Coordinated **Hard Sphere Mixture (CHaSM)**: A simplified model for oxide and silicate melts at mantle pressures and temperatures

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Abstract

We develop a new model to understand and predict the behavior of oxide and silicate melts at extreme temperatures and pressures, including deep mantle conditions like those in the early Earth magma ocean. The **Coordinated Hard Sphere Mixture (CHaSM)** is based on an extension of the hard sphere mixture model, accounting for the range of coordination states available to each cation in the liquid. By utilizing approximate analytic expressions for the hard sphere model, this method is capable of predicting complex liquid structure and thermodynamics while remaining computationally efficient, requiring only minutes of calculation time on standard desktop computers. This modeling framework is applied to the MgO system, where model parameters are trained on a collection of crystal polymorphs, producing realistic predictions of coordination evolution and the equation of state of MgO melt over a wide range of pressures and temperatures. We find that the typical coordination number of the Mg cation evolves continuously upward from 5.25 at 0 GPa to 8.5 at 250 GPa. The results produced by CHaSM are evaluated by comparison with predictions from published first-principles molecular dynamics calculations, indicating that CHaSM is accurately capturing the dominant physics controlling the behavior of oxide melts at high pressure. Finally, we present a simple quantitative model to explain the universality of the increasing grüneisen parameter trend for liquids, which directly reflects their pro-

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gressive evolution toward more compact solid-like structures upon compression. This general behavior is opposite that of solid materials, and produces steep adiabatic thermal profiles for silicate melts, thus playing a crucial role in magma ocean evolution.

Keywords: High Pressure Melts, Silicate Liquids, Grüneisen Parameter, Magma Ocean, Liquid Thermodynamics

1. Introduction

Understanding the behavior of silicate and oxide liquids at mantle pressures is crucial to reconstructing evolution of Earth and other terrestrial planets, both today and in the distant past. While molten silicates are primarily restricted to the shallow mantle today, their material properties directly determined the Earth's evolutionary path as it cooled from a nearly whole-mantle magma ocean to its present-day solid state.

Recent first-principles theoretical calculations and experimental shock-wave investigations (Stixrude et al., 2009; Mosenfelder et al., 2009) indicate that the adiabatic profiles of molten MgSiO_3 as well as a wide collection of other silicate melts (Thomas et al., 2012; Asimow, 2012)) are significantly steeper than previously thought. Giant impact simulations indicate that events like the moon-forming impact efficiently deliver heat to great depths, supporting the possibility of a deep potentially whole-mantle magma ocean early in Earth's history (Nakajima and Stevenson, 2014). The evolution of this planetary-scale magma ocean as it cools and crystallizes is dominated by the poorly understood behavior of silicates at extreme pressures and temperatures. Probing these conditions is difficult for both theory and experiment, and further challenges are posed by the large relevant compositional space, including at least MgO , SiO_2 , and spin-dependent FeO . The primary tool for computational work, first-principles molecular dynamics (FPMD), has been used to probe the behavior of a variety of silicate liquid compositions across the MgO-SiO_2 binary (e.g. Stixrude and Karki, 2005; Karki et al., 2006, 2007; de Koker et al., 2008, 2013) as well as iron-rich silicate liquid Fe_2SiO_4 (Muñoz Ramo and Stixrude, 2014). While extremely powerful, this approach has limitations including high computational cost, lower bounds on temperature due to relaxation constraints, as well as restrictions to simulation length and time scales that

are many orders of magnitude smaller than those relevant to the Earth or experimental methods. These limitations invite the parallel development of new theoretical methods for investigating the behavior of molten oxides and silicates.

Though there is much about the structure of high-pressure silicate melts that we do not yet understand, there is a growing consensus amongst experimental and theoretical studies that the evolution of cation coordination number plays a critical role in silicate liquid compression. Nuclear Magnetic Resonance (NMR) spectroscopy probes the local bonding environment around particular target atoms within a material. Numerous ^{29}Si -NMR and ^{27}Al -NMR studies over the last two decades have examined the evolution of cation coordination number (signifying the number of oxygens bonded to each cation), showing its smooth increase with compression from 4 to 6 for these network forming cations based on measurements of quenched glasses, thought to represent frozen snapshots of the liquid structure (e.g., [Xue et al., 1991](#); [Yarger et al., 1995](#); [Lee, 2011](#)). These ex-situ spectroscopy studies on glasses are nicely complemented by in-situ melt studies that measure diffuse x-ray diffraction signals for laser- or furnace-heated samples at high pressures. With carefully designed experiments for the cubic-anvil press ([Funamori et al., 2004](#)), Paris-Edinburgh press ([Yamada et al., 2011](#); [Wang et al., 2014](#)), and diamond anvil cell ([Sanloup et al., 2013](#)), recent studies have measured in-situ x-ray structure factors for silicate melts over a range of elevated pressures. By transforming and integrating these data, they found upward evolution of cation coordination with compression. These experimental findings all compare well with FPMD calculations, which show progressive cation coordination evolution for all cations within the melt, indicating that coordination evolution must play a major role in accommodating compression for oxide and silicate melts over a wide range of conditions.

As a complement to accurate first-principles calculations, we have developed the Coordinated **H**ard **S**phere **M**ixture (**CHaSM**), which represents oxide and silicate liquids by tracking the relative populations of differently coordinated cation species (clusters) as a function of temperature and pressure. This model is based on extending the standard hard sphere mixture model ([Mansoori et al., 1971](#)), which was recently applied to silicate liquids by [Jing and Karato \(2011\)](#). In order to reasonably represent

compression-induced changes to internal energy, we implement a perturbation to the standard hard sphere model, in which the internal energy is represented by empirical cluster potentials that are coordination dependent. Using entirely analytic expressions and the principle of free energy minimization, we determine the relative populations of the different coordination states. We also demonstrate how the equations of state for a set of solid structures can be used to train appropriate values for the cluster potentials, thus providing a fully predictive model for oxide liquids that does not require fitting any liquid data.

Shock wave experiments indicate that all silicate liquids maintain much steeper adiabatic profiles at extreme pressures than their solid counterparts (Thomas et al., 2012; Asimow, 2012). This is a consequence of the compression behavior of the thermodynamic grüneisen parameter γ :

$$\left. \frac{dT}{dP} \right|_S = \gamma \left(\frac{T}{K_S} \right) \quad (1)$$

where γ gives the proportionality constant for the adiabatic temperature path and K_S is the adiabatic bulk modulus. The function $\gamma(V)$ is thus a crucial property for understanding early Earth evolution, as it largely determines the thermal profile through the convecting (nearly adiabatic) magma ocean. Both theoretical calculations and experiments show that the grüneisen parameter increases upon compression not just for silicate melts but for nearly all liquids (McQueen and Marsh, 1960; Knopoff and Shapiro, 1970; Boehler and Kennedy, 1977), which is opposite to the well-understood behavior of solid materials. Unfortunately, we do not yet have a mechanistic understanding of why this property behaves so counterintuitively. We propose a simple and entirely general explanation, which provides accurate quantitative predictions along with important qualitative insights about the general properties of liquids.

We begin this paper by first reviewing the physics behind the Hard Sphere model, previous geological applications, and the variational perturbation approach in Section 2. In Section 3, we present the framework for our new model, the Coordinated Hard Sphere Mixture (CHaSM), taking special care to explicitly connect the model parameters to the physical aspects of oxide melt structure. In Section (4), we present a first application of CHaSM to the MgO melt system, demonstrating how its parameters can

85 be trained on solid data in order to obtain predictions of melt behavior over a wide
 86 pressure-temperature range. In Section 5, we review the existing experimental and
 87 computational evidence considering the grüneisen parameter behavior of liquids and
 88 present a simple model that provides a general explanation of these data, while also
 89 providing testable quantitative predictions. Finally in Section 6, we review our find-
 90 ings and discuss future prospects for this new modeling effort.

91 2. The Hard Sphere Model

92 Unlike crystalline solids, whose compression behavior is dominated by the en-
 93 ergetic cost of bond-length shortening, liquid equations of state are influenced by
 94 their compression-induced structural evolution. The Hard Sphere model successfully
 95 describes simple liquids based on its approximate representation of atomic spatial
 96 distributions, capturing the associated configurational entropies and how they evolve
 97 with pressure.

98 2.1. Intro to Hard Spheres and Simple Liquids

99 In a hard sphere fluid, liquid particles are described as a collection of non-overlapping
 100 and non-deformable spheres, reflecting the short-range electronic repulsive forces that
 101 give atoms their finite size. Like the ideal gas this model is devoid of energy interac-
 102 tions, and thus obtains its rich behavior entirely from entropic and kinetic energy terms.
 103 The details of the basic hard sphere model are readily found in statistical physics text-
 104 books, but we reproduce all the necessary equations in [Appendix A](#).

105 Absence of long-range order is a defining characteristic of liquids, and thus their
 106 structure must be characterized probabilistically. The Radial Distribution Function
 107 (RDF), denoted $g(r)$, is used to describe the time-averaged liquid structure, expressing
 108 how particle density varies with separation distance:

$$g(r) \equiv \frac{\rho(r)}{\langle \rho \rangle} \quad \text{and} \quad \mathcal{P}(r)dr = 4\pi r^2 \langle \rho \rangle g(r)dr \quad (2)$$

109 The RDF is computed in atomic simulations by averaging the number of particles lying
 110 within spherical shells over a range of sizes.

Figure 1: Comparison of the standard Hard Sphere (HS) and variational Hard Sphere (HS-V) models to Monte Carlo (MC) simulations for a toy single-component melt tuned to have compression behavior similar to MgO at 3000 K. Panel (a) compares the Radial Distribution Function (RDF) curves from the HS and MC models; (b) illustrates the pair potential parameters, defining the energy well position r^0 , depth E^0 , and width σr^0 ; (c) compares the equation of state predictions for the MC, HS, and HS-V models at 3000 K and 7000 K; and (d) shows the evolution of d_{HS} for the HS and HS-V models in light and heavy weight lines, respectively.

111 To demonstrate the hard sphere model, we compare its predictions to those of
 112 atomic simulation, where atomic positions and their effect on total energy are directly
 113 modeled. Unlike the hard sphere model, atomic simulations account for interaction en-
 114 ergies by representing them with either first-principles quantum mechanics or empirical
 115 potentials, which describe the shape of the energy well for pairwise atomic interactions
 116 (see Figure 1b). These simulations can either use the molecular dynamics (MD) or
 117 molecular Monte Carlo (MC) approaches, where atomic positions are varied according
 118 to either Newtonian mechanics or random proposals, respectively. Both methods pro-

119 duce consistent predictions of liquid structure and thermodynamics, though dynamical
120 quantities like diffusivity or viscosity are typically restricted to MD simulations.

121 For a simple demonstration, we explore a single-component reference liquid whose
122 pair potential has been chosen to reproduce the 3000 K isotherm of MgO melt (Karki
123 et al., 2006). This toy example shows the general characteristics of liquids while re-
124 taining temperature and pressure scales appropriate to silicate and oxide melts. Fig-
125 ure 1(a) compares the RDF curve from the Hard Sphere model to the precise structure
126 obtained from empirical Monte Carlo simulation (using a basic random-walk Monte
127 Carlo scheme in MATLAB). Both curves demonstrate the primary structural features of
128 all liquids: a sharp inner edge to the particle density and decaying density oscillations
129 with increasing distance. The inner edge is a direct consequence of finite particle size
130 resulting from repulsive interactions, and is thus well represented by the hard sphere
131 diameter d_{HS} . The density oscillations reflect the liquid’s short-range order, where each
132 subsequent maximum corresponds to a shell of next-nearest neighboring particles. At
133 great distance, all ordering is lost as the density asymptotically approaches the average
134 bulk value, with $g(r) = 1$. The hard sphere model achieves this successful approxi-
135 mation of liquid structure with only a single free parameter, d_{HS} . Furthermore, its an
136 entirely analytic model (see Appendix A), resulting in nearly instantaneous calcula-
137 tions in contrast to the long convergence times needed for atomic simulations.

138 In addition to structure, the hard sphere model also estimates thermodynamic prop-
139 erties like pressure and Helmholtz Free energy by estimating the entropy associated
140 with the predicted liquid structure. The isothermal equation of state is shown in Fig-
141 ure 1c for both the HS model and MC simulations, in the light weight curves and open
142 symbols, respectively. The 3000 K and 7000 K hard sphere diameters, shown by the
143 light weight lines in panel d, were determined by matching the reference bulk mod-
144 ulus¹. The HS model matches the MC results well in the low pressure-region, but
145 begins to deviate significantly at 3000 K and 7000 K for pressures exceeding 10 GPa

¹ The basic HS model curves in Figure 1 include an additional background potential term to roughly capture the attractive Coulombic field. This negative pressure term is important for representing near-ambient pressure properties.

and 40 GPa, respectively. The failure of the basic hard sphere model to extend to high pressures reflects the inadequacy of assuming fixed hard sphere sizes.

2.2. Variational Approach to Hard Spheres

The variational hard sphere model, developed by Mansoori and Canfield (1969), address this limitation by adding a structural energy perturbation to the hard sphere model, which is used to estimate the structure and entropy of the liquid. The hard sphere size is then determined by minimizing the total Helmholtz free energy (with respect to its value):

$$F^{\text{HS-V}}(V, T) = \min_{d_{\text{HS}}} \left\{ F^{\text{HS}}(V, T, d_{\text{HS}}) + E^{\text{struc}}(V, d_{\text{HS}}) \right\} \quad (3)$$

This approach has the advantage of eliminating hard sphere size as a free parameter, allowing the model to determine its optimal value.

To estimate the structural energy, we must choose a pair potential to describe the pairwise interactions. Though many potential functional forms exist (e.g. Lennard-Jones, Buckingham, Mie, etc.), we use the Morse potential for its flexibility and easily interpreted tunable parameters:

$$E_*^{\text{Morse}}(r_*) = \exp \left[-2 \frac{(r_* - 1)}{\sigma} \right] - 2 \exp \left[- \frac{(r_* - 1)}{\sigma} \right] \quad (4)$$

with, $E_* = E/E^0$ and $r_* = r/r^0$

where the energy and length scales defining the depth and position of the energy well are given by E^0 and r^0 , and the normalized width of the energy well is defined by σ (see Figure 1b). The total structural energy is then just an RDF-weighted average over pairwise particle interactions:

$$\begin{aligned} E^{\text{struc}} &= \frac{1}{2} \int_0^\infty E^{\text{pot}}(r) \mathcal{P}(r) dr \\ &= 2\pi \langle \rho \rangle \int_0^\infty E^{\text{pot}}(r) r^2 g(r) dr \end{aligned} \quad (5)$$

where E^{pot} is the pair potential and the factor of $\frac{1}{2}$ prevents double counting.

Standard numerical minimization of the total free energy (Equation 3) is used to infer the appropriate hard sphere sizes, shown by the heavy-weight lines in Figure 1d,

167 which are seen to shrink with both increasing temperature and pressure. This is in-
 168 tuitively reasonable since reducing the hard sphere size is accomplished by climbing
 169 up the short-range repulsive slope of the potential, which requires energy that can be
 170 provided either thermally or by doing mechanical work on the system. The free energy
 171 surface as a function of volume and temperature is easily calculated, and numerical
 172 derivatives yield desired thermodynamic quantities, such as entropy, pressure, com-
 173 pressibility, etc. In Figure 1(c), we can see that the variational method extends the hard
 174 sphere model's accuracy across the entire explored pressure range. By eliminating all
 175 free parameters, the variational approach thus transforms the hard sphere model from
 176 an empirical data-fitting procedure into a predictive model for simple liquids.

177 2.3. Previous Application of Hard Spheres to Silicate Liquids

178 Despite the ~70 year history of the hard sphere model (Percus and Yevick, 1958),
 179 hard sphere theory is rather new to the study of silicate melts. The first notable ap-
 180 plication to geologic systems was presented by Guillot and Sarda (2006), where the
 181 compression of MORB, silica, and olivine composition liquids up to 10 GPa were
 182 modeled to investigate high-pressure noble gas solubility. The effective hard sphere
 183 sizes were determined empirically by fitting 1 bar melt density measurements.

184 More recently, Jing and Karato (2011) calibrated oxide-specific hard spheres us-
 185 ing liquid density and bulk modulus measurements in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$
 186 system. With least-squares minimization, they obtained best-fit HS diameters
 187 for each oxide component. Further refinements incorporated empirical corrections for
 188 temperature- and volume-dependence of the sphere sizes, but the absence of any physi-
 189 cal model for these corrections limits their predictive power for out-of-sample data. As
 190 pointed out by the authors, these limitations are evident in the non-physical values for
 191 some of these terms (e.g. the sign of the temperature dependence for MgO spheres).

192 Despite the limitations of the empirical procedure employed by both Jing and
 193 Karato (2011) and Guillot and Sarda (2006), these studies demonstrated the potential
 194 power of the hard sphere model for describing pressure-, temperature-, and composition-
 195 dependent trends for oxide and silicate melt properties. These investigators used the
 196 HS model as a physically-motivated averaging kernel, allowing them to interpolate

197 within the fitted dataset. Extrapolation was fairly limited, however, as the hard spheres
 198 were not strongly connected with physically meaningful aspects of liquid structure,
 199 thus confining it to pressures generally below ~ 20 GPa. Compositionally-induced
 200 structure changes, such as the Ca-dependent Fe-coordination evolution inferred in Guo
 201 et al. (2013), are also inaccessible to this empirical approach. Motivated by both the
 202 successes and shortcomings of these earlier works, we extend the hard sphere model-
 203 ing framework to directly incorporate the general structural attributes of dense oxide-
 204 silicate melts.

205 **3. Coordinated Hard Sphere Mixture (CHaSM)**

206 Evidence from diffraction studies, NMR spectroscopy, and FPMD simulations all
 207 indicate that cation coordination evolution is a common compression mechanism across
 208 all oxide and silicate melts. Despite this fact, there has been almost no development
 209 of simple theories for oxide melts that account for these coordination effects (a notable
 210 exception is the empirical thermodynamic modeling of amorphous SiO_2 by Ghiorso
 211 (2004)). We thus develop the **Coordinated Hard Sphere Mixture** model (CHaSM),
 212 adding coordination-dependent structural and vibrational perturbations to the varia-
 213 tional hard sphere model. Using the analytic formulation of the HS mixture model,
 214 CHaSM predicts the compression of silicate and oxide melts by determining the evo-
 215 lution of the cation coordination populations while remaining computationally effi-
 216 cient, needing only minutes on a standard desktop computer. Following a classical
 217 approach, CHaSM uses empirical potentials trained on the well-understood behavior
 218 of solid polymorphs, giving a fully predictive model for oxide liquids.

219 *3.1. Connecting Hard Spheres directly to Oxide Liquid Structure*

220 Previous applications of hard spheres to silicate systems suffered from their am-
 221 biguous link to atomic-scale melt structure. Since these melts are composed of charged
 222 ions with strong multi-body interactions, it is impractical to represent individual ions
 223 as hard spheres. Previous investigators side-stepped this complication, using the HS
 224 method as an empirical fitting function without providing physical justification for the
 225 extension from simple liquids to ionic melts.

Figure 2: Cartoon of oxide liquids and solids using charge-neutral ionic clusters. Panel (a) schematically represents a one-dimensional pseudo-lattice of oxygens (in red) and cations (in blue) with bonds represented by black springs. Panel (b) portrays the structure using ionic clusters, each containing a single cation and shared oxygens. Internal vibrational motions are represented by small black springs and cluster interactions are represented by the large black springs. Panel (c) represents the coordination-dependence of both internal vibrations and cluster interactions, where oxygen sharing is represented by fractional symbols.

226 To construct a physically-rooted hard sphere model, we consider a simplified car-
 227 toon of solid or melt structure as a set of coordinated ionic clusters, depicted in Fig-
 228 ure 2. Panel (a) shows the condensed material as a pseudo-lattice of bonded cations
 229 and oxygens. These ions can be grouped, much like molecules in a gas, yielding the
 230 set of charge-neutral ionic clusters shown in panel (b). Each clustered particle is cen-
 231 tered on a single cation, with shared oxygens between neighboring clusters. As with

polyatomic gas molecules, we must account for the internal vibrational modes of each cluster (shown by small internal springs), in addition to cluster-cluster interactions (represented by the larger springs). Internal oscillators are used to account for the additional entropy and free energy associated with the relative motions of bonded ions. Finally, we recognize that the both cluster interactions and internal oscillations can depend on coordination number, as depicted in panel (c).

This conceptual structural model is justified both experimentally and theoretically by the radial distribution functions of silicate liquids, which universally show primary peaks corresponding to well-defined cation-oxygen bond lengths and average coordination numbers (for reviews, see [Mysen and Richet 2005](#) and [Karki 2015](#)). Furthermore, the NMR work of ([Stebbins et al., 1985](#)) shows that the atomic structure of oxide and silicate melts is fully dynamic, with bonds constantly breaking and reforming, even at equilibrium. Each cations evolves through a set of coordination states, where the relative time spent in each state reflects the coordination populations.

3.2. *CHaSM Free Energy Contributions*

Since coordinated ionic clusters represent roughly independent structural units, they are perfectly suited for direct representation using hard spheres. The total Helmholtz free energy of the CHaSM liquid is thus given:

$$F^{\text{Tot}} \approx F^{\text{HS}} + E^{\text{struc}} + F^{\text{osc}} \quad (6)$$

where F^{HS} is the standard hard sphere mixture model term, E^{struc} is the structural contribution to the internal energy, and F^{osc} captures the internal oscillation contribution to each ionic cluster, which depend on the vibrational properties of both the individual bonded ions and the ionic clusters. As depicted in Figure 2, coordination number affects both the structural energy (through the cluster interactions) and the internal oscillations. In the next section, we present a method for estimating the potential parameters using the thermodynamic properties of solid crystals, and thus we assume for the current discussion that their values are known. (The full expressions for each of these terms are presented in Appendices A-E.) Given the dependencies of each term,

Figure 3: Unit cell structures and cation coordination polyhedra for six polymorphs of MgO displayed along a coordination spectrum (created using VESTA, Momma and Izumi, 2011). Though only the NaCl structure (periclase) is stable under terrestrial conditions, all structures can be theoretically studied and provide insight into the coordination-dependence of the clusters potentials for MgO.

the total free energy can be written:

$$F^{\text{Tot}} = F^{\text{Tot}}(V, T, \vec{X}, \mathbf{d}_{\text{HS}}, \mathbf{p}_{\text{HS}}) \quad (7)$$

where the free energy is a function of the thermodynamic state variables volume V , temperature T , and composition $\vec{X}$, as well as the Hard Sphere diameters $\mathbf{d}_{\text{HS}}$ and populations $\mathbf{p}_{\text{HS}}$ specific to each coordination number and oxide component.

Using an extended form of the variational approach to Hard Spheres, discussed in Section 2.2, the optimal hard sphere diameters and coordination populations are determined using free energy minimization:

$$F^{\text{liq}}(V, T, \vec{X}) = \min_{\mathbf{p}_{\text{HS}}, \mathbf{d}_{\text{HS}}} \{F^{\text{Tot}}\} \quad (8)$$

where this expression is analogous to Equation 3 for an evolving mixture of hard spheres. Due to its analytic underpinnings, this expression is rapidly evaluated enabling numerical minimization, predicting both coordination populations and total free energy.

4. A First Application to MgO Melt

As a first demonstration, we apply CHaSM to the MgO system, which is relatively simple yet vital to our understanding of the Earth. MgO exists as the mineral periclase

(in the B1 or NaCl structure) over a large pressure range extending up to 400-500 GPa, where it is predicted to transform to the denser CsCl (or B2) structure (Karki, 1997; Schleife et al., 2006; Jaffe et al., 2000; Joshi et al., 2012). Despite such stable behavior, other analog AB crystal systems indicate that MgO could potentially adopt a range of structures including the distorted NiAs structure and the low-coordination h-MgO (a buckled boron nitride structure), zincblende (B3), and wurtzite (B4) structures. Ab initio studies of these MgO polymorphs provide useful information about the coordination-dependence of atomic interactions in this system.

4.1. Training Potentials on Solid Structures

It is standard practice to use sets of well-characterized crystal structures to train ionic potential parameters, describing the interactions of cation-oxygen and oxygen-oxygen pairs (e.g. Leinenweber and Navrotsky, 1988; Matsui, 1994, 1996; Gale, 1998; Guillot and Sator, 2007). Despite its successes, ionic potentials have demonstrated limited transferability to extreme near-endmember compositions (as shown by Guillot and Sator (2012) for very FeO- or SiO₂-rich melts) or to very high pressures (as shown by Spera et al. (2011) for MgSiO₃ melt at lower-mantle pressures). Both of these issues likely stem from the challenge of approximating ionic interactions over a wide range of local environmental conditions. It is unsurprising that simple analytic forms, such as the Buckingham or Morse potentials, are not flexible enough to represent coordination numbers that span from ~4 to ~12.

The development of accurate coordination-dependent ionic potentials would directly address this difficulty, but represents a substantial undertaking that deserves full attention in future studies. For CHaSM, we need only represent the dependence of total structural energy on cluster separation distances, and thus we adopt an empirical fitting approach to determine approximate ionic cluster potentials. Though more limited than coordination-dependent ionic potentials, it is much simpler to train the fewer free parameters and eliminates the need to explicitly include Coulombic interactions, as their energetic impact is folded into the pairwise interactions of the charge-neutral clusters.

For training our MgO cluster potentials, we rely on the dataset produced by Schleife

et al. (2006)², which examined all of the available structures shown in Figure 3. The published energy-volume curves for the six potential structures of MgO are shown in Figure 4. Representing each crystal as a set of coordinated ionic clusters centered on the cation positions, we model the internal energy with a Morse potential (Equation (4)), summing over cluster pairs out to a cutoff distance large enough for convergence.

In addition to the direct interaction energy, we introduce a correction to account for the strong distortions present in some of the structures like NiAs and hMgO. The cluster potentials developed here are appropriate for near-ideal atomic arrangements produced by regular packing schemes. Distorted structures have the freedom to adjust relative ionic positions, internal to the clusters, reducing the true energy cost of apparently unfavorable arrangements. To account for this discrepancy, we apply a simple additive energy offset correction:

$$\Delta E_{\text{corr}}^0 = - \sum_i w_i \left(E_{\text{pair}}(d_{\text{Mg-Mg}}^i) - E_{\text{pair}}(\langle d_{\text{Mg-Mg}} \rangle) \right) \quad (9)$$

where w_i is the weight of the i^{th} nearest-neighbor cation at a distance $d_{\text{Mg-Mg}}^i$, and $\langle d_{\text{Mg-Mg}} \rangle$ is the average cation separation distance at zero pressure (see Appendix F). This expression approximates the energetic benefit of shifting neighboring cations from their observed positions to their average separation distances, which better reflect the configuration's true energy cost. This corrective term is only significant for highly distorted structures like NiAs and hMgO, where it is large and negative.

Parameter variations are fit in log-space to the MgO polymorph data assuming quadratic coordination-dependence:

$$\delta \theta_{\text{pot}} = \log_e \theta_{\text{pot}}(\text{CN}) - \log_e \theta_{\text{pot}}(6) = k_2 \Delta \text{CN}^2 + k_1 \Delta \text{CN} \quad (10)$$

where the fractional deviation of the potential parameters, $\delta \theta_{\text{pot}} = (\delta r^0, \delta E^0, \delta \sigma)$, is expressed relative to their fitted values at CN=6. The ambient pressure cation separation distances, $\log_e d_{\text{Mg-Mg}}(\text{CN})$, also help to constrain the equilibrium position values, $\log_e r^0(\text{CN})$, and are constrained to have the same slope and curvature (k_1 and k_2) al-

²Self-consistent calculation of energies for all structures within a single study is crucial, since each study introduces an arbitrary energy offset.

Figure 4: First-principles energy-volume curves for six solid polymorphs of MgO (Schleife et al., 2006), with the best-fit coordinated cluster potential model (panel a). Using 9 free parameters, plus an additional offset parameter, we obtain a good fit to the data with a goodness-of-fit (explained fraction of the variance) of $R^2 = 0.986$ (without the highly distorted NiAs structure; see text for details). Residuals are higher for more distorted structures, like NiAs and hMgO, as expected. Panels (b) and (c) show the linear variation of relative bond-length and relative cation separation distance with coordination number, which reflect atomic packing efficiency.

Table 1: Best-fit Coordination-Dependent Morse Cluster Potential for MgO

	$\theta_{\text{pot}}(6)$	k_2	k_1
r^0	3.4359 Å	+0.0045	-0.0441
E^0	0.6902 eV	-0.0174	+0.0088
σ	0.2658	-0.0010	-0.0138

Morse potential parameters (Equation 4) are assumed to vary quadratically with coordination number, as given by Equation (10).

lowing only a relative offset to freely vary, as shown by the dashed and solid red lines in Figure 5(a). An arbitrary energy offset parameter is also fit, reflecting that only relative energies are thermodynamically important.

We use standard least-squares regression to infer the coordination-dependent cluster potential for MgO, excluding the NiAs dataset (see Table 1 for best-fit values). As can be seen in Figure 4(a), the NiAs structure deviates non-negligibly from the model curve, reflecting the limitations of the simple distortion correction term given by Equation 9. Furthermore, this structure is strongly disfavored as it forces all coordination

polyhedra into energetically unfavorable distortions, and is only stable to small perturbations, indicating that a liquid with complete configurational freedom is unlikely to sample similar atomic geometries. Nevertheless, the model still provides a good qualitative match to the metastable NiAs curve, and the residuals to the other structures are all reasonable. . The goodness-of-fit can be quantified in terms of the explained fraction of the variance $R^2 = 1 - \text{Var}(E_{\text{resid}})/\text{Var}(E_{\text{data}})$, with a value of 1 corresponding to a *perfect* fit. Excluding NiAs, the best-fit model gives a value of $R^2 = 0.99$ (which drops to $R^2 = 0.9$ if NiAs is included). Linear fits to normalized bond-lengths and cation separation distances, which both reflect atomic packing efficiency, are shown in panels b and c of Figure 4. The NiAs structure is the only outlier from these atomic packing trends, supporting its exclusion from the global fit. These quantities play an important role in the internal oscillation contribution to the free energy, as detailed in [Appendix D](#).

The best-fit polynomials for the Morse potential parameters are shown in Figure 5 in terms of the fractional deviation from the fitted values at CN=6. Panel (a) shows the systematic decrease of the equilibrium radius with increasing coordination, mirroring the Mg–Mg distance trend, in red solid and dashed lines. Also shown are the variation of the energy-well depth and width, in gray and blue lines, respectively. In Panel (b), the effect of these trends on the predicted energy wells is shown, highlighting that the lowest equilibrium energy occurs for CN=6, reflecting the strong stability of periclase. From this figure, we can also see that the minimum energy coordination state, given by the lowest energy curve at each distance, evolves upward with compression, revealing the primary driver for compression-induced coordination evolution in oxide liquids.

4.2. Determining Liquid Properties using CHaSM

Now that we can evaluate structural energies using the potentials obtained above, we apply CHaSM to determine average melt structure and thermodynamics. In this section, we demonstrate how to use the free energy minimization framework, introduced in Section 3.2, to calculate the thermodynamic properties of oxide liquids, specifically applying them to the MgO system.

We begin by representing a complex coordinated liquid in terms of a set of nearly-

Figure 5: Best-fit dependence of cluster potential parameters on coordination number, in terms of fractional deviations from their reference value, $\delta\theta_{\text{pot}} = \log_e \theta_{\text{pot}}(\text{CN}) - \log_e \theta_{\text{pot}}(6)$. Panel (a) shows the variation of the position, depth, and width parameters in red, gray, and blue lines, respectively. Also plotted are the cation separation distances of the MgO polymorphs (symbols defined in Figure 4) and the corresponding fitted trend, shown in the red-dashed line, as discussed in the text. Panel (b) displays the corresponding potential energy wells, color-coded by coordination state.

independent cation coordination states. The essential insight behind this procedure—that coordination state occupancies can be treated as internal order parameters that are varied to minimize the total free energy—follows from the work of Ghiorso (2004). In that investigation, the author calibrated a thermodynamic model for SiO_2 by empirically fitting observed coordination statistics from MD simulations of liquid and amorphous silica. The resulting model recovered evolving coordination populations, by modeling the energetic competition between volumetric work (akin to the structural energy) and the entropy of mixing. While this model is confined to pure silica and is limited by its need to train on liquid MD output, it demonstrates the explanatory power of the independent coordination-state assumption. Single-component liquids are thus

viewed as a set of ionic clusters whose behavior changes gradually with coordination. Heterogeneous interactions (e.g. between 4- and 5-coordinated Mg) are thus rather similar to homogeneous ones, and the proportion of heterogeneous interactions is limited by the peaked coordination distributions. Given coordination state independence, we are allowed to consider each state in isolation, greatly simplifying the calculation.

Using the variational method, we determine the optimal hard sphere size for each fixed-coordination liquid by separately minimizing its total free energy. Though coordination states are discretized, the structural energy of each state is not truly given by a single value as represented by this model, but rather a distribution of values reflecting continuous distortions of bonding polyhedra. Just as for crystal polymorphs, where fractional coordination numbers represent distortions from ideal bonding geometries, we approximate distorted states by considering non-integer values of the coordination number. This choice smooths over unphysical kinks in the energy surface that otherwise arise (a sampling frequency of 0.25 is sufficient for a converged result). Using standard optimization routines (available in MATLAB[®]) to minimize the free energy, we determine the set of coordination-specific free energy curves for 3000 K MgO shown in Figure 6(a). Panel (b) shows the same free energy curves with the minimum energy envelope subtracted off, drawing attention to the compression-induced increase of the preferred coordination state from ~ 4.5 at $30 \text{ \AA}^3$ to ~ 8 at $10 \text{ \AA}^3$.

Treating these fixed-coordination liquids as a set of non-interacting states, we use Boltzmann's factors to estimate the equilibrium population distribution:

$$p_i \propto \exp(-\Delta F_i/k_B T) \quad (11)$$

where ΔF_i is the free energy difference from the minimum, $k_B T$ is the thermal energy scale, and p_i is the population of the i^{th} coordination state³. By examining the energetic spread of coordination states relative to the thermal energy scale $k_B T$ (shown by the red-shaded region), we can roughly determine which states are well-populated, yielding a coordination spread of ± 1 at 3000 K.

³ This equation is defined in terms of free energies F_i , instead of the internal energies E_i , to account for entropy variations, because the coordination states are degenerate macrostates rather than true microstates.

Figure 6: Free energy compression curves for hypothetical fixed-coordination MgO melts at 3000 K, with cation coordination number ranging between 3 and 9; for visual clarity, only integer coordination states are color-coded (panel a). To emphasize the evolution of preferred coordination state with compression, the minimum energy envelope is removed in panel (b), showing steady increase in the dominant coordination state from 4 to 8 over the calculated volume range. The red shaded region indicates the thermal energy scale, $k_B T$, which determines the range of well populated coordination states about the dominant value (about ± 1).

400 The coordination population distributions for MgO at 3000 K, obtained by applying
 401 Equation (11) to the relative free energies, are shown in Figure 7a. Panel (b) shows the
 402 evolving median coordination state, with the 68% and 95% population intervals in the
 403 solid line, and dark and light gray bands, respectively, displaying the smooth upward
 404 trend of the average coordination number with compression. Also shown in red is the
 405 corresponding evolution at 7000 K, where higher temperatures broaden the population
 406 distributions and shift the peak to higher coordination numbers, reflecting the drive
 407 toward more compact liquid particles, as shown for the toy-model in Figure 1d.

408 We repeat this procedure over a grid of points in volume-temperature space, to
 409 obtain the coordination populations over a range of conditions. The total free en-

Figure 7: Evolution of the coordination populations for MgO melt at 3000 K. Panel (a) shows color-coded curves for the relative populations of each coordination state (with bins centered on integer values), and (b) shows the continuous evolution of coordination with compression, where the median, 68%, and 95% population intervals are indicated by the black line, dark gray, and light gray bands, respectively. For comparison, the median and 68% population bounds are also shown for 7000 K, in the solid and dashed red lines.

energy is given by a weighted average of the independent contributions from each coordination state combined with the free energy of mixing term from [Appendix A](#), $F_{\text{liq}} = \sum_i p_i F_i + F^{\text{mix}}$. Each equilibrium configuration is calculated in a few seconds, and the entire range of conditions is finely sampled in minutes.

To determine all of the thermodynamic properties of interest, we must represent these samples with a smooth free energy surface appropriate for calculating successive temperature and volume derivatives. We use a *log-EOS*, which is simply a Taylor expansion in logarithmic strain, defined as $\epsilon \equiv \log_e(V/V_r)$, where V_r is a convenient reference volume. Unlike other EOS forms, the log-EOS function retains a polynomial form even if the zero-pressure volume is not known a-priori, allowing basic polynomial

Figure 8: Derivative equation of state properties, pressure and entropy, for MgO melt. The main panel shows the pressure-volume isotherms color-coded by temperature, which agree well with first-principles results from [Karki et al. \(2006\)](#) at 3000 K and 7000 K, shown in the blue and red crosses, respectively. The inset figure displays the entropy-compression evolution, where the blue cross corresponds to the ambient pressure entropy of 10.5 per atom from [de Koker and Stixrude \(2009\)](#), which should be compared with the value of 9.8 indicated by the open circle. The reference volume of $V_{10}^{\text{ref}} = 20.2 \text{ \AA}^3$, defined at 10 GPa, accounts for a systematic scaling offset of the CHaSM results and should be compared to the first principles value of $22.5 \text{ \AA}^3$.

420 regression for inferring the coefficients of each free energy isotherm. We find that a 4th
 421 order expansion is fully sufficient to explain the variation to within the precision of the
 422 model. Finally, we capture the temperature dependence of the coefficients using spline
 423 interpolation. This straightforward method provides a complete description of the free
 424 energy surface that is thermodynamically consistent and smooth up to the highest-order
 425 derivatives of interest.

426 Given the full free energy surface for MgO melt, we obtain the isothermal pressure
 427 and entropy curves through differentiation shown in Figure 8. Also plotted in blue and

red crosses are the first principles calculated values from [Karki et al. \(2006\)](#) for MgO at 3000 K and 7000 K, respectively. CHaSM’s agreement with this simulation is quite remarkable, given the >4–5 orders of magnitude difference in computational resources for these methods. This comparison uses scaled volumes, as is common practice for theoretical calculations, since even first principles MD simulations produce systematic errors in reference volumes of ~6-13%, as estimated from the typical ~2 GPa empirical pressure correction ([Van de Walle and Ceder, 1999](#); [Oganov et al., 2001](#); [Stixrude and Karki, 2005](#)) applied to silicate melts with reference bulk moduli of ~15-30 GPa ([Jing and Karato, 2011](#)). Given the simplicity of CHaSM and the approximate nature of the cluster potentials utilized in this work, we are quite satisfied with a volumetric difference of ~9% for a reference pressure of 10 GPa. We can also see in the inset figure that the 3000 K ambient pressure entropy predicted by CHaSM matches the first principles value to within ~6% ([de Koker and Stixrude, 2009](#)). This level of agreement in terms of entropy stems from CHaSM’s accounting for the internal oscillations of each ionic cluster, in contrast to simpler hard sphere approaches that all drastically underestimate the entropy.

5. Understanding the Grüneisen Parameter Evolution of Liquids

As discussed in the introduction, the grüneisen parameter determines the slope of the adiabat, governing the thermal profiles in convecting systems (see Equation 1). Its thermodynamic definition is:

$$\gamma \equiv - \left. \frac{\partial \log_e T}{\partial \log_e V} \right|_S = \frac{\alpha K_T V}{C_V} \quad (12)$$

where α is the thermal expansion, K_T is the isothermal bulk modulus, and C_V is the heat capacity at constant volume. Using this equation, we evaluate the compression evolution of the grüneisen parameter for a set of isotherms for MgO melt, shown in Figure 9. The increase with compression, opposite that of solids, is nearly universal for liquids. The magnitude of the increase is in reasonable agreement with first principles calculations, though our values are systematically lower by ~0.1 to 0.2 ([de Koker and Stixrude, 2009](#)). We also find a substantial temperature dependence for γ , another

Figure 9: The thermodynamic grüneisen parameter (γ) of MgO melt, predicted by CHaSM, is plotted for a set of color-coded isotherms, displaying the universal increasing trend with compression for liquids. Also plotted are the mode grüneisen parameters at 3000 K for the ionic cluster and internal oscillator vibrations, shown in circles and triangles, respectively (determined using Equations 13 and 15). The weighted average of these two vibrational modes yields the total vibrational grüneisen parameter, shown in blue crosses, which provides an excellent match to the thermodynamic trend at 3000 K.

distinguishing general feature of liquids. CHaSM predicts that γ and temperature are positively correlated for MgO melt, while first principles investigation obtained a dependence of similar magnitude but opposite sign (de Koker and Stixrude, 2009). It is unclear, however, whether this disagreement is a result of the MD simulations themselves, or rather of the parametric modeling needed to predict $\gamma(V, T)$ from a limited set of MD simulation runs affected by statistical noise.

The widespread paradoxical γ -behavior of liquids was first remarked upon by Knopoff and Shapiro (1970), who observed that the grüneisen parameter of water increases consistently for volumetric compressions of up to 20%. They also found a strong positive correlation with temperature, much like our findings for MgO, in contrast to the near

465 temperature-independent behavior of solids. Since then, similar behavior has been
466 seen for a wide array of liquids, including: cryogenic Ar; organic solvents like pen-
467 tane, ethanol and methanol; metallic liquids like mercury; and a variety of silicates in
468 the CMASF compositional system (Brown et al., 1987; Amoros et al., 1988; Boehler
469 and Ramakrishnan, 1980; Asimow, 2012).

470 Observed for nearly every liquid type—including neutral atomic, molecular, metal-
471 lic, and partially ionic silicate liquids—the grüneisen behavior of liquids requires a gen-
472 eral explanation befitting its broad insensitivity to chemistry. From statistical physics,
473 it is easy to show that increasing γ is a natural outcome of the basic hard sphere model,
474 as noted by Jing and Karato (2011), resulting from the evolution of the packing frac-
475 tion η with increasing compression. Unfortunately, this result cannot be quantitatively
476 generalized to multi-component or highly compressed liquids.

477 Within the Earth science community, the currently favored explanation rests on an
478 analogy to the behavior of solid MgSiO_3 polymorphs, which individually show de-
479 creasing γ -trends, but between which there is a systematic upward shift with increas-
480 ing coordination number. Since a compressing liquid effectively samples ionic clusters
481 that are similar to increasingly higher pressure polymorphs, we might expect a corre-
482 sponding increasing trend in γ (Stixrude and Karki, 2005). Like the basic hard sphere
483 behavior, this cation coordination model revolves around structural evolution, but it
484 also fails to generalize since most non-oxide liquids do not undergo cation coordina-
485 tion evolution. Even for oxide or silicate melts, it does not provide testable quantitative
486 estimates, as it relies on a qualitative interpolation argument. This uncertainty is most
487 notable for molten silica with $\gamma = 0$ at ambient pressure (Asimow, 2012), in contrast
488 to its low-pressure solid polymorphs which show a wide-range of values of roughly
489 0, 0.3, and 0.6 for α -quartz, coesite, and β -quartz, respectively, despite all possessing
490 four-coordinated silica tetrahedra (Boehler, 1982; Hemley, 1987; Williams et al., 1993;
491 Welche et al., 1998).

492 To calibrate our intuition, we review the well-understood behavior of crystalline
493 solids where the entropy is dominated by atomic vibrations. The thermodynamic
494 grüneisen parameter (Equation 12) can be directly interpreted in terms of the volume-
495 dependence of the angular frequency ω of each vibrational mode in the crystal (Grüneisen,

496 1912, 1926):

$$\gamma_i = -\frac{\partial \log_e \omega_i}{\partial \log_e V} = -\frac{1}{2} \frac{V}{\omega_i^2} \frac{\partial \omega_i^2}{\partial V} \quad (13)$$

497 where γ_i is the mode-specific grüneisen parameter, and the total thermodynamic value
498 can be shown to be a weighted average of the individual mode contributions,

$$\gamma = \frac{\sum C_{V,i} \gamma_i}{\sum C_{V,i}} \quad (14)$$

499 with a weights equal to the mode-specific heat capacity, $C_{V,i}$ (e.g. Kieffer, 1976).

500 To better understand the vibrational definition of γ , we introduce an approximate
501 expression for the particle vibrational frequency, representing independent oscillation
502 of each particle about its average position:

$$m\omega^2 = \hat{k}_{\text{tot}} = \nabla^2 E_{\text{struc}} \approx \sum_j N_j \hat{k}_j \quad (15)$$

$$\hat{k}_j = \frac{1}{6} \left[E''_{\text{pot}}(r_j, \theta_{\text{pot}}) + \frac{2}{r_j} E'_{\text{pot}}(r_j, \theta_{\text{pot}}) \right]$$

503 where $\hat{k}_{\text{tot}}$ is the total restoring force constant of each particle and $\hat{k}_j$ represents the
504 contribution by interactions with the N_j particles occupying the j^{th} particle distance.
505 This expression is obtained by taking a second derivative of the structural energy with
506 respect to perturbations in particle position (see for example Roy et al., 1974) and also
507 forms the basis of the internal oscillator correction within CHaSM (see Appendix D).

508 This expression provides a crude representation of the shortest wavelength phonons
509 in a material, akin to the Einstein model, providing useful semi-quantitative insights for
510 solid materials. First, we can see that the temperature-independence of the grüneisen
511 parameter (e.g. Soga and Anderson, 1966) should arise for nearly-harmonic vibra-
512 tions, where the force constant is independent of amplitude, as assumed by the quasi-
513 harmonic model (e.g. Gale and Rohl, 2003). It is also well established from both
514 experiments and theory that γ always decreases with compression for solid phases
515 (e.g. McQueen and Marsh, 1960; Anderson, 1968; Roberts and Rupp, 1971; Boehler,
516 1982).

517 The first investigation to examine the application of these ideas to liquids, (Knopoff
518 and Shapiro, 1970), put forward its own simple semi-quantitative model, appealing to

519 the development of progressively larger solid-like clusters within the liquid as it is com-
520 pressed. The authors showed that for a 1D monatomic crystal, the growth of solid-like
521 clusters would generate the observed behavior as the quantity and value of vibrational
522 mode frequencies evolved with increasing cluster size. This explanation using local vi-
523 brations in a liquid is attractive due to its generality, but the over-simplified derivation
524 lacks quantitative predictive ability for real complex liquids.

525 In contrast to solids, where the average particle distances are defined uniquely by
526 the crystal structure and the volume, liquids contain typical particle separations corre-
527 sponding to successive shells of neighboring particles. The sizes and occupancies of
528 these neighboring shells evolve with compression, reflecting the development of short-
529 range order as expressed in the radial distribution function (see [Appendix D](#)). When
530 applied to liquids, this approximation becomes paradoxically more accurate, since the
531 long-wavelength phonons that it neglects are largely absent from liquid dynamics. Par-
532 ticle trajectories within a liquid are stochastic and complex, combining both oscillatory
533 and diffusive motions (e.g., [Angelani and Foffi, 2007](#); [Trachenko and Brazhkin, 2013](#)).
534 We therefore interpret Equation (15) as an approximate expression for the vibrational
535 component of motion experienced by each particle in response to interactions with the
536 time-averaged liquid structure surrounding it.

537 As CHaSM enables us to calculate the frequencies of these motions, we can directly
538 test whether the solid-derived theories for the grüneisen parameter can be extended to
539 liquids. We thus calculate the effective mode grüneisen parameters (Equation 13) for
540 CHaSM’s ionic-cluster and internal oscillator vibrations using the complete expres-
541 sions for vibrational frequencies in [Appendix D](#), as shown by the open symbols in
542 Figure 9. The internal oscillator vibration represents the independent relative motions
543 of the bonded Mg and O ions, and the cluster vibration represents the motions of each
544 coordinated ionic cluster relative to its environment (where bonded Mg and O ions
545 move roughly in-phase with one another). Using the standard heat capacity weighted
546 average, we combine these two contributions into the total vibrational grüneisen pa-
547 rameter, shown in the blue crosses, which yields an excellent match to the thermody-
548 namically determined values in the solid blue line. Unlike for nearly-harmonic solids,
549 the vibrational frequencies determined by CHaSM are functions of both volume and

550 temperature, $\omega(V, T)$, reflecting how thermally-induced structural evolution alters the
 551 average atomic environment, influencing restoring forces.

Determining the average vibrational γ value from the local vibrational modes within a liquid clearly yields a predictive quantitative model for its thermodynamic grüneisen parameter. Behavioral differences between liquids and solids can thus be understood by decomposing the possible sources of volume-dependence for atomic vibrations:

$$\begin{aligned}
 \frac{d\omega^2}{dV} \approx \frac{\partial}{\partial V} \left(\sum_j N_j \hat{k}_j \right) \approx & \quad \text{solids \& liquids} \\
 & + \underbrace{\sum_j N_j \frac{\partial \hat{k}_j}{\partial r_j} \left(\frac{dr_j}{dV} \right)}_{\text{bond length compression}} \bigg|_{\text{geom}} \\
 & \quad \text{liquids only} \\
 & + \underbrace{\sum_j N_j \frac{\partial \hat{k}_j}{\partial r_j} \left(\frac{dr_j}{dV} \right)}_{\text{short-range order development}} \bigg|_{\text{struc}} + \underbrace{\sum_j \frac{\partial N_j}{\partial V} \hat{k}_j + \sum_j N_j \frac{\partial \hat{k}_j}{\partial \theta_{\text{pot}}} \frac{d\theta_{\text{pot}}}{dV}}_{\text{environment-dependent pot interactions}}
 \end{aligned} \tag{16}$$

552 where the potential parameter vector is represented by θ_{pot} . We can understand the
 553 qualitatively different γ -behavior of liquids and solids, related to vibrations through
 554 Equation 13, by considering the expected volume-dependence of each term in this ex-
 555 pression.

556 In the case of solids, where atomic structures are constrained by symmetry, com-
 557 pression is accomplished predominately by bond-length reduction, represented by the
 558 first term in Equation (16). This leads to the normal solid-like compression behavior of
 559 decreasing γ , which is a direct consequence of the non-linear repulsive potential that
 560 dominates short-range interactions as demonstrated by [Anderson \(1968\)](#). Liquids, on
 561 the other hand, are able to dynamically adjust their structure in order to minimize free
 562 energy, compressing by a combination of structural relaxation, $(dr_j/dV)_{\text{struc}}$, and solid-
 563 like fixed-structure compression, $(dr_j/dV)_{\text{geom}}$. This corresponds directly in the hard
 564 sphere framework to an initial compression at fixed packing fraction—where the ratio
 565 of hard sphere volume to total volume is held constant—and then allowing the hard
 566 sphere size to expand to minimize total free energy. Due to short-range non-linear re-
 567 pulsive forces, the hard sphere size always grows during relaxation, reducing the large

568 repulsive energy cost of closely spaced particles.

569 As liquid packing fraction increases to better accommodate compression, short-
570 range order further develops, increasing the number of nearest neighbors, given by
571 dN_j/dV . The two short-range order terms in Equation (16) have competing effects on
572 the vibrational frequency, but the *exponential* drop (due to increasing nearest neighbor
573 distance, r_j) dominates over the *linear* rise (due to increasing shell occupancy, N_j). This
574 net frequency drop with compression provides a negative contribution to the grüneisen
575 parameter for liquids. The strength and duration of the effect are limited, however:
576 as the liquid is compressed, its packing fraction rises reflecting a more compact and
577 solid-like structure. The potential for further structural evolution is reduced, however,
578 as the contrast between liquid and solid diminishes.

579 The final term in the vibrational frequency reflects the dependence of pairwise inter-
580 actions on the local-environment. Within the CHaSM framework, this manifests as the
581 cation coordination dependence of the cluster potentials, $\theta_{\text{pot}}(\text{CN})$. The compression-
582 induced evolution of cation coordination state provides a crucial structural degree of
583 freedom that lowers the overall energy by significantly reducing the curvature of the
584 free-energy surface. This decrease in material stiffness lowers the compression trend of
585 the vibrational restoring force, thus providing a negative contribution to γ whose mag-
586 nitude falls with compression, similar to the short-range order contribution discussed
587 above. This similarity is perfectly natural, since the bonding coordination-dependence
588 of the cluster potentials is designed to capture the development of short-range order at
589 atomic-bonding length-scales.

590 Given the opposing effects of the geometric and structural contributions to the
591 grüneisen parameter, we can see that the liquid-like behavior of γ should be limited
592 to a material-specific compression range. Once the contrast between liquid and solid
593 structures is sufficiently small, the negative contribution of the liquid-specific terms can
594 no longer overwhelm the positive fixed-geometry term, and solid-like behavior will de-
595 velop. This implies that liquids with close-packed structures, like molten iron, cannot
596 access the necessary structural degrees of freedom and should thus display solid-like γ -
597 trends under all P-T conditions, as supported by the experimentally observed structure
598 (Shen et al., 2004) and theoretically calculated γ -trends of molten iron over a broad

range of pressures (Vocadlo et al., 2003). In contrast, the room temperature grüneisen parameter of mercury, also a metallic liquid, shows the usual increasing trend up to its freezing point (Boehler and Ramakrishnan, 1980), as it evolves from an initial self-coordination number of 6 at ambient pressure up to a close-packed structure near 12 at the freezing point (Kruh et al., 1963). We further expect that particularly open low density structures with low cation coordination numbers, such as liquid silica, should demonstrate markedly strong grüneisen parameter evolution, reflecting the large initial contrast between the liquid and solid structures. This matches the experimentally observed and theoretically calculated behavior of silica, which evolves from $\gamma = 0$ at ambient pressure to $\gamma \sim 1$ at two-fold compression (Asimow, 2012; de Koker and Stixrude, 2009).

This model thus provides a simple explanation of why increasing grüneisen parameter upon compression does not occur in solid structures, but should be generally present up to some threshold pressure for nearly all liquids. The ability of liquids to adjust their structures in order to minimize free energy is a generic consequence of the lack of long-range order present in all liquids, and so it is natural to expect such universal behavior. Similar to compression, thermally-driven structural evolution in liquids also affects the packing efficiency and so imposes an analogous temperature dependence to vibrational frequencies. We therefore expect that liquids should generally exhibit temperature dependence of the grüneisen parameter, as first observed by Knopoff and Shapiro (1970).

6. Discussion and Conclusions

We present a new simplified model for representing the structure and thermodynamics of oxide and silicate melts. The Coordinated **H**ard **S**phere **M**ixture (CHaSM) provides an extension to the standard hard sphere mixture model, which accounts for the evolution of local cation coordination number, a primary compression mechanism for oxide melts. Atoms in the liquid are represented as a set of neutrally-charged ionic clusters, each composed of a single cation surrounded by a shell of shared bonded oxygens. CHaSM is based on the principle of free energy minimization, where the

628 sizes and populations of the coordinated ionic clusters (represented by hard spheres),
 629 are directly predicted by the model as a function of volume and temperature. Unlike
 630 previous adaptations of hard sphere theory to silicate melts, CHaSM accounts for the
 631 internal oscillations of bonded ions and so is able to accurately predict thermodynamic
 632 properties related to entropy, making it uniquely suited to the exploration of high P-T
 633 melt properties such as grüneisen parameter evolution.

634 As a first application, we demonstrate how the CHaSM framework accurately pre-
 635 dictes the thermodynamic properties of MgO melt over a wide pressure-temperature
 636 range. Coordination-dependent interactions between clusters are described by poten-
 637 tials that are trained on data from solid polymorphs, which sample the energetics of
 638 structures over a wide range of coordination values. Using these potentials, CHaSM
 639 estimates coordination state evolution and equation of state properties that compare
 640 favorably with first principles calculations, despite the 4 to 5 order of magnitude dif-
 641 ference in computation time. As a statistical physics model, CHaSM does not suffer
 642 from the convergence issues that confront MD simulations and thus extends naturally to
 643 near-solidus temperatures, enabling future comparison with laboratory measurements
 644 at experimentally attainable temperatures.

645 Finally we present a simple new approach to understanding grüneisen parameter
 646 evolution characteristics common to nearly all liquids. By considering pairwise inter-
 647 actions, typical vibrational frequencies are determined from the average liquid structure
 648 of MgO for ionic clusters and the bonded ions that comprise them. Analysis of different
 649 contributions to the particle restoring force shows why compression-induced growth in
 650 the grüneisen parameter is such a universal feature of liquids, reflecting their ability to
 651 evolve toward more compact and solid-like structures upon compression. By focusing
 652 only on independent particle motions, this approximation neglects any role played by
 653 longer wavelength vibrations. The close match between our local vibrational model
 654 and the calculated thermodynamic grüneisen parameter from CHaSM indicates that,
 655 despite its simplicity, this model accurately captures most of the important physics.

656 The next challenge for CHaSM is extension to a broad geologically interesting
 657 chemical system. This can be achieved while improving accuracy up to moderate
 658 pressures ($\lesssim 30$ GPa) by implementing standard ionic potentials for modeling struc-

659 tural energies. Similar to our approach for MgO polymorphs in this investigation, we
 660 can identify coordination-dependent structural trends, like those in Figure 4, across a
 661 broad collection of minerals throughout a geologically relevant chemical system like
 662 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$. These trends in ionic pair distances reflect the in-
 663 fluence of cation coordination on the atomic packing geometry. By initially limiting
 664 investigation to moderate pressures and intermediate compositions, we can make use
 665 of existing ionic potentials, like those of Matsui (1994, 1996) and Guillot and Sator
 666 (2007), while avoiding the transferability limits of the potentials induced by significant
 667 coordination evolution. The approximations of CHaSM could also be directly tested
 668 against empirical MD simulations using the same ionic potentials. As discussed in
 669 Section 4.1, the CHaSM framework would also greatly benefit from the development
 670 of coordination-dependent ionic potentials, enabling significantly more accurate calcu-
 671 lations over broader ranges of chemistry and pressure. The training of such potentials
 672 should greatly expand the general reach of empirical atomic simulation techniques,
 673 though it is likely to require input from first-principles calculations on solid phases to
 674 constrain the greater number of free parameters.

675 Given that CHaSM provides a complete description of the free energy surface of
 676 the liquid, we will also be able to carry out melting curve calculations by combining it
 677 with the thermodynamic properties of the solid phases, allowing direct comparison with
 678 high-pressure melting experiments (e.g. Ohtani, 1983; Knittle et al., 1989; Boehler,
 679 2000; Ohtani, 2009; Andraut et al., 2011). The results of such an investigation will
 680 also be interesting to compare with the recent first-principles work on the MgO-SiO_2
 681 binary by de Koker et al. (2013).

682 As the CHaSM model is extended to a broad chemical system, we might also begin
 683 incorporating constraints from liquid data as well. This could be accomplished as a
 684 perturbation to the model parameters trained on solid structures, leading to solutions
 685 that are loosely guided by the solid-derived values, rather than fixed to them. Such an
 686 approach might eliminate the need for volumetric scaling, for instance, while improv-
 687 ing the zero-pressure entropy values. Though we expect these sorts of implementation
 688 details to evolve over time, we are confident that CHaSM provides the necessary frame-
 689 work to produce accurate predictions of melt thermodynamics, as it remains tied to a

690 simplified yet realistic physical picture of oxide and silicate melts.

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Appendix A. Generalized Hard Sphere Mixture

The complete set of expressions for the equation of state of a hard sphere mixture is presented in [Mansoori et al. \(1971\)](#). For completeness, we include these expressions here, which represent the total free energy for a hard sphere mixture as a sum of terms:

$$F^{\text{HS}} = F^{\text{gas}} + F^{\text{mix}} + \Delta F^{\text{HS}} \quad (\text{A.1})$$

where F^{gas} is the standard ideal gas contribution (see Equation A.2), F^{mix} is the entropic mixing contribution associated with random mixing of liquid particles (see Equation

895 A.3), and ΔF^{HS} is the adjustment to the ideal gas accounting for the finite volume
 896 occupied by liquid particles or ionic clusters (see Equation A.7).

897 The two ideal contributions are the ideal gas and ideal mixing terms. The free
 898 energy of an ideal gas is:

$$\begin{aligned} F^{\text{gas}} &= -k_B T \log_e Q^{\text{gas}} \\ \log_e Q^{\text{gas}} &= \log_e V + \frac{3}{2} \log_e \left(\frac{mk_B T}{2\pi} \right) + 1 \end{aligned} \quad (\text{A.2})$$

899 where k_B is Boltzmann's constant, Q^{gas} is the canonical partition function of the ideal
 900 gas, and the mass m and volume V are expressed in atomic units (e.g., proton masses
 901 and bohr³). The entropic mixing contribution to the free energy is:

$$\begin{aligned} F^{\text{mix}} &= -TS^{\text{mix}} \\ S^{\text{mix}} &= -k_B \sum_j^{\text{CN}} \bar{p}_j \log_e \bar{p}_j \end{aligned} \quad (\text{A.3})$$

902 This is just the ideal entropy of mixing for the set of integer coordination states, where
 903 $\bar{p}_j$ refers to the binned population of the j^{th} coordination state.

904 The analytic form of the hard sphere free energy correction, which accounts for the
 905 volume occupied by the hard spheres, is somewhat complex but easily evaluated. We
 906 begin with the expression for the packing fraction:

$$\eta_i \equiv \frac{V_i}{V} = p_i \frac{\pi}{6V} d_i^3 \quad \text{where} \quad \eta = \sum_i^{\text{HS}} \eta_i \quad (\text{A.4})$$

907 where p_i and d_i are the population and diameter of the i^{th} hard sphere, and η_i is its
 908 contribution to the total packing fraction. We must also define the compressibility
 909 factor Z , expressed as a function of the packing fraction:

$$Z = \frac{\hat{P}V}{k_B T} \approx [1 + \eta + \eta^2 - 3\eta(y_1 + y_2\eta) - \eta^3 y_3](1 - \eta)^{-3} \quad (\text{A.5})$$

910 where the needed additional relations are:

$$\begin{aligned}
y_1 &= \sum_{i=1} \sum_{j>i} \Delta_{ij} (d_i + d_j) (d_i d_j)^{-1/2} \\
y_2 &= \sum_{i=1} \sum_{j>i} \Delta_{ij} \sum_{k=1}^N \left(\frac{\eta_k}{\eta} \right) \frac{(d_i d_j)^{1/2}}{d_k} \\
y_3 &= \left[\sum_{i=1} \left(\frac{\eta_i}{\eta} \right)^{2/3} p_i^{1/3} \right]^3 \\
\Delta_{ij} &= \left[\frac{(\eta_i \eta_j)^{1/2}}{\eta} \right] \left[\frac{(d_i - d_j)^2}{d_i d_j} \right] (p_i p_j)^{1/2}
\end{aligned} \tag{A.6}$$

911 It is important to note that while symbol $\hat{P}$ has the units of pressure, it refers to the true
912 pressure only if we are considering the basic hard sphere model where the hard sphere
913 populations and sizes are fixed. Otherwise, hard sphere evolution introduces additional
914 pressure terms not accounted for in this expression.

915 These are all combined to express the contribution to the free energy of the liquid:

$$\begin{aligned}
\frac{\Delta F_{HS}}{k_B T} &= -\frac{3}{2} (1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)(1 - \eta)^{-1} + \\
&\quad \frac{3}{2} (1 - y_1 - y_2 - \frac{1}{3} y_3)(1 - \eta)^{-2} + (y_3 - 1) \log_e(1 - \eta)
\end{aligned} \tag{A.7}$$

916 By combining all of the expressions in this section through Equation (A.1), we can
917 evaluate the total contributions to the free energy from the standard hard sphere mix-
918 ture model. If these expressions are used within a variational scheme where evolving
919 hard sphere sizes and populations are determined by free energy minimization (e.g.,
920 Equation 8), then pressure and entropy must be determined numerically from the ther-
921 modynamic derivatives $P = -\partial F / \partial V_T$ and $S = -\partial F / \partial T_V$.

922 **Appendix B. Hard Spheres with Structural Perturbation**

923 The variational approach to hard spheres allows the incorporation of a structural
924 perturbation into the free energy expression, which captures the dependence of the
925 internal energy on the structure of the liquid. This variational method was developed
926 by [Mansoori and Canfield \(1969\)](#), and the relevant expressions are reproduced below.

927 In the standard variational Hard Sphere approach (Equation 3), the structural energy
928 contribution is approximated using the radial distribution function $g(r)$, together with

929 the pair potential $u(r)$:

$$E^{\text{struc}} = \frac{1}{2} \int_0^\infty \mathcal{P}(r)u(r)dr = 2\pi\rho \int_{d_{\text{HS}}}^\infty ru(r) \cdot rg(r)dr \quad (\text{B.1})$$

930 [Mansoori and Canfield \(1969\)](#) showed that the above integral for the structural
931 perturbation energy E^{struc} can be simplified using a Laplace transformation:

$$E^{\text{struc}} = 2\pi\rho \int_0^\infty U(s)G(s)ds \quad (\text{B.2})$$

932 where $G(s) = \mathcal{L}\{rg(r)\}$ and $U(s) = \mathcal{L}^{-1}\{ru(r)\}$ are the Laplace and inverse Laplace
933 transforms of the expressions involving the RDF and pair potential functions, respec-
934 tively. The expression for $G(s)$ has a simple functional form given by Percus-Yevick
935 theory (e.g. [Percus and Yevick, 1958](#); [Lebowitz, 1964](#); [Yuste et al., 1998](#)):

$$\begin{aligned} G(s) &= \frac{\exp(-sd_{\text{HS}})}{2\pi s^2} \frac{L^{(0)} + sL^{(1)}}{1 - 1/V \cdot [\phi_2(sd_{\text{HS}}) \cdot d_{\text{HS}}^3 L^{(0)} + \phi_1(sd_{\text{HS}}) \cdot d_{\text{HS}}^2 L^{(1)}]} \\ \phi_n(x) &\equiv x^{-(n+1)} \left(\sum_{m=0}^n \frac{(-x)^m}{m!} - \exp(-x) \right) \\ L^{(0)} &= 2\pi \frac{1 + 2\eta}{(1 - \eta)^2} \\ L^{(1)} &= 2\pi d_{\text{HS}} \frac{1 + \frac{1}{2}\eta}{(1 - \eta)^2} \end{aligned} \quad (\text{B.3})$$

936 Using this expression, we can take a numerical inverse Laplace transform of $G(s)$ to
937 calculate the radial distribution function. Even more efficient, however, is to take ad-
938 vantage of the form of the Morse potential in order to yield extremely rapid structural
939 energy calculations.

940 The Morse potential (Equation XXX) can be rewritten in the simple form

$$E_{\text{Morse}} = A_r \exp(-k_r r) - A_a \exp(-k_a r) \quad (\text{B.4})$$

941 where r and a subscripts refer to the contributions of the repulsive and attractive in-
942 teractions, respectively. The proper values of these parameters are determined as a
943 function of coordination number based on the cluster potential model reported in Ta-
944 ble 1. Using standard transform tables, we determine the inverse Laplace transform of
945 $rE_{\text{Morse}}(r)$:

$$U(s) = A_r \delta'(s - k_r) - A_a \delta'(s - k_a) \quad (\text{B.5})$$

946 where $\delta'(x - b)$ is the derivative delta function, which returns the derivative of the
 947 function it operates on evaluated at $x = b$. Thus we can now trivially compute the
 948 structural energy integral:

$$E^{\text{struc}} = 2\pi\rho \int_0^\infty [A_r\delta'(s-k_r) - A_a\delta'(s-k_a)]G(s)ds = 2\pi\rho[-A_rG'(k_r) + A_aG'(k_a)] \quad (\text{B.6})$$

949 This expression shows that the total structural energy can be determined for a Morse
 950 potential by evaluating $G(s)$, Equation B.3, at a few discrete points to calculate the nu-
 951 merical derivative, in place of a costly inverse Laplace transform followed by numerical
 952 integration.

953 **Appendix C. Bond Energy Model**

954 In an oxide or silicate melt, variations in bond distance and bond angle occur due to
 955 the vibrational motions of individual ions, which contribute to the overall free energy of
 956 the melt. We incorporate these entropic sources of free energy into the CHaSM model
 957 as the internal oscillator correction term, F^{osc} found in Equation (6), which accounts
 958 for the internal degrees of freedom available to the individual ions within each ionic
 959 cluster. In order to derive the value of F^{osc} , we must first obtain a reasonable description
 960 of the vibrational energy resulting from the individual ions. We therefore construct a
 961 bond energy model that accounts for variations in internal energy due to Mg-O bond
 962 length changes.

963 In this section, we derive a structural energy description of MgO in terms of its
 964 bonding characteristics, by fitting the energy volume curves of the MgO polymorphs
 965 with a coordination-dependent bond potential. We use the basic Born ionic potential
 966 form:

$$E_{\text{bond}} = E_R - E_{\text{coul}} = \text{CN} \cdot A_r^{\text{bond}} \left(\frac{d_{\text{bond}}}{a_0} \right)^{-n_r} - E_{\text{coul}} + \Delta E_0 \quad (\text{C.1})$$

967 where CN is the cation coordination number, n_r is repulsive exponent, A_r^{bond} scales the
 968 strength of the repulsive interaction, and d_{bond} is the Mg-O bond length, scaled by the
 969 Bohr radius $a_0 = 0.529\text{\AA}$, and ΔE_0 is an arbitrary energy offset parameter that is shared
 970 by all polymorphs. For crystalline solids, the Coulomb energy contribution is readily

Table C.2: Best-fit Coordination-Dependent Bond-Energy Potential for MgO

θ_{bond}	k_2	k_1	k_0
$\log_e A_r^{\text{bond}}$	+0.0398	+0.1345	+6.8563
n_r	+0.0219	+0.1456	+4.5055

971 evaluated using the Madelung lattice energy

$$E_{\text{coul}} = \frac{q^2 M}{d_{\text{bond}}/a_0} \quad (\text{C.2})$$

972 where $q = 2$ is the ionic charge, and M is the Madelung constant, which takes typical
 973 values from 1 to 1.8, depending on coordination and the detailed structure of the solid
 974 (Hoppe, 1966).

975 We fit the bond-potential model to the MgO polymorph data, assuming that the
 976 parameter values $\theta_{\text{bond}} = (\log_e A_r^{\text{bond}}, n_r)$ depend quadratically on coordination number

$$\theta_{\text{bond}} = k_2 \Delta \text{CN}^2 + k_1 \Delta \text{CN} + k_0 \quad (\text{C.3})$$

978 where $\Delta \text{CN} = \text{CN} - 6$. The quality of the resulting fit is similar to that of the cluster
 979 potential model, with best-fit values given in Table C.2⁴.

980 Appendix D. Vibrational Motions

981 To directly connect the hard sphere model to the atomic structure of oxide melts,
 982 we account not only for the configurational entropy contribution to the free energy, but
 983 also the added vibrational component due to the individual ions. This free energy cor-
 984 rection is represented by the internal oscillation term, F^{osc} , in the CHaSM free energy
 985 expression (Equation 6). To derive the expression for this term, we must first obtain
 986 the vibrational frequencies of the cluster and bond-energy potential models.

⁴Though the bond potential form is similar to the classic Born-Landé approximation for lattice energy, the parameter values differ due to the introduction of ΔE_0 , which allows us to better represent compressibilities and vibrational properties, rather than absolute lattice energies.

We rely on the approximate expression for restoring force-constants given in Equation (15), derived by taking a second derivative of the structural energy with respect to displacements of the particle from equilibrium, where the sum is replaced by an integral to better reflect liquid structure:

$$\hat{k}_{\text{MgO}^{[\text{CN}]}} = m_{\text{MgO}} \cdot \omega_{\text{MgO}^{[\text{CN}]}}^2 \approx \frac{4\pi}{V} \int_{d_{\text{HS}}}^{\infty} r \hat{k}_{[\text{CN}]}(r) \cdot r g_{[\text{CN}]}(r) dr \quad (\text{D.1})$$

$$\hat{k}_{[\text{CN}]}(r) = \frac{1}{6} \left[E''_{\text{pot}}(r, \text{CN}) + \frac{2}{r} E'_{\text{pot}}(r, \text{CN}) \right]$$

where $\hat{k}_{\text{MgO}^{[\text{CN}]}}$ is the total effective restoring force constant acting on ionic cluster particles with cation coordination of CN, $\hat{k}_{[\text{CN}]}(r)$ is the contribution to the restoring force due to interactions at a distance r , and $E_{\text{pot}}(r, \text{CN})$ defines the coordination-dependent cluster potential energy interaction. This expression estimates a representative restoring force constant and frequency for individual ionic clusters, akin to the Einstein model, and is thus incapable of representing true phonon modes involving many particles. In this calculation, the local environment of each particle, given by the RDF $g_{[\text{CN}]}(r)$, is held fixed and is thus assumed uncorrelated with the particle vibration. Despite these approximations, this expression is nevertheless useful for obtaining a rough estimate of the oscillatory motions within the liquid, and is in fact considerably more accurate for liquids than it is for solids, since the long-wavelength phonon modes that are neglected do not play an important role in liquid energetics due to the lack of long-range order.

We can simplify this expression for the Morse cluster potential using the same Laplace transform approach used in Section Appendix B, taking the inverse Laplace transform of the $r\hat{k}(r)$ term, yielding:

$$\hat{k}_{\text{MgO}^{[\text{CN}]}} = \frac{2\pi}{3} \rho d_{\text{HS}}^3 \left\{ \int_0^{\infty} [-k_r^2 A_r \delta'(s - k_r) + k_a^2 A_a \delta'(s - k_a)] \cdot G(s) ds \right. \\ \left. - \frac{1}{d_{\text{HS}}} \int_0^{\infty} [+k_r A_r \delta(s - k_r) - k_a A_a \delta(s - k_a)] \cdot G(s) ds \right\}$$

$$\hat{k}_{\text{MgO}^{[\text{CN}]}} = \frac{2\pi}{3} \rho d_{\text{HS}}^3 \left\{ -k_r^2 A_r G'(k_r) + k_a^2 A_a G'(k_a) - \frac{k_r}{d_{\text{HS}}} A_r G(k_r) + \frac{k_a}{d_{\text{HS}}} A_a G(k_a) \right\} \quad (\text{D.2})$$

where the simplified Morse potential parameters (A_r, k_r, A_a, k_a) are defined by Equation B.4, and $G(s)$ is the Laplace transform of the hard sphere RDF, given by Equation

1007 (B.3). This expression is rapidly evaluated just as the structural energy given by Equa-
 1008 tion (B.6).

1009 Finally, we must also determine the restoring force constant for the bond energy
 1010 model, which describes the vibrations of individual ions in response to bond stretch-
 1011 ing. When considering displacements of individual ions, we use the bond energy equa-
 1012 tion (C.1), and consider the total Coulombic attraction of each of the coordinated ions
 1013 $|E_{\text{coul}}| = \text{CN} \cdot q^2/(r/a_0)$, forgoing the use of the Madelung constant since we neglect
 1014 such longer-range interactions for the disordered liquid (and they contribute much less
 1015 to the curvature anyway). Since the bond energy model relies only on directly bonded
 1016 ions, we can use a simplified discrete form of the restoring force equation:

$$\hat{k}_{\text{bond}} = \frac{1}{6} \left[E''_{\text{bond}}(r) + \frac{2}{r} E'_{\text{bond}}(r) \right]_{r=d_{\text{bond}}} \quad (\text{D.3})$$

1017 Since the form of E_{bond} is just a simple polynomial in $1/r$, evaluation of this expression
 1018 is trivial using the coordination dependent bond energy parameters given in Table C.2.
 1019 Though this expression neglects longer-range interactions beyond bonded neighbors,
 1020 this approximation is not unreasonable for liquids, and thus should provide a decent
 1021 first-order estimate of the vibrational properties of the individual ions.

1022 Appendix E. Internal Oscillation Correction

1023 Up to this point, we have presented two alternate models for the oxide melt sys-
 1024 tem, one in terms of ionic clusters and the other using bond energies (Appendix B-
 1025 Appendix D). The clear advantage of the ionic cluster model is that it enables the use
 1026 of hard sphere theory to represent liquid structure and configurational entropy, but has
 1027 the downside of not accounting for the independent motions of the ions within each
 1028 cluster. To overcome this issue, we introduce an additional internal oscillator term,
 1029 F^{osc} , which represents the missing part of the vibrational free energy. To derive the
 1030 expression for F^{osc} , we begin with the quasi-harmonic expression for vibrational free
 1031 energy:

$$F^{\text{qha}} = \sum_i \left\{ \frac{1}{2} \hbar \omega_i + k_B T \log_e \left[1 - \exp \left(-\frac{\hbar \omega_i}{k_B T} \right) \right] \right\} \quad (\text{E.1})$$

1032 where ω_i is the frequency of the i^{th} vibrational mode. This expression simplifies in the
 1033 high temperature limit to:

$$F_i^{\text{vib}} \approx 3k_B T \log_e \left(\frac{\hbar \omega_i}{k_B T} \right) \quad (\text{E.2})$$

1034 where the factor of 3 reflects the three independent oscillation directions. The vi-
 1035 brational frequency is simply determined from the restoring force constant $\hat{k}$ and the
 1036 particle mass m , given by $\omega = \sqrt{\hat{k}/m}$.

1037 We can now compare the total approximate vibrational free energy (using Equation
 1038 E.2) for the two alternative vibrational models of the system:

$$\begin{aligned} \frac{F_{\text{Tot}}^{\text{vib}}}{3k_B T} &\approx \frac{1}{2} \log_e \left(\frac{\hat{k}_{\text{bond}}}{m_{\text{Mg}}} \right) + \frac{1}{2} \log_e \left(\frac{\hat{k}_{\text{bond}}}{m_{\text{O}}} \right) + \log_e \left(\frac{\hbar}{k_B T} \right) && \text{Bond Energy} \\ &\approx \frac{1}{2} \log_e \left(\frac{\hat{k}_{\text{MgO}^{[\text{CN}]}}}{m_{\text{MgO}}} \right) + \frac{1}{2} \log_e \left(\frac{\hat{k}_{\text{osc}}}{m_{\text{osc}}} \right) + \log_e \left(\frac{\hbar}{k_B T} \right) && \text{Ionic Cluster} \end{aligned} \quad (\text{E.3})$$

1039 where the first line expresses the individual atomic vibrations using the bond-energy
 1040 model, and the second line provides the CHaSM-derived free energy in terms of the
 1041 cluster vibrations and the effective internal oscillations. The restoring force constants
 1042 $\hat{k}_{\text{bond}}$ and $\hat{k}_{\text{MgO}^{[\text{CN}]}}$ are given by Equations (D.3) and (D.2), and thus we can solve for
 1043 internal oscillator character characteristics:

$$\begin{aligned} \hat{k}_{\text{osc}} &= \hat{k}_{\text{bond}}^2 / \hat{k}_{\text{MgO}^{[\text{CN}]}} \quad , \quad m_{\text{osc}} = m_{\text{Mg}} m_{\text{O}} / m_{\text{MgO}}, \\ \omega_{\text{osc}} &= \sqrt{\hat{k}_{\text{osc}} / m_{\text{osc}}} \end{aligned} \quad (\text{E.4})$$

1044 where the internal oscillator mass and force constant both have a similar form, and
 1045 the mass is simply the reduced mass of the ionic pair. Finally, we can evaluate the
 1046 quasi-harmonic model for a three-dimensional oscillator with frequency ω_{osc} :

$$F^{\text{osc}} = \frac{3}{2} \hbar \omega_{\text{osc}} + 3k_B T \log_e \left[1 - \exp \left(-\frac{\hbar \omega_{\text{osc}}}{k_B T} \right) \right] \quad (\text{E.5})$$

1047 By combining this expression for F^{osc} with those for the structural energy E^{struc} (Equa-
 1048 tion B.6) and the hard sphere free energy F^{HS} (Equation A.1), we have all of the pieces
 1049 needed to evaluate the CHaSM free energy model.

1050 Appendix F. Fractional Coordination Numbers and Bond Lengths

1051 For non-ideal or distorted structures, the consideration of fractional coordination
 1052 numbers can be useful in examining geometric trends with coordination environment.
 1053 Furthermore, the calculation of average ion-pair distances like bond lengths requires a
 1054 clear understanding of how to weight neighboring ions that occupy a range of distances.
 1055 This topic was examined in detail by Hoppe (1979), who used an exponential averaging
 1056 scheme to give greater weight to closer neighbors in determining effective coordination
 1057 numbers and average bond lengths. In this work, we make use of a more recent alterna-
 1058 tive weighting scheme, the Solid Angle Nearest Neighbor (SANN) method (van Meel
 1059 et al., 2012), which provides geometrically intuitive estimates that better reflect the
 1060 differences between the structures examined in this study.

1061 The SANN method identifies the relative importance of neighboring atoms as pro-
 1062 portional to the apparent solid angle, Ω_i , they present to the central atom:

$$\Omega_i = 2\pi[1 - \cos \theta_i] = 2\pi(1 - r_i/R) \quad (\text{F.1})$$

1063 where the set of neighboring atoms are considered to lie within a neighborhood shell
 1064 of radius R , and r_i is the distance to the i^{th} neighbor. The size of the neighborhood is
 1065 determined by requiring that the total solid angle of all m neighbors is complete, with
 1066 $4\pi = \sum_i^m \Omega_i$. The neighborhood shell radius can thus be determined with:

$$\left(R = \sum_i^m \frac{r_i}{(m-2)} \right) < r_{m+1} \quad (\text{F.2})$$

1067 where the number of neighbors m is increased until the inequality criterion is met.

1068 Extending this procedure from van Meel et al. (2012), we define the coordination
 1069 weight of each neighbor as the solid angle relative to that of the closest neighbor:

$$\text{CN}_{\text{SA}} = \sum_i^m w_i \quad \text{with} \quad w_i = \frac{\Omega_i}{\Omega_1} = \frac{1 - r_i/R}{1 - r_1/R} \quad (\text{F.3})$$

1070 where the total coordination number is just the sum of the weights. This definition is
 1071 trivial to calculate, parameter free, and yields the intuitive result that the coordination
 1072 weight for the nearest neighbor is defined to be one. Using this coordination defini-
 1073 tion based on solid angles, we recover the expected values for ideal structures as well

1074 as finding smooth systematic behavior for the set of progressively more coordinated
1075 structures of MgO. We can also use this coordination weighting factor to determine
1076 other quantities of interest through weighted averaging, like the average bond length
1077 $\langle d_{\text{bond}} \rangle = \sum_i w_i r_{\text{Mg-O},i}$ or cation separation distance $\langle d_{\text{Mg-Mg}} \rangle = \sum_i w_i d_{\text{Mg-Mg},i}$. This
1078 minor extension of the Solid Angle Nearest Neighbor method provides a simple and
1079 powerful tool for characterizing local atomic structure.