

Combined molecular dynamics – experimental investigation of oxidic slag properties

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ABSTRACT

Recycling and decarbonization current metallurgical processes is key for our planet's future and in both cases, digital twinning will play an important role. However, the various modelling techniques being used for digital twinning require a lot of input values on variables such as viscosities, diffusion coefficients and surface energies that need to be known as a function of temperature, atmosphere and composition, but which are not widely available, such as in databases, for molten slag phases. The need for more accurate data on physical slag properties is clear and will be extremely relevant for making more realistic and quantitative simulations. Some of these properties are difficult to determine, which is inherent to the very high pyrometallurgical temperatures. Therefore, this work focuses on some aspects related to determining electrical conductivities, viscosities and surface tensions of slags via a combined experimental-modelling method.

Besides experimental work, molecular dynamics (MD) simulations can be used to investigate oxidic slag physical properties. With MD simulations, one can follow the time evolution of a system (consisting of atoms or molecules) by integrating Newton's equation of motion. The input for an MD simulation mainly consists of a force field as well as initial positions, velocities and mass of each atom. The determination of the transport properties in existing literature of MD simulations in oxidic systems, is typically based on incorrect assumptions. For example, to determine the ionic conductivity, the frequently-used Einstein-Stokes equation fails to take into account all ionic types and neglects correlated motion. Furthermore, the viscosity determination via the Einstein-Stokes formula also assumes independent motion of the different ions. This paper gives a brief overview of the opportunities and challenges related to the use of MD simulations for oxidic slag systems.

INTRODUCTION

Metals are indispensable in our future society as they will become even more important in the years to come, given the energy transition we are embarking on (Gregoir and Acker, 2022). Their use has increased immensely in the past decennia due to the growing global demand for electronic consumer goods and high-tech solutions for the transition towards a carbon neutral society (Gregoir and Acker, 2022). Pyrometallurgy (often in combination with electro- and hydrometallurgy) is one of the most important techniques used in extractive operations of ores and scrap (Ebin and Isik, 2016). Upon pyrometallurgical processing, the impurities are typically collected in a slag (metal oxide) phase which floats on top of a liquid metal or liquid matte (metal sulphides) phase (Mills, 2011).

In order to meet the climate objectives, more emphasis is put on recycling as well as on decarbonization the existing metallurgical production methods. Current operations have been working fine for decades, but will need to be adapted when more scrap and carbon-less technologies are employed. For both recycling and decarbonization, electric furnaces will play a key role (Allanore, 2013). For the operation and design of electric furnaces, the electrical conductivity of the slag is a crucial property as in electric furnaces, thermal energy is generated primarily by the Joule effect, which is inversely related to the slag conductivity. However, data on slag conductivity is unfortunately scarce.

The physical properties, except for the electrical conductivity, of slags from primary production are well studied as they have long been used in the industry. They are catalogued in the 'Slag Atlas' (VDEh, 1995). In contrast, only limited research is available on slag conductivities and for all relevant properties, data for slags originating from feeds of secondary materials is scarce. The composition of these new types of slag can indeed vary significantly depending on the market supply of secondary resources. These great variations in slag composition result in a large variability in slag properties, amongst which the electrical conductivity. In pyrometallurgical slags, properties are rather described by structure-property relationships than purely as a function of composition. This is because slags have a very specific molecular structure, as discussed in the following section, and the slag property variations can be explained qualitatively with the variations in these structures.

SLAG PROPERTIES AND STRUCTURE

The slag composition has a direct influence on the slag structure and in turn physical slag properties depend on the slag structure. The dependence of slag properties on the slag structure has been described in a qualitative way, but not quantitatively as the relations are not yet fully understood. Furthermore, the various properties depend differently on the slag structure. As the network structure

becomes more polymerized the resistance to viscous flow will increase and the viscosity will increase. The polymeric network also hinders the movement of cations and thus a more polymerized slag has a lower electrical conductivity (Mills *et al.*, 2013). Electrical conduction in silicate slags results from an applied electrical field and takes place through two parallel mechanisms, ionic and electronic conduction. Ionic conduction involves the movement of cations through the silicate network. The structural dependence of the ionic conduction is currently assumed to be the same as for the slag's viscosity (Zhang *et al.*, 2011; Li *et al.*, 2016; Thibodeau and Jung, 2016a).

Previous experiments of electrical conductivities showed a minor influence of substitution of MgO with CaO (Kawahara *et al.*, 1978), which is in contrast to the substitution effect of these ions on the viscosity (Gao *et al.*, 2014) (showing an increased viscosity when Ca^{2+} was substituted by Mg^{2+}). Furthermore, our recent work on electrical conductivity experiments showed that substitution of PbO with CaO clearly decreases the electrical conductivity (FIG 1 Left), whereas viscosity predictions from Factsage indicate an increasing viscosity trend at a constant temperature. Hence, the trends observed in viscosity based on changes in the slag structure, cannot be directly translated into the same relationships for electrical conductivities, which has been the standard hypothesis and operating method for years (Zhang *et al.*, 2011; Li *et al.*, 2016).

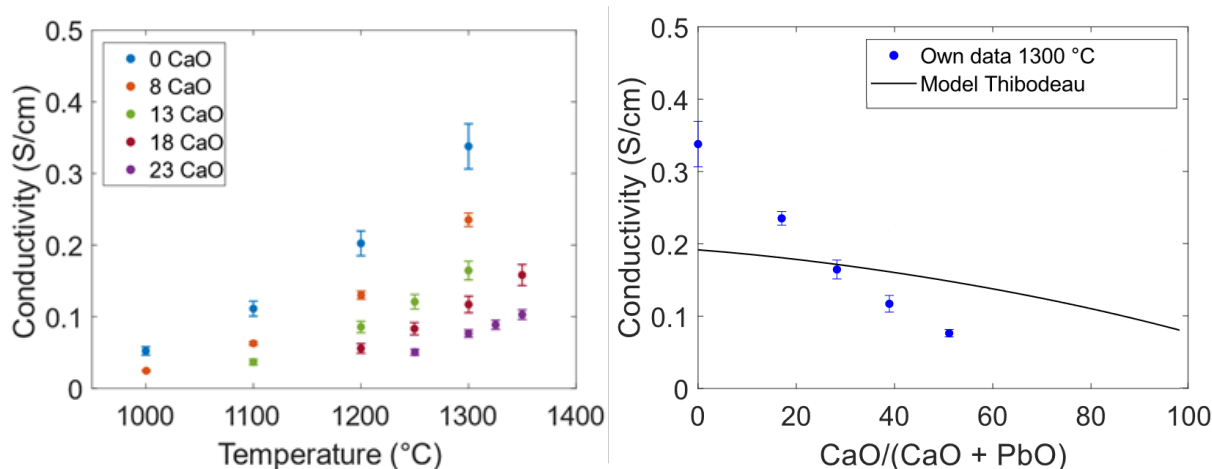


FIG 1 - Influence of the substitution of CaO with PbO on the electrical conductivity in a SiO_2 -CaO-PbO slag (at 1300°C) at various temperatures. [Unpublished results] and compared with existing model by Thibodeau *et al.* (Thibodeau and Jung, 2016a).

The most recent structure-property model for electrical conductivities is the one by Thibodeau *et al.* (Thibodeau and Jung, 2016b) (black line in right part of FIG 1). It is a semi-empirical model, as is very common to use in slag property descriptions: it is based on the abovementioned description of the slag structure, assuming similar correlations as for the slag's viscosity with the slag's structure. This description contains several model parameters which are typically fitted to available experimental results. The model uses temperature and slag composition as input parameters. However, for electrical conductivities, there is an insufficient amount of data, so that in the description of the ionic contribution, the following assumptions are made: (i) there is no interaction between different cations, (ii) the network is only generated via SiO_2 and Al_2O_3 , the latter for which the amphoteric character is neglected, and (iii) the possible amphoteric effect of Fe_2O_3 is neglected.

To optimize this model, less assumptions, more data and more fundamental molecular insights into the slag properties are necessary. However, pyrometallurgical experiments remain very difficult to perform due to the extremely high temperatures. Molecular dynamics modelling of slag structures and their physical properties could reveal a lot of fundamental knowledge provided the simulations account for the complexity of the slag structure as observed experimentally, which can be checked by experimental validation of the simulations. That is why a combined experimental-modelling approach is very promising. More information on the experimental methodology, considering both the set-up development and an investigation of influencing parameters, can be found in the following references: (Boeykens, Bellemans and Verbeken, 2022; Boeykens *et al.*, 2023). Specific focus was put on the reproducibility of the results, the measurement technique itself (comparing Electrochemical Impedance spectroscopy (EIS) versus single frequency measurements) and comparing crucible materials (Pt-Ir versus Al_2O_3). The crucible material had a clear influence on the

conducting path, but the resulting conductivity values for the liquid PbO-SiO₂ slags were of similar order. It should be noted, however, that the measurements in Al₂O₃ are unstable over time as the conductivity decreases continuously during the experiment due to crucible dissolution.

MOLECULAR DYNAMICS SIMULATIONS

Given the fact that the slags are highly dynamic systems due to the high temperature conditions, it is highly desirable to perform atomistic level simulations at the temperatures of interest to capture the nature behind their peculiar behaviour. With Molecular Dynamics (MD) simulations, one can follow the time evolution of a given system of particles, atoms or molecules, by integrating Newton's equation of motion. In principle, the forces between the atoms have to be determined from first principles, i.e. based on underlying quantum mechanical techniques. Density Functional Theory (DFT) is the most popular method for this purpose thanks to its attractive trade-off between accuracy and computational efficiency. However, yet for the systems of interest, consisting of 10³–10⁴ atoms, DFT is still computationally very intensive. Therefore, initially classical force fields Molecular Dynamics (MD) simulations can be used. These atomistic simulations are based on classical interatomic potentials and can account for a substantially larger number of atoms and allow calculation of dynamic properties for larger systems and at higher temperatures (Alder and Wainwright, 2004; Vandenhaute, Rogge and Van Speybroeck, 2021).

Overview of MD studies on slags

Molecular dynamics has already been used to study the properties of several slag systems, mostly molten silicate systems consisting of several thousands of atoms. The following paragraphs give a non-exhaustive overview of molecular dynamics studies focusing on various attention points for MD studies in slag systems.

The FeO-SiO₂ and CaO-SiO₂ systems were investigated by Seo and Tsukihashi (Seo and Tsukihashi, 2004, 2005). The structural properties such as pair distribution functions and the fractions of oxygen ion species (bridging non-bridging and free oxygen), self-diffusion coefficients, enthalpy, entropy and the Gibbs free energy of mixing were determined. The results were in good agreement with the previously determined experimental values. Takei et al. (Takei *et al.*, 2000) calculated the metastable immiscibility region in the Al₂O₃-SiO₂ system from the thermodynamic structural data obtained by MD simulations. The immiscibility gap range was narrower compared with previous reported data.

Wu et al. (Wu *et al.*, 2015) also investigated several binary systems. They calculated the viscosity and electric conductivity of CaO-SiO₂ and CaO-Al₂O₃ systems with different CaO contents. With the increase of the CaO content, the melt viscosity decreased, while the electrical conductivity was enhanced in both systems. Belashchenko et al. (Belashchenko, Ostrovski and Skvortsov, 2001) investigated structural, thermodynamic and transport properties of the binary CaO-FeO, MgO-SiO₂, FeO-SiO₂, CaO-SiO₂ and CaO-Al₂O₃ and the ternary CaO-FeO-SiO₂ systems. It should be noted that the electrical conductivity was derived based on the simplifying Nernst-Einstein equation.

However typically, no real systematic approach of binary to higher order systems can be found in literature and most other molecular dynamics investigations go immediately to complex systems with 4, 5 or even 7 components. One exception are the studies by Zheng et al. (Zheng *et al.*, 2012, 2014), who used MD simulations to model calcium aluminosilicate ternary systems, CaO-SiO₂-Al₂O₃. They first investigated systems with a fixed CaO content and varying molar ratios between SiO₂ and Al₂O₃, investigating the change of self-diffusion coefficients and structure. They used the Qⁿ species description to illustrate the polymerization of the slag. The sequence of diffusivity for four atoms was Ca>Al>O>Si, with the self-diffusion coefficients of Al, Si and O sharing close values and similar variation trends with compositions, indicating that O atoms move cooperatively with network-forming atoms in [SiO₂] and [Al₂O₃] tetrahedra. It is one of the few studies investigating the network-forming tetrahedra, but unfortunately they missed on the opportunity to investigate the charge compensation effect in more detail.

Wu et al. (Wu et al., 2016) investigated the effect of CaO/SiO₂ ratio in a slag with 5 components (CaO-SiO₂-Al₂O₃-FeO) on structural properties and viscosity of the melt. The viscosity decreased and the atomic self-diffusion coefficients increased with the increase in basicity, which is in line with

the expectations from structure-property relations in slags. However, when higher Al_2O_3 contents were used, more complex structures were obtained, indicating that not only SiO_2 was structurally incorporated into the polymer network, but that also Al_2O_3 is taking up a role as network forming component. This in turn requires charge compensating cations to retain charge neutrality within the melt, but this was not investigated in detail. It should be noted that the electrical conductivity was derived based on simplifying the Einstein-Stokes equation.

Gel'chinskii et al. (Gel'chinskii *et al.*, 2011) investigated the multicomponent SiO_2 - CaO - Al_2O_3 - MgO - CaF_2 - Na_2O - K_2O - FeO mixture and compared their results to experimental density values. In this system, and in simpler systems with alkali ions, a more thorough investigation could result in more insights into the mixed alkali effect.

Zhang et al. (Zhang, Zhang, Peng, *et al.*, 2014) investigated the structure of CaO - SiO_2 - Al_2O_3 - TiO_2 slags with varying amounts of TiO_2 and varying CaO/TiO_2 ratios. They validated the structural parameters of the liquid slag in the MD simulations with Fourier-transform infrared (FT-IR) spectroscopic analysis of quenched slags. They found that the replacement of CaO by TiO_2 has little effect on the degree of polymerization in the system. However, it should be noted that they compared the structural parameters of the liquid slag from the MD simulations to the experimental structure obtained from quenched slag. It is highly probable that during the liquid-to-glass transition in experiments there is some sort of structural change taking place, so that a direct comparison between the two states is not optimal.

Zhang et al. (Zhang, Zhang, Liu, *et al.*, 2014) further investigated the structure of the CaO - SiO_2 - Al_2O_3 - MgO - TiO_2 and the relationship with experimentally determined viscosity values for varying basicity and TiO_2 additions. Some of their results indicated the viscosity decreased with increasing basicity and TiO_2 content. They also found that TiO_2 had more network breaking than network forming characteristics, which is somewhat unexpected, but might be due to the relatively high Al_2O_3 amounts. This indicates the potential of molecular dynamics simulations, but it is clear from the different references and corresponding remarks above that attention should be paid on the MD simulation set-up and post-processing for validation.

MD simulations set-up

The force field is an essential ingredient for the MD simulations and should represent all interatomic interactions. So far, interactions in silicate melts are typically represented by a Born-Mayer-Huggins (BMH) potential function:

$$U_{ij}(r) = \frac{Z_i Z_j}{r_{ij}} + B_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

This potential is composed of the long-range Coulomb interaction, short range repulsion and attractive van der Waals force. This force field considers a melt as a completely ionic solution during the simulation. The charge distribution on each atom is represented by a point charge whose magnitude is identified with the formal charge of the ion in the corresponding oxide (e.g. for SiO_2 : $q_{\text{Si}}=+4e^-$, $q_{\text{O}}=-2e^-$). In this equation, $U_{ij}(r)$ is the interatomic-pair potential; Z_i and Z_j are the selected charges, and in order to ensure the transferability of the interaction potential with the melt composition, the valence assigned to the atoms is usually kept fixed for all compositions; r_{ij} represents the distance between atoms i and j ; B_{ij} and C_{ij} are energy parameters for the pair ij describing the repulsion at short distances and van der Waals attractive forces, respectively; and $1/\rho_{ij}$ is a e-folding length characterizing the radially symmetric decay of electron repulsion energy between atom pair ij . This BMH potential is sometimes also referred to as Buckingham potential, based on the description by Matsui et al. (Matsui, 1996).

Aside from the BMH potential, other potentials have been mentioned in the context of oxidic slags. For example, Wu et al. (Wu *et al.*, 2016) used a BMH potential function in combination with a Lennard-Jones (L-J) two-body potential function:

$$U_{ij}(r) = D_0 \left\{ \left(\frac{R_0}{r_{ij}} \right)^{12} - 2 \left(\frac{R_0}{r_{ij}} \right)^6 \right\}$$

With D_0 is the depth of the potential well; R_0 is the distance at which the potential reaches its minimum, at R_0 the potential function has the value $-D_0$. These authors claimed this is necessary because there are no accurate parameters for Fe-Fe, Fe-Al, Fe-Si and Fe-Ca pairs corresponding to the BMH function. Unfortunately, they did not carefully refer to the original paper for the BMH potential, as these parameters are well described for example for Fe-containing slags by Guillot et al. (Guillot and Sator, 2007).

The work of Mongalo et al. (Mongalo, Lopis and Venter, 2016) is also worth mentioning. They first used a Morse potential, based on the description by Pedone et al. (Pedone *et al.*, 2006), which corresponds to the second term in the following equation:

$$U_{ij}(r) = \frac{Z_i Z_j e^2}{r_{ij}} + D_{ij} \left[\left\{ 1 - \exp(-a_{ij}(r_{ij} - r_0)) \right\}^2 - 1 \right] - \frac{C_{ij}}{r_{ij}^{12}}$$

The Morse function is typically used in modeling bonded interactions in covalent systems (e.g., the hydroxide ion in ionic systems) where the different parameters have a certain physical meaning. This is not the case here because the Coulomb term is explicitly included in the full potential expression, and D_{ij} , a_{ij} , and r_0 should be simply considered as parameters.

The study by Mongalo (Mongalo, 2018) is one of the few studies mentioning a comparison of different force fields. Unfortunately, they seemed to have made a copying mistake for the parameter values for the BMH potential. Furthermore, originally, Pedone et al. (Pedone *et al.*, 2006) mentioned the following for O-O bond: The term C/r^{12} is needed only in MD simulations and in free energy calculation at high temperature and pressure. In fact, the C_{OO} term can range between 22 and 100 eV \AA^{12} without altering the results of free energy minimization at room temperature. Mongalo, on the other hand, stated for all C_{ij} terms that "This term is only necessary to model the interactions at high temperature and pressure. Since the simulations were performed at atmospheric pressure, this term is not required and was therefore not used.". It is clear that Pedone et al. only made the remark referring to the O-O bond, where Mongalo interpreted it much broader. Therefore, it is not clear whether the conclusion of Mongalo (Mongalo, 2018) is indeed correct. He concluded that the Morse potential predicts the experimental densities with better accuracy than the Buckingham potential.

This brings to the attention that various force field expressions and the corresponding parameters are typically developed by fitting to a certain aspect of the system being investigated. This can result in for example a very good correspondence of some of the structural or transport properties, but large deviations for other properties. A possible solution is the use of DFT-derived force field and parameters, which happens in ab-initio MD simulations. Since 2015 more and more ab-initio MD simulations have been used, as increased computational power now also allows calculations of this type for the highly disordered slag systems (Harvey, Gheribi and Asimow, 2015; Sajid et al., 2020a, 2020b; He et al., 2021).

Besides the force field, the remainder of the simulations is more similar to MD simulations in other (non-slag) systems. Typically, the MD simulations are performed in isobaric and isothermal ensemble (NPT) which implies that the simulations run while keeping the number of particles, sample pressure and the temperature of the systems constant. Temperature is controlled by the velocity scaling method and pressure is controlled by Parrinello and Rahmann method (Parrinello and Rahman, 1998).

In the simulation process, an appropriate number (typically a couple of thousands) of atoms of each type are placed in the representative volume element with random initial configurations and then the volume of the cell is determined by the atom numbers and the density. Periodic boundary conditions are typically employed on all sides of the model box to create an infinite system with no boundaries. At the beginning of each simulation, the initial temperature is fixed at a certain very high value (e.g. 4000 K) for a few thousand steps to mix the system completely and eliminate the effect of the initial configuration. Then, the temperature is cooled down to the temperature of interest with a cooling rate that is extremely large compared to the experimental values. The control over the system temperature is achieved by rescaling the velocity of each particle. At equilibrium, the system is relaxed and finally different transport and structure properties for different systems can be calculated and analysed as described below.

Properties derivable by MD simulations and points of attention

In MD simulations, the atomic structure of melts is commonly described in terms of radial distribution functions (RDF), which represent the probabilities for finding pairs of atoms at a certain distance r . The peak positions of the RDF represent the most probable interatomic distances of the different coordination shells. In addition, the coordination numbers (CN) can be determined by a numerical integration of the first peak of the RDF.

As a first property, the diffusion coefficients are determined based on the mean square displacement (MSD). This MSD can be generated by statistical analysis of the particles trajectory. MSD indicates the average displacement of a certain atom during a fixed time t and is defined by the following equation:

$$MSD = \frac{1}{N} \left\langle \sum_i^N [\vec{r}_i(t) - \vec{r}_i(0)]^2 \right\rangle$$

where N is the number of atoms, $r_i(t)$ is the position of atom i at time t and the angle brackets express an ensemble average taken over time. In literature, the self-diffusion coefficient of a selected ion i (D_i) is typically calculated from the slopes of MSD of ions as a function of time:

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_i^N [\vec{r}_i(t) - \vec{r}_i(0)]^2 \right\rangle$$

The determination of the other transport properties in the abovementioned references, is typically based on incorrect assumptions, such as independent motion of different ions. The electrical conductivity (σ) is typically calculated by combining the diffusion coefficient and the Nernst–Einstein equation:

$$\sigma = D \frac{nq^2}{k_B T}$$

Where n is the number of the carrier atoms in a unit volume and q is the charge of the ion. It should be emphasized that the frequently used Nernst-Einstein equation, should actually be extended to also take into account all ionic types:

$$\sigma^{NE} = \frac{e^2}{kTV} \sum_j N_j Z_j^2 D_j$$

With e the elementary charge, V the simulation box volume, Z_j the charge of the ion and N_j the number of ions of this type. However, this equation still assumes independent migration of ions and neglects correlated motion. As experimental results in Fig. 1 have shown, this is not the case. Hence, a more accurate analysis requires the application of the more general Einstein relationship:

$$\sigma^E = \frac{e^2}{6kTV} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_i^N \sum_j^N Z_i Z_j [\vec{r}_i(t) - \vec{r}_i(0)] [\vec{r}_j(t) - \vec{r}_j(0)] \right\rangle$$

This more realistic analysis results in better correspondence with experimental values, as shown by the work of Mongalo et al. (Mongalo, Lopis and Venter, 2016). They compared experimentally measured slag conductivities reported in the slag atlas (VDEh, 1995) compared to MD values with either the Nernst-Einstein equation or the more general Einstein equation and they showed that the Nernst-Einstein approximation overestimates the experimental conductivities, by 40% to 100%, which can be ascribed to neglecting the correlation between different atom types. However, it should also be noted that experimental data they investigated were derived from the slag atlas. Some compositions and conditions they addressed, should actually result in not-fully liquid slag systems. The presence of solids has a definite influence on the measured electrical conductivity (Zhang *et al.*, 2023), but the slag atlas did not mention any presence of these solids.

CONCLUSION: OPPORTUNITIES AND CHALLENGES FOR MD SIMULATIONS IN SLAGS

With the increasing importance of electric furnaces, the need for new data on electrical conductivity of slags is high. As the experimental measurement of this data is extremely intricate, the benefit of using a combined modelling – experimental approach to determine slag electrical conductivities has been illustrated in this work. Of course, the experiments should be performed with the utmost care to ensure only measurement of the desired property so that no unwanted side effects are taken into account. These effects are not present during MD simulations, as long as they are executed in a dedicated way so that they represent the real systems. Hence, the molecular dynamics simulations should be post-processed in such a way that no a priori assumptions, of for example independent motion of different types of ions, are used to assure the resulting transport properties within the liquid slags are correct. For the experimental validation of structural properties, it should be emphasized that the liquid to glass transition could have had an effect on the structural parameters so that care should be taken in comparing these two states. It is also noted that the MD technique could elucidate many remaining questions regarding slag structure and specific structural effects such as the charge compensation effect and mixed alkali effect and their influence on the slag properties. However, a systematic investigation is currently lacking to allow for this. Finally, it should be mentioned that the ab-initio MD technique holds great promise, as the force field and the corresponding parameters are derived from first principles and thus are not derived with a specific focus property to be optimized for.

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