

Molecular Dynamics and Monte Carlo Simulations of Molten Alkali Carbonates

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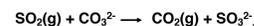
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Abstract

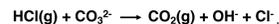
While molten alkali carbonates possess important geochemical and industrial applications due to their properties at high temperatures and pressures, many of their physical and surface properties remain unknown. Experimentally, they have been observed to efficiently remove gaseous HCl from chlorine-rich coal via scattering studies, but the interface has not yet been characterized using simulation methods. Here, we attempt to characterize the molten alkali carbonate interface via scattering studies with gaseous HCl as well as determine various dynamic properties. We examine a previously published force field and describe the development of a novel one using the Lennard-Jones potential equation for interfacial and bulk liquid characterization. We also describe the parameterization of Lennard-Jones constants for lithium, sodium, and potassium ions. While our scattering study results do not yet match the experimentally determined ones, an adjustment of HCl parameters and the addition of dissociative abilities of HCl will likely resolve this discrepancy.

Introduction

In coal burning power plants, gaseous SO₂ waste is removed via a reaction with limestone or other solid carbonates via the reaction



Carbonates can also remove HCl from chlorine-rich coal during these SO₂ waste removal processes via the reaction



While solid limestone can be adequate for waste removal process, reaction times can be lengthy due to sintering of the limestone at certain temperatures, impeding HCl transport. Thus, recent attention has been brought to molten carbonates as a reaction source. In the liquid form, problems with sintering would not arise as the surface is continuously renewed.¹

Experimental scattering studies have been used to characterize the molten alkali carbonate liquid-vapor interface. In a scattering study, one molecule impinges upon the surface of another, and the impinging molecule can have one of three possible trajectories. It can inelastically scatter without reacting, thermally equilibrate at the surface and desorb, or absorb into the bulk liquid, as can be seen in Figure 1. One such series of scattering studies with gaseous HCl showed that approximately 31% of impinging molecules were absorbed into the bulk carbonate liquid.¹

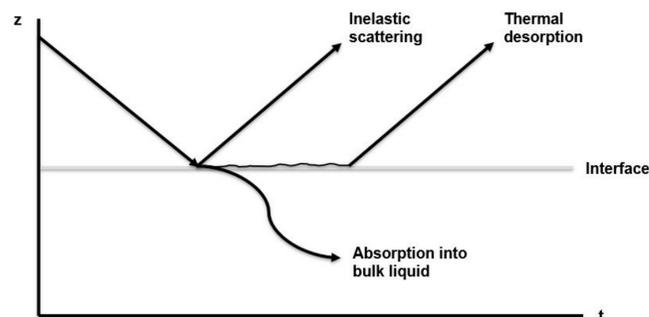


Figure 1. The possible outcomes of an impinging HCl molecule. A molecule which inelastically scatters will hit the interface and immediately bounce back off. A molecule which thermally desorbs will stay at the surface of the interface for a short time. If a molecule dissolves into the bulk, it will stay there for the duration of the simulation.

Molecular dynamics (MD) simulations are useful due to their ability to document changes in a system over time. A few variations of the carbonate mixture studied by Nathanson et. al. have been studied using MD simulations.²⁻⁵ For example, Corradini et. al. recently examined structural and dynamic properties of the Li₂CO₃-K₂CO₃ eutectic mixture.⁶ The MD simulation presented here includes only Li₂CO₃, yet it will likely eventually be altered to include the mixture components present in the experiment by Nathanson et. al.

Simulation Methods

Classical molecular dynamics and Monte Carlo simulations have been used to characterize molten alkali carbonates and perform scattering studies with gaseous HCl. The intramolecular potential used is from Corradini et. al and is given by

$$U_{intra} = \frac{1}{2} k_{C-O} (r_{ij} - r_{C-O})^2 + B_{O-O} e^{\rho_{O-O} (r_{ij} - r_{O-O})}$$

where r_{C-O} is the equilibrium carbon-oxygen bond distance of 1.16 Å. The repulsive exponential term for oxygen-oxygen interactions preserves both the 120 degree bond angles and the planarity of the carbonate molecules.

The intermolecular potential consists of a long-range Coulombic term, a repulsive term, and a dispersive term, given by

$$U_{inter} = \frac{q_i q_j}{r_{ij}} + B_{ij} e^{-\rho_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6}$$

where B_{ij} , ρ_{ij} , and C_{ij} are constants parameterized by Corradini et. al.⁶ Electrostatic forces were calculated using a damped shift potential described by Fennell and Gezelter.⁷ We chose a flexible model which will eventually accommodate dissociative HCl molecules.

Pair	B_{ij} (kJ/mol)	ρ_{ij} (Å ⁻¹)	C_{ij} (kJ Å ⁶ /mol)
Li-O	15.0 x 10 ⁵	0.175	0
O-O	5.0 x 10 ⁵	0.253	2300.0

Table 1. Values used for the repulsive and dispersive intermolecular potential terms.⁶ Extrapolation from these values was required to account for the presence of an HCl molecule.

Using these potential equations and parameters, we consider two systems: One of 216 CO₃²⁻ and 432 Li⁺ molecules, and one of 216 CO₃²⁻, 268 Li⁺, and 164 K⁺ molecules. The initial setups were identical for both the molecular dynamics and Monte Carlo simulations. For each, a cubic system was prepared with box lengths corresponding to the densities given by Corradini et al.⁶ For scattering studies performed on the eutectic system, an interface was prepared by extending the length of the box in the z direction to 100 Å. The molecules were arranged in an arbitrary crystalline pattern, and the system was allowed to equilibrate over the course of 500 ps. The leapfrog method was used to move forward in time, and a time step of 0.5 fs was used. To prepare the system for HCl scattering, one HCl molecule was placed above or below the bulk liquid and given a trajectory toward the interface with a velocity derived from the Boltzmann distribution. If the molecule was placed below the interface, it was given a velocity in the positive z direction. If the molecule was placed above the interface, it was given a velocity in the negative z direction.

Classical molecular dynamics and Monte Carlo simulations are also being used to develop and study a novel Lennard-Jones model. The Li₂CO₃-K₂CO₃ eutectic mixture (62:38 mol %) systems are also being studied here, and the molecular dynamics and Monte Carlo simulations are set up identically to those described above. Studies with pure Li₂CO₃, Na₂CO₃, and K₂CO₃ are also being conducted. However, no interfacial studies have yet been conducted with these systems. The intramolecular potential remains the same as described above, but the intermolecular potential is that of Lennard-Jones:

$$U_{NB} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where the values of σ and ϵ are described in Table 2.

Atom	σ (Å)	ϵ (kJ/mol)
Carbon	1.700	5.975 E-22
Oxygen	1.480	1.459 E-21
Lithium	1.074	1.271 E-22
Sodium	2.179	3.508 E-23
Potassium	4.262	3.561 E-24

Table 2. Values of σ and ϵ for Lennard-Jones Interactions.⁸ Adjustments are being made to the cation parameters in order to more closely match experimentally determined densities (see Figure 4). These parameters are listed such that $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$.

Interfacial Characterization

In order to further characterize the interface, the longitudinal density profile for the molten Li₂CO₃ system was determined using the potential from Corradini et. al. The atoms' relative densities were plotted as a function of their location in the z direction. This allowed us to see the distribution of carbon, lithium, and oxygen atoms at the interface and in the bulk liquid.

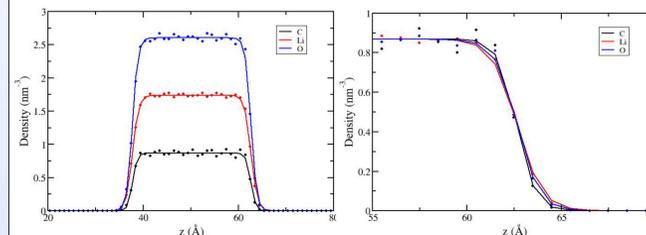


Figure 2. Left: Longitudinal density profile for the molten Li₂CO₃ system. The molecules are contained in an approximately 25 Å x 25 Å x 25 Å space and centered at 50 Å in the z direction. The differences in the relative densities are consistent with the molecular stoichiometry of Li₂CO₃. Right: Stoichiometrically adjusted density profile of the Li₂CO₃ interface.

Atom	C	Li	O
t (Å)	2.15	2.91	2.55

Table 3. 90-10 thickness of carbon, lithium, and oxygen molecules. Near the liquid-vapor interface, there is a higher than expected distribution of lithium atoms.

HCl Scattering Studies

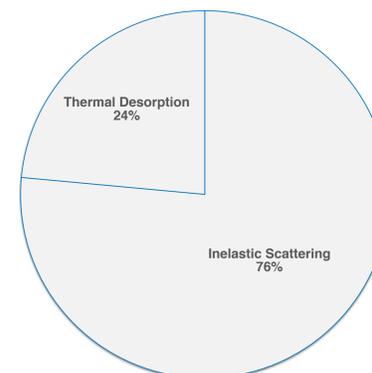


Figure 3. Results of preliminary scattering studies. Approximately three quarters of the incoming HCl molecules inelastically scattered and the remaining quarter remained at the surface of the interface for a short time before scattering (thermal desorption). In comparison, Nathanson et. al. found that about a third of the HCl molecules dissolved into the bulk liquid.

These results do not yet match those of Nathanson et al. for a few reasons. More careful parameterization is necessary, as our rough extrapolations for intermolecular interactions involving HCl likely do not accurately describe behavior which matches experiment. In addition, the HCl molecules in our studies are non-dissociative, and giving them the ability to dissociate will give them the ability to more closely mimic their behavior in a physical space. Perhaps less important is the fact that our studies were performed with a pure Li₂CO₃ interface, while the experimental studies were performed using the Na₂CO₃-Li₂CO₃-K₂CO₃ (31:44:25 mol %) eutectic mixture. However, implementing all of these changes will likely resolve this discrepancy. Many more scattering study trials will also have to be performed, and the fact that none of the molecules absorbed into the bulk liquid could simply be the result of a small sample size.

Lennard-Jones Parameterization

Adjustments to the Lennard-Jones parameters are currently being made in order to more closely match the experimental behavior of alkali carbonates at a range of temperatures. The values of σ and ϵ for the lithium, sodium, and potassium ions are being adjusted, and the resulting density of the systems are calculated and compared to experimental results. Figure 4 details the results of these adjustments.

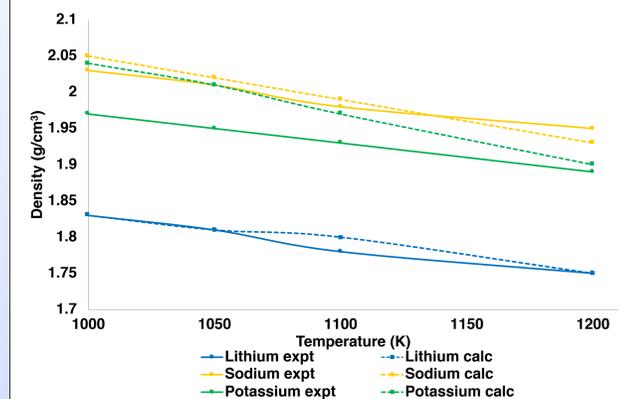
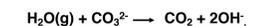


Figure 4. Comparison of experimentally determined densities of alkali carbonates to calculated densities using adjusted Lennard-Jones parameters. While there is relatively close agreement for lithium and sodium carbonate, more significant adjustments to the Lennard-Jones parameters for the potassium ion need to be done.

Conclusions and Future Work

We have performed HCl scattering studies on a pure Li₂CO₃ interface and have begun to characterize it using classical molecular dynamics and Monte Carlo simulations. More careful parameterization of HCl interactions are needed to prevent inconsistencies between our results and those of Nathanson et al. Scattering studies involving water are also a possibility, as water interacts with the molten carbonate via the reaction



Determining whether water molecules inelastically scatter, thermally desorb, or absorb into the bulk liquid would be useful for further alkali carbonate characterization. We are also still in the process of developing a model which employs Lennard-Jones intermolecular potential equations. More density studies of the system are needed, as there is not perfect agreement between experimental densities and our Lennard-Jones model. Continued adjustment of the interaction parameters is likely necessary. Other dynamic properties such as surface tension, diffusion coefficients, and other properties which are experimentally known can also be studied using these simulations. Further characterization of the molten alkali carbonate interface and bulk liquid are still needed in order to more completely characterize the molten alkali carbonate system.

References

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Acknowledgments

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