

### S3.F. The Ginzburg-Landau Theory of Superconductors

Order parameter for a superconductor is the complex wave function  $\Psi(r)$  of the superconducting state ( Bose condensate of Cooper pairs ). This brings in certain quantum characteristics into the Ginzburg-Landau theory. Since the macroscopic induction field  $\mathbf{B}$  is the average of the microscopic field dealt with in quantum mechanics, the natural thermodynamic function is therefore the Helmholtz free energy  $A(T, \mathbf{B}, \Psi)$ , instead of the Gibbs free energy  $G(T, \mathbf{H}, \Psi)$  expected from purely thermodynamic considerations.

Since the Helmholtz free energy density must be real, it takes the form [ in Gaussian units ]

$$a(\mathbf{r}, T, \mathbf{B}, \Psi) = a_n(T) + \alpha_1 \Psi^* \Psi + \frac{1}{2} \alpha_2 (\Psi^* \Psi)^2 + \frac{1}{2m} \left| \frac{\hbar}{i} \nabla_r \Psi - \frac{q}{c} \mathbf{A} \Psi \right|^2 + \frac{1}{8\pi} \mathbf{B}^2 \quad (3.155)$$

where  $a_n(T)$  is the (uniform, or  $r$ -independent) Helmholtz free energy density of the normal conductor at  $\mathbf{B} = 0$ .  $q$  &  $m$  are the charge & mass of a Cooper pair, respectively.  $c$  is the speed of light,  $\hbar$  the Planck's constant, and the induction field  $\mathbf{B}$  is related to the vector potential  $\mathbf{A}$  by

$$\mathbf{B}(\mathbf{r}) = \nabla_r \times \mathbf{A}(\mathbf{r}) \quad (3.154)$$

In general, the expansion coefficients  $\alpha_j$  are real functions of  $T$  &  $\mathbf{B}$ . Furthermore, for the sake of global stability,  $\alpha_2 > 0$  [ see §3.G.1 ].

Note that, as usual [ c.f. ideal gas ], the natural thermodynamic free energy is equated with the total energy (or Hamiltonian) in mechanics.

**Reminder:** while  $\mathbf{p} = \frac{\hbar}{i} \nabla_r$  is the canonical momentum, the operator

$$m \dot{\mathbf{r}} = \frac{\hbar}{i} \nabla_r - \frac{q}{c} \mathbf{A} = \mathbf{p} - \frac{q}{c} \mathbf{A} \quad (3.154a)$$

is the mechanical momentum operator.

Incidentally, the Gibbs free energy density is given by the Legendre transform

$$g(\mathbf{r}, T, \mathbf{H}, \Psi) = a(\mathbf{r}, T, \mathbf{B}, \Psi) - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{B} \quad (3.156)$$

The Helmholtz free energy is obtained by integrating (3.155) over the volume  $V$  of the system

$$\begin{aligned} A(T, \mathbf{B}, \Psi) &= \int_V d^3 r a(\mathbf{r}, T, \mathbf{B}, \Psi) \\ &= \int_V d^3 r \left[ a_n(T) + \alpha_1 \Psi^* \Psi + \frac{1}{2} \alpha_2 (\Psi^* \Psi)^2 + \frac{1}{2m} \left| \frac{\hbar}{i} \nabla_r \Psi - \frac{q}{c} \mathbf{A} \Psi \right|^2 + \frac{1}{8\pi} \mathbf{B}^2 \right] \end{aligned} \quad (3.157)$$

Since  $\Psi$  is complex, it corresponds to 2 real variables, and hence 2 degrees of freedom, which can be taken as either  $(\text{Re } \Psi, \text{Im } \Psi)$  or the more popular choice  $(\Psi, \Psi^*)$ . Owing to (3.154), the state variables in  $A$  can be taken as  $(T, \Psi, \Psi^*, \mathbf{A})$ . As discussed in Chap 2, equilibrium states are extrema of the properly chosen (or natural) thermodynamic free energy. Thus, for each degree of freedom  $f$ ,

$$\begin{aligned} 0 = \delta A &= \int d^3 r \left[ \frac{\partial a}{\partial f} \delta f + \frac{\partial a}{\partial \nabla_r f} \cdot \delta(\nabla_r f) \right] \\ &= \int d^3 r \left[ \left( \frac{\partial a}{\partial f} - \nabla_r \cdot \frac{\partial a}{\partial \nabla_r f} \right) \delta f + \nabla_r \cdot \left( \frac{\partial a}{\partial \nabla_r f} \delta f \right) \right] \quad [ \delta(\nabla_r f) = \nabla_r(\delta f) \text{ used. } ] \end{aligned}$$

$$= \int_V d^3r \left( \frac{\partial a}{\partial f} - \nabla_r \cdot \frac{\partial a}{\partial \nabla_r f} \right) \delta f + \oint_S dS \mathbf{n} \cdot \frac{\partial a}{\partial \nabla_r f} \delta f \quad (3.157a)$$

where  $\mathbf{S} = \mathbf{n} S$  is the surface with outward normal  $\mathbf{n}$  that encloses the system. Since  $\delta f$  is arbitrary, (3.157a) is satisfied if & only if

$$\frac{\partial a}{\partial f} - \nabla_r \cdot \frac{\partial a}{\partial \nabla_r f} = 0 \quad \& \quad \mathbf{n} \cdot \frac{\partial a}{\partial \nabla_r f} \Big|_S = 0 \quad (3.157b)$$

For  $f = \Psi$ , we have

$$\begin{aligned} & \alpha_1 \Psi^* + \alpha_2 (\Psi^* \Psi) \Psi^* - \frac{q}{m c} \mathbf{A} \cdot \left( -\frac{\hbar}{i} \nabla_r \Psi^* - \frac{q}{c} \mathbf{A} \Psi^* \right) - \frac{\hbar}{m i} \nabla_r \cdot \left( -\frac{\hbar}{i} \nabla_r \Psi^* - \frac{q}{c} \mathbf{A} \Psi^* \right) = 0 \\ \rightarrow & \alpha_1 \Psi^* + \alpha_2 (\Psi^* \Psi) \Psi^* - \frac{1}{m} \left( \frac{\hbar}{i} \nabla_r + \frac{q}{c} \mathbf{A} \right) \cdot \left( -\frac{\hbar}{i} \nabla_r \Psi^* - \frac{q}{c} \mathbf{A} \Psi^* \right) = 0 \\ & \alpha_1 \Psi^* + \alpha_2 (\Psi^* \Psi) \Psi^* + \frac{1}{m} \left( \frac{\hbar}{i} \nabla_r + \frac{q}{c} \mathbf{A} \right)^2 \Psi^* = 0 \end{aligned} \quad (3.158a)$$

and

$$\mathbf{n} \cdot \left( -\frac{\hbar}{i} \nabla_r \Psi^* - \frac{q}{c} \mathbf{A} \Psi^* \right) \Big|_S = 0 \quad (3.158b)$$

Instead of working (3.157b) for  $f = \Psi^*$ , we can take the complex conjugate of (3.158a-b) to get the same result as

$$\alpha_1 \Psi + \alpha_2 (\Psi^* \Psi) \Psi + \frac{1}{m} \left( -\frac{\hbar}{i} \nabla_r + \frac{q}{c} \mathbf{A} \right)^2 \Psi = 0 \quad (3.158)$$

$$\mathbf{n} \cdot \left( \frac{\hbar}{i} \nabla_r \Psi - \frac{q}{c} \mathbf{A} \Psi \right) \Big|_S = 0 \quad (3.158c)$$

Using (3.154a), we see that (3.158 b & c) state the obvious fact that, on the surface, the velocity in the normal direction must vanish.

Now, from (3.154),

$$B_i = \epsilon_{ijk} \frac{\partial A_k}{\partial x_j} \equiv \epsilon_{ijk} A_{k,j} \quad [ \text{Implicit summation over repeated indices.} ]$$

$$\rightarrow \frac{\partial B_i}{\partial A_m} = 0 \quad \frac{\partial B_i}{\partial A_{m,n}} = \epsilon_{ijk} \delta_{mk} \delta_{nj} = \epsilon_{inm}$$

$$\therefore \frac{\partial B^2}{\partial A_m} = \frac{\partial B_i B_i}{\partial A_m} = 2 B_i \frac{\partial B_i}{\partial A_m} = 0$$

$$\frac{\partial B^2}{\partial A_{m,n}} = 2 B_i \frac{\partial B_i}{\partial A_{m,n}} = 2 \epsilon_{inm} B_i$$

$$\frac{\partial \mathbf{B} \cdot \mathbf{H}}{\partial A_{m,n}} = H_i \frac{\partial B_i}{\partial A_{m,n}} = \epsilon_{inm} H_i$$

$$\rightarrow \nabla_r \cdot \frac{\partial B^2}{\partial \nabla_r A_m} = \partial_n \frac{\partial B^2}{\partial A_{m,n}} = 2 \epsilon_{inm} \partial_n B_i = -2 (\nabla \times \mathbf{B})_m$$

$$\nabla_r \cdot \frac{\partial \mathbf{B} \cdot \mathbf{H}}{\partial \nabla_r A_m} = \partial_n \frac{\partial H_i B_i}{\partial A_{m,n}} = \epsilon_{inm} \partial_n H_i = -(\nabla \times \mathbf{H})_m$$

Also,

$$\frac{\partial}{\partial A_m} \left| \frac{\hbar}{i} \nabla_r \Psi - \frac{q}{c} \mathbf{A} \Psi \right|^2 = \frac{\partial}{\partial A_m} \left[ \left( -\frac{\hbar}{i} \partial_j \Psi^* - \frac{q}{c} A_j \Psi^* \right) \left( \frac{\hbar}{i} \partial_j \Psi - \frac{q}{c} A_j \Psi \right) \right]$$

$$\begin{aligned}
&= -\frac{q}{c} \delta_{mj} \Psi^* \left( \frac{\hbar}{i} \partial_j \Psi - \frac{q}{c} A_j \Psi \right) + \left( -\frac{\hbar}{i} \partial_j \Psi^* - \frac{q}{c} A_j \Psi^* \right) \left( -\frac{q}{c} \delta_{mj} \Psi \right) \\
&= -\frac{q}{c} \left[ \Psi^* \left( \frac{\hbar}{i} \partial_m \Psi - \frac{q}{c} A_m \Psi \right) + \left( -\frac{\hbar}{i} \partial_m \Psi^* - \frac{q}{c} A_m \Psi^* \right) \Psi \right] \\
&= -\frac{q}{c} \left[ \frac{\hbar}{i} (\Psi^* \partial_m \Psi - \Psi \partial_m \Psi^*) - \frac{2q}{c} A_m \Psi^* \Psi \right]
\end{aligned}$$

Therefore, for  $f = \mathbf{A}$ , we have

$$\begin{aligned}
&-\frac{q}{2mc} \left[ \frac{\hbar}{i} (\Psi^* \nabla_r \Psi - \Psi \nabla_r \Psi^*) - \frac{2q}{c} \mathbf{A} \Psi^* \Psi \right] + \frac{1}{4\pi} \nabla \times \mathbf{B} = 0 \\
\rightarrow \nabla_r \times \mathbf{B} &= \frac{4\pi}{c} \left[ \frac{q\hbar}{2mi} (\Psi^* \nabla_r \Psi - \Psi \nabla_r \Psi^*) - \frac{q^2}{mc} \mathbf{A} \Psi^* \Psi \right] \quad (3.159a) \\
&= \frac{4\pi}{c} \mathbf{J}
\end{aligned}$$

where

$$\mathbf{J} = \frac{q\hbar}{2mi} (\Psi^* \nabla_r \Psi - \Psi \nabla_r \Psi^*) - \frac{q^2}{mc} \mathbf{A} \Psi^* \Psi \quad (3.162)$$

is the **total current density**. Since all normal pathways are shortened out by the superconducting component,  $\mathbf{J}$  is also the **super-current density**.

The surface part is

$$\begin{aligned}
&n_n \frac{\partial}{\partial A_{m,n}} \left( \frac{1}{8\pi} \mathbf{B}^2 \right) \Big|_S = 0 = \frac{1}{4\pi} \epsilon_{inm} n_n B_i \Big|_S \\
\rightarrow \mathbf{n} \times \mathbf{B} \Big|_S &= 0 \quad (3.159b)
\end{aligned}$$

which means that on the surface, either  $\mathbf{B} = 0$  or  $\mathbf{B}$  is normal to the surface. In either case, the tangential components of  $\mathbf{B}$  must vanish.

Now, the particle flux is defined as

$$\mathbf{J}_p = \frac{\hbar}{2mi} (\Psi^* \nabla_r \Psi - \Psi \nabla_r \Psi^*)$$

Therefore, the current density due to the motion of the Cooper pairs is

$$\mathbf{J}_q = \frac{q\hbar}{2mi} (\Psi^* \nabla_r \Psi - \Psi \nabla_r \Psi^*) \quad (3.159c)$$

and (3.159a) becomes

$$\nabla_r \times \mathbf{B} = \frac{4\pi}{c} \mathbf{J}_q - \frac{4\pi q^2}{mc^2} \mathbf{A} \Psi^* \Psi \quad (3.159d)$$

In the absence of particle flux, (3.159d) reduces to

$$\begin{aligned}
\nabla_r \times \mathbf{B} &= -\frac{4\pi q^2}{mc^2} \mathbf{A} \Psi^* \Psi \\
&= \nabla_r \times (\nabla_r \times \mathbf{A}) = \nabla_r (\nabla_r \cdot \mathbf{A}) - \nabla_r^2 \mathbf{A} \quad (3.159e)
\end{aligned}$$

In the Coulomb gauge,

$$\nabla_r \cdot \mathbf{A} = 0$$

and (3.159e) becomes the **London equation**,

$$\nabla_r^2 \mathbf{A} = \frac{1}{\lambda^2} \mathbf{A} \quad (3.159f)$$

where

$$\lambda = \sqrt{\frac{m c^2}{4 \pi q^2 \Psi^* \Psi}} = \text{penetration depth} \quad (3.170a)$$

$\lambda$  is so named because, in the immediate vicinity of a surface of outward normal  $\hat{n}$ , the solution of (3.159f) is

$$\mathbf{A}(r) = \hat{n} A_0 e^{r \cdot \hat{n} / \lambda} = \hat{n} A_0 e^{-d / \lambda} \quad (3.171a)$$

where  $d = -r \cdot \hat{n}$  is the distance beneath the surface for point  $r$ .

Thus,  $\mathbf{A}$  drops to zero rapidly beyond a depth larger than  $\lambda$  beneath the surface.

This proves the **Meissner effect**, which states that  $\mathbf{B} = 0$  in the bulk of a superconductor.

Now,  $\mathbf{H}$ , as given by the Ampere's law, arises solely from currents due to mobile charges. In the present case, this means

$$\nabla_r \times \mathbf{H} = \frac{4 \pi}{c} \mathbf{J}_q \quad (3.171b)$$

so that (3.159d) becomes

$$\nabla_r \times (\mathbf{B} - \mathbf{H}) = -\frac{1}{\lambda^2} \mathbf{A} \quad [ (3.170a) \text{ used. } ]$$

$$\rightarrow \nabla_r \times \mathbf{M} = -\frac{1}{4 \pi \lambda^2} \mathbf{A} = \frac{1}{c} \mathbf{J}_M \quad (3.171c)$$

where the magnetization  $\mathbf{M}$  is defined by

$$\mathbf{B} = \mathbf{H} + 4 \pi \mathbf{M}$$

and  $\mathbf{J}_M$  is the **magnetization current density**. (3.162) then becomes

$$\mathbf{J} = \mathbf{J}_q + \mathbf{J}_M \quad (3.171d)$$

Returning to the phase transition aspect of the problem, we solve the equilibrium condition (3.158) for the order parameter  $\Psi$ . Using

$$\begin{aligned} \left( -\frac{\hbar}{i} \nabla_r + \frac{q}{c} \mathbf{A} \right)^2 \Psi &= \left( -\frac{\hbar}{i} \nabla_r + \frac{q}{c} \mathbf{A} \right) \cdot \left( -\frac{\hbar}{i} \nabla_r \Psi + \frac{q}{c} \mathbf{A} \Psi \right) \\ &= -\hbar^2 \nabla_r^2 \Psi - \frac{\hbar q}{i c} [\mathbf{A} \cdot \nabla_r \Psi - \nabla_r \cdot (\mathbf{A} \Psi)] + \frac{q^2}{c^2} \mathbf{A}^2 \\ &= -\hbar^2 \nabla_r^2 \Psi - \frac{\hbar q}{i c} (\nabla_r \cdot \mathbf{A}) \Psi + \frac{q^2}{c^2} \mathbf{A}^2 \end{aligned}$$

(3.158) becomes

$$\alpha_1 \Psi + \alpha_2 (\Psi^* \Psi) \Psi - \frac{1}{m} \left[ \hbar^2 \nabla_r^2 \Psi + \frac{\hbar q}{i c} (\nabla_r \cdot \mathbf{A}) \Psi - \frac{q^2}{c^2} \mathbf{A}^2 \right] = 0 \quad (3.164a)$$

As discussed in association with the London's equation (3.159f),  $\mathbf{A} = 0$  in the bulk of a superconductor.

Hence, for  $\Psi \neq 0$ , (3.164a) becomes

$$\alpha_1 \Psi + \alpha_2 (\Psi^* \Psi) \Psi - \frac{\hbar^2}{m} \nabla_r^2 \Psi = 0 \quad (3.164b)$$

which also applies to the normal state ( $\Psi = 0$ ) in the absence of magnetic fields ( $\mathbf{A} = 0$ ).

Taking the complex conjugate gives

$$\alpha_1 \Psi^* + \alpha_2 (\Psi^* \Psi) \Psi^* - \frac{\hbar^2}{m} \nabla_r^2 \Psi^* = 0 \quad (3.164c)$$

Thus, it is legitimate to assume  $\Psi$  is real since (3.164b & c) become the same equation

$$\alpha_1 \Psi + \alpha_2 \Psi^3 - \frac{\hbar^2}{m} \nabla_r^2 \Psi = 0 \quad (3.164d)$$

Consider now a homogeneous superconductor that occupies the upper half ( $z \geq 0$ ) of the 3-D space.  $\Psi$  thus varies only in the  $z$ -direction so that (3.164d) simplifies to

$$\frac{\hbar^2}{m} \frac{d^2 \Psi}{dz^2} = \alpha_1 \Psi + \alpha_2 \Psi^3 \quad \text{with} \quad \Psi = \Psi_0 = \text{const} \quad \text{as} \quad z \rightarrow \infty \quad (3.164e)$$

Using

$$\frac{d^2 \Psi}{dz^2} = \frac{d}{dz} \left( \frac{d\Psi}{dz} \right) = \frac{d\Psi}{dz} \frac{d}{d\Psi} \left( \frac{d\Psi}{dz} \right) = \frac{1}{2} \frac{d}{d\Psi} \left( \frac{d\Psi}{dz} \right)^2$$

(3.164e) becomes

$$\frac{\hbar^2}{2m} \left( \frac{d\Psi}{dz} \right)^2 = \frac{1}{2} \alpha_1 \Psi^2 + \frac{1}{4} \alpha_2 \Psi^4 + C \quad [C = \text{const.}] \quad (3.164f)$$

Hence,

$$\begin{aligned} \frac{\hbar^2}{2m} \left( \frac{d\Psi}{dz} \right)^2 = 0 &= \frac{1}{2} \alpha_1 \Psi_0^2 + \frac{1}{4} \alpha_2 \Psi_0^4 + C & \text{as } z \rightarrow \infty & (3.164g) \\ \frac{\hbar^2}{m} \frac{d^2 \Psi}{dz^2} = 0 &= \alpha_1 \Psi_0 + \alpha_2 \Psi_0^3 \end{aligned}$$

Since  $\Psi$  must be real in the superconducting phase,

$$\Psi_0^2 = -\frac{\alpha_1}{\alpha_2} = \alpha \geq 0 \quad \forall T \leq T_c \quad (3.164h)$$

so that (3.164g) gives

$$C = \frac{1}{2} \alpha_2 \alpha^2 - \frac{1}{4} \alpha_2 \alpha^2 = \frac{1}{4} \alpha_2 \alpha^2$$

Since we must have  $\alpha_2 > 0$  for all  $T$  to maintain global stability, we have

$$\alpha \geq 0 \quad \rightarrow \quad \alpha_1 \leq 0 \quad \forall T \leq T_c$$

(3.164f) thus becomes

$$\begin{aligned} \frac{\hbar^2}{m \alpha_2} \left( \frac{d\Psi}{dz} \right)^2 &= -\alpha \Psi^2 + \frac{1}{2} \Psi^4 + \frac{1}{2} \alpha^2 \\ &= \frac{1}{2} (\alpha - \Psi^2)^2 \\ &= \frac{1}{2} (\Psi_0^2 - \Psi^2)^2 \end{aligned} \quad (3.167a)$$

Setting

$$f(z) = \frac{\Psi(z)}{\Psi_0} \quad \rightarrow \quad f(\infty) = 1 \quad [ (3.164e) \text{ used. } ]$$

(3.167a) becomes

$$\frac{\hbar^2}{m \alpha_2} \left( \frac{df}{dz} \right)^2 = \frac{1}{2} (1 - f^2)^2$$

Setting

$$\xi = \sqrt{\frac{\hbar^2}{m \alpha_2}} = \text{coherence length} \quad (3.165)$$

we have

$$\xi^2 \left( \frac{df}{dz} \right)^2 = \frac{1}{2} (1 - f^2)^2 \quad (3.167)$$

*Mathematica* [ see §Code ] gives the general solution to (3.167) as

$$f(z) = \frac{e^{\sqrt{2} z/\xi} - C}{e^{\sqrt{2} z/\xi} + C} \quad [ C = \text{const.} ]$$

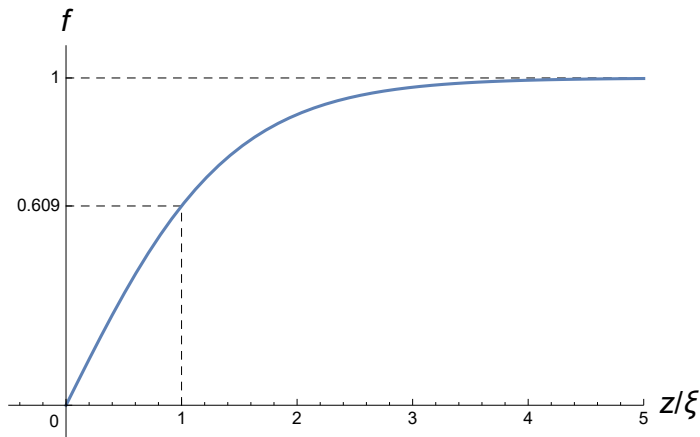
Putting in the boundary condition  $f(0) = 0$ , we have

$$f(z) = \frac{e^{\sqrt{2} z/\xi} - 1}{e^{\sqrt{2} z/\xi} + 1} = \tanh \frac{z}{\sqrt{2} \xi} \quad (3.168)$$

or

$$\Psi(z) = \Psi_0 \tanh \frac{z}{\sqrt{2} \xi}$$

As shown in Fig.3.38, the order parameter  $\Psi$  attains its bulk value  $\Psi_0$  only a few coherence lengths away from the boundary at  $z = 0$ .



**Fig.3.38.** Plot of  $f\left(\frac{z}{\xi}\right)$  showing  $f \approx 1$  for  $\frac{z}{\xi} > 4$ .

If we neglect the variation near the surface, then

$$\Psi \approx \Psi_0 = \sqrt{-\frac{\alpha_1}{\alpha_2}} \quad [ (3.164h) \text{ used.} ]$$

and (3.170a) becomes

$$\lambda = \sqrt{\frac{m c^2 \alpha_2}{4 \pi q^2 (-\alpha_1)}} \quad (3.170)$$

## Code

$$\text{eq} = \xi^2 (f'[z])^2 == \frac{1}{2} (1 - f[z]^2)^2;$$

```
sol = DSolve[eq, f, z]
```

$$\text{Out[*]} = \left\{ \left\{ f \rightarrow \text{Function}\left[ \{z\}, \frac{e^{\frac{\sqrt{2}z}{\xi}} - e^{2c_1}}{e^{\frac{\sqrt{2}z}{\xi}} + e^{2c_1}} \right] \right\}, \left\{ f \rightarrow \text{Function}\left[ \{z\}, \frac{1 - e^{\frac{\sqrt{2}z}{\xi} + 2c_1}}{1 + e^{\frac{\sqrt{2}z}{\xi} + 2c_1}} \right] \right\} \right\}$$

```
In[*]:= fs[z_] := f[z] /. sol[[1]] /. C[1] -> 0 // ExpToTrig // Simplify
```

```
In[*]:= fs[z]
```

$$\text{Out[*]} = \text{Tanh}\left[\frac{z}{\sqrt{2}\xi}\right]$$

```
In[*]:= Plot[fs[z \xi], {z, 0, 5},
  PlotRange -> {{-.5, 5}, {-.1, 1.1}},
  AxesLabel -> {"z/\xi", "f"},
  Ticks -> {All, {0, fs[\xi] // N[#, 3] &, 1}},
  Prolog -> {Dashed, Line[{{0, 1}, {5, 1}}],
  Line[{{1, 0}, {1, fs[\xi]}]}, Line[{{0, fs[\xi]}, {1, fs[\xi]}]},
  Text["0", {-.1, -.05}]
}
]
```