

ANALYTIC MULTIPHASE EQUATION OF STATE FOR MgO. D. C. Swift,¹ N. D. Drummond,² O. Heuzé,³ R. G. Kraus,⁴ and G. J. Ackland,⁵ ¹Lawrence Livermore National Laboratory, U.S.A. (e-mail dswift@llnl.gov), ²University of Lancaster, U.K., ³Commissariat à l'Energie Atomique, France, ⁴Harvard University, U.S.A., ⁵University of Edinburgh, U.K.

MgO is an important prototype and end-member constituent for the mantle of rocky planets. Planetary structures and the response to impacts depend on the equation of state (EOS), notably including any phase transitions. MgO adopts the B1 crystal structure under ambient conditions, and has been predicted to change to B2 under compression. There are large variations in theoretical predictions of this transition [1-4] and of the conditions for shock melting [5-6]; experimental observations are inconsistent or unclear [7].

We have previously constructed equilibrium B1-B2 EOS for MgO, in tabular form, using ab initio electronic structure calculations based on density functional theory (DFT) and the quasiharmonic approximation for lattice vibrations [3,8]. This EOS reproduced mechanical and thermal data in the B1 phase very satisfactorily [8]. More recently, we have developed multi-phase EOS for several materials in which each single-phase EOS is represented analytically [9-12]. It is desirable to use analytic forms when including experimental data in the construction of an EOS, and the availability of a separate EOS for each phase makes it possible to investigate the effect of kinetics in phase transitions. Accordingly, analytic EOS of the Mie-Grüneisen form were fitted to the previous DFT-derived states. The EOS was expressed in terms of mass density and internal energy, which is most efficient for continuum dynamics (hydrocode) simulations. The Mie-Grüneisen EOS omits the detailed physics of the theoretical EOS, and minor parameter adjustments were required to reproduce the theoretical B1-B2 phase boundary. In particular, the Mie-Grüneisen heat capacity was over-simplified with respect to the phonon modes.

An approximate liquid EOS was constructed, based on the B1 EOS with vacancies and additional entropy. Again, the parameters in the liquid EOS could be adjusted to reproduce the melting curve. Given the large discrepancy between experimental [7] and theoretical [5,6] melting curves, two sets of liquid parameters were derived. We had hoped to use the resulting liquid EOS to predict the locus of the B2-liquid boundary, but it was unphysical. This may, of course, be caused by inadequacy of the Mie-Grüneisen EOS, but it is also an indication that the liquid EOS is significantly different above the B2 region than the B1, suggesting the possible existence of a liquid-liquid phase boundary.

An asymptotic case of phase change kinetics was investigated, in which each single phase was allowed to persist if it had the lowest free energy, i.e. no Maxwell construction was performed. This case is significant, as it represents the behavior of a substance in dynamic situations, where there may be insufficient time for equilibration of pressure and temperature between spatially distinct regions. This treatment also exhibits hysteresis in the history of states induced during pressurization and depressurization (or heating and cooling), because the pressure in the composite EOS does not increase monotonically with compression. For an EOS whose independent variables are mass density and specific internal energy (a thermodynamic potential), the effective thermodynamic potential is given by the specific entropy. The stable phase has the highest specific entropy.

Interestingly, the principal shock Hugoniot calculated using this kinetic treatment appears to agree closely with pressure-temperature states measured for a decaying shock [13], corresponding to the B1-B2 region of the EOS. Given the variation between different melting curves, and the misbehavior of the B1-based liquid EOS for melting from B2, no clear conclusions were drawn on the location and shape of the melt transition.

Future work includes the application of a more general description of heat capacity in the Mie-Grüneisen EOS, and the application of these techniques to other substances including Fe and SiO₂.

- [1] Karki B. B., Ackland G. J., and Crain J. (1997), *J. Phys.: Condens. Matter* 9, 8579. [2] Strachan A., Cagin T. and Goddard W. A. III (1999) *Phys. Rev. B* 60, 15084. [3] Drummond N. D. and Ackland G. J. (2002), *Phys. Rev. B* 65, 184104. [4] Oganov A. and Dorogokupets P. (2003), *Phys. Rev. B* 67, 224110. [5] Alfe D. (2005), *Phys. Rev. Lett.* 94, 235701. [6] Belonoshko A. et al (2010), *Phys. Rev. B* 81, 054110. [7] Zerr A. and Boehler R. (1994) *Nature* 371, 506. [8] Luo S.-N., Swift D. C., Mulford R. N., Drummond N. D., and Ackland G. J. (2004), *J. Phys.: Cond. Matt.* 15, 4435. [9] Missonnier M., and Heuzé O. (2006), *Am. Inst. Phys. Conf. Proc.* 845, 262. [10] Heuzé O. (2006), *Am. Inst. Phys. Conf. Proc.* 845, 212. [11] Hebert D., Bertron I., and Heuzé O. (2009), *Am. Inst. Phys. Conf. Proc.* 1195, 1205. [12] Swift D. C. and Heuzé O., to appear. [13] McWilliams R. S. et al, in preparation.