Appendix: Thermodynamic relations and Equation of State

Rosenfeld and Tarazona (1998) derive an expression from a fundamental-measure energy functional for hard spheres and thermodynamic perturbation theory for the functional dependence of the potential energy (*U*) on volume (*V*) and temperature (*T*) in a dense classical liquid:

$$U(V,T) = a(V) + b(V)T^{3/5} \tag{1}$$

This expression beautifully represents the potential energy-temperature relations along a given isochore obtained from our MD simulations of liquid Mg_2SiO_4 (Appendix Fig. 1, Appendix Table 1).

The *a(V)* and *b(V)* functions may be parameterized using simple polynomials of volume (Appendix Fig. 2, Appendix Table 2, e.g. Saika-Voivod et al., 2000).

Given the representation of *U* embodied in Equation 10, the internal energy, *E*, is obtained by addition of the kinetic energy, $\frac{3n}{2}RT$, where *n* in this case is seven, the number of atoms in the formula unit of Mg_2SiO_4 liquid:

$$E(V,T) = a(V) + b(V)T^{3/5} + \frac{3n}{2}RT \tag{2}$$

From Equation 11 the isochoric heat capacity is readily obtained by differentiation with respect to *T* at constant *V*

$$C_V = \frac{3}{5}\frac{b(V)}{T^{2/5}} + \frac{3n}{2}R \tag{3}$$

It should be appreciated that since values of the function *b*(*V*) are positive (e.g., Appendix Fig, 2b), the heat capacity of a Rosenfeld-Tarazona fluid will decrease with increasing temperature asymptotically to the value 3*nR*/2.

An internally consistent equation of state (EOS) may be constructed from Equation 11 by first finding an expression for the Helmholtz free energy (*A*), which is formally defined as

$$A(V,T) = E(V,T) - TS(V,T) \tag{4}$$

The temperature- and volume-dependence of the entropy (*S*) may be obtained from Equation 11 and the thermodynamic identity $dE = TdS - PdV$. From this identity it follows that

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

and

$$\left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

which together permit the entropy to be evaluated as

$$S(V,T)=S(V_0,T_0)+\frac{1}{T_0}\int_{V_0}^{V}\left[\left.\left(\frac{\partial E}{\partial V}\right)_T\right|_{T_0}+P(V,T_0)\right]dV+\int_{T_0}^{T}\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT \tag{5}$$

Substitution of Equation 11 into Equation 14 gives a model expression

$$\begin{aligned}S(V,T)&=S(V_0,T_0)\\&+\frac{1}{T_0}\left[a(V)+T_0^{3/5}b(V)-a(V_0)-T_0^{3/5}a(V_0)+\int_{V_0}^{V}P(T_0,V)dV\right]\\&-\frac{3}{2}\left(\frac{1}{T^{2/5}}-\frac{1}{T_0^{2/5}}\right)b(V)+\frac{3n}{2}R\ln\left(\frac{T}{T_0}\right)\end{aligned} \tag{6}$$

Note that the entropy is defined *relative to that at a reference volume* (V_0) *and temperature* (T_0) – that is, with respect to an unspecified constant - and that the model expression requires adoption of an EOS along the reference isotherm [$P(T_0, V)$]. The selection of this EOS is arbitrary.

Substitution of Equations 11 and 15 into Equation 13 gives a model expression for the Helmholtz free energy compatible with Equation 10

$$\begin{aligned}A(V,T)&=a(V)+T^{3/5}b(V)+\frac{3n}{2}RT-TS(V_0,T_0)\\&-\frac{T}{T_0}\left[a(V)+T_0^{3/5}b(V)-a(V_0)-T_0^{3/5}a(V_0)+\int_{V_0}^{V}P(T_0,V)dV\right]\\&+T\frac{3}{2}\left(\frac{1}{T^{2/5}}-\frac{1}{T_0^{2/5}}\right)b(V)-\frac{3n}{2}RT\ln\left(\frac{T}{T_0}\right)\end{aligned} \tag{7}$$

An EOS is obtained from Equation 16 by differentiation, i.e., $P=-\left(\frac{\partial A}{\partial V}\right)_T$:

$$P=\left(\frac{T}{T_0}-1\right)\frac{da(V)}{dV}+\frac{5}{2}T^{3/5}\left[\left(\frac{T}{T_0}\right)^{2/5}-1\right]\frac{db(V)}{dV}+\frac{T}{T_0}P(T_0,V) \tag{8}$$

This result demonstrates that a Rosenfeld-Tarazona compatible EOS – $P(V,T)$ – can be built from any isothermal EOS of choice, and that the temperature dependence of the pressure arises through the parameterization of the potential energy of the fluid. In this paper we adopt for $P(T_0, V)$ the Universal EOS of Vinet at al. (1986; 1987; 1989)

$$P(T_0,V)=\frac{3K_v(1-x)e^{\eta(1-x)}}{x^2} \tag{9}$$

where $\eta=\frac{3}{2}\left(K_v^{'}-1\right)$ and $x=\left(\frac{V}{V_v}\right)^{1/3}$. In Equation 18, K_v, $K_v^{'}$ and V_v are constants (fit parameters of the EOS), whose values correspond to the bulk modules, its pressure derivative, and the zero pressure volume, respectively, all at the temperature T_0. A fit to the nominal ~3500 K MD data for Mg_2SiO_4 liquid is presented in Appendix Table 3. The model EOS is presented and compared to the MD simulation data in Appendix Figure 3.

In the low temperature limit, the Helmholtz energy (Eq. 16) reduces to $A(V,T) \approx a(V)$, and by inspection of Appendix Fig. 2a it is clear that in the case of our model calculations for Mg_2SiO_4 liquid there is a range of volume over which the liquid is thermodynamically unstable with respect to unmixing at sufficiently low-*T*; this region corresponds to the portion of the curve that is concave down, and in this case the coexisting liquids differ in structure but are identical in composition. The loci of (*V,T*)-points corresponding to zero-curvature of *A* is known as the spinoidal and is given by the thermodynanic condition of phase instability (Prigogine and Defay, 1954): $\left(\partial P/\partial V\right)_T = 0$, which from Equation 17 is

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = \left(\frac{T}{T_0} - 1\right)\frac{d^2 a(V)}{dV^2} + \frac{5}{2}T^{3/5}\left[\left(\frac{T}{T_0}\right)^{2/5} - 1\right]\frac{d^2 b(V)}{dV^2} + \frac{T}{T_0}\frac{dP(T_0,V)}{dV} \tag{10}$$

for our thermodynamic model. The highest temerature that satisfies Equation 19 is the *critical point* (the temperature of the onset of unmixing). We find this *T* to be below 100 K, a condition corresponding to the deeply supercooled region.

A compete set of thermodynamic functions can be developed from Equations 16 and 17 and the numerical evaluation of these functions requires no further paramterization of the MD data.

The Gibbs free energy ($G = A + PV$) is

$$\begin{aligned} G(V,T) = {} & a(V) + T^{3/5}b(V) + \frac{3n}{2}RT - TS(V_0,T_0) \\ & - \frac{T}{T_0}\left[a(V) + T_0^{3/5}b(V) - a(V_0) - T_0^{3/5}a(V_0) + \int_{V_0}^{V} P(T_0,V)\,dV\right] \\ & + T\frac{3}{2}\left(\frac{1}{T^{2/5}} - \frac{1}{T_0^{2/5}}\right)b(V) - \frac{3n}{2}RT\ln\left(\frac{T}{T_0}\right) \\ & + \left(\frac{T}{T_0} - 1\right)V\frac{da(V)}{dV} + \frac{5}{2}T^{3/5}\left[\left(\frac{T}{T_0}\right)^{2/5} - 1\right]V\frac{db(V)}{dV} + \frac{T}{T_0}VP(T_0,V) \end{aligned} \tag{11}$$

The coefficient of "thermal pressure," $\left(\frac{\partial P}{\partial T}\right)_V$, is given as

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T_0}\frac{da(V)}{dV} + \frac{3}{2}T^{-2/5}\left[\frac{5}{3}\left(\frac{T}{T_0}\right)^{2/5} - 1\right]\frac{db(V)}{dV} + \frac{P(T_0,V)}{T_0} \tag{12}$$

The bulk modulus, $K = -V\left(\frac{\partial P}{\partial V}\right)_T$, is found to be

$$K = -\left(\frac{T}{T_0} - 1\right) V \frac{d^2 a(V)}{dV^2} - \frac{5}{2} T^{3/5} \left[\left(\frac{T}{T_0}\right)^{2/5} - 1\right] V \frac{d^2 b(V)}{dV^2} - \frac{T}{T_0} V \frac{dP(T_0,V)}{dV} \qquad (13)$$

and, since $\alpha K = \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$, the isothermal coefficient of expansion (α) may be written

$$\alpha = -\frac{\frac{1}{T_0}\frac{da(V)}{dV} + \frac{3}{2} T^{-2/5} \left[\frac{5}{3}\left(\frac{T}{T_0}\right)^{2/5} - 1\right] \frac{db(V)}{dV} + \frac{P(T_0,V)}{T_0}}{V\left\{\left(\frac{T}{T_0} - 1\right)\frac{d^2 a(V)}{dV^2} + \frac{5}{2} T^{3/5} \left[\left(\frac{T}{T_0}\right)^{2/5} - 1\right] \frac{d^2 b(V)}{dV^2} + \frac{T}{T_0}\frac{dP(T_0,V)}{dV}\right\}} \qquad (14)$$

Finally, our model expression for the Grüneisen parameter, $\gamma = \frac{\alpha K V}{C_V}$, is given by

$$\gamma = \frac{\frac{V}{T_0}\frac{da(V)}{dV} + \frac{3}{2} V T^{-2/5} \left[\frac{5}{3}\left(\frac{T}{T_0}\right)^{2/5} - 1\right] \frac{db(V)}{dV} + \frac{V P(T_0,V)}{T_0}}{\frac{3}{5}\frac{b(V)}{T^{2/5}} + \frac{3n}{2} R} \qquad (15)$$

Appendix Table 1. Coefficients for the Rosenfeld-Tarazona (1998) model expression for the potential energy of a dense fluid: $U(V,T) = a(V) + b(V)T^{3/5}$

ρ (kg/m^3)	b (V) (*kJ*/mol)	σ	a (V) (*kJ*/mol)	σ
2753.83	4.518	0.011	–5803.4	1.5
3000.07	4.569	0.0043	–5825.9	0.58
3075.07	4.574		–5829.2	
3150.07	4.595	0.0067	–5833.4	0.91
3225.08	4.608		–5836.1	
3300.08	4.644	0.0099	–5839.7	1.3
3500.08	4.744	0.024	–5845.9	3.3
3800.09	5.122	0.016	–5871.2	2.3
3900.09	5.330	0.0084	–5886.8	1.3
4200.10	5.835	0.021	–5895.6	3.2
4350.10	6.094	0.015	–5890.3	2.3
4500.10	6.388	0.011	–5880.0	1.7

Notes: Model equations are compared to MD simulation data in Figure 12 (in text).

Appendix Table 2. Polynomial parameterizations of the Rosenfeld-Tarazona (1998) functions for the potential energy

i	$a(V)$ (kJ/mol)	$b(V)$ ($kJ/K^{3/5}$mol)
0	19790.2	52.7838
1	–437356.	–471.962
2	3046190.	1706.03
3	–11179100.	–2690.69
4	23103100.	1553.34
5	–26316700.	
6	14597600.4	
7	–2621980.	

Notes: $a(V)=\sum_{0}^{n} a_i V^i$ and $b(V)=\sum_{0}^{n} b_i V^i$; V has units cm^3/gm or 1000 × the quantity in units of m^3/kg (see Appendix Fig. 1).

Appendix Table 3. Parameterization of the Universal EOS (Eq. 9) along the nominal 3500 K isotherm ($T_0 = 3582.75 \pm 45.75$ K)

Parameter	Value	Units
V_v	8.08642×10^{-4}	m^3/kg
K_v	0.131575	GPa
K'_v	11.8272	

Note: The standard error on residuals for pressure recovery from this EOS is 0.059 GPa.

Note that the references cited in this appendix are included in the reference list of the article, except for one which is below.

Prigogine, I. and Defay, R. (1954) Chemical Thermodynamics, 543 p., Longmans Green and Co., New York.