

Solid-Liquid thermodynamic database in the MgO-FeO-SiO₂ system from 20 to 140 GPa

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In this document, you will find the thermodynamic models and parameters used in Boukaré et al. (2015).

1. Gibbs free energy of the solid *end-members*

We write the Helmholtz Free energy as follows,

$$\begin{aligned} F(V, T) &= F(V_0, T_0) + (F(V, T_0) - F(V_0, T_0)) + (F(V, T) - F(V, T_0)) \\ &= F(V_0, T_0) + F_{V_0, T_0}^c(V) + F^{th}(V, T) \end{aligned} \quad (1)$$

where the so-called cold part, $F_{V_0, T_0}^c(V)$ describes the volume dependence of F at $T = T_0$ and the thermal part $F^{th}(V, T)$ accounts for the effects of thermal agitation.

1.1. The cold part, $F_{V_0, T_0}^c(V)$

We follow Stixrude and Lithgow-Bertelloni (2005) and De Koker and Stixrude (2009) where the cold part is the volume integrale of the 3rd order Birch-Murnaghan equation of state (EoS),

$$F_{V_0, T_0}^c(V) = 9K_0 \left[\frac{1}{2}f^2 + \frac{1}{2}(K' - 4)f^3 \right] \quad (2)$$

and,

$$f = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{2/3} - 1 \right] \quad (3)$$

where K_0 is the incompressibility and K' its pressure derivative at $T = T_0$ and $V = V_0$.

1.2. The thermal part, $F^{th}(V, T)$

The thermal part, $F^{th}(V, T)$, is computed using the Debye approximation,

$$F^{th}(V, T) = 9nRT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \epsilon^2 \ln(1 - e^{-\epsilon}) d\epsilon \quad (4)$$

where n is the number of atoms of the chemical specie in question (e.g., for MgO, $n = 2$) and R is the universal gas constant. $\theta_D(V, T_0)$ is the Debye temperature,

$$\theta_D = \theta_0 e^{\frac{\gamma_0 - \gamma}{q}} \quad (5)$$

where the Grüneisen parameter, γ , is reduced to

$$\gamma = \gamma_0 \left(\frac{V}{V_0} \right)^q \quad (6)$$

where q is a constant and γ_0 is Grüneisen parameter of reference at $V = V_0$. For solids, the Gibbs function, G , is computed from the Helmholtz free energy, F . Maxwell's relations give:

$$G = F + V \left(\frac{\partial F}{\partial V} \right)_T \quad (7)$$

and

$$\left(\frac{\partial F}{\partial V} \right)_T = -P \quad (8)$$

2. Gibbs free energy of the liquid *end-members*

We consider here three end-members in the liquid phase (MgO)_l, (FeO)_l et (SiO₂)_l. Sadly, each end-member has its own EoS, hence a specific Gibbs function.

- For (MgO)_l, we follow exactly the model described in Liebske and Frost (2012) and De Koker and Stixrude (2009).
- For (SiO₂)_l, it has been shown that the variation of its incompressibility requires a 5th order Birch-Murnaghan EoS (De Koker and Stixrude, 2009; Sanloup et al., 2013). However, the thermodynamic model of De Koker and Stixrude (2009) is hard to reproduce. Consequently, we fit their FPMD calculation with a simple exponential EoS. We then derived the self-consistent thermodynamic potentials associated with this EoS.
- For (FeO)_l, we need a simple well-behaved thermodynamic model as we inverse various experimental data for the thermodynamic parameters of liquid FeO (Boukaré et al., 2015).

For the liquids end-members, we summarize in Table 1 the mathematical functions that describe the key ingredients of the thermodynamic models: the EoS, the thermal capacity (or equivalent) and the Grüneisen parameter (or equivalent).

End-members	EoS	C_V (ou eq.*)	γ (ou eq.*)
MgO	3 rd order BM**	Constant	Linear in V
FeO	Murnaghan	Linear in T	Exponential in V
SiO ₂	Exponential	Linear in V and T	Function of V et T

Table 1: We summarize here the mathematical formalism that describe the key ingredients (EoS, thermal capacity, C_V and Grüneisen parameter, γ) used to build the Gibbs function of the liquid *end-members*. *eq : equivalent. **BM: Birch-Murnaghan.

2.1. Liquid MgO [Liebske et al, 2012][DeKoker et al, 2009]

For liquid MgO, the Helmotz free energy is also decomposed into a cold and a thermal part. The cold part, $F_{T_0}^c(V)$ for liquid MgO is the same as for the solids (equation 2). While the thermal part of the solid end-members is developed using the vibrational approach, the thermal part of F is obtained by integrating an entropy model.

We have,

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT \quad (9)$$

By using the definition of C_V , the thermodynamic identity $dF = -SdT - PdV$ and the definition of the Grüneisen parameter $\gamma = \alpha V K_T / C_V$, we get,

$$dS = \alpha K_T dV + \frac{C_V}{T} dT = \frac{\gamma C_V}{V} dV + \frac{C_V}{T} dT \quad (10)$$

Assuming that $C_V = C_{V_0}$ is constant and $\gamma = \gamma_0 \left(\frac{V}{V_0} \right)^q$ (equation 6), we obtain,

$$S(V, T) = S_0 + C_{V_0} \frac{\gamma_0}{q} \left[\left(\frac{V}{V_0} \right)^q - 1 \right] + C_{V_0} \ln \frac{T}{T_0} \quad (11)$$

We have,

$$S(V, T) = - \left(\frac{\partial F}{\partial T} \right)_V \quad (12)$$

It turns out that,

$$F_{V_0, T_0}^{th}(T) = -S_0(T - T_0) - C_{V0} \left[T \ln \left[\frac{T}{T_0} \right] - (T - T_0) \right] - C_{V0} \frac{\gamma_0}{q} (T - T_0) \left[\left(\frac{V}{V_0} \right)^q - 1 \right] \quad (13)$$

2.1.1. *SiO₂ liquide (home-made)*

De Koker and Stixrude (2009); DeKoker et al. (2013) describe the Gibbs free energy of liquid SiO₂ with high degree polynomial functions. However, they do not provide the coefficients required to reproduce the Gibbs function. Here, we develop a simple Gibbs function for liquid SiO₂ that we use to fit the FPMD calculations of De Koker and Stixrude (2009).

We start with the following equation of state.

$$P(V, T_0) = P(V_0, T_0) + F(V) \quad (14)$$

where,

$$F(V) = p_0 \text{Exp}[p_1 V] + p_2 \text{Exp}[p_3 V] \quad (15)$$

We use an exponential function to describe the EoS as it allows to reproduce very precisely high order Birch-Murnaghan EoS with four parameters (from 0 to 140 GPa, liquid SiO₂ requires a 5th order BM).

FPMD calculations show a volume dependance of C_V (see Figure 1). We choose,

$$C_V = C_V^0 + C_V^1 V + C_V^2 T \quad (16)$$

(C_V^2 seems absolutely useless, can't remember why I have this guy) and Maxwell relations imposes,

$$\left(\frac{\partial \alpha K_T}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial C_V}{\partial V} \right)_T = \frac{C_V^1}{T} \quad (17)$$

FPMD calculations also show a volume dependance of αK_T (see Figure 1). We choose,

$$\alpha K_T = f_1 V^{f_2} + C_V^1 \ln \left[\frac{T}{T_0} \right] \quad (18)$$

Note that the last term on the right-hand side of equation 18 is constrained by equation 16 through equation 17. By integrating equation 18, we can add the thermal pressure to the EoS (equation 14) using,

$$\left(\frac{\partial P}{\partial T} \right)_V = \alpha K_T. \quad (19)$$

We get,

$$P(V, T) = P(V_0, T_0) + F(V) + (T - T_0) f_1 V^{f_2} + C_V^1 \left[T \ln \left[\frac{T}{T_0} \right] - (T - T_0) \right] \quad (20)$$

From the definition of αK_T and C_V , we can build the entropy (equation 10),

$$S(V, T) = S(V_0, T_0) + (C_V^0 + C_V^1 V) \ln \left[\frac{T}{T_0} \right] + C_V^2 (T - T_0) + C_V^1 (V - V_0) \ln \left[\frac{T}{T_0} \right] \quad (21)$$

The others thermodynamic potential (F , G , E ...) can then be obtained by integration.

In Figure 1, we show our fits of the FMPD calculations of De Koker and Stixrude (2009) for the internal energy, $E(V, T)$, the EoS, $P(V, T)$, the thermal capacity at constant volume, C_V and αK_T . The best fitting thermodynamic parameters are shown in Table 2.

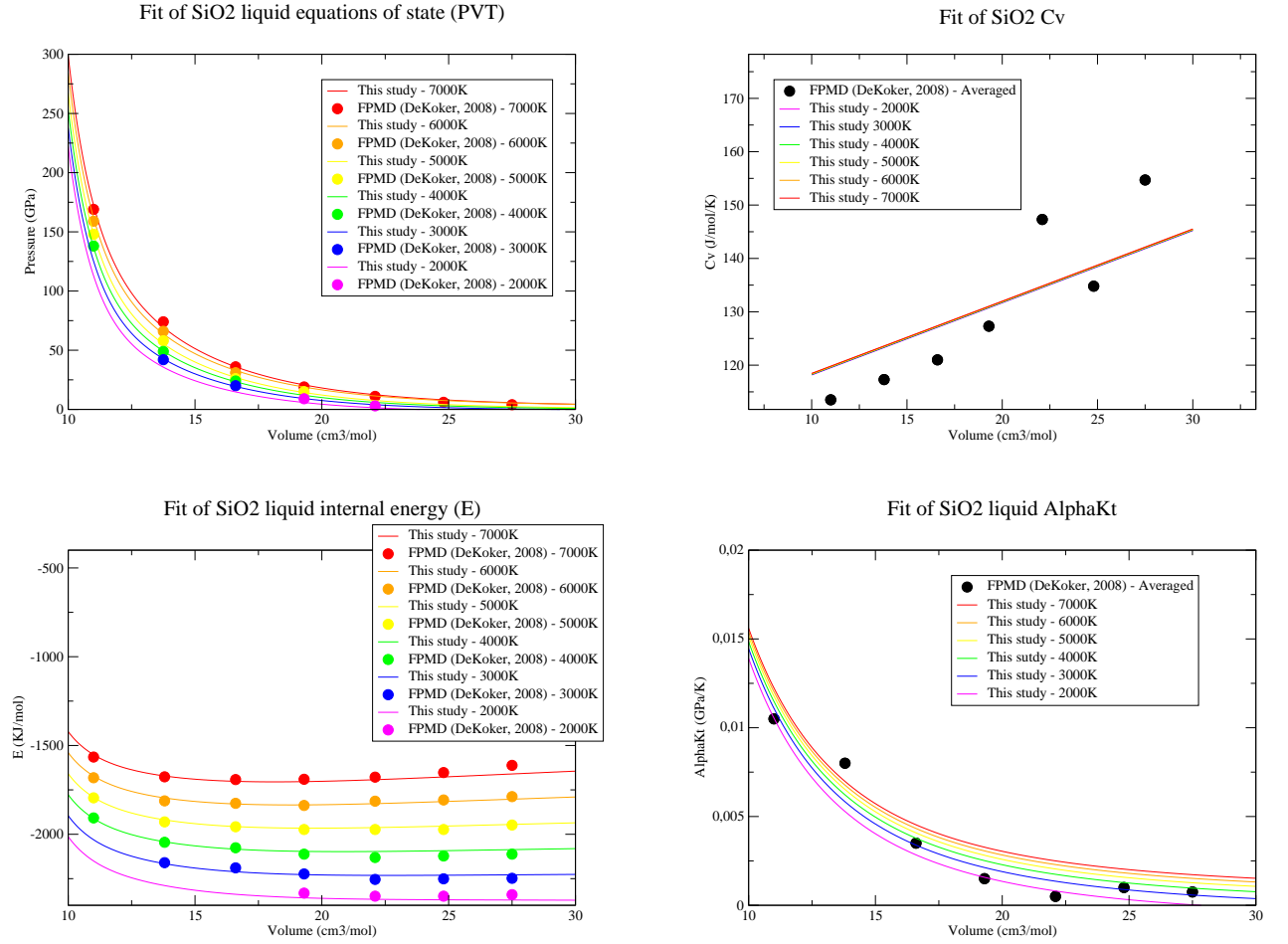


Figure 1: We fit the FPMD calculations of De Koker and Stixrude (2009) with our Gibbs function. The best fitting parameters can be found in Table 2.

2.1.2. FeO liquide (home-made)

Taking into account the limited amount of observations available for the iron liquid oxyde end member, we start from a simple Murnaghan expression Murnaghan (1951)

$$\frac{\rho_0}{\rho} \approx (1 + n \frac{P}{K_0^T})^{-\frac{1}{n}} \quad (22)$$

as the density ρ is mostly a function of the pressure P . To account for the minor effect of temperature T , we choose a linear correction:

$$\frac{\rho_0}{\rho} = (1 + n \frac{P}{K_0^T})^{-\frac{1}{n}} + A(P)\alpha_0(T - T_0) \quad (23)$$

where $A(P)$ is a yet unknown function of P . We assume, as what is usually done with solid EOS Anderson (1979) that

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \alpha_0 K_0^T \left(\frac{\rho}{\rho_0}\right)^{1-q} \quad (24)$$

which using (23) constrains A and leads to the semi-empirical EOS

$$\frac{\rho_0}{\rho} = (1 + n \frac{P}{K_0^T})^{-\frac{1}{n}} + (1 + n \frac{P}{K_0^T})^{-\frac{n+q}{n}} \alpha_0(T - T_0) \quad (25)$$

The shape of this last equation is certainly arbitrary. However it is a simple, mathematically well behaved equation, with a limited number of parameters, 5, a reference density ρ_0 , thermal expansion α_0 , compressibility K_0 , and two exponents n and q .

From the Maxwell relation $\partial(1/\rho)/\partial T|_P = -\partial S/\partial P|_T$, we can derive the pressure dependence of the entropy according to (25) and we choose as a general entropy parametrization:

$$S = S_0 + C_0(T - T_0) + C_1 \log \frac{T}{T_0} + \frac{\alpha_0 K_0}{q \rho_0} \left(1 + n \frac{P}{K_0^T}\right)^{-\frac{q}{n}} \quad (26)$$

Finally, we obtain an expression for the reference potential by using

$$d\mu_0 = \frac{1}{\rho} dP - S dT \quad (27)$$

which is

$$\begin{aligned} \mu_0 = & G_0 - S_0(T - T_0) \\ & - C_1 \left(T \log \left(\frac{T}{T_0} \right) - (T - T_0) \right) \\ & - \frac{C_0}{2} (T - T_0)^2 \\ & - \frac{\alpha_0 K_0^T}{\rho_0 q} \left(1 + n \frac{P}{K_0^T}\right)^{-\frac{q}{n}} (T - T_0) \\ & + \frac{K_0^T}{\rho_0(n-1)} \left(1 + n \frac{P}{K_0^T}\right)^{1-\frac{1}{n}} \end{aligned} \quad (28)$$

MgO Liquid		FeO Liquid		SiO ₂ Liquid	
T_0	3000.0	T_0	2000	T_0	4000
V_0	16.46	P_0	20	V_0	27.4
K_0	34	ρ_0	3.82641	p_0	1447.2
K'	4.5	K_0	30.961	p_1	-0.24865
γ_0	0.96	α_0	-9.54849	p_2	10.27×10^6
γ'	-0.37	q	-0.97	p_3	-1.1258
C_v	56	n	3.26	f_1	7.45
S_0	173.5	S_0	175.617	f_2	-2.701
F_0	-843.89	$C_{p,0}$	3.0×10^{-3}	S_0	275
		$C_{p,1}$	73.7532	$C_{v,0}$	0.10451
		G_0	-1153.52	$C_{v,1}$	0.1353×10^{-2}
				$C_{v,2}$	0.6×10^{-7}
				F_0	-2030.3

Table 2: Thermodynamic parameters of the liquid end-members. The expression of the Helmutz Free Energy, $F(V,T)$, is derived in section 2.

	Unit	Mg-Perovskite	Fe-Perovskite	Periclase	Wustite	Sthishovite
T_0	K	300.0	300.0	300.0	300.0	300.0
V_0	$10^{-6} \text{ m}^{-3} / \text{mol}$	24.45	25.49	11.24	12.256	14.02
K_0	GPa	251	272	161	149	314
K'	-	4.14	4.1	4.8	3.6	3.8
γ_0	-	1.57	1.57	1.3	1.41	1.37
q	-	1.1	1.1	1.7	0.5	2.8
θ_0	-	905	871	767	417	1108
F_0	kJ/mol	-1408	-1048	-569	-165	-819

Table 3: Thermodynamic parameters of solids phases. The expression of the Helmutz Free Energy, $F(V,T)$, is derived in section 1.

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