A self-consistent optimization of multicomponent solution properties: *ab initio* molecular dynamic simulations and the MgO-SiO₂ miscibility gap under pressure

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ABSTRACT

We propose a new approach to parameterizing the Gibbs energy of a multicomponent solution as a function of temperature, pressure and composition. It uses the quasichemical model in the second nearest neighbour approximation and considers both a polynomial representation (for low pressure) and an exponential decay representation (for moderate-to-high pressure) of the excess molar volume v^{xs} to extend thermodynamic behaviour to elevated pressure. This approach differs from previous configuration-independent regular or associated solution-type models of multicomponent silicate liquids at elevated pressure and can account for any structural or short-range order data that may be available. A simultaneous least squares fit of the molar volume and the molar enthalpy of mixing data obtained from First Principles Molecular Dynamics (FPMD) simulations at various pressures enables complete parameterization of the excess thermodynamic properties of the solution. Together with consistently optimized properties of coexisting solids, this enables prediction of pressure-temperature-composition phase diagrams associated with melting. Although the method is extensible to natural multicomponent systems, we apply the procedure as a first test case to the important planetary model system MgO-SiO₂ using FPMD data found in the literature. One key result of this optimization, which depends only on the derived excess properties of the liquid phase, is that the consolute temperature of the SiO₂-rich miscibility gap is predicted to decrease with increasing pressure. This appears to be in

disagreement with available experimental constraints and suggests possible thermodynamic inconsistency between FPMD data and experimental phase equilibrium data in the 0-5 GPa pressure range. We propose a new thermodynamic consistency criterion relating the signs of v^{xs} and other excess properties and discuss the need for precise calculations of derivatives of excess properties. Finally, the potential reappearance of the miscibility gap in the MgO-SiO₂ system above 5 GPa is discussed in light of this work.

I. Introduction

Our ability to describe the range of evolutionary pathways for terrestrial planets and to identify, through interpretation of available data, the particular pathway that the Earth followed depends on our understanding of the thermo-physical properties of Earth materials subjected to a wide range of conditions. In particular, multi-component liquid and solid solutions of oxides, metals and silicates are complex phases whose behavior at elevated pressure (P) and temperature (T) can, at best, be characterized experimentally only at sparsely sampled compositions and (P , T) points. This is one reason that there has been a historical divide between the relatively coarse, configuration-independent models of liquid solutions adopted in geochemistry — where high-pressure experimental constraints are few and the refined (Ghiorso and Sack, 1995; Bottinga and Weill, 1970), parameter-rich, configuration-dependent models preferred in ambient pressure materials science — where data are densely sampled and abundant (Pelton et al., 2000). The continuing advances in numerical tools such as First Principles Molecular Dynamics (FPMD) simulations, though, should eventually provide the densely sampled data on both macroscopic and microscopic properties needed to make progress in multicomponent solution models for high-pressure geochemistry. Applying such simulations, however, often requires derived results obtained by fitting or interpolating the simulation data. The accuracy of the fitting and interpolation method and the accuracy of the simulations themselves then both contribute to uncertainties in this approach. It is our purpose in this contribution to introduce a fully self-consistent scheme for interpolation of multi-component FPMD results extending to high pressure and to discuss the advantages of this approach compared to previous methods. We then attempt a first test case by applying it to the only internally consistent set of FPMD calculations of a geochemically important model system of which we are aware, the MgO-SiO₂ simulation data of de Koker *et al.* (2013). We consider the differences between the inferences drawn from our new

interpolation and the interpolation scheme of de Koker *et al.* (2013); test whether the resulting phase diagrams match available experimental constraints; and speculate whether the disagreements might arise from the experiments, the simulations, or the interpolation schemes.

The particular feature and system that we choose to focus on is the asymmetrical equilibrium miscibility gap in the liquid phase of the MgO-SiO₂ binary system. This binary is both an essential step towards a full understanding of the mantles of terrestrial planets, as these are the two major oxides that dominate the overall compositions, and an important test case of the capabilities of the method, because a comprehensive set of simulations have already been done (de Koker *et al.*, 2013) and substantial experimental data are available to constrain some aspects of the phase diagram and to test the prediction of other aspects. The miscibility gap was originally measured by Ol'shanskii (1951) and Hageman and Oonk (1986) and more recently by Hudon *et al.* (2004, 2005). The miscibility gap is a useful feature to focus on because its accurate prediction provides a very sensitive test of the ability of any modeling method to capture the compositional dependence of the excess Gibbs energy of the liquid relative to the pure end members. By 5 GPa, the rising liquidus surface overtakes the miscibility gap and it disappears from the equilibrium phase diagram, as found experimentally by Dalton and Presnall (1997). The flat shape and upwards concavity of the SiO₂ liquidus in this region is, however, a clear indication that the repulsive energetic tendency of the melt is still present under these equilibrium conditions and suggests the consolute point is not far below the liquidus. The question that arises is whether the miscibility gap may reappear at higher pressure. If it does, it implies that non-ideal mixing relations persist or even increase with increasing pressure. Such behaviour might be surprising, since immiscibility is often associated with mixing of unlike species and, with increasing pressure, the SiO₂ component in silicate liquids shifts from four-coordinated, network-forming behaviour towards six-coordinated structures nominally more similar to those adopted by the MgO component. While actual formation of liquids silicic enough to encounter this miscibility gap (or its multicomponent extension) in the Earth is speculative, we feel that examination of the MgO-SiO₂ miscibility gap provides basic insight into the energetics of liquid solutions, the relationship between microstructure and macroscopic thermodynamics, and the internal consistency of various modeling and fitting approaches. In this work we refrain from presenting complete predicted phase diagrams at high pressure that depend

on the assessment of high-pressure solid phases as well as the liquid solution, in order to focus our discussion on the accuracy of the liquid solution model itself.

As pointed out by de Koker *et al.* (2013), FPMD simulations can allow the definition of the Gibbs energy of geologically important multicomponent solutions for a large range of pressure and temperature, but this requires a statistical analysis and post-treatment of the evolution of internal energy and pressure data obtained in different thermodynamic ensembles (canonical ensemble, micro-canonical ensemble, etc.). We emphasize that the miscibility gap, in particular, is sensitive to the excess Gibbs energy of the solution relative to the end members, and so it is important to focus on how this excess quantity is derived. To model MgO-SiO₂ binary liquids, de Koker *et al.* (2013) proceeded through several steps. (a) They carried out canonical ensemble (NVT) FPMD simulations at several discretely sampled compositions, temperatures, and volumes. (b) They fit the simulation results for each discrete melt composition to a self-consistent formulation of the Helmholtz free energy involving ideal gas, excess, and electronic contributions (de Koker and Stixrude, 2009) in which the excess term is a polynomial expansion in dimensionless temperature and in a volume parameter akin to finite-strain (Davies, 1973), followed by a Legendre transform to assess the Gibbs energy function $G(P,T)$ of each discrete melt composition. Finally (c), they obtained the composition-dependent function $G(P,T,X)$, the excess properties of the liquid solution, and computed phase diagrams by interpolating empirically among the Gibbs energy functions of each composition using an asymmetric regular solution model and by incorporating models of the solid phases and constraints from the 1 atm phase diagram.

(a) Supercomputers are still limited in the number of FPMD simulations which can be done in order to generate, within a reasonable amount of time, a useful set of thermo-physical data. For that reason, simulations belonging to the canonical ensemble (NVT) are most often used for exploring the thermodynamic behaviour of solutions, rather than more laborious simulations performed in the isothermal-isobaric (NPT) ensemble. In this context, it is important to point out the differences in precision of predictions between those first-order properties that are direct simulation outputs — such as the internal energy, the equilibrium volume, the equilibrium pressure and the equilibrium temperature — and second order properties that are derived from interpolation among these direct simulation outputs. This category includes both

properties defined at constant composition — such as the thermal expansion coefficient, the bulk modulus, the Grüneisen parameter, etc. — and functions of composition such as chemical potential, configurational entropy, excess Gibbs energy, etc.

(b) The direct evaluation of second order thermo-physical parameters from finite differences, statistical fluctuations, or thermodynamic integration of MD simulations is typically subject to large errors due to the technical limitations of simulation time and statistical sampling of the simulations. Hence, in the work of de Koker *et al.* (2013), second order thermo-physical properties at fixed composition are calculated from Maxwell relations applied to a Helmholtz energy model parameterized for each studied composition using internal energy and pressure results. This strategy ensures that all thermo-physical properties are self-consistent for each specific composition.

(c) Compositional systematics of the binary system are obtained by de Koker *et al.* (2013) by then interpolating among the self-consistent Gibbs energy functions fitted to simulation data at each composition. But this approach does not guarantee that the resulting excess properties (referred to pure liquid SiO₂ and MgO) are behaving self-consistently if, for example, different expansion orders are used for different compositions in the system. The question of whether or not the miscibility gap reappears at high pressures, in particular, addresses the precise definition of the excess thermodynamic properties of the melt, not the absolute values of its thermodynamic functions. In this context, the self-consistent definition of compositional derivatives is paramount in predicting the phase diagram.

In this paper, we present a new procedure for optimizing the molar enthalpy of mixing and molar volume data obtained from FPMD simulations at different pressures. This results in a complete set of fully coherent thermo-physical properties of the binary system using classical thermodynamics. The modified quasichemical model, in the second nearest neighbour approximation proposed by Pelton and Blander (1986) and presented in section II of this work, is used to define the thermodynamic properties at 0 GPa as in previous work (Hudon *et al.*, 2005; Wu *et al.*, 1993). Excess thermo-physical properties at higher pressures are predicted by integrating the equation defining the excess volume v^{xs} of the considered single phase. This procedure is applied to the MgO-SiO₂ system using the NVT-FPMD simulation data presented by de Koker *et al.* (2013), and certain features of the phase diagram (in particular, the pressure-

temperature-composition evolution of the miscibility gap) is predicted. The result appears inconsistent with experimental phase diagrams and this may point to shortcomings of current-generation FPMD simulations themselves as a basis for constructing a thermodynamic model. The possible origins of such inconsistency are beyond the scope of the current work. We limit ourselves here to recommending better sampling techniques for future FPMD studies of silicate melts in order to ensure that 1) the partition function at high temperature and high pressure is adequately sampled, 2) the thermo-physical properties obtained from these simulations reflect their true equilibrium behaviour, and 3) the functional form of the excess volume reflects a fundamental understanding of the link between internal energy, structure and volume.

The present work is organized as follows: the classical thermodynamic description of the thermo-physical behaviour of multicomponent liquid solutions is presented in section II. Approaches used to represent v^{xs} as a function of T , P and X are presented in section III. The thermodynamic model parameterization procedure for the MgO-SiO₂ liquid solution at P_0 is explained in section IV. Results of the parameterization of v^{xs} for the MgO-SiO₂ binary system using different approaches and the resulting derived thermo-physical excess properties are given in section V and section VI respectively. The predicted MgO-SiO₂ phase diagram in the SiO₂-rich region for different pressures is presented in section VII. We close with some perspectives in section VIII and conclusions in section IX.

II. Classical thermodynamic description of the thermo-physical properties of multicomponent liquid solutions

We summarize here (more detail is given in Appendix 1) the basis of a thermodynamic model for mixing in multicomponent liquid solutions that explicitly takes account of short-range atomic ordering and its extension to high pressure. Such a model requires definition of the Gibbs energy of mixing as a function of configuration and composition, a correct formulation of the configurational entropy, and a formulation of the excess volume. Together these enable determination of the configuration parameters by Gibbs energy minimization. We discuss each element in turn.

II-A The modified quasichemical model in the second nearest neighbour approximation

The modified quasichemical model in the second nearest neighbour approximation was presented in detail by Pelton and Blander (1986). For silicate melts, it involves the definition of a cation second nearest neighbour quasichemical reaction. For MgO-SiO₂, the following reaction is defined:

The variation of the molar Gibbs energy of the quasichemical model reaction $\Delta g_{\text{Si-Mg}}^{\text{QC}}$ was originally expressed as a polynomial in the component equivalent fractions and temperature T :

$$\Delta g_{\text{Si-Mg}}^{\text{QC}} = \sum_{i+j \geq 0} (\omega_{ij} + \eta_{ij} T) Y_{\text{SiO}_2}^i Y_{\text{MgO}}^j \quad (2)$$

Pelton *et al.* (2000) later introduced excess parameters of this quasichemical reaction that can be a function of pair fractions. The general definition of Y_i , the equivalent pair fraction of species i , is:

$$Y_i = \frac{z_i \cdot X_i}{\sum_{j=1}^s z_j \cdot X_j} \quad (3)$$

where X_i is the molar fraction of the i^{th} species in the melt. An equivalent partial coordination number for each species, z_i , is introduced in the thermodynamic model to modify the position of the minimum in the molar Gibbs energy of mixing function as explained by Pelton and Blander (1986). The partial coordination numbers define the total coordination number of the solution $z_{\text{tot.}}$:

$$z_{\text{tot.}} = \sum_{i=1}^s z_i \cdot X_i \quad (4)$$

The number of moles of second nearest neighbour pairs i - j , n_{i-j} , is related to the number of moles of each system species via the following mass balance:

$$z_i \cdot n_i = 2n_{i-i} + \sum_{j \neq i}^s n_{i-j} \quad (5)$$

II-B The configurational entropy of mixing

In this work, the molar configurational entropy of mixing of the modified quasichemical model in the second nearest neighbour approximation, $\Delta s^{QC,config.}$, is used:

$$\Delta s^{QC,config.} = -R \cdot \left[\sum_{i=1}^s X_i \ln(X_i) + \frac{z_{tot.}}{2} \left[\sum_{i=1}^s X_{ii} \ln\left(\frac{X_{ii}}{Y_i^2}\right) + \sum_{j>i}^s \sum_{i=1}^s X_{ij} \ln\left(\frac{X_{ij}}{2 \cdot Y_i Y_j}\right) \right] \right] \quad (6)$$

This model (Pelton *et al.*, 2000) involves the introduction of second nearest neighbour pair fractions X_{ij} . Although more recent modifications have been made to this model (Pelton *et al.*, 2000) especially for the definition of $z_{tot.}$ as a function of the chemical composition, we decided to use this original model for comparison with previous similar thermodynamic assessments (Hudon *et al.*, 2004, 2005; Wu *et al.*, 1993). We emphasize the critical advantage of the quasichemical method, as compared to the regular solution or associated solution approach commonly adopted in geochemical solution modeling: that the explicit consideration of microscopic order in the quasichemical approach makes the configurational entropy internally consistent with the excess enthalpy of the solution.

II-C Total Gibbs energy of mixing at ambient pressure

With all the variables of this model properly presented, one can define the total Gibbs energy of mixing for the SiO₂-MgO binary system at ambient pressure:

$$\Delta G^{QC,mix.}(T, P_0, \underline{X}) = -T \left(n_{tot.} \cdot \Delta s^{QC,config.} \right) + \frac{n_{Si-Mg}}{2} \Delta g_{Si-Mg}^{QC} \quad (7)$$

where the chemical composition vector is defined as $\underline{X} = [X_1, X_2, \dots, X_s]$. The total Gibbs energy of the solution is obtained by minimizing eq. 7 constrained by the mass balances presented previously. The equilibrium abundance of each pair is governed by eq. 7: a large and negative value for Δg_{Si-Mg}^{QC} will favor the presence of Mg-Si pairs in the melts at the expense of Mg-Mg and Si-Si pairs, while a large and positive value will favor unmixing, i.e. the formation of Mg-Mg and Si-Si pairs. If $\Delta g_{Si-Mg}^{QC} = 0$, no pairs are favored and the solution is said to be ideal. This thermodynamic model is therefore an implicit function of the pair fractions. If pressure

dependent terms are added to eq. 2 as proposed in the simplified approach of Robelin *et al.* (2007) to define density of molten salts, then the model is also an implicit function of pressure, as pair fractions will evolve as a function of this variable.

Finally, configuration-independent contributions that will not affect the magnitude of each pair fraction in the melt, also called Bragg-Williams-like excess parameters, can be added to eq. 7. Such excess terms, i.e. Margules parameters, are familiar from models more commonly used in geochemistry such as the regular and associated solution models. For the MgO-SiO₂ binary system, configuration-independent molar excess Gibbs energy $\Delta g^{BW, xs}$ takes the following general form:

$$\Delta g_{Si-Mg}^{BW, xs} = \frac{z_{tot.}}{2} \left[Y_{SiO_2} Y_{MgO} \sum_{i+j \geq 0} (\omega_{ij} + \eta_{ij} \cdot T) \cdot Y_{SiO_2}^i Y_{MgO}^j \right] \quad (8)$$

II-D The effect of pressure through the excess volume

The energetic effects of pressure on silicate melts are based on the explicit definition of a function describing the change in molar excess Gibbs energy upon compression:

$$\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X}) = \int_{P_0}^P v^{xs}(T, P, \underline{X}) dP \quad (9)$$

with:

$$v^{xs}(T, P, \underline{X}) = v^{solution}(T, P, \underline{X}) - \sum_{i=1}^s X_i \cdot v_i^0(T, P) \quad (10)$$

The function $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$ defined in eq. 9 represents the molar Gibbs energy change associated with modifying the equilibrium state of the melt from a reference pressure P_0 (atmospheric pressure) to a final pressure P at a given T and composition. In eq. 10, $v^{solution}$ is the molar volume of the solution and v_i^0 represents the molar volume of each constitutive species i of the solution. As presented here, the analytical form of $v^{xs}(T, P, \underline{X})$ and its resulting integrated expression with respect to pressure will depend on the thermodynamic model considered, as well as assumptions regarding its behaviour as a function of the internal structure of the solution. In

this case we considered that the excess volume goes to zero as a function of pressure. The complete definition of the total Gibbs energy of silicate melts using this approach is presented in Appendix 1.

II-E *Distinctions between configuration-dependent and configuration-independent excess parameters at P_0*

As stated previously, the quasichemical model in the second nearest neighbor pair approximation permits variation of the degree of Short Range Order (SRO) in the solution via variation of the molar Gibbs energy of the quasichemical reaction Δg_{A-B}^{QC} . It has been shown in our recent studies on metallic systems (Harvey *et al.*, 2011, 2012) that configuration-independent excess contributions could also be physically present in the solution, even if a certain degree of SRO is observed. For example, if volume relaxation effects occur in the NPT ensemble then excess terms will be needed to adequately represent the Gibbs energy of the solution, but this should not affect or depend on the speciation. As proposed by Pelton and Kang (2007), a combination of different configuration-dependent (quasichemical) and configuration-independent (Bragg-Williams) excess parameters can be used to model the system with a higher degree of accuracy.

In the case of the MgO-SiO₂ binary system at ambient pressure, the previous thermodynamic assessment using this model reported by Wu *et al.* (1993) considered only the presence of configuration-dependent excess terms. In this system, it is reasonable to assume that the maximum amount of SRO will occur at a molar composition of $X_{SiO_2} = 1/3$ where two Mg²⁺ cations and one Si⁴⁺ cation form an ionic complex Mg₂SiO₄. In the solid state, Mg₂SiO₄ is the most stable compound of the system (Fei *et al.*, 1990). A negative and configuration-dependent enthalpy term should be added to the thermodynamic model to represent this physical behaviour. According to Hudon and Baker (2002a, b), one explanation of the origin of the liquid miscibility gap observed in this liquid slag system is due to the difference in cation size between Si⁴⁺ and Mg²⁺. Hence, the positive enthalpy contribution inducing the miscibility gap should reasonably be modelled using configuration-independent excess terms. New FPMD molar enthalpy of mixing data simulated at 0 GPa are also available and could modify the thermodynamic assessment of this system. For these reasons, we decided to perform a new thermodynamic assessment of the MgO-SiO₂ system at ambient pressure.

By analogy and as a direct consequence of these observations, it is important to explore the possibility of using configuration-independent and configuration-dependent excess volumes in this work.

III. Choices of excess volume expressions

If we suppose, for the moment, that the excess volume is configuration independent, then an analytical form for $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$ can be obtained. Although we mentioned earlier that configuration-dependent parameters are permissible and might be expected in the parameterization procedure, the thermo-physical properties obtained from FPMD simulations by de Koker *et al.* (2013) do not in practice require such parameters.

III-A Configuration-independent Bragg-Williams polynomial representation of the excess volume for low pressure

For low pressures (a few GPa), one can assume that the molar excess volume can be expanded as a function of the species equivalent fractions, temperature and pressure according to the following power series:

$$v^{xs}(T, P, \underline{X}) = Y_1 Y_2 \sum_{i+j \geq 0} \left[\sum_{q \geq 0} [l_{ij}^q + k_{ij}^q \cdot T] (P - P_0)^q \right] Y_1^i Y_2^j \quad (11)$$

Note that when $q=2$, eq. 11 is the excess function equivalent of the equation of state used by Ghiorso (2004a, b, c; Ghiorso and Kress, 2004) (if a and b are equal to 0). Derived excess thermodynamic properties of this formalism can be found in Appendix 2.

Because derived properties such as isothermal compressibility and volumetric thermal expansivity data can also be available for the solution, it is important to define the excess isothermal compressibility β_T^{xs} and the excess volumetric thermal expansivity α_V^{xs} :

$$\beta_T^{xs} \equiv -\frac{1}{v^{xs}} \left(\frac{\partial v^{xs}}{\partial P} \right)_T \quad (12)$$

$$\alpha_V^{xs} \equiv \frac{1}{v^{xs}} \left(\frac{\partial v^{xs}}{\partial T} \right)_P \quad (13)$$

297 These two excess physical properties are not extensive properties and thus cannot be evaluated
 298 from simple mixing rules. In order to define and use simple mixing rules, the following two
 299 extensive physical quantities are introduced:

$$300 \quad \Gamma^{xs} \equiv \left(\frac{\partial v^{xs}}{\partial P} \right)_T = -v^{xs} \beta_T^{xs} \quad (14)$$

$$301 \quad \Omega^{xs} \equiv \left(\frac{\partial v^{xs}}{\partial T} \right)_P = v^{xs} \alpha_v^{xs} \quad (15)$$

302 Γ^{xs} is the extensive excess isothermal compressibility of the solution, whereas Ω^{xs} is the
 303 extensive excess isobaric thermal expansion. These two derived extensive excess properties can
 304 be used to parameterize the expression defining the excess volume:

$$305 \quad \Gamma^{xs}(T, P, \underline{X}) = \left(\frac{\partial v^{xs}}{\partial P} \right)_T = Y_1 Y_2 \sum_{i+j \geq 0} \left[\sum_{q \geq 1} q \cdot (l_{ij}^q + k_{ij}^q \cdot T) (P - P_0)^{q-1} \right] Y_1^i Y_2^j \quad (16)$$

$$306 \quad \Omega^{xs}(T, P, \underline{X}) = \left(\frac{\partial v^{xs}}{\partial T} \right)_P = Y_1 Y_2 \sum_{i+j \geq 0} \left[\sum_{q \geq 0} k_{ij}^q (P - P_0)^q \right] Y_1^i Y_2^j \quad (17)$$

307 To allow the excess volume to vary as a function of both pressure and temperature, at least one
 308 l_{ij}^1 and one k_{ij}^0 parameter have to be assigned a non-zero value according to eqs. 16 and 17.
 309 Moreover, if β_T^{xs} varies as a function of pressure, then at least one l_{ij}^{2+n} parameter with $n \geq 0$
 310 should be used.

311 These two physical quantities ultimately lead to the expression of β_T^{xs} and α_v^{xs} as a function of
 312 the pure species (Γ_i, Ω_i) and the solution physical properties ($\Gamma^{solution}, \Omega^{solution}$):

$$313 \quad \beta_T^{xs} = - \left[\frac{\Gamma^{solution} - \sum_{i=1}^s x_i \Gamma_i}{v^{xs}} \right] \quad (18)$$

$$\alpha_v^{xs} = \frac{\Omega^{solution} - \sum_{i=1}^s x_i \Omega_i}{v^{xs}} \quad (19)$$

We will see that these two last equations can be used to judge the validity and coherence of the data.

III-B Configuration-independent Bragg-Williams exponential decay representation of the excess volume for moderate-to-high pressure and high temperature

For moderate-to-high pressure and temperature, the limiting behavior of v^{xs} is not clearly established in the literature. Proposing a functional form of v^{xs} under these extreme conditions becomes a difficult task. In order to reproduce the set of thermo-physical properties presented by de Koker *et al.* (2013), we are using here one of their important FPMD simulation observations, i.e. “the volume of mixing becomes increasingly ideal at elevated pressure. Indeed v^{xs} is essentially zero over most of the lower mantle”. This assumption is consistent with, though not required by, shock wave experiments of Asimow and Ahrens (2010) on three compositions along a different multicomponent silicate liquid join, the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ binary. The volume of the intermediate composition, at high temperature along the Hugoniot, can be predicted from the end-member equations of state, whereas the excess volume inferred at low temperature is prone to high uncertainties (Asimow and Ahrens, 2010). Following de Koker *et al.* (2013), the limiting behaviour of v^{xs} at high pressure and temperature is assumed to be as follows:

$$\lim_{T \rightarrow \infty} v^{xs}(T, P, \underline{X}) = 0 \quad (20)$$

$$\lim_{P \rightarrow \infty} v^{xs}(T, P, \underline{X}) = 0 \quad (21)$$

According to eqs. 20 and 21, the excess volume becomes increasingly ideal for both elevated pressure and temperature. To respect eqs. 20 and 21 simultaneously, the following expression is proposed:

$$v^{xs}(T, P, \underline{X}) = Y_1 Y_2 \sum_{i+j \geq 0} \left[\left[a_{ij} + b_{ij} T + c_{ij} (P - P_0) \right] \exp \left[d_{ij} (P - P_0) + f_{ij} T \right] \right] Y_1^i Y_2^j \quad (22)$$

Excess thermodynamic properties such as I^{xs} and Ω^{xs} (equivalent to eq. 16 and eq. 17) derived from this specific representation of v^{xs} are presented in Appendix 2. Important limitations of this functional form must be stated at this point. According to the calculated self-diffusivities of Si and Mg cations in MgO-rich silicate melts obtained by de Koker *et al.* (2008), the FPMD simulations of de Koker *et al.* (2013) are most probably not run long enough (6 ps) for two immiscible liquids to develop, even when the liquid lies inside the spinodal region. Indeed, a first indication that can be used to qualitatively assess the necessary time to relax silicate melt structures in MD simulations can be found in the work of Karki *et al.* (2013). These authors evaluated the viscosity of MgO-SiO₂ melts at ambient pressure. In their work, the authors present the evolution of the normalized stress auto-correlation function as a function of the MD simulation time. As the amount of SiO₂ increased, the relaxation time drastically increased, going up to the ns scale for pure SiO₂ liquid. A reasonable relaxation time at 3000 K and atmospheric pressure would be well above 30 ps for SiO₂-rich melt. However, this is not a sufficient criterion since any given configuration can be relaxed. In order to 1) reach the equilibrium state and 2) simulate enough configurations to sample adequately the partition function, much longer simulation times would be required. In this case, self-diffusion coefficient could be used to qualitatively assess the suitable relaxation/equilibration time for each composition. This topic has been covered in the recent work of Harvey and Asimow (2015).

Obviously, eq. 22 applies to single-phase regions only, though in some cases that single liquid may be metastable or unstable. We will see in section VIII how the miscibility gap calculated from this formulation compares to the available experimental data for the MgO-SiO₂ system (Dalton and Presnall, 1997; Hudon *et al.*, 2004, 2005). The high-pressure limiting behaviour of equation (22) is not based on fundamental physical concepts or experimental observations; it is motivated by the interpretation of de Koker *et al.* (2013) and therefore should allow a self-consistent thermo-physical interpolation of the FPMD data. The assumption of the temperature limiting behaviour of v^{xs} , eq. 22, on the other hand, is believed to be reasonable, because any system at high temperature will tend towards the ideal gas limit.

III-C. Configuration-dependent quasichemical-like excess volume formulations

As presented in section II, the thermodynamic behaviour of liquid silicate melts can be expressed, in part, as a function of second nearest neighbour pair fractions X_{ij} . Eqs. 11 and 22

describing v^{xs} might thus, in principle, be re-written as a function of these variables. In this work, we did not explore this option because the FPMD simulations show that the largest excess volume phenomena are present on the SiO₂-rich side of the system where configuration-independent contributions are dominant. However, for completeness we note that in situations where excess volume does need to be written in terms of configuration-dependent pair fractions, a problem arises from the pressure and temperature dependencies of the X_{ij} . No analytical form for $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$ can be obtained in this case. To partially circumvent this problem one can change the order of evaluation, beginning from a general form for $\Delta g_{AB}(T, P, X_{ij})$, and numerically evaluating all thermo-physical properties from Gibbs energy minimization.

IV. Thermodynamic model parameterization procedure of the MgO-SiO₂ liquid solution at P_0

The classical scheme for the parameterization of the selected thermodynamic model, in this case the modified quasi-chemical model in the second nearest neighbour formalism (Pelton and Blander, 1986), is found extensively in the literature. A new approach that considers simultaneously both thermodynamic and structural self-consistent data was presented recently in the case of metallic systems (Harvey *et al.*, 2011, 2012). To apply this self-consistent approach, enthalpy, entropy, and structural data at P_0 for each potentially stable solution have to be evaluated in order to completely represent their respective thermo-physical behaviour. Phase diagram data are used in this case to validate the parameterization or to fine-tune the excess properties of the solution. One has to remember that multi-phase equilibria are defined by common tangents and that, accordingly, a small local shift in the Gibbs energy of a given solution could potentially drastically affect the phase assemblage.

The recent FPMD study of de Koker *et al.* (2013) provides the most complete set of self-consistent thermo-physical data as a function of T , P and X for any multi-component silicate liquid, in this case the MgO-SiO₂ binary. However, de Koker *et al.* (2013) did not have access to a direct method for evaluating the mixing entropy at P_0 and did not present partial distribution functions needed to evaluate structural data such as second nearest neighbour pair fractions. Therefore we performed a classical thermodynamic parameterization at P_0 to accurately obtain the Gibbs energy function of the liquid solution at this pressure. Other thermodynamic

assessments for this system were proposed by Wu *et al.* (1993), Holland and Powell (2003) and Ghiorso *et al.* (2002).

Figure 1: Results of the CALPHAD method thermodynamic assessment of the MgO-SiO₂ liquid phase at 0 GPa: A) molar enthalpy of mixing; B) SiO₂-liquid activity data (note, this plot continues into the stability fields of Mg₂SiO₄ and MgSiO₃; the metastable liquid is plotted for illustration purposes); C) molar entropy of mixing; D) liquid-liquid miscibility gap; and E) Entire phase diagram.

Table 1: Thermodynamic parameters of the MgO-SiO₂ liquid solution obtained for P₀

Excess parameter	Numerical value
Z_{Mg}	1.3774
Z_{Si}	2.7548
Δg_{Si-Mg}^{QC}	
ω_{00}^{QC}	-58576 J·mol ⁻¹
η_{00}^{QC}	-17.99 J·mol ⁻¹ ·K ⁻¹
$\Delta g_{Si-Mg}^{BW,xs}$	
η_{00}^{BW}	23.43 J·mol ⁻¹ ·K ⁻¹
ω_{70}^{BW}	239325 J·mol ⁻¹
η_{70}^{BW}	-86.19 J·mol ⁻¹ ·K ⁻¹

We performed a CALPHAD method thermodynamic assessment of the liquid phase using FactSage software (Bale *et al.*, 2009), with an emphasis on accurately fitting the FPMD molar heat of mixing data of de Koker *et al.* (2013). In our approach, the thermodynamic description of each solid phase and of pure MgO(liq.) and SiO₂(liq.) is taken directly from the work of Wu *et al.* (1993). The resulting properties and optimized phase diagrams are shown in Figure 1 and the thermodynamic parameters of the quasichemical model are presented in Table 1.

FPMD enthalpy of mixing data obtained by Zhang (2011) at 4000 K are also shown in Fig. 1A. These results highlight the potentially large uncertainty in evaluating thermodynamic properties with this technique. Zhang (2011) attributed this large uncertainty to several factors. MD simulations are sensitive to initial configuration; integration of the equations of motion identifies only local minima and samples a limited part of the Gibbs energy surface of the solution. Zhang (2011) used three initial configurations. The resulting standard deviation of the total energy is between 10 and 50 kJ/mol, which could induce a potentially large absolute error in calculating molar heat of mixing. It is unclear whether such errors are present in the results of de Koker *et al.* (2013), who begin each simulation only from a single initial configuration. Moreover, the total simulation time directly impacts the statistical analysis required to evaluate thermodynamic properties of the system. This statistical analysis is also used to ensure that the simulations are ergodic. Short simulation times, given the low self-diffusivity of Si at some of the state points and compositions studied, limits the number of chemical configurations sampled by MD simulations. The simulations of de Koker *et al.* (2013) and of Zhang (2011) used similar simulation times (6ps) and number of atoms (≈ 100), suggesting that the apparently better internal precision and lower reported uncertainties de Koker *et al.* (2013) may result from the use of only one initial configuration for each state point; it is difficult to tell from the published record.

Wasserman *et al.* (1993) reported a maximum in the enthalpy of mixing of MgO-SiO₂ melts of +22 kJ/mol at $X_{\text{SiO}_2} = 0.7$, obtained by classical MD simulations at 5000 K and 5 GPa with an accuracy of 10 kJ/mol, while predicting all negative values at 50 GPa. As a basis of comparison, the calculated molar enthalpy of mixing obtained by Wu *et al.* (1993) in their thermodynamic assessment of the MgO-SiO₂ system is presented in Fig 1A.

Entropy parameters of the quasichemical model for the liquid phase presented in Table 1 are obtained by fitting experimental activity data reported by Kambayashi and Kato (1983, 1984) and of Rein and Chipman (1965) (Fig. 1B) as well as the liquid-liquid miscibility gap data of Hageman and Oonk (1986) in the SiO_2 -rich side of the phase diagram (Fig. 1D). FPMD alone cannot provide the absolute entropy of a given equilibrium state unless an approach such as the thermodynamic integration method is implemented to overcome this limitation. It is therefore of fundamental importance to use all these thermodynamic data to fine-tune the entropy of the solution. A comparison between the predicted molar entropy of mixing obtained in this work and by Wu *et al.* (1993) is presented in Fig. 1C. Finally, the entire liquidus of the MgO-SiO_2 system obtained from the present thermodynamic assessment is compared to that of Wu *et al.* (1993) in Fig. 1E. We did not use the temperatures and compositions of the eutectic and peritectic points as constraints because this makes the liquid model strongly dependent on the adopted solid models; hence the detailed liquidus topology in the middle of the diagram is a prediction or confirmation of our model rather than a fit forced by the calibration. There is a discrepancy in the liquidus between the two assessments, up to 150°C , between $X_{\text{SiO}_2} = 0.4$ and $X_{\text{SiO}_2} = 0.6$. This error is caused by a change of about 2 kJ/mol in the Gibbs energy of the liquid phase, which is relatively small compared to typical errors of FPMD simulations. In general phase diagram topologies are sensitive to differences in Gibbs energy below the resolution of FPMD simulations and the accurate prediction of phase equilibria data requires additional tuning such as the incorporation of univariant temperatures and compositions as constraints.

V. Parameterization procedure of $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$

To calculate the effect of pressure on the Gibbs energy function calibrated at P_0 in section IV, we attempt to parameterize $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$ using both eq. 11 and eq. 22.

Note that all the equations of section III and corresponding Appendixes must be multiplied by a coordination number factor $z_{\text{tot}}/2$ to conform with the quasichemical formalism implemented in the *FactSage* software. The numerator of this coordination number factor is the equivalent coordination number of the solution (eq. 4), while the denominator is the coordination number of the classical quasichemical model ($z_{\text{classical}} = 2$). For a given set of excess parameters in eqs. 11

and 22, $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$ scales by the equivalent coordination number of the solution according to this formalism, so all thermodynamic properties presented in section III are normalized by this factor.

Figs. 2A and 2B present the results of the least squares fitting of FPMD molar volume and enthalpy of mixing data at 3000 K and each pressure reported by de Koker *et al.* (2013) to the following functions:

$$\left(\frac{v^{xs}(\underline{X})}{Z_{tot.}/2} \right)_{T,P} = Y_{SiO_2} Y_{MgO} \left[(\beta_{00})_{T,P} + (\beta_{70})_{T,P} Y_{SiO_2}^7 \right] \quad (24)$$

$$\left(\frac{\Delta h_{P_0 \rightarrow P}^{xs}(\underline{X})}{Z_{tot.}/2} \right)_{T,P} = \left(\frac{h_P^{xs}(\underline{X}) - h_{P_0}^{xs}(\underline{X})}{Z_{tot.}/2} \right)_{T,P} = Y_{SiO_2} Y_{MgO} \left[(\omega_{00})_{T,P} + (\omega_{70})_{T,P} Y_{SiO_2}^7 \right] \quad (25)$$

The general form of these equations is similar to the BW excess parameter function used in section IV to fit the thermo-physical properties at P_0 . The same powers (0th and 7th) were adopted for the excess configuration-independent parameters at P_0 and allowed description of the miscibility gap in the silica-rich region. Note that open symbols in Fig. 2B are apparently anomalous FPMD data of de Koker *et al.* (2013) that were excluded from the least squares fitting procedure.

Figure 2: Results of the least squares fitting of A) $\left(\frac{v^{xs}}{z_{tot.}/2}\right)$ and B) $\left(\frac{h_p^{xs} - h_{p_0}^{xs}}{z_{tot.}/2}\right)$ as a function of Y_{SiO_2} at each pressure. Symbols represent the FPMD data of de Koker *et al.* (2013), while solid lines are functions fitted in this work. Open symbols in B) are FPMD data of de Koker *et al.* (2013) that are not considered in the least squares fitting procedure.

The fitted parameters defining $\left(\frac{v^{xs}}{z_{tot.}/2}\right)$ and $\left(\frac{h_p^{xs} - h_{p_0}^{xs}}{z_{tot.}/2}\right)$ using eqs. 24 and 25 at each pressure are summarized in Figs. A-1 and A-2 (Appendix 3). The observation that v^{xs} tends to zero as pressure increases, made by de Koker *et al.* (2013), is consistent with these results, with the excess volume parameters (Fig. A-1) tending to zero and the excess enthalpy parameters (Fig. A-2) converging to constants at high pressure. These observations motivate the general form of eq. 22 for moderate-to-high pressures (section III-B).

V-A Low pressure polynomial representation of v^{xs} (below 10 GPa)

Figure 3: Results of the parameterization of eqs. 11 and A2-3 that allows the description of A) v^{xs} and B) h_p^{xs} as a function of X_{SiO_2} and P . Symbols in this figure are the FPMD data of de Koker *et al.* (2013) while the lines are the results obtained from eqs. 11 and A2-3.

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497 At low pressure, i.e. below 10 GPa, we assume that the parameters of both $\left(\frac{v^{xs}}{z_{tot.}/2}\right)$ and
 498 $\left(\frac{h_p^{xs} - h_{p_0}^{xs}}{z_{tot.}/2}\right)$ are linear functions of pressure, i.e. $q = 1$ in eq. 11 (Figs. A-1 and A-2 in Appendix 3
 499 make it clear that this assumption does not apply over larger pressure ranges). As mentioned
 500 previously, this is the minimum requirement for defining Γ . Also, both enthalpy (l_{ij}^q) and
 501 entropy (k_{ij}^q) parameters are used in order to fit simultaneously these two thermodynamic
 502 properties as a function of pressure and to define Ω . Enthalpy parameters are obtained first by
 503 fitting molar heat of mixing data (see eq. A2-3). Molar volume data are then used to
 504 parameterize the entropy terms. Optimized parameters for eq. 11 using this procedure are
 505 presented in Table 2.

506

507 Table 2: Optimized parameters of eq. 11 defining $\left(\frac{v^{xs}}{z_{tot.}/2}\right)$

Parameter	Value
l_{00}^0	-4.214E-06 J/(mol·Pa)
l_{70}^0	-3.014E-05 J/(mol·Pa)
l_{00}^1	2.184E-16 J/(mol·Pa ²)
l_{70}^1	1.672E-15 J/(mol·Pa ²)
k_{00}^0	3.823E-10 J/(mol·K·Pa)
k_{70}^0	2.674E-09 J/(mol·K·Pa)
k_{00}^1	-8.265E-21 J/(mol·K·Pa ²)

$$k_{70}^1 \quad -1.185\text{E-}19 \text{ J}/(\text{mol} \cdot \text{K} \cdot \text{Pa}^2)$$

V.B Moderate pressure exponential decay representation of v^{xs} (at 10-25 GPa)

For moderate pressures, eq. A2-6 is used to describe the FPMD data obtained by de Koker *et al.* (2013); fit parameters are given in Table 3. In this formalism, v^{xs} tends to zero as pressure goes to infinity. In fact, v^{xs} is almost 0 at about 40 GPa (Fig. 4A). The FPMD data do not cover enough temperatures to constrain the limiting behavior of v^{xs} as a function of temperature, so no f_{ij} parameters are used in this work. Using this formalism, it is possible to fit all raw thermodynamic data of de Koker *et al.* (2013) at 3000K with fairly good precision.

Figure 4: Results of the parameterization of eqs. 22 and A2-6 that allows the description of A) v^{xs} and B) h_p^{xs} as a function of X_{SiO_2} and P . Symbols in this figure are the FPMD data of de Koker *et al.* (2013) while the lines are the results obtained from eqs. 22 and A2-6.

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Table 3: Optimized parameters of eq. 22 defining $\left(\frac{v^{xs}}{z_{tot.}/2}\right)$

Parameter	Value
a_{00}	-4.933E-06 J/(mol·Pa)
a_{70}	-3.777E-05 J/(mol·Pa)
b_{00}	5.693E-10 J/(mol·K·Pa)
b_{70}	4.429E-09 J/(mol·K·Pa)
c_{00}	--
c_{70}	--
d_{00}	-1.059E-10 (Pa ⁻¹)
d_{70}	-1.328E-10 (Pa ⁻¹)

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525 **VI. Calculation of derived thermo-physical excess properties**

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The proposed v^{xs} parameterizations enable calculation of derived excess properties such as Γ^{xs} and Ω^{xs} (defined in section III). Comparisons between the predicted behaviour of these two derived excess properties at 0 GPa and 3000 K using the polynomial representation of v^{xs} (valid for low pressure) and the data reported by de Koker *et al.* (2013) are presented in Figs. 5 and 6.

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Figure 5: A) Γ^{xs} as a function of X_{SiO_2} for the MgO-SiO₂ melts at 0 GPa and 3000 K. Filled circles represent the data reported by de Koker *et al.* (2013); the solid line represents the results obtained in this work using the polynomial representation of v^{xs} , eq. 11. B) Magnification of the region showing the results obtained in this work (solid line). Filled circles now represent the data reported by de Koker *et al.* (2013) modified by referencing Γ^{xs} with respect to SiO₂ (liquid) having an isothermal bulk modulus of 12.2 GPa as proposed by de Koker and Stixrude (2009) for a 1st order expansion in θ .

These figures reveal important considerations when estimating derived excess properties from molecular dynamic simulations and parameterized Equations of State (EOS) for each studied composition. The first observation is the noticeable difference between Γ^{xs} obtained in this work compared to the data obtained by de Koker *et al.* (2013) using a 2nd-order expansion in dimensionless temperature (θ). This is a surprising result, since v^{xs} is well fitted in the low-pressure range using our approach (Fig. 3). However, de Koker and Stixrude (2009) demonstrate the effect of the order of the finite strain expansion on the resulting thermo-physical properties at 0 GPa for liquid SiO₂. The isothermal bulk modulus and its pressure derivative are highly sensitive to the order of the polynomial expansion in θ . The isothermal bulk modulus of 12.2 GPa that results from the 1st order expansion in θ would generate a set of Γ^{xs} values of amplitude much closer to our result (Fig. 5B). This is an important conclusion: the necessity of using a higher order finite strain expansion informs us that the behavior in temperature of liquid SiO₂ is of a complex form compared to MgO, Mg₂SiO₄ and MgSiO₃. It is critical in a future study to analyse carefully the low temperature FPMD simulations of liquid SiO₂ to see whether this complex behavior is reproducible or is instead a convergence issue with FPMD simulations of highly viscous melts at high pressure and low temperature.

Figure 6: Ω^{xs} as a function of X_{SiO_2} for the MgO-SiO_2 melts at 0 GPa and 3000 K. Filled circles represent the data reported by de Koker *et al.* (2013); the solid line represents the results obtained in this work using the polynomial representation of v^{xs} (eq. 11).

The second observation is related to the precision of the calculation of Ω^{xs} . According to our work, Ω^{xs} calculated at 0 GPa and 3000 K is always positive and displays a smooth general behaviour similar to the other self-consistent excess properties. On the other hand, the Ω^{xs} data of de Koker *et al.* (2013) are scattered and of both signs. This may result from the indirect calculation procedure of the volumetric thermal expansion, α_v , which was not directly determined by de Koker *et al.* (2013) from the dependence of v^{xs} on T at $P=0$ GPa. Instead, the authors used the following thermodynamic identities,

$$\frac{1}{\beta_T} = V \left(\frac{\partial^2 F}{\partial V^2} \right)_T \quad (26a)$$

$$\frac{\alpha_v}{\beta_T} = - \left(\frac{\partial^2 F}{\partial V \partial T} \right) \quad (26b)$$

where F is the Helmholtz energy, in order to evaluate α_v from their parameterized EOS at each composition. This procedure is strictly equivalent to evaluating α_v from the macroscopic Grüneisen parameter γ :

$$\alpha_v = \frac{\gamma \cdot c_v \cdot \beta_T}{V} \quad (27)$$

where c_v is the molar heat capacity at constant volume. The error transfer from each thermo-physical property in eq. 27 is an important contribution to the scatter of the data seen in Fig. 6.

Moreover, Ω^{xs} values obtained from the FPMD data of de Koker *et al.* (2013), although scattered, seem to be distributed in two distinct regions: mostly positive deviations from ideality in MgO-rich melts and mostly negative deviations from ideality in SiO₂-rich melts. The uncertainty in locating these two regions and the definition of Ω^{xs} suggest a new thermodynamic criterion relating the sign of v^{xs} and Ω^{xs} . In section III-B, we mentioned that the v^{xs} function should converge to zero as the temperature increases without limit. In the case of uniformly negative excess volumes at 0 GPa (as reported by de Koker *et al.* (2013) for the MgO-SiO₂ system), a uniformly positive Ω^{xs} function (i.e. $\left(\frac{\partial v^{xs}}{\partial T}\right)_p > 0$) is necessary to reach the limit defined by eq. 20. On the other hand, a negative Ω^{xs} function should be expected alongside positive excess volumes at 0 GPa and finite temperature. Of course, violations of this principle over limited temperature ranges are possible, but require in turn even stronger converging behaviour beyond the studied range.

We do not propose a similar criterion for Γ^{xs} because the validity of eq. 21 is not based on fundamental physical principles. Moreover, it will be shown in section VII that this hypothesis is not valid and, most importantly, is inconsistent with the experimental phase diagram at low-to-moderate pressures for the MgO-SiO₂ system.

VII. Predicted evolution of MgO-SiO₂ miscibility gap

Figure 7: The liquid-liquid miscibility gap in the MgO-SiO₂ binary system as a function of pressure. The experimental data at 0 GPa of Ol'shanskii (1951), Hageman and Oonk (1986) and of Hudon *et al.* (2004) for 1 GPa and 1.5 GPa are compared to the miscibility gaps predicted in this work using the polynomial (dashed and dot lines) and exponential decay (dashed lines) representations. This is not an equilibrium phase diagram; solid phases are suppressed to emphasize relations within the (possibly metastable) liquid phase only.

A decisive test for judging whether fitting the FPMD data of de Koker *et al.* (2013) with the v^{xs} equations proposed in this work captures the excess properties of the liquid solution is to predict the MgO-SiO₂ solvus on the SiO₂-rich side. In this region there is a miscibility gap at low pressure. The predicted MgO-SiO₂ miscibility gaps at each pressure obtained using the polynomial representation (eq. 11) and the exponential representation (eq. 22) are compared to the thermodynamic data given by Hudon *et al.* (2004) based on their experimental results (Fig. 7). In this figure, all solid phases are suppressed and only phase equilibrium data associated with the miscibility gap are considered. The prediction that results from our excess volume parameterization based on the FPMD data is a strongly decreasing consolute temperature from 0 to 5 GPa. According to the thermodynamic assessment of Hudon *et al.* (2004), however, the consolute temperature of the miscibility gap increases gently with pressure. This result awaits confirmation from experiments over a wider pressure range: in Fig. 7, consolute temperatures

between 1 and 1.5 GPa are well within the scatter of the 0 GPa experiments. Nevertheless, our prediction of decreasing consolute point behaviour with increasing pressure is inconsistent with that of Hudon *et al.* (2004).

Figure 8: The silica liquidus in the MgO-SiO₂ binary at 5 GPa as a function of the weight fraction of SiO₂. Filled circles represent the data of Dalton and Presnall (1997); lines are the predicted liquidus obtained from the parameterization of the liquid phase in this work (solid line) and from Hudon *et al.* (2004) (dashed line).

It might be argued however that the most accurate set of data at 0 GPa is provided by Ol'shanskii (1951), contrary to what was claimed previously by Wu *et al.* (1993), in which case a decrease of consolute temperature with pressure, consistent with our model, would in fact reproduce the data of Hudon *et al.* (2005). But there is a further experimental constraint on the change in position of the solvus to be obtained by considering the silica liquidus data of Dalton and Presnall (1997) at 5.0 GPa (Fig. 8). According to these data, the liquid-liquid miscibility gap disappears by 5.0 GPa because of the significant increase of the melting point of SiO₂ with pressure (Hudon *et al.*, 2002) (proposed by Hudon *et al.* (1994)). The disappearance of the miscibility gap thus does not require a decrease of the consolute temperature. In fact the relatively flat shape of the experimental liquidus is a clear indication of a still-strong tendency toward demixing and suggests that the miscibility gap is not far below the liquidus at 5 GPa and therefore lies at higher temperature than the 1 bar consolute point. Although the shape of the liquidus depends only of

liquid-phase mixing properties, the absolute position of the calculated liquidus is sensitive to the Gibbs energy of the coexisting silica phase (in this case coesite). We chose the thermodynamic assessment of Hudon *et al.* (2002) to define the Gibbs energy function of coesite, but the uncertainty in the coesite liquidus is small enough that the conclusion that a strongly flattened liquidus at 5 GPa implies an increase in metastable consolute temperature is probably robust.

If the consolute temperature does in fact increase with pressure, then it is possible that the miscibility gap could reappear at higher pressures, where the rate of increase in liquidus temperature is much lower. Ultimately, the stable (not metastable) reappearance of a miscibility gap will be confirmed by performing equilibrium calculations that also account for the potential presence of the relevant SiO₂ polymorphs for these particular equilibrium conditions. To achieve this objective, an accurate representation of the P-T unary phase diagram of SiO₂ up to potentially very high pressure (50-100 GPa) is necessary and represent by itself a scientific challenge in geochemistry.

The disagreement at present between experimental observations and the self-consistent prediction calibrated upon first principles calculations, however, suggests that it is premature at this time to assess the very high-pressure behaviour of the miscibility gap. Further tests and independent calculations are needed to trace the source of the discrepancy to the experiments, to the interpolation method proposed here, or to the inherent accuracy of current FPMD simulations as a probe of mixing relations among SiO₂-rich liquids.

XIII. Discussion

Despite careful study, the evolution of the liquid-liquid miscibility gap in the MgO-SiO₂ binary system at high pressure is still not consistently accounted for. The shape of the experimental liquidus obtained by Dalton and Presnall (1997) at 5 GPa implies that the consolute point remains close to the liquidus and a potential reappearance of the miscibility gap at higher pressures is not impossible. It may be that the magnitude of the positive enthalpy of mixing in the liquid increases as a function of pressure, contrary to result derived from our self-consistent fit to the FPMD data of de Koker *et al.* (2013). In this scenario, the use of metastable single-phase simulation results at state points where the true equilibrium is a two-phase existence might bias the estimates of enthalpy of mixing. For instance, the FPMD heat of mixing data reported by

de Koker *et al.* (2013) at 0 GPa and 2000 K show that it would be energetically more favorable to form two immiscible liquids at $0.4 \leq X_{\text{SiO}_2} \leq 1$. The failure of the calculations to exsolve shows the need for caution in applying this method to potentially immiscible solutions, even though the entropic effects of mixing, which do not influence the equations of motion in molecular dynamics, might favour single-phase mixing by a Gibbs energy criterion.

Furthermore, Zhang (2011) showed that FPMD results are highly sensitive to initial configurations. Assuming that de Koker *et al.* (2013) started their simulations with a single-phase liquid solution, the energetic driving force inducing the formation of the miscibility gap at low pressure could have been insufficient. It is also possible that de Koker *et al.* (2013) reported thermodynamic properties of a two-phase liquid-liquid system. Where a miscibility gap is suspected it is important to analyze Si-Si, Si-Mg and Mg-Mg partial radial distribution functions and their change with pressure to detect incipient or complete exsolution.

Unfortunately, the existing literature on both classical and *ab initio* molecular dynamics of multicomponent silicate melts cannot resolve the origin of the inconsistency highlighted here. MD simulations of pure pseudo-unary liquids such as MgO (Alfè, 2005; Belonoshko and Dubrovinsky, 1996a; Karki *et al.*, 2006; Lacks *et al.*, 2007; Liu *et al.*, 2004) or SiO₂ (Benoit *et al.*, 2000; Carre *et al.*, 2008; Demiralp *et al.*, 1999; Feuston and Garofalini, 1988; Hassanali and Singer, 2007; Herzbach *et al.*, 2005; Karki *et al.*, 2007; Mitra *et al.*, 1981; Paramore *et al.*, 2008; Soules, 1990; Soules *et al.*, 2011; Takada *et al.*, 2004; Tangney and Scandolo, 2002; Tsuneyuki *et al.*, 1988; Vashishta *et al.*, 1990; Woodcock *et al.*, 1976) cannot provide any evidence regarding the importance of second-nearest neighbour SRO or its effect on thermo-physical properties at conditions relevant to Earth's mantle. Moreover, previous classical MD simulations of MgO-SiO₂ melts (Belonoshko and Dubrovinsky, 1996a; Ben Martin *et al.*, 2009; Oganov *et al.*, 2000; Spera *et al.*, 2011) did not explore the entire range of composition and do not address the present issue. Other classical MD simulations have been performed on geologically relevant multicomponent compositions (Ben Martin *et al.*, 2012; Guillot and Sator, 2007; Matsui *et al.*, 2000; Spera *et al.*, 2009) but in each case these studies examined only the thermo-physical properties of specific melt compositions and not excess properties of the solutions.

As the quasichemical model is unfamiliar to most geochemists, it will be interesting in the future to compare in greater detail the microscopic consequences of quasichemical solution models to those of the more familiar associated solution approaches. As an example, there is clearly a relationship in a statistical sense between the Si-Si pair fraction abundance of the quasichemical model, on the one hand, and the populations of “Q-species” (i.e. the number of Si-O-Si bridging oxygens coordinating each Si atom) considered by associated solution models (Hovis et al., 2004). Furthermore, the extent to which the points of minimum configurational entropy arising in a quasichemical model correspond to the precisely ordered compositions that result from assumed changes in the mixing species of an associated model, will clearly depend on the amplitude of the excess enthalpy of solution. For a value as negative as that optimized by Wu et al. for MgO-SiO₂ (-37.3 kJ/mol), the quasichemical approach will more nearly yield a perfectly ordered solution at the Mg₂SiO₄ composition that it would for the less negative enthalpy minimum given by the de Koker et al. simulation (-24.0 kJ/mol).

IX. Conclusion and perspectives

We present a new fully self-consistent approach to parameterizing the Gibbs energy of a multicomponent solution as a function of temperature, pressure and composition, using two representations of the excess volume. A well-constrained optimization following the usual CALPHAD practice for enthalpy and entropy of mixing at ambient pressure is obtained using FPMD data or activity-composition measurements and solid-liquid or two-liquid phase equilibrium constraints. Then the simultaneous least squares fit of molar volume and enthalpy of mixing data from FPMD simulations over a range of pressure results in the complete parameterization of the effect of pressure on the excess Gibbs energy of mixing, $\Delta g_{P_0 \rightarrow P}^{xs}(T, P, \underline{X})$. We tested the utility of this approach for multicomponent silicate liquids of interest in geological science using the published FPMD simulations data of de Koker *et al.* (2013) for the MgO-SiO₂ system. This exercise leads to several conclusions:

1. In the 0-25 GPa pressure range, a marked decrease with increasing pressure of the consolute temperature of the miscibility gap in the SiO₂-rich part of the system is predicted. This appears to be inconsistent with the phase equilibrium data. An increase in

the consolute temperature is more consistent with the 5.0 GPa liquidus data of Dalton and Presnall (1997).

2. Derived properties, such as the excess components of volumetric thermal expansion and isothermal compressibility, that are functions of composition and pressures are more accurately described using a consistent approach, as opposed to stitching together distinct equations of state fitted to each studied composition.
3. Thermodynamic inconsistencies between directly measured properties such as v^{xs} and derived excess thermo-physical properties via a given EOS (e.g., finite strain expansion), are easily detected with our approach.
4. A new thermodynamic criterion relating the sign of v^{xs} and its temperature dependence Ω^{xs} , based on the expected high temperature ideal limit, is proposed in section VI and should be tested in the future.

It may be assumed that the FPMD simulations of de Koker *et al.* (2013) have been performed with state-of-the-art methodology. Hence the evidence of discrepancies between predictions based on those simulations and experimental data urge caution concerning the accuracy of the Gibbs energy function derived from thermo-physical properties of liquids computed by FPMD simulations. In any particular case, a discrepancy could of course also be due to inconsistent experimental results used in the optimization. Comparable studies of more systems with independent experimental inputs are needed to generalize this conclusion. However, Zhang (2011) proposed valuable recommendations concerning the requisite simulation time for FPMD and the need to use multiple initial conditions. Increasing computational power should make it routine to carry out and establish confidence in such accurate simulations. FPMD simulations will eventually be the tool of choice for constraining the thermodynamic behaviour of multicomponent liquid solutions under extreme conditions of pressure and temperature, and the need for a strategy such as that presented here for interpolating among and making predictions from such simulations will become increasingly evident.

Modelling of systems that are subject to liquid-liquid immiscibility is not a simple matter. Indeed, as noted in this work, numerical modelling of liquid structure and properties is complicated by the tendency to unmix, in particular between the solvus and the spinodal where

the second liquid must nucleate before unmixing will take place, requiring calculation times potentially longer than those achievable with current computer resources.

Acknowledgements

We would like to thank Dr. James Sangster and Dr. Pierre Hudon for their constructive criticisms of the present work as well as the editors and reviewers at GCA for pushing us to improve the manuscript. This work was supported in part by Defence Research and Development Canada and by the US NSF through award EAR-1426526.

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