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Monte Carlo Simulation to Understand the Working Mechanism of The Electrolytes Lithium Hexafloorophosphate and Ethylene Carbonate

Hubertus Ngaderman, Ego Srivajawaty Sinaga
Department of Physics, Universitas Cenderawasih, Jayapura, 99581, Indonesia

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Corresponding Author:

Hubertus Ngaderman,
Email: ngadermanh@gmail.com

ABSTRACT

Monte Carlo (MC) simulations provide a powerful approach to investigate electrolyte–electrode interactions and to optimize battery design. This study aims to determine the entropy and average energy of a lithium salt–ethylene carbonate (EC) system, as these parameters are essential for evaluating the Boltzmann factor. The Boltzmann factor was derived from entropy concepts and the principle of maximum entropy, which involves the Boltzmann constant (k) and the number of accessible states (Ω). Simulations were performed using Lennard–Jones parameters within a canonical ensemble framework to compute entropy and energy for systems with varying atom numbers. Results show that the system entropy for two atom types (200 atoms) was 6.67×10^{7} kJ·mol^{-1}·K^{-1}. For three atom types (300 atoms), the equilibrium entropy reached 1.1×10^{10} kJ·mol^{-1}·K^{-1}, and for four atom types (400 atoms), 1.3×10^{13} kJ·mol^{-1}·K^{-1}. When reduced to five atom types with only 300 atoms (to minimize computational cost), the entropy was 2.4×10^{8} kJ·mol^{-1}·K^{-1}. The simulations, employing the Metropolis criterion, successfully identified globally stable configurations, providing new insights into entropy-driven behavior in lithium battery electrolytes.

1. INTRODUCTION

Commercial lithium-ion batteries typically use lithium hexafluorophosphate ($LiPF_6$) as the electrolyte salt in organic solvents because it has high ionic conductivity and good thermal stability. Organic solvents such as ethylene carbonate (EC) and diethyl carbonate (DEC) were used because they can form a stable solid electrolyte interphase (SEI) layer on the electrode surface. The use of $LiPF_6$ and organic solvents, such as EC and DEC, has become standard in the lithium-ion battery industry due to their excellent performance and high stability (Zhang et al., 2022). The commonly used anode is graphite, while the cathode is typically a lithium metal oxide, such as lithium cobalt oxide ($LiCoO_2$) or lithium iron phosphate ($LiFePO_4$) (Dai & Zhu, 2024).

Molecular simulations and ab initio calculations can help to understand the behavior of $Li^+$and PF_6^- ions in lithium-ion battery electrolytes, including solvation, diffusion, and interactions with solvents such as EC and EMC (Aoyagi & Otani, 2019; Kuganathan, 2022; Mabrouk et al., 2024). Simulation results indicate that solvent structure and ion-solvent interactions influence electrolyte performance. Simulations can also help to understand the electrolyte degradation mechanisms and their impact on battery performance (Tian et al., 2023). Several studies have used simulations to study

solvation, diffusion, and ion-solvent interactions in electrolytes, including the use of the Lennard-Jones 12-6 potential to study the reaction between the cation Li^+ and the anion PF_6^- with the solvent EC (Ngaderman & Sinaga, 2024; Sinaga et al., 2024). Thus, simulations can help researchers develop better electrolytes and improve overall battery performance.

Given the above background, the researcher conducted a study titled Monte Carlo Simulation to Understand the Working Mechanism of Lithium Hexafluorophosphate and Ethylene Carbonate Electrolytes. Several researchers have used MC simulations to study the behavior of lithium-ion batteries. MC simulations are used to predict the performance of lithium-ion batteries, such as predicting battery capacity and cycle life. MC simulations are also used to study electrolyte behavior, such as investigating the structure of the solvent with Li^+ and PF_6^- ions (Hossain et al., 2020). Electrolytes generally consist of lithium salts and organic solvents. A good electrolyte must have high ionic conductivity, high thermal and chemical stability (Chou et al., 2021).

Research on lithium-ion batteries shows that the growth of lithium dendrites can cause safety issues and poor battery performance (Pant et al., 2024). MC simulations have been used to study the dendrite formation process and other properties of the Li-GIC (lithium-graphite intercalation compound) system, which shows promise as an anode material due to its high storage capacity and good stability (Anniés et al., 2021) . MC simulations and MC kinetic models have been also used to understand the electrolyte and electrode behavior, optimize battery design, and comprehend phenomena occurring within batteries (Yu et al., 2023). Thus, simulations can help to improve the battery performance, safety, and lifespan. MC simulations were used by Saul (Perez-Beltran et al., 2024) to understand the formation of the SEI layer and lithium ion electrodeposition in batteries, and the research results showed that SEI formation affects battery performance because the SEI acts as a protective layer that regulates lithium ion flow, prevents side reactions, and reduces internal resistance. Factors such as current density, electrode potential, and lithium-ion solvation structure also influence the lithium-ion electrodeposition process. Thus, optimal SEI formation can improve battery performance by reducing unwanted side reactions, thereby enhancing efficiency, safety, and battery lifespan. The composition and physicochemical properties of the SEI also play a crucial role in regulating the electrodeposition process and battery performance. The physicochemical properties of the SEI include chemical composition, morphological structure, ionic conductivity, and thermal stability. The chemical composition of the SEI determines the type and number of components that form the SEI, while the morphological structure of the SEI influences the shape and size of the SEI particles or layers. The ionic conductivity of the SEI determines its ability to conduct ions, and the thermal stability of the SEI determines its ability to withstand temperature changes without degradation. Therefore, a kinematic understanding of lithium ion electrodeposition is crucial for improving battery performance and stability by optimizing the physicochemical properties of the SEI(Perez-Beltran et al., 2024).

Computer simulations aid in the development of lithium-ion battery technology by understanding the interactions between lithium ions and materials and testing the stability and efficiency of the intercalation process (Xu et al., 2024). Simulations also show that CO_2 is formed during chemical reactions in the electrolyte and plays a role in enhancing the formation of inorganic compounds such as Li_2CO_3, which can stabilize the SEI layer and reduce the decomposition of organic solvents (Spotte-Smith et al., 2022). CO_2 has positive implications for battery performance and safety, but uncontrolled accumulation can pose safety risks (Chen et al., 2020). Therefore, optimizing CO_2 concentration and electrolyte design is crucial for balancing battery performance and safety. Computer simulations are key to the development of next-generation lithium-ion batteries.

The objective of this study is to determine the entropy variable and the average energy of the system, which consists of lithium salt and the organic solvent EC. These variables are essential because knowing them allows the derivation of the Boltzmann factor. Naturally, these variables must first be maximized in order to reach thermal equilibrium. In performing Monte Carlo (MC) steps, achieving thermal equilibrium is a necessary condition

Entropy is critically important in research because it enables the derivation of the Boltzmann factor, which describes the relative probability of a system possessing a certain energy at a given temperature. Entropy must be maximized to achieve thermal equilibrium in Monte Carlo (MC)

simulations, which is a crucial step toward reaching the global minimum. The Boltzmann factor can be derived from the concept of entropy and the principle of maximum entropy, which are related to the Boltzmann constant (k) and the number of accessible states (Ω). Researchers use parameters epsilon (ε) and sigma (σ) from the Lennard-Jones potential, along with the canonical ensemble, to study the system (Parashar & Jha, 2020). Thus, a deep understanding of entropy and the Boltzmann factor is essential in the simulation and analysis of thermodynamic systems.

The strategy of entropy enhancement for improving lithium battery cathode performance has been demonstrated by Ajayi et al. (2024), involving the incorporation of multiple atomic species to increase configurational entropy. Higher configurational entropy can improve material properties such as capacity and structural stability by making the system more adaptable to environmental changes. Specifically, increasing the number of atomic species enhances the thermodynamic stability of cathode materials, regulates redox processes, and reduces oxygen release. The greater atomic diversity increases the number of possible configurations, thereby strengthening configurational entropy (Lin et al., 2025; Yuxin et al., 2025).

Beyond cathodes, entropy engineering has also been applied to electrolytes. Guo et al. (2024) reported the development of sulphide-based argyrodite solid electrolytes through the introduction of Cl and Br atoms, leading to high configurational entropy. These LiPSClBr electrolytes exhibited ionic conductivity as high as 6.9 $mS \cdot cm^{-1}$ at room temperature, along with high areal capacity (>6 $mAh \cdot cm^{-2}$) and good stability. The enhanced configurational entropy was identified as the key factor driving improved lithium-ion conductivity and overall electrochemical performance.

Monte Carlo (MC) simulations provide a useful framework to understand such entropy-driven phenomena at the molecular scale. In particular, they can capture solvation events between $LiPF_6$ salt and ethylene carbonate (EC) solvent, where molecular motion occurs randomly. These simulations offer valuable insights into microscopic processes, including solvation behaviour, lithium dendrite formation, and the development of the solid electrolyte interphase (SEI). Consequently, MC simulations represent a powerful tool for elucidating complex interactions in lithium-ion battery systems.

2. METHOD

This study uses the MC simulation method with the Metropolis algorithm to calculate entropy variables, atomic positions, and average energy. The simulation is run using Scilab software version 6.1.1. In this simulation, the values of epsilon (ε) and sigma (σ) are standard parameters in the Lennard-Jones potential to describe interatomic interactions. The non-bonding interaction parameters and charges for EC were obtained from the study by Masia et al. (2004) , while the parameters for PF_6 were obtained from the study by Jorn et al. (2013) . However, the Lennard-Jones sigma parameter for phosphorus was taken from the universal force field (UFF) developed by Rappé et al. (1992; 1993).

Table 1. Non-bonded LJ parameters used for the simulation of $LiPF_6$ dissolved in EC.

Atomic pair	**ε (kJ/mol)**	**σ (Å)**	**Atomic pair**	**ε (kJ/mol)**	**σ (Å)**
Lithium - lithium	0.4315	1.4424	hydrogen-hydrogen	0.12552	2.5
Carbon-Carbon	0.2761	3.5	phosphorus-phosphor	0.0035	3.1
Oxygen-oxygen	0.4017	3.405	Fluor-fluor	0.12015	2.9347

In the case of the code, the values of ε and σ used can be seen in Table 1. These values are taken from several references; for example, the ε and σ values for oxygen are 0.096 kcal/mol (0.4017 kJ/mol) and 3.405 Å . The epsilon and sigma values for hydrogen are 0.030 kcal/mol (0.12552 kJ/mol) and 2.5 Å (Rappé et al., 1992). These values may vary depending on the type of atom and environmental conditions. Researchers will intentionally make the conditioning dependent on the atom type and environmental conditions. The epsilon and sigma values may vary depending on the intrinsic properties of the atom, external factors, and the system environment. The epsilon and sigma values are not universal and should be chosen with critical consideration and validated with experimental data or ab

initio simulations (Erickson et al., 2011). The epsilon and sigma values in the coding appear to be valid in the context of MC simulations for systems consisting of lithium, carbon, oxygen, hydrogen, and phosphorus atoms.

The values of epsilon and sigma for interactions between different atoms (for example, lithium–carbon) are calculated using commonly applied combination rules, such as the Lorentz–Berthelot rule, as shown in the coding script, with one example illustrated in the equation below.

$$\varepsilon_{LiC} = \sqrt{(\varepsilon_{LiLi} + \varepsilon_{CC})} \quad (1)$$

$$\sigma_{LiC} = (\sigma_{LiLi} + \sigma_{CC}) / 2 \quad (2)$$

Equations (1) and (2) were intentionally implemented in the coding script using the Scilab 6.1.1 programming language, where ε_{LiC} represents the Lennard-Jones potential energy for lithium-carbon interactions, and σ_{LiC} denotes the Lennard Jones radius for lithium-carbon. The code applies the Lorentz-Berthelot combination rule to calculate the Lennard-Jones interaction parameters between different atoms.

The script for calculating the Lennard-Jones interaction parameters for three types of atoms-lithium, carbon, and oxygen is included in the coding as follows:

$$\varepsilon_{LiO} = \sqrt{(\varepsilon_{LiLi} + \varepsilon_{OO})} \quad (3)$$

$$\sigma_{LiO} = (\sigma_{LiLi} + \sigma_{OO}) / 2 \quad (4)$$

$$\varepsilon_{CO} = \sqrt{(\varepsilon_{CC} + \varepsilon_{OO})} \quad (5)$$

$$\sigma_{CO} = (\sigma_{CC} + \sigma_{OO}) / 2 \quad (6)$$

Equations (1), (2), (3), (4), (5), and (6) were implemented using the Lorentz-Berthelot rules. By applying the Lorentz-Berthelot rules, the Lennard-Jones interaction parameters between different atoms can be calculated based on the interaction parameters of identical atoms, thereby simplifying the computation of interactions between dissimilar atoms.

The values of entropy and average energy are calculated at each simulation step and printed every 10 steps. The values of entropy and average energy equal to zero are merely the initialization of the corresponding variables with an initial value of zero. The command used for this purpose applies the structure "if modulo(i,10) == 0 then". This command prints the values of average energy and entropy every 10 steps during the program execution. The script for displaying these values employs the printf command in Scilab 6.1.1. The "If" structure must be terminated with the "end" statement in the code.

The unit of entropy may vary depending on the context. However, in thermodynamics, the commonly used units of entropy are J/K (Joule per Kelvin), kJ/K (kilojoule per Kelvin), or cal/K (calorie per Kelvin). In the coding script, it can be written as: "entropy = average_potential_energy / T". Entropy is calculated as the average potential energy divided by the temperature (T), so the unit of entropy will depend on the units of average potential energy and temperature. For example, if the average potential energy has the unit of kJ/mol and the temperature is expressed in Kelvin (K), then the entropy unit will be kJ/(mol·K).

Entropy is defined as a measure of the disorder or randomness of a system. The maximum entropy principle states that systems tend towards a state with maximum entropy in thermodynamic equilibrium. By applying the principle of maximum entropy, a probability distribution of a system having a certain energy (E) can be derived, known as the Boltzmann distribution. This probability distribution can be calculated using the formula.

$$P(E) \approx exp(-E/kT) \quad (7)$$

Where P(E) is the probability of the system having energy E, k is Boltzmann's constant, and T is the temperature. The Metropolis criterion allows the system to accept energy-increasing changes with temperature-dependent probabilities and energy differences, allowing the system to explore a wider configuration space and achieve a more optimal configuration. The MC simulation will continue to run until predefined stopping criteria are reached, such as the maximum number of iterations or energy convergence. The Metropolis criterion is a method to determine whether a change in atomic position is accepted or rejected in an MC simulation. The Metropolis criterion is based on the Boltzmann

distribution, which describes the probability of a system being in a certain state. Where *P(E)* is the probability of the system having energy *E*, *k* is Boltzmann's constant, and *T* is the temperature. The Metropolis criterion allows the system to accept energy-increasing changes with temperature-dependent probabilities and energy differences, allowing the system to explore a wider configuration space and achieve a more optimal configuration. The MC simulation will continue to run until predefined stopping criteria are reached, such as the maximum number of iterations or energy convergence. The Metropolis criterion is a method to determine whether a change in atomic position is accepted or rejected in an MC simulation. The Metropolis criterion is based on the Boltzmann distribution, which describes the probability of a system being in a certain state.

In MC simulations, the Metropolis criterion is used to ensure that the system is in thermal equilibrium at a given temperature. The Metropolis criterion can be explained as follows: (1) Calculate the energy change (ΔE) associated with the change in atomic position. (2) If $\Delta E \leq 0$, then the change in atomic position is accepted. (3) If $\Delta E > 0$, then the change in atomic position is accepted with probability $\exp(-\Delta E/kT)$, where k is Boltzmann's constant and T is the temperature. In the Metropolis criterion, the probability of accepting a change in atomic position is determined by the factor $\exp(-\Delta E/kT)$. If ΔE is large and positive, then the probability of accepting a change in atomic position will be small. Conversely, if ΔE is small or negative, then the probability of accepting the change in atomic position will be large. The Metropolis criterion is used to ensure that the system is in thermal equilibrium at a given temperature and that the distribution of atomic positions corresponds to the Boltzmann distribution. By using the Metropolis criterion, MC simulations can produce realistic and accurate atomic configurations. The use of Boltzmann factors in MC simulations allows the system to "jump" out of shallow energy valleys and seek more globally stable configurations. The Boltzmann factor enables the system to accept new configurations with higher energy than the current energy, thus allowing the system to break out of the local minimum and seek a more optimal configuration. Accordingly, the system can achieve a more optimized and realistic configuration instead of just being stuck in a shallow local minimum.

Probability density is a function that describes the probability distribution of a random variable. In the context of MC simulation, probability density is used to describe the probability distribution of system states. Detailed equilibrium, as explained earlier, is a condition that requires the transition probabilities between two states a certain relationship. The link between probability density and detailed equilibrium is as follows: if a system has a stable probability density, the system must satisfy the detailed equilibrium condition. That is, if the system is in equilibrium, the transition probabilities between the two states must quench the detailed equilibrium relationship so that the probability distribution of the system remains stable. In the context of the Metropolis algorithm, the desired probability density is the Boltzmann distribution, which describes the probability distribution of the system state in thermal equilibrium. The Metropolis algorithm uses detailed equilibrium to ensure that the resulting samples are accurate and representative of the Boltzmann distribution. In canonical ensembles, the temperature is considered constant because the total energy of the system is considered fixed.

The use of this factor allows the system to escape from shallow energy wells and search for a more globally stable configuration. If the system becomes trapped in a local minimum, the Monte Carlo (MC) simulation program does not stop automatically. The MC simulation continues running and attempts to find a more globally stable configuration using the Metropolis criterion. If the system is trapped in a local minimum, the MC simulation keeps testing changes in atomic positions and accepts or rejects those changes based on the Metropolis criterion. This part of the script is the implementation of the Metropolis algorithm in the MC simulation. The command if delta_energy ≤ 0 means that if the change in energy (delta_energy) is less than or equal to 0, the position change is accepted. This is because a negative change in energy indicates that the system is becoming more stable. The command rand() < exp(-beta * delta_energy) means that if the change in energy (delta_energy) is greater than 0, the position change is accepted with a certain probability. This probability is calculated using the Boltzmann distribution, which is exp(-beta * delta_energy), where beta is the inverse of temperature (1/(R*T)) and rand() is a random number between 0 and 1. If this random number is less than the Boltzmann probability, the position change is accepted. If the position change is accepted, the initial

potential energy is updated to the new potential energy. If the position change is rejected, the atom's position is restored to its previous state.

A modified flow chart for the Monte Carlo (MC) simulation code with six atom types—lithium, carbon, oxygen, hydrogen, phosphorus, and fluorine—is presented in Figure 1. The procedure consists of three main stages. (A) Initialization: (A1) define the number of atoms for each atom type; (A2) specify the simulation box size (L); (A3) set the temperature (T) and the universal gas constant (R); (A4) assign the Lennard–Jones parameters for all possible atom pairs (e.g., Li–Li, Li–C, Li–O, Li–H, Li–P, Li–F, C–C, C–O, C–H, C–P, C–F, O–O, O–H, O–P, O–F, H–H, H–P, H–F, P–P, P–F, and F–F); and (A5) initialize the atomic positions randomly. (B) Monte Carlo simulation: for a predefined number of steps, the algorithm (B1) randomly selects an atom, (B2) updates its position, (B3) recalculates the potential energy considering interactions with all other atoms, (B4) evaluates the energy change, (B5) accepts or rejects the new position based on the Boltzmann probability, (B6) updates the average potential energy, and (B7) records entropy and average energy values. (C) Visualization: the final stage includes (C1) visualizing the initial and final positions of each atom type, (C2) plotting entropy as a function of the number of steps, and (C3) plotting average potential energy as a function of the number of steps.

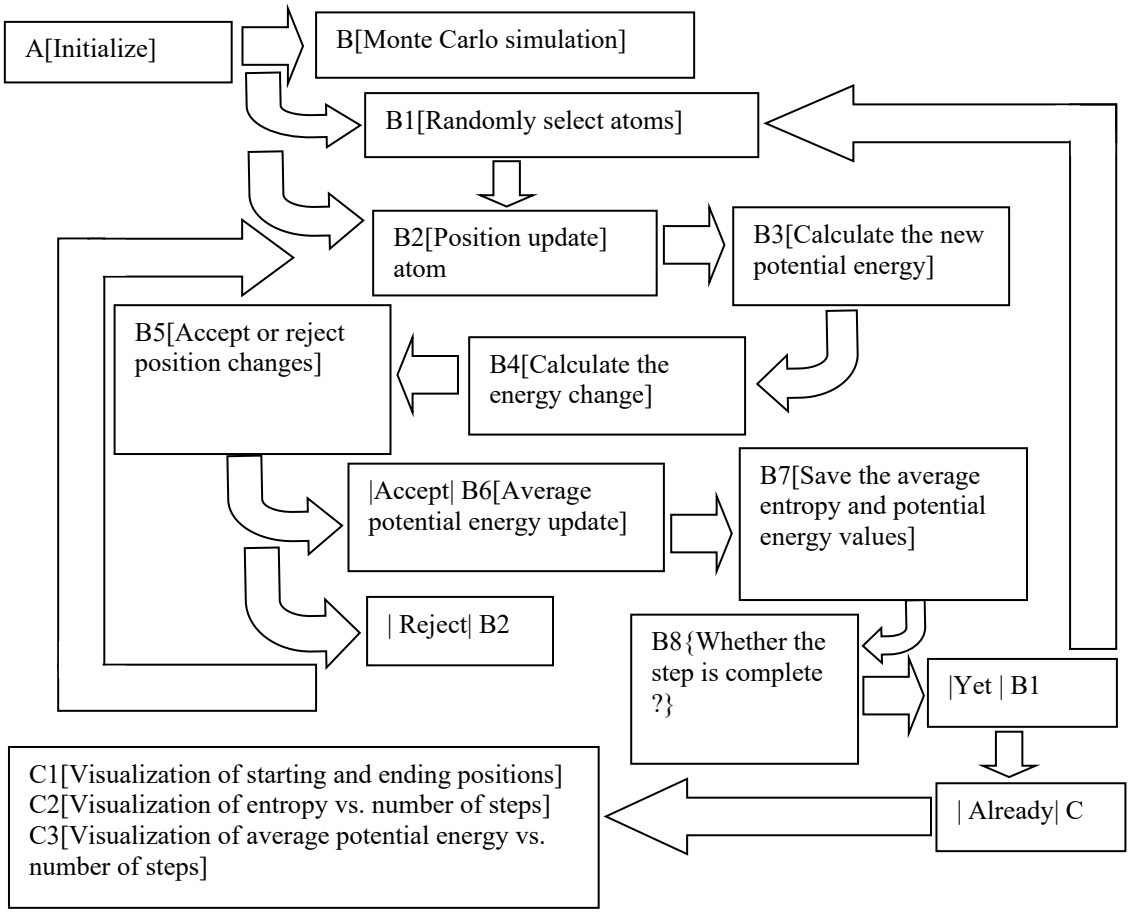

Figure 1. Flow chart for MC simulation code for five atoms, lithium, carbon, oxygen, hydrogen, and phosphorus atoms: (A) Initialization. (B) MC simulation, iterate as many steps as specified. (C) Visualization.

In the script, the number of lithium and carbon atoms is defined as N_Li = 100 and N_C = 100. A similar approach is applied to other atom types, such as oxygen, hydrogen, and phosphorus, each consisting of 100 particles, but written separately for each case. The initial positions of the atoms are generated using commands such as position = rand(N_Li, 3) * L and position_C = rand(N_C, 3) * L, where the program assigns random coordinates within the simulation box (L) to distribute 100 atoms randomly. In addition, the code initializes entropy and average energy variables to zero, which does not

imply that the system's entropy or energy is actually zero. Instead, these values are set to zero at the start to prepare the variables for subsequent calculations. For example, energy_potential_flat = 0 initializes the scalar variable, while entropy_vector = zeros(1, step) creates an entropy vector of size *step* with initial values of zero. Similarly, energy_potential_flat_vector = zeros(1, step) initializes the average potential energy vector with the same size and zero entries. These initializations ensure that the variables are properly defined before being updated during the simulation.

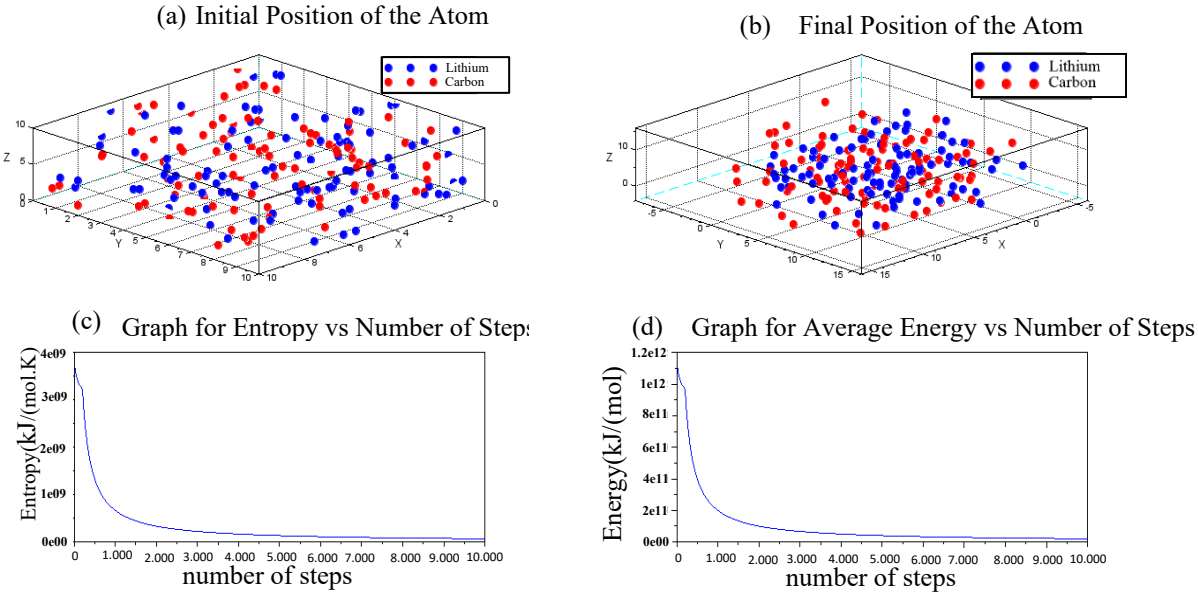

Figure 2. Monte Carlo (MC) simulation with ε and σ values for lithium–lithium, carbon–carbon, and lithium–carbon interactions. (a) Initial atomic positions, (b) final atomic positions, (c) entropy versus number of steps (10,000 steps), and (d) average potential energy versus number of steps. Stabilization of both entropy and potential energy indicates that the system has reached equilibrium.

3. RESULTS AND DISCUSSION

The results of the simulations are presented in Figures 2–6, with the Lennard–Jones parameters (ε and σ) obtained from Table 1. These figures illustrate solvation events involving $LiPF_6$ salt and the solvent ethylene carbonate $(CH_2O)_2CO$. Figure 2 specifically shows the Monte Carlo (MC) simulation results for lithium–lithium, carbon–carbon, and lithium–carbon interactions, where entropy is plotted against the number of simulation steps. In this case, the simulation was run for 10,000 steps. The appropriate number of MC steps depends on various factors, including the desired level of accuracy, system complexity, temperature, and other simulation parameters. Generally, larger systems and higher temperatures require more steps to achieve equilibrium. For relatively simple systems, 10,000–100,000 steps may be sufficient, whereas more complex systems may require 100,000–1,000,000 steps or more. In this study, running 10,000 steps for a system of 100 lithium and 100 carbon atoms required approximately 20 minutes of computation time. Equilibrium was assessed by monitoring key parameters such as average potential energy and entropy. Once these quantities stabilized, the system was considered to have reached equilibrium, confirming that the number of steps used was adequate for the present simulations.

In Markov chains, a stationary state refers to a condition in which the probability distribution of the system no longer changes with time. Once the system reaches this state, the probability distribution remains constant for all subsequent steps, as illustrated in Figure 2 (Entropy vs. Number of Steps and Average Energy vs. Number of Steps). In Monte Carlo (MC) simulations using the Metropolis algorithm, thermal equilibrium corresponds to the stationary state of the Markov chain. At this point, the system's probability distribution follows the Boltzmann distribution, which characterizes systems in thermal equilibrium.

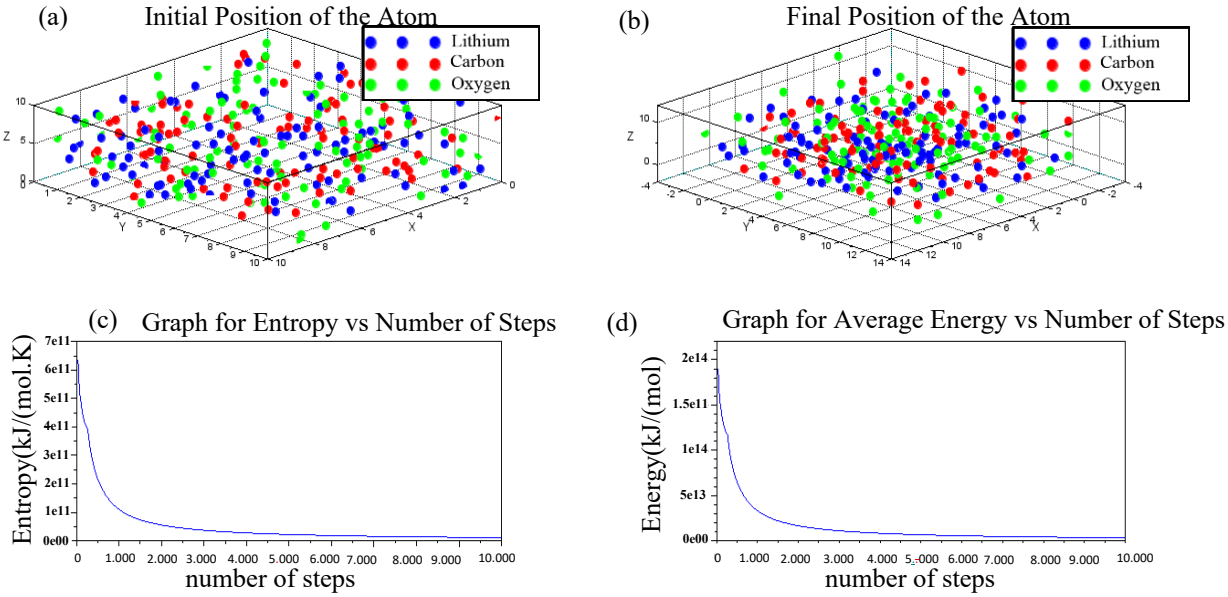

Figure 3. Monte Carlo (MC) simulation with ε and σ values for lithium–lithium, carbon–carbon, oxygen–oxygen, lithium–oxygen, oxygen–carbon, and lithium–carbon interactions. (a) Initial atomic positions, (b) final atomic positions, (c) entropy versus number of steps (10,000 steps), and (d) average potential energy versus number of steps. Stabilization of entropy and potential energy confirms that the system has reached equilibrium.

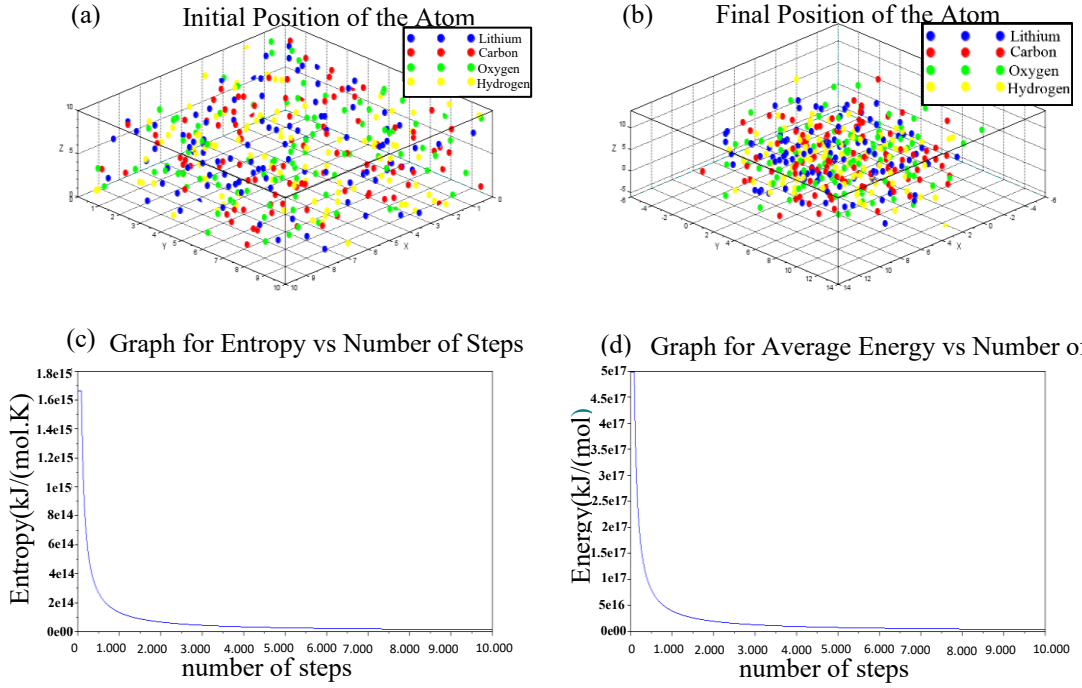

Figure 4. Monte Carlo (MC) simulation with ε and σ values for lithium–lithium, carbon–carbon, oxygen–oxygen, hydrogen–hydrogen, lithium–oxygen, oxygen–carbon, lithium–carbon, lithium–hydrogen, carbon–hydrogen, and oxygen–hydrogen interactions. (a) Initial atomic positions, (b) final atomic positions, (c) entropy versus number of steps (10,000 steps), and (d) average potential energy versus number of steps. Stabilization of entropy and potential energy indicates that the system has reached equilibrium.

During the simulations, entropy and average energy values were calculated at each step and recorded every 10 steps (Figure 2). At the 10,000th step, the entropy reached equilibrium at 6.67×10^7 kJ·mol^{-1}·K^{-1}, while the average energy stabilized at 2×10^{10} kJ·mol^{-1}. Figure 3 presents the MC

simulation results with ε and σ values for lithium–lithium, carbon–carbon, oxygen–oxygen, lithium–oxygen, oxygen–carbon, and lithium–carbon interactions, as listed in Table 1.

The Monte Carlo (MC) simulation results for lithium–carbon–oxygen interactions are shown in Figure 3, where entropy is plotted against the number of steps (10,000 steps). As noted earlier, the appropriate number of simulation steps depends on factors such as accuracy, system complexity, and temperature. Compared to the simpler two-atom system in Figure 2, this three-atom system is more complex and therefore ideally requires more steps to reach equilibrium. However, the simulation was still limited to 10,000 steps, given that the system remained a canonical ensemble at a standard temperature of 300 K. Running the simulation for 100 lithium, 100 carbon, and 100 oxygen atoms required approximately 40 minutes of computation.

Equilibrium was determined by monitoring entropy and average potential energy. Stabilization of both parameters indicates that the system has reached equilibrium. At the 10,000th step, entropy reached 1.1×10^{10} kJ·mol^{-1}·K^{-1}, while average potential energy stabilized at 3.3×10^{12} kJ·mol^{-1} (Figure 3). These values were obtained using the Boltzmann factor, which enables the system to escape shallow energy valleys and explore more globally stable configurations. If the system becomes trapped in a local minimum, the MC simulation does not terminate; rather, it continues to attempt position updates using the Metropolis criterion until a more stable configuration is identified.

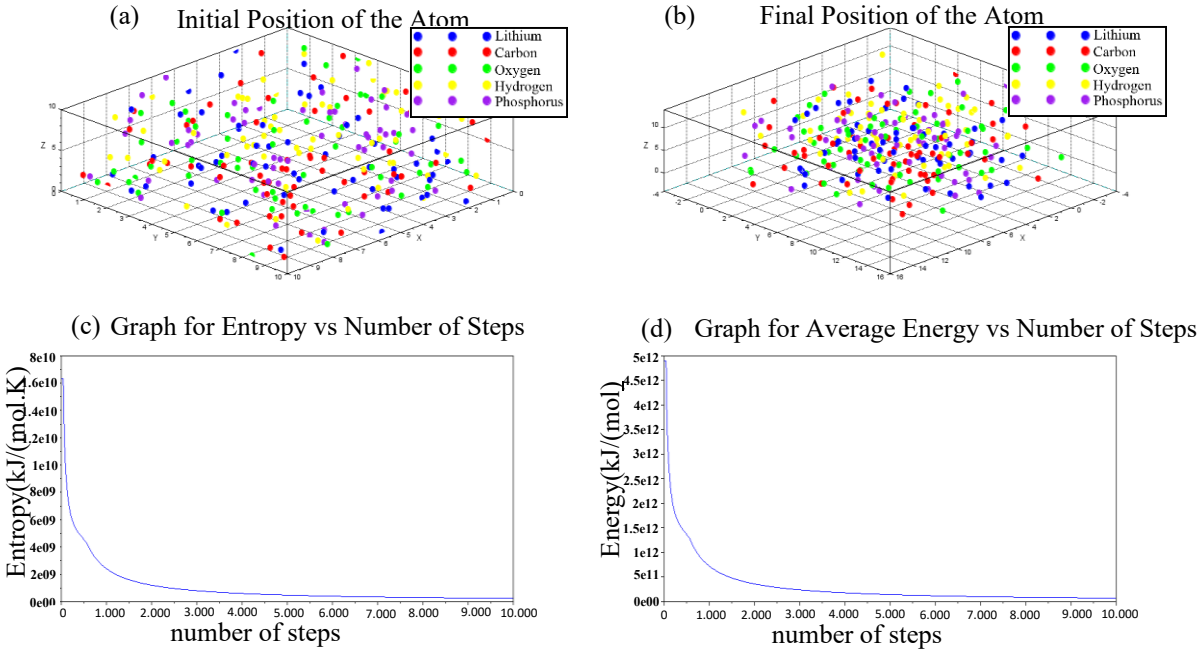

Figure 5. Monte Carlo (MC) simulation with ε and σ values for lithium–lithium, carbon–carbon, oxygen–oxygen, hydrogen–hydrogen, phosphorus–phosphorus, lithium–oxygen, oxygen–carbon, lithium–carbon, lithium–hydrogen, carbon–hydrogen, oxygen–hydrogen, lithium–phosphorus, carbon–phosphorus, oxygen–phosphorus, and hydrogen–phosphorus interactions. (a) Initial atomic positions, (b) final atomic positions, (c) entropy versus number of steps (10,000 steps), and (d) average potential energy versus number of steps. Stabilization of entropy and potential energy indicates that the system has reached equilibrium.

Figure 4 presents the MC simulation for four atom types: lithium, carbon, oxygen, and hydrogen, with interaction parameters (ε and σ) defined as shown in Figure 1. At 10,000 steps, entropy reached 1.3×10^{13} kJ·mol^{-1}·K^{-1} and average potential energy stabilized at 3.3×10^{15} kJ·mol^{-1}. Notably, the entropy for the four-atom system (1.3×10^{13} kJ·mol^{-1}·K^{-1}) was significantly higher than that of the three-atom system (1.1×10^{10} kJ·mol^{-1}·K^{-1}), demonstrating that increasing atomic diversity enhances system disorder. The Boltzmann factor again played a critical role in guiding the system toward more stable global configurations.

Figure 5 extends the simulation to five atom types—lithium, carbon, oxygen, hydrogen, and phosphorus—with ε and σ parameters defined for all pairwise interactions (see Figure 1). At 10,000 steps, the entropy stabilized at 2.4×10^{8} kJ·mol^{-1}·K^{-1}, while the average potential energy reached 7.2×10^{10} kJ·mol^{-1}. Interestingly, this entropy value is lower than that obtained for the four-atom system (1.3×10^{13} kJ·mol^{-1}·K^{-1}). Although entropy would typically increase with additional atom types, in this case the total particle number was deliberately reduced to 300 atoms (60 atoms per type) to minimize computational cost. Running simulations with 100 atoms per type was found to be prohibitively time-consuming.

Figure 6 further extends the simulation to six atom types—lithium, carbon, oxygen, hydrogen, phosphorus, and fluorine—with ε and σ parameters defined for all pairwise interactions. At 10,000 steps, the entropy stabilized at 3.11×10^{13} kJ·mol^{-1}·K^{-1}, while the average potential energy reached approximately 9.32×10^{15} kJ·mol^{-1}. These results demonstrate that the addition of fluorine atoms significantly increased system entropy compared to the five-atom case, reflecting the enhanced configurational complexity and interaction diversity of the system.

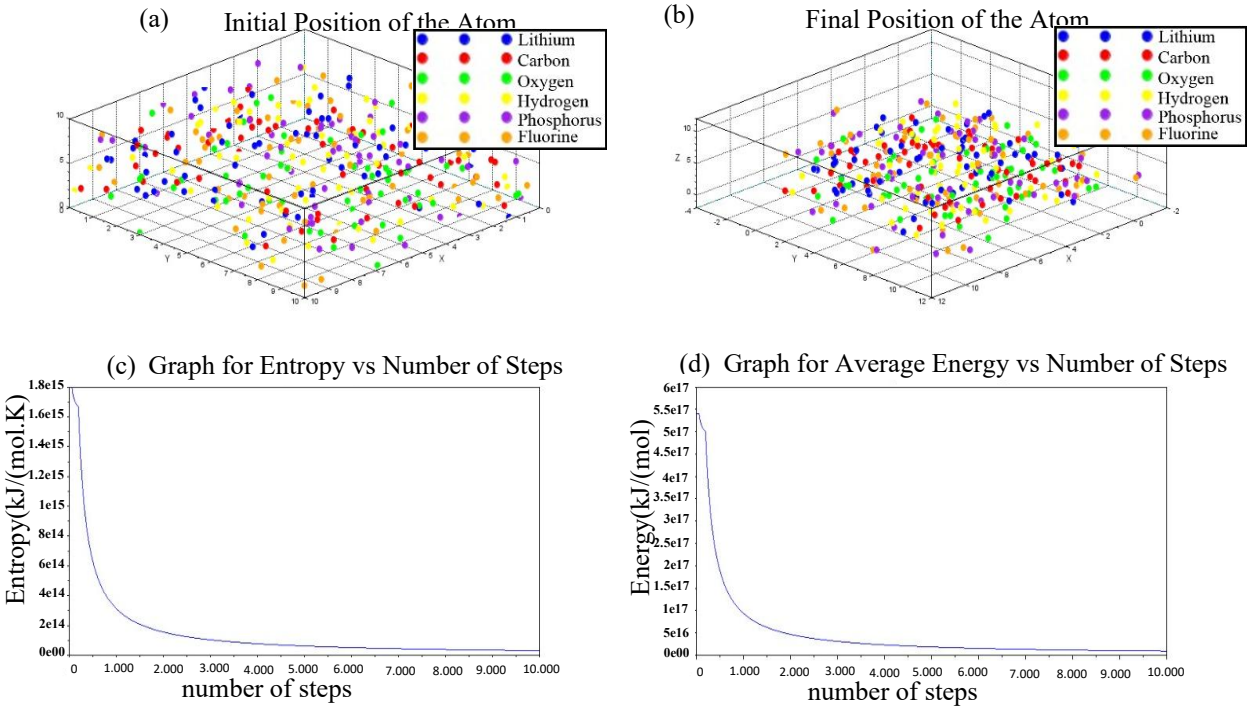

Figure 6. Monte Carlo (MC) simulation with ε and σ values for lithium–lithium, carbon–carbon, oxygen–oxygen, hydrogen–hydrogen, phosphorus–phosphorus, fluorine–fluorine, lithium–oxygen, oxygen–carbon, lithium–carbon, lithium–hydrogen, carbon–hydrogen, oxygen–hydrogen, lithium–phosphorus, carbon–phosphorus, oxygen–phosphorus, hydrogen–phosphorus, lithium–fluorine, carbon–fluorine, oxygen–fluorine, hydrogen–fluorine, and phosphorus–fluorine interactions. (a) Initial atomic positions, (b) final atomic positions, (c) entropy versus number of steps (10,000 steps), and (d) average potential energy versus number of steps. Stabilization of entropy and potential energy indicates that the system has reached equilibrium.

The universal gas constant (R) plays a specific role in ensuring unit consistency and in entropy-related calculations within the Monte Carlo (MC) simulation. In the coding framework, the Lennard–Jones potential energy (ε) is expressed in kJ·mol^{-1}; for example, ε for lithium is relatively small, at 0.4315 kJ·mol^{-1} (Table 1). To maintain consistent units, R = 8.314 J·mol^{-1}·K^{-1} was converted to 0.008314 kJ·mol^{-1}·K^{-1}. Entropy calculations in thermodynamics frequently involve R, with the Boltzmann constant (kB) applied at the molecular scale, and R at the molar scale (Ma et al., 2025).

Configurational entropy is particularly significant in advanced battery materials. In lithium-rich layered oxides (LRLOs), increasing configurational entropy enhances electrochemical performance by stabilizing the material structure (Ajayi et al., 2025; Samuel et al., 2024). Similarly, high-entropy oxides (HEOs) are characterized by intrinsically high entropy, where configurational entropy contributes to both structural stability and electrochemical properties. In such systems, R is fundamental to the calculation and classification of configurational entropy (Lin et al., 2025; Yuxin et al., 2025).

A system with high entropy is primarily characterized by configurational entropy. The configurational mixing entropy (ΔS_{conf}), calculated using R, provides a basis for classifying materials as follows: (1) $\Delta S_{conf} > 1.5R \rightarrow$ high-entropy materials; (2) $1.0R < \Delta S_{conf} < 1.5R \rightarrow$ medium-entropy materials; and (3) $\Delta S\_conf < 1.0R \rightarrow$ low-entropy materials (Lin et al., 2025; Yuxin et al., 2025). Table 2 summarizes this classification, with $R = 8.314$ J·mol^{-1}·K^{-1}.

For the first case, a system consisting of 100 lithium atoms and 100 carbon atoms (200 total) was simulated. The initial entropy was 6.659792×10^6 kJ·mol^{-1}·K^{-1}, and the final entropy was 6.659792×10^6 kJ·mol^{-1}·K^{-1}. To simplify presentation, only the first digit before the decimal point is reported in Table 2. The resulting ΔS_{conf} was 0.0018 kJ·mol^{-1}·K^{-1}, equivalent to 1.8 J·mol^{-1}·K^{-1} after conversion for consistency with R. Based on this value, the lithium–carbon system is classified as a medium-entropy material. These entropy values were obtained from the Monte Carlo simulation results presented in Figure 2.

For the second case, the system consisted of 100 lithium, 100 carbon, and 100 oxygen atoms (300 total). The initial entropy was $1.1066951168 \times 10^{10}$ kJ·mol^{-1}·K^{-1}, and the final entropy was $1.1066951168 \times 10^{10}$ kJ·mol^{-1}·K^{-1}. As with the previous case, only the first digit before the decimal point was reported in Table 2 for clarity. The calculated ΔS_{conf} was 0.0025 kJ·mol^{-1}·K^{-1}, equivalent to 2.5 J·mol^{-1}·K^{-1} after conversion. Based on this value, the lithium–carbon–oxygen system is classified as a high-entropy material. These results were obtained from the Monte Carlo simulation presented in Figure 3.

For the third case, the system included 100 lithium, 100 carbon, 100 oxygen, and 100 hydrogen atoms (400 total). The initial entropy was $1.3155251118 \times 10^{13}$ kJ·mol^{-1}·K^{-1}, while the final entropy was $1.3155251118 \times 10^{13}$ kJ·mol^{-1}·K^{-1}. Again, only the first digit before the decimal point was reported in Table 2. The corresponding ΔS_{conf} was 0.040 kJ·mol^{-1}·K^{-1}, or 40 J·mol^{-1}·K^{-1}, placing this system firmly in the high-entropy material category. The entropy values were obtained from the Monte Carlo simulation shown in Figure 4.

Table 2. For lithium and carbon atoms, ΔS_{conf} is 1.8 J/mol.K, classifying the material as a medium-entropy material. For lithium, carbon, and oxygen atoms, ΔS_{conf} is 2.5 J/mol.K (high-entropy material). For lithium, carbon, oxygen, and hydrogen atoms, ΔS_{conf} is 40 J/mol.K (high-entropy material).

No	Atom	Number of atoms	Initial Entrophy	Final Entrophy	ΔS_{conf} (J/mol.K)	Classification
1	lithium and carbon	200	2.337907	2.336107	1.8	Medium-entropy material
2	lithium, carbon and oxygen	300	7.996499	7.998999	2.5	high-entropy material
3	lithium, carbon, oxygen dan hydrogen	400	3.7725	3.812500	40	high-entropy material
4	Lithium Atom, carbon, oxygen, hydrogen and phosphorus	360	8.324649	8.346649	22	high-entropy material

4. CONCLUSION

Solvation event where the LiPF6 salt and the solvent ethylene carbonate $(CH_2O)_2CO$ interact. In this MC simulation, the number of steps is 10,000, for two types of atoms, the entropy value is 6 x $67x10^7$ kJ/mol.K, and the average energy is $2x10^{10}$ kJ/mol for three kinds of atoms with an amount of 300 pieces. If the entropy is stable, the system has reached equilibrium, and the value is $1.1x10^{10}$

kJ/mol.K, and the average energy is $3.3x10^{12}$ kJ/mol. The simulation will continue to run and try to find a more globally stable configuration using the Metropolis criterion. If the system is trapped inside the local minimum, the simulation will try to change the atom's position and accept or reject the change. The entropy value for four types of atoms is larger than that of 3, 1.3×10^{13} kJ/mol.K. The entropy value for five kinds of atoms is $2.4x10^{8}$ kJ/mol.K, and the average energy is $7.2x10^{10}$ kJ/mol. The entropy value is smaller than that of the four types of atoms because the researcher intentionally reduces the number of particles, 300 atoms, to shorten the running time. The same thing also applies to 6 atoms: lithium, carbon, oxygen, hydrogen, phosphorus and fluorine. The number of particles is 360 atoms, so the entropy value is 3.11×10^{13} kJ/mol.K. Overall, the entropy is affected by the number of atoms, interactions between particles, and environmental conditions. The number of atoms affects entropy because the greater the number of atoms, the greater the disorder or randomness increases. Strong interactions between the salt and the solvent can reduce the system's entropy, while weak interactions (van der Waals interactions) can increase the system's entropy. The phase change of LiPF6 salt and EC solvent can increase the system's entropy because the liquid phase has higher disorder than the solid phase. The interaction between LiPF6 salt and EC solvent affects the system's entropy.

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