A new approach to the equation of state of silicate melts: An application of the theory of hard sphere mixtures

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Abstract

A comparison of compressional properties of silicate solids, glasses, and liquids reveals the following fundamental differences: (1) Liquids have much smaller bulk moduli than solids and glasses and the bulk moduli of various silicate melts have a narrow range of values; (2) Liquids do not follow the Birch’s law of corresponding state as opposed to solids and glasses; (3) The Grüneisen parameter increases with increasing pressure for liquids but decreases for solids; (4) The radial distribution functions of liquids show that the interatomic distances in liquids do not change upon compression as much as solids do.

The last observation indicates that the compression of silicate melts occurs mostly through the geometrical arrangement of various units whose sizes do not change much with compression, i.e., the entropic mechanism of compression plays a dominant role over the internal energy contribution. All of the other three observations listed above can be explained by this point of view. In order to account for the role of the entropic contribution, we propose a new equation of state for multi-component silicate melts based on the hard sphere mixture model of a liquid. We assign a hard sphere for each cation species that moves in the liquid freely except for the volume occupied by other spheres. The geometrical arrangement of these spheres gives the entropic contribution to compression, while the Columbic attraction between all ions provides the internal energy contribution to compression. We calibrate the equation of state using the experimental data on room-pressure density and room-pressure bulk modulus of liquids. The effective size of a hard sphere for each component in silicate melts is determined. The temperature and volume dependencies of sphere diameters are also included in the model in order to explain the experimental data especially the melt density data at high pressures. All compressional properties of a silicate melt can be calculated using the calibrated sphere diameters. This equation of state provides a unified explanation for most of compressional behaviors of silicate melts and the experimental observations cited above including the uniformly small bulk moduli of silicate melts as well as the pressure dependence of Grüneisen parameters. With additional data to better constrain the key parameters, this equation of state will serve as a first step toward the unified equation of state for silicate melts.

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1. INTRODUCTION

Compressional properties of silicate melts including density and its pressure (or temperature) derivative, i.e., bulk modulus (or thermal expansivity), are crucial to our understanding of many geological problems such as the generation and differentiation of silicate melts in the Earth’s mantle, and the evolution of a melt layer (e.g., the putative magma ocean) in a planet. Important issues in this regard include the density of melts with various chemical compositions under deep Earth conditions (i.e., equation of state (EOS)) and the variation of some thermodynamic properties such as the Grüneisen parameter with compression. In order to understand these issues, a physically sound model is needed for the compression of molten materials under deep Earth conditions.

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However, unlike the solid and gaseous states of a matter for which there are widely accepted idealized models such as a crystal lattice and an ideal gas, describing the properties of liquids is challenging because they are nearly as dense as solids yet there is no long-range order in atomic positions (see textbooks, e.g., Egelstaff, 1994; March and Tosi, 2002; Barrat and Hansen, 2003; Hansen and McDonald, 2006). In the past, purely empirical equations of state were frequently employed for silicate melts. One such type of EOS is the Taylor expansion of volume in terms of pressure (e.g., Lange and Carmichael, 1987, 1990; Kress and Carmichael, 1991). The effect of liquid composition on volume is studied by the ideal mixing model first developed by Bottinga and Weill (1970). In the Bottinga–Weill model, the molar volume of a melt is a linear function of the partial molar volume of each oxide component \( \text{SiO}_2 \), for example in the melt, implying that the compression of a complex liquid can be modeled as a sum of the compression of individual solid-like components. Similarly, higher order coefficients in the Taylor expansion are calculated from properties of oxide components by assigning bulk modulus for each component oxide (e.g., Lange and Carmichael, 1987). This type of approach was employed in the widely used software package MELTS (Ghiorso and Sack, 1995) for the modeling of phase equilibria in magmatic systems. Apart from the obvious limitation that such an approach works only to a low degree of compression (Lange and Carmichael, 1987), there is a fundamental issue for the basic concept behind this approach: An implicit assumption is that the compression of a complex liquid such as a silicate melt can be viewed as the weighted average of compression of individual oxide components. As we will show in this paper, existing data on bulk moduli and radial distribution functions of silicate melts suggest that such a solid-based model of compression is unlikely valid for the compression of silicate melts.

A modified version of a curve-fitting approach has recently been proposed by Ghiorso and his co-worker (Ghiorso, 2004a,b,c; Ghiorso and Kress, 2004) using the Padé approximation. In this approach, some complications such as the influence of mixing of \( \text{SiO}_2 \) species with different Si–O coordination numbers are included. However, this is again an entirely empirical approach and the formula used in their approach has no strong physical basis.

Another group of equations of state borrows directly the ideas developed for solids. These include the widely used third-order Birch–Murnaghan EOS (Birch, 1947) and the Vinet EOS (Vinet et al., 1986). Many studies for silicate liquids at high pressure employ the Birch–Murnaghan EOS (e.g., Rigden et al., 1989; Agee, 1998; Stixrude and Karaki, 2005). Also, it was utilized in pMELTS (Ghiorso et al., 2002), the revised version of MELTS, for the modeling of phase equilibria up to 3 GPa. Similarly, Stixrude and Karaki (2005) explained the calculated trend in Grüneisen parameters using the behavior of Grüneisen parameters of the corresponding solids. The physical basis for the Birch–Murnaghan EOS is that the thermodynamics of a given material is completely characterized by the volumetric strain and that the influence of temperature can be included through the temperature dependence of parameters such as bulk modulus. Such an approach is valid when the major contribution to the free energy is the internal energy. However, as we will demonstrate in this paper, several observations strongly suggest that it is not the internal energy that changes most upon compression of a silicate melt: the factor that plays the most important role in the compression of silicate melts is entropy. In these cases, concepts borrowed from solids may not be applied to liquids.

The modern theories of liquids (see textbooks, e.g., Hansen and McDonald, 2006) may provide a more promising way to obtain the EOS for silicate liquids. These theories relate the microscopic description of atomic configurations and interactions in liquids to thermodynamic properties with the help of classical statistical mechanics. The key to this approach is to make adequate approximations for the interatomic potentials of atoms (and/or ions) and the correlation functions of atomic configurations. Among various equations that have been proposed (Hansen and McDonald, 2006), a simple but widely used equation is the hard sphere equation of state (Reiss et al., 1959; Thiele, 1963; Wertheim, 1963), which successfully calculates the entropic contribution through the excluded volume effect of rigid molecules in liquids. As we will show in this paper, the hard sphere EOS can naturally explain some of the most distinct compressional behaviors of silicate liquids. Guillot and Sarda (2006) first applied the hard sphere EOS to describe the compression of some silicate melts such as peridotitic and basaltic melts up to 10 GPa, demonstrating the applicability of the hard sphere EOS to silicate melts. However, their approach cannot be applied to study the effect of melt composition since the silicate melt was treated as a single component system with an average sphere diameter defined for all melt components. A more critical problem is that the hard sphere EOS oversimplifies the interatomic potential between atoms by neglecting the cohesion energy of liquids, which results in an infinite molar volume at zero pressure. Therefore the EOS had to be scaled to a reference data point in Guillot and Sarda (2006) to obtain the hard sphere diameter. In order to describe more realistic ionic liquids with Coulombic interactions, many charged hard sphere mixture models (e.g., Caccamo and Malescio, 1989; Blum et al., 1992; Rosenfeld, 1993) have been developed using statistical mechanics in the liquid state physics literature. Despite the sophisticated formulations of these models, which often involve integral equations, the application of these models are often limited to simple cases such as binary mixtures with equally sized and charged ions, i.e., the restricted primitive model (e.g., Blum et al., 1992; Fisher and Levin, 1993; Zhou and Stell, 1995; Zhou et al., 1995; Guillot and Guissani, 1996). Since the purpose of this paper is to develop a simple model for the equation of state of complex silicate liquids that can be readily used for geochemical and geophysical modeling, we choose an alternative approach by modifying the model of hard sphere mixtures (Lebowitz, 1964; Lebowitz et al., 1965; Mansoori et al., 1971) using some empirical approximations for the Coulombic potential energy and soft repulsion between spheres to account for the experimental data of silicate liquids.
In this paper, we will first review the experimental (and computational) observations on the compressional properties of silicate liquids, solids, and glasses and discuss the differences in the compressional behaviors of these states. We will show that these differences can be explained by the important contribution of entropy as opposed to internal energy. We will then propose a new equation of state for silicate liquids that provides a unified explanation for all the observations based on the modified hard-sphere model of liquids, which emphasizes the entropic contribution to compression.

2. A REVIEW OF OBSERVATIONS ON COMPRESSIONAL PROPERTIES

2.1. Comparison of density and bulk modulus

In this section we will discuss the observations on the compressional properties of silicate liquids, solids, and glasses and compare the differences in the compressional behaviors of these states. We will show that the differences are due to the large differences in the compressibility of the solid phases as compared to the liquid phases, which is due to the large entropy contribution.

If temperature (T) and volume (V, see Table 1 for the definition of symbols) are chosen as the independent variables, then the isothermal EOS of a material can be given by the volume derivative of the Helmholtz free energy ($F$) of the material as,

$$ P = -\left(\frac{\partial F}{\partial V}\right)_{T} = -\left(\frac{\partial U}{\partial V}\right)_{T} + T\left(\frac{\partial S}{\partial V}\right)_{T}, $$

which contains both the internal energy contribution and the entropy contribution. The second-order volume derivative of free energy ($F$) gives the isothermal bulk modulus $K_{T}$

$$ K_{T} = -V\left(\frac{\partial P}{\partial V}\right)_{T} = V\left(\frac{\partial^{2} U}{\partial V^{2}}\right)_{T} - TV\left(\frac{\partial^{2} S}{\partial V^{2}}\right)_{T}, $$

which also has two contributions.

Fig. 1 compares the density and bulk modulus of silicate liquids and solids with the same compositions at room pressure. We can see that the densities of silicate liquids are only slightly smaller (by 10–20%) than those of the corresponding solids, whereas the bulk moduli of silicate liquids are much smaller (a factor of 3–6) than those of their solid counterparts. Therefore the large difference in bulk moduli between liquid and solid silicates is not due to the difference in density. That is, the compression of silicate liquids does not follow the Birch’s law of corresponding state (e.g., Birch, 1961; Anderson and Nafe, 1965; Chung, 1972; Shankland, 1972) (for more details on Birch’s law see Appendix A). It should also be noted that the bulk moduli of silicate liquids have a relatively narrow range (17–27 GPa for the liquids plotted) in contrast to the corresponding solids (56–134 GPa).

Additional information on compression mechanisms can be gathered by comparing the bulk modulus as a function of density (or molar volume) for a given composition in different states (liquid, glass, and solid). Fig. 2 plots the bulk moduli of solid, glass and liquid states of CaMgSi$_2$O$_6$ (diopside or Di), CaAl$_2$Si$_2$O$_8$ (anorthite or An), and NaAl$_2$Si$_2$O$_6$ (albite or Ab) as a function of molar volume per atom. It is clear that the data of glasses and crystalline

Table 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$\bar{M}$</td>
<td>Molar mass (molar formula weight)</td>
</tr>
<tr>
<td>$\bar{V}$</td>
<td>Molar volume</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of atoms per formula</td>
</tr>
<tr>
<td>$\bar{M}_n$</td>
<td>$\bar{M}/n$</td>
</tr>
<tr>
<td>$K_T$</td>
<td>Mean atomic weight</td>
</tr>
<tr>
<td>$a$</td>
<td>Isothermal bulk modulus</td>
</tr>
<tr>
<td>$C_V$</td>
<td>Thermal expansivity</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Constant pressure specific heat</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Grüneisen parameter</td>
</tr>
<tr>
<td>$(\partial K_T/\partial T)_T/\bar{V}$</td>
<td>Intrinsic temperature dependence of bulk modulus</td>
</tr>
<tr>
<td>$\delta_T$</td>
<td>Pressure derivative of bulk modulus</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Anderson–Grüneisen parameter</td>
</tr>
<tr>
<td>$q$</td>
<td>Volume of the $i$th melt component</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Effective sphere diameter</td>
</tr>
<tr>
<td>$\bar{V}_m$</td>
<td>Volume occupied by a mole of molecules</td>
</tr>
<tr>
<td>$f_{ij}$</td>
<td>Interactions among different spheres</td>
</tr>
<tr>
<td>$f_{ij}$</td>
<td>Dimensionless compressibility factor</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Exponent of the attractive term in EOS</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Exponent of the repulsive term in EOS</td>
</tr>
<tr>
<td>$\eta_T$</td>
<td>Temperature dependence of sphere diameter</td>
</tr>
<tr>
<td>$\zeta_T$</td>
<td>Volume dependence of sphere diameter</td>
</tr>
<tr>
<td>$\delta_T$</td>
<td>Temperature dependence of $\bar{V}_m$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Temperature dependence of $\zeta_T$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Volume dependence of $\delta_T$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Dependence of $\zeta$ on packing fraction</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Temperature dependence of the volume of spheres</td>
</tr>
<tr>
<td>$\epsilon_{Na_2O-Al_2O_3}$</td>
<td>Cross composition term</td>
</tr>
</tbody>
</table>
solids for these silicates fall on the same lines on this plot, which implies that glasses have the same compression mechanism as crystals. On the contrary, liquids are significantly more compressible than solids and glasses compared at the same molar volume. This implies that the differences in bulk modulus between liquids and solids (and glasses) cannot be attributed to the differences in molar volume (mean interatomic distance) only: the entropy contribution to compression must be important for liquids.

2.2. The pressure dependence of Grüneisen parameter

Another important difference in compressional properties between liquids and solids is the volume (pressure) dependence of Grüneisen parameter. The Grüneisen parameter ($\gamma$) and its volume dependence ($\gamma'$) are defined as (Anderson, 1995)

$$\gamma = \frac{2K_{\text{v}}V}{C_{\text{V}}}$$

(3)

and

$$\gamma' = \frac{\partial \ln \gamma}{\partial \ln V}.$$  

(4)

It has been demonstrated by first-principles molecular dynamics (FPMD) studies (Stixrude and Karki, 2005; Karki et al., 2006, 2007; de Koker et al., 2008; Stixrude et al., 2009) that the Grüneisen parameters of liquids including MgSiO$_3$, Mg$_2$SiO$_4$, SiO$_2$, and MgO increase with increasing compression ($\gamma'$ in Eq. (4) is negative) as opposed to solids for which the Grüneisen parameters decrease upon compression (Anderson, 1995). This observation has also been supported by shock-wave studies on silicate liquids (Mosenfelder et al., 2009; Asimow and Ahrens, 2010). Other non-metallic liquids including water and some organic liquids also have the negative volume dependence ($\gamma < 0$) (Boehler and Kennedy, 1977; Brown et al., 1988).
The interatomic potential may be separated into the short-range repulsive part and the long-range attractive part (see textbooks on theories of liquids, e.g., Hansen and McDonald, 2006). Molecular dynamics simulations on liquids have shown that the repulsive part of the potential controls the structure (or geometrical arrangement) of the liquids (Chandler, 1978). The repulsive potential can be further simplified as the hard sphere potential, where the molecules in the liquids are considered as rigid spheres (with infinite strength) and they can move freely as far as they do not overlap. The mutual interaction of molecules is included only by the excluded volume effect (i.e., influence of finite size of spheres). The pressure in the hard sphere model is caused entirely by the entropy and the EOS of a liquid takes a form that resembles that of a gas, viz.,

\[ P = \frac{RT}{V} \Phi(f), \]

where \( \Phi \) is the molar volume of the liquid, \( R \) is the gas constant, and \( \Phi(f) \) is a function that represents the excluded volume effect with \( f \) being the packing fraction defined as

\[ f = \frac{V_m}{V}, \]

where \( V_m \) is the volume occupied by a mole of spheres. For a monatomic liquid, \( V_m \) is given by

\[ V_m = \frac{1}{6} \pi \sigma^3 N_A, \]

where \( \sigma \) is the diameter of hard spheres; \( N_A \) is Avogadro’s constant. By taking the volume derivative of Eq. (5), and using \( (\partial f/\partial V)_T = -f/V \), one can obtain the bulk modulus of the hard sphere liquids as

\[ K_T = \frac{RT}{V} \Gamma(f) = \frac{RT}{V} \frac{d}{dT} [\Phi(f)]. \]

The key is to formulate \( \Phi(f) \) in Eqs. (5) and (8) for various physical models of liquids.

For the one-component system, the equation of state of hard sphere liquids can be given as (Reiss et al., 1959; Thiele, 1963; Wertheim, 1963),

\[ \Phi(f) = \frac{1 + f + f^2}{(1 - f)^3}, \]

and hence

\[ \Gamma(f) = \frac{1 + 4f + 4f^2}{(1 - f)^4}. \]

Eq. (9) successfully explains the results from numerical simulations on hard sphere liquids (e.g., Henderson, 1964). Guillot and Sarda (2006) first applied the hard sphere EOS to the compression of some silicate melts assuming the melt is a single component system. Although the effect of composition cannot be studied by the one-component hard-sphere EOS, the success of Guillot and Sarda (2006) shows its potential as a starting point for a more precise EOS for silicate liquids. To illustrate this, here we show that the hard sphere EOS naturally explains the compressional properties of silicate liquids reviewed in Section 2.

First, as seen from Eq. (8) the bulk modulus of a hard sphere liquid depends strongly on the packing fraction of the liquid, which is a result of the entropy-dominated compression (through the excluded volume effect). Upon compression, the bulk modulus increases as the packing
fraction increases (Fig. 4a). Guillot and Sarda (2006) discovered that for a wide range of melt compositions including silica, MORB, peridotite, komatite, and olivine melts, the reduced density \( \rho' \) (defined as \( N_s \sigma^2 / T \)) “is remarkably constant” (\( \rho' = 0.803 \pm 0.025 \)). Therefore the packing fraction (Eqs. (6) and (7)) takes a narrow range of \( \sim 0.42 \pm 0.01 \) at room pressure. This corresponds to a narrow range of bulk modulus that is consistent with the observation (Fig. 1b).

Second, the hard sphere model predicts a volume (pressure) dependence of Grüneisen parameter that is consistent with the observations for non-metallic liquids. To demonstrate this, we calculate the volume dependence of Grüneisen parameter (Eq. (3)) using the volume dependencies of thermal expansivity, bulk modulus, and heat capacity. The volume dependence of heat capacity has not been measured experimentally for silicate liquids, but was estimated to be relatively small and negligible using thermodynamic relations (Bottinga, 1985). Results of first-principles molecular dynamic simulations on silicate liquids (e.g., Stixrude and Karki, 2005; Karki et al., 2006, 2007; de Koker et al., 2008) showed the change in heat capacity over the pressure range of 130 GPa is about 10%. From thermodynamic relations (Eqs. (8) and (13)) taking a narrow range of

\[
\frac{\partial \ln T}{\partial \ln V} = \frac{1}{2} \frac{(1-f)(1+f+f^2)}{1+4f+4f^2}.
\]  

\[\delta_T = \frac{(\partial \ln K_T)}{(\partial \ln V)} .\]  

For the simple hard sphere EOS, \( z \) can be obtained by taking the temperature derivative of Eq. (5) as

\[z = \frac{1}{K_T} \left( \frac{\partial P}{\partial T} \right)_T = \frac{1}{T} \frac{(1-f)(1+f+f^2)}{1+4f+4f^2} .\]  

Then \( K'_T \) and \( \delta_T \) can be obtained by taking the volume derivatives of Eqs. (8) and (13)

\[
K'_T = \frac{1+9f+2f^2}{1+f-2f^2},
\]

\[
\delta_T = \frac{f(4+3f^2+2f^3)}{(1-f^2)(1+f)},
\]

Fig. 4b shows the calculated \( K'_T \) and \( \delta_T \) as functions of \( f \) for the simple hard sphere liquid. The Grüneisen parameter as a function of volume is therefore given by

\[\gamma = \gamma_0 \left( \frac{T_0}{T} \right)^q ,\]

with

\[q = \delta_T - K'_T + 1.\]

From thermodynamic relations

\[K'_T - \delta_T = \frac{1}{zK_T} \left( \frac{\partial K_T}{\partial T} \right)_T .\]

is the intrinsic temperature dependence of bulk modulus. This quantity controls the behavior of \( \gamma \) upon compression. For materials following the Birch’s law, \( K'_T = \delta_T \) (Anderson, 1989) and \( q = 1 \), which is consistent with observations (e.g., Anderson, 1974; Boehler and Ramakrishnan, 1980; Stixrude and Lithgow-Bertelloni, 2005). For hard sphere liquids, from Eqs. (14) and (15), we have

\[K'_T - \delta_T = \frac{(1+f)^2}{1-f^3} .\]

Therefore for a packing fraction (\( f \)) larger than 0, \( K'_T - \delta_T > 1 \), and \( q < 0 \) for hard sphere liquids, which means that the Grüneisen parameter increases with increasing pressure.

These predictions agree qualitatively with the observations summarized in Section 2. However, the hard sphere model cannot make quantitative predictions to actual silicate liquids given the complex interatomic interactions.

![Fig. 4. Results of the simple hard sphere equation of state for a liquid with a molar volume of 20 cm³/mol at 1673 K. (a) P and Kₜ as functions of packing fraction. (b) Kₜ' and δₜ as functions of packing fraction.](image-url)
that differ from the hard sphere potential. In the following, we will make some modifications to the hard sphere model in two different but closely related aspects. First, when we treat actual silicate liquids with complex compositions, we need to extend this equation of state to a multi-component system. Second, in the simplest form, the hard sphere EOS involves only the entropy term. Changes in internal energy will certainly occur in a realistic liquid. This effect needs to be included in the actual application of this type of equation of state to silicate melts under deep Earth conditions.

### 3.2. Equation of state for hard sphere mixtures

We adopt the equation of state for a hard sphere mixture generalized from Eq. (9) by solving the Percus–Yevick equation (Lebowitz, 1964; Lebowitz et al., 1965) to account for the multiple components in silicate liquids such as SiO$_2$ and MgO. It should be noted that similar equations with higher accuracy have been developed for the hard sphere mixtures (Mansoori et al., 1971; Hansen-Goos and Roth, 1981; Mansoori et al., 1971; Hansen-Goos and Roth, 1981) but we use the Percus–Yevick equation as a starting point for its simplicity. For a liquid composed of neutrally charged hard spheres of different sizes (i.e., no interaction between the hard spheres except for the excluded volume effect), $\Phi(f)$ becomes

$$\Phi(f, y_1, y_2) = \frac{1 + (1 - 3y_1)f + (1 - 3y_2)f^2}{(1 - f)^2}, \tag{20}$$

where

$$f = \frac{\gamma}{\rho} = \sum_{i=1}^{m} f_i, \tag{21}$$

$m$ is the number of components in the liquid and

$$\gamma = \frac{\sum_{i=1}^{m} X_i \rho_i}{\rho} = \frac{1}{6} \pi N_A \sum_{i=1}^{m} X_i \sigma_i^3, \tag{22}$$

$$f_i = \frac{\rho_i X_i}{\rho} = \frac{1}{6} \pi \rho \sigma_i^3 X_i N_A, \tag{23}$$

where $\sigma_i$ and $X_i$ are the hard sphere diameter and the mole fraction of the $i$-th component. $X_i$ is normalized as $\sum_{i=1}^{m} X_i = 1$. $y_1$ and $y_2$ are the parameters representing the interaction of spheres with different sizes. They are functions of $\sigma_i$ and $X_i$, and are independent of molar volume.

$$y_1 = \sum_{j \neq i}^{m} \Delta_{ij}(\sigma_i + \sigma_j)(\sigma_i \sigma_j)^{-1/2}, \tag{24}$$

$$y_2 = \sum_{j \neq i}^{m} \Delta_{ij} \sum_{k=1}^{m} \left( f_j \right)^{1/2} \frac{(\sigma_i \sigma_j)^{1/2}}{\sigma_k}, \tag{25}$$

with

$$\Delta_{ij} = \frac{[(f_i f_j)^{1/2}/f_i][((\sigma_i - \sigma_j)^2/\sigma_i \sigma_j)][X_i X_j]^{1/2}}{(f_i f_j)^{1/2}/f_i}. \tag{26}$$

Again, the bulk modulus can be obtained by taking the volume derivative of the equation of state (Ashcroft and Langreth, 1967; Tomczyk, 1977; Suski and Tomczyk, 1981)

$$\Gamma(f, y_1, y_2) = \left. \frac{\partial}{\partial \gamma} (\Phi f) \right|_{\gamma}$$

$$= \frac{1 + (4 - 6y_1)f + (4 - 3y_1 - 9y_2)f^2}{(1 - f)^3}, \tag{27}$$

### 3.3. Attractive force and the internal energy contribution

The hard sphere mixture model developed for neutrally charged spheres cannot be applied to real liquids directly because there is no attractive force and the zero-pressure volume is infinite (see Eqs. (5) and (20)). Since we will use room-pressure data to place constraints on sphere sizes, it is necessary to introduce the attractive interaction. The attraction in silicate liquids comes mainly from the Coulombic interactions between cations (such as Mg$^{2+}$ and Si$^{4+}$) and anions (O$^-$) in the liquids. The straightforward approach is to develop a theory for charged hard sphere mixtures. Despite the vast literature on this subject, available analytical models are mostly limited to the simplest case: the restricted primitive model for binary mixtures with equally sized and charged ions (Blum et al., 1992; Fisher and Levin, 1993; Zhou and Stell, 1995; Zhou et al., 1995; Guillot and Guissani, 1996), which is far less complicated than real silicate liquid.

Since our purpose is to develop a simple equation of state for silicate liquids that can be readily used for geochemical and geophysical modeling, we choose a more empirical approach by modifying the hard sphere EOS with a mean-field adjustment. Longuet-Higgins and Widom (1964) showed that for simple molecular liquids, the structure of liquids is mostly determined by the steeply changing repulsive potential, which can be approximated as the hard sphere potential, whereas the slowly varying attractive potential can be introduced as a uniform negative background potential. This mean field approach was later extended to ionic liquids by Itami and Shimoji (1980) and McBroom and McQuarrie (1983). Following this approach, we consider a silicate liquid as a mixture of hard spheres corresponding to different melt components such as SiO$_2$ and MgO, and consider the electrostatic energy as a uniformly distributed negative background potential, which does not change the structure of a liquid but will modify the thermodynamic properties of liquids. Then the cohesion energy can be viewed as a liquid analog of the Madelung energy of solids. The equation of state is given as

$$P = \frac{RT}{\rho} \Phi(f, y_1, y_2) - A, \tag{28}$$

where $\mu$ is an exponent that depends on the nature of the attractive force and is 4/3 for the Coulombic attraction and $A$ is a constant of volume that describes the importance of the internal energy contribution. $A$ can be evaluated by setting $P = 0$ in Eq. (28),

$$A = RT \Phi_0 \rho_0^{-\mu}, \tag{29}$$

where $\Phi_0 = \Phi(f_0, y_{01}, y_{02})$ and subscript “0” represents room pressure values. Substituting (29) back into (28), one gets

$$P = \frac{RT}{\rho} \left[ \Phi - \Phi_0 \rho_0^{-\mu} \right]. \tag{30}$$

The isothermal bulk modulus can then be obtained as

$$K_T = \frac{RT}{\gamma} \left[ \Gamma - \mu \Phi_0 \rho_0^{-\mu} \right]. \tag{31}$$
where \( \Phi \) and \( \Gamma \) are given in Eqs. (20) and (27). At \( P = 0 \), the room-pressure bulk modulus is

\[
K_{T0} = \frac{RT}{V_0} \left[ \Gamma_0 - \mu \Phi_0 \right].
\]  

(32)

4. APPLICATION OF THE EQUATION OF STATE TO SILICATE LIQUIDS

We consider a 5-component system including SiO\(_2\), Al\(_2\)O\(_3\), FeO, MgO, and CaO (hereafter referred to as the CMA SF system) as an example to demonstrate how the proposed EOS is applied to real silicate liquids.

4.1. Application of the equation of state to room-pressure data

In this section, we calibrate the proposed EOS using room-pressure data on density (or molar volume) and bulk modulus. The proposed EOS (Eq. (30)) has a few parameters including the room-pressure molar volume \( V_0 \) and the volume occupied by a mole of the hard spheres \( V_m \). Both \( V_0 \) and \( V_m \) are compositional dependent. \( V_0 \) also depends on temperature. \( V_m \) is calculated from the hard sphere diameters \( (r_i) \) (Eq. (22)).

The room-pressure molar volume \( (V_0) \) is well described by the ideal mixing model (e.g., Bottinga and Weill, 1970; Lange, 1997), viz.,

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Sources of room-pressure relaxed sound velocity data.</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>Sample</td>
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<tr>
<td></td>
<td>SiO(_2)-MgO-CaO</td>
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<tr>
<td>Secco et al. (1991)</td>
<td>SiO(_2)-Al(_2)O(_3)-MgO-CaO</td>
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<tr>
<td>Rivers and Carmichael (1987)</td>
<td>SiO(_2)-MgO-CaO</td>
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<tr>
<td></td>
<td>SiO(_2)-Al(_2)O(_3)-CaO</td>
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<tr>
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<td>SiO(_2)-CaO</td>
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<tr>
<td></td>
<td>SiO(_2)-Al(_2)O(_3)-MgO-CaO</td>
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<td></td>
<td>SiO(_2)-FeO</td>
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<td>SiO(_2)-Na(_2)O</td>
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<td>SiO(_2)-K(_2)O</td>
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<td>SiO(_2)-MgO</td>
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<td>SiO(_2)-Al(_2)O(_3)-MgO-CaO</td>
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<td>SiO(_2)-MgO-Na(_2)O</td>
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<td></td>
<td>SiO(_2)-Al(_2)O(_3)-FeO-MgO-CaO-Na(_2)O</td>
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<tr>
<td>Kress et al. (1988)</td>
<td>SiO(_2)-Al(_2)O(_3)-Na(_2)O</td>
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</tr>
<tr>
<td></td>
<td>SiO(_2)-Na(_2)O</td>
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</tr>
</tbody>
</table>
\[
V_0 = \sum_{i=1}^{n} \tau_{0i} X_i. \tag{33}
\]

Note that the mole fraction defined in this study is different from the common definition used in the ideal mixing model, since a mole of Al\textsubscript{2}O\textsubscript{3} has two moles of Al\textsuperscript{3+} cations and hence will be considered as two moles of spheres. As a result, the molar volume for Al\textsubscript{2}O\textsubscript{3}, which is half of the molar volume of Al\textsubscript{2}O\textsubscript{3}, must be applied in Eq. (33). The ideal mixing model is widely used and can give excellent results on melt densities (within 1% to experimental values). Therefore the same approach is applied here to calibrate \( V_0 \). The hard sphere diameter \( \sigma_i \) for each melt component is then calibrated by room-pressure bulk modulus using Eq. (32). The room-pressure bulk modulus can be obtained by ultrasonic sound velocity measurements

\[
\frac{1}{K_{T0}} = \frac{V_0}{c^2} + \frac{V_0 \kappa_0^2}{C_{P0}}, \tag{34}
\]

where \( c \) is the measured sound velocity for silicate liquids. \( \kappa_0 \) and \( C_{P0} \) are room-pressure values of the thermal expansivity and heat capacity of silicate liquids, which can be calculated by the ideal-mixing model (e.g., Lange and Navrotsky, 1992; Lange, 1997). For the CMASF system, we start from the most recent data set on sound velocity given by Ai and Lange (2008) to calibrate our equation of state. In addition to this data set, results of Webb and Courtial (1996), Secco et al. (1991), and Rivers and Carmichael (1987) are also included in the calibration. Only relaxed sound velocity data that do not depend on the frequency of the measurements are used. The sources of the experimental data used in the calibration are summarized in Table 2. Excluding the data for FeO-bearing liquids, this data set is similar to the one used in Ai and Lange (2008) to calibrate the ideal-mixing model of compressibility for CMAS liquid. In total, 170 observations are included in the data set for 21 different compositions. Room-pressure molar volume and thermal expansivity are calculated from the ideal-mixing model. Partial molar quantities except for the FeO component are from the calibration of Lange (1997). For the FeO component, results of Kress and Carmichael (1991) are used. Room-pressure heat capacity \( C_{P0} \) is calculated from the calibration of Lange and Navrotsky (1992).

A non-linear least squares regression with five parameters in total for the 5-component system was conducted.

Regressed results of \( \sigma_i \) for each cation are listed in Table 3 along with the one-sigma error (\( \sigma \)) estimates for the parameters. Fig. 5 shows the comparison of the predicted

![Fig. 5. Comparison of the predicted room-pressure bulk modulus \( K_{T0} \) for the CMASF system using the proposed EOS and parameters in Table 3 with experimental data. Symbols with different colors represent different melt compositions. Symbols with the same color are for the same melt composition but measured at different temperatures and frequencies. The diagonal line shows 1:1 correlation of the axes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).](image)

![Fig. 6. Comparison of the predicted room-pressure bulk modulus \( K_{T0} \) for CaMgSi\textsubscript{2}O\textsubscript{6} (Di) liquid with experimental results. The red dashed curve is the calculated \( K_{T0} \) using temperature-independent sphere diameters in Table 3; the blue solid curve is the calculated \( K_{T0} \) using temperature-dependent sphere diameters in Table 4; The black solid circles are the experimental results of Ai and Lange (2008). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).](image)
and experimental measurements for the different melt compositions represented by different colors. The overall goodness of the fit is fair with a maximum residual in \( K_{\rho_0} \) of about 2 GPa (10%). The adjusted \( R^2 \) is 0.848 and the root mean squared error (s) of the fit is 0.589. A detailed analysis of Fig. 5 reveals that with one parameter for each melt component, the proposed model can explain the effect of composition fairly well. However, the predicted results for each composition at various temperatures are less satisfactory. For example, Fig. 6 shows that the predicted \( K_{\rho_0} \) for the diopside (D) melt increases with increasing temperature (dashed line), which is opposite to the temperature dependence of experimental data (solid circles) from Ai and Lange (2008). This comparison indicates that the model with constant sphere sizes can explain properties such as the compositional dependence but must be modified in order to explain the temperature dependence of bulk modulus.

4.2. Temperature dependence of sphere diameters

We introduce the temperature dependence of hard sphere diameters by considering the fact that the repulsive potential between two spheres in the liquids is not precisely the hard sphere potential, i.e., spheres have finite strength. As a result, the potential energy is higher but remains finite when the distance between spheres is smaller. At a higher temperature, the kinetic energy is higher due to the higher average velocity of the spheres. The kinetic energy can be converted to the potential energy of spheres during the elastic collision of spheres, and as a result the effective sphere diameters decrease with increasing temperature (e.g., Stillinger, 1961; Andersen et al., 1971). For the inverse power law repulsive potential that was widely used for soft spheres (e.g., Rowlinson, 1964; Ben-Amotz and Stell, 2004), the effective sphere diameter (\( \sigma \)) can be evaluated by equating the repulsive potential energy to the kinetic energy at temperature \( T \)

\[
\frac{e}{\sigma^s} = k_b T.
\]

where \( e \) is a constant, \( s \) is the power of the potential. Therefore the effective hard-sphere diameter for the \( i \)-th component is

\[
\sigma_i(T) = \sigma_{i,ref} \left( \frac{T_{ref}}{T} \right)^{\frac{1}{s_i}},
\]

where \( \sigma_{i,ref} \) is the hard sphere diameter at the reference temperature \( T_{ref} \). Therefore we can define the temperature dependence of \( \sigma_i \) as

\[
\eta_i = \frac{d \ln \sigma_i}{d \ln T} = -\frac{1}{s_i}.
\]

Using the same set of experimental data for the CMASF system in Table 2, we conduct another non-linear least squares regression to constrain \( \sigma_{i,ref} \) and \( \eta_i \) (10 parameters in total for the 5-component system, which is identical to the number of parameters used in the ideal-mixing model when calculating room-pressure bulk modulus). Calibrated \( \sigma_{i,ref} \) and \( \eta_i \) with one-sigma error estimates for each component are listed in Table 4. The relative uncertainties in the fitted hard sphere diameters are rather small (~0.1–0.3%). However, the uncertainties in the temperature dependence of hard sphere diameter are large because the temperature range in sound velocity measurements (see Table 2) is not very large (less than 250 K, and only 100 K for many compositions). It should also be noted that \( \eta_i \) is positive for the MgO component, which is inconsistent with our physical picture of the temperature effect on hard-sphere diameters. This may be either due to the complex interaction between different melt components (for example, the Mg-O coordination likely depends on temperature and melt composition (George and Stebbins, 1998)), or due to the narrow temperature range of the sound velocity data, which will be better constrained when experimental data for a larger temperature range become available.

The predicted bulk moduli for CMAS liquids using the parameters in Table 4 are compared with experimental

<table>
<thead>
<tr>
<th>Component</th>
<th>( \sigma_{i,ref} ) (nm)</th>
<th>( \eta_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>0.3356 ± 0.0004</td>
<td>-0.08 ± 0.01</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.3012 ± 0.0003</td>
<td>-0.04 ± 0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>0.2744 ± 0.0004</td>
<td>-0.01 ± 0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2627 ± 0.0007</td>
<td>0.14 ± 0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3102 ± 0.0006</td>
<td>-0.02 ± 0.02</td>
</tr>
</tbody>
</table>

Reference temperature (\( T_{ref} \)) is 1673 K. Uncertainties represent one \( \sigma \) error estimates. The adjusted \( R^2 \) for the regression is 0.981. The root mean squared error (s) of the fit is 0.073.

Fig. 7. Comparison of the predicted room-pressure bulk modulus \( K_{\rho_0} \) for the CMASF system with experimental measurements. Blue circles represent the predictions of the proposed EOS and parameters in Table 4; red squares represent the predictions of Ai and Lange (2008). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
results in Fig. 7. The overall fit has been significantly improved from the previous regression (Fig. 5). The adjusted $R^2$ is 0.981 and the root mean squared error ($s$) of the fit is 0.073. We also compare our results with those of the ideal-mixing model by Ai and Lange (2008) in Fig. 7 as similar data sets were used for the calibration of both models. The predictions made by the proposed EOS are as good as the ideal-mixing model. The solid line in Fig. 6 shows that the calculated room-pressure bulk modulus for CaMgSi$_2$O$_6$ (Di) liquid as a function of temperature is consistent with the experimental observations from Ai and Lange (2008). Thus the proposed equation of state with temperature-dependent sphere diameters can reproduce the room-pressure bulk modulus and its temperature dependence well at least for the Di composition (but not limited to the Di composition as suggested by the improved fitting in Fig. 7 from Fig. 5).

### 4.3. Calibrations for liquids with more components

Using the same approach demonstrated for the CMASF system, we also calibrate our proposed EOS for liquids with seven components including CaO, MgO, FeO, Al$_2$O$_3$, SiO$_2$, Na$_2$O, and K$_2$O (CMASFNK). Again, the room-pressure molar volume, thermal expansion, and heat capacity are calculated from the ideal-mixing model as for the CMASF system. In addition to the sound velocity data for the CMASF system, experimental data from Kress et al. (1988) and Rivers and Carmichael (1987) on Na- and K-bearing melts are included in the calibration (Table 2). There is only one composition that contains K$_2$O in the data set. Results on K$_2$SiO$_3$ from Rivers and Carmichael (1987) are excluded since the sample dissolved a significant amount of MoO$_2$ (4.7 wt%) in the melt. Some other ultrasonic results on the potassium-bearing liquids including Bockris and Kojonen (1960) and Baidov and Kunin (1968) are not included in the regression since the measured sound velocities cannot be confirmed to be relaxed (Lange and Carmichael, 1990; Kress and Carmichael, 1991). In total, there are 259 observations of sound velocity data for 37 different liquid compositions.

The calibrated hard sphere diameters and their temperature dependencies for the 7-component system are listed in Table 5. The uncertainties in the parameters for the K$_2$O component are quite large compared to other components due to the limited number of samples that contain K$_2$O. Reference temperature ($T_{ref}$) is 1673 K. Uncertainties represent one-$s$ error estimates. The adjusted $R^2$ for the regression is 0.963. The root mean squared error ($s$) of the fit is 0.431.

### Table 5

Calibrated hard-sphere diameters and their temperature dependences for melt components in the CMASFNK system using Eq. (32).

<table>
<thead>
<tr>
<th>Component</th>
<th>$\sigma_{i,T_{ref}}$ (nm)</th>
<th>$\eta_i = d \ln \sigma_i / d \ln T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>0.3371 ± 0.0005</td>
<td>-0.06 ± 0.02</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.3031 ± 0.0006</td>
<td>-0.12 ± 0.03</td>
</tr>
<tr>
<td>FeO</td>
<td>0.2730 ± 0.0008</td>
<td>-0.04 ± 0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2610 ± 0.0013</td>
<td>0.08 ± 0.06</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3065 ± 0.0009</td>
<td>0.01 ± 0.03</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.3517 ± 0.0010</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.4007 ± 0.0037</td>
<td>0.17 ± 0.15</td>
</tr>
</tbody>
</table>

Reference temperature ($T_{ref}$) is 1673 K. Uncertainties represent one-$s$ error estimates. The adjusted $R^2$ for the regression is 0.963. The root mean squared error ($s$) of the fit is 0.431.

Fig. 8. Comparison of the predicted room-pressure bulk modulus $K_T$ for the CMASFNK system using the proposed EOS with experimental data. Red squares represent Na$_2$O-bearing liquids and blue circles represent Na$_2$O-free compositions. (a) Regression results without the interaction term between Na$_2$O and Al$_2$O$_3$ (regressed parameters are in Table 5); (b) regression with the interaction term between Na$_2$O and Al$_2$O$_3$ (regressed parameters are in Table 6). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
we calculate the compressional curves for a few peridotitic melts (Fig. 9a) and basaltic melts (Fig. 9b) whose densities were measured by the sink/float experiments (Agee and Walker, 1993; Suzuki et al., 1998; Suzuki and Ohtani, 2003). It can be seen that the predicted densities of all melt compositions are somewhat smaller than the experimental data especially at high pressures. The assumption of constant sphere size at high pressure has to be modified in order to explain the density data at high pressure.

A straightforward modification is to introduce the volume dependence of the sphere diameters. For the $i$-th component,

$$\sigma_i(T) = \sigma_0(T) \left( \frac{T}{T_0} \right)^{\frac{2}{3}},$$

where $\xi_i$ defines the deformability of the $i$-th sphere and is assumed to be independent of $T$ and $T$ for simplicity. The volume of molecules changes upon compression can be defined as a deformability parameter, viz.,

$$\xi_i \equiv \left( \frac{\partial \ln T_i}{\partial \ln V_i} \right)_T = \frac{1}{\mathcal{V}_m} \sum_{i=1}^{m_i} \mathcal{V}_m \xi_i.$$

The volume derivatives of all other quantities that depend on $\mathcal{V}_m$ should also be modified accordingly using Eq. (40). For example, the volume dependence of packing fraction changes to

$$\frac{df}{d\mathcal{V}} = f (\xi - 1).$$

Similarly, the equation of state should be different than Eq. (28) since it is obtained by taking the volume derivative of Helmholtz free energy of the liquids. The entropic contribution (excluded volume effect) to the Helmholtz free energy has the form of (e.g., Hansen and McDonald, 2006)

$$F_{ev} = RT \left[ \ln \frac{f}{1 - f} + \frac{3}{2} \left( \frac{2f - f^2}{1 - f^2} \right) \right].$$

Taking the volume derivative of Eq. (42) gives

$$P_{ev} = \frac{RT}{\mathcal{V}} \left( 1 - \xi \right) \Phi,$$

which is different from Eq. (5) by a factor of $(1 - \xi)$ due to the deformability of the spheres. The attractive energy term (Coulombic term) remains the same as in Eq. (28) since it is a long-range interaction and does not depend on $\mathcal{V}_m$.

In addition to the entropic contribution and the attractive energy term, the repulsive energy also needs to be considered to account for the strain energy stored in the deformed spheres. We assume the repulsive potential takes the same inverse power-law form for all melt components, that is, $U_{rep} \propto 1/\sigma_m \propto 1/\mathcal{V}_m^{-1}$, where $\nu = s/3 + 1$. Note that the repulsive energy is a short-range potential, which controls the local structure of a liquid and hence should be a function of $\mathcal{V}_m$. Based on the results of ionic crystals, $s$ can be related to $K_{Tm}$ of the material (e.g., Poirier, 2000) as $K_{Tm} = (s + 7)/3$. If $K_{Tm}$ is 4 as in the case of many crystals, then $s$ has a value of about 5. The pressure due to the repulsive energy can be given by

### Table 6

Calibrated hard-sphere diameters and their temperature dependencies for melt components in the CMASFNK system using Eq. (32) with the Na$_2$O–Al$_2$O$_3$ interaction term (Eq. (38)).

<table>
<thead>
<tr>
<th>Component</th>
<th>$\sigma_{r,T/C}$ (nm)</th>
<th>$\eta_i = \partial \ln \sigma_i / \partial \ln T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>0.3370 ± 0.0004</td>
<td>−0.06 ± 0.01</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.3010 ± 0.0004</td>
<td>−0.05 ± 0.02</td>
</tr>
<tr>
<td>FeO</td>
<td>0.2732 ± 0.0006</td>
<td>−0.04 ± 0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2607 ± 0.0010</td>
<td>0.10 ± 0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3084 ± 0.0007</td>
<td>−0.05 ± 0.02</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.3466 ± 0.0008</td>
<td>−0.04 ± 0.03</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.4010 ± 0.0026</td>
<td>0.16 ± 0.11</td>
</tr>
<tr>
<td>Na$_2$O–Al$_2$O$_3$</td>
<td>0.17 ± 0.01*</td>
<td></td>
</tr>
</tbody>
</table>

Reference temperature ($T_{ref}$) is 1673 K. Uncertainties represent one standard error estimates. The adjusted $R^2$ for the regression is 0.981. The root mean squared error (s) of the fit is 0.221. *CN$_{Na_2O-Al_2O_3}$ is a non-dimensional parameter.
Combining Eqs. (43), (44), and (28), we obtain the modified equation of state considering the deformability of spheres

\[ P = \frac{RT}{V}\left(1 - \frac{1}{n}\right) - \frac{A}{V_m^\mu} + \frac{f}{V_m^\nu}, \]  

(45)

where \( \mu = 4/3 \) and \( \nu = 8/3 \); \( A \) and \( B \) are constants that do not depend on volume. \( B \) can be obtained by letting \( \xi = 1 \) and \( P = 0 \). Eq. (45) then reduces to

\[ B = \frac{V_m^{\nu-1}}{V_m^0} A. \]  

(46)

Constant \( A \) can be obtained by letting \( \xi = 0 \) and \( P = 0 \). The result for \( A \) is the same as in Eq. (29). Substituting Eq. (29) and (46) back to Eq. (45), the final form of the equation of state can be derived as

\[ P = \frac{RT}{V}\left(1 - \frac{1}{n}\right) - \Phi_0\left(\frac{V_0}{V}\right)^{\mu-1} + \varsigma\Phi_0\left(\frac{V_m^0}{V_m}\right)^{\nu-1}, \]  

(47)

and the bulk modulus can be obtained by taking the volume derivative of Eq. (47)

\[ K_T = \frac{RT}{V}\left(1 - \frac{1}{n}\right)^2\Gamma + \left(\varsigma + (1 - \varsigma)\varsigma\right) - \mu\Phi_0\left(\frac{V_m^0}{V_m}\right)^{\mu-1} + \Phi_0\left(\varsigma - \varsigma + (v - 1)\varsigma^2\right)\left(\frac{V_m^0}{V_m}\right)^{\nu-1}. \]  

(48)

where

\[ \varsigma = \frac{\partial \xi}{\partial \ln V} = \frac{1}{V_m^0} \sum_{i=1}^{n} X_i V_m^i \varsigma_i^2 - \varsigma. \]  

(49)

The room-pressure bulk modulus is thus given by

\[ K_{T0} = \frac{RT}{V_0}\left(1 - \frac{1}{n}\right)^2\Gamma_0 + \Phi_0(2\varsigma_0 + (v - 2)\varsigma_0^2 - \mu). \]  

(50)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample</th>
<th>Pressure (GPa)</th>
<th>Temperature (K)</th>
<th>Sources</th>
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<td>Suzuki et al. (1998)</td>
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<td>Suzuki and Ohtani (2003)</td>
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<td>Pyrolite</td>
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<td>Suzuki and Ohtani (2003)</td>
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<td>Picritic</td>
<td>Picrite</td>
<td>14.5</td>
<td>2773</td>
<td>Ohtani and Maeda (2001)</td>
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<tr>
<td>Komatititic</td>
<td>Komatite</td>
<td>8.9</td>
<td>2173</td>
<td>Agee and Walker (1993)</td>
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<tr>
<td></td>
<td>Komatite</td>
<td>6</td>
<td>2073</td>
<td>Agee and Walker (1993)</td>
</tr>
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<td>Basaltic</td>
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<td>1673</td>
<td>Agee (1998)</td>
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<tr>
<td></td>
<td>MORB</td>
<td>14.9</td>
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<tr>
<td></td>
<td>MORB</td>
<td>15.1</td>
<td>2773</td>
<td>Ohtani and Maeda (2001)</td>
</tr>
</tbody>
</table>
The deformability of spheres \( (n_i) \) must be constrained by high-pressure experimental data. Table 7 summarizes the density data determined from sink/float experiments. A regression was conducted using Eqs. (47) and (50) simultaneously with data in Tables 2 and 7 by minimizing
\[
\frac{1}{2} P_i \left( \frac{P_i}{C_0} P \right)^2 + P_j \left( \frac{K_{T_0}}{C_0} K \right)^2
\]
where \( P_i \) is the pressure for the \( i \)-th density measurement and \( K_{T_0} \) is the bulk modulus for the \( j \)-th bulk modulus measurement. The regressed parameters are listed in Table 8. Predicted compression curves are plotted as solid lines in Fig. 10a for peridotitic melts and in Fig. 10b for basaltic melts. In contrast to Fig. 9a and b, the density data at high pressure can be reproduced very well. The residuals in calculated density and experimental measurements are less than 1% and about

<table>
<thead>
<tr>
<th>Component</th>
<th>( n_{i,T_{ref}} ) (nm)</th>
<th>( n_i = (\partial \ln n_i / \partial \ln T)<em>{T</em>{ref}} )</th>
<th>( n_i = 3(\partial \ln n_i / \partial \ln \bar{T})<em>{T</em>{ref}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>0.365 ± 0.001</td>
<td>−0.02 ± 0.01</td>
<td>0.62 ± 0.04</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.328 ± 0.002</td>
<td>−0.03 ± 0.01</td>
<td>0.66 ± 0.06</td>
</tr>
<tr>
<td>FeO</td>
<td>0.257 ± 0.008</td>
<td>0.00 ± 0.02</td>
<td>−0.68 ± 0.28</td>
</tr>
<tr>
<td>MgO</td>
<td>0.277 ± 0.002</td>
<td>0.00 ± 0.02</td>
<td>0.22 ± 0.07</td>
</tr>
<tr>
<td>CaO</td>
<td>0.335 ± 0.003</td>
<td>−0.14 ± 0.02</td>
<td>0.66 ± 0.08</td>
</tr>
</tbody>
</table>

Reference temperature \( (T_{ref}) \) is 1673 K. Uncertainties represent one \( \sigma \) error estimates.

The diameters of spheres \( (n_i) \) need to be constrained by high-pressure experimental data. Table 7 summarizes the density data determined from sink/float experiments. A regression was conducted using Eqs. (47) and (50) simultaneously with data in Tables 2 and 7 by minimizing
\[
\sum (P_i - \bar{P})^2 + \sum (K_{T_0} - \bar{K})^2
\]
where \( P_i \) is the pressure for the \( i \)-th density measurement and \( K_{T_0} \) is the bulk modulus for the \( j \)-th bulk modulus measurement. The regressed parameters are listed in Table 8. Predicted compression curves are plotted as solid lines in Table 8. Predicted compression curves are plotted as solid lines in Fig. 10a for peridotitic melts and in Fig. 10b for basaltic melts. In contrast to Fig. 9a and b, the density data at high pressure can be reproduced very well. The residuals in calculated density and experimental measurements are less than 1% and about

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<th>( n_i = 3(\partial \ln n_i / \partial \ln \bar{T})<em>{T</em>{ref}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>0.3612 ± 0.0006</td>
<td>−0.03 ± 0.01</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.3242 ± 0.0006</td>
<td>−0.02 ± 0.01</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>0.2935 ± 0.0007</td>
<td>−0.02 ± 0.02</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2827 ± 0.0007</td>
<td>0.08 ± 0.01</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3311 ± 0.0008</td>
<td>−0.12 ± 0.02</td>
<td>0.53 ± 0.01</td>
</tr>
</tbody>
</table>

Reference temperature \( (T_{ref}) \) is 1673 K. Uncertainties represent one \( \sigma \) error estimates.

\( * \) \( n \) takes the same value for all melt components.
0.5% for most compositions, which are similar to the experimental uncertainties. Therefore the introduction of the deformability of spheres can significantly improve the fitting for high-pressure density data.

Since the regressed values of \( \xi_i \) have large uncertainties due to the limited data at high pressures, we may simplify the model by using an average \( \xi \) in the regression. Using the same data sets (Tables 2 and 7), we can obtain the EOS parameters in Table 9. Predicted compression curves based on this model are shown as dashed lines in Fig. 10a and b. It can be seen that the density data can be reproduced quite well by using a single \( \xi = 0.53 \) for all components, although there exists some difference between the predicted compression curves.

4.5. Predictions of other compressional properties at high pressure

In this section we use a Fe-rich peridotitic melt composition MA (see Suzuki et al. (1998) for the chemical composition of this melt) as an example to demonstrate how the proposed equation of state can be applied to calculate compressional properties at high pressure including bulk modulus \( (K_T) \), thermal expansivity \( (\alpha) \), and Grüneisen parameter \( (\gamma) \). Bulk modulus \( (K_T) \) can be calculated directly from Eq. (48). Fig. 11a shows the calculated \( K_T \) as a function of pressure for the MA melt at 2603 K. The pressure derivative of bulk modulus \( (K_T') \) is estimated to be about 7.0. Thermal expansivity \( (\alpha) \) as a function of pressure can be obtained by taking the temperature derivative of Eq. (47). The detail derivation of thermal expansivity at high pressure is presented in Appendix B. Fig. 11b shows that thermal expansivity for the MA melt decreases from about \( 7 \times 10^{-3} K^{-1} \) at room pressure to about \( 4 \times 10^{-3} K^{-1} \) at 25 GPa. From Eq. (11), The volume dependence of thermal expansivity \( (\delta_\alpha) \) can be estimated to be about 2.1, which is much smaller than the typical values for solids (about 4).

Given the calculated results for bulk modulus \( (K_T) \), and thermal expansivity \( (\alpha) \) at high pressure, Grüneisen parameter \( (\gamma) \) can be calculated using Eq. (3). Fig. 11c shows that the predicted Grüneisen parameters for the MA melt decreases with compression. The volume dependence of Grüneisen parameter \( (\delta_\gamma) \) can be estimated (from its definition in Eq. (4)) to be about \(-3.9\), which is a negative value in contrast to \( q = 1 \) for materials that follow Birch’s law. According to Eq. (17), the negative value of \( q \) for liquids comes mainly from the distinct thermal properties of liquids represented by a small value of \( \delta_\gamma \) compared to \( K_T' \), which is a direct consequence of the entropy contribution as

![Graphs showing predicted compressional properties at high pressures for the peridotitic melt MA at 2603 K. (a) Bulk modulus; (b) thermal expansivity; (c) Grüneisen parameter.](http://example.com/fig11.png)
demonstrated by the simple hard-sphere model. If we compare the predicted volume dependence of Grüneisen parameter \( (\varphi) \) with previous results on silicate liquids, we find that the calculated value is somewhat smaller (larger in absolute value) than the estimates (about \(-1.6\) to \(-2.0\)) from numerical simulations and shock-wave experiments on the MgSiO\(_3\) and MgSiO\(_3\) liquids (Stixrude and Karki, 2005; Mosenfelder et al., 2009). Two factors may contribute to this discrepancy: basically the influence of compression and temperature. (1) The prediction of the Grüneisen parameter for the MA melt is based on the calibration of EOS using experimental data up to only 25 GPa, but the observations are based on shock-wave experiments and numerical simulations that cover a much larger range of pressure from room pressure to 130 GPa. The extrapolation of the EOS to such high pressures will introduce some uncertainty in the calculated Grüneisen parameter due to the uncertainties in the calibrated sphere diameters and their volume dependencies. (2) The calculated volume dependence of Grüneisen parameter \( (\varphi) \) is obtained for an isothermal compression at 2603 K, but both shock-wave data and numerical simulation results were obtained at very high temperatures from 3000 to 6000 K or even higher and \( \varphi \) was assumed to be a constant of temperature in these studies. That is, the previous estimated \( \varphi \) is an average value over a wide range of high temperatures. We will discuss the application of our EOS to these very high pressure–temperature conditions in the next section.

4.6. Application of the EOS to extreme pressures up to 130 GPa

Our previous calibration of the EOS parameters (Tables 8 and 9) is limited to sink/float data up to 25 GPa. The

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**Fig. 12.** Comparison of predicted density for Di (blue circles) and Di\(_{64}\)An\(_{36}\) (red circles) with shock-wave data. (a) EOS parameters in Table 9 are used; (b) shock data are included in the calculation; (c) the deformability of spheres is assumed to depend on the packing fraction of the liquid. Parameters in Table 11 are used. The diagonal line shows 1:1 correlation of the axes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
validation of this calibration at very high pressures may be examined by the density data determined by shock-wave experiments from 5 to 130 GPa (e.g., Rigden et al., 1988, 1989; Miller et al., 1991; Chen et al., 2002; Asimow and Ahrens, 2010). Fig. 12a compares the calculated density for Di (diopside) and D64An36 (diopside–anorthite eutectic) using the proposed EOS and parameters in Table 9 to the density determined by shock-wave experiments (Asimow and Ahrens, 2010). The shock temperatures for the data are calculated based on the P–V–T EOS provided in Asimow and Ahrens (2010) (Table 10). The difference between the predicted density and experimental data is less than 1% at 40 GPa, but increases with pressure and can be as large as 10% at pressures higher than 80 GPa. Consequently, the previous calibration may not be applicable to pressures higher than 40 GPa.

Ideally, we can incorporate all shock-wave data into our data set to extend the pressure range of the EOS. However, most shock data currently available have poorly estimated shock temperatures due to two major reasons: (1) The volume dependence of the Grüneisen parameter ($q$) is often assumed to be 1 in these calculations, which is not consistent with the new observations for liquids (e.g., Asimow and Ahrens, 2010); (2) The specific heat ($C_V$) is often assumed to be 3R/mol atm (the Dulong–Petite value for solid materials), which could be more than 50% less than the real liquid values (Richet and Neuville, 1992). The combination of these two can result in an uncertainty in shock temperature of more than 1000 K, which is a serious problem for the EOS calibration given the large thermal expansivity of silicate melts at high pressure. Therefore we will only include the shock data for Di and D64An36 melts from Asimow and Ahrens (2010) to calibrate our EOS since the Grüneisen parameter and its volume dependence ($q$) were better determined from their data without just assuming $q = 1$. Anorthite (An) melt has also been studied in Asimow and Ahrens (2010) but will not be included in the calibration because the data show some very complicated compressional behavior (a possible abrupt structural change at high pressure), which may require two equations of state for both pressure ranges below and above the transition pressure.

Since shock data for only two compositions will be included in the calculation, the deformability of spheres ($\zeta$) for each melt component will be difficult to resolve at high pressure. Consequently, we will use a single deformability parameter ($\zeta$) for all components for the calibration. In addition, the shock temperatures are higher when the pressures are higher, which makes the volume dependence of sphere diameters hard to be isolated from the temperature dependence. To avoid this trade-off between the temperature and volume dependencies, we use the same temperature dependence of sphere diameters in Table 9 calibrated by using ultrasonic data and sink/float data. After including the shock data for Di and D64An36 (Table 10), the new regression gives a higher deformability ($\zeta = 0.63$) compared to the previous value of 0.53. Fig. 12b compares the predicted density with that determined by shock experiments. Although the calculation of the density at pressures higher than 80 GPa is improved, the calculated melt densities are too high at relatively low pressures due to the high deformability of spheres. This means the predicted melts are too compressible at relatively low pressures but not compressible enough at high pressures. A likely reason for this is that the deformability of spheres may not be constant but depend on the packing fraction of the liquid when the EOS is applied over a wide range of pressures such as from room pressure to 130 GPa.

A simple way to model this behavior is to define the deformability of spheres to be a linear function of the packing fraction as

$$\zeta \equiv \left( \frac{\partial \ln V_m}{\partial \ln \rho} \right)_T = \zeta_0 + \tau (f - f_0),$$

(51)

where $\zeta_0$ is the deformability of spheres at room pressure and $\tau$ determines how packing fraction influences $\zeta$. The equation of state remains the same as Eqs. (47), (48), and (50), but it should be noted that $\zeta = (\partial \zeta / \partial \ln \rho)_T$ in Eq. (48) becomes

$$\zeta = -\tau (1 - \zeta).$$

(52)

To solve the EOS, $f$ and $V_m$ can be expressed as functions of $\rho$. Using Eq. (51), it can be shown that

$$\frac{d \ln V}{d \ln f} = \frac{1}{(\zeta_0 - 1) + \tau (f - f_0)}.$$  

(53)

Then $V$ can be integrated out as a function of $f$. After some manipulation, one obtains

$$f = f_0 \frac{\tau f_0 + (1 - \zeta_0)}{\tau f_0 + (1 - \zeta_0)(V/V_0)^{(f_0/(f_0 - 1 - \zeta_0))}}.$$  

(54)

Then the volume of spheres at high pressure can be obtained from

$$V_m = f V.$$  

(55)
Table 11
Calibrated sphere diameters and their temperature and volume dependencies for melt components in the CMASF system assuming that the deformability of spheres depends on packing fraction.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\sigma_{r,ref}$ (nm)</th>
<th>$\eta_i = (\partial \ln \sigma_i / \partial \ln T)_T$</th>
<th>$\zeta_0$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>$0.350 \pm 0.002$</td>
<td>$-0.03 \pm 0.01^a$</td>
<td>$0.31 \pm 0.03^b$</td>
<td>$0.84 \pm 0.05^b$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>$0.315 \pm 0.001$</td>
<td>$-0.02 \pm 0.01^a$</td>
<td>$0.84 \pm 0.05^b$</td>
<td>$0.84 \pm 0.05^b$</td>
</tr>
<tr>
<td>FeO</td>
<td>$0.287 \pm 0.001$</td>
<td>$-0.02 \pm 0.02^a$</td>
<td>$0.84 \pm 0.05^b$</td>
<td>$0.84 \pm 0.05^b$</td>
</tr>
<tr>
<td>MgO</td>
<td>$0.279 \pm 0.001$</td>
<td>$0.08 \pm 0.01^a$</td>
<td>$0.84 \pm 0.05^b$</td>
<td>$0.84 \pm 0.05^b$</td>
</tr>
<tr>
<td>CaO</td>
<td>$0.325 \pm 0.001$</td>
<td>$-0.12 \pm 0.02^a$</td>
<td>$0.84 \pm 0.05^b$</td>
<td>$0.84 \pm 0.05^b$</td>
</tr>
</tbody>
</table>

Reference temperature ($T_{ref}$) is 1673 K. Uncertainties represent one $\sigma$ error estimates.

$^a$ Same values of $\eta_i$ in Table 9 are used.

$^b$ All melt components have the same values of $\zeta_0$ and $\tau$.

Again, we use Eqs. (47) and (50) to calibrate all the data including sound velocity data (Table 2), sink/float density data (Table 7), and the shock-wave density data (Table 10). The regressed $\zeta_0$ and $\tau$ are 0.31 and 0.84, respectively (Table 11). Given that the packing fractions for Di and Di$_{64}$-An$_{36}$ change from about 0.4-0.5 at room pressure to about 0.65-0.75 at 130 GPa, the deformability of solids increases from 0.31 to about 0.5. Fig. 13 shows the comparison of the predicted density with experimental data. The experimental data can be reproduced well and no systematic deviation is observed in this case. Consequently, with a packing-fraction dependent deformability, the proposed EOS can be successfully applied to model density data at extreme pressures up to 130 GPa.

Now we can calculate the Grüneisen parameter at extreme pressures up to 130 GPa Eq. (3). The formulation to calculate the thermal expansivity ($\chi$) is given in Appendix B. The calculated Grüneisen parameters for the peridotitic melt MA at high pressures and various temperatures from 2000 to 6000 K are plotted in Fig. 13 and compared with observations. It can be seen that the volume dependence of Grüneisen parameter ($q$) increases with temperature from about $-3$ at 2000 K to about $-2$ at 4000 K and to about $-1$ at 6000 K. The predicted $q$ at 4000 K are consistent with the observations that were averaged over 3000–6000 K. A likely explanation for the temperature effect on $q$ is that with increasing temperature the packing fraction is smaller due to small sphere diameters and as we have demonstrated in Fig. 4b for the simple hard sphere liquid, the difference between the pressure derivative of bulk modulus ($K'_q$) and volume dependence of thermal expansivity ($\delta q$) is smaller at lower packing fraction. That is, $q$ increases with decreasing packing fraction (the absolute value of $q$ decreases) and eventually becomes 0 for the ideal gas.

5. DISCUSSION

5.1. Interpretation of the sphere diameters

The hard sphere (deformable sphere actually) picture is a simplification of the very complex structure of silicate melts, which varies dramatically depending on the melt composition and pressure (e.g., McMillan and Wolf, 1994; Stebbins, 1995; Wolf and McMillan, 1995; Mysen and Richet, 2005, and references therein). This means that the sphere diameters cannot be measured directly and cannot provide the complete structural information of melts. It is however interesting to compare the inferred sphere diameters from our model with the bond lengths in crystalline solids (Fig. 14). It can be seen that for the components with 6-fold coordination including FeO, MgO, CaO, Na$_2$O, and K$_2$O, there is a correlation between the calibrated sphere diameters and bond lengths in the crystals. This correlation suggests that the short-range order for the 6-fold species is correctly represented by the proposed model. For the components with the 4-fold coordination including SiO$_2$ and Al$_2$O$_3$, however, they do not follow the high-coordination trend. The possible explanation is that the geometry of the effective volume (excluded volume) occupied by species with 4-fold coordination deviates considerably from a sphere, essentially due to the strong directional covalent bonding in these species. Therefore a large empty space is included if we treat the excluded volumes of these species as spheres. This implies that if the coordination of these species (SiO$_2$, Al$_2$O$_3$) changes to 6-fold, the influence of the directed covalent bonding will become weak and the sphere volumes of these species will become smaller. Thus this provides a possible explanation for the high deformability of spheres for SiO$_2$ and Al$_2$O$_3$ compared to MgO: the deformability parameter ($\zeta_0$) is 0.62 for SiO$_2$ and 0.66 for Al$_2$O$_3$, but only 0.22 for MgO (Table 8). With increasing pressure, SiO$_2$ and Al$_2$O$_3$ can undergo a gradual...
parameters listed in Table 11 be used. In total 12 parameters are required to better constrain the EOS at high pressures for wide ranges of temperature and melt compositions. Therefore the use of the proposed EOS for very MgO poor melts: only two compositions include FeO. The temperature data up 25 GPa from sink/float experiments. The bulk modulus data and high-pressure density data up 25 GPa from sink/float experiments. The bulk modulus data focus mainly on SiO$_2$–Al$_2$O$_3$–MgO–CaO melts: only two compositions include FeO. The temperature range in these measurements is within 300 K, which limits the calibration of the temperature dependence of sphere diameters. On the other hand, most melts in sink/float experiments are ultramafic to mafic composition. Therefore the use of the proposed EOS for very MgO poor melts at high pressures may produce larger uncertainties. In addition, there is a trade-off between the sphere diameter and its temperature and volume dependencies. More density measurements and maybe sound velocity measurements at high pressures for wide ranges of temperature and melt compositions are required to better constrain the EOS parameters.

5.2. Limitations of the model and future developments

We recommend the EOS parameters listed in Table 8 be used to calculate compressional properties of silicate melts when pressure is lower than 40 GPa. Fifteen parameters in total are calibrated for the CMASF system based on room-pressure bulk modulus and high-pressure density data up 25 GPa from sink/float experiments. The bulk modulus data focus mainly on SiO$_2$–Al$_2$O$_3$–MgO–CaO melts: only two compositions include FeO. The temperature range in these measurements is within 300 K, which limits the calibration of the temperature dependence of sphere diameters. On the other hand, most melts in sink/float experiments are ultramafic to mafic composition. Therefore the use of the proposed EOS for very MgO poor melts at high pressures may produce larger uncertainties. In addition, there is a trade-off between the sphere diameter and its temperature and volume dependencies. More density measurements and maybe sound velocity measurements at high pressures for wide ranges of temperature and melt compositions are required to better constrain the EOS parameters.

For pressures higher than 40 GPa, we recommend the parameters listed in Table 11 be used. In total 12 parameters are used in this calibration. The packing-fraction dependence of deformability becomes more important at extreme pressures. Density data including shock-wave data and first-principles molecular dynamics calculations at extreme pressure and temperature conditions are critical to constrain the EOS behavior under such conditions. It is possible that the functional forms for the temperature and volume dependencies of sphere diameters may need further modifications with more data become available. In that case, the first-principles molecular dynamics calculations, which are helpful to find the link between microscopic properties and the model parameters, may provide some insights and guidelines for such modifications.

At the current stage, we have not considered the effect of oxidation state of the FeO component. Fe$_2$O$_3$ is expected to have very different properties than FeO (e.g., Kress and Carmichael, 1991). Volatile components such H$_2$O and CO$_2$ are also very important to the density of silicate liquids (Lange, 1994).

We have made simple empirical approximations for the cohesion energy and the soft repulsive potential of hard spheres. This means that the structure of liquids is not explicitly modeled in the EOS, but represented by the sphere parameters and their temperature and volume dependencies. As a result, the sphere diameters cannot be measured directly and the exact structural information cannot be derived from the equation of state. For example, the effect of increasing coordination for the network modifiers such as SiO$_2$ and Al$_2$O$_3$ with increasing compression may contribute to the deformability of those spheres as we discussed in the previous section, but the exact coordination of these species cannot be calculated. Polymerization is another complication introduced by the network-forming components like SiO$_2$ and Al$_2$O$_3$, which can be linked to other network-forming components through bridging oxygen to form a chain-like or a three-dimensional network of molecules (for the review of polymerization refer to Mysen and Richet, 2005, and the references therein). Polymerization may reduce the entropy of the liquids and in turn affect the other properties such as compressibility and viscosity. If this effect is important, compositional dependent sphere diameters may be needed to model the network-forming components. However, since most data on density and bulk modulus can be explained well by the proposed EOS, the effect of polymerization on the entropic contribution to compression (excluded volume of spheres) is likely small. This on the other hand means that the proposed model cannot be applied to study the liquid structure and structure-related properties such as transport properties without introducing more parameters for the structural information.

ACKNOWLEDGMENTS

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APPENDIX A. BULK MODULUS–MOLAR VOLUME RELATIONSHIP FOR SOLIDS AND BIRCH’S LAW

Birch’s law is an empirical relationship between elastic constants (wave velocities) and density proposed by Birch (1961). Its physical interpretations and implications have been discussed in detail in many works (e.g., Birch, 1961; Anderson and Nafe, 1965; Chung, 1972; Shankland, 1972). Here we summarize the main conclusions below.

For solids, the free energy is mainly from the interatomic potential energy. Therefore the bulk modulus of solids is controlled by the molar volume or mean interatomic distance. For a given material, the volume derivatives of bulk modulus at constant temperature or constant pressure are given by

\[
\frac{\partial \ln K_T}{\partial \ln V} = -K'_T
\]

and

\[
\frac{\partial \ln K_T}{\partial \ln V} = -\delta_T,
\]

where \(K'_T\) is the pressure derivative of bulk modulus and \(\delta_T\) is the Anderson–Grüneisen parameter. If we define mean atomic weight as \(\bar{M}_a = M/n\), where \(M\) is the molar formula weight and \(n\) is the number of atoms in a chemical formula. Then we can define the volume derivative of bulk modulus at constant mean atomic weight (regardless if the temperature or pressure are constant) as

\[
\frac{\partial \ln K_T}{\partial \ln V} = -\chi.
\]

\(\chi\) is a constant of \(\approx 4\) for many crystalline oxides and silicates with the same mean atomic weight. For a small range of \(M\), Eq. (A3) reduces to a linear relationship between the bulk sound velocity and density as demonstrated by Chung (1972)

\[
v_k = a(M) + b\rho,
\]

where \(v_k = (K/\rho)^{1/2}\). Eq. (A4) is the original form of Birch’s law proposed by Birch (1961).

Essentially, Birch’s law says that the volume dependencies of bulk modulus at constant temperature, pressure, and mean atomic weight are roughly the same, that is

\[
K' = \delta = \chi
\]

The similar values of anharmonic parameters \(K', \delta, \) and \(\chi\) are confirmed by many experiments (e.g., Anderson et al., 1971; Liebermann and Ringwood, 1973).

APPENDIX B. THERMAL EXPANSIVITY AT HIGH PRESSURE

Thermal expansivity as a function of pressure can be obtained by taking the temperature derivative of Eq. (47)

\[
\alpha = \frac{1}{K_T} \left( \frac{\partial P}{\partial T} \right)_T.
\]

where the temperature derivative of \(\Phi(f, y_1, y_2)\) is needed. \(y_1\) and \(y_2\) are small in the composition range of this study (\(<0.03\)) since the sphere diameters are close to each other. Therefore we can simplify the evaluation of Eq. (A6) by neglecting the temperature dependencies of \(y_1\) and \(y_2\) as

\[
\left( \frac{\partial \Phi}{\partial T} \right)_f = f \left( \frac{\partial \Phi}{\partial T} \right)_0 \left( \frac{\partial \ln f}{\partial T} \right)_0 = (\Gamma - \Phi) \frac{\partial \ln V_m}{\partial T},
\]

and

\[
\left( \frac{\partial \Phi_0}{\partial T} \right)_f = f_0 \left( \frac{\partial \Phi_0}{\partial f_0} \right) \left( \frac{\partial \ln f_0}{\partial T} \right)_0 = (\Gamma_0 - \Phi_0) \frac{\partial \ln V_{m^0}}{\partial T} + \lambda_0,
\]

where

\[
\lambda_0 = \frac{\partial T}{\partial T} \frac{\partial \ln V_0}{\partial T} = \frac{\partial \ln V_0}{\partial T}
\]

is the room-pressure thermal expansivity of a liquid. Using Eqs. (A7) and (A8), Eq. (A6) can be reduced to

\[
\left( \frac{\partial P}{\partial T} \right)_f = \frac{P}{T} + \frac{RT}{V} \left[ (1 - \xi)\theta(\Gamma - \Phi) - ((\theta_0 - \lambda_0)(\Gamma_0 - \Phi_0)
\]

\[
+ \omega \Phi + (\xi(\theta_0 - \lambda_0)(\Gamma_0 - \Phi_0) + \omega \Phi_0
\]

\[
+ \xi(\gamma - 1)(\theta_0 - \lambda_0)\Phi_0) \frac{\partial \ln V_{m^0}}{\partial T} \right],
\]

where \(\theta\) and \(\omega\) are related to the temperature dependence of the volume of spheres

\[
\theta \equiv \left( \frac{\partial \ln V_m}{\partial T} \right)_0 = \frac{1}{V_m} \sum_{i=1}^{n} X_i \frac{\partial V_m}{\partial \theta_i} = \lambda_0 \xi,
\]

\[
\theta_0 \equiv \left( \frac{\partial \ln V_{m^0}}{\partial T} \right)_0 = \frac{1}{V_{m^0}} \sum_{i=1}^{n} X_i \frac{\partial V_{m^0}}{\partial \theta_i},
\]

and

\[
\omega \equiv \left( \frac{\partial \xi}{\partial T} \right)_f = \frac{1}{V_m} \sum_{i=1}^{n} X_i \frac{\partial \xi}{\partial \theta_i} = \theta \xi - \xi \xi - \lambda_0(\xi + \xi^2),
\]

with

\[
\xi_0 = \frac{\partial \xi}{\partial T} \frac{\partial V_{m^0}}{\partial T} = \theta \xi + \lambda_0 \zeta_0.
\]

Note that here \(\eta_{m^0}\) is defined as the temperature dependence of sphere diameters at constant liquid volume. When temperature changes, the total volume of the liquid also changes due to the thermal expansion. Since the sphere diameters are also volume dependent, the second term on the right hand side of Eq. (A14) thus represents the effect of thermal expansion.

For the case that the deformability of spheres is a linear function of the packing fraction (Eq. (51)), Eq. (A10) remains valid, but \(\theta\) and \(\omega\) should be evaluated as
\[
\theta = \frac{12\tau f_0 + (1 - \zeta_0)}{\tau f_0 + (1 - \zeta_0)} \left( \frac{\theta_0 - \theta_0}{\ln(1 - \zeta_0)} \right) - \frac{\tau f_0(\theta_0 - \theta_0) + (1 - \zeta_0)(\theta_0/\theta_0)^{1/(1 - \zeta_0)} \left( \tau f_0(\theta_0 - \theta_0/\theta_0)^{1/(1 - \zeta_0)} \right)}{\tau f_0 + (1 - \zeta_0)(\theta_0/\theta_0)^{1/(1 - \zeta_0)}},
\]

(A15)

and

\[
\omega = \tau(\theta - f \theta_0) \quad \text{(A16)}
\]

REFERENCES


