# An Effective Partial Charge model for Bulk and Surface Properties of cubic ZrO$_2$, Y$_2$O$_3$ and Yttrium-Stabilised Zirconia - Supplementary Material

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# S1 Comparison of spectral properties obtained via MM and QM MD

Due to the differences in system size as well as the simulation time between the MD simulations carried out at MM and QM level discussed in the main article, it cannot be expected that identical spectra arise from the Fourier transform of the associated velocity autocorrelation functions. In addition, the difference in the description of the system (i.e. a pair-wise additive potential model versus a many-body description based on density functional theory) will also have a strong impact in the difference of the system. Of course, it can hardly be expected that a simplified potential model will yield an identical description of the system than a quantum chemical treatment, no matter how rigorous the interaction potentials have been parameterised.

In this work the overall agreement of the vibrational wave numbers has been one critereon in identifiying a suitable parameterisation, *i.e.* the vibrational bands observed in the MM
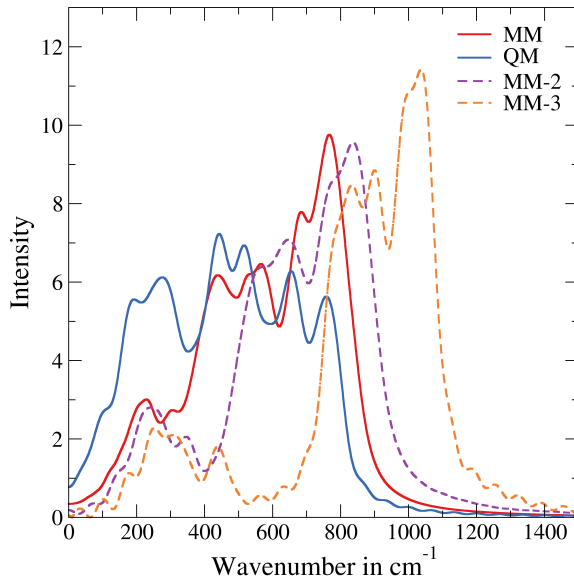


Figure S1: Comparison of the vibrational power spectrum for c-ZrO$_2$ obtained via three different MM parameterisations compared to the QM MD reference (blue). While the range of the observed wave numbers in case of the potential labelled MM (red) is similar to that obtained in QM case (blue), the spectra obtained for parametrisations MM-2 and MM-3 (dashed) are shifted to higher wave numbers. This implies that the associated vibrational modes are subject to higher effective force constants.

MD simulations should not be shifted with respect to the QM reference. To clarify this point, figure 3 of the main article (comparision between the spectra obtained from the QM MD simulation with the one resulting from the selected MM potential model in a classical simulation of c-ZrO$_2$) is reproduced in figure S01. In addition, the spectra of two alternative parameterisations labelled MM-2 and MM-3 are included (dashed lines). The latter two potentials also provide an adequate structural description of the system along with a good agreement of the density at 298 K (these potentials have been identified via isodensity lines similar as shown in figure 1 of the main article). However, in these cases the spectra are shifted towards higher wave numbers out of the range observed in the QM MD simulation.

This is an indication that on average the curvature of the potential (second derivative of the potential with repect to the nuclear coordinates) tends to be higher compared to the QM MD case. Since the masses of the involved Zr and O atoms are of course identical, the underlying vibrational modes can be expected to have similar reduced masses. Based on this analysis it can be concluded that out of the available options depicted in the figure S1, the potential model shown in red (labelled as MM) is indeed the best choice, as it shares the majority of features with the quantum chemical MD result. In this context, the agreement of the range of wave numbers from 100 to 1000 cm$^{-1}$ was the main focus, as this implies that the vibrational modes show comparable effective force constants.

## S2  Impact of System Composition

The yttrium-stabilised zirconia (YSZ) model systems employed in this work were constructed via substitution of randomly selected Zr atoms by Y and the deletion of randomly selected oxygen atoms. Therefore, it proved of particular interest to probe the impact of the randomised cationic lattice on the diffusive properties of the oxide ions. For this reason two additional random systems (Configurations #2 and #3) have been constructed in addition to the one employed in the actual study for the example YSZ9.5 (Configuration #1, see Figure 7 in the main article).

The resulting Arrhenius representation of the associated oxygen diffusion coefficient D

depicted in Figure S2 shows that within numerical noise all three systems show a nearly identical temperature dependence of D. The associated activation energies determined from the slope of a linear regression applied in the temperature range of 1000 to 1900K ($0.53 \cdot 10^{-3}$ to $1.0 \cdot 10^{-3} \mathrm{K}^{-1}$) amount to 0.80. 0.82 and 0.82eV for configurations #1, #2 and #3, respectively. This implies that the overall diffusive properties are mainly dependent on the temperature of the system as well as the number of vacancies in the anionic lattice. Due to the good overall agreement between the three different data sets, no further test configurations were considered.
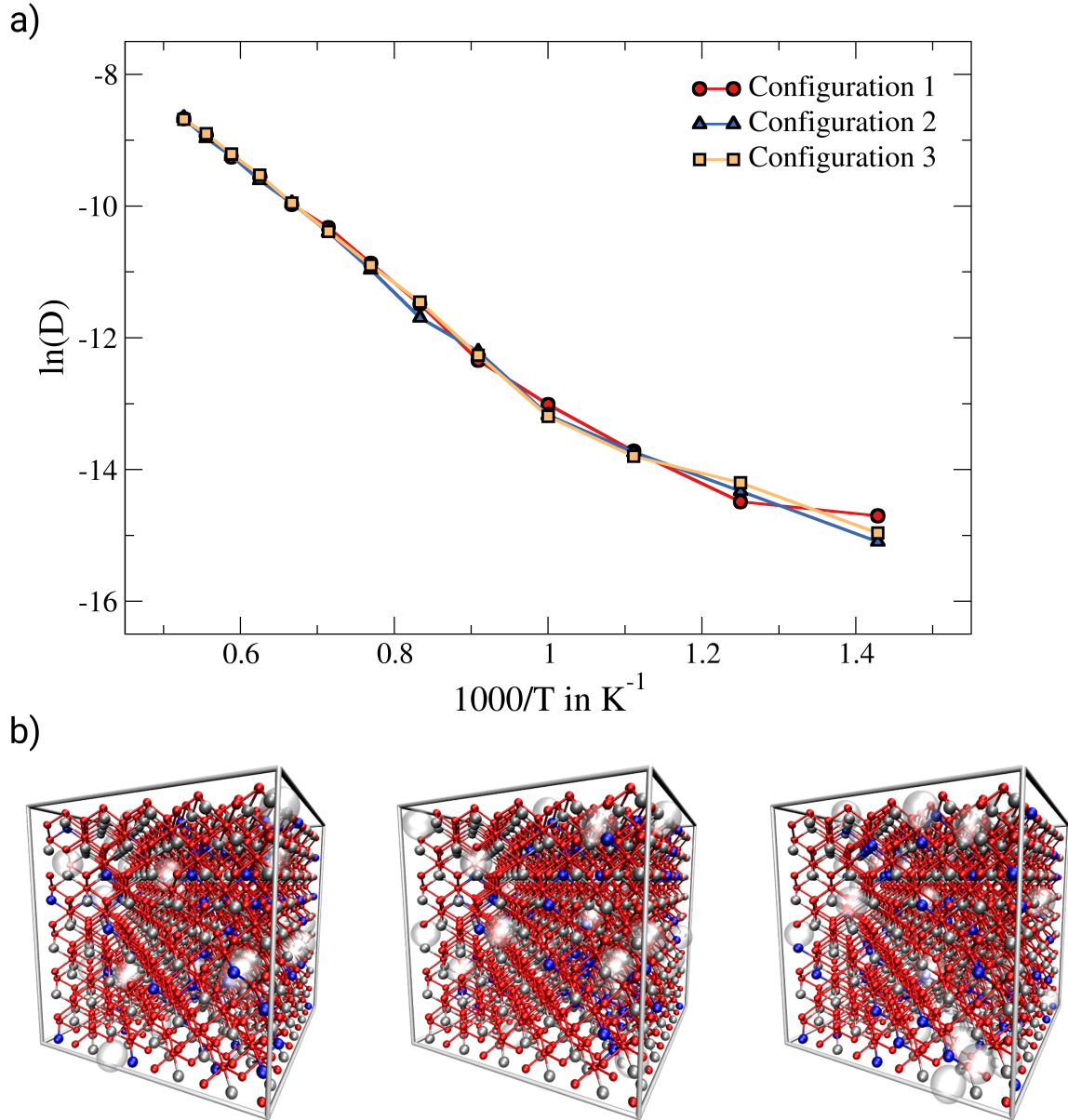
a)



b)



Figure S2: a) Arrhenius representation of the diffusion coefficient obtained for three different randomised configurations of cubic YSZ9.5 using the reduced charge model developed in this work (D in $nm^2ps^{-1}$). b) Initial configurations of the three investigated YSZ9.5 systems. The substitution of Zr by Y and deletion of oxygen atoms was determined via a random selection of atoms (silver: Zr, blue: Y, red: O, white spheres: O vacancies).

## S3 Analysis of the Surface Stability

In the following the structures obtained for 2d-periodic c-$ZrO_2$(110), c-$ZrO_2$(111), c-$Y_2O_3$(110) and c-$Y_2O_3$(111) model systems via low-temperature (10K) MD simulations employing the interaction potential developed in this work as well as the full-charge potential models of Schelling *et al.*[1] and Brinkman *et al.*[2] are compared.

## References

(1) Schelling, P. K.; Phillpot, S. R.; Wolf, D. Mechanism of the Cubic-to-Tetragonal Phase Transition in Zirconia and Yttria-Stabilized Zirconia by Molecular-Dynamics Simulation. *J. Am. Ceram. Soc.* **2001**, *84*, 1609–1619.

(2) Brinkman, H.; Briels, W.; Verweij, H. Molecular dynamics simulations of yttria-stabilized zirconia. *Chem. Phsy. Lett.* **1995**, *247*, 386 – 390.
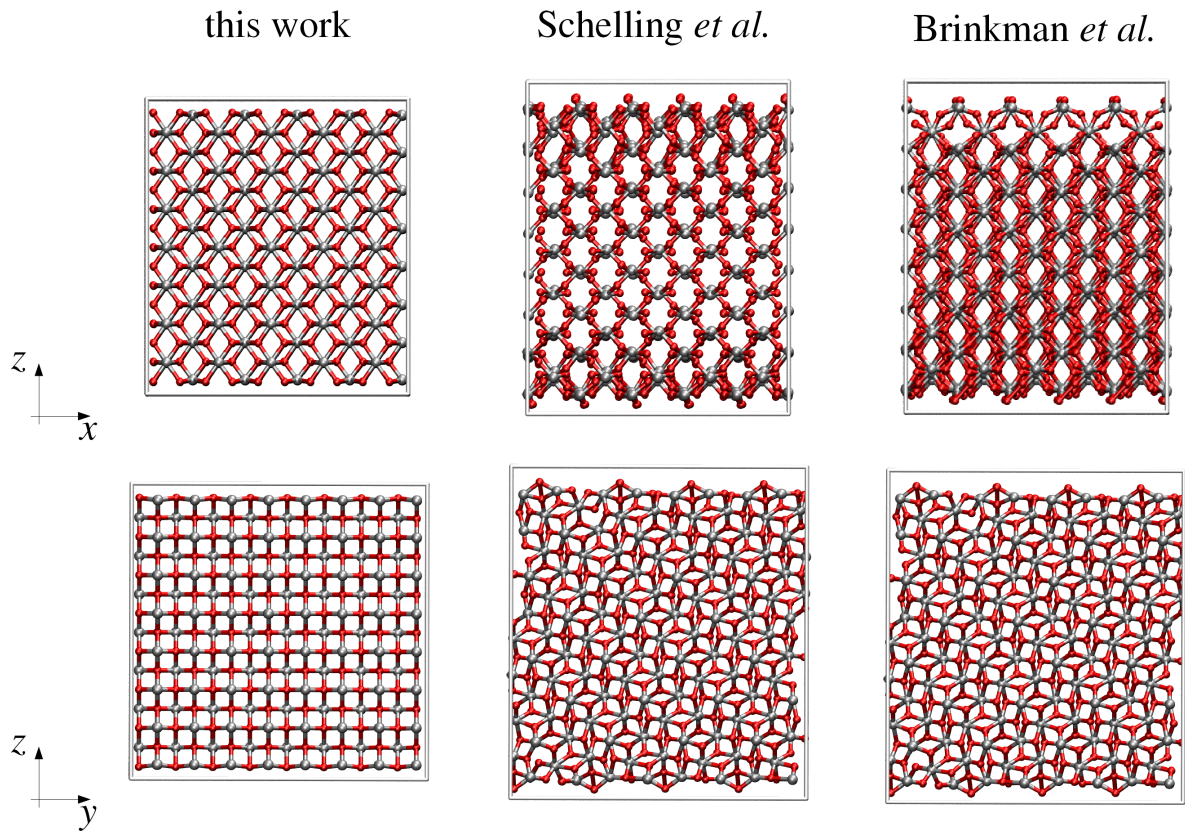
Figure S3: Comparison of the structure of a 2d-periodic c-ZrO$_2$(110) model system determined via low temperature (10K) molecular dynamics using the partial charge model developed in this study to results obtained via the full-charge potentials by Schelling *et al.* and Brinkman *et al.* under the same conditions. The $z$-axis represents the non-periodic direction.
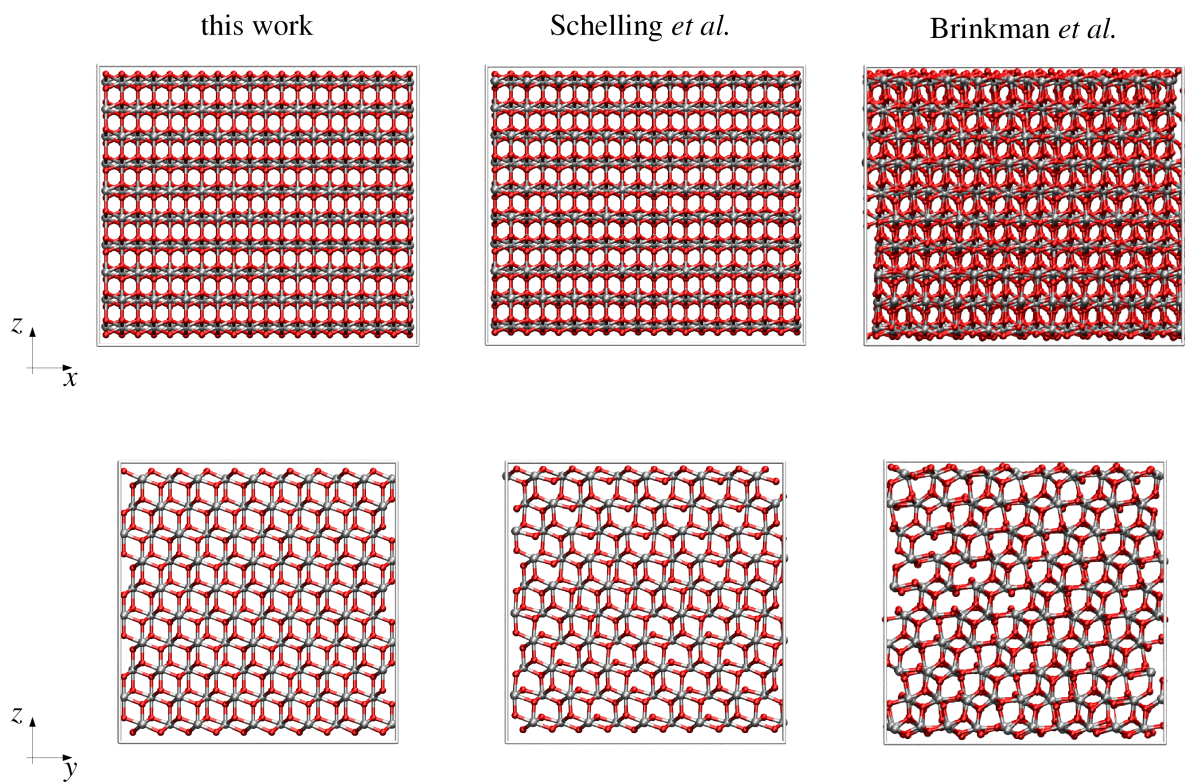
Figure S4: Comparison of the structure of a 2d-periodic c-ZrO$_2$(111) model system determined via low temperature (10K) molecular dynamics using the partial charge model developed in this study to results obtained via the full-charge potentials by Schelling *et al.* and Brinkman *et al.* under the same conditions. The $z$-axis represents the non-periodic direction.
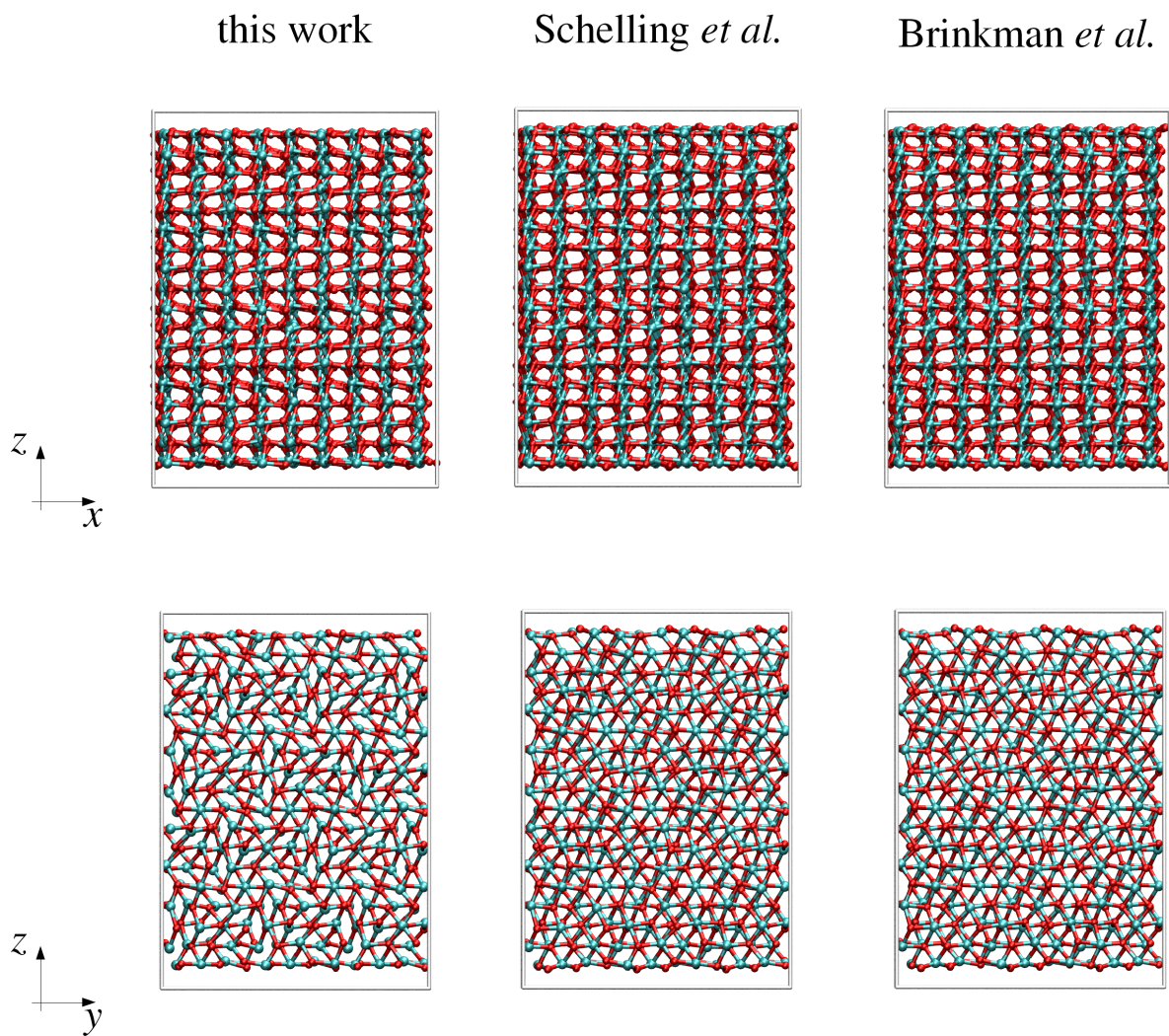
this work          Schelling *et al.*          Brinkman *et al.*



Figure S5: Comparison of the structure of a 2d-periodic c-$Y_2O_3$(110) model system determined via low temperature (10K) molecular dynamics using the partial charge model developed in this study to results obtained via the full-charge potentials by Schelling *et al.* and Brinkman *et al.* under the same conditions. The $z$-axis represents the non-periodic direction.
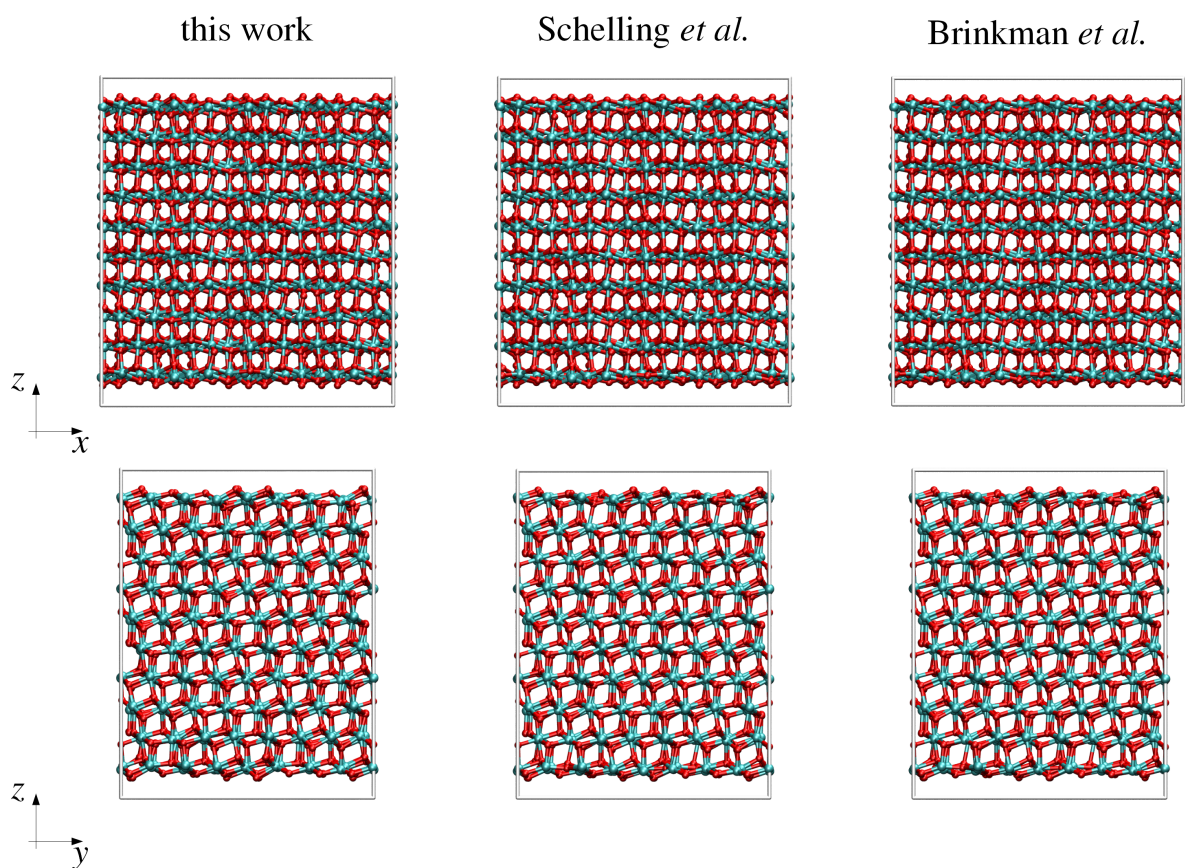
Figure S6: Comparison of the structure of a 2d-periodic c-$Y_2O_3$(111) model system determined via low temperature (10K) molecular dynamics using the partial charge model developed in this study to results obtained via the full-charge potentials by Schelling *et al.* and Brinkman *et al.* under the same conditions. The $z$-axis represents the non-periodic direction.