

Atoms at finite temperatures

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Abstract

These are working notes written as a first step in understanding atomic potentials and atomic structure in finite-temperature systems.

1 Thomas-Fermi Theory

As a first step, we consider the Thomas-Fermi theory at finite temperatures. This is my version of the discussion of temperature-dependent Thomas-Fermi theory given in the seminal work of Feynman, Metropolis, and Teller [1]. Later, we will make detailed comparisons with results from that paper.

In the discussion to follow, we imagine that a material is divided into neutral cells, each containing a single nucleus (charge Z) and Z electrons. We isolate an individual neutral cell and treat it in a thermodynamic average sense, ignoring the interaction between neighboring cells. These cells are later considered to be spherical; the radius of each cell is taken to be the Wigner-Seitz radius determined from the material density ρ_m (g/cm³) and the atomic weight A (g/mol) by:

$$\begin{aligned}\Omega &= \frac{A}{\mathcal{A}\rho_m} \\ R &= \left(\frac{3\Omega}{4\pi}\right)^{1/3},\end{aligned}$$

where $\mathcal{A} = 6.022 \times 10^{23}$ is Avagadro's number and Ω is the atomic volume.

1.1 Elementary formulas

We consider an atom with N electrons moving in a potential $V(r)$. We suppose that locally the electrons are moving in a box of side L and depth $V(r)$. The number of states in momentum interval d^3p is

$$d^3N = 2 \frac{L^3}{(2\pi)^3} d^3p,$$

so that the particle density is

$$\rho = \frac{N}{L^3} = \frac{1}{\pi^2} \int_0^{p_f} p^2 dp = \frac{p_f^3}{3\pi^2},$$

at zero temperature, assuming levels up to the Fermi level p_f are occupied. At finite temperature T this generalizes to

$$\rho = \frac{1}{\pi^2} \int_0^\infty \frac{p^2 dp}{[1 + e^{(E-\mu)/kT}]},$$

where E is the particle energy, μ is the chemical potential, and $k = 8.617342 \times 10^{-5}$ eV/K is Boltzmann's constant. Taking advantage of the energy-momentum relation

$$\frac{p^2}{2m} + V(r) = E,$$

we may change the independent variable to E . We have $pdp = mdE$, from which follows

$$\rho = \frac{m}{\pi^2} \int_{V(r)}^\infty \frac{pdE}{[1 + e^{(E-\mu)/kT}]}$$

With the further change of variable $\epsilon = E - V$, $p = \sqrt{2m\epsilon}$, we obtain

$$\rho = \frac{(2m)^{3/2}}{2\pi^2} \int_0^\infty \frac{\sqrt{\epsilon} d\epsilon}{[1 + e^{(\epsilon+V(r)-\mu)/kT}]}$$

It is convenient to write this expression in terms of the Fermi integral

$$I_{1/2}(x) = \int_0^\infty \frac{y^{1/2} dy}{[1 + e^{y-x}]}$$

We find that

$$\rho(r) = \frac{(2mkT)^{3/2}}{2\pi^2} I_{1/2}(x) \tag{1}$$

with

$$x = [\mu - V(r)]/kT.$$

For low temperatures, x is large and

$$I_{1/2} \approx \frac{2}{3} x^{3/2}.$$

The corresponding low temperature approximation to ρ is

$$\rho(r) \approx \frac{(2m[\mu - V(r)])^{3/2}}{3\pi^2},$$

which agrees with the zero temperature result provided we identify the low-temperature limit of the chemical potential $\mu(T)$ with the Fermi energy,

$$\lim_{T \rightarrow 0} \mu(T) = E_f.$$

In the finite-temperature case, $\mu(T)$ is determined from the normalization condition for a neutral atom ($N = Z$),

$$Z = \int \rho(r) d^3 r = 4\pi \int_0^R r^2 \rho(r) dr ,$$

where we have replaced the box by a spherical cavity of radius R .

1.2 Self-consistent potential

Let us assume a nucleus of charge Z surrounded by a cloud of Z electrons with density ρ , and let us determine $\rho(r)$ self-consistently using the considerations of the previous section. We ignore exchange and determine $V(r)$ from the Poisson equation:

$$\nabla^2 V = -4\pi\rho . \quad (2)$$

(We use atomic units here) Assuming spherical symmetry, the solution to this equation that reduces to the nuclear Coulomb potential at the origin is

$$V(r) = -\frac{Z}{r} + \frac{1}{r} \int_0^r 4\pi s^2 \rho(s) ds + \int_r^R 4\pi s \rho(s) ds .$$

This potential satisfies Eq. (2) and the boundary conditions

$$V(R) = 0 \quad \text{and} \quad \frac{dV}{dr}(R) = 0 .$$

1.3 Self-Consistent TF Code

We wrote a small FORTRAN code “thomas.f” to evaluate the Thomas-Fermi potential $V(r)$ for a cavity of a given radius. The input parameters are the nuclear charge Z , the cavity radius R (a.u.), the temperature range $[T_1, T_2, dT]$, and two initial guesses for the chemical potential μ (μ_1, μ_2). These initial guesses are chosen so that $F(\mu_1) \times F(\mu_2) < 0$, where

$$F(\mu) = Z - 4\pi \int_0^R r^2 \rho(r) dr . \quad (3)$$

The initial guesses insure that the normalization condition $F(\mu) = 0$ is satisfied for some value of μ in the interval (μ_1, μ_2) . The density $\rho(r)$ is evaluated on the standard 500 point atomic grid from Eq. (1). (The Fermi integral $I_{1/2}(x)$ in Eq. (1) is evaluated at each point on the grid using an adaptive 15-point Gaussian quadrature rule from QUADPACK.) Starting from a Coulomb potential $V(r) = -Z/r$, $\rho(r)$ is evaluated and normalized by solving $F(\mu) = 0$ from Eq. (3) using the subroutine “root.f” downloaded from NETLIB which is based on the secant method. After finding $\rho(r)$ and the corresponding value of μ , the Hartree screening function $Y(r)$

$$Y(r) = \int_0^r 4\pi s^2 \rho(s) ds + r \int_r^R 4\pi s \rho(s) ds$$

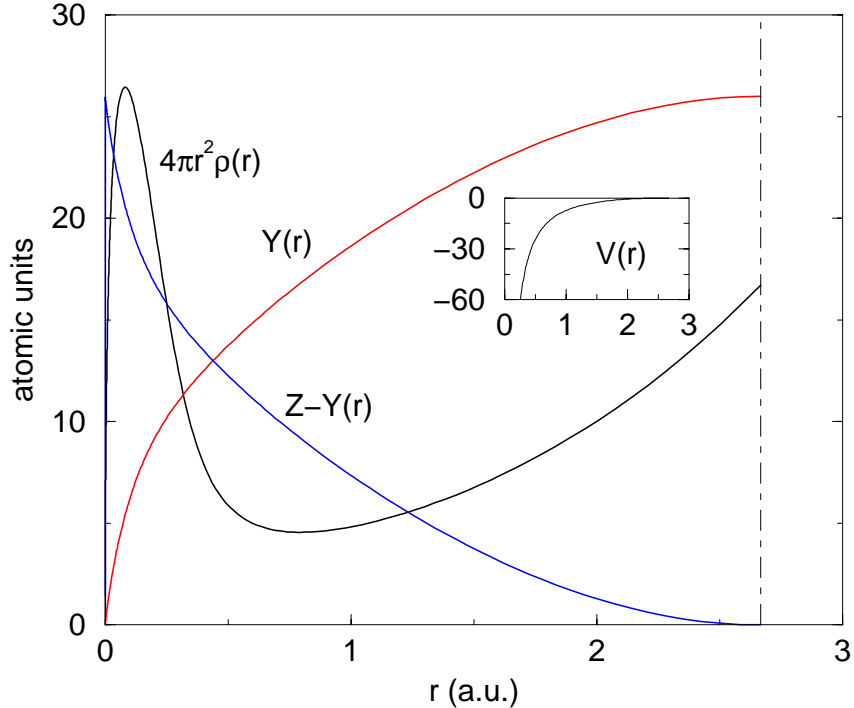


Figure 1: The radial electron density $4\pi r^2 \rho(r)$, the Hartree screening function $Y(r)$ and the “effective” charge $Z - Y(r)$ are shown as functions of r for Fe ($Z=26$, $A= 55.845$) at density $\rho_m = 7.874$ corresponding to $R = 2.6672$. The temperature in this example is $T = 10$ a.u. = 272.1 eV. The insert shows the potential $V(r)$. Note that V and its derivative vanish at $r = R$.

is evaluated and a new effective charge $Z_{\text{eff}} = Z - Y(r)$ is determined. This charge is used to obtain a new potential and the whole process is repeated until the chemical potential has converged between successive iterations to a relative accuracy $\epsilon < 10^{-7}$. The iteration scheme is repeated for each temperature in the interval $[T_1, T_2, dT]$.

Solutions to the above equation for Fe ($Z = 26$) at temperature $kT = 10$ (a.u.) are shown in Fig. 1. The cell radius is $R = 2.6672$ (a.u.) based on normal iron density 7.874 g/cm^3 and atomic weight $A = 55.845 \text{ g/mol}$.

1.4 Pressure

Now, we evaluate the pressure at the surface of the containing sphere $r = R$. Note that the potential and its gradient vanish at the surface. Therefore, the forces on the electron cloud vanish at the surface and the particles move as free particles. One sixth of the electrons move in the

x direction, one sixth in the y direction and one sixth in the z direction. Consider those electrons in a tube of length l_x and area A_x moving along x . The momentum transferred to the surface on an elastic collision is $2p_x$. The force per unit area on A_x by an electron inside the tube having momentum p_x is therefore

$$T_{xx} = 2p_x \times \frac{v_x}{l_x} \times \frac{1}{A_x} = 2 \frac{p_x^2}{mA_x l_x}.$$

The pressure on the surface is

$$P = \frac{1}{6} [T_{xx} + T_{yy} + T_{zz}] = \frac{p^2}{3m} \times \frac{N}{V},$$

where N/V is the density of particles with momentum p at the surface. Average this over a thermal distribution to obtain

$$d^3 P = 2 \frac{d^3 p}{(2\pi)^3} \frac{p^2}{3m} \frac{1}{[1 + e^{(E-\mu)/kT}]},$$

giving

$$\begin{aligned} P &= \frac{1}{3\pi^2 m} \int_0^\infty \frac{p^4 dp}{[1 + e^{(E-\mu)/kT}]} \\ &= \frac{1}{3\pi^2} \int_0^\infty \frac{p^3 dE}{[1 + e^{(E-\mu)/kT}]} \\ &= \frac{(2m)^{3/2}}{3\pi^2} \int_0^\infty \frac{E^{3/2} dE}{[1 + e^{(E-\mu)/kT}]} \\ &= \frac{(2mkT)^{5/2}}{6m\pi^2} I_{3/2}(\mu/kT), \end{aligned}$$

where

$$I_{3/2}(x) = \int_0^\infty \frac{y^{3/2} dy}{[1 + e^{y-x}]}$$

It should be mentioned that the formula for pressure obtained here is in complete agreement with that derived in Ref. [2] from the Helmholtz free energy F using thermodynamic arguments.

	[F]	$8.23872181 \times 10^{-8}$ N
Atomic units of force and length:	[L]	$5.291772083 \times 10^{-11}$ m
	[P]	294.2100996 Mbar

In Table 1, we compare the results of the present calculation of the chemical potential and pressure with the examples given in Table IX in the paper of Feynman, Metropolis, and Teller [1]. We see that with two exceptions, which are obvious misprints, the present calculations are in agreement with those of [1]. The results for P are also in agreement with values from [3].

In the upper panel of Fig. 2, we plot the chemical potential as a function of temperature for Fe at the normal density $\rho_m = \rho_0 = 7.874$ gm/cc

Table 1: Comparison of output from the Thomas-Fermi code with results from Table XI of Feynman, Metropolis, and Teller [1]. The cavity radius a and the temperature T are input parameters. The chemical potential from Ref. [1] is inferred from their tabulated values of β_b .

T(keV)	a(Å)	μ (keV)	μ [1]	P(Mbar)	P [1]
0.2231	1.259	-0.5581	-0.5576	581.2	581.5
0.4926	1.274	-1.6991	-1.6925	1646.	1665.
0.1476	2.977	-0.6639	-0.6615	28.44	28.97
0.2381	3.101	-1.2152	-1.2142	51.34	51.40
0.5297	2.944	-3.1282	-3.1257	170.1	170.9
0.2366	0.966	-0.4269	-0.4193	1333.	1375.
14.660	0.757	-97.191	-97.182	332300.	166000.
0.2923	1.787	-1.1140	-1.1077	311.4	3.179
0.9892	2.844	-6.5628	-6.5571	391.2	392.4
0.3416	4.292	-2.1988	-2.1860	33.40	34.54
0.0326	3.567	-0.1190	-0.1154	1.518	1.703

and at density $0.1 \rho_0$. The chemical potential is small and positive at $T = 0$ and decreases monotonically with T . In the lower panel, we plot the pressure, which increases monotonically from $P = 4.103$ Mbar at $T = 0$ for density ρ_0 and from $P = 0.012$ Mbar for density $0.1 \rho_0$. The results for P are in agreement with values given in Fig. 3 of Cowan and Ashkin [3].

1.5 Kinetic and Potential Energies

The kinetic energy of the atom under consideration is

$$\begin{aligned}
 E_{\text{kin}} &= \int_0^R 4\pi r^2 dr \int \frac{p^2}{2m} \frac{d^3p}{(2\pi)^3} \frac{1}{[1 + e^{(E-\mu)/kT}]} \\
 &= \frac{1}{m\pi} \int_0^R r^2 dr \int_0^\infty \frac{p^4 dp}{[1 + e^{(E-\mu)/kT}]} \\
 &= \frac{2}{\pi} (2mkT)^{3/2} kT \int_0^R I_{3/2}(x) r^2 dr, \tag{4}
 \end{aligned}$$

where $x = [\mu - V(r)]/kT$. Integrating by parts, the integral on the last line of Eq. (4) may be transformed to

$$\int_0^R I_{3/2}(x) r^2 dr = \frac{R^3}{3} I_{3/2}(\mu/kT) + \frac{1}{3kT} \int_0^R r^3 \frac{dI_{3/2}(x)}{dx} \frac{dV}{dr} dr. \tag{5}$$

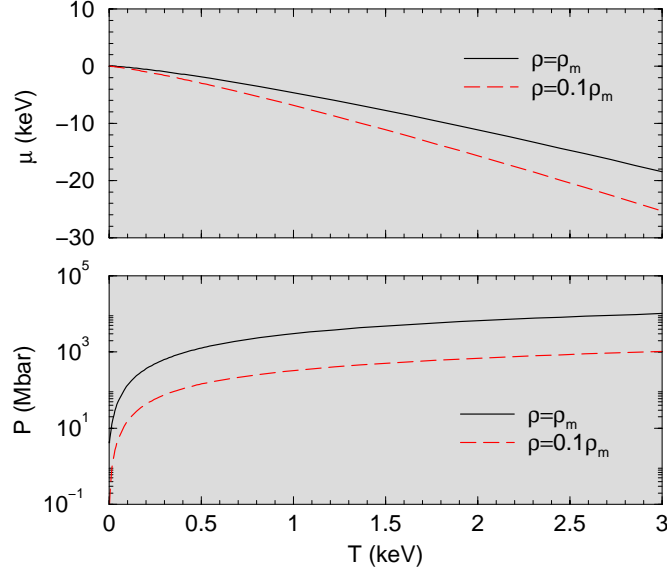


Figure 2: The chemical potential $\mu(T)$ and the pressure P are shown as functions of temperature T for Fe ($Z=26$, $A= 55.845$) at density $\rho_m = 7.874$ gm/cc corresponding to $R = 2.667 a_0$ and at and density $0.1 \rho_m$.

The derivative of $I_{3/2}(x)$ is easily evaluated as

$$\begin{aligned}
 \frac{dI_{3/2}(x)}{dx} &= - \int_0^\infty y^{3/2} d \left[\frac{1}{1 + e^{y-x}} \right] \\
 &= \frac{3}{2} \int_0^\infty \frac{y^{1/2} dy}{[1 + e^{y-x}]} \\
 &= \frac{3}{2} I_{1/2}(x) .
 \end{aligned} \tag{6}$$

With the aid of Eqs. (5) and (6), we can rewrite the kinetic energy from Eq. (4) as

$$\begin{aligned}
 E_{\text{kin}} &= \frac{2}{\pi} (2mkT)^{3/2} kT \left\{ \frac{R^3}{3} I_{3/2}(\mu/kT) + \frac{1}{2kT} \int_0^R r^3 I_{1/2}(x) \frac{dV}{dr} dr \right\} \\
 &= \frac{4\pi R^3}{3} \frac{(2mkT)^{3/2} kT}{2\pi^2} I_{3/2}(\mu/kT) + \frac{(2mkT)^{3/2}}{\pi} \int_0^R I_{1/2}(x) \left(r \frac{dV}{dr} \right) dr \\
 &= \frac{3}{2} P \Omega + \frac{1}{2} \int_0^R 4\pi r^2 \rho(r) \left(r \frac{dV}{dr} \right) dr ,
 \end{aligned} \tag{7}$$

where $\Omega = 4\pi R^3/3$ is the volume of the containing cell. Since

$$r \frac{dV}{dr} = \frac{Z}{r} - \frac{1}{r} \int_0^r 4\pi s^2 \rho(s) ds ,$$

the second term in (7) may be written

$$\begin{aligned}
& \frac{1}{2} \int_0^R 4\pi r^2 \rho(r) \left(r \frac{dV}{dr} \right) dr \\
&= \frac{1}{2} \int_0^R 4\pi r^2 \rho(r) \frac{Z}{r} dr - \frac{1}{2} \int_0^R 4\pi r \rho(r) dr \int_0^r 4\pi s^2 \rho(s) ds \\
&= -\frac{1}{2} (E_{e-n} + E_{e-e}) = -\frac{1}{2} E_{\text{pot}} , \tag{8}
\end{aligned}$$

where E_{pot} is the total potential energy. We have written $E_{\text{pot}} = E_{e-n} + E_{e-e}$, where E_{e-n} is the electron-nucleus potential energy and E_{e-e} is the electron-electron potential energy. Combining the above equations, we obtain a generalized ‘‘virial’’ theorem

$$E_{\text{kin}} = \frac{3}{2} P \Omega - \frac{1}{2} E_{\text{pot}} \tag{9}$$

1.6 Other Thermodynamic Quantities

Other important thermodynamic quantities are also given in [1]. We write out explicit formulas for entropy S , the internal energy U and the Helmholtz free energy F following notes of Rozsnyai [4]. (Rozsnyai’s definition of internal energy is the usual sum kinetic and potential energies; it differs from the definition given in [1] where the $T = 0$ free-space energy is subtracted out.) (The definition of internal energy in these notes is the usual sum kinetic and potential energies; it differs from the definition given in [1] where the $T = 0$ free-space energy is subtracted out.)

The entropy S for a collection of fermions is given by the expression

$$TS = -kT \sum_i [n_i \ln n_i + (1 - n_i) \ln (1 - n_i)] ,$$

where

$$n_i = \frac{1}{[1 + e^{(\epsilon_i - \mu)/kT}]}$$

is the number of states at energy ϵ_i . This can be rearranged to give

$$\begin{aligned}
TS &= -kT \sum_i \left[n_i \ln \left(\frac{n_i}{1 - n_i} \right) + \ln (1 - n_i) \right] \\
&= \sum_i [n_i \epsilon_i - n_i \mu] - kT \sum_i \ln (1 - n_i) \\
&= E_{\text{kin}} + E_{e-n} + 2E_{e-e} - \mu N - kT \sum_i \ln (1 - n_i) . \tag{10}
\end{aligned}$$

The sum on the last line of Eq. (10) can be expressed in terms of the kinetic energy. To this end, we write

$$\begin{aligned}
\sum_i \ln (1 - n_i) &\equiv \int d^3 r \int \frac{2d^3 p}{(2\pi)^3} \ln \left(\frac{e^{(E-\mu)/kT}}{1 + e^{(E-\mu)/kT}} \right) \\
&= \frac{2(2mkT)^{3/2}}{\pi} \int_0^R r^2 dr \int_0^\infty y^{1/2} dy \ln \left(\frac{e^{y-x}}{1 + e^{y-x}} \right) . \tag{11}
\end{aligned}$$

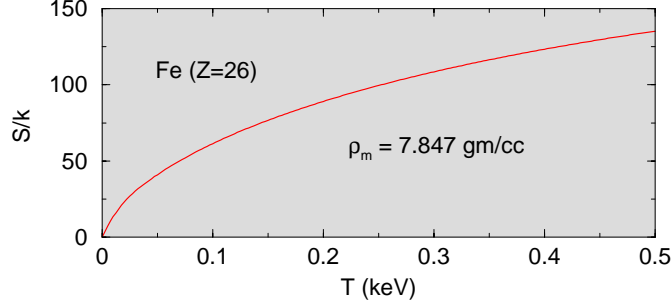


Figure 3: The entropy S/k is shown as functions of temperature T for Fe ($Z=26$, $A= 55.845$) at density $\rho_m = 7.874$ corresponding to $R = 2.6672$ a.u.

The integral over y in Eq. (11) can be integrated by parts to give

$$\int_0^\infty y^{1/2} dy \ln \left(\frac{e^{y-x}}{1 + e^{y-x}} \right) = -\frac{2}{3} \int_0^\infty \frac{y^{3/2} dy}{[1 + e^{y-x}]} = -\frac{2}{3} I_{3/2}(x). \quad (12)$$

It follows that

$$-kT \sum_i \ln(1 - n_i) = \frac{2}{3} kT \frac{2(2mkT)^{3/2}}{\pi} \int_0^R r^2 dr I_{3/2}(x) = \frac{2}{3} E_{\text{kin}}$$

Combining, we have

$$TS = \frac{5}{3} E_{\text{kin}} + E_{e-n} + 2E_{e-e} - \mu N \quad (13)$$

$$= \frac{5}{2} P \Omega + \frac{1}{6} E_{e-n} + \frac{7}{6} E_{e-e} - \mu N. \quad (14)$$

A plot of the (dimensionless) ratio of the entropy to Boltzmann's constant S/k as a function of T for Fe ($Z=26$, $A= 55.845$) at density $\rho_m = 7.874$ (gm/cc) is given in Fig. 3. Values of S from this plot are in agreement with values given in Fig. 5 in Ref. [3].

The internal energy U is

$$U = E_{\text{kin}} + E_{\text{pot}} = \frac{3}{2} P \Omega + \frac{1}{2} E_{e-n} + \frac{1}{2} E_{e-e}. \quad (15)$$

From thermodynamics, we know that

$$dU = dQ - Pd\Omega = TdS - Pd\Omega.$$

The Helmholtz free energy F is defined in terms of the internal energy U by

$$F = U - TS = -P\Omega + \frac{1}{3} E_{e-n} - \frac{2}{3} E_{e-e} + N\mu. \quad (16)$$

From the first of these it follows that

$$dF = -SdT - Pd\Omega.$$

Table 2: Contributions to energies and entropy of Fe ($Z = 26$, $A = 55.845$) at density $\rho_m = 7.874$ (gm/cc) are evaluated for the cases considered in Table 1. The present values of energies are in agreement with values from Ref. [1] and from the extensive tables in [5].

T(keV)	a(Å)	E_{pot}/kTZ	E_{kin}/kTZ	$P\Omega/kTZ$	S/k
0.2231	1.259	-13.53	7.548	0.5227	87.53
0.4926	1.274	-5.439	3.762	0.6947	126.6
0.1476	2.977	-20.18	10.86	0.5112	116.5
0.2381	3.101	-11.62	6.780	0.6465	148.8
0.5297	2.944	-4.225	3.348	0.8238	195.1
0.2366	0.966	-12.98	7.256	0.5107	74.63
14.660	0.757	-0.0612	1.514	0.9888	236.9
0.2923	1.787	-9.679	5.757	0.6113	122.2
0.9892	2.844	-1.748	2.246	0.9147	226.9
0.3416	4.292	-7.143	4.738	0.7774	197.0
0.0326	3.567	-97.87	49.26	0.2125	56.51

From this, it follows in turn that the Helmholtz free energy is a thermodynamic function of the “natural” variables of the problem (Ω and T). We have

$$S = -\left.\frac{\partial F}{\partial T}\right|_{\Omega} \quad P = -\left.\frac{\partial F}{\partial \Omega}\right|_T$$

In Table 2, we list values of the potential energy E_{pot} , the kinetic energy E_{kin} , the product $P\Omega$, and the entropy S for those cases considered in Table 1. The values of the energies are in agreement with values given in Table XI of Ref. [1].

References

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