]= $\frac{3}{2} + \frac{3\,\mathrm{Log}[T]}{2} + \mathrm{Log}[\mathrm{Cosh}[\frac{B}{T}]] - \frac{B\,\mathrm{Tanh}[\frac{B}{T}]}{T}$

In[∘]:= $GT = -\int S\,dT$

Out[∘]= $-\frac{3}{2}T\,\mathrm{Log}[T] - T\,\mathrm{Log}[\mathrm{Cosh}[\frac{B}{T}]]$

In[∘]:= $M = \mathrm{Tanh}[\frac{B}{T}]$

Out[∘]= $\mathrm{Tanh}[\frac{B}{T}]$

In[∘]:= $GB = -\int M\,dB$

Out[∘]= $-T\,\mathrm{Log}[\mathrm{Cosh}[\frac{B}{T}]]$

In[ ]:=
```
(* M(B) *)
Plot[M /. T → 1, {B, -5, 5}, PlotRange → {{-5, 5}, 1.2 {-1, 1}},
        AxesLabel → {"B", "M" }, Ticks → None
]
```

In[ ]:=
```
(* G(B) *)
Plot[GB /. T → 1, {B, -5, 5}, PlotRange → All,
        AxesLabel → {"B", "G(B)" }, Ticks → None,
        PlotStyle → Red
]
```

In[ ]:=
```
(* S(T) *)
Plot[S /. B → 1, {T, .6, 2}, PlotRange → {{.6, 2.1}, 2.5 {-1, 1}},
        AxesLabel → {"T", "S" }, Ticks → None
]
```

In[ ]:=
```
(* G(T) *)
Plot[GT /. B → 1, {T, .6, 2}, PlotRange → {{.6, 2.1}, 2.5 {-1, .1}},
        AxesLabel → {"T", "G(T)" }, Ticks → None,
        PlotStyle → Red
]
```