

Supplementary Information for
**“The crucial role of transient tri-coordinated oxygen in the flow of
silicate melts”**

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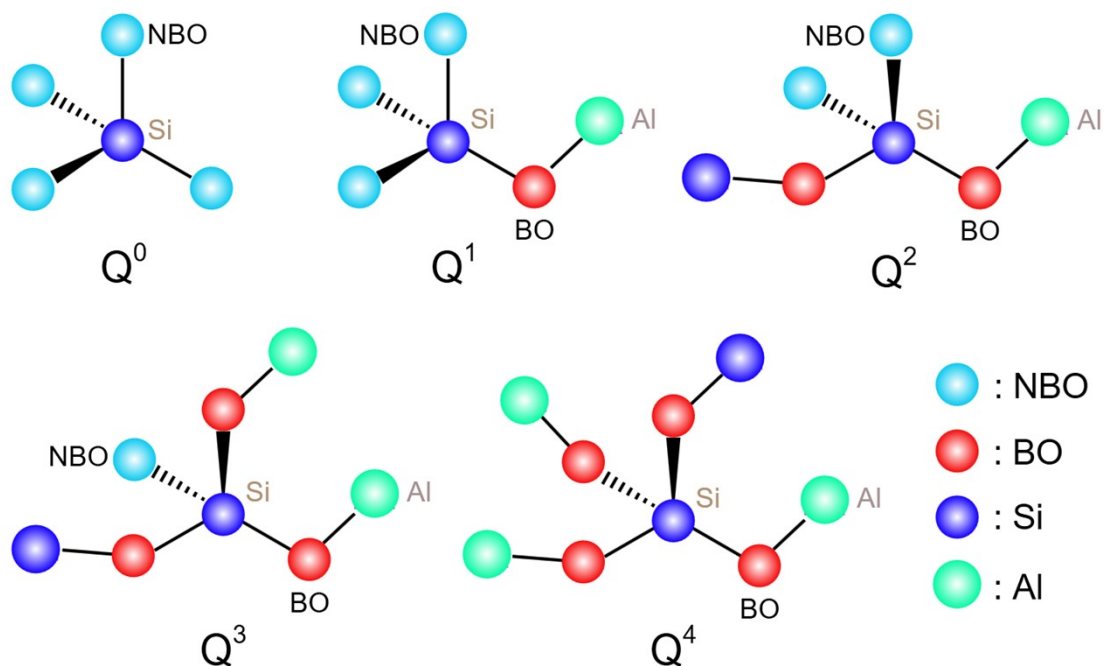
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Table S1 Chemical compositions of samples (mol fraction)

Sample	SiO ₂	Al ₂ O ₃	CaO
1	50	50	0
2	47.20	47.20	5.6
3	44.70	44.70	10.6
4	42.45	42.45	15.1
5	40.40	40.40	19.2

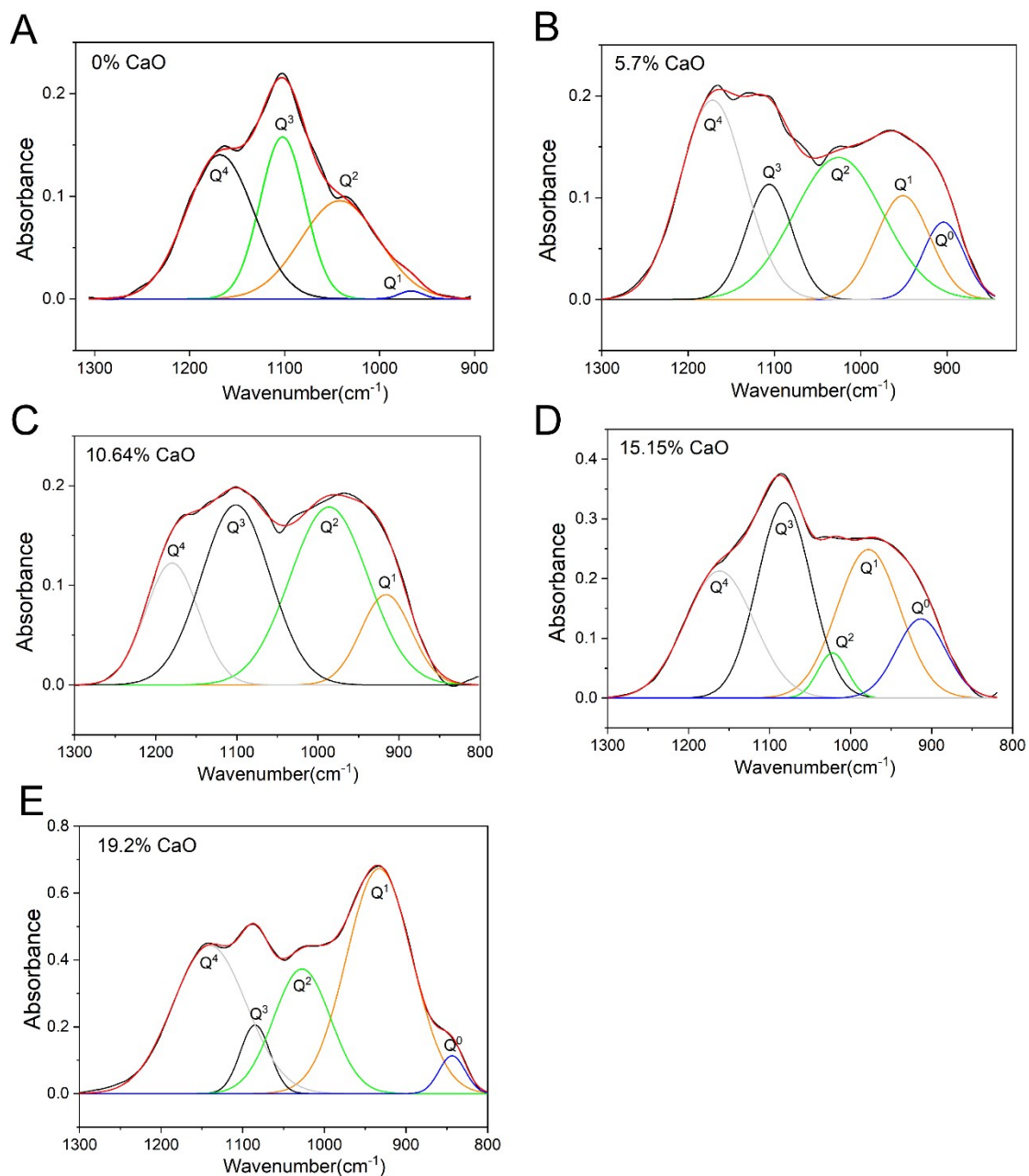


Supplementary Figure. S1. Schematic diagram of Q^n structural unit.

The value n represents the number of bridging oxygens around a Si atom, where ($n = 0, 1, 2, 3, 4$). According to the traditional theory of polymerization, melt viscosity is directly proportional to the degree of polymerization. As the content of Q^3 and Q^4 increases in the system, indicating a higher degree of polymerization, the melt viscosity also rises. We use the value R , defined as $(Q^3+Q^4)/(Q^0+Q^1+Q^2)$, to characterize the degree of polymerization. A higher R value indicates an elevated degree of polymerization, with a greater number of bridging oxygens in the melt, resulting in higher melt viscosity.

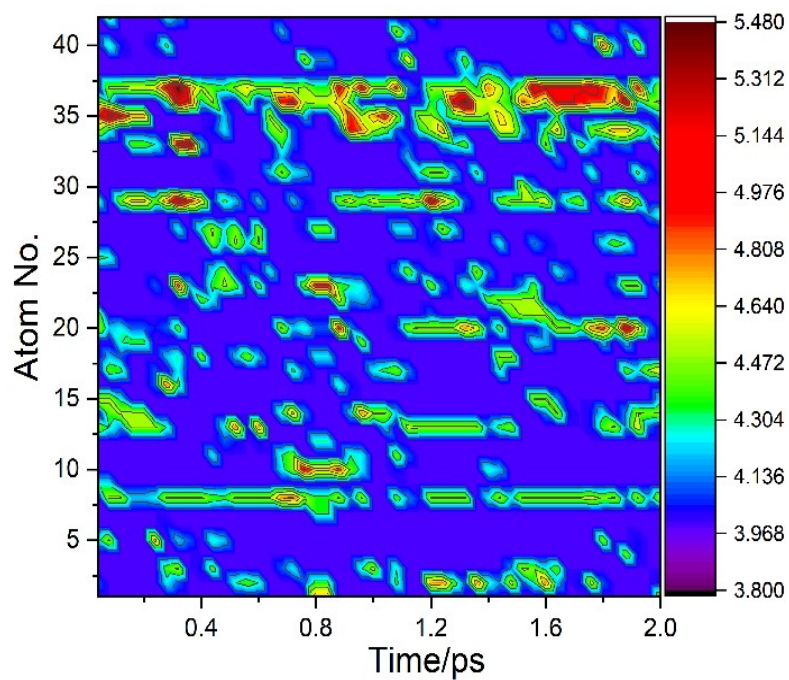
In this paper, we investigate the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system with a $\text{SiO}_2\text{:Al}_2\text{O}_3$ ratio of 1:1, where the molar content of Al_2O_3 exceeds 40 mol%, making it a typical aluminum-rich system. This system is not only suitable for studying the transformation of tri-coordinated oxygen structures but also amplifies the charge

compensation effect of alkaline oxides. From Figure R-2, it can be observed that when the CaO content is below 10.64%, the proportion of Q⁴ and Q³ structural units in the melt increases with the CaO content. However, when the CaO content exceeds 10.64%, the proportions of Q³ and Q⁴ decrease abruptly, while Q¹ and Q⁰ content increase. The main factor driving this shift in trend is the fluctuation in CaO content, resulting in changes to the phase composition of the quenching slag. Additionally, when the CaO content is below 10.6%, Ca²⁺ acts as a charge compensator. The charge compensating ability of Ca²⁺ is generally considered to be twice that of Na⁺, and Ca²⁺ promotes the involvement of more Al³⁺ in forming a network structure, leading to an increase in Q³ and Q⁴ content, thereby enhancing the R value. When the CaO content exceeds this threshold, Ca²⁺ starts to disrupt the melt structure. The quantities of Q⁰ and Q¹ increase in the quenched slag, while Q⁴ content significantly decreases, resulting in a decrease of approximately 40% in the R value. Currently, we still have limited understanding of the structures formed and the chemical nature when charge compensation occurs in alkaline oxides.



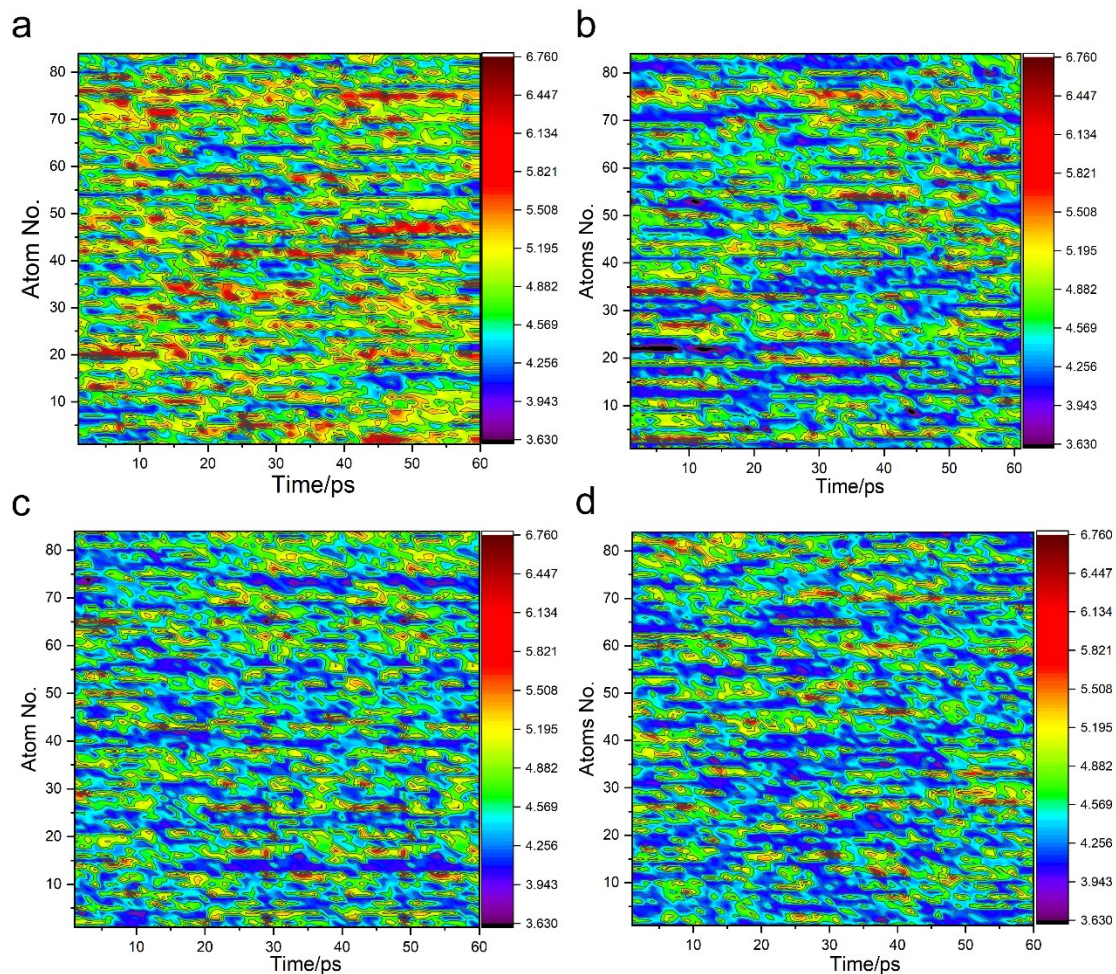
Supplementary Figure. S2. FTIR experimental results. (A) 0% CaO, (B) 5.7% CaO, (C) 10.64% CaO, (D) 15.15% CaO, (E) 19.2% CaO.

Q⁰: 880-850 cm⁻¹, Q¹: 920-900 cm⁻¹, Q²: 1000-950 cm⁻¹, Q³: 1100-1050 cm⁻¹, Q⁴: 1200-1060 cm⁻¹.



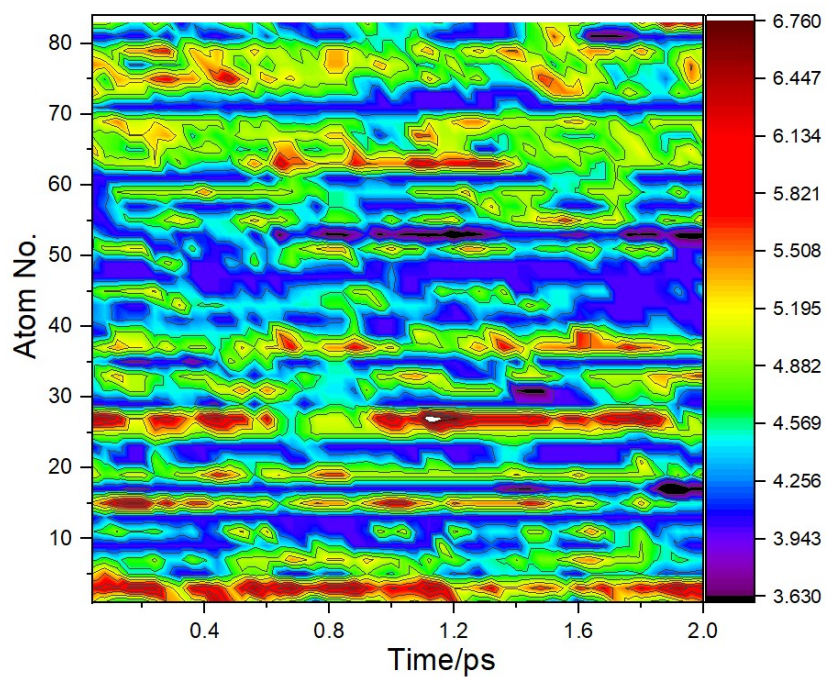
Supplementary Figure. S3. Transient CN analysis of Si for 2 ps

The transient coordination analysis diagram of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ (5.7%) system. The vertical axis represents the atomic number and the color represent the CN of the corresponding atoms.



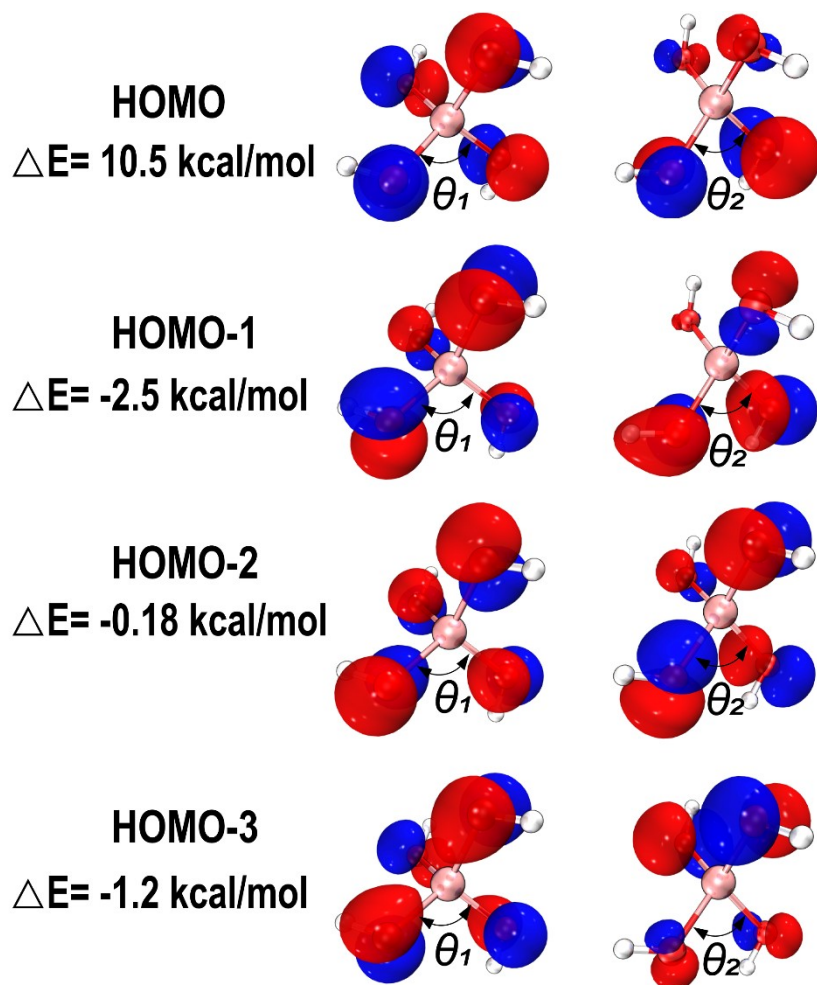
Supplementary Figure. S4. Transient CN analysis of Al for 60 ps.

Temporal evolution of the coordination numbers, for **(a)** Si at 2000 K in the SiO₂-Al₂O₃ system, **(b)** Si at 2000 K in the SiO₂-Al₂O₃-CaO (5.7%) system. **(c)** Si at 2000 K in the SiO₂-Al₂O₃-CaO (10.64%) system. **(d)** Si at 2000 K in the SiO₂-Al₂O₃-CaO (15.15%) system. (The vertical coordinate in the transient coordination analysis diagram represents the atomic number, with colors closer to red indicating a higher coordination number and closer to purple indicating a lower coordination number.)

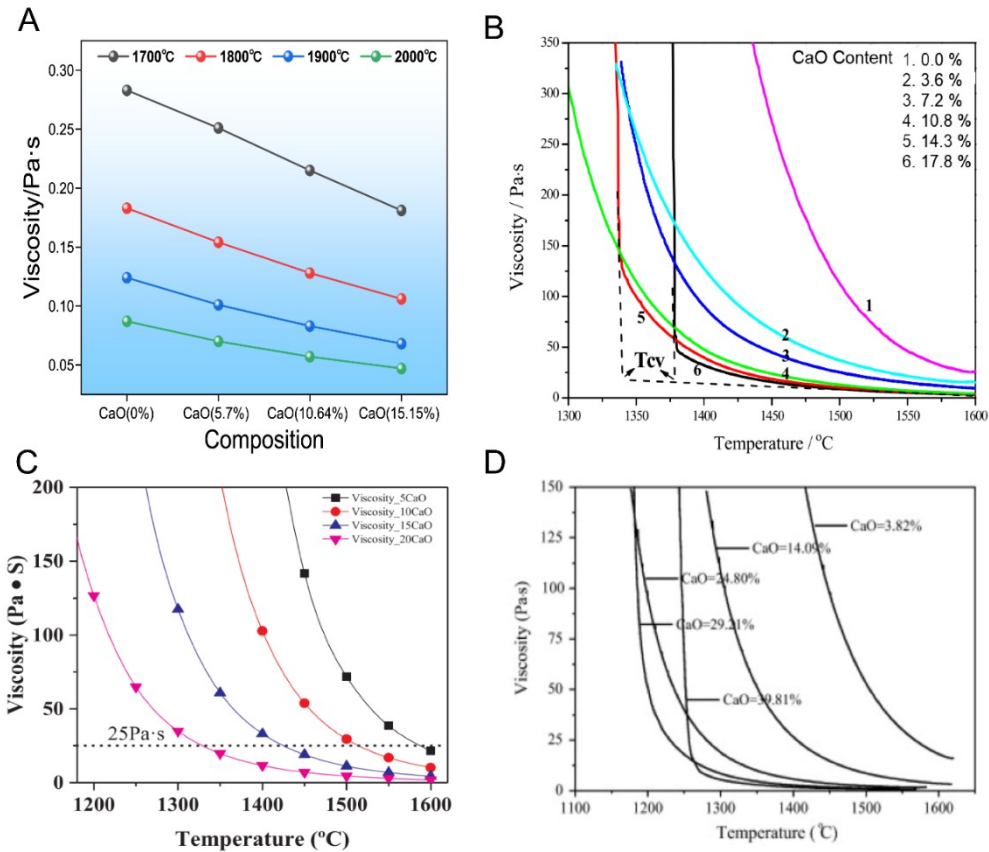


Supplementary Figure. S5. Transient CN analysis of Al for 2 ps.

The transient coordination analysis diagram of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ (5.7%) system. The vertical axis represents the atomic number and the color represent the CN of the corresponding atoms.



Supplementary Figure. S6. Comparison of the occupied orbitals for different O-Al-O angles of $\text{Al}(\text{OH})_4^-$. ($\theta_1=105^\circ$, $\theta_2=84^\circ$, $\Delta E=E_{02}-E_{01}$)



Supplementary Figure. C1. In comparison with previous studies on the impact of CaO on viscosity. (A). The viscosity curves in this article. (B). The viscosity curves by Ge et al ^[1]. (C). The viscosity curves by Dai et al ^[2]. (D). The viscosity curves by Kong et al ^[3].

As shown in Figure R-2, in similar systems, previous research has focused on the influence of CaO content on the entire viscosity-temperature curve. As evident from Figures 1B, C, and D, at a fixed temperature, the viscosity of the system decreases with an increase in CaO content. The trend of viscosity changes caused by CaO content in this paper is consistent with the previous research.

Explanation of abbreviations:

VMD: Visual molecular dynamics (Software)

OVITO: The open visualization tool (Software)

BO: Bridging oxygen

TO: Tri-coordinated oxygen

NBO: Nonbridging oxygen

NMR: solid-state nuclear magnetic resonance

AIMD: Ab initio molecular dynamics

FTIR: Fourier transform infrared spectroscopy

MD: Classical molecular dynamics

LAMMPS: Large-scale atomic/molecular massively parallel simulator (Software)

BMH: Born–Mayer–Huggins (BMH) potential (potential function)

NVT: Canonical ensemble, abbreviated as NVT, represents a system with a fixed number of particles (N), volume (V), and temperature (T).

R.I.N.G.S: Structural analysis software

PBE: Perdew-Burke-Ernzerhof. PBE is an exchange-correlation functional primarily employed for computing the electronic structure within materials. The PBE functional falls under the category of generalized gradient approximation.

CP2K: Molecular simulation software

RDF: Radial distribution function. The radial distribution function, also known as the pair correlation function, describes how the particle density changes as a function of the distance from a reference atom.

CN: Coordination number

References:

1. Z. Ge, L. Kong, J. Bai, et al. Effect of CaO/Na₂O on slag viscosity behavior under entrained flow gasification conditions. *Fuel Process. Technol.*, 2018, **181**, 352-360.
2. X. Dai, J. Bai, Q. Huang, et al. Viscosity temperature properties from molecular dynamics simulation: The role of calcium oxide, sodium oxide and ferrous oxide. *Fuel*, **2019**, 237, 163-169.
3. L. Kong, J. Bai, W. Li, et al. The internal and external factor on coal ash slag viscosity at high temperatures, Part 3: Effect of CaO on the pattern of viscosity–temperature curves of slag. *Fuel*, 2016, **179**, 10-16.