Large Scale Simulations

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INTRODUCTION

In this chapter we will focus on molecular dynamics (MD) simulations with large numbers of atoms (N > 1000). Typically, *ab initio* or First Principles Molecular **D**ynamics (FPMD) calculations are performed with smaller clusters of say 100 or fewer atoms. This choice is largely due to limitations in computing resources. The simulation procedure we will explore in this chapter is known as Empirical Pair-Potential Molecular Dynamics (EPPMD). EPPMD does not rely upon estimating the forces between atoms with **D**ensity Functional Theory (DFT) as an approximation to the solution of the quantum mechanical problem, which is the computationally costly aspect of FPMD. Rather, EPPMD estimates forces between atoms from an empirical parameterization of a classical description of the potential energy, whose spatial derivative captures the pairwise-additive attractive and repulsive forces between all atoms. Because the interatomic force calculation is classical, its computational cost is minimal, and this encourages the application of EPPMD to simulations involving large numbers of atoms. Additionally, whereas FPMD simulations are typically run for durations on the order of a few picoseconds, EPPMD simulations may be extended to much longer durations (2-10 nanoseconds), which permits investigation of transport properties such as shear viscosity and phonon thermal conductivity (Fig. 1) using Green-Kubo theory (Kubo, 1966). The longer durations of EPPMD runs (with up to order 10⁷ time steps) are again a consequence of the computational efficiency derived from the classical force field approximation. In this chapter we are going to refer to long duration molecular dynamics simulations involving large numbers of atoms as Large Scale Simulations (LSS).

The main advantage of LSS is to improve the counting statistics associated with estimating equilibrium properties, including of course the equilibrium structure, as well as the ability to monitor dynamical fluctuations over a long enough time interval to estimate transport properties with better precision (Nevins and Spera, 2007). In any MD simulation there is an inherent uncertainty in every

ensemble-averaged property, for example, fluctuations in temperature (σ_T) and pressure (σ_P) scale as $N^{-\frac{1}{2}}$ (McQuarrie, 2000) in calculations carried out in the NEV or microcanonical ensemble¹. This scaling implies that the uncertainty in temperature (T) or pressure (P) - that is the location of the state point in T-Pspace - is ~ 9 times smaller in a MD simulation of, say, 8000 atoms compared to one with 100 atoms; a significant difference when one is faced with the task of constructing an Equation of State (EOS) or an Arrhenian description of a transport property such as the liquid shear viscosity over a broad region of T-P space. Similarly, equilibrium structures are determined by estimating a Radial Distribution Function (RDF) for atom-pairs (e.g. O about Si, O about O, etc.), and these RDFs are more accurately determined when there are more atoms available for An example is illustrated in Figure 2, for an important geoliquid, counting. MqSiO₃. Both cubes in Figure 2 contain the same number density of atoms and are dawn to scale; the positions of the atoms are projected onto the front face of the cube. It is obvious from examination of the figure that an RDF developed for O about Mg, for example will be better estimated by averaging 1600 Mg positions in the right box compared to 20 in the left. The consequences become especially acute if long range RDF features (second and third nearest neighbor configurations) are the subject of interest.

An advantage of LSS when computed using EPPMD is that a large number of state points may be simulated using a well tested potential to explore subtleties in the thermodynamic relations, without the expenditure of an excessive amount of computing resources. An excellent illustration of this is the work of Poole et al. (2005) on the density minimum in liquid water and its energetic relation to the liquid-liquid critical point found in the supercooled amorphous state. These authors performed 2,718 state point simulations (with $N \sim 5000$) to explore the energy surface at sufficient detail to resolve the effect.

The important caveat to appreciate when evaluating the advantages of LSS computed using EPPMD is the necessity of utilizing a well-tested and verified pair-potential. There is, of course, no sense in doing a large number of fast computations if the results of the effort are nonsensical. But, if the empirical pair-potential of interest has been parameterized from first principles studies and/or can be shown to yield results that are supported by experimental observations, then its use can be justified, especially if the computational regimen is supplemented and cross-checked against *ab initio* calculations. In some cases, where it is necessary to account for electron transfer (as in atoms with variable valence states) or where the spin state configuration of the outer electron orbitals is at issue, EPPMD cannot be easily applied, and a full quantum mechanical description of the forces must be used.

¹ A calculation where the total number of atoms, the total energy of those atoms, and the volume occupied by those atoms is fixed by initial conditions of the simulation.

In considering the application of EPPMD in LSS it is important to appreciate that all MD simulations — even DFT based FPMD — are approximations (Cohen et al., 2008). It is critical to understand the limitations of these approximations and to choose a technique that is suitable for the problem at hand. In this regard an analogy may be drawn between EPPMD and FPMD techniques and the geophysical interpretation of Earth structure from seismologic observations. Although no geophysicist would seriously contemplate that the Earth's interior is radially symmetric, huge advances in understanding the structure and mineralogical constitution of the Earth were made in the last century by making precisely this assumption. More recently, the assumption of radial symmetry has been relaxed and seismic tomography has revealed a more richly detailed and refined picture. But, to a decent approximation, many problems in geochemistry and geophysics can be productively addressed assuming radial symmetry. The EPPMD method is like the seismological assumption of radial symmetry. It is not as accurate as FPMD based calculations, but its careful application in computational chemistry can provide an essential data set of materials and transport properties upon which more rigorous and costly calculations may be contextualized.

Our interests in LSS are directed towards the thermodynamic and transport properties of silicate melts and glasses, especially at elevated pressure. LSS is ideally suited to investigating these substances because of their chemical complexity and their propensity to develop marked changes in short-range structure as temperature and (especially) pressure varies. The ultimate goal of our work is to formulate approximate but useful equations of state and transport properties for multicomponent liquids in the system CaO-MgO-FeO-SiO₂-TiO₂-Al₂O₃-K₂O-Na₂O-H₂O with a focus on melts of natural composition. These results can then be used with analogous properties of crystalline phases to compute phase equilibria within terrestrial planets, and address mass and heat transport phenomena central to magma dynamics.

We are going to focus this chapter on what to do with LSS results obtained on amorphous materials, using as an example EPPMD simulations recently completed on molten MgSiO₃. We think that it is better to illustrate the analysis of MD data using a concrete example rather than talk about that analysis in the abstract. We hope that our approach will provide the reader with a template for performing a rigorous evaluation of LSS results that can readily be applied to other amorphous materials. The chapter will begin with a formalism for thermodynamic analysis of MD state point arrays. Having developed the thermodynamic treatment, we will then touch on issues of polyamorphism and the calculation of the shock Hugoniot. Evaluation of melt structure will follow and we will explore the relation between structure and density and other thermodynamic properties. Following that we will examine transport properties. Finally we will comment on the feasibility of LSS studies that are based upon FPMD.

THERMODYNAMIC ANALYSIS

Traditionally, thermodynamic models are constructed from physical experimental data because thermodynamics provides a theoretical framework for interpolating and extrapolating these measurements without the necessity of performing a new experiment for every situation of interest. Additionally, thermodynamic analysis allows an experiment of one kind, say the measurement of the density of a liquid, to be used in estimating another property that would be difficult or impossible to measure, for instance, the variation of the Gibbs free energy with pressure. When the experimental basis for determining the properties of a system are founded on MD simulations however, the utility of constructing thermodynamic models from the results is less obvious. Why not simply compute the properties of the system at every point of interest? This reasoning is especially acute if the basis for the simulation is EPPMD running on multiprocessor machines in optimized mode for which the computational cost is modest. The answer to this argument is that thermodynamics provides more than a convenient interpolative scheme. The principles of thermodynamics permit conclusions to be drawn about the topology of the energy surface and a model facilitates the representation and analysis of that surface as a smooth continuous function. It is essential both that a model be constructed from MD simulation data and that this model be fully constrained by a sufficient number of state points to adequately embody the topological features of the energy surface. Once thermodynamic models for multicomponent liquids are available for instance, solid-liquid equilibria and the phenomenon of melting can be better explored using all the standard tools of equilibrium thermodynamics.

Perhaps the best way to illustrate the arguments of the previous paragraph is to develop an example of thermodynamic analysis of EPPMD data in LSS that we have recently calculated for MgSiO₃ liquid (Spera et al., 2010; see also Nevins et al., 2009). The data are obtained using NEV simulation and the pair-potential from Oganov et al. (2001), derived specifically for MgSiO₃ composition based on DFT calculations and semi-empirical methods utilizing ionization potential, electron affinity and other chemical properties for O, Mg and Si. The Oganov pair-potential energy between two atoms *i* and *j* has the Buckingham (1938) form:

$$V(r_{ij}) = \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} + A_{ij} e^{-\frac{r_{ij}}{B_{ij}}} - \frac{C_{ij}}{r_{ij}^6}$$
(1)

where q_i , q_j are the effective charges on species *i* and *j*, r_{ij} is the distance between the pair *i-j*, *e* is the charge of the electron, ε_0 , is the vacuum permittivity, A_{ij} and C_{ij} are energy parameters describing repulsive and van der Waals attractive forces, respectively and B_{ij} is a e-folding length characterizing the radiallysymmetric decay of electron repulsion energy between atom pair *i-j*.

In Figure 3 we illustrate results of 72 EPPMD LSSs of MgSiO₃ liquid (N=8000) based on the Oganov pair-potential. These results are typical of state

point grids computed by NEV MD in that computations are performed along chosen isochors with internal energies selected to map out isotherms. The state points in Figure 3 have uncertainties in pressure smaller than the size of the symbols, a direct consequence of using 8000 atoms in the simulations. The associated temperature fluctuations are on the order of 25 K. These results constitute a data set from which a thermodynamic model may be constructed.

How to go about making this thermodynamic model generates some important considerations. The rule is: always formulate first an expression for the energy (either the internal energy, enthalpy, Helmholtz energy, or Gibbs free energy) and formally manipulate this expression using thermodynamic identities to retrieve internally consistent equations for the derivative properties. Importantly, when formulating a thermodynamic model for any substance, one should not start by fitting an EOS — that is a relationship between pressure, temperature and density or volume — to the data set, unless it can be established that the EOS is a proper derivative of an energy function; in this context a necessary (but not sufficient condition) is that the thermodynamic identify:

$$V\alpha K + K\frac{\partial\alpha}{\partial P} = V + \frac{1}{K}\frac{\partial K}{\partial T}$$
(2)

(Prigogene and Defay, 1954; *V* is the volume, α is the isothermal coefficient of thermal expansion, *K* is the isothermal bulk modulus, *T* is the temperature, and *P* is the pressure) must hold for any adopted EOS.

A thermodynamic model will be created for these MD data by developing an equation for the Helmholtz energy. As a staring point we will use a temperature-potential energy scaling law derived by Rosenfeld and Tarazona (1998) from a fundamental-measure energy functional for hard spheres and thermodynamic perturbation theory. Their postulated expression relates the potential energy (E_P) of a substance to temperature according to

$$E_{P} = a + bT^{\frac{3}{5}}$$
(3)

where a and b are unspecified functions of volume but not temperature (note that at absolute zero, *a* is identical to the internal energy of the material). One does not need to assume that Equation (3) holds; MD simulation results can be used to test the applicability of Rosenfeld-Tarazona (RT) scaling to dense high temperature silicate liquids. Clearly, when MD generated values of E_P are plotted versus $T^{3/5}$, linear correlations are expected if RT scaling is valid. Potential energy-temperature relations are plotted in Figure 4 for the state point arrays shown in Figure 3. Indeed, RT scaling holds with model errors on the order of 0.01% in $E_{P.}$ We have found previously (Nevins et al., 2009; Martin et. al., 2009; Ghiorso et al., 2009; Spera et al., 2009) that the Rosenfeld-Tarazona scaling law applies equally well to a wide variety of silicate melts - polymerized and unpolymerized, strong and fragile - over a broad range of compressions and temperatures. Although originally proposed to be applicable to "cold, dense" liquids, RT scaling appears to extend to "hot, dense" geoliquids as well. It is important to emphasize that application of RT scaling to thermodynamic modeling of silicate

liquids is an assumption that is easily tested directly using simulation results. To date, this test has succeeded in every case that we have examined.

From Equation (3), the internal energy (E) is given by

$$E = E_P + \frac{3n}{2}RT \tag{4}$$

where *n* is the number of atoms in the formula unit of the simulated substance (i.e., for MgSiO₃, n = 5) and *R* is the universal gas constant in units of energy/g-K. The right-hand term in Equation (3) is the classical high-temperature limit of the kinetic energy, which can be shown to hold for these MD simulation results (to within 0.01%). Substitution of Equation (3) into Equation (4) gives a Rosenfeld-Tarazona compatible model expression for the internal energy

$$E = a + bT^{\frac{3}{5}} + \frac{3n}{2}RT$$
(5)

A derivation of the Helmholtz energy (*A*) from Equation (5) was first developed by Saika-Voivod et al. (2000). Following their algorithm, we start with the thermodynamic identity,

$$A = E - TS \tag{6}$$

which illustrates that the Helmholtz energy depends on the entropy of the system (S). Fortunately, an expression for entropy is easily constructed. Start by writing the total derivative of S as

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V} dT + \left(\frac{\partial S}{\partial V}\right)_{T} dV$$
(7)

The two partial derivatives in Equation (7) may be rewritten using the first law of thermodynamics (dE = TdS - PdV, under the assumption of reversibility) as

$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_{V} dT + \left[\frac{1}{T} \left(\frac{\partial E}{\partial V} \right)_{T} + \frac{P}{T} \right] dV$$
(8)

and this expression may be integrated along a path from some reference volume (V_0) and reference temperature (T_0) to V, T_0 and then from V, T_0 to V, T:

$$S - S_{V_0,T_0} = \frac{1}{T_0} \int_{V_0}^{V} \left[\left(\frac{\partial E}{\partial V} \right)_T + P_{T_0} \right] dV + \int_{T_0}^{T} \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V dT$$
(9)

Substitution of Equation (5) into Equation (9) and carrying out the integrations results in a Rosenfeld-Tarazona compatible model expression for the entropy

$$S = S_{V_0,T_0} + \frac{1}{T_0} \left[a - a_{V_0} + T_0^{\frac{3}{5}} \left(b - b_{V_0} \right) + \int_{V_0}^{V} P_{T_0} \, dV \right] - \frac{3}{2} \left(\frac{1}{T^{\frac{2}{5}}} - \frac{1}{T_0^{\frac{2}{5}}} \right) b + \frac{3n}{2} R \ln \left(\frac{T}{T_0} \right)$$
(10)

The subscripts V_0 and T_0 denote evaluation of the quantity under the specified conditions. It is worth noting that the entropy can only be known to within an arbitrary constant (S_{V_0,T_0}). From Equations (6) and (10) the Helmholtz energy may be written:

$$A = a + T^{\frac{3}{5}}b + \frac{3n}{2}RT - TS_{V_0,T_0} - \frac{T}{T_0} \left[a - a_{V_0} + T_0^{\frac{3}{5}} \left(b - b_{V_0} \right) + \int_{V_0}^{V} P_{T_0} \, dV \right] + T \frac{3}{2} \left(\frac{1}{T^{\frac{2}{5}}} - \frac{1}{T_0^{\frac{2}{5}}} \right) b - \frac{3n}{2}RT \ln \left(\frac{T}{T_0} \right)$$
(11)

and by standard thermodynamic transformations both the Gibbs free energy (G = A + PV) and the enthalpy (H = E + PV) may be derived from Equations (5) and (11).

A Rosenfeld-Tarazona compatible EOS is obtained from Equation (11) by differentiation,

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T} = \left(\frac{T}{T_{0}} - 1\right)\frac{da}{dV} + \frac{5}{2}T^{\frac{3}{5}}\left[\left(\frac{T}{T_{0}}\right)^{\frac{3}{5}} - 1\right]\frac{db}{dV} + \frac{T}{T_{0}}P_{T_{0}}$$
(12)

There are several interesting features of this expression that are worth taking a moment to ponder. Let us first focus on the last term in the expression involving P_{T_0} . This term is the pressure variation along the T_0 isotherm. To evaluate it, either the ρ -P relations of state points along some reference isotherm must be interpolated or alternately, these points may be fitted to some appropriate function. Of course, this function would be nothing more than an *isothermal* equation of state, such as the 3rd order Birch-Murnaghan equation (Birch, 1939, 1952):

$$P_{T_0} = \frac{3}{2} K \left(x^7 - x^5 \right) \left[1 - \frac{3}{4} \left(4 - K^{\dagger} \right) \left(x^2 - 1 \right) \right], \ x = \left(\frac{V_{T_0, P_0}}{V_{T_0}} \right)^{\frac{1}{3}}$$
(13)

which is derived from strain theory, or the Universal EOS (Vinet et al., 1986):

$$P_{T_0} = \frac{3K(1-x)e^{\eta(1-x)}}{x^2}, \ \eta = \frac{3}{2}(K'-1), \ x = \left(\frac{V_{T_0}}{V_{T_0,P_0}}\right)^{\frac{1}{2}}$$
(14)

which is derived from a generalized bonding potential function, or alternately by a purely empirical expression (e.g. Saika-Voivod et al., 2000):

$$P_{T_0} = \sum_{i} \frac{C_i}{V_{T_0}}$$
(15)

In all cases, the parameters of the representations (V_{T_0,P_0} , K, K', c_i) are constants.

The temperature dependence of the pressure in the EOS embodied in Equation (12) is determined in part from scaling P_{T_0} by T/T_0 and in part from the volume

dependence of the intercepts and slopes of the E_P versus $T^{3/5}$ relations. The functional form of this expression is not necessarily compatible with alternate temperature dependent extensions of the more commonly used equations of state, for example the thermal pressure correction to the Universal EOS (Vinet et al., 1987) or the Mie-Grüneisen extension of the Birch-Murnaghan equation. The reverse is also true: These alternate temperature-dependent EOS formalisms will

not recover the E_P vrs. $T^{3/5}$ scaling of Rosenfeld-Tarazona theory. In other words, the practice of applying a "pressure correction" to the Universal or Birch-Murnaghan EOS is generally incompatible with RT scaling.

In order to use Equation (12) in practice for the dataset displayed in Figure 3 we must obtain a(V) and b(V) as differentiable functions of volume and we must select a way to represent P_{T_0} . A polynomial expansion in volume works well

for the Rosenfeld-Tarazona parameters, i.e.

$$a = \sum_{i=0}^{N} a_i V^i, \quad b = \sum_{i=0}^{N} b_i V^i$$
(16)

2/ T

(Fig. 5) and the Universal EOS (Eqn. 14) recovers the ρ -P relations along the 4000 K isotherm (with $V_0 = 0.408031$ cc/g, K = 13.6262 GPa, and K' = 7.66573). The smooth curves plotted in Figure 3 are computed from this parameterization and Equations (5) and (12).

Having derived a thermodynamic model from the MD state points, one may explore a few derivative thermodynamic properties as an illustration. The temperature derivative of the pressure (Eqn. 12) along an isochore is the "thermal pressure" coefficient, which for the Rosenfeld-Tarazona form is given by г

$$\alpha K = \left(\frac{\partial P}{\partial T}\right)_{V} = \frac{1}{T_0} \frac{da}{dV} + \frac{3}{2} T^{-\frac{2}{5}} \left[\frac{5}{3} \left(\frac{T}{T_0}\right)^{\frac{2}{5}} - 1\right] \frac{db}{dV} + \frac{P_{T_0}}{T_0}$$
(17)

and is equal to the product of the isothermal coefficient of thermal expansion (α) and the isothermal bulk modulus (K). Plots of the thermal pressure coefficient for our example liquid are shown in Figure 6. For many solids, αK is approximately a constant, and this fact is utilized in many temperature-dependent EOS formulations, including that of Vinet et al. (1987). The constancy of αK is certainly not the case for simulated MgSiO₃ liquid and one reason for this may be rooted in the observation that the structure (cation-oxygen coordination) of this liquid changes dramatically as a function of pressure below ~50 GPa (this issue is investigated in greater detail below). The pressure variation of the bulk modulus,

$$K = -\left(\frac{T}{T_0} - 1\right) V \frac{d^2 a}{dV^2} - \frac{5}{2} T^{\frac{3}{5}} \left[\left(\frac{T}{T_0}\right)^{\frac{3}{5}} - 1 \right] V \frac{d^2 b}{dV^2} - \frac{T}{T_0} V \frac{dP_{T_0}}{dV}$$
(18)

by contrast behaves as might be expected of a typical solid and to first order (and perhaps surprisingly) is linear and not influenced by changes in melt structure. It follows then that the isothermal coefficient of thermal expansion,

$$\alpha = -\frac{\frac{1}{T_0} \frac{da}{dV} + \frac{3}{2} T^{-\frac{2}{5}} \left[\frac{5}{3} \left(\frac{T}{T_0} \right)^{\frac{2}{5}} - 1 \right] \frac{db}{dV} + \frac{P_{T_0}}{T_0}}{V \left\{ \left(\frac{T}{T_0} - 1 \right) \frac{d^2a}{dV^2} + \frac{5}{2} T^{\frac{3}{5}} \left[\left(\frac{T}{T_0} \right)^{\frac{2}{5}} - 1 \right] \frac{d^2b}{dV^2} + \frac{T}{T_0} \frac{dP_{T_0}}{dV} \right\}}$$
(19)

will exhibit a pressure dependence reflecting the non-linearity in αK and that is borne out by the MD simulation data (Fig. 7). These observations (Figs. 6 and 7) demonstrate an interesting generalization about the thermodynamic properties of liquids that undergo a strong pressure dependent cation-oxygen packing. If a matrix of second partial derivatives (the Hessian matrix) is formed of any energetic potential that fully characterizes the thermodynamic state of the liquid, say the Helmholtz free energy, then the on-diagonal elements of that matrix, e.g.,

$$\frac{\partial^2 A}{\partial V^2} = -\frac{\partial P}{\partial V} = \rho K \tag{20}$$

and

$$\frac{\partial^2 A}{\partial T^2} = -\frac{\partial S}{\partial T} = -\frac{C_V}{T} = \frac{3}{5} \frac{b(V)}{T^{\frac{1}{5}}} - \frac{3n}{2} \frac{R}{T}$$
(21)

will not be strong functions of the changes in cation-oxygen packing. This conclusion is illustrated in Figure 8 by noting that the pressure dependence of the plotted quantities is not dramatically different below 50 GPa, where SiO^[4] and SiO^[5] dominate (see below), when compared to higher pressures, where SiO^[6] dominates². By contrast, the off-diagonal Hessian elements, e.g.,

$$\frac{\partial^2 A}{\partial T \partial V} = -\frac{\partial P}{\partial T} = -\alpha K \tag{22}$$

will reveal a sensitivity to melt structure, as illustrated in Figure 6, where the pressure-dependence of the thermal pressure coefficient is seen to be dramatically different below and above 50 GPa. The on-diagonal Hessian elements are responding to the bulk properties of the liquid, what in the thermodynamics of solid solutions is normally referred to as the vibrational contribution to the energy. Energetic contributions arising from changes in the basic configurational units or building blocks that comprise the liquid are typically second order and while present in the on-diagonal elements, they are overwhelmed by the vibrational contribution and are only readily detectable in the off-diagonal terms of the Hessian. These considerations explain why the thermal Grüneisen parameter,

$$\gamma = \frac{\alpha K V}{C_V} \tag{23}$$

which is essentially a scaling of the thermal pressure coefficient, displays such a strong dependence on pressure below 50 GPa and essentially no pressure dependence above that (Fig. 9).

Polyamorphism

A thermodynamic model that has been constructed from LSS MD data can be used to investigate the topology of the energy surface and to probe that topology for evidence of phase instability. This is an especially useful technique when

² Notation: XY^[n] implies *n* atoms of type "Y" surround, in nearest neighbor coordination, the central atom "X."

it is applied to simulation data on liquids, where an analysis of the topology of the energy surface affords an understanding of the phenomena of polyamorphism. Polyamorphism refers to the equilibrium coexistence of two or more amorphous phases that have the same composition, temperature and pressure but differ in structure and hence density. It is analogous to polymorphism which occurs when a crystalline phase undergoes a phase transition from one structural form to another (e.g. quartz to coesite) and is similar to compositional unmixing, which occurs in isostructural solid and liquid solutions when phases of differing composition coexist in thermodynamic equilibrium.

Polyamorphism has been observed experimentally in liquid phosphorous (Katayama et al., 2000, 2004) and other compounds and has been identified in molecular dynamics studies of liquid H₂O (Poole et al., 2005), SiO₂ (Saika-Voivod et al., 2000), and liquid CaAl₂Si₂O₈ (Ghiorso et al., 2009). Tanaka (2000) discusses the thermodynamics of polyamorphism and presents methods for developing models that describe its energetic consequences.

A sufficient criteria for the development of polyamorphism is violation of the so-called condition of mechanical stability (Prigogene and Defay, 1954) which states that the derivative, $\partial^2 A / \partial V^2$ must be positive for a homogeneous phase. This condition is equivalent to K > 0 (Eqn. 20). Using the Rosenfeld Tarazona EOS (Eqn. 12), the locus of points that define a zero in *K* is:

$$0 = -\left(\frac{T}{T_0} - 1\right)\frac{d^2a(V)}{dV^2} - \frac{5}{2}T^{\frac{3}{5}}\left[\left(\frac{T}{T_0}\right)^{\frac{2}{5}} - 1\right]\frac{d^2b(V)}{dV^2} - \frac{T}{T_0}\frac{dP(T_0, V)}{dV}$$
(24)

and a solution of this expression corresponds to an implicit surface in *V*-*T*-*P* space. This surface is known as the spinodal. Note, that although pressure is not explicit in Equation (24), its value is implied by any (*V*,*T*) pair *via* the EOS (Eqn. 12, or equivalent). Equation (24) or its equivalent is usually solved by selecting a *T* or *V* (=1/ ρ) and calculating the remaining variable by iteration. This process will always result in either two real roots, one real root, or two complex roots. Solutions of the first kind correspond to the limbs of the spinodal, while a solution of the second kind gives the critical point for the onset of unmixing.

Utilizing the Rosenfeld-Tarazona EOS calibrated above for MgSiO₃ liquid, we can illustrate calculation of the spinodal and its critical end point. Our first consideration in performing this examination is to consider qualitatively the topology of the energy surface and address the question of whether we expect polyamorphism to occur at all. The answer is "yes" and we know this by examining the Helmholtz energy in the low-temperature limit. From Equation (11), $\lim_{T\to 0} A = a$, which tells us that in a thermodynamic model of the liquid that follows a

Rosenfeld-Tarazona scaling law, the variation of Helmholtz free energy at zero T is simply given by a(V). This function is plotted in Figure 5a, and we note that the curve has two points of inflection, which means that within the volume interval

cally unstable. The inflection points are the limbs of the spinodal, in this case at zero kelvin. It is also worth noting from Figure 5a that the limbs of the spinodal *do not* correspond to the densities of hypothetical equilibrium coexisting liquid phases. These equilibrium compositions are exterior to the spinodal, that is at both lower and higher densities than the spinodal points, and are defined by the intersection of a line of mutual tangency to the *a*(*V*) curve at both locations.

Now that we know that a spinodal exists for this liquid, we can solve Equation (24) by choosing suitable temperatures, finding volume-roots until a temperature is reached — the critical temperature (T_c) — where the points of inflection coalesce to a single critical volume (V_c) or density (ρ_c). The results of these calculations are plotted in Figure 10 for our example LSS MgSiO₃ data set. We find that in this case the critical point for liquid-liquid unmixing is at a temperature well below the stable liquid field, that is within the thermodynamic stability field of solid MgSiO₃ (enstatite), so it is very unlikely that polyamorphism will ever be observed in this liquid. However, other silicate liquid compositions, such as CaAl₂Si₂O₈ liquid, appear to have critical end points for liquid-liquid unmixing within the stable liquid field (Ghiorso et al., 2009), a prediction that awaits verification by physical experimentation. The general expectation is that polyamorphism is an expected phenomena in molten silicates because they tend to form strongly bonded covalent localized structural units (Kurita and Tanaka, 2005).

Hugoniot

One final example of what can be done with a thermodynamic model derived from LSS MD studies involves calculation of the shock-wave Hugoniot. The Hugoniot is a univariant curve in *V-T-P*-space that characterizes the final states of a series of shock experients of varying intensity that originate from the same set of initial conditions (Anderson, 1989). The Hugoniot curve is modeled by finding *V-T-P* points that simultaneously satisfy an EOS and a constraint

$$E - E_{i} = \frac{1}{2} (P - P_{i}) (V_{i} - V)$$
(25)

(Anderson, 1989) that results from a combination of the conservation of mass, momentum and energy equations. The subscript *i* refers to the initial shock conditions.

For a substance that obeys the Rosenfeld-Tarazona EOS (Eqn. 12), Equation (25) reduces to

$$C_1 T^{\frac{3}{5}} + C_2 T = C_3 \tag{26}$$

where

$$C_1 = b + \frac{5}{4} \frac{db}{dV} \left(V_i - V \right) \tag{27}$$

$$C_{2} = \frac{3n}{2}R - \frac{V_{i} - V}{2T_{0}} \left(\frac{da}{dV} + \frac{5}{2}T_{0}^{\frac{3}{5}}\frac{db}{dV} + P_{T_{0}}\right)$$
(28)

and

$$C_{3} = a_{V_{i}} - a + \frac{1}{2} \left(\frac{da}{dV} \Big|_{V_{i}} - \frac{da}{dV} \right) (V_{i} - V) + T_{i}^{\frac{3}{5}} \left(b_{V_{i}} + \frac{5}{4} \frac{db}{dV} \Big|_{V_{i}} (V_{i} - V) \right)$$

$$+ T_{i} \left[\frac{3n}{2} - \frac{V_{i} - V}{2T_{0}} \left(\frac{da}{dV} \Big|_{V_{i}} + \frac{5}{2} T_{0}^{\frac{3}{5}} \frac{db}{dV} \Big|_{V_{i}} + P_{T_{0}} \right) \right]$$
(29)

In Figure 11 we plot a calculated Hugoniot for our example MgSiO₃ liquid for initial conditions of 1832 K and zero pressure (the metastable melting temperature for enstatite). The inset of this figure shows the Hugoniot curve translated into alternate coordinates

$$U_{s} = V_{i} \left(\frac{P - P_{i}}{V_{i} - V}\right)^{\frac{1}{2}}, \quad U_{p} = \left[\left(P - P_{i}\right)\left(V_{i} - V\right)\right]^{\frac{1}{2}}$$
(30)

where U_s and U_p are the shock and particle velocities, respectively. The calculated Hugoniot shows very high-shock temperatures at elevated pressures (~10000 K at 125 GPa). For comparison, we have also plotted an isentrope for this liquid calculated by solving Equations (10) and (12) simultaneously while holding the system entropy at a value defined by the initial conditions of the shock. Note that the isentrope also climbs in T with increasing P, but far less dramatically than the Hugoniot. The data points are from Akins et al. (2004) with properties inferred from the experimental shock wave studies of solids and glasses that underwent melting during compression.

STRUCTURAL FEATURES

LSS MD studies are ideally suited for investigation of structural changes that take place in a substance as a function of *T* and *P*. This is especially true for non-crystalline materials, where the absence of both long-range order and lattice symmetry constraints requires the statistical evaluation of nearest neighbor atomic coordinations to fully characterize the structural state. The difficulty of this task is further exacerbated if the material is chemically complex, because under these circumstances more atoms are required to sample all possible structural configurations. As an example, consider the LSS MD study on MgSiO₃ used in the previous section. For amorphous substances, short-range nearest neighbor structure is determined by statistical analysis of atom locations using partial pair correlation functions (radial distribution functions, RDF) expressed as:

$$g_{ij}(r) = \frac{V}{N^2} \left\langle \sum_{i=1}^{N} \sum_{j=1, i \neq j}^{N} \delta(r - r_{ij}) \right\rangle$$
(31)

For two atoms *i* and *j*, Equation (31) gives the normalized averaged distribution of atom *i* around a central *j* atom within a defined cut off distance. *V* is the volume of

atom corresponding to the first minimum in the RDF that follows the first maximum. This cut off distance is uniquely determined by the position of the minimum for each isobar shown in Figure 12. We plot these average O-O coordination numbers in Figure 13, along with values calculated in an identical way from RDFs for oxygen about silicon and oxygen about magnesium. The results in this example are fascinating for a variety of reasons. The most striking observation is the abrupt change in average coordination number of O-O between about 65 and 85 GPa. What is happening is that the minimum in the O-O RDF abruptly shifts location over this pressure interval, as can be seen in Figure 12 (with details illustrated in the inset). The same abrupt shift in minima location is *not* displayed by the RDFs for Si-O or Mg-O, and one can see from Figure 13 that the bulk liquid density, which is essentially a linear function of average Si-O coordination number, does not respond to this fundamental rearrangement of the oxygen packing. We will see later that the transport properties are affected by this rearrangement.

atom. By convention, the average coordination number of oxygen about oxygen is defined by numerical integration of $g_{\Omega,\Omega}(r)$ up to a distance from the central

Further details of the structural variation can be scrutinized by counting the number of configurations of a given kind up to the cut-off radius of the RDF and forming a distribution of occurrences of each unit. For example, in the case of oxygen about oxygen, we would count the number of OO^[1], OO^[2], OO^[3], etc., that are found within the cut off radius for each oxygen atom in the simulation and average these quantities to obtain a probability distribution or number abundance of particular configurations. This procedure allows us to examine the "speciation" of the liquid as a function of changing intensive variables. Figure 14 shows these results along a ~3500 K isotherm for the liquid, and from them one can visualize the changes in Si-O coordination as a function of pressure and understand better the oxygen about oxygen rearrangements that accompany the abrupt change in average coordination number.

Microscopic to macroscopic

One of the great advantages of calculating an extensive array of state points using MD simulations of materials is the opportunity to explore the relationship between the microscopic and the macroscopic, that is, the relation between structural change and the variation in bulk physical properties. We have already seen for example that qualitatively the bulk density of our example MgSiO₃ liquid is strongly correlated to the average oxygen coordination number of silicon (Fig. 13). There are a number of approaches to making these relationships more quantitative and to explore more deeply the kinds of structural transformations that accompany changes in T and P. In a liquid like MgSiO₃ for instance, the variation in oxygen coordination number of Si is probably not independent of that of Mg, since the same oxygen atoms are likely involved in both cation coordination polyhedra. The degree of correlation amongst changes in structural features that take place as a function of T and P, reduces the number of degrees of freedom and directly impacts the *configurational* entropy associated with the effects.

A simple way to visualize these correlations is to construct a cluster dendrogram from a correlation coefficient matrix that is in turn constructed from the abundances of various species or configurational units along a specified isobar or isotherm. For example, Figure 15 illustrates a cluster dendrogram obtained from examination of the abundances of cation-oxygen and oxygen-oxygen nearest neighbor coordination polyhedra at 12 state points along the ~3500 K isotherm for our MgSiO₃ example liquid. For those unfamiliar with cluster analysis, the degree of correlation is represented by vertical linkages which are positioned to indicate high to low correlation by their location right to left on the diagram. Thus, SiO^[6] and MgO^[7] are very highly correlated as are SiO^[7] and MgO^[9], but the first group is more weakly correlated to the second. All four configurations however, are uncorrelated to the abundance of SiO^[4]. The dendrogram enables a visual assessment of the extent of correlation between structural units in the liquid and from it we can conclude that there are essentially three principal groupings or combinations of structural units that vary independently as a function of pressure along the isotherm. This result is important because it emphases that the number of "independent" modes of structural variation is three, despite the myriad ways of counting the atomic configurations.

To further quantify this assessment of structural correlation, a principal component analysis (PCA) can be performed on the same matrix of correlation coefficients (R) used in making the cluster dendrogram of Figure 15. PCA performs an eigenvector/eigenvalue decomposition of the R-matrix, yielding weighted linear combinations (eigenvectors) of the abundances of structural configurations and the amount of variance (eigenvalue) associated with each linear combination. The eigenvectors are, of course, uncorrelated and may be ranked in order of decreasing variance. As would be expected from our dendrogram, we find that the first three eigenvectors account for 99% of the variance, so there are only three independent measures of structural variation operative in this example. The coefficients of these three principal eigenvectors demonstrate which of the original structural configurations contribute and in what proportion. These coefficients are plotted on the bar graph in Figure 16. Focusing just on the first eigenvector, we can see that it embodies the transformation from low- to highcoordination number of O about Si,Mg. The second eigenvector largely accounts for intermediate Si-O, Mg-O and O-O configurations, while the third captures the O-O coordination number shift at pressures of ~ 70 GPa. With the PCA, we can make the quantitative connection between structure and some macroscopic property.

We will illustrate this connection by constructing an equation for the volume of MgSiO₃ liquid on the assumption of ideal mixing of Si-O, Mg-O, and O-O configuration units, i.e.

$$V = \sum_{i} v_{\text{Si},i} \left\{ \text{SiO}^{[i]} \right\} + \sum_{i} v_{\text{Mg},i} \left\{ \text{MgO}^{[i]} \right\} + \sum_{i} v_{\text{O},i} \left\{ \text{OO}^{[i]} \right\}$$
(32)

where the $v_{x,i}$ are partial molar volumes of the "species" XO^[i] and the curly brackets denote the fractional abundance of each which respect to the total Si, Mg and O in a mole of MgSiO₃. The analysis of the previous paragraphs shows that not all XO^[i] species vary in abundance independently. To fit the model embodied in Equation (32), regression techniques that deal properly with this correlation must be employed. One such technique is Singular Value Analysis (SVA, Press et al., 1999) which uses PCA to estimate the number of "independent" variables in the least squares problem and performs the regression analysis in this "reduced" variable space. The output of a SVA procedure is a set of regression coefficients on the original correlated variables that are not overdetermined because they incorporate the intrinsic correlation determined from the PCA analysis. We use SVA to fit Equation (32) to the volume-structure data for MgSiO₃ liquid along the 3500 K isotherm; the three principal eigenvectors of structure variation (Fig. 16) are used to perform the regression. The model coefficients so obtained are plotted in Figure 17. The model recovers the volume of the liquid along the entire isotherm with errors on recovery never exceeding 1%.

The first thing that should be noticed about the model "partial molar volumes" plotted in Figure 17 is that the trends for each element form a logical pattern. There is a general decease in the intrinsic volume of SiO^[1] and MgO^[1] units as *i* increases; the reversal of this trend for i > 7 (Si) and > 9 (Mg) may be real or may be an artifact of low abundances of these configurations in the liquid (Fig. 14). The minimum in volume of OO^[12] is especially interesting. An icosahedron or polyhedron with 20 faces and 12 vertices is one of the classical Platonic solids and represents an optimal way to pack equal volume spheres. The volume of a single regular oxygen icosahedron is about 2.18 d_0^3 where d_0 is the diameter of an oxygen anion. Taking the diameter of oxygen to be 0.275 nm gives a volume of 27.3 cc/mol for a mole of oxygen icosahedra, surprisingly close to the volume minimum for the OO^[12] species shown on Figure 17. Perhaps the most important consequence of this analysis is the realization that once volume is successfully parameterized in terms of abundances of structural units in the liquid, then the internal energy and all dependent thermodynamic properties are similarly parameterized because E is consistent with the Rosenfeld-Tarazona scaling law (Eqn. 5). The a(V) and b(V) functions of volume (Fig. 5) now become functions of melt structure. Obviously, this analysis could be pursued farther by investigating multiple isotherms and developing a more comprehensive formalism, but we will not develop the example further here. We hope that we have illustrated, however, the potential for LSS MD studies to elucidate the relationship between microscopic and macroscopic properties and to demonstrate the importance of carrying out a comprehensive post-simulation analysis of MD results so that variation of physical properties can be understood in the context of fundamental measures of material structure.

TRANSPORT PROPERTIES

We turn now from discussing static equilibrium properties determined from LSS MD studies to the estimation of transport properties. By transport properties we mean diffusivity, viscosity, thermal conduction, and related irreversible phenomena that can be studied by examining dynamical fluctuations within the simulation volume. Even more so than with equilibrium properties, the estimation of transport properties by MD benefits enormously from LSS and especially from long-duration simulations (Fig. 1). Here we focus upon the shear viscosity of liquid MgSiO₃ and related self-diffusion of O, Si and Mg. Once again, we will emphasize the strong correlation that exists between the macroscopic and microscopic worlds.

Viscosity

Shear viscosity can be computed from LSS MD results using linear response theory embodied as the Green-Kubo (GK) relations. Shear viscosity is determined by studying the temporal decay of appropriate stress components (both off and on-diagonal; Rapaport, 1995). The GK expression for the shear viscosity is given by integration of the stress (pressure) autocorrelation function,

$$\eta = \frac{V}{3kT} \int_0^\infty \left\langle \sum_{x < y} \sigma_{xy}(t) \sigma_{xy}(0) \right\rangle dt$$
(33)

where η is the shear viscosity, *V* is the system volume, *T* is the temperature, *k* is Boltzmann's constant, and σ_{ij} refers to the *ij* component of the stress tensor. In addition to σ_{xy} , used in Equation (33), the decay of temporal autocorrelations: σ_{xz} , σ_{yz} , ($\sigma_{xx} - \sigma_{yy}$) and ($\sigma_{yy} - \sigma_{zz}$), also provide independent GK values for the shear viscosity. The reported MD-derived viscosity at a given state point is the average of the five independently computed values following the method detailed in Nevins and Spera (2007). Viscosity estimates are made from long simulation runs of ~2 ns, with a sampling window width of ~2, ~5, or ~10 ps, and a time interval between the start of successive sampling windows of ~10 fs. As an approach is made to the computer glass transition, longer and longer simulation durations are required in order to compute a precise shear viscosity. Details may be found in the study of Morgan and Spera (2001).

Continuing with our example involving MgSiO₃ liquid, we plot in Figure 18 shear viscosity computed using the GK method at 17 state points along a nominal 3500 K isotherm. The viscosity increases by a factor of \sim 32 from low pressure to 100 GPa and is extrapolated to increase by a factor of 110 across the entire terrestrial mantle (to the core-mantle boundary at 135 GPa). This increase

has important dynamical implications for convective mixing, chemical stratification and crystal fractionation in the terrestrial planet magma oceans. The activa-

tion energy (Q) for viscous flow, defined from the Boltzmann relation, $\eta \sim e^{Q/RT}$,

has a pressure dependence of ~1 cc/mol, but Figure 18 demonstrates that there is an abrupt change in slope in $\log_{10} \eta$ versus *P* at ~70 GPa. This decrease in *Q* occurs over the same pressure interval where the oxygen about oxygen coordination polyhedra display a dramatic reconfiguration (Fig. 14a). Recall, that over the same pressure interval there are no significant rearrangements of Si-O or Mg-O configurations (Figs. 14b,c) nor are there significant perturbations in pressure dependences of the thermodynamic properties, demonstrating that in this liquid the anion-anion oxygen packing strongly influences relative atomic motion and by inference other transport phenomena. The average oxygen about oxygen coordination number in the high-pressure region is ~11, quite close to the maximum packing efficiency associated with icosahedra. The difference from the ideal limit of CN=12 may be related to the irregularity of packing presumably associated with the agitated thermal state or intrinsic mobility of oxygen in the hightemperature (~ 3500 K) liquid.

Self-Diffusivity

Another transport property that can be readily examined with LSS MD is self-diffusivity. In a continuous system, the diffusion coefficient D is defined by combining Fick's first and second laws to give,

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{34}$$

where C(r,t) is the local density or concentration of some atom as a function of position (*r*) and time (*t*). Equation (34) applies both to diffusion of one species through another in response to a spatial gradient in chemical potential and to self-diffusion, which is the relative motion of one species generated by dynamical fluctuations in an otherwise equilibrium state. MD results can be used to compute diffusivities associated with chemical potential gradients, but this requires more effort because the effects of all atoms must be taken into account; self-diffusivities are simpler to compute and are addressed here. At the discrete particle level concentration, *C* may be written using the Dirac delta function, $\delta(r)$, as

$$C(\vec{r},t) = \sum_{j=1}^{N_a} \delta(\vec{r} - \vec{r}_j(t))$$
(35)

For large *t*, the Einstein expression (McQuarrie, 2000) for the Mean Square Displacement (MSD) is related to the diffusion coefficient by

$$D = \frac{1}{6N_{a}t} \left\langle \sum_{j=1}^{N_{a}} \left[\vec{r}_{j}(t) - \vec{r}_{j}(0) \right]^{2} \right\rangle$$
(36)

where N_a refers to the number of atoms of species 'a' and the quantity in brackets represents the MSD of the a^{th} atom type. Unfolded atomic trajectories are used in the calculation of the self-diffusivity (Rapaport 1995). At each state point, the MSD for a particular species is accumulated from the unfolded atom trajectories and a plot of MSD *versus* time is made. Following a brief (< 1 ps) ballistic transport regime not of immediate interest, the MSD average over all atoms of the same type becomes linear, and the slope of this average is directly proportional to the self-diffusivity.

Self-diffusivity of O, Mg and Si are plotted in Figure 19 for our example MgSiO₃ liquid along the ~3500 K isotherm (see Nevins et al., 2009 for additional isotherms). At very low P (~ 0 GPa) there is a small region of "anomalous" diffusion for Si and O (and perhaps Mg) in which increasing pressure increases the diffusivity; there is also a cross over in Mg and O self-diffusivity at ~ 2 GPa. Of special significance are the breaks in slope ~70 GPa, where the rate of decrease of all diffusivities diminishes over a 10 GPa interval. This observation implies that

the activation volume (V_i^o) for tracer diffusion, given by $\begin{pmatrix} \partial \ln D_i \\ \partial P \end{pmatrix}_T = \frac{-V_i^o}{RT}$, is

smaller at this pressure, where the average O-O mean coordination number decreases abruptly, than at pressures above or below the transition interval. Just below this pressure the mean oxygen around oxygen CN is ~15 as noted on Figure 13. This packing polyhedra becomes unstable with respect to the more efficiently packed irregular icosahedra of mean CN ~11. Clearly, the oxygen packing exerts a first-order effect on the mobility of oxygen, especially its pressuredependence. The recurring theme is that microscopic structure does indeed map into macroscopic properties and that LSS allows one to investigate the connections rather easily.

Eyring relation

Because independent values of self-diffusivity and shear viscosity are available from the LSS MD simulations, the applicability of the Eyring et al. (1982) relation can be addressed. Typically the Eyring or closely-related Stokes-Einstein relation is used to estimate shear viscosity from self-diffusion data (or vice versa) by assuming a length scale ('size') of the atom or cluster of atoms involved in the activated process of atom mobility. Ambiguity generally arises, however, in selecting the 'size' of the activated cluster *a priori*.

The Eyring formulation is based on a phenomenological picture involving a jump of a particular atom from one coordination environment to another. These environments can be characterized by a size related to the atom cluster involved in the diffusive event. The Eyring relationship between self-diffusivity and viscosity is

$$\xi \left(\frac{V}{nN_A}\right)^{\frac{1}{3}} = \frac{kT}{D\eta} \tag{37}$$

where *n* is the number of atoms per formula unit, *V* is the molar volume, N_A is Avogadro's number and ξ +1 is the number of atoms in the activated complex.

The ratio $kT/\eta D$ defines a scale-length, λ , associated with the size of the "activated cluster" involved in atomic mobility and viscous shear flow. In Figure 20, both $kT/\eta D$ and ξ are plotted for oxygen along the nominal 3500 K isotherm for our MgSiO₃ example data set. As would be expected, λ decreases rapidly with pressure from around 1.8 nm at 1 bar to 0.2 nm for P ~150 GPa. The number of atoms (ξ +1) in the activated cluster changes from a ~7-9 at low pressure to a smaller activated unit of 2-3 atoms according to the Eyring relation. The plateau in λ and ξ for 65 < P < 85 GPa is consistent with the unusual behavior in the shear viscosity and self-diffusion discussed previously. The rapid reorganization of the oxygen packing in the melt over the interval 65-85 GPa abates but does not negate the trend in λ and ξ .

THE FUTURE - LSS IN THE CONTEXT OF FPMD

We close this chapter with a few remarks concerning the future of LSS MD studies. Historically, EPPMD is the method generally chosen for LSS. The reason for this is that large numbers of atoms can be used in the simulation without the prohibitive consumption of computing resources. The LAMMPS code (Plimpton, 1995) for example, a modified version (Nevins, 2009) of which was utilized for all of the example results provided in this chapter, has computational costs that scale as N log N for long-range forces, permitting calculations with large N to be handled routinely. By contrast, FPMD uses DFT for estimation of forces between atoms, and the majority of commonly used computational packages that implement this technique have computational costs that scale at N^3 (or the cube of the number of electrons, Ordejón et al., 2000). Of course, the advantage of a DFT description of atomic forces is that it is closer approximation to a complete guantum mechanical solution, and therefore presumably more accurate. While it may be argued that EPPMD on well characterized systems is entirely adequate as long as results are spot checked against FPMD, there is considerable more uncertainty involved in using EPPMD as an exploratory tool in temperature. pressure and composition regimes where the underlying pair-potential has not been adequately tested. And, as mentioned above, there are material calculations involving free electrons for example, that are simply beyond the capabilities of the EPPMD method. On the other hand, transport property estimates of shear viscosity and thermal conductivity are generally thought to be beyond the reach of current FPMD methodology.

The future for LSS based upon DFT is not gloomy, however. Computational advances (e.g. SIESTA: Soler, et al. 2002) demonstrate methods for the calculation of total energies and forces that scales linearly with the number of atoms in the system. Codes based on these algorithmic advances enable electronic structure and MD computations on larger systems (N~10³) with modest computational costs. In the near future, we can envision large-scale FPMD simulations of long duration, and the capability of creating a dense grid of state points that enclose the *P*-*T* range of interest. LSS using FPMD will potentially provide us with the best data source for thermodynamic modeling and exploration of the causal relationship between microscopic structure and macroscopic properties of geomaterials. This kind of calculation may very well be within reach in the not too distant future.

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Figure Legends

Figure 1. Typical time scales for various molecular dynamics calculations. The value

labeled as "Debye frequency" refers to the reciprocal of $\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}} v_s$, where *N* is the

number of atoms in the simulation, *V* is the volume and v_s is the sound speed of the material of interest; a typical value is shown.

Figure 2. Visual comparison of the number density of atoms an MD simulation with 100 atoms (left) and 8000 atoms (right). The atoms are randomly placed in the cube and do not overlap; all atoms are projected to the front face. Atoms are coded to indicate O, Si and Mg, with the overall stoichiometry: MgSiO₃.

Figure 3. EPPMD using LSS and the pair-potential of Oganov et al. (2001) on MgSiO₃ liquid. Results were computed using the NEV ensemble along 16 isochors at evenly spaced temperatures over the range 2500-5000 K. *Upper panel*: density (ρ) plotted as a function of pressure (*P*). *Lower panel*: Internal energy (*E*) plotted as a function of pressure uncertainty (i.e. MD pressure fluctuations) are smaller than the size of the symbols.

Figure 4. Test of the Rosenfeld-Tarazona (1998) scaling law for the data set of Figure 3. Potential energy (E_p) is plotted as a function of temperature (T). Deviations from the

linear scaling relation, $E_p = a(V) + b(V)T^{\frac{3}{5}}$, are less than 0.01%.

Figure 5. Polynomial functions fitted to the slopes (*b*) and intercepts (*a*) of the Rosenfeld-Tarazona scaling relations (Fig. 4), parameterized as a function of specific volume (V). Uncertainties on *a* and *b* are plotted as one sigma and are derived from fitting straight lines to the scaling relations.

Figure 6. Thermal pressure (=aK) for the data set of Figure 3. The points are calculated by finite difference of simulation results along computed isochors. Uncertainties are plotted as one sigma and estimated by error propagation. The curves are model estimates calculated from Equation (17).

Figure 7. The isothermal coefficient of thermal expansion (α) for the data set of Figure 3. The points are calculated by finite difference of simulation results and uncertainties are plotted as one sigma and estimated by error propagation. The curves are model estimates calculated from Equation (19).

Figure 8. Evaluation of the on-diagonal terms of the Hessian matrix of the Helmholtz energy for the data set of Figure 3. The points are calculated by finite difference of simulation results and uncertainties are plotted as one sigma and estimated by error propagation. The curves are model estimates calculated from Equation (21) (Fig. 8a) and Equation (20) (Fig. 8b).

Figure 9. The thermal Grüneisen parameter (Υ) for the data set of Figure 3. The points are calculated by finite difference of simulation results and uncertainties are plotted as

one sigma and estimated by error propagation. The curves are model estimates calculated from Equation (23).

Figure 10. Evaluation of the critical phenomena for liquid-liquid unmixing in MgSiO₃ liquid based upon the data set of Figure 3. The critical point for the onset of unmixing is shown by the *large dot*; its critical density, pressure and temperature are indicated. The *heavy curve* traces the spinode, which encloses a region of mechanical instability. The remaining curves are isotherms calculated from the model EOS (Eqn. 12).

Figure 11. Calculated Hugoniot curve (Eqns. 16-28; *heavy curve*) and isentrope (Eqn. 10; *normal curve*) for MgSiO₃ liquid based upon the data set of Figure 3. *Dashed curves* are isotherms calculated from the model EOS (Eqn. 12). The dots indicate coordinates obtained from shock waves studies (Akins et al., 2004) and are labeled according to estimated shock temperature. The inset shows the Hugoniot curve mapped into the alternate coordinate space defined in terms of particle (U_p) and shock (U_s) velocities.

Figure 12. Radial distribution functions (Eqn. 31) for oxygen-oxygen pairs calculated from simulation results for the data set of Figure 3 plotted as a function of distance from the central oxygen atom. Inset shows a blow up of the shift in the position of the minimum over the pressure interval ~65 to ~85 GPa.

Figure 13. Average coordination number (CN) for oxygen about oxygen, oxygen about Mg and oxygen about silicon calculated from simulation results for the data set of Figure 3.

Figure 14. Oxygen packing configurations calculated from simulation results for the data set of Figure 3. Concentrations are plotted as fractional abundances. Figure 14a: Oxygen about oxygen configurations. Figure 14b: Oxygen about silicon configurations. Figure 14c: Oxygen about magnesium configurations.

Figure 15. Cluster dendrogram of correlated abundances of O-O, Si-O, and Mg-O configurations (i.e. Fig. 14). Correlations are denoted by the vertical linakges which are placed from right to left to indicate strong to weak correlation. Groupings are computed by averaging to reduce the correlation matrix.

Figure 16. Principal component analysis of the matrix of correlation coefficients relating abundances of O-O, Si-O, and Mg-O configurations (i.e. Fig. 14) in MgSiO₃ liquid (data set of Fig. 3). The coefficients of the first three eigenvectors are plotted, with coefficients for each configuration indicated by the length of the vertical bar in the graph. Note that some configurations contribute positively and some negatively to the eigenvectors and that each eigenvector is denoted by a different fill pattern. The first three eigenvectors have associated eigenvalues indicating that they account for 99% of the observed structural variance in the liquid over the entire pressure range of this isotherm (~3500 K).

Figure 17. Partial molar volumes of O-O, Si-O, and Mg-O configurational units (i.e. Fig. 14) in MgSiO₃ liquid (data set of Fig. 3) along the \sim 3500 K isotherm over the pressure range zero to \sim 150 GPa. Values are estimated using singular value decomposition fitting techniques utilizing results from the principal component analysis displayed in

Figure 16. These estimates are strongly correlated as they are derived from only three independent measures of structural variation. See text for further explanation.

Figure 18. Shear viscosity (η) computed using Green-Kubo relations from long-duration MD simulations using the pair-potential of Oganov et al. (2001) on MgSiO₃ liquid. Error bars are one sigma estimates. Calculations were performed along a nominal ~3500 K isotherm. Note the break in slope of the viscosity-pressure relations over the pressure interval ~ 65 - 85 GPa.

Figure 19. Self-diffusivity (*D*) of O, Mg, and Si calculated from MD simulation results for the data set of Figure 3. Note the displacement over the pressure interval $\sim 65 - 85$ GPa.

Figure 20. Evaluation of the Eyring relation (left vertical axis) computed from shear viscosity (Fig. 18) and oxygen self-diffusion data (Fig. 19) for the data set of Figure 3. On the right vertical axis the Eyring characteristic length is translated into a quantity reflecting the number of atoms (ξ +1) in the activated complex for transport.



8000 atoms















































