CONTRIBUTIONS TO MEAN-CLUSTER MODELING OF STRUCTURED MATERIALS - APPLICATIONS TO LITHIUM-ION BATTERIES

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BY

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Abstract

One of the questions arising as regards to structured materials is how one can compute their cluster concentrations. Specifically, we are interested in deriving the concentrations of the micro-structures in the NMC (Nickel-Manganese-Cobalt) layer of the cathodes of Li-ion batteries. A simulated annealing approach has been used lately for detecting the structure of the whole lattice which is computationally heavy. Here we propose a mathematical model, called cluster approximation model, in the form of a dynamical system for describing the concentrations of different clusters inside the lattice. However, the dynamical system is hierarchical which requires to be truncated. Truncation of the hierarchical system is performed by the nearest-neighbor closure scheme. Also, a novel framework is proposed for an optimal closure of the dynamical system in order to enhance the accuracy of the model. The parameters of the model are reconstructed by the least square approach as a constrained optimization problem by minimizing the mismatch between the experimental data and the model outputs. The model is validated based on the experimental data on a known Li-ion battery cathode and different approximation schemes are compared. The results clearly show that the proposed approach significantly outperforms the conventional method.

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Symbols

E_i	Local energy of the i-th oxygen site
$C(TM_i)$	Charge of the i-th transition metal
$P(\Delta E)$	Probability assigned to an element swap
C_i	Marginal probability of finding a singlet in the i state
C_{ij}	Probability of finding a pair in the ij state
$C_{\overline{ijk}}$	Probability of finding a linear triplet in the ijk state
$C_{\widehat{ijk}}$	Probability of finding an open triplet in the ijk state
$C_{\widehat{\overline{ijk}}}$	Probability of finding a triangular triplet in the ijk state
k_i	Rate constant
Q_i	Equilibrium constant
$P_{i/j}$	Conditional probability of being in state i with a neighbor in state j
Q_{ij}	Pair correlation of nearest-neighbor elements
T_{ijk}	Triple correlation of a triplet
θ	Probability of finding a closed triplet in a lattice
N	Population size
m	Number of neighbors of each site
β_i	Ratios of equilibrium constants
F	Cost functional of regression problem
J	Cost functional of inverse problem
$\widetilde{C}$	Experimental concentrations

$\widetilde{Q}$	Experimental equilibrium constants
T	Final time

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Chapter 1

Introduction

Lithium-ion batteries are one of the emerging technologies that are impacting our lives significantly. They are the leading technology used in the portable electronic devices such as tablets and phones [26]. Also, they are getting more attention in the field of electric vehicles [37], where the combination of electricity and carbon fuel is used to mitigate the carbon footprint. The technology has also found applications in aerospace engineering and medical devices such as hearing aids. It has given rise to miniaturized high-density rechargeable power sources to be used in small medical devices for drug-delivery and glucose sensing applications [25]. The technology still needs to develop in the field of power supply systems, leaving a huge gap in the industry to be filled by emerging technologies. Lithium-ion batteries present great potential as regards to sustainable energies and mitigation of carbon emission [23].

Different materials have been used for the chemistry of batteries, however, lithium is among the most promising ones. Light weight, high electropositivity, wide accessibility and being nontoxic are some of the reasons that lithium is the primary choice for batteries [24]. Also, high energy-to-weight ratio, low self-discharge, excellent cycle life and no memory effect are the other advantages of lithium batteries over its rivals [30, 31]. In addition to all these advantages, lithium is highly reactive which makes its safe use challenging. This problem is addressed by using compounds of lithium, rather than the metallic lithium. These compounds provide ionic lithium used in the reversible reactions inside the battery.

Each battery cell consists of four parts, namely, cathode, anode, electrolyte and separator. During the charge of the battery, lithium ions migrate from the cathode toward the anode through the electrolyte. However, the reverse happens during the discharge of the battery. The intercalation and insertion of lithium ions occurs on the surface of the cathode material, which is the solid host for arriving ions. The electrolyte contains a solvent which provides the medium for migration of lithium ions. The separator is a barrier which prevents the direct contact of the cathode and anode (short-circuit), while letting lithium ions pass through it. The schematic of a Li-ion battery is shown in figure 1.1. Normally, Li-ion batteries are named after their cathode type, which is a lithium metal oxide material such as lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium nickel cobalt aluminum oxide (NCA) and nickel manganese oxide (NMO) [24]. Later, Co was added to $Li(Ni_{1/2}Mn_{1/2})O_2$ to further enhance its structure stability [27, 30]. This new cathode is commercially called NMC cathode and has the chemical composition $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. It has a layered structure where layers of oxygen are surrounded by a lithium layer and a transition metal layer. NMC cathodes have been investigated widely with different stoichiometries of metals in the NMC layer. Recently, a new generation of Li-rich and Mn-rich batteries has been introduced such as Li_2MnO_3, which have higher capacities than normal NMC cathodes [28]. Also, a significant irreversible capacity loss during the first charge/discharge cycle of the cathode is associated with these high capacity batteries which has impeded their commercial use [46, 47]. Some examples of these newly introduced materials can be found in [32, 33]. Although these materials are being explored for high capacity batteries, the crystal structure of their cathodes is not yet completely understood [36]. Moreover, the capacity enhancement of these Li-excess batteries and the irreversible capacity loss during the first cycle are attributed to their local microscopic structures of the NMC layer [34, 36]. Further refinement and commercialization of these batteries requires knowledge on their microscopic structure and ordering of the elements in the NMC layer of the cathode.

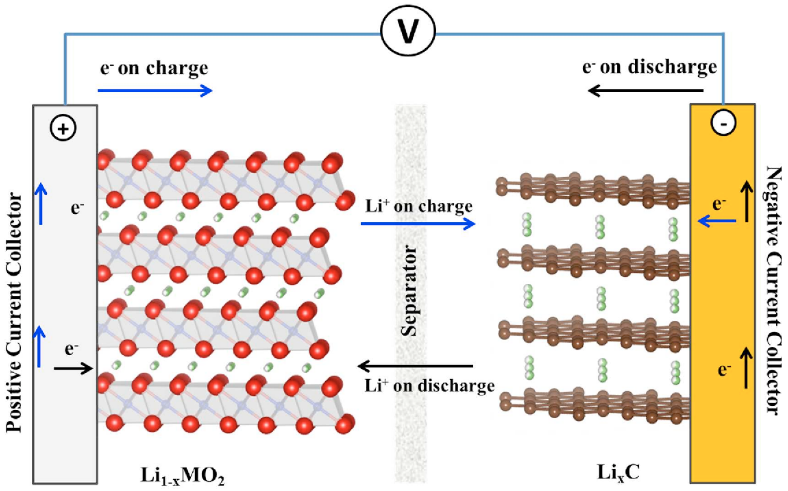


Figure 1.1: Schematic of a Li-ion battery [49].

The aforementioned problem is addressed by mathematical modeling [13,48]. Harris et al. [13] has used NMR spectroscopy data [35] to find the structures corresponding to different temperatures of the system. Simulated annealing is a stochastic optimization method designed in analogy to annealing solid materials and is based on an iterative Monte-Carlo algorithm. The structure of the lattice is randomly initialized at the start of the process and each site is filled with elements chosen at random. At each iteration of the Monte-Carlo algorithm microscopic rearrangements of the elements of two different sites are performed and the change in the energy is used to control the update at each iteration. Accepting only those element swaps that lead to a lower energy state of the lattice will result in a rapid quenching of the system from the highest to the lowest temperature and consequently the meta-stable state of the system [22]. In order to prevent this situation, the Metropolis-Hastings algorithm is used in which steps that result in a higher energy level of the lattice are incorporated in the simulation in a controlled manner.

The cathode of Li-ion batteries has a layered structure where each layer of oxygen is surrounded by a layer of Li and a NMC layer as shown in figure 1.2. Due to the triangular structure of the lattice, each oxygen site is surrounded by three Li ions on the above layer and 3 transition metals on the lower layer. Transition metals could be Ni, Mn or Co for the NMC cathodes. As the oxygen element tends to remain in the oxidation state of -2, the lowest energy state is obtained when it is surrounded by the elements that contribute $+2$ to the state of the oxygen. As each neighbor element contributes $1/6$ of its charge to the oxygen state, a total charge balance of $+12$ is required around the oxygen site to be in the lowest energy state. Each Li ion has a charge of $+1$ and three lithium ions are in the lower layer of the oxygen site. Hence, charge balance of $+9$ is needed from three transition metals in a triangle. Therefore, the local energy balance on each oxygen site is defined as [13]

$$E_i = |C(TM_1) + C(TM_2) + C(TM_3) - 9|, \tag{1.1}$$

where C represents the charge of each transition metal atom in a triangle and E_i is the energy balance on the i-th oxygen site. In this algorithm two elements of the lattice are randomly chosen and swapped with each other. Every element swap in the transition metal layer affects 6 triangles on each site. The local energy change is calculated based on the change on the energy of each one of these triangles. if $\Delta E \leq 0$, the element swap is accepted and the lattice configuration is updated. However, if $\Delta E > 0$, a probability is assigned to its displacement. Based on the Boltzmann distribution, the probability of the displacement is calculated as

$$P(\Delta E) = \begin{cases} \exp(-\frac{\Delta E}{T}) & \text{if} \quad \Delta E > 0 \\ 1 & \text{if} \quad \Delta E \leq 0 \end{cases} \tag{1.2}$$

where T is the temperature at which the swap is happening. Note that the concept of temperature being used here is not equivalent to the physical temperature of the system. This parameter is a pseudo-temperature which accounts for the term $k_B\theta$ in the Boltzmann distribution, k_B being the Boltzmann constant and θ being the thermodynamic temperature of the system. T for the initial state and the final state of the lattice is chosen in a way that simulation slowly converges to the equilibrium state. Next, a randomly generated number with uniform distribution in (0,1) is compared to $P(\Delta E)$ and the element swap is accepted only if the probability is higher than the random number. This allows the system to step back to the higher energy states in order to avoid rapid quenching of the system to a state corresponding to a local minimum. These steps are repeated sufficiently many times such that the system reaches equilibrium. The choice of how the temperature is decreased is arbitrary, however, the equilibrium state must be reached at the end of the process for every arbitrarily chosen temperature profile.

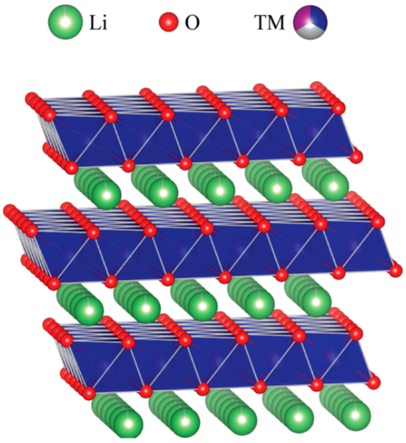
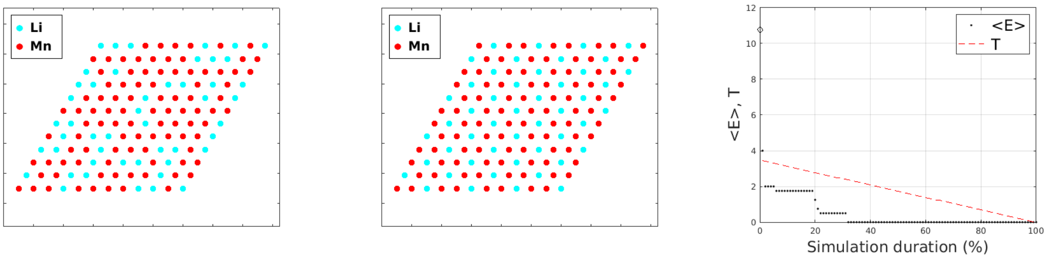


Figure 1.2: Schematic of the NMC cathode [13].

One of the know materials used as the cathode in Li-ion batteries is $Li[Li_{1/3}Mn_{2/3}]O_2$.

The simulated annealing method has been validated on this material by Harris, et al. [13]. The initial state of the algorithm had a high energy and was generated randomly. However, the final state had the lowest energy state and its structure matched the crystal structure of this material. In order to reach the equilibrium, 10^5 iterations were used. At equilibrium, each triangle consists of two Mn elements and one Li element. Figure 1.3 demonstrates the results of the simulated annealing experiment and its energy state before and after the simulation. In this example the temperature was reduced linearly, giving it enough time to stabilize. Hence, there will be two states of the lattice, the initial random state and the final equilibrium state. Note that an equilibrium state is occurring at each specific temperature by giving the lattice enough time to reach equilibrium at that temperature.



(a) (b) (c)

Figure 1.3: (a) Initial random state, (b) final ordered state of the lattice for $Li_{1/3}Mn_{2/3}$ system and (c) the local energy change of the lattice (black) and linear decrease of temperature (red). Blue and red circles represent Li ions (or negative ions in the cluster approximation model) and Mn ions (or positive ions in the cluster approximation model) respectively.

In order to obtain the micro-structure concentrations, we consider two different types of clusters of size 2 (2-clusters) and 3 (3-clusters) as shown in figure 1.4. 2-clusters or pairs consist of 2 nearest neighbor elements. 3-clusters are clusters containing 3 elements which can be in the shape of a triangle (triangular 3-cluster), an open triplet with 120 degree bond (open 3-cluster) or linear. The pair and triangular concentrations have been calculated for each lattice. Table 1.1 demonstrates the results for the initial and final states of the lattice. As can be observed, the $Li-Li$ pair does not exist in the final state of the $Li_{1/3}Mn_{2/3}$ structure. Similarly, all triangles are in the form of $Mn - Mn - Li$ and concentrations of all other triangles are zero. For simplicity, Mn and Li elements are represented by $+$ and $-$ from now on. Note that these notations are not an indicator of the charge of the elements.

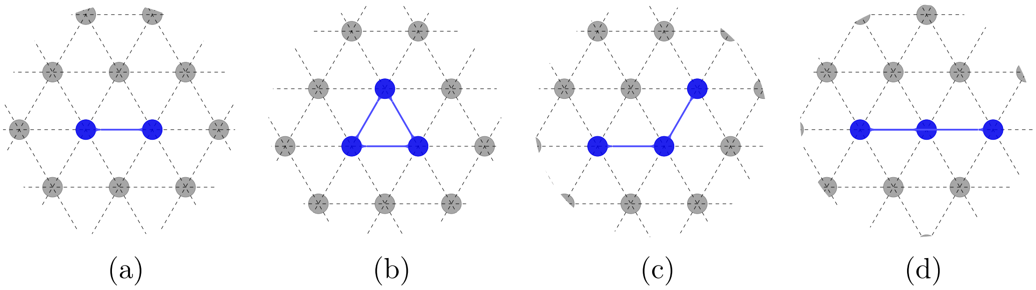

(a) (b) (c) (d)

Figure 1.4: Schematic of (a) 2-cluster, (b) triangular 3-cluster, (c) open 3-cluster and (d) linear 3-cluster.

	Pair Concentrations	
Cluster Type	Initial State	Final State
C_{++} or C_{MnMn}	0.5065	0.3325
C_{--} or C_{LiLi}	0.1143	0.0000
C_{+-} or C_{MnLi}	0.1896	0.3338
	Triangular Concentrations	
	Initial State	Final State
C_{+++} or C_{MnMnMn}	0.4049	0.0000
C_{---} or C_{LiLiLi}	0.0330	0.0000
C_{++-} or C_{MnMnLi}	0.1184	0.3333
C_{+--} or C_{MnLiLi}	0.0689	0.0000

Table 1.1: Pair concentrations and triangular concentrations calculated for the initial state and the final state of the lattice of the $Li_{1/3}Mn_{2/3}$ system.

The simulated annealing approach has some advantages. Specifically it allows for the direct matching of NMR spectroscopy data to the model outputs. However, it is computationally heavy as it is based on the random visits of lattice states. One reason for this excessive cost is that the simulated annealing approach predicts an entire lattice structure. On the other hand, for comparison with the results of NMR spectroscopy we only need information about concentrations of certain clusters. In contrast, we would like to propose a novel approach called cluster approximation, which attempts to build dynamical systems for the evolution of concentrations of different clusters. Thus, instead of obtaining the whole structure of the lattice, we will be looking into approximations of concentrations of micro-structures inside the lattice. This method has been inspired from Ben-Avraham et al [1]. The cluster approximation models have applications in random sequential adsorption in determining the structure of different polymers [38]. They also have been extensively used in ecology for determining the propagation of a disease [4]. The only difference in our model is that the NMC layer of cathodes have a triangular shaped lattice which requires different truncation strategies than those used in the random sequential adsorption processes. Pair approximation along with a novel approximation scheme is used to truncate the hierarchy of the dynamical systems.

The goal of this work is to find approximations of the concentrations of different clusters inside the lattice. Cluster approximation model is developed at different levels, however, the parameters of this model are unknown. In order to find the parameters of the model, we will try to minimize the mismatch between the model outputs and the experimental results (which are the simulated annealing results in this document), which is called "inverse modeling". An inverse problem, in contrast to a forward problem, is comprised of using the actual data and measurements in order to deduce the values of the parameters that characterize a physical system [39]. Inverse problems have been widely used in many different fields of technology such as engineering, electrochemistry [44,45], machine learning [40], biomedical imaging [41], psychology [42], geophysics [43], etc. The goal is to obtain better predictions of desired properties via indirect measurements. We will use this approach to obtain the parameters of the constructed dynamical model.

In chapter 2 and 3 we will build the dynamical model, with respect to clusters of size 2 and 3 respectively. We will also propose the analytic solution of the dynamical system at equilibrium. Chapter 4 presents computational frameworks for calculating the parameters of the model. It also proposes a new approach for truncating the hierarchical systems. Chapter 5 presents the results. Chapter 6 discusses the obtained results and provides some conclusions.

Chapter 2

Two-Element Model

In this chapter, we will be developing a system of evolution equations for a lattice containing two types of elements. For simplicity, plus $(+)$ and minus $(-)$ are the symbols that will be used for each type of element. This notation is not an indicator of the charge of the elements. Two different, yet interconnected, models have been developed, namely, a two-cluster model and triangular-cluster model. The former seeks to generate evolution equations for concentrations of cluster of size 2 (pair concentrations), however, the latter generates a system for the evolution of triangular clusters (clusters with 3 elements in each vertex of a triangle). In order to formulate the cluster approximation model on a 2D lattice, one needs to know the lattice type of the transition metal layer of the cathode. Harris et al. [13] supposed that TM layer of cathode holds triangular lattice shape in which each element has 6 nearest neighbors as shown in figure 2.1. Ben-Avraham et al. [1] introduced an approach called the "window method" for a 1D system that considers swaps of nearest-neighbor elements in order to derive rate equations for the rate of change in concentrations of specific clusters. In other words, this model predicts the concentrations of different clusters inside the lattice. However, our definition of concentration is different from its original meaning. Concentration of a specific cluster is defined as the probability of picking one cluster of the same size and shape from the lattice being in the desired state and is denoted by C. In this method, each element inside a cluster can swap with its nearest neighbors to build or destroy specific clusters with a particular rate constant. In the 2D lattice case, each element can swap with any of its nearest neighbors to produce or destroy a specific cluster within the window. In the two-cluster model, we are interested in determining probabilities of clusters of size 2 (2-clusters). Figure 2.1 demonstrates all possible ways that a neighbor can swap with an element inside a specific cluster. These element swaps will be used in order to generate system of evolution equations in the next sections.

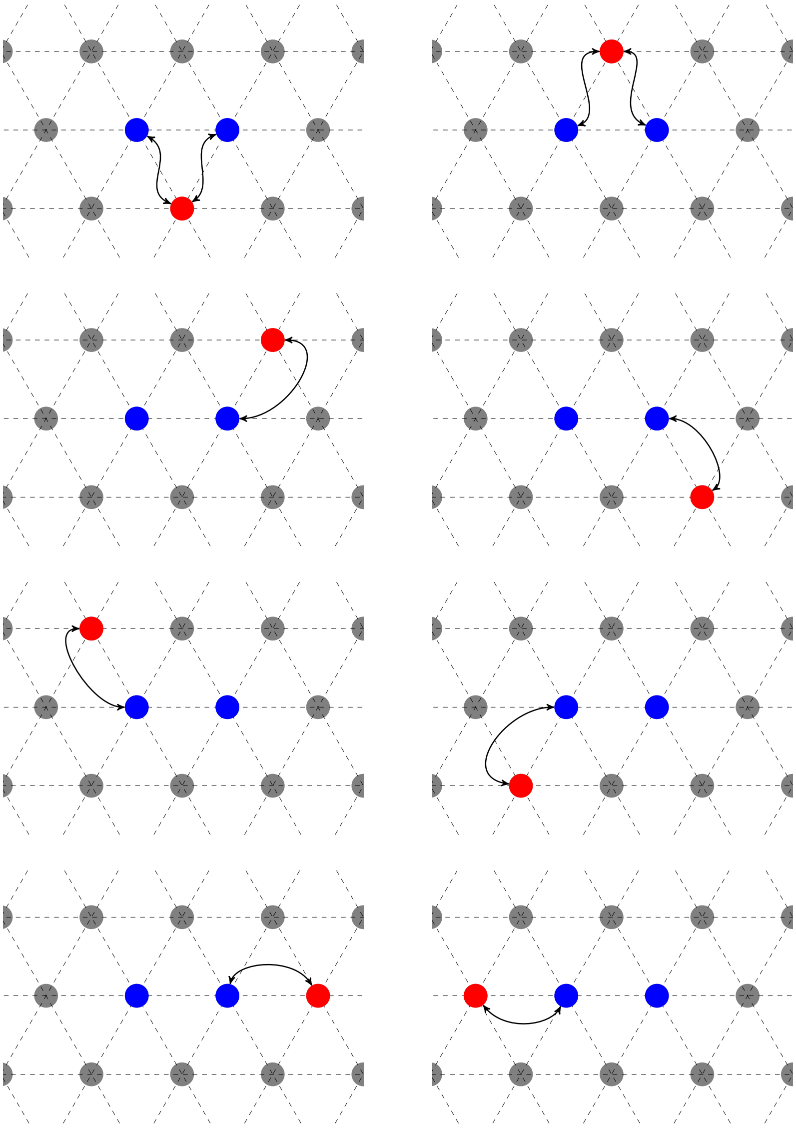


Figure 2.1: Schematic of a triangular lattice structure - possible element swaps in a two-cluster model. Elements shown in blue represent a window in which the probability of the cluster inside the window is to be determined. The element shown in red represents a nearest neighbor to at least one of the elements inside the window. Black arrows indicate a possible swap between one of the elements inside the window and the nearest neighbor element.

2.1 Evolution of Two-Clusters

In order to derive rate equations for each cluster type one needs to consider all possible 3-clusters that may produce or destroy that particular cluster by swapping the third element with one of the elements inside the window. Considering 2-clusters with two types of elements (positive (⊕) and negative (⊖) elements), four distinct configurations can be observed inside the window: (⊕⊕), (⊖⊖), (⊕⊖) and (⊖⊕). All possible ways that these configurations can be destroyed or produced are discussed in the following sections.

Remark. *The normalization condition states that the sum of the concentrations (or probabilities) of all possible n-clusters should be equal to one, where n denotes the size of the cluster [1]:*

$$\sum_{X_1,X_2,\ldots,X_n} C_{(X_1,X_2,\ldots,X_n)} = 1, \tag{2.1}$$

in which $1, 2, 3, .., n$ *indices denote different sites of the lattice where each two subsequent ones are nearest neighbors to each other and* X *denotes the state of that specific site (which could be ⊕ or ⊖ in this example). Applying this to 1-clusters and 2-clusters in our model, the following equations are derived from the normalization condition:*

$$C(\oplus) + C(\ominus) = 1 \tag{2.2.1}$$

$$\begin{gathered} C(\oplus\oplus) + C(\ominus\ominus) + C(\oplus\ominus) + C(\ominus\oplus) = 1 \\ \Rightarrow C(\oplus\oplus) + C(\ominus\ominus) + 2C(\oplus\ominus) = 1. \end{gathered} \tag{2.2.2}$$

As can be observed the concentration of $(+-)$ *and* $(-+)$ *clusters are the same as stated in Theorem 7.1.1 in Appendix. Equation* (2.2.1) *is satisfied by all configurations of the system. In the upcoming sections, we introduce a rate equation for one of* $(+-)$ *or* $(-+)$ *clusters as they are translations of each other.*

2.1.1 Production and Destruction of (⊕⊕) Cluster

In this section, we investigate possible reactions that will produce or destroy the (⊕⊕) cluster via nearest neighbor element swaps. The window method introduced by Ben-Avraham et al. [1] is used to generate the rate equations. This method states that one has to determine a window in which the elements are in the desired state before the destruction (or after the production) by swapping with one of the nearest neighbor elements outside the window. In each of the reactions in figure 2.2, the neighbor element (highlighted in red) will swap with one of the elements of the window (highlighted in blue) to produce a (⊕⊕) cluster. Also, figure 2.3 illustrates all possible ways to destroy a (⊕⊕) cluster inside the blue window.

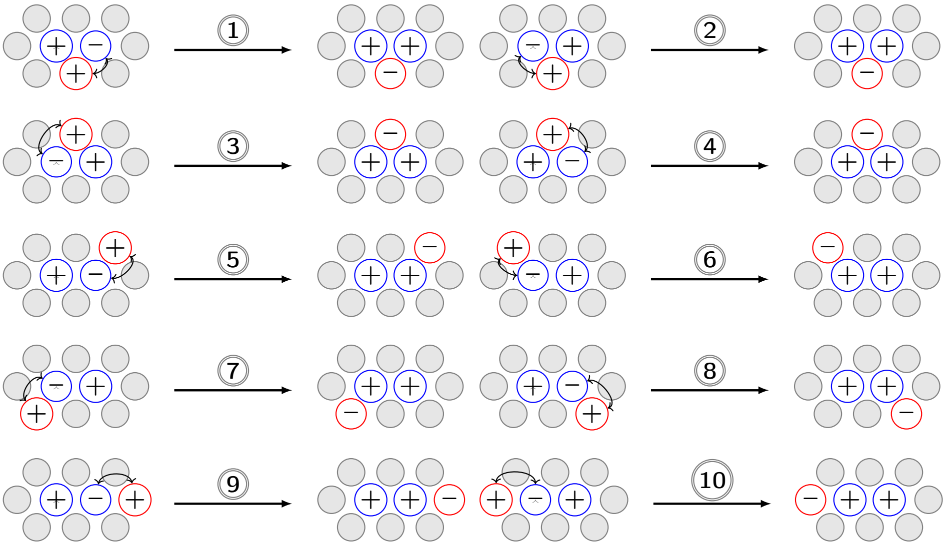


Figure 2.2: All possible reactions to produce a (⊕⊕) cluster.

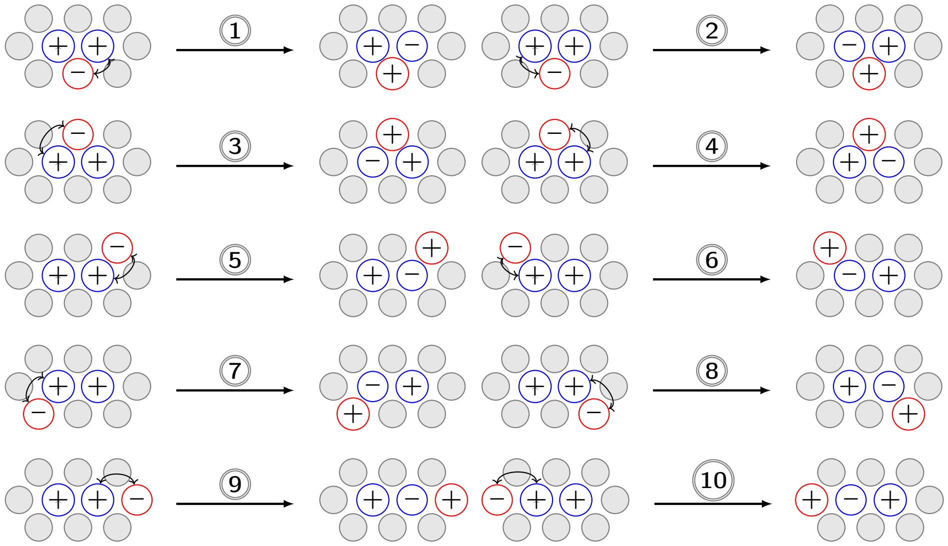


Figure 2.3: All possible reactions to destroy a $(\oplus\oplus)$ cluster.

Some assumptions must be taken into consideration prior to deriving the rate equations:

- Some of the reactions in figure 2.2 and 2.3 are indeed symmetry transformations of the others due to the translational and reflectional symmetry of the system. Theorems 7.1.2 and 7.1.3 in Appendix state how these translations can occur in the lattice. In both figures, each one of the following groups of reactions can be obtained from one reaction inside the group by performing suitable rotations and reflections: (1 & 2 & 3 & 4), (5 & 6 & 7 & 8) and (9 & 10). Thus, according to the translational and reflectional symmetry of the system, these reactions can be considered the same in deriving rate equations.

- Considering reactions 1, 2, 3 and 4 in figure 2.2 and 2.3, it can be observed that production or reduction of a $(\oplus\oplus)$ cluster does not affect the total count of $(\oplus\oplus)$ clusters. In other words, all of the aforementioned reactions have one $(\oplus\oplus)$ cluster and two $(\oplus\ominus)$ clusters on the left hand side of the reaction and the count remains the same on the right hand side too. However, the orientation of the clusters has been altered. Hence, translational symmetry of the system dictates to eliminate all reactions (element swaps) that take place in a triangular-shaped cluster in deriving the rate of change for each cluster type.

- Reaction 5 (reaction 9) has 4 (2) translations. This means the aforesaid reactions have to be accounted 4 (2) times with the same rate constant in deriving the rate equations for the system.

Taking into account all these factors, the number of unique reactions for deriving rate equations will reduce significantly. Figure 2.4 demonstrates all of the reactions with a unique rate constant written as reversible reactions for producing or destroying a ($\oplus\oplus$) cluster.

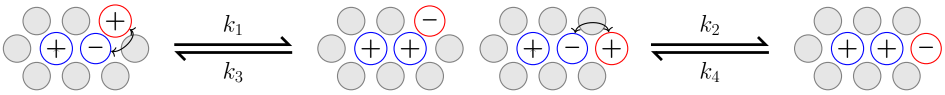


Figure 2.4: Unique reversible reactions, after considering translational symmetries, to destroy or produce a ($\oplus\oplus$) cluster.

k_1 to k_4 are called rate constants. Each unique reaction has a unique rate constant. The rate constant has the unit of $1/time$ and controls the evolution of different clusters through a reaction. It links the concentration of reactants to the rate of the chemical reaction. These parameters are unknown in our physical system and they will be discussed thoroughly in chapter 4 and 5. Considering reactions in figure 2.4, the following rate equation can be deduced to govern the system for a ($\oplus\oplus$) cluster:

$$\begin{aligned}\frac{d}{dt}C\left(\begin{smallmatrix} & \bullet & \bullet & \bullet & \\ \bullet & \oplus & \oplus & \bullet \\ & \bullet & \bullet & \bullet & \end{smallmatrix}\right) &= 4k_1C\left(\begin{smallmatrix} & \bullet & \bullet & \oplus & \\ \bullet & \oplus & \ominus & \bullet \\ & \bullet & \bullet & \bullet & \end{smallmatrix}\right) + 2k_2C\left(\begin{smallmatrix} & \bullet & \bullet & \bullet & \\ \bullet & \oplus & \ominus & \oplus \\ & \bullet & \bullet & \bullet & \end{smallmatrix}\right) \\ &\quad -4k_3C\left(\begin{smallmatrix} & \bullet & \bullet & \ominus & \\ \bullet & \oplus & \oplus & \bullet \\ & \bullet & \bullet & \bullet & \end{smallmatrix}\right) - 2k_4C\left(\begin{smallmatrix} & \bullet & \bullet & \bullet & \\ \bullet & \oplus & \oplus & \ominus \\ & \bullet & \bullet & \bullet & \end{smallmatrix}\right).\end{aligned} \tag{2.3}$$

Note that each site in the lattice can be in the ($\oplus$) or ($\ominus$) state and ($\bullet$) indicates an unspecified state.

2.1.2 Production and Destruction of (⊖⊖) Cluster

In a very similar way, the reactions for producing or destroying (⊖⊖) clusters will be generated using nearest neighbor element swaps. According to assumptions introduced in section 2.1.1, i.e. translational and rotational symmetries and dismissing of triangular-shaped clusters, the unique reactions to produce or destroy a (⊖⊖) cluster will reduce to ones shown in figure 2.5.

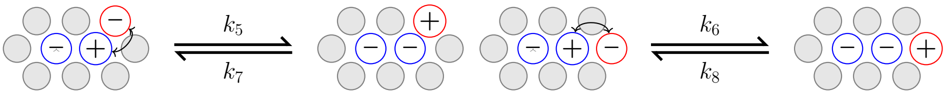


Figure 2.5: Unique reversible reactions, after considering translational symmetries, to destroy or produce a (⊖⊖) cluster.

In order to study the behavior of (⊖⊖) cluster in the lattice, the following rate equation can be inferred from unique reactions in figure 2.5:

$$\begin{aligned}\frac{d}{dt}C\left(\begin{smallmatrix} & \bullet & \bullet & \bullet \\ \bullet & \ominus & \ominus & \bullet \\ & \bullet & \bullet & \bullet \end{smallmatrix}\right) &= 4k_5C\left(\begin{smallmatrix} & \bullet & \bullet & \ominus \\ \bullet & \ominus & \oplus & \bullet \\ & \bullet & \bullet & \bullet \end{smallmatrix}\right) + 2k_6C\left(\begin{smallmatrix} & \bullet & \bullet & \bullet \\ \bullet & \ominus & \oplus & \ominus \\ & \bullet & \bullet & \bullet \end{smallmatrix}\right) \\ &\quad -4k_7C\left(\begin{smallmatrix} & \bullet & \bullet & \oplus \\ \bullet & \ominus & \ominus & \bullet \\ & \bullet & \bullet & \bullet \end{smallmatrix}\right) - 2k_8C\left(\begin{smallmatrix} & \bullet & \bullet & \bullet \\ \bullet & \ominus & \ominus & \oplus \\ & \bullet & \bullet & \bullet \end{smallmatrix}\right).\end{aligned} \tag{2.4}$$

2.1.3 Production and Destruction of (⊕⊖) Cluster

Before deriving the corresponding rate equations, one should note that (⊕⊖) and (⊖⊕) clusters are mirror reflections of each other and it is intuitive to assume equal concentrations for them. According to Ben-Avraham et al. [1], cluster probabilities are independent of the position of the cluster on the lattice. Theorem 7.1.1 explains linear relations between 2-clusters. Consequently, the translational invariance of clusters in the lattice allows us to deduce the rate equation for one of these clusters only. Again, the triangular-shaped clusters will be disregarded as they do not affect the count of clusters. Also, the clusters with translations will get the same rate constant, however, they will be accounted by the number of their translations in deriving the rate equations. Moreover, the reactions that produce or destroy a (⊕⊖) cluster are the same as the reactions that destroy or produce a (⊕⊕) or (⊖⊖) cluster. Hence, these type of reactions are repetitions of the previous ones as demonstrated in figure 2.6.

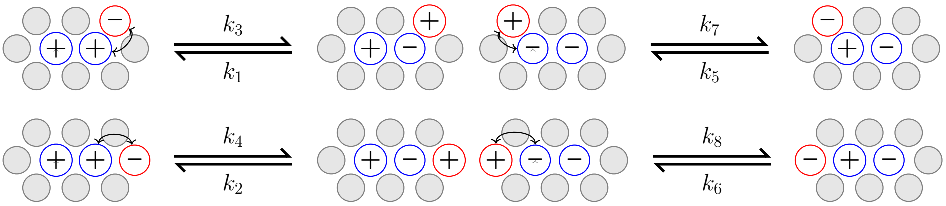
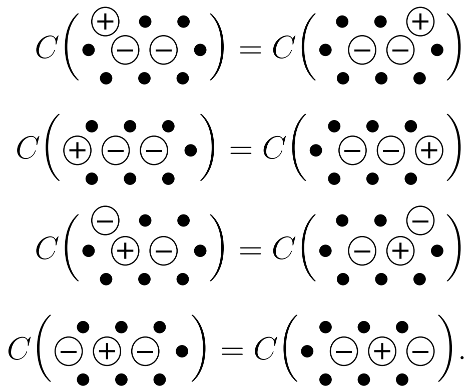


Figure 2.6: Unique reversible reactions, after considering translational symmetries, to destroy or produce a (⊕⊖) cluster is shown.

It is noticeable that all rate constants in figure 2.6 are repetitions from prior reactions for producing or destroying (⊕⊕) or (⊖⊖) clusters. Some of these reactions may not be found directly in figures 2.4 or 2.5, however, their translations can be marked there. The rate equation for calculating the concentration of (⊕⊖) cluster can be derived as follows:

$$
\begin{aligned}
\frac{d}{dt}C\left(\begin{smallmatrix} & \bullet & & \bullet & & \bullet & \\ \bullet & & \oplus & & \ominus & & \bullet \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) = {} & 2k_3C\left(\begin{smallmatrix} & \bullet & & \bullet & & \ominus & \\ \bullet & & \oplus & & \oplus & & \bullet \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) + 2k_7C\left(\begin{smallmatrix} & \bullet & & \bullet & & \oplus & \\ \bullet & & \ominus & & \ominus & & \bullet \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) \\
& + k_4C\left(\begin{smallmatrix} & \bullet & & \bullet & & \bullet & \\ \bullet & & \oplus & & \oplus & & \ominus \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) + k_8C\left(\begin{smallmatrix} & \bullet & & \bullet & & \bullet & \\ \bullet & & \ominus & & \ominus & & \oplus \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) \\
& - 2k_1C\left(\begin{smallmatrix} & \bullet & & \bullet & & \oplus & \\ \bullet & & \oplus & & \ominus & & \bullet \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) - 2k_5C\left(\begin{smallmatrix} & \bullet & & \bullet & & \ominus & \\ \bullet & & \ominus & & \oplus & & \bullet \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) \\
& - k_2C\left(\begin{smallmatrix} & \bullet & & \bullet & & \bullet & \\ \bullet & & \oplus & & \ominus & & \oplus \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right) - k_6C\left(\begin{smallmatrix} & \bullet & & \bullet & & \bullet & \\ \bullet & & \ominus & & \oplus & & \ominus \\ & \bullet & & \bullet & & \bullet & \end{smallmatrix}\right).
\end{aligned}
\tag{2.5}
$$

Note that in writing eq. (2.5), the following 3-cluster concentrations have been replaced by their equivalents to make the equations consistent with eq. (2.3) and (2.4). All these relations have been presented as Theorems 7.1.2 and 7.1.3



(2.6)

As can be observed in eq. (2.3), (2.4) and (2.5), there are two types of bonds involved in deriving rate equations. The first type is the linear 3-cluster in which the two bonds are colinear. This can be called a linear cluster. The second type is the cluster in which there is an obtuse angle of 120 degrees between the bonds due to the triangular shape of the lattice. Note that in deriving rate equations, there is no acute angle as we disregarded all triangular-shaped 3-clusters. For simplicity, we will change the notation for writing down cluster concentrations from now on. To do so, linear clusters will be represented as linear combination of elements with a straight line on them as $[\overline{(\bullet\bullet\bullet)}]$, and angled clusters will be shown as linear combination of elements with a hat sign on them as $[\widehat{(\bullet\bullet\bullet)}]$. Applying the new notation on previous equations, the following set of rate equations will be obtained

$$\frac{d}{dt}C_{++} = 4k_1 C_{\widehat{+-+}} + 2k_2 C_{\overline{+-+}} - 4k_3 C_{\widehat{++-}} - 2k_4 C_{\overline{++-}}, \tag{2.7.1}$$

$$\frac{d}{dt}C_{--} = 4k_5 C_{\widehat{-+-}} + 2k_6 C_{\overline{-+-}} - 4k_7 C_{\widehat{--+}} - 2k_8 C_{\overline{--+}}, \tag{2.7.2}$$

$$\begin{aligned}\frac{d}{dt}C_{+-} &= 2k_3C_{\widehat{++-}} + 2k_7C_{\widehat{--+}} + k_4C_{\overline{++-}} + k_8C_{\overline{--+}} \\ &\quad -2k_1C_{\widehat{+-+}} - 2k_5C_{\widehat{-+-}} - k_2C_{\overline{+-+}} - k_6C_{\overline{-+-}}\,. \end{aligned} \tag{2.7.3}$$

Also, the normalization condition can be modified to a dynamic form. By taking derivative with respect to time from eq. $(2.2.2)$, the following equation will be generated:

$$\frac{d}{dt}C_{++} + \frac{d}{dt}C_{--} + 2\frac{d}{dt}C_{+-} = 0. \tag{2.8}$$

This equation is satisfied by the system of evolution equations. Moreover, considering reversible reactions in figure 2.4 and 2.5, the rate of forward reaction will be equal to the rate of backward reaction in chemical equilibrium. Also, the concentration of each cluster remains constant at equilibrium or steady state of the system, meaning that the left hand side of the system of ODEs will be zero and it will convert to a system of algebraic equations. As we are interested in equilibrium state of reactions, a linear equation can be written for each pair of parameters in equilibrium. Q_i, $i = 1, ..., 4$ denotes the equilibrium constant for each reversible reaction

$$k_1C_{\widehat{+-+}} = k_3C_{\widehat{++-}} \Rightarrow Q_1 = \frac{k_1}{k_3} = \frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}}, \tag{2.9.1}$$

$$k_2C_{\overline{+-+}} = k_4C_{\overline{++-}} \Rightarrow Q_2 = \frac{k_2}{k_4} = \frac{C_{\overline{++-}}}{C_{\overline{+-+}}}, \tag{2.9.2}$$

$$k_5C_{\widehat{-+-}} = k_7C_{\widehat{--+}} \Rightarrow Q_3 = \frac{k_5}{k_7} = \frac{C_{\widehat{--+}}}{C_{\widehat{-+-}}}, \tag{2.9.3}$$

$$k_6C_{\overline{-+-}} = k_8C_{\overline{--+}} \Rightarrow Q_4 = \frac{k_6}{k_8} = \frac{C_{\overline{--+}}}{C_{\overline{-+-}}}. \tag{2.9.4}$$

It is notable that Q_i can be obtained from the results of a simulated annealing experiment. Also, eq. $(2.7.3)$ can be seen as the summation of eq. $(2.7.1)$ and $(2.7.2)$ in the equilibrium state. The analytical solution of these equations corresponding to the equilibrium will be presented in the upcoming sections.

Generally, cluster approximation model in 2D can be formulated in many different ways. In the previous approach, 2-clusters were subject of interest and our aim was to find concentrations of different 2-clusters in terms of 3-clusters. However, this approach cannot be used for comparing the results to the experimental NMR data. Therefore, we propose another type of formulation, namely triangular-cluster model, as described in the following section.

2.2 Evolution of Triangular-Clusters

The same approach can be implemented in another level of cluster concentrations. This level of 2D cluster approximation model considers triangular 3-clusters. Harris et al [13] has extracted the concentrations of triangular 3-clusters of the NMC layer of the cathode using NMR spectroscopy and simulated annealing experiment results have been matched to the data. Hence, we are interested in the evolution of triangular 3-clusters. In this approach, concentration of triangular clusters will be written in terms of 4-clusters. By doing so, the resulting concentrations of cluster approximation model can be matched to the experimental NMR data. In order to build the model, we need to consider all nearest neighbor sites to a triangular cluster. Figure 2.7 highlights all nearest neighbors to at least one of the elements in the triangular cluster. We will be considering all possible element swaps between the elements inside the triangle and one of the external elements. Each swap can alter the ordering of the elements and it can affect the cluster concentrations. Starting from an initial condition for the structure of the system, elements can swap with specific rates to destroy current clusters and build new ones. Our effort is to find the rate constants specific to each reaction. Figure 2.7 demonstrates all possible element swaps between an element inside the triangle and an external one. These configurations will be used in order to derive rate equations for each specific cluster.

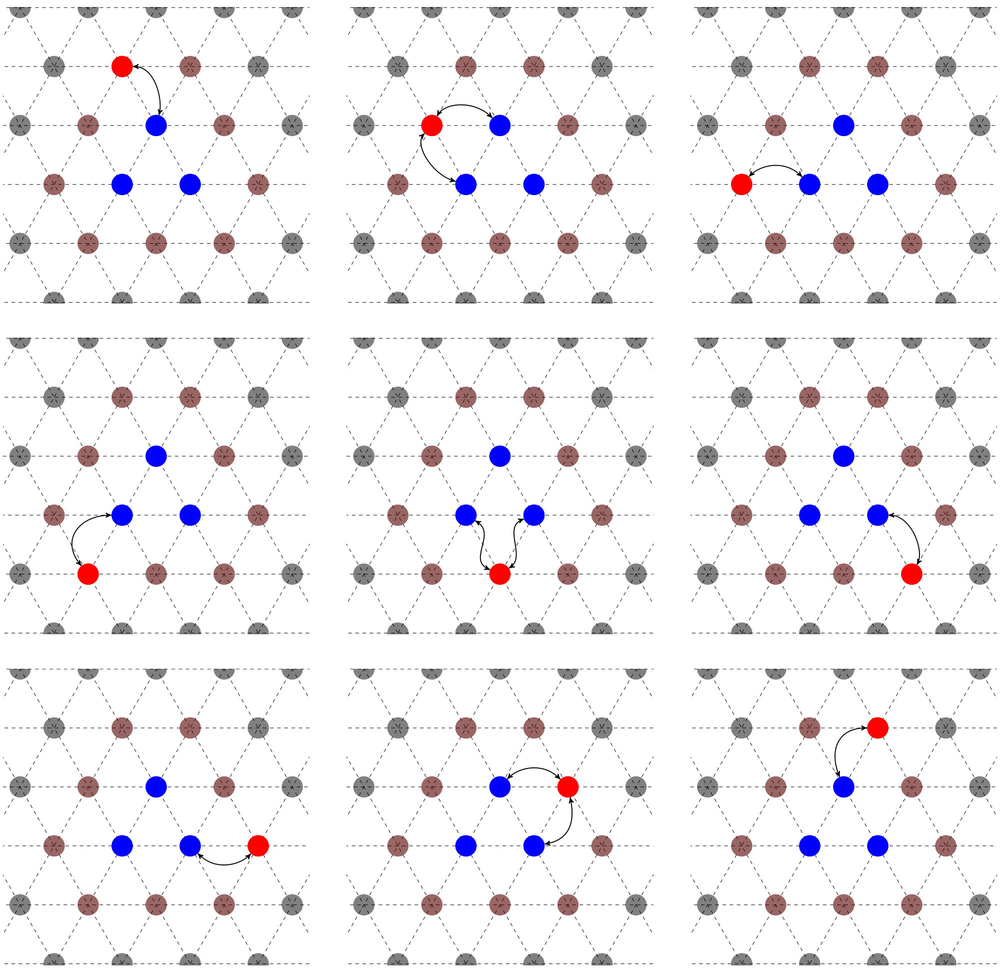


Figure 2.7: Schematic of a tringular lattice - possible element swaps in a triangular-cluster model. Blue elements form a triangle inside the window of desired elements. Red elements are the nearest neighbor elements to at least one of the elements inside the window, with bright red one being the desired one. Black arrows indicate a possible swap between elements outside and inside a window.

In this section two types of elements will be considered in the model, namely, positive and negative elements. As triangular 3-clusters are the subject of interest, 8 configurations for building a 3-cluster can be found, in which some of them are rotations of the others. Unique configurations are as follows: $\left(\overset{\oplus}{\oplus\oplus}\right)$, $\left(\overset{\ominus}{\ominus\ominus}\right)$, $\left(\overset{\ominus}{\oplus\oplus}\right)$, $\left(\overset{\oplus}{\ominus\ominus}\right)$. Note that $\left(\overset{\oplus}{\oplus\ominus}\right)$, $\left(\overset{\oplus}{\ominus\oplus}\right)$, $\left(\overset{\ominus}{\oplus\ominus}\right)$ and $\left(\overset{\ominus}{\ominus\oplus}\right)$ can be obtained by rotating other clusters as stated by Theorem 7.1.4 in Appendix. Our focus will be on deriving rate equations for the first 4-clusters.

Remark. *The normalization condition introduced in eq.* (2.1) *states that sum of the concentrations (or probabilities) of all possible n-clusters should be equal to one, where n denotes the size of the cluster [1]. Normalization condition for single site clusters and 2-clusters has been investigated previously in eq.* (2.2). *In the current setting we are interested in triangular 3-clusters. eq.* (2.10) *illustrates this condition*

$$\begin{aligned} & C\left(\overset{\oplus}{\oplus\oplus}\right) + C\left(\overset{\ominus}{\ominus\ominus}\right) + C\left(\overset{\ominus}{\oplus\oplus}\right) + C\left(\overset{\oplus}{\oplus\ominus}\right) \\ & + C\left(\overset{\oplus}{\ominus\oplus}\right) + C\left(\overset{\oplus}{\ominus\ominus}\right) + C\left(\overset{\ominus}{\oplus\ominus}\right) + C\left(\overset{\ominus}{\ominus\oplus}\right) = 1 \\ \Rightarrow & C\left(\overset{\oplus}{\oplus\oplus}\right) + C\left(\overset{\ominus}{\ominus\ominus}\right) + 3C\left(\overset{\ominus}{\oplus\oplus}\right) + 3C\left(\overset{\oplus}{\ominus\ominus}\right) = 1. \end{aligned} \tag{2.10}$$

Some terms in eq. (2.10) *are rotations of each other as stated by Theorem 7.1.4 in Appendix. By taking derivative with respect to time of eq.* (2.10), *following equation will be generated:*

$$\frac{d}{dt}C\left(\overset{\oplus}{\oplus\oplus}\right) + \frac{d}{dt}C\left(\overset{\ominus}{\ominus\ominus}\right) + 3\frac{d}{dt}C\left(\overset{\ominus}{\oplus\oplus}\right) + 3\frac{d}{dt}C\left(\overset{\oplus}{\ominus\ominus}\right) = 0. \tag{2.11}$$

The rate equations derived in this section should satisfy this normalization condition.

2.2.1 Production and Destruction of ($\overset{\oplus}{\oplus\oplus}$) Cluster

In order to derive rate equation for $\left(\overset{\oplus}{\oplus\oplus}\right)$ cluster, all possible element swaps that will produce or destroy this cluster will be considered. Figure 2.8 and 2.9 demonstrate all potential reactions for producing or destroying a $\left(\overset{\oplus}{\oplus\oplus}\right)$ cluster. In each figure, reactions 1 and 3 are distinct, however, another reactions can be obtained by rotating or flipping unique ones. For example, reactions 4, 7, 8, 11 and 12 are translations of reaction 3. Theorems 7.1.4 and 7.1.5 in Appendix can shed some light on the translational symmetries of the system in this model. Similarly, reactions 2, 5, 6, 9 and 10 can be obtained by rotating or flipping reaction 1. The same concept can be used in destroying the clusters in figure 2.9. In each of these figures, one elements outside the window is swapped by one of the elements inside the window in order to produce or destroy the desired cluster.

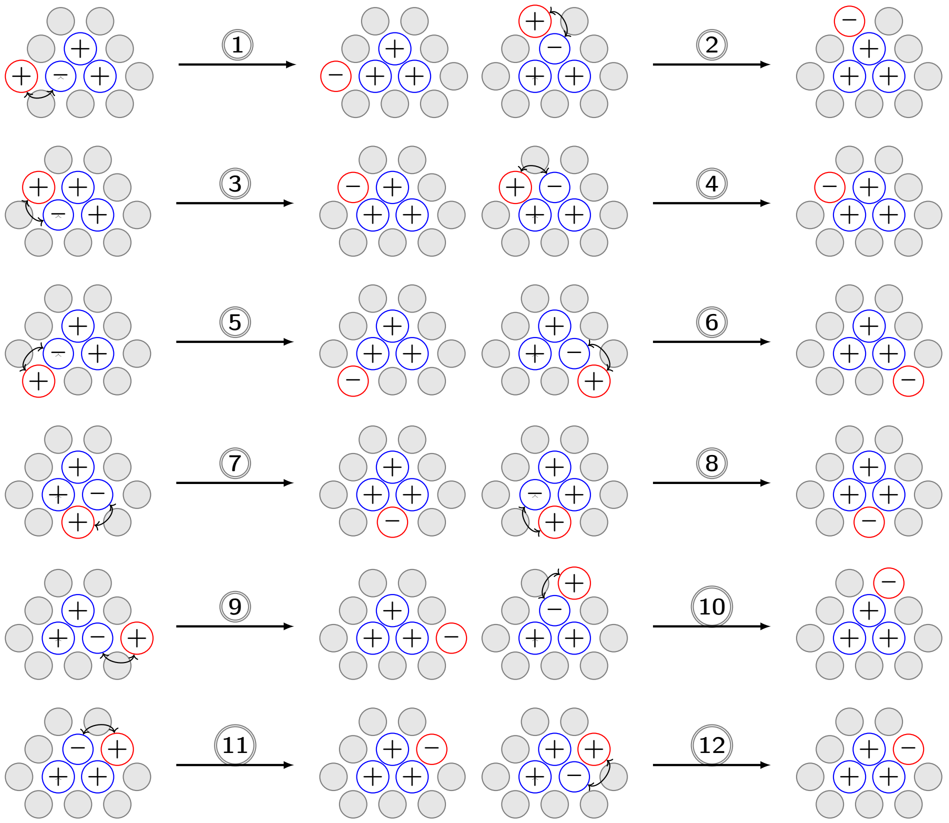


Figure 2.8: All possible reactions to produce a ($\overset{\oplus}{\oplus\oplus}$) cluster.

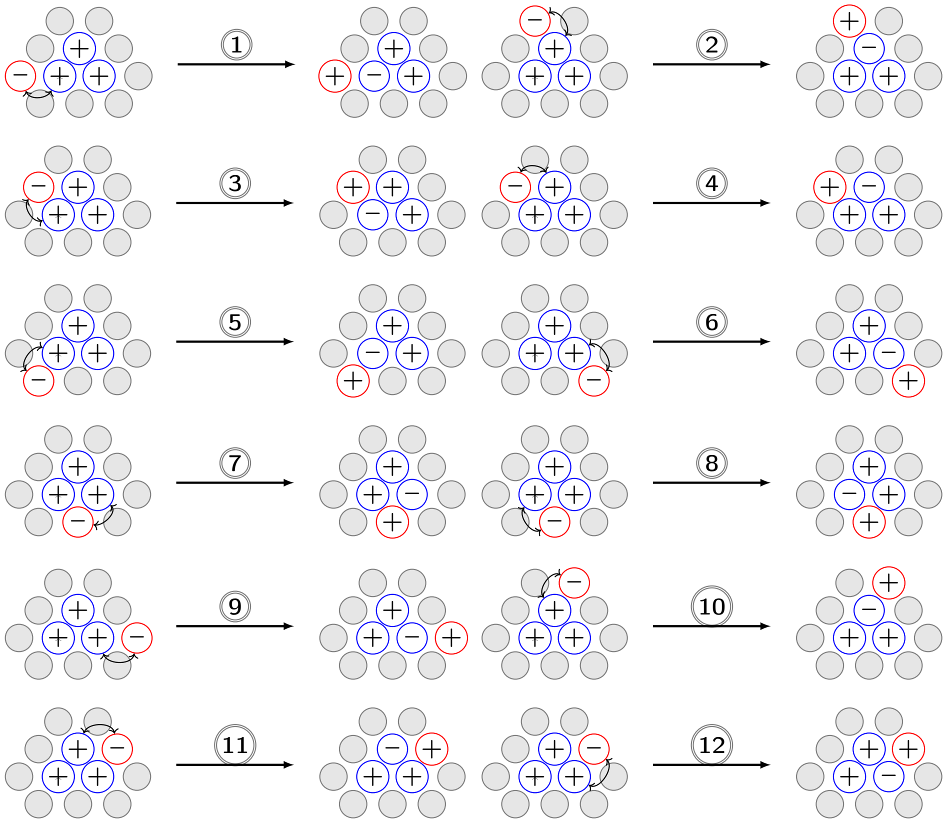


Figure 2.9: All possible reactions to destroy a ($\overset{\oplus}{\oplus\oplus}$) cluster.

Consequently, unique reactions in producing or destroying a $\left(\overset{\oplus}{\oplus\oplus}\right)$ cluster can be condensed to reactions described in figure 2.10.

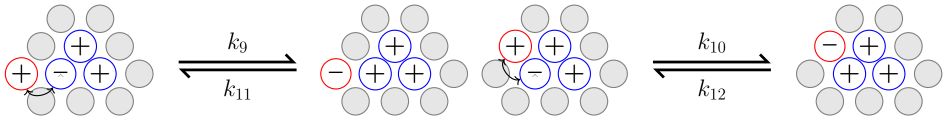


Figure 2.10: Unique reversible reactions, after considering translational symmetries, to produce or destroy a ($\overset{\oplus}{\oplus\oplus}$) cluster.

Notably, reaction 1 in figures 2.8 and 2.9 is repeated 6 times considering all translations. Same translations are happening for reaction 3. Hence, each one of the reactions will be accounted for 6 times in deriving the rate equation. Given the reversible and unique reactions in figure 2.10, the following rate equation can be deduced for $\left(\overset{\oplus}{\oplus\oplus}\right)$

cluster

$$\begin{aligned}\frac{d}{dt}C\left(\overset{\oplus}{\oplus\oplus}\right) &= 6k_9C\left(\oplus\,\overset{\oplus}{\ominus\oplus}\right)+6k_{10}C\left(\overset{\oplus\oplus}{\ominus\oplus}\right)\\ &-6k_{11}C\left(\ominus\,\overset{\oplus}{\oplus\oplus}\right)-6k_{12}C\left(\overset{\ominus\oplus}{\oplus\oplus}\right).\end{aligned} \tag{2.12}$$

2.2.2 Production and Destruction of ($\overset{\ominus}{\ominus\ominus}$) Cluster

Similarly, all possible element swaps that will destroy or produce the ($\overset{\ominus}{\ominus\ominus}$) cluster will be considered. Again, each reaction will have 6 translational symmetries. All unique reactions in destroying or producing a ($\overset{\ominus}{\ominus\ominus}$) cluster can be summed up to the reversible reactions described in figure 2.11.

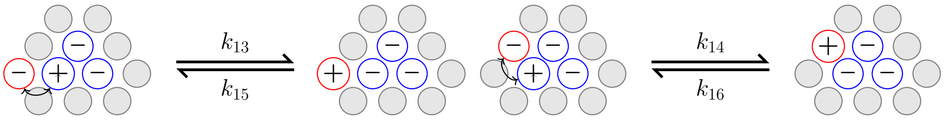


Figure 2.11: Unique reversible reactions, after considering translational symmetries, to produce or destroy a ($\overset{\ominus}{\ominus\ominus}$) cluster.

Considering reversible and unique reactions, with 6 translations for each one, following rate equation can be deduced for ($\overset{\ominus}{\ominus\ominus}$) cluster.

$$\begin{aligned}\frac{d}{dt}C\left(\overset{\ominus}{\ominus\ominus}\right) &= 6k_{13}C\left(\ominus\,\overset{\ominus}{\oplus\ominus}\right)+6k_{14}C\left(\overset{\ominus\ominus}{\oplus\ominus}\right)\\ &-6k_{15}C\left(\oplus\,\overset{\ominus}{\ominus\ominus}\right)-6k_{16}C\left(\overset{\oplus\ominus}{\ominus\ominus}\right)\end{aligned} \tag{2.13}$$

2.2.3 Production and Destruction of ($\overset{\ominus}{\oplus\oplus}$) Cluster

Deriving rate equation for ($\overset{\ominus}{\oplus\oplus}$) cluster can be accomplished by considering all possible element swaps that will destroy or produce this cluster. Note that some of these reactions will be repetitions of the previous ones, as the production or destruction of this cluster may result in destruction or production of the ($\overset{\oplus}{\oplus\oplus}$) cluster respectively. Also, some new reactions with unique rate constants will be introduced here. Again, due to the symmetries of the system, the number of unique reactions will be reduced significantly. Figure 2.12 displays all of these unique reactions with their rate constants.

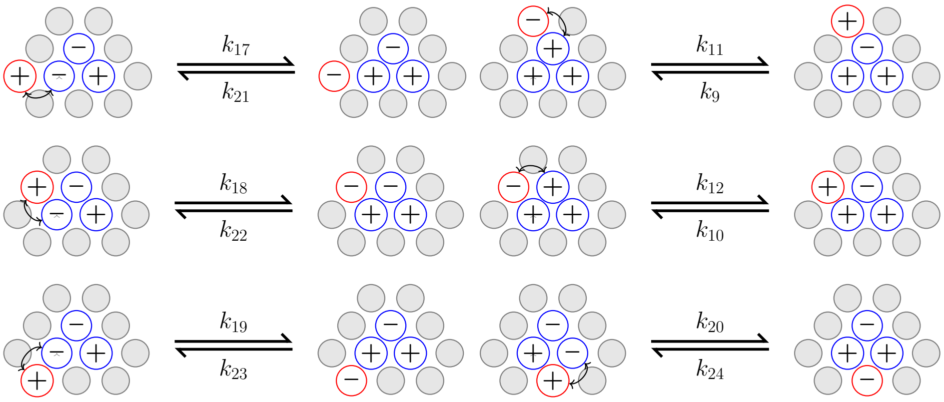


Figure 2.12: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\ominus}{\oplus\oplus})$ cluster.

In order to deduce rate equation for this cluster, reversible reactions in figure 2.12 will be considered. Each of the reactions for producing or destroying the $(\overset{\ominus}{\oplus\oplus})$ cluster have 2 translations and hence each term on the right hand side of the Eq. (2.14) will have a coefficient of 2

$$\begin{aligned}\frac{d}{dt}C\left(\overset{\ominus}{\oplus\,\oplus}\right) = {}& 2k_{17}C\left(\oplus\,\overset{\ominus}{\ominus\,\oplus}\right) + 2k_{11}C\left(\ominus\,\overset{\oplus}{\oplus\,\oplus}\right) + 2k_{18}C\left(\begin{matrix}\oplus\,\ominus\;\; \\ \;\;\ominus\,\oplus\end{matrix}\right) \\ &+2k_{12}C\left(\begin{matrix}\ominus\,\oplus\;\; \\ \;\;\oplus\,\oplus\end{matrix}\right) + 2k_{19}C\left(\oplus\,\overset{\oplus}{\ominus\,\ominus}\right) + 2k_{20}C\left(\begin{matrix}\oplus\,\oplus\;\; \\ \;\;\ominus\,\ominus\end{matrix}\right) \\ &-2k_{21}C\left(\ominus\,\overset{\ominus}{\oplus\,\oplus}\right) - 2k_{9}C\left(\oplus\,\overset{\oplus}{\ominus\,\oplus}\right) - 2k_{22}C\left(\begin{matrix}\ominus\,\ominus\;\; \\ \;\;\oplus\,\oplus\end{matrix}\right) \\ &-2k_{10}C\left(\begin{matrix}\oplus\,\oplus\;\; \\ \;\;\ominus\,\oplus\end{matrix}\right) - 2k_{23}C\left(\ominus\,\overset{\oplus}{\oplus\,\ominus}\right) - 2k_{24}C\left(\begin{matrix}\ominus\,\oplus\;\; \\ \;\;\oplus\,\ominus\end{matrix}\right).\end{aligned} \tag{2.14}$$

2.2.4 Production and Destruction of $(\overset{\oplus}{\ominus\ominus})$ Cluster

In this section, the $(\overset{\oplus}{\ominus\ominus})$ cluster will be considered to derive the rate of change of its concentration based on the reactions that can produce or destroy this cluster. Similarly, the number of unique reactions will diminish significantly by applying translation invariance rules. Figure 2.13 demonstrates all unique reactions with their rate constants. Note that all of the reactions stated here have been introduced in prior sections. Hence this process will not add to the number of unique parameters of the cluster approximation model.

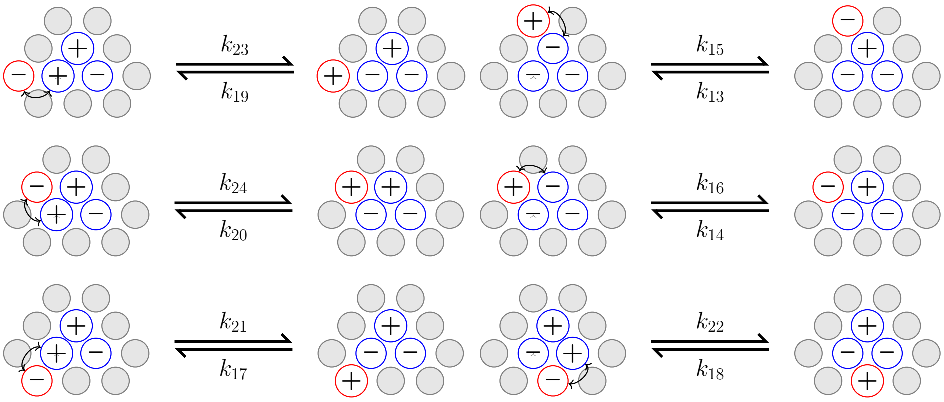


Figure 2.13: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $\left(\overset{\oplus}{\ominus\ominus}\right)$ cluster.

Deriving rate equation for $\left(\overset{\oplus}{\ominus\ominus}\right)$ cluster is facilitated by considering the reversible reactions in figure 2.13. Again, each term in the rate equation has a coefficient of 2 due to number of translations of each reaction in the system

$$\begin{aligned}\frac{d}{dt}C\left(\overset{\oplus}{\ominus\ominus}\right) = {} & 2k_{23}C\left(\ominus\,\overset{\oplus}{\oplus\ominus}\right) + 2k_{15}C\left(\oplus\,\overset{\ominus}{\ominus\ominus}\right) + 2k_{24}C\left(\overset{\ominus\oplus}{\oplus\ominus}\right)\\ & +2k_{16}C\left(\overset{\oplus\ominus}{\ominus\ominus}\right) + 2k_{21}C\left(\ominus\,\overset{\ominus}{\oplus\oplus}\right) + 2k_{22}C\left(\overset{\ominus\ominus}{\oplus\oplus}\right)\\ & -2k_{19}C\left(\oplus\,\overset{\oplus}{\ominus\ominus}\right) - 2k_{13}C\left(\ominus\,\overset{\ominus}{\oplus\ominus}\right) - 2k_{20}C\left(\overset{\oplus\oplus}{\ominus\ominus}\right)\\ & -2k_{14}C\left(\overset{\ominus\ominus}{\oplus\ominus}\right) - 2k_{17}C\left(\oplus\,\overset{\ominus}{\ominus\oplus}\right) - 2k_{18}C\left(\overset{\oplus\ominus}{\ominus\oplus}\right).\end{aligned} \tag{2.15}$$

Additionally, triangular 3-clusters were the focus of the current modeling. For simplicity, concentrations of triangular clusters, which up to now has been denoted $C\left(\overset{\textcircled{z}}{\textcircled{x}\textcircled{y}}\right)$, will be written as $C(\widehat{xzy})$, where, the element in the middle (z, in this example) is the apex of the triangle. Moreover, as can be observed in equations (2.12), (2.13), (2.14) and (2.15), there are two types of 4-clusters involved in rate equations. Generally, these clusters can take one of the following forms: $\left(\substack{\textcircled{o}\textcircled{x} \\ \textcircled{x}\textcircled{x}}\right)$ or $\left(\textcircled{o}\overset{\textcircled{x}}{\textcircled{x}\textcircled{x}}\right)$, where, $\textcircled{x}$ denotes a site inside the triangular 3-cluster and $\textcircled{o}$ denotes an outlier to the triangle. For simplicity, we will change the notations from now on. If the 4-cluster has an outlier with a bond with two elements of the triangle, this type of cluster will be denoted $C(\ddot{o}\widehat{xxx})$, where two dots on top of "o" imply the two bonds. Conversely, if the 4-cluster has an outlier with a bond with only one element of the triangle, this type of cluster will be denoted $C(\dot{o}\widehat{xxx})$, where one dot on top of "o" denotes one bond. All previous rate equations can be then re-written in the following more compact format

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{+++})} &= 6k_9C_{(\dot{+}\widehat{-++})} + 6k_{10}C_{(\ddot{+}\widehat{-++})} \\ &\quad -6k_{11}C_{(\dot{-}\widehat{+++})} - 6k_{12}C_{(\ddot{-}\widehat{+++})},\end{aligned} \tag{2.16.1}$$

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{---})} &= 6k_{13}C_{(\dot{-}\widehat{+--})} + 6k_{14}C_{(\ddot{-}\widehat{+--})} \\ &\quad -6k_{15}C_{(\dot{+}\widehat{---})} - 6k_{16}C_{(\ddot{+}\widehat{---})},\end{aligned} \tag{2.16.2}$$

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{+-+})} &= 2k_{17}C_{(\dot{+}\widehat{--+})} + 2k_{11}C_{(\dot{-}\widehat{+++})} + 2k_{18}C_{(\ddot{+}\widehat{--+})} \\ &\quad +2k_{12}C_{(\ddot{-}\widehat{+++})} + 2k_{19}C_{(\dot{+}\widehat{-+-})} + 2k_{20}C_{(\ddot{+}\widehat{-+-})} \\ &\quad -2k_{21}C_{(\dot{-}\widehat{+-+})} - 2k_9C_{(\dot{+}\widehat{-++})} - 2k_{22}C_{(\ddot{-}\widehat{+-+})} \\ &\quad -2k_{10}C_{(\ddot{+}\widehat{-++})} - 2k_{23}C_{(\dot{-}\widehat{++-})} - 2k_{24}C_{(\ddot{-}\widehat{++-})},\end{aligned} \tag{2.16.3}$$

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{-+-})} &= 2k_{23}C_{(\dot{-}\widehat{++-})} + 2k_{15}C_{(\dot{+}\widehat{---})} + 2k_{24}C_{(\ddot{-}\widehat{++-})} \\ &\quad +2k_{16}C_{(\ddot{+}\widehat{---})} + 2k_{21}C_{(\dot{-}\widehat{+-+})} + 2k_{22}C_{(\ddot{-}\widehat{+-+})} \\ &\quad -2k_{19}C_{(\dot{+}\widehat{-+-})} - 2k_{13}C_{(\dot{-}\widehat{+--})} - 2k_{20}C_{(\ddot{+}\widehat{-+-})} \\ &\quad -2k_{14}C_{(\ddot{-}\widehat{+--})} - 2k_{17}C_{(\dot{+}\widehat{--+})} - 2k_{18}C_{(\ddot{+}\widehat{--+})}.\end{aligned} \tag{2.16.4}$$

This system of equations is determined in terms of 24 unique parameters by defining the evolution of 4 concentrations. Also, the concentrations of 3-clusters are written in terms of concentrations of 4-clusters. This modeling approach thus leads to a hierarchy of equations in which concentration of n-clusters are described by concentrations of $(n+1)$-clusters. Solving this system of equations is therefore impossible. One remedy to this issue is to truncate the hierarchy of the equations at some level, which will be discussed in the next section.

Also, the degree of freedom of system (2.16) can be reduced by introducing the equilibrium constants into the model rather than the rate constants. As we are interested in the equilibrium state of the system, rate of the forward reaction will be equal to the rate of the reverse reaction in equilibrium. Thus, the reactions rates can be grouped pairwise to produce the following identities

$$k_9 C_{(\dot{+}\widehat{-++})} = k_{11} C_{(\dot{-}\widehat{+++})} \Rightarrow Q_5 = \frac{k_9}{k_{11}} = \frac{C_{(\dot{-}\widehat{+++})}}{C_{(\dot{+}\widehat{-++})}}, \tag{2.17.1}$$

$$k_{10} C_{(\ddot{+}\widehat{-++})} = k_{12} C_{(\ddot{-}\widehat{+++})} \Rightarrow Q_6 = \frac{k_{10}}{k_{12}} = \frac{C_{(\ddot{-}\widehat{+++})}}{C_{(\ddot{+}\widehat{-++})}}, \tag{2.17.2}$$

$$k_{13} C_{(\dot{-}\widehat{+--})} = k_{15} C_{(\dot{+}\widehat{---})} \Rightarrow Q_7 = \frac{k_{13}}{k_{15}} = \frac{C_{(\dot{+}\widehat{---})}}{C_{(\dot{-}\widehat{+--})}}, \tag{2.17.3}$$

$$k_{14} C_{(\ddot{-}\widehat{+--})} = k_{16} C_{(\ddot{+}\widehat{---})} \Rightarrow Q_8 = \frac{k_{14}}{k_{16}} = \frac{C_{(\ddot{+}\widehat{---})}}{C_{(\ddot{-}\widehat{+--})}}, \tag{2.17.4}$$

$$k_{17} C_{(\dot{+}\widehat{--+})} = k_{21} C_{(\dot{-}\widehat{+-+})} \Rightarrow Q_9 = \frac{k_{17}}{k_{21}} = \frac{C_{(\dot{-}\widehat{+-+})}}{C_{(\dot{+}\widehat{--+})}}, \tag{2.17.5}$$

$$k_{18} C_{(\ddot{+}\widehat{--+})} = k_{22} C_{(\ddot{-}\widehat{+-+})} \Rightarrow Q_{10} = \frac{k_{18}}{k_{22}} = \frac{C_{(\ddot{-}\widehat{+-+})}}{C_{(\ddot{+}\widehat{--+})}}, \tag{2.17.6}$$

$$k_{19} C_{(\dot{+}\widehat{-+-})} = k_{23} C_{(\dot{-}\widehat{++-})} \Rightarrow Q_{11} = \frac{k_{19}}{k_{23}} = \frac{C_{(\dot{-}\widehat{++-})}}{C_{(\dot{+}\widehat{-+-})}}, \tag{2.17.7}$$

$$k_{20} C_{(\ddot{+}\widehat{-+-})} = k_{24} C_{(\ddot{-}\widehat{++-})} \Rightarrow Q_{12} = \frac{k_{20}}{k_{24}} = \frac{C_{(\ddot{-}\widehat{++-})}}{C_{(\ddot{+}\widehat{-+-})}}. \tag{2.17.8}$$

These equilibrium constants will be used in the following section along with the closed dynamical system to obtain an approximate equilibrium solution.

2.3 Moment Closure Approximation

There are many instances of developing hierarchical system of equations, specifically in reaction-diffusion models that appear in ecology [2–5, 8]. Some models are introduced without individuality, on a continuous space, although others are individual-based in a network-based space [9]. Our problem lies in the second category where moment closure models and mean-field approximations are used for closing the hierarchy of equations. Cluster approximation model results in a set of hierarchical ODE equations such as eq. (2.7) and eq. (2.16) which is not closed and hence not solvable. The hierarchy has to get truncated at some level to reach a closed dynamical system. The truncation is performed by some approximations, in which higher order terms can be written in terms of lower order ones. There is no single answer to this type of approximations. Ben-Avraham et al. [1] suggests a class of approximations in 1D lattices known as (n, m) approximations, where n defines the cluster size and m denotes the overlap between clusters. The simplest case in this class corresponds to zero overlap ($m = 0$) between clusters where the correlations between different clusters are completely ignored. Assuming a cluster in the form of $(X_1X_2X_3...X_nX_{n+1}...)$, the $(n, 0)$ approximation is introduced as [1]:

$$C_{(X_1X_2X_3...X_nX_{n+1}...)} = C_{(X_1X_2X_3...X_n)}C_{(X_{n+1}X_{n+2}...)}, \tag{2.18}$$

where $1, .., n$ denote different sites of the lattice and X denotes the state of that particular site. However, in a more complex setting, the correlation is allowed for one site in the lattice. Hence, the $(n, 1)$ approximation can be written as:

$$C_{(X_1X_2X_3...X_nX_{n+1}...)} = C_{(X_1X_2X_3...X_n)}\frac{C_{(X_nX_{n+1}...)}}{C_{(X_n)}}. \tag{2.19}$$

In this setting, the second factor implies the conditional probability of having a cluster in state $(X_nX_{n+1}X_{n+2}...)$, given that site n is in state (X_n). The overlap between the clusters could be increased to account for larger correlations. The $(n, n-1)$ approximation is the most exact one as it takes care of translation invariance automatically [1]. This approximation was used to solve the 1D system of ODEs, however, it cannot be generalized to a higher dimensional setting.

Hierarchical systems of equations are appearing in the field of ecology for modeling population and evolution dynamics. Different types of regular lattices, such as linear, hexagonal, square and triangular have been studied in this field. The assumption is that each site can only interact with its nearest neighbors [11]. The methods proposed in this field establish a closed dynamical system by using two components: first, the global densities of the lattice sites to be in a specified state (these probabilities are not dependent on the state of the neighbors), and second, local densities or conditional probabilities that a randomly sampled nearest neighbor of a site is in a specified state [2]. Mean-field approximation and pair-approximation methods have been proposed to decouple clusters which are referred to as moment-closure methods [6, 11].

The state of a site is denoted by S where $S \in \{+, -\}$ for a two particle system. Global densities are denoted by C_S, giving the probability that a randomly chosen site in the lattice is in state S. Similarly, $C_{SS'}$ is the global density of a cluster being in state SS'. Also, local densities are denoted by $P_{S/S'}$, giving the probability that a randomly chosen nearest neighbor of a site in state S' is in state S. Indeed, the local densities are distinguished from global densities by the effect of nearest-neighbor correlations. These local densities can be expressed in terms of global densities [2, 11]

$$C_{SS'} = C_{S'S} = C_S P_{S'/S} = C_{S'} P_{S/S'}, \tag{2.20.1}$$

$$\sum_{S \in \{+,-,0\}} C_S = 1, \tag{2.20.2}$$

$$\sum_{S \in \{+,-,0\}} P_{S/S'} = 1 \;\; for\ any\ S' \in \{+,-,0\}. \tag{2.20.3}$$

The first equation also satisfies the translation symmetry of the system. Notably, in our model, the process of deriving rate equations is spatially homogeneous and hence global densities are independent of their location in the lattice [11].

2.3.1 Two-Element Two-Cluster Model

In order to close the system of ODEs in eq. (2.7), one should write triplet densities in terms of densities of pairs and singlets. The approximation that we use here is called pair approximation as it neglects three-site correlations and decouples them into smaller clusters [2,4]. Considering a cluster in the form of ⓘⓙⓚ, the ⓚ element is the nearest neighbor of ⓙ element and is non-nearest neighbor of ⓘ element. In the pair approximation method, we neglect the effect of ⓚ element on the ⓘ element. In other words, it assumes correlation between nearest neighbors only and neglects the effect of non-nearest neighbors on each other. Hence, the correlation between non-nearest-neighbor sites is approximately reconstructed through nearest-neighbor correlations [11]. In eq. (2.7), triplet densities can be written as multiplication of doublet densities and local densities as stated here

$$C_{(\widehat{+-+})} = C_{+-} P_{(\widehat{+/+-})}, \tag{2.21}$$

where the first term in the right hand side of the equation is the global probability of a randomly chosen site being in state $(+-)$, and the second term is the conditional probability that a randomly chosen nearest neighbor site of $(+-)$ cluster is in state $(+)$.

Mean-Field Theory The mean-field approximation completely overlooks the spatial structure of the lattice. Hence, the local densities such as $P(+/+)$ are assumed to be equal to singlet densities as $C(+)$. This is true in the case where the lattice is completely random [3]. We are not going to apply mean-field approach to our system of equations.

Pair Approximation Assuming a square lattice in the pair approximation method, the term $P_{(+/+-)}$ is approximated by $P_{(+/-)}$, meaning that the probability of finding a randomly sampled nearest neighbor of $(-)$ in state $(+)$ is not affected by its nearest neighbor. Underlying this assumption is the fact that those two nearest neighbors of $(-)$ are not nearest neighbors of each other and elements will be less affected by distant neighbors [2, 3, 11]. Figure 2.14 explains this assumption in a square lattice. In this figure, $P_{(0/+0)}$ in the left is replaced by $P_{(0/+)}$ in a square lattice [4, 11].

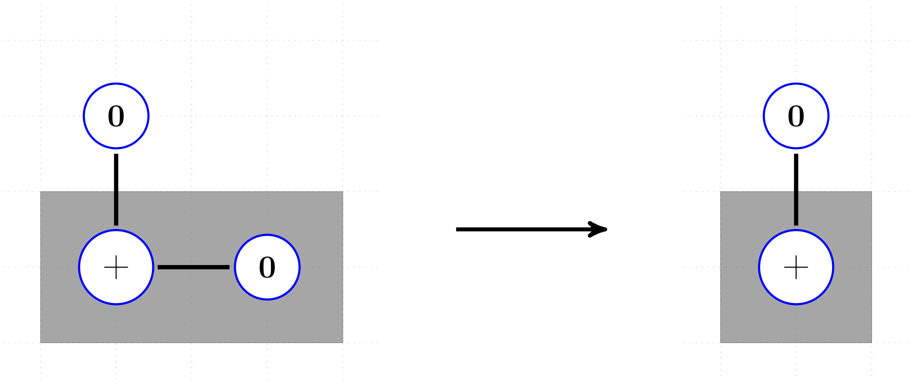


Figure 2.14: The underlying assumption of pair approximation method.

First, let us apply this concept on a 1D ring of elements. Assuming a triplet in the form of $(-++)$, the global density of this cluster can be expressed in terms of densities of smaller ones (assuming that the window under consideration is $(++)$) as follows:

$$C_{(-++)} = P_{(-/++)}C_{(++)} \approx P_{(-/+)}C_{(++)} = \frac{C_{(-+)}}{C_{+}}C_{(++)}. \tag{2.22}$$

Surprisingly, this equation is the same as applying the $(2, 1)$ approximation on the cluster introduced by Ben-Avraham et al [1]. As another example, if we assume a 4-cluster in the form of $(- + ++)$, it can be expressed in terms of densities of triplets by using the same concept

$$C_{(-+++)} = P_{(-/+++)}C_{(+++)} \approx P_{(-/++)}C_{(+++)} = \frac{C_{(-++)}}{C_{(++)}}C_{(+++)}. \tag{2.23}$$

Equation (2.23) also can be seen as the $(3, 2)$ approximation of the $(- + ++)$ cluster. All in all, this approximation method could be considered as an extension of the (n, m) approximation in higher dimensions. The idea of pair approximation is to write triplet densities in terms of pair densities. The knowledge of spatial geometry of the lattice can assist in finding better approximations for lattices with fixed number of neighbors per element (regular lattices) [12]. Even if the lattice sites have variable number of neighbors, some methods for approximation are proposed by Morris [6] and Rand [7].

Ordinary Pair Approximation Let us start by considering a random lattice in which each element is randomly connected to n other neighbors. If the size of the lattice is too large, it would be less likely that pair elements have neighbors in common. Following this assumption, a nearest neighbor to an element will have no correlation with other neighbors of aforementioned element [12]. Thus, the probability of a triplet being in state (ijk) can be written as stated in eq. (2.24). Note that element i and element k will not be nearest neighbors

$$C_{ijk} = C_i C_j C_k Q_{ij} Q_{jk} T_{ijk}, \tag{2.24}$$

where C_i, C_j and C_k denotes the global densities of singlets, Q_{ij} and Q_{ik} are the pair correlation of nearest neighbors and T_{ijk} is the triple correlation of the chain. Notice that there is no Q_{ik} term in the equation as they are not nearest neighbors and their correlation is presented in T_{ijk}. Pair correlations of nearest neighbors can be found as follows

$$Q_{ij} = \frac{C_{ij}}{C_i C_j}. \tag{2.25}$$

Van Baleen [12] suggests that there is no deterministic way of finding triple correlations and some assumptions have to be made in order to close the hierarchical system of equations. The standard pair approximation method is derived by neglecting all triple correlations as $T_{ijk} = 1$ of every triple clusters [12]

$$P_{i/jk} = \frac{C_{ijk}}{C_{jk}} = \frac{C_i C_j C_k Q_{ij} Q_{jk}}{C_j C_k Q_{jk}} = C_i Q_{ij} = P_{i/j}. \tag{2.26}$$

Hence, for a chain-like triplet, k element can be overlooked and $P_{i/jk}$ can be estimated by $P_{i/j}$ in this method [12].

Improved Pair Approximation Similarly triplet densities in triangular lattices can be broken down into smaller clusters by using the same concept. However, triplets can be chain-like (with an obtuse angle between pairs) or triangular (with an acute angle between pairs). Thus, the triple correlation term will have an effect in calculations. The probability that a randomly chosen triplet is in a closed state (and not an open chain) is denoted by θ. For a triangular lattice, θ is equal to $2/5$ as demonstrated in figure 2.15 [12].

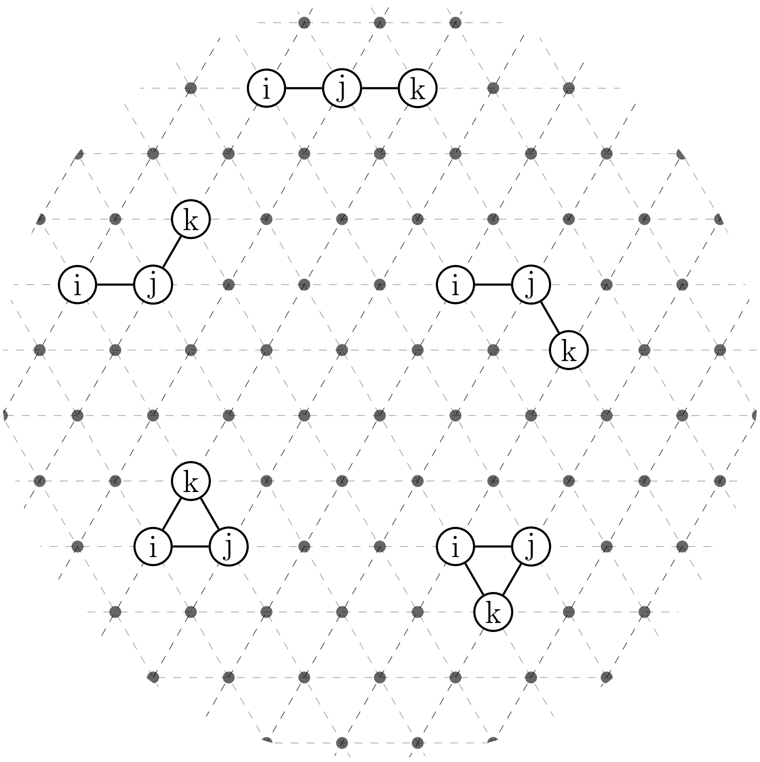


Figure 2.15: Schematic of a 2D triangular lattice - Different types of 3-clusters.

Knowing the value of θ, the triplet densities for an open-chain and a closed-chain can be calculated as [12]

$$C_{\angle ijk} = C_i C_j C_k Q_{ij} Q_{jk} T_{\angle ijk}, \tag{2.27.1}$$

$$C_{\triangle ijk} = C_i C_j C_k Q_{ij} Q_{jk} Q_{ki} T_{\triangle ijk}. \tag{2.27.2}$$

Notice that Q_{ki} is included for a triangle cluster. Taking into account these relations, one can write:

$$P_{i/jk} = P_{i/j}((1-\theta)T_{\angle ijk} + \theta Q_{ik} T_{\triangle ijk}). \tag{2.28}$$

There is no *a priori* assumption that triple correlations should be the same. A naive approximation of triple correlations is that $T_{\triangle ijk} = T_{\angle ijk} = 1$. Considering eq. (2.28), it will hold to be true only if $Q_{ik} = 1$, which means that the elements i and k are totally uncorrelated. This assumption is similar to the random lattice assumption with no triple correlations. Another approach could be to consider $T_{\angle ijk} = 1$ and $T_{\triangle ijk} = 1/Q_{ik}$. This also has the same effect as the previous assumption as it eliminates the effect of θ from calculations [12]. In the two-cluster model, open chain triplets are merely used in deriving rate equations and triangular correlations have been totally neglected. Disregarding the fact that elements i and k have correlations, triplet densities can be viewed as a random lattice model. Alternatively, in deriving rate equations in a two-cluster model, there are 3 different types of triplets: triangular triplet, open triplet with a 120 degree angle between bonds and open triplet with 180 degree angle between bonds. In our model, different types of triplets are distinguished and hence eq. (2.28) cannot be used in our calculations. The reason is that this equation disregards the structure of the triplets and evaluates all as one. In other words, it seeks to present a mean-field solution for finding $P_{i/jk}$ conditional probability regardless of the configuration of the triplets. Nonetheless, we are looking for specific approximations for each configuration of the triplet, as the triangular and chain-like triplets have been discretely expressed in our model.

Morris [6] and Keeling [7] have proposed a formula for approximating the number of closed or open triplets in a specific state of (ijk) for a regular lattice with fixed number of neighbors per site by taking into account the clumping effect of triangles in the lattice. Each regular lattice can be defined by two parameters: number of neighbors per site and proportion of triangles to triplets, which determines the clumping intensity of the lattice. For instance, a triangular lattice has $m = 6$ neighbors per site and $\theta = 2/5$. The total number of open (i, j, k) paths and closed $< i, j, k >$ paths can be approximated by eq. (2.29) for a general regular lattice [5–7, 10]

$$(i,j,k) = (1-\theta)\frac{(m-1)}{m}\frac{(ij)(jk)}{(j)}, \tag{2.29.1}$$

$$< i,j,k > = \frac{\theta N}{m}\frac{(m-1)}{m}\frac{(ij)(jk)(ki)}{(i)(j)(k)}. \tag{2.29.2}$$

Note that N is the population size. (ij) denotes the number of nearest neighbor pairs in state ij and (i) denotes the total number of sites in state i. These approximations can provide total number of open and closed paths in a particular state and fail to produce corresponding probabilities. One approach is to divide each term by its corresponding aggregate number in order to calculate probabilities. For a regular lattice with N elements grid, total number of pairs can be approximated by mN and total number of triplets by $m(m-1)N$ [7]. By applying this conversion eq. (2.30) will be achieved

$$C_{\angle ijk} = \frac{(i,j,k)}{m(m-1)N} = (1-\theta)\frac{1}{m(m-1)N}\frac{(m-1)}{m}\frac{\frac{(ij)}{mN}\frac{(jk)}{mN}}{\frac{(j)}{N}}\frac{m^2N^2}{N} = (1-\theta)\frac{C_{ij}C_{jk}}{C_j}, \tag{2.30.1}$$

$$C_{\triangle ijk} = \frac{<i,j,k>}{m(m-1)N} = \frac{1}{m(m-1)N}\frac{\theta N}{m}\frac{(m-1)}{m}\frac{\frac{(ij)(jk)(ki)}{m^3N^3}}{\frac{(i)(j)(k)}{N^3}}\frac{m^3N^3}{N^3} = \theta\frac{C_{ij}C_{jk}C_{ki}}{C_iC_jC_k}. \tag{2.30.2}$$

As can be seen, a chain-like triplet can be approximated by assuming correlation between nearest neighbors merely. This is the same as eq. $(2.27.1)$ by assuming a factor of $(1-\theta)$ as the triple correlation. Also, all pair correlations for a triangular triplet have been considered and a factor of θ represents the triple correlation. Notice that in two-cluster model there are two types of chain-like triples with 120 degree angle and 180 degree angle between bonds. Referring to figure 2.15, there are 2 configurations involving a 120 degree angle and one configuration with 180 degree angle for a triple site to be in state (ijk). Hence, there is $1/3$ probability that the chain-like triplet is a straight triplet and $2/3$ for the other one. It can be proposed that concentrations for each type of triplets can be estimated as in eq. (2.31) where $\overline{ijk}$ denotes a straight cluster, $\widehat{ijk}$ denotes an open triplet with 120 degree bonds and $\widehat{\overline{ijk}}$ denotes a closed triangle with 60 degree bonds

$$C_{\overline{ijk}} = (1-\theta)\frac{1}{3}\frac{C_{ij}C_{jk}}{C_j}, \tag{2.31.1}$$

$$C_{\widehat{ijk}} = (1-\theta)\frac{2}{3}\frac{C_{ij}C_{jk}}{C_j}, \tag{2.31.2}$$

$$C_{\widehat{\overline{ijk}}} = \theta\frac{C_{ij}C_{jk}C_{ki}}{C_iC_jC_k}. \tag{2.31.3}$$

Based on this approximation, we can rewrite the system of ODEs in eq. (2.7) as a closed system of equations as follows:

$$\begin{aligned}\frac{d}{dt}C_{++} &= 4k_1\frac{2}{3}(1-\theta)\frac{C_{+-}^2}{C_-} + 2k_2\frac{1}{3}(1-\theta)\frac{C_{+-}^2}{C_-}\\ -4k_3\frac{2}{3}(1-\theta)&\frac{C_{++}C_{+-}}{C_+} - 2k_4\frac{1}{3}(1-\theta)\frac{C_{++}C_{+-}}{C_+},\end{aligned} \tag{2.32.1}$$

$$\begin{aligned}\frac{d}{dt}C_{--} &= 4k_5\frac{2}{3}(1-\theta)\frac{C_{+-}^2}{C_+} + 2k_6\frac{1}{3}(1-\theta)\frac{C_{+-}^2}{C_+}\\ -4k_7\frac{2}{3}(1-\theta)&\frac{C_{--}C_{+-}}{C_-} - 2k_8\frac{1}{3}(1-\theta)\frac{C_{--}C_{+-}}{C_-},\end{aligned} \tag{2.32.2}$$

$$\begin{aligned}\frac{d}{dt}C_{+-} = 2k_3\frac{2}{3}(1-\theta)&\frac{C_{++}C_{+-}}{C_+} + 2k_7\frac{2}{3}(1-\theta)\frac{C_{--}C_{+-}}{C_-}\\ +k_4\frac{1}{3}(1-\theta)&\frac{C_{++}C_{+-}}{C_+} + k_8\frac{1}{3}(1-\theta)\frac{C_{--}C_{+-}}{C_-}\\ -2k_1\frac{2}{3}(1-\theta)&\frac{C_{+-}^2}{C_-} - 2k_5\frac{2}{3}(1-\theta)\frac{C_{+-}^2}{C_+}\\ -k_2\frac{1}{3}(1-\theta)&\frac{C_{+-}^2}{C_-} - k_6\frac{1}{3}(1-\theta)\frac{C_{+-}^2}{C_+}.\end{aligned} \tag{2.32.3}$$

A two-cluster model is developed for a two-element model with 3 independent nonlinear equations and 8 unique parameters. The aim is to deduce rate constants $k_1, ..., k_8$ from some knowledge of concentrations. As we are interested in equilibrium state of the system, evolutionary system of equations can be converted to the algebraic system of equations in equilibrium. After applying moment closure approximations to the model and simplifying them, following system of equations will govern the system in equilibrium

$$4k_1\frac{C_{+-}^2}{C_-} + k_2\frac{C_{+-}^2}{C_-} - 4k_3\frac{C_{++}C_{+-}}{C_+} - k_4\frac{C_{++}C_{+-}}{C_+} = 0, \tag{2.33.1}$$

$$4k_5\frac{C_{+-}^2}{C_+} + k_6\frac{C_{+-}^2}{C_+} - 4k_7\frac{C_{--}C_{+-}}{C_-} - k_8\frac{C_{--}C_{+-}}{C_-} = 0, \tag{2.33.2}$$

$$k_1C_{\widehat{+-+}} = k_3C_{\widehat{++-}} \Rightarrow Q_1 = \frac{k_1}{k_3} = \frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}} = \frac{C_{++}C_-}{C_{+-}C_+}, \tag{2.33.3}$$

$$k_2C_{(\overline{+-+})} = k_4C_{(\overline{++-})} \Rightarrow Q_2 = \frac{k_2}{k_4} = \frac{C_{(\overline{++-})}}{C_{(\overline{+-+})}} = \frac{C_{++}C_-}{C_{+-}C_+}, \tag{2.33.4}$$

$$k_5C_{\widehat{-+-}} = k_7C_{\widehat{--+}} \Rightarrow Q_3 = \frac{k_5}{k_7} = \frac{C_{\widehat{--+}}}{C_{\widehat{-+-}}} = \frac{C_{--}C_+}{C_{+-}C_-}, \tag{2.33.5}$$

$$k_6C_{(\overline{-+-})} = k_8C_{(\overline{--+})} \Rightarrow Q_4 = \frac{k_6}{k_8} = \frac{C_{(\overline{--+})}}{C_{(\overline{-+-})}} = \frac{C_{--}C_+}{C_{+-}C_-}, \tag{2.33.6}$$

$$C_{++} + C_{--} + 2C_{+-} = 1, \tag{2.33.7}$$

where Q_1 to Q_4 are the equilibrium constants for unique reversible reactions of two-cluster model. As can be seen, each equilibrium constant has a unique definition. Taking closer look at the reversible reactions of figure 2.4, Q_1 and Q_2 both represent destruction of $(+-)$ cluster and production of $(++)$ cluster. The only difference is in the angle of the bonds, which is a 120 degree angle for the first one and straight for the second. However, the after applying the approximation both are expressed in the same terms. Also, to make the equations more consistent, the moment closure approximations have to be used not only for the rate equations, but also for the derivation of equilibrium constants to have a valid meaning and value. Hence,eq. (2.33.3) to (2.33.6) have been written in terms of pair and single concentrations.

The rate constants are not individually important in solving the system in equilibrium. Nonetheless, the ratios of parameters, which are called equilibrium constants play vital roles in controlling the system at the equilibrium. In other words, there are no bounds in choosing rate constants (unless they have to be positive to be plausible in a physical system), however, their ratios determine how different clusters are engaged in reversible reactions in the system. Taking into account all these factors, we can re-write system of equations in eq. (2.33) in terms of ratios of rate constants in order to diminish the degree of freedom of the underdetermined system. The complete derivation of equations can also be found in Appendix 7.2

$$(4Q_1\beta_1 + Q_2)\frac{C_{+-}^2}{C_-} - (4\beta_1 + 1)\frac{C_{++}C_{+-}}{C_+} = 0, \tag{2.34.1}$$

$$(4Q_3\beta_2 + Q_4)\frac{C_{+-}^2}{C_+} - (4\beta_2 + 1)\frac{C_{--}C_{+-}}{C_-} = 0, \tag{2.34.2}$$

$$Q_1 = Q_2 = \frac{C_{++}C_-}{C_{+-}C_+},\ Q_3 = Q_4 = \frac{C_{--}C_+}{C_{+-}C_-},\ \beta_1 = \frac{k_3}{k_4},\ \beta_2 = \frac{k_7}{k_8}, \tag{2.34.3}$$

where β_1 and β_2 are newly introduced ratios. This transformation leads to 2 unique reactions and 4 equilibrium constants namely, Q_1-Q_4. Substituting eq. (2.34.3) into the (2.34.1) and (2.34.2), the rate equations will be satisfied for all real values of β_1 and β_2. Note that the newly introduced parameters β_1 and β_2 are the ratios of the rate constants that do not correspond to a same reversible reaction, however, equilibrium constants are defined as the ratios of the rate constants which correspond to the forward and reverse reactions of the same reversible reaction. Intuitively, k_3 and k_4 are the only reaction rates that lead to the destruction of $(++)$ cluster. Indeed, β_1 is the ratio of rate constants for destroying a $(++)$ cluster in an angled element swap versus the straight one. Hence, it is a representative of the tendency of particles to swap in an angled position rather than a straight position. Similarly, β_2 represents the tendency of destruction of $(--)$ cluster in the angled bond versus the straight one. All in all, the result indicates that the values of β_1 and β_2 are not a key factor in determining the equilibrium state of the system, however, they might be influential in intermediate states that will lead to the equilibrium.

Some other methods have been developed for moment closure models in which $P_{i/jk} = \epsilon P_{i/j}$. In the ordinary pair approximation model $\epsilon = 1$ for all different types of elements. However, improved pair approximation methods seek to find an optimal value for ϵ via comparing their results to computer simulations. The choice of ϵ is highly dependent to the dynamics of each specific problem [4]. These types of improvements in the approximation are discussed in chapters 4 and 5.

2.3.2 Two-Element Triangular-Cluster Model

Another approach to derive rate equations was based on considering triangular triples and the reactions that can produce or destroy these reactions. Hence, 4-clusters will be involved in the model and have to be approximated by smaller clusters to close the dynamical system. Equation (2.16) is an instance of this formulation for the two-element model. The approximation method for this case is called triple approximation [6]. Instead of closing hierarchical equations at the level of pairs by writing third order clusters in terms of second order ones, it is necessary to truncate this hierarchy in the level of triplets by writing fourth-order densities in terms of smaller ones [8].

First, let us have a closer look at eq. (2.31) and its derivation. The coefficient in equations $(2.31.1)$, $(2.31.2)$ and $(2.31.3)$ is equal to $1/5$, $2/5$ and $2/5$ respectively. This coefficient actually represents the probability of finding the corresponding cluster shape in the lattice. For instance, there is $1/5$ probability that we can find the (ijk) triple as a straight line. Moreover, putting coefficients aside, eq. 2.31.1 and 2.31.2 have been derived by assuming no correlation between non-nearest neighbors. Hence, for both of them we can write

$$C_{\overline{ijk}} = (1-\theta)\frac{1}{3}C_{ijk} = (1-\theta)\frac{1}{3}C_{ij}P_{ij/k} \approx (1-\theta)\frac{1}{3}C_{ij}P_{j/k} = (1-\theta)\frac{1}{3}C_{ij}\frac{C_{jk}}{C_j}. \tag{2.35}$$

Derivation of eq. (2.31.2) is the same. However, eq. 2.31.3 is for a triangle whose density will be estimated by assuming pair correlations between all pairs. Similarly, all of these equations can be obtained from eq. (2.27) by neglecting triple correlations in the lattice. The only difference is that we have added a coefficient which accounts for the spatial structure of each configuration.

Considering the triangular-cluster model, the target is to write 4-cluster concentrations in terms of triangular clusters. We will be applying the same concept to this model, knowing that there are two distinct spatial structures for 4-clusters. Figure 2.16 demonstrates these spatial structures. As can be observed, there is $1/3$ probability that a 4-cluster in state $hijk$ is in the closed shape and $2/3$ probability otherwise. These coefficients are indeed the coefficients of the concentration terms.

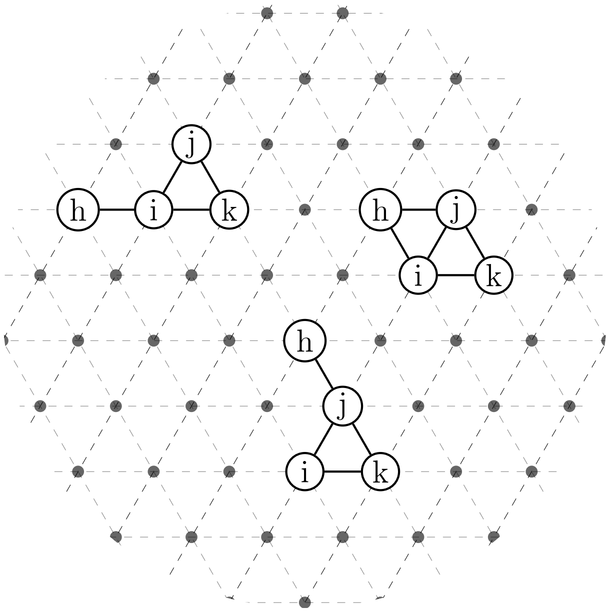


Figure 2.16: Schematic of a 2D triangular lattice - Different types of 4-clusters.

Considering a 4-cluster in a closed shape, its concentration can be broken down as

$$C_{\ddot{h}\widehat{ijk}} = \frac{1}{3} C_{\widehat{ijk}} P_{h/\widehat{ijk}} \approx \frac{1}{3} C_{\widehat{ijk}} P_{h/ij} = \frac{1}{3} C_{\widehat{ijk}} \frac{C_{\widehat{ijh}}}{C_{ij}}. \tag{2.36}$$

Note that $P_{h/\widehat{ijk}}$ is the probability that a randomly chosen nearest neighbor of a triangle in state ijk is in state h. But, due to the fact that we are looking for that particular neighbor which forms a closed structure with the triangle, the coefficient $1/3$ have also been included. As long as element h is not a nearest neighbor of element k, their correlation will be neglected and $P_{h/\widehat{ijk}}$ can be approximated by $P_{h/ij}$ [2]. It is notable that if we extend eq. (2.36) to triple densities based on singlets, pairs and triple correlations as in eq. (2.27), we obtain a definition for a 4-cluster density which complies by the concept introduced in eq. (2.27). The only difference is that all triple and quartet correlations have been neglected.

Similarly, considering an open 4-cluster, the element h is the nearest neighbor of i only. So its correlation with j and k will be neglected

$$C_{\dot{h}\widehat{ijk}} = \frac{2}{3} C_{\widehat{ijk}} P_{h/\widehat{ijk}} \approx \frac{2}{3} C_{\widehat{ijk}} P_{h/i} = \frac{2}{3} C_{\widehat{ijk}} \frac{C_{ih}}{C_i}. \tag{2.37}$$

This equation is true if i and j sites are actually occupied by the same elements. Otherwise, it has to be rewritten for each one of them with a $1/3$ coefficient.

Taking into account these approximations, system of ODEs (2.16) can be rewritten in the following closed format

$$\begin{aligned}\frac{d}{dt}C_{\widehat{+++}} &= 6k_9\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} + 6k_{10}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}}\\ &\quad -6k_{11}\frac{2}{3}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} - 6k_{12}\frac{1}{3}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}},\end{aligned} \tag{2.38.1}$$

$$\begin{aligned}\frac{d}{dt}C_{\widehat{---}} &= 6k_{13}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_+} + 6k_{14}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{+-}}\\ &\quad -6k_{15}\frac{2}{3}C_{\widehat{---}}\frac{C_{(+-)}}{C_-} - 6k_{16}\frac{1}{3}C_{\widehat{---}}\frac{C_{\widehat{--+}}}{C_{--}},\end{aligned} \tag{2.38.2}$$

$$\begin{aligned}\frac{d}{dt}C_{\widehat{++-}} &= 2k_{17}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-} + 2k_{11}\frac{2}{3}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} + 2k_{18}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}\\ &\quad +2k_{12}\frac{1}{3}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} + 2k_{19}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-} + 2k_{20}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}\\ &\quad -2k_{21}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+} - 2k_9\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} - 2k_{22}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}\\ &\quad -2k_{10}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} - 2k_{23}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+} - 2k_{24}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}},\end{aligned} \tag{2.38.3}$$

$$\begin{aligned}\frac{d}{dt}C_{\widehat{--+}} &= 2k_{23}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+} + 2k_{15}\frac{2}{3}C_{\widehat{---}}\frac{C_{(+-)}}{C_-} + 2k_{24}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}}\\ &\quad +2k_{16}\frac{1}{3}C_{\widehat{---}}\frac{C_{\widehat{--+}}}{C_{--}} + 2k_{21}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+} + 2k_{22}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}\\ &\quad -2k_{19}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-} - 2k_{13}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_+} - 2k_{20}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}\\ &\quad -2k_{14}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{+-}} - 2k_{17}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-} - 2k_{18}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}.\end{aligned} \tag{2.38.4}$$

As can be observed, the quartet densities have been written in terms of triplets and doublets. Hence, as we are interested in the equilibrium state of the system, the following system of equations can be solved to calculate triplet and doublet densities

$$\begin{aligned} 6k_9\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} + 6k_{10}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} \\ -6k_{11}\frac{2}{3}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} - 6k_{12}\frac{1}{3}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} = 0, \end{aligned} \tag{2.39.1}$$

$$\begin{aligned} 6k_{13}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_+} + 6k_{14}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{+-}} \\ -6k_{15}\frac{2}{3}C_{\widehat{---}}\frac{C_{(+-)}}{C_-} - 6k_{16}\frac{1}{3}C_{\widehat{---}}\frac{C_{\widehat{--+}}}{C_{--}} = 0, \end{aligned} \tag{2.39.2}$$

$$\begin{aligned} 2k_{17}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-} + 2k_{11}\frac{2}{3}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} + 2k_{18}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}} \\ +2k_{12}\frac{1}{3}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} + 2k_{19}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-} + 2k_{20}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}} \\ -2k_{21}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+} - 2k_9\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} - 2k_{22}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}} \\ -2k_{10}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} - 2k_{23}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+} - 2k_{24}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}} = 0, \end{aligned} \tag{2.39.3}$$

$$C_{\widehat{+++}} + C_{\widehat{---}} + 3C_{\widehat{++-}} + 3C_{\widehat{--+}} = 1. \tag{2.39.4}$$

Also, to reduce the degree of freedom in the system equilibrium constants can be taken into account as in eq. (2.17). Note that equilibrium constants are written in terms of 4-clusters which needs to be approximated by smaller clusters. Consistency of equations dictates us to break down 4-clusters into 3-clusters and further to 2-clusters. Hence, the equilibrium constants are all approximated by pair and single concentrations. The equations (2.39.1) to (2.39.3) need to be re-written in terms of equilibrium constants rather than the rate constants. Equation (2.40) demonstrates the system of equations after applying moment closure approximation and substituting constants with ratios

$$2Q_5\beta_3\frac{C_{++}C_{+-}^3}{C_+^2C_-^2}+Q_6\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2}-2\beta_3\frac{C_{++}^3C_{+-}}{C_+^4}-\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}=0, \tag{2.40.1}$$

$$2Q_7\beta_4\frac{C_{--}C_{+-}^3}{C_-^2C_+^2}+Q_8\frac{C_{--}^2C_{+-}^3}{C_-^4C_+^2}-2\beta_4\frac{C_{--}^3C_{+-}}{C_-^4}-\frac{C_{--}^3C_{+-}^2}{C_-^5C_+}=0, \tag{2.40.2}$$

$$\begin{aligned}2Q_9\beta_5\beta_7\frac{C_{--}C_{+-}^3}{C_-^3C_+}+Q_{10}\beta_7\frac{C_{--}C_{+-}^4}{C_-^4C_+^2}+2Q_{11}\beta_6\frac{C_{--}C_{+-}^3}{C_-^3C_+}\\+Q_{12}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}-2\beta_5\beta_7\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\beta_7\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}\\-2\beta_6\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}=0,\end{aligned} \tag{2.40.3}$$

$$\begin{aligned}Q_5=\frac{k_9}{k_{11}}=\frac{C_{++}^2C_-^2}{C_{+-}^2C_+^2},\ Q_6=\frac{k_{10}}{k_{12}}=\frac{C_{++}C_-}{C_{+-}C_+},\ Q_7=\frac{k_{13}}{k_{15}}=\frac{C_{--}^2C_+^2}{C_{+-}^2C_-^2},\\ Q_8=\frac{k_{14}}{k_{16}}=\frac{C_{--}C_+}{C_{+-}C_-},\ Q_9=\frac{k_{17}}{k_{21}}=\frac{C_{++}C_-^2}{C_{--}C_+^2},\ Q_{10}=\frac{k_{18}}{k_{22}}=\frac{C_{++}C_-}{C_{+-}C_+},\\ Q_{11}=\frac{k_{19}}{k_{23}}=\frac{C_{++}C_-^2}{C_{--}C_+^2},\ Q_{12}=\frac{k_{20}}{k_{24}}=\frac{C_{+-}C_-}{C_{--}C_+},\ \beta_3=\frac{k_{11}}{k_{12}},\\ \beta_4=\frac{k_{15}}{k_{16}},\ \beta_5=\frac{k_{21}}{k_{22}},\ \beta_6=\frac{k_{23}}{k_{24}},\ \beta_7=\frac{k_{22}}{k_{24}}.\end{aligned} \tag{2.40.4}$$

The complete derivation of equations can be found in Appendix 7.3. As can be observed, some new ratios have been introduced in the equations which are unknown. However, for all values of β_3 to β_7 the system of rate equations will be satisfied. Also, Q_5 to Q_{12} can be found using reversible reactions in equilibrium and momentum closure models.

To recapitulate, a regular triangular lattice is considered with two types of elements in it. The concentration of micro-structures inside the lattice can be described by writing the rate equations for different types of clusters, using two-cluster or triangular-cluster model. In each model, the system of hierarchical equations is not closed. The pair approximation model is proposed to truncate the hierarchy of the equations at the level of 2-clusters or 3-clusters. Also, to make the system of equations determined, ratios of rate constants were used at equilibrium rather than rates constants itself. The state of the system at equilibrium is dependant on the values of the equilibrium constants.

Analytical solution for the equations in equilibrium were proposed in this section. Also, the calculation of the rate constants will be investigated in the chapters 4 and 5. In the next chapter, the three-element model will be proposed, which is a representative of the NMC cathodes in Li-ion batteries.

Chapter 3

Three-Element Model

The previous chapter developed a cluster approximation model for different types of clusters based on existence of 2 types of elements in the lattice, namely, plus (⊕) and minus (⊖). The cluster approximation model can be modified to account for interactions between 3 types of elements in a 2D lattice. This formulation is representative of NMC layer in Li-ion batteries, as it consists of Nickel, Manganese and Cobalt. Interactions between 3 different types of elements will be considered in order to predict the concentration of micro-structures in the lattice. Similar to the two-element setting, deriving rate equations for each specific cluster requires us to contemplate all possible 3-clusters that may produce or destroy the cluster of interest by swapping nearest-neighbor elements. Here, 3 different types of elements (positive (⊕), negative (⊖) and neutral (ⓞ) elements) are considered. It is notable that the name of these elements does not correspond to their charge, as the model has no assumptions on the charge of the elements.

3.1 Evolution of Two-Clusters

The 3 types of elements can have different interactions with each other to form a variety of 2-clusters. Combinations of these elements can create the following configurations in building a 2-cluster: ($\oplus\oplus$), ($\ominus\ominus$), ($\circledcirc\circledcirc$) ($\oplus\ominus$), ($\ominus\oplus$), ($\oplus\circledcirc$), ($\circledcirc\oplus$), ($\ominus\circledcirc$) and ($\circledcirc\ominus$). We will be examining all possible ways that these configurations will be destroyed or produced in order to derive rate equations for each one of them. Note that translations of the 2-clusters will have the same concentration as stated by translational symmetry in Theorem 7.1.1.

Remark. *The normalization condition for the three-element model states that the sum of the concentrations of all possible 2-clusters should be equal to one. The same statement is true for the 1-clusters. Some of the concentrations have symmetries which require to be accounted for. The following equations will be derived from the normalization condition:*

$$C(\oplus) + C(\ominus) + C(\circledcirc) = 1, \tag{3.1.1}$$

$$C(\oplus\oplus) + C(\ominus\ominus) + C(\circledcirc\circledcirc) + 2C(\oplus\ominus) + 2C(\oplus\circledcirc) + 2C(\ominus\circledcirc) = 1. \tag{3.1.2}$$

Eq. (3.1.1) *is satisfied for all configurations at all times of the system. By taking the derivatives of eq.* (3.1.2)*, the following equation will be generated:*

$$\begin{aligned} &\frac{d}{dt}C(\oplus\oplus) + \frac{d}{dt}C(\ominus\ominus) + \frac{d}{dt}C(\circledcirc\circledcirc) \\ +2&\frac{d}{dt}C(\oplus\ominus) + 2\frac{d}{dt}C(\oplus\circledcirc) + 2\frac{d}{dt}C(\ominus\circledcirc) = 0. \end{aligned} \tag{3.2}$$

The normalization condition introduced in eq. (3.2) *is satisfied by the rate equations introduced in the following sections.*

The rate of change in the concentration of each one of these clusters will be derived in terms of concentrations of bigger clusters as stated in the following sections. Note that each reaction has some translational symmetries and the coefficients introduced in the derivation of rate equations represent the number of translations that each reaction can have.

3.1.1 Production and Destruction of (⊕⊕) Cluster

In each of the reactions in figure 3.1, the neighbor element (highlighted in red) will swap with one of the elements of the window (highlighted in blue) to produce a (⊕⊕) cluster in the forward reaction. Conversely, the reverse reactions illustrate all possible ways to destroy a (⊕⊕) cluster inside the blue window. Figure 3.1 shows all possible unique reactions to produce or destroy a (⊕⊕) cluster.

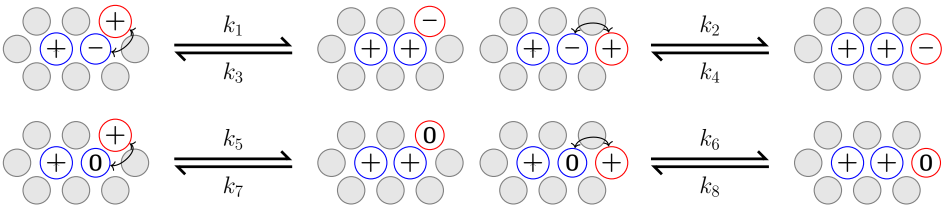


Figure 3.1: Unique reactions, after considering translational symmetries, to destroy or produce a (⊕⊕) cluster.

According to the forward and backward reactions in the figure 3.1, the rate equation for the rate of change of ⊕⊕ cluster will be derived as follows. Note that this equation is similar to the equation derived for the two-element model with additional terms for the interaction of ⊕ and ⓞ elements

$$\begin{aligned}\frac{d}{dt}C_{++} = 4k_1C_{\widehat{+-+}} + 2k_2C_{\overline{+-+}} - 4k_3C_{\widehat{++-}} - 2k_4C_{\overline{++-}} \\ +4k_5C_{\widehat{+0+}} + 2k_6C_{\overline{+0+}} - 4k_7C_{\widehat{++0}} - 2k_8C_{\overline{++0}}.\end{aligned} \tag{3.3}$$

3.1.2 Production and Destruction of (⊖⊖) Cluster

Similarly, all possible unique reactions to produce or destroy the (⊖⊖) cluster are shown in figure 3.2. Each one of these reactions have some translational symmetries, which have been taken care of in the derivation of the rate equation in eq. (3.4).

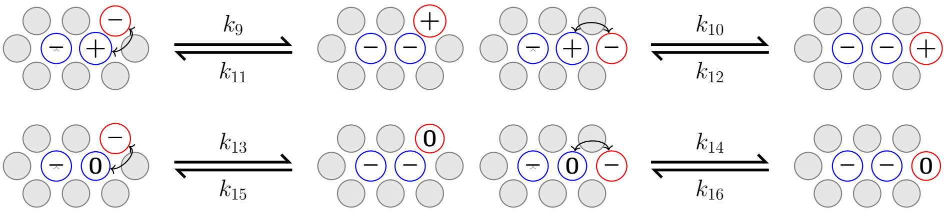


Figure 3.2: Unique reactions, after considering translational symmetries, to destroy or produce a (⊖⊖) cluster.

8 specific rate constants are introduced in this rate equation

$$\begin{aligned}\frac{d}{dt}C_{--} = {} & 4k_9C_{\widehat{-+-}} + 2k_{10}C_{\overline{-+-}} - 4k_{11}C_{\widehat{--+}} - 2k_{12}C_{\overline{--+}} \\ & +4k_{13}C_{\widehat{-0-}} + 2k_{14}C_{\overline{-0-}} - 4k_{15}C_{\widehat{--0}} - 2k_{16}C_{\overline{--0}}.\end{aligned} \tag{3.4}$$

3.1.3 Production and Destruction of (⓪⓪) Cluster

In each of the reactions in figure 3.3, one of the nearest-neighbor elements will swap with one of the elements of the window to form a (⓪⓪) cluster in the forward reaction. Conversely, the backward reactions will destroy this specific cluster.

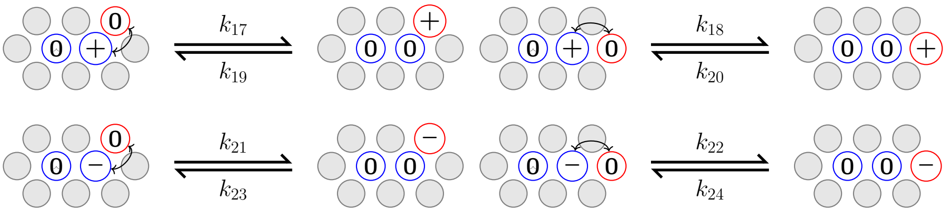


Figure 3.3: Unique reactions, after considering translational symmetries, to destroy or produce a (⓪⓪) cluster.

The rate equation for the rate of change in concentration of ⓪⓪ cluster is shown in eq. (3.5) by accounting for the translations of each reaction

$$\begin{aligned} \frac{d}{dt}C_{00} = 4k_{17}C_{\widehat{0+0}} + 2k_{18}C_{\overline{0+0}} - 4k_{19}C_{\widehat{00+}} - 2k_{20}C_{\overline{00+}} \\ +4k_{21}C_{\widehat{0-0}} + 2k_{22}C_{\overline{0-0}} - 4k_{23}C_{\widehat{00-}} - 2k_{24}C_{\overline{00-}}. \end{aligned} \tag{3.5}$$

3.1.4 Production and Destruction of (⊕⊖) Cluster

In order to find the reaction rate for the (⊕⊖) cluster, one needs to look for the neares-neighbor element swaps that may build or destroy this specific cluster inside the 2-cluster window. This can be accomplished by considering all interactions between different types of elements. All possible unique reactions to produce or destroy this cluster are shown in figure 3.4. Note that the number of translations that each reaction can have is not equal to that of previous clusters.

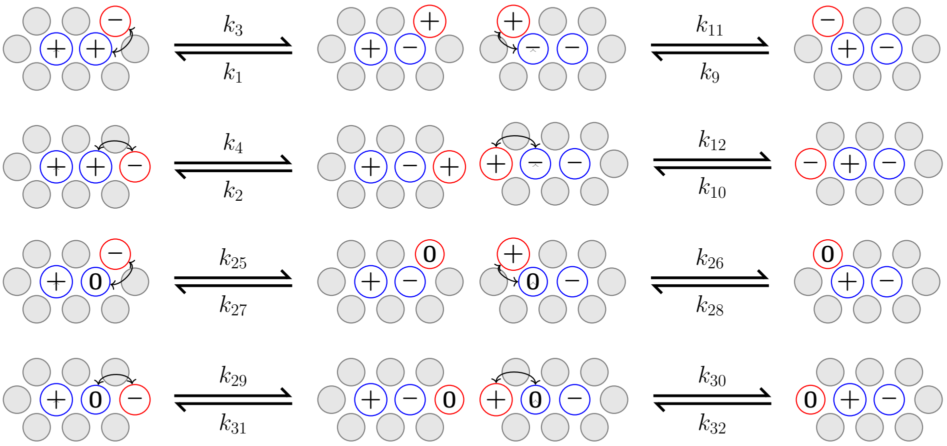


Figure 3.4: Unique reactions, after considering translational symmetries, to destroy or produce a (⊕⊖) cluster.

The rate equation for the (⊕⊖) cluster will be presented as

$$
\begin{aligned}
\frac{d}{dt}C_{+-} = 2k_3C_{\widehat{++-}} + 2k_{11}C_{\widehat{--+}} - 2k_1C_{\widehat{+-+}} - 2k_9C_{\widehat{-+-}} \\
+k_4C_{\overline{++-}} + k_{12}C_{\overline{--+}} - k_2C_{\overline{+-+}} - k_{10}C_{\overline{-+-}} \\
2k_{25}C_{\widehat{+0-}} + 2k_{26}C_{\widehat{-0+}} - 2k_{27}C_{\widehat{+-0}} - 2k_{28}C_{\widehat{-+0}} \\
+k_{29}C_{\overline{+0-}} + k_{30}C_{\overline{-0+}} - k_{31}C_{\overline{+-0}} - k_{32}C_{\overline{-+0}}.
\end{aligned}
\tag{3.6}
$$

3.1.5 Production and Destruction of (⊕ⓞ) Cluster

Similar to the ⊕⊖ cluster, the reversible reactions for producing or destroying the (⊕ⓞ) cluster are introduced by figure 3.5. Note that some of these reversible reactions are repetitions or translations of the other reactions, thereby their unique rate constant have been utilized here.

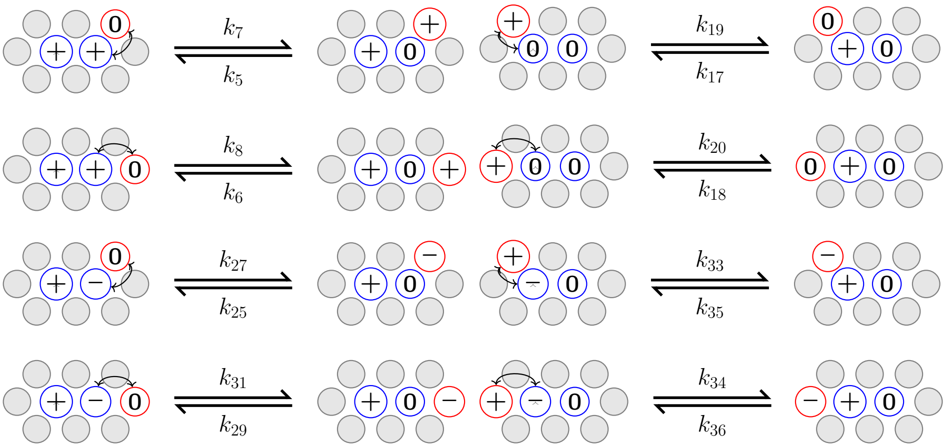


Figure 3.5: Unique reactions, after considering translational symmetries, to destroy or produce a (⊕ⓞ) cluster.

The rate equation for stating the concentration of the ($\oplus$$\textcircled{o}$) cluster is derived as

$$\begin{aligned}\frac{d}{dt}C_{+0} = 2k_7C_{\widehat{++0}} + 2k_{19}C_{\widehat{00+}} - 2k_5C_{\widehat{+0+}} - 2k_{17}C_{\widehat{0+0}} \\ +k_8C_{\overline{++0}} + k_{20}C_{\overline{00+}} - k_6C_{\overline{+0+}} - k_{18}C_{\overline{0+0}} \\ 2k_{27}C_{\widehat{+-0}} + 2k_{33}C_{\widehat{0-+}} - 2k_{25}C_{\widehat{+0-}} - 2k_{35}C_{\widehat{0+-}} \\ +k_{31}C_{\overline{+-0}} + k_{34}C_{\overline{0-+}} - k_{29}C_{\overline{+0-}} - k_{36}C_{\overline{0+-}}.\end{aligned} \tag{3.7}$$

3.1.6 Production and Destruction of ($\ominus$$\textcircled{o}$) Cluster

All possible unique reactions to produce or destroy the ($\ominus$$\textcircled{o}$) cluster are shown in figure 3.6. It is worth mentioning that all of these reactions are repetitions of the ones in figures 3.2, 3.3, 3.4 and 3.5 with their specific rate constants. Thereby, this equation is the complement of all other rate equations in (3.3)-(3.7) and satisfies the aforesaid normalization condition.

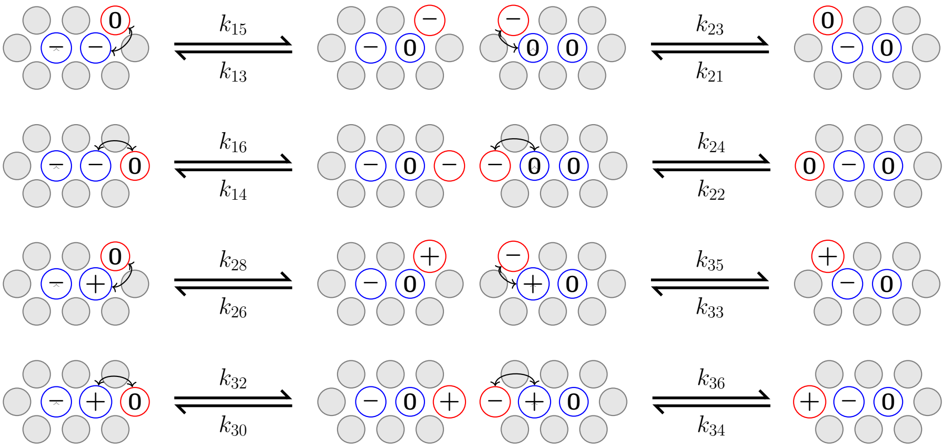


Figure 3.6: Unique reactions, after considering translational symmetries, to destroy or produce a ($\ominus$$\textcircled{o}$) cluster.

The following equation represents the rate of change in the concentration of the

(⊖⊚) cluster

$$\begin{aligned}\frac{d}{dt}C_{-0} = {} & 2k_{15}C_{\widehat{--0}} + 2k_{23}C_{\widehat{00-}} - 2k_{13}C_{\widehat{-0-}} - 2k_{21}C_{\widehat{0-0}} \\ & +k_{16}C_{\overline{--0}} + k_{24}C_{\overline{00-}} - k_{14}C_{\overline{-0-}} - k_{22}C_{\overline{0-0}} \\ & 2k_{28}C_{\widehat{-+0}} + 2k_{35}C_{\widehat{0+-}} - 2k_{26}C_{\widehat{-0+}} - 2k_{33}C_{\widehat{0-+}} \\ & +k_{32}C_{\overline{-+0}} + k_{36}C_{\overline{0+-}} - k_{30}C_{\overline{-0+}} - k_{34}C_{\overline{0-+}}.\end{aligned} \tag{3.8}$$

In summary, the following set of rate equations has been derived for the rate of change of specific clusters in the three-element model. These equations satisfy the normalization condition introduced in eq. (3.2). Hence, one of the equations in eq. (3.9) is redundant and can be dropped

$$\begin{aligned}\frac{d}{dt}C_{++} = {} & 4k_{1}C_{\widehat{+-+}} + 2k_{2}C_{\overline{+-+}} - 4k_{3}C_{\widehat{++-}} - 2k_{4}C_{\overline{++-}} \\ & +4k_{5}C_{\widehat{+0+}} + 2k_{6}C_{\overline{+0+}} - 4k_{7}C_{\widehat{++0}} - 2k_{8}C_{\overline{++0}},\end{aligned} \tag{3.9.1}$$

$$\begin{aligned}\frac{d}{dt}C_{--} = {} & 4k_{9}C_{\widehat{-+-}} + 2k_{10}C_{\overline{-+-}} - 4k_{11}C_{\widehat{--+}} - 2k_{12}C_{\overline{--+}} \\ & +4k_{13}C_{\widehat{-0-}} + 2k_{14}C_{\overline{-0-}} - 4k_{15}C_{\widehat{--0}} - 2k_{16}C_{\overline{--0}},\end{aligned} \tag{3.9.2}$$

$$\begin{aligned}\frac{d}{dt}C_{00} = {} & 4k_{17}C_{\widehat{0+0}} + 2k_{18}C_{\overline{0+0}} - 4k_{19}C_{\widehat{00+}} - 2k_{20}C_{\overline{00+}} \\ & +4k_{21}C_{\widehat{0-0}} + 2k_{22}C_{\overline{0-0}} - 4k_{23}C_{\widehat{00-}} - 2k_{24}C_{\overline{00-}},\end{aligned} \tag{3.9.3}$$

$$\begin{aligned}\frac{d}{dt}C_{+-} = {} & 2k_{3}C_{\widehat{++-}} + 2k_{11}C_{\widehat{--+}} - 2k_{1}C_{\widehat{+-+}} - 2k_{9}C_{\widehat{-+-}} \\ & +k_{4}C_{\overline{++-}} + k_{12}C_{\overline{--+}} - k_{2}C_{\overline{+-+}} - k_{10}C_{\overline{-+-}} \\ & +2k_{25}C_{\widehat{+0-}} + 2k_{26}C_{\widehat{-0+}} - 2k_{27}C_{\widehat{+-0}} - 2k_{28}C_{\widehat{-+0}} \\ & +k_{29}C_{\overline{+0-}} + k_{30}C_{\overline{-0+}} - k_{31}C_{\overline{+-0}} - k_{32}C_{\overline{-+0}},\end{aligned} \tag{3.9.4}$$

$$\begin{aligned}\frac{d}{dt}C_{+0} = {} & 2k_{7}C_{\widehat{++0}} + 2k_{19}C_{\widehat{00+}} - 2k_{5}C_{\widehat{+0+}} - 2k_{17}C_{\widehat{0+0}} \\ & +k_{8}C_{\overline{++0}} + k_{20}C_{\overline{00+}} - k_{6}C_{\overline{+0+}} - k_{18}C_{\overline{0+0}} \\ & +2k_{27}C_{\widehat{+-0}} + 2k_{33}C_{\widehat{0-+}} - 2k_{25}C_{\widehat{+0-}} - 2k_{35}C_{\widehat{0+-}} \\ & +k_{31}C_{\overline{+-0}} + k_{34}C_{\overline{0-+}} - k_{29}C_{\overline{+0-}} - k_{36}C_{\overline{0+-}},\end{aligned} \tag{3.9.5}$$

$$
\begin{aligned}
\frac{d}{dt}C_{-0} = 2k_{15}C_{\widehat{--0}} + 2k_{23}C_{\widehat{00-}} - 2k_{13}C_{\widehat{-0-}} - 2k_{21}C_{\widehat{0-0}} \\
+k_{16}C_{\overline{--0}} + k_{24}C_{\overline{00-}} - k_{14}C_{\overline{-0-}} - k_{22}C_{\overline{0-0}} \\
+2k_{28}C_{\widehat{-+0}} + 2k_{35}C_{\widehat{0+-}} - 2k_{26}C_{\widehat{-0+}} - 2k_{33}C_{\widehat{0-+}} \\
+k_{32}C_{\overline{-+0}} + k_{36}C_{\overline{0+-}} - k_{30}C_{\overline{-0+}} - k_{34}C_{\overline{0-+}}.
\end{aligned}
\tag{3.9.6}
$$

As can be observed, these equations form a hierarchical system of ODEs, in which the rate of change of each cluster concentration is given in terms of higher order clusters. One solution to this problem is the truncation of this hierarchy, which will be investigated in the next sections.

3.2 Evolution of Triangular-Clusters

In this section, the triangular cluster model will be developed for a system consisting of 3 types of elements, namely, positive, negative and neutral ones. The goal of this section is to find the concentrations of 3-clusters with the shape of a triangle. As mentioned before, there are three different spatial shapes of a triplet in the lattice: closed triplets or triangles, open triplets with 180 degree bonds and open triplets with 120 degree bonds. Triangular concentrations are a matter of interest as we are seeking to match the predictions of the cluster approximation model with the NMR spectroscopy results. There are 10 different combinations for a triangle with three particles: $\left(\overset{\oplus}{\oplus\oplus}\right)$, $\left(\overset{\ominus}{\ominus\ominus}\right)$, $\left(\overset{\circledcirc}{\circledcirc\circledcirc}\right)$, $\left(\overset{\ominus}{\oplus\oplus}\right)$, $\left(\overset{\oplus}{\ominus\ominus}\right)$, $\left(\overset{\circledcirc}{\oplus\oplus}\right)$, $\left(\overset{\oplus}{\circledcirc\circledcirc}\right)$, $\left(\overset{\circledcirc}{\ominus\ominus}\right)$, $\left(\overset{\ominus}{\circledcirc\circledcirc}\right)$, $\left(\overset{\circledcirc}{\oplus\ominus}\right)$. As stated by Theorem 7.1.4, there are some other configurations which are rotational translations of these triangles. In this section, the focus will be on obtaining rate equations for the rate of change of concentrations of these triangles, thereby establishing a dynamical system in order to comprehend the behavior of the triangular clusters.

Remark. *The normalization condition can be written for the triangular clusters with 3 types of species. This condition was investigated previously in eq.* (2.2) *for single site clusters and 2-clusters. In the current setting we are interested in triangular 3-clusters. The following equation represents this condition*

$$
\begin{aligned}
&\mathrm{c}\left(\overset{\oplus}{\oplus\oplus}\right)+\mathrm{c}\left(\overset{\ominus}{\ominus\ominus}\right)+\mathrm{c}\left(\overset{\circledcirc}{\circledcirc\circledcirc}\right)+\mathrm{c}\left(\overset{\ominus}{\oplus\oplus}\right)+\mathrm{c}\left(\overset{\oplus}{\oplus\ominus}\right)+\mathrm{c}\left(\overset{\oplus}{\ominus\oplus}\right)\\
&+\mathrm{c}\left(\overset{\oplus}{\ominus\ominus}\right)+\mathrm{c}\left(\overset{\ominus}{\oplus\ominus}\right)+\mathrm{c}\left(\overset{\ominus}{\ominus\oplus}\right)+\mathrm{c}\left(\overset{\circledcirc}{\oplus\oplus}\right)+\mathrm{c}\left(\overset{\oplus}{\oplus\circledcirc}\right)+\mathrm{c}\left(\overset{\oplus}{\circledcirc\oplus}\right)\\
&+\mathrm{c}\left(\overset{\oplus}{\circledcirc\circledcirc}\right)+\mathrm{c}\left(\overset{\circledcirc}{\oplus\circledcirc}\right)+\mathrm{c}\left(\overset{\circledcirc}{\circledcirc\oplus}\right)+\mathrm{c}\left(\overset{\circledcirc}{\ominus\ominus}\right)+\mathrm{c}\left(\overset{\ominus}{\ominus\circledcirc}\right)+\mathrm{c}\left(\overset{\ominus}{\circledcirc\ominus}\right)\\
&+\mathrm{c}\left(\overset{\ominus}{\circledcirc\circledcirc}\right)+\mathrm{c}\left(\overset{\circledcirc}{\ominus\circledcirc}\right)+\mathrm{c}\left(\overset{\circledcirc}{\circledcirc\ominus}\right)+\mathrm{c}\left(\overset{\circledcirc}{\oplus\ominus}\right)+\mathrm{c}\left(\overset{\circledcirc}{\ominus\oplus}\right)+\mathrm{c}\left(\overset{\ominus}{\oplus\circledcirc}\right)\\
&\qquad+\mathrm{c}\left(\overset{\ominus}{\circledcirc\oplus}\right)+\mathrm{c}\left(\overset{\oplus}{\ominus\circledcirc}\right)+\mathrm{c}\left(\overset{\oplus}{\circledcirc\ominus}\right)=1,\\
&\Rightarrow \mathrm{c}\left(\overset{\oplus}{\oplus\oplus}\right)+\mathrm{c}\left(\overset{\ominus}{\ominus\ominus}\right)+\mathrm{c}\left(\overset{\circledcirc}{\circledcirc\circledcirc}\right)\\
&+3\mathrm{c}\left(\overset{\ominus}{\oplus\oplus}\right)+3\mathrm{c}\left(\overset{\oplus}{\ominus\ominus}\right)+3\mathrm{c}\left(\overset{\circledcirc}{\oplus\oplus}\right)\\
&+3\mathrm{c}\left(\overset{\oplus}{\circledcirc\circledcirc}\right)+3\mathrm{c}\left(\overset{\circledcirc}{\ominus\ominus}\right)+3\mathrm{c}\left(\overset{\ominus}{\circledcirc\circledcirc}\right)+6\mathrm{c}\left(\overset{\circledcirc}{\oplus\ominus}\right)=1.
\end{aligned}
\tag{3.10}
$$

Some terms in eq. (3.10) *are translations of each other as stated by Theorem 7.1.4. By taking derivatives of eq.* (3.10)*, the following equation is generated*

$$
\begin{aligned}
&\frac{d}{dt}\mathrm{c}\left(\overset{\oplus}{\oplus\oplus}\right)+\frac{d}{dt}\mathrm{c}\left(\overset{\ominus}{\ominus\ominus}\right)+\frac{d}{dt}\mathrm{c}\left(\overset{\circledcirc}{\circledcirc\circledcirc}\right)\\
&+3\frac{d}{dt}\mathrm{c}\left(\overset{\ominus}{\oplus\oplus}\right)+3\frac{d}{dt}\mathrm{c}\left(\overset{\oplus}{\ominus\ominus}\right)+3\frac{d}{dt}\mathrm{c}\left(\overset{\circledcirc}{\oplus\oplus}\right)\\
&+3\frac{d}{dt}\mathrm{c}\left(\overset{\oplus}{\circledcirc\circledcirc}\right)+3\frac{d}{dt}\mathrm{c}\left(\overset{\circledcirc}{\ominus\ominus}\right)+3\frac{d}{dt}\mathrm{c}\left(\overset{\ominus}{\circledcirc\circledcirc}\right)+6\frac{d}{dt}\mathrm{c}\left(\overset{\circledcirc}{\oplus\ominus}\right)=0.
\end{aligned}
\tag{3.11}
$$

This condition will be investigated after deriving all rate equations for different 3-clusters.

3.2.1 Production and Destruction of ($\overset{\oplus}{\oplus\oplus}$) Cluster

In order to derive the rate equation for the $\left(\overset{\oplus}{\oplus\oplus}\right)$ cluster, all possible element swaps that will build or destroy this cluster will be considered. Figure 2.8 and 2.9 in the previous sections demonstrate all potential reactions for producing or destroying a $\left(\overset{\oplus}{\oplus\oplus}\right)$ cluster by considering interactions between $\oplus$ and $\ominus$ elements. Currently, the $\circledcirc$ element is also added to the model, which requires us to contemplate the interactions of ⊕ element with it. The rules for producing and destroying this triangle are the same as before, with similar translational symmetries. The possible reversible reactions that are unique are presented in figure 3.7.

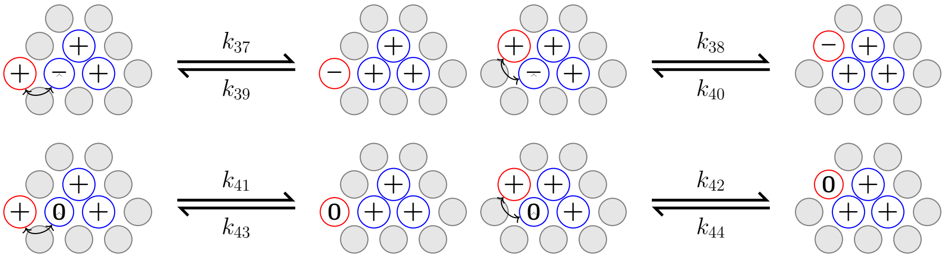


Figure 3.7: Unique reversible reactions, after considering translational symmetries, to produce or destroy a ($\overset{\oplus}{\oplus\oplus}$) cluster.

Notably, each one of the reversible reactions have 6 translational symmetries, as referred to in the previous sections, and will be accounted for 6 times in deriving the rate equations. The rate equation for this cluster can be derived by subtracting its rate of production from its rate of destruction

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{+++})} &= 6k_{37}C_{(\dot{+}\widehat{-++})} + 6k_{38}C_{(\ddot{+}\widehat{-++})} - 6k_{39}C_{(\dot{-}\widehat{+++})} - 6k_{40}C_{(\ddot{-}\widehat{+++})} \\ &+6k_{41}C_{(\dot{+}\widehat{0++})} + 6k_{42}C_{(\ddot{+}\widehat{0++})} - 6k_{43}C_{(\dot{0}\widehat{+++})} - 6k_{44}C_{(\ddot{0}\widehat{+++})}.\end{aligned} \tag{3.12}$$

3.2.2 Production and Destruction of ($\overset{\ominus}{\ominus\ominus}$) Cluster

Similarly, deriving the rate equation for the ($\overset{\ominus}{\ominus\ominus}$) cluster requires considering all possible element swaps that will destroy or produce this cluster. Figure 3.8 demonstrates all potential reactions for producing or destroying a ($\overset{\ominus}{\ominus\ominus}$) cluster, considering interactions of ⊖ with ⊕ and ⓪ elements.

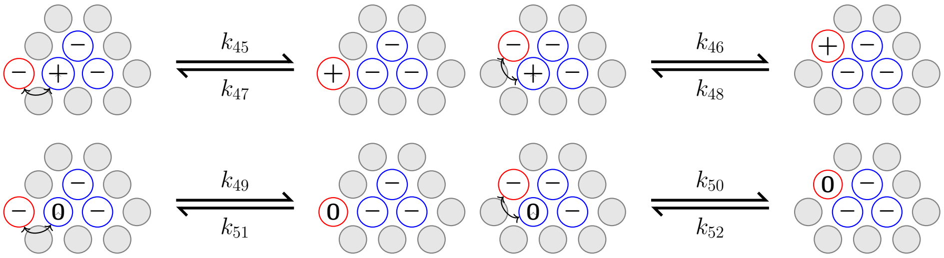


Figure 3.8: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\ominus}{\ominus\ominus})$ cluster.

Considering reversible and unique reactions in figure 3.8, the following rate equation can be deduced for $(\overset{\ominus}{\ominus\ominus})$ cluster

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{---})} = {} & 6k_{45}C_{(\dot{-}\widehat{+--})} + 6k_{46}C_{(\ddot{-}\widehat{+--})} - 6k_{47}C_{(\dot{+}\widehat{---})} - 6k_{48}C_{(\ddot{+}\widehat{---})} \\ & +6k_{49}C_{(\dot{-}\widehat{0--})} + 6k_{50}C_{(\ddot{-}\widehat{0--})} - 6k_{51}C_{(\dot{0}\widehat{---})} - 6k_{52}C_{(\ddot{0}\widehat{---})}.\end{aligned} \tag{3.13}$$

3.2.3 Production and Destruction of $(\overset{\textcircled{o}}{\textcircled{o}\textcircled{o}})$ Cluster

Following the same rules, we will derive the rate equation for a $(\overset{\textcircled{o}}{\textcircled{o}\textcircled{o}})$ cluster. We will consider interactions of $\textcircled{o}$ element with $\oplus$ and $\ominus$ elements. The following reversible reactions will be found with their specific rate constants.

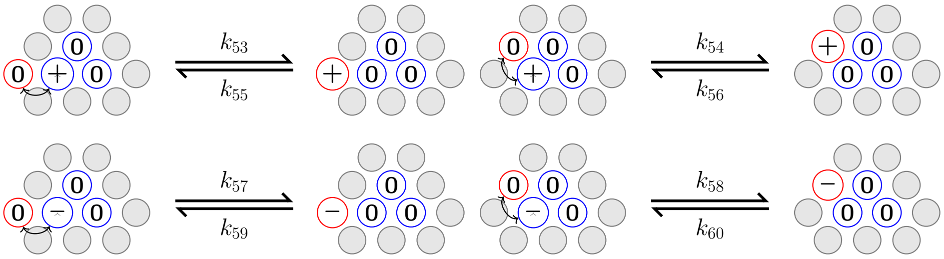


Figure 3.9: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\textcircled{o}}{\textcircled{o}\textcircled{o}})$ cluster.

Considering reversible and unique reactions in figure 3.9, the following rate equation can be deduced for $\left(\overset{\circledcirc}{\circledcirc\circledcirc}\right)$ cluster.

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{000})} &= 6k_{53}C_{(\dot{0}\widehat{+00})} + 6k_{54}C_{(\ddot{0}\widehat{+00})} - 6k_{55}C_{(\dot{+}\widehat{000})} - 6k_{56}C_{(\ddot{+}\widehat{000})} \\ &+6k_{57}C_{(\dot{0}\widehat{-00})} + 6k_{58}C_{(\ddot{0}\widehat{-00})} - 6k_{59}C_{(\dot{-}\widehat{000})} - 6k_{60}C_{(\ddot{-}\widehat{000})}.\end{aligned} \tag{3.14}$$

3.2.4 Production and Destruction of $\left(\overset{\ominus}{\oplus\oplus}\right)$ Cluster

Deriving the rate equation for the $\left(\overset{\ominus}{\oplus\oplus}\right)$ cluster can be accomplished by considering all possible element swaps that will destroy or produce this cluster. Figure 3.10 demonstrates these reactions. Note that translational symmetries are taken into account to reduce number of reactions.

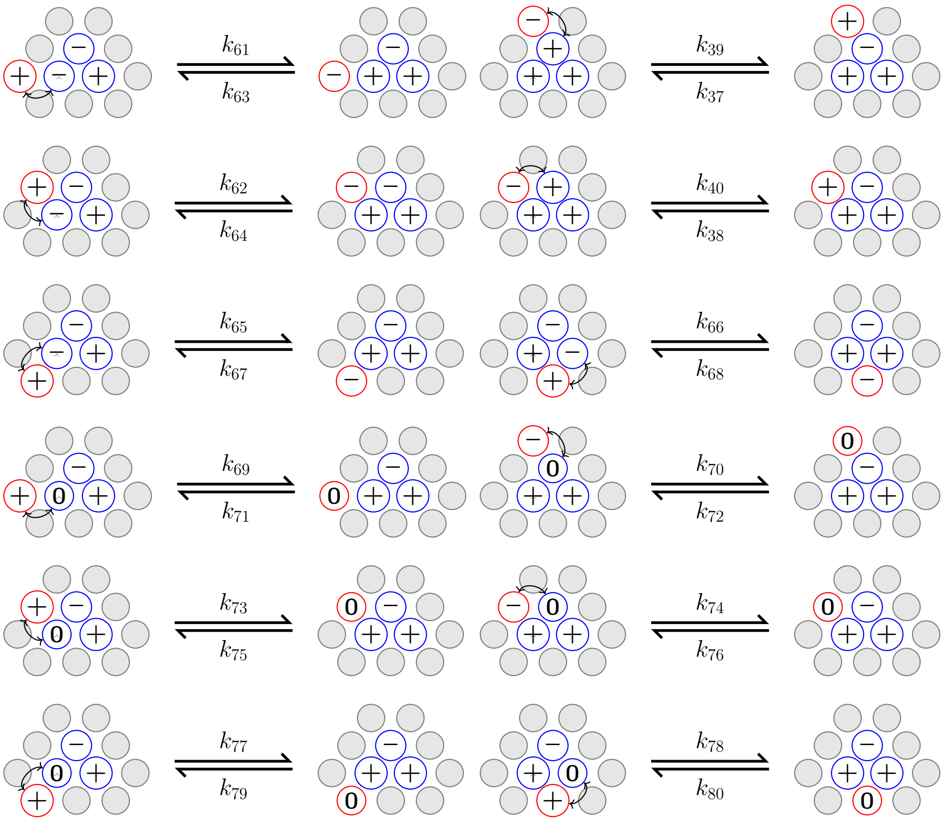


Figure 3.10: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $\left(\overset{\ominus}{\oplus\oplus}\right)$ cluster.

Each one of the reactions in figure 3.10 for producing or destroying the $\left(\overset{\ominus}{\oplus\oplus}\right)$ cluster has 2 translational symmetries. Here we have introduced the unique ones and will account for each one of them two times in the equation. Some of the rate constants are the same as some of the previous ones, however, some new constants have been added to the system to account for interactions between $\oplus$ and $\ominus$ elements

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{+-+})} = {} & 2k_{61}C_{(\dot{+}\widehat{--+})} + 2k_{39}C_{(\dot{-}\widehat{+++})} - 2k_{63}C_{(\dot{-}\widehat{+-+})} - 2k_{37}C_{(\dot{+}\widehat{-++})} \\ & +2k_{62}C_{(\ddot{+}\widehat{--+})} + 2k_{40}C_{(\ddot{-}\widehat{+++})} - 2k_{64}C_{(\ddot{-}\widehat{+-+})} - 2k_{38}C_{(\ddot{+}\widehat{+-+})} \\ & +2k_{65}C_{(\dot{+}\widehat{-+-})} + 2k_{66}C_{(\ddot{+}\widehat{+--})} - 2k_{67}C_{(\dot{-}\widehat{++-})} - 2k_{68}C_{(\ddot{-}\widehat{++-})} \\ & +2k_{69}C_{(\dot{+}\widehat{0-+})} + 2k_{70}C_{(\dot{-}\widehat{0++})} - 2k_{71}C_{(\dot{0}\widehat{+-+})} - 2k_{72}C_{(\dot{0}\widehat{-++})} \\ & +2k_{73}C_{(\ddot{+}\widehat{0-+})} + 2k_{74}C_{(\ddot{-}\widehat{+0+})} - 2k_{75}C_{(\ddot{0}\widehat{+-+})} - 2k_{76}C_{(\ddot{0}\widehat{+-+})} \\ & +2k_{77}C_{(\dot{+}\widehat{0+-})} + 2k_{78}C_{(\ddot{+}\widehat{+0-})} - 2k_{79}C_{(\dot{0}\widehat{++-})} - 2k_{80}C_{(\ddot{0}\widehat{++-})}.\end{aligned} \tag{3.15}$$

3.2.5 Production and Destruction of $\left(\overset{\oplus}{\ominus\ominus}\right)$ Cluster

Similarly, the rate of change of the $\left(\overset{\oplus}{\ominus\ominus}\right)$ cluster can be obtained by looking into the reactions that will build or destroy this cluster. In addition to the interactions between $\oplus$ and $\ominus$ elements, the ⓪ element would also come into play. Figure 3.11 demonstrates all possible unique reactions after considering translational symmetries to produce or destroy this cluster. Note that some of the reactions might be similar to previous ones.

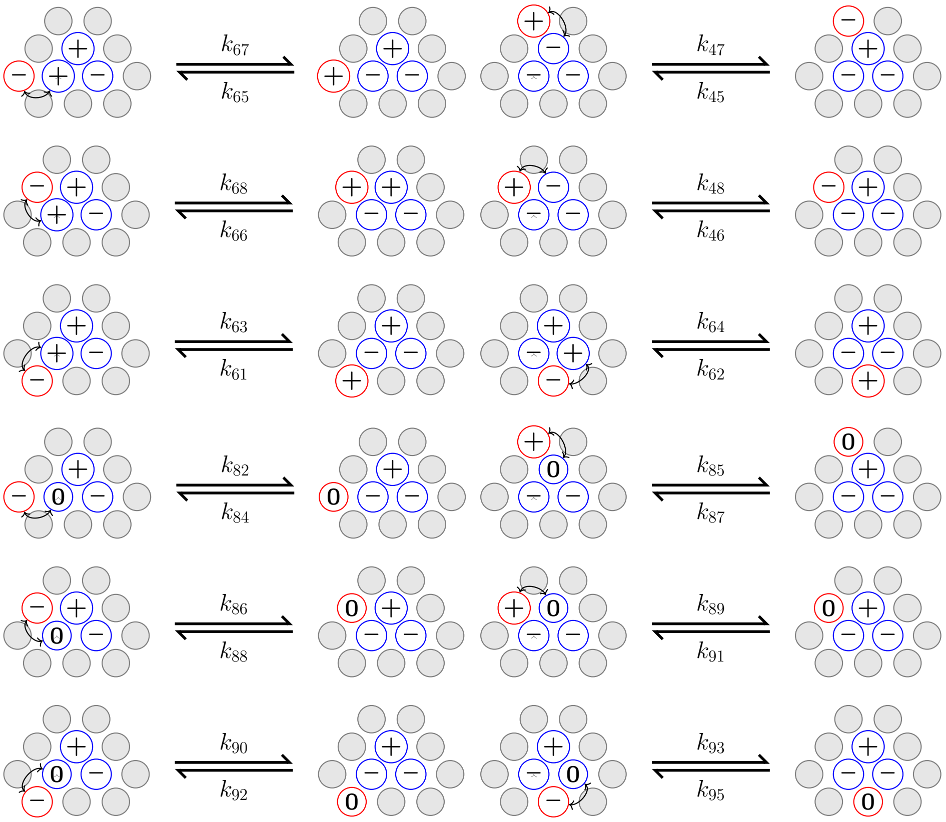


Figure 3.11: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\oplus}{\ominus\ominus})$ cluster.

One can write the rate equation for the $(\overset{\oplus}{\ominus\ominus})$ cluster by considering the reversible reactions in figure 3.11. Again, each term in the rate equation has a coefficient of 2 due to translation invariance of the system

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{-+-})} = {} & 2k_{67}C_{(\dot{-}\widehat{++-})} + 2k_{47}C_{(\dot{+}\widehat{---})} - 2k_{65}C_{(\dot{+}\widehat{-+-})} - 2k_{45}C_{(\dot{-}\widehat{+--})} \\ & +2k_{68}C_{(\ddot{-}\widehat{++-})} + 2k_{48}C_{(\ddot{+}\widehat{---})} - 2k_{66}C_{(\ddot{+}\widehat{-+-})} - 2k_{46}C_{(\ddot{-}\widehat{+--})} \\ & +2k_{63}C_{(\dot{-}\widehat{+-+})} + 2k_{64}C_{(\ddot{-}\widehat{+-+})} - 2k_{61}C_{(\dot{+}\widehat{--+})} - 2k_{62}C_{(\ddot{+}\widehat{--+})} \\ & +2k_{82}C_{(\dot{-}\widehat{0+-})} + 2k_{85}C_{(\dot{+}\widehat{0--})} - 2k_{84}C_{(\dot{0}\widehat{-+-})} - 2k_{87}C_{(\dot{0}\widehat{+--})} \\ & +2k_{86}C_{(\ddot{-}\widehat{0+-})} + 2k_{89}C_{(\ddot{+}\widehat{-0-})} - 2k_{88}C_{(\ddot{0}\widehat{-+-})} - 2k_{91}C_{(\ddot{0}\widehat{+--})} \\ & +2k_{90}C_{(\dot{-}\widehat{0-+})} + 2k_{93}C_{(\ddot{-}\widehat{0-+})} - 2k_{92}C_{(\dot{0}\widehat{--+})} - 2k_{95}C_{(\ddot{0}\widehat{--+})}.\end{aligned} \tag{3.16}$$

3.2.6 Production and Destruction of $(\overset{\textcircled{o}}{\oplus\oplus})$ Cluster

Likewise, the dynamics of the $(\overset{\textcircled{o}}{\oplus\oplus})$ cluster can be represented by some reversible reactions. Figure 3.12 demonstrates all potential reactions for producing or destroying this cluster by considering interaction between different elements.

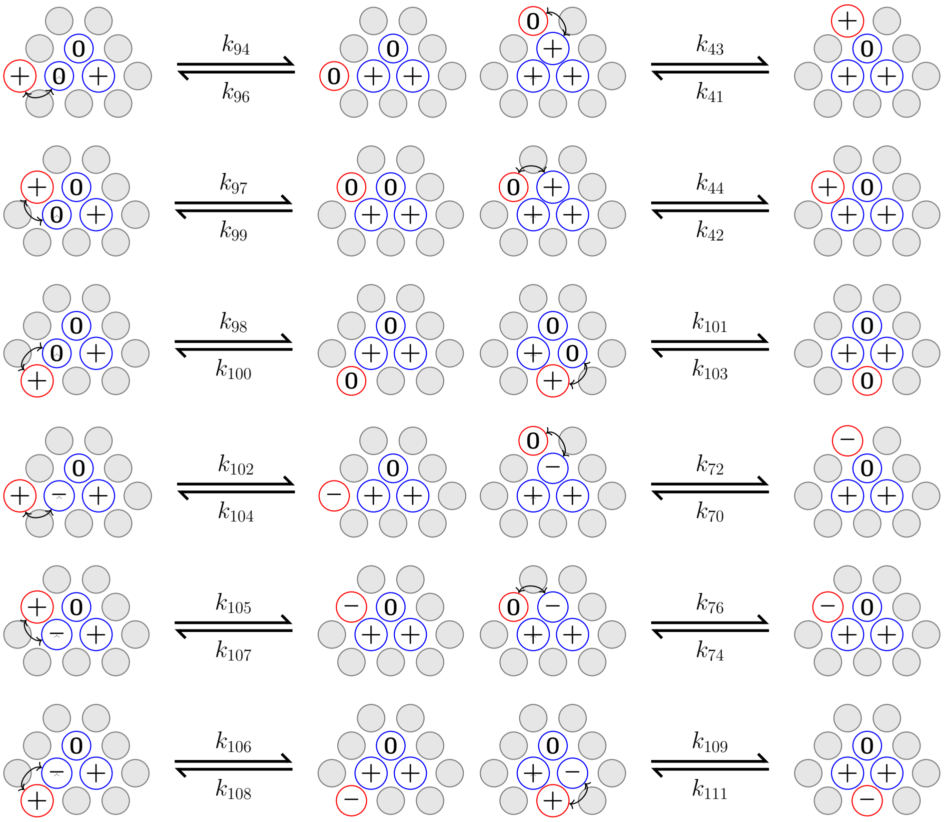


Figure 3.12: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\textcircled{o}}{\oplus\oplus})$ cluster.

Each of the reactions in figure 3.10 for producing or destroying the $(\overset{\textcircled{o}}{\oplus\oplus})$ cluster has 2 translations. Here we have introduced the unique ones only and will account for each one of them two times in the equation

$$
\begin{aligned}
\frac{d}{dt}C_{(\widehat{+0+})} = {} & 2k_{94}C_{(\dot{+}\widehat{00+})} + 2k_{43}C_{(\dot{0}\widehat{+++})} - 2k_{96}C_{(\dot{0}\widehat{+0+})} - 2k_{41}C_{(\dot{+}\widehat{0++})} \\
& +2k_{97}C_{(\ddot{+}\widehat{00+})} + 2k_{44}C_{(\ddot{0}\widehat{+++})} - 2k_{99}C_{(\ddot{0}\widehat{+0+})} - 2k_{42}C_{(\ddot{+}\widehat{+0+})} \\
& +2k_{98}C_{(\dot{+}\widehat{0+0})} + 2k_{101}C_{(\ddot{+}\widehat{+00})} - 2k_{100}C_{(\dot{0}\widehat{++0})} - 2k_{103}C_{(\ddot{0}\widehat{++0})} \\
& +2k_{102}C_{(\dot{+}\widehat{-0+})} + 2k_{72}C_{(\dot{0}\widehat{-++})} - 2k_{104}C_{(\dot{-}\widehat{+0+})} - 2k_{70}C_{(\dot{-}\widehat{0++})} \\
& +2k_{105}C_{(\ddot{+}\widehat{-0+})} + 2k_{76}C_{(\ddot{0}\widehat{+-+})} - 2k_{107}C_{(\ddot{-}\widehat{+0+})} - 2k_{74}C_{(\ddot{-}\widehat{+0+})} \\
& +2k_{106}C_{(\dot{+}\widehat{-+0})} + 2k_{109}C_{(\ddot{+}\widehat{+-0})} - 2k_{108}C_{(\dot{-}\widehat{++0})} - 2k_{111}C_{(\ddot{-}\widehat{++0})}.
\end{aligned}
\tag{3.17}
$$

3.2.7 Production and Destruction of $\left(\overset{\oplus}{\circledcirc\circledcirc}\right)$ Cluster

In a similar manner, one can find a set of reversible reactions in which the $\left(\overset{\oplus}{\circledcirc\circledcirc}\right)$ cluster can be found on one side of the reactions. Figure 3.13 demonstrates all possible reactions of such type.

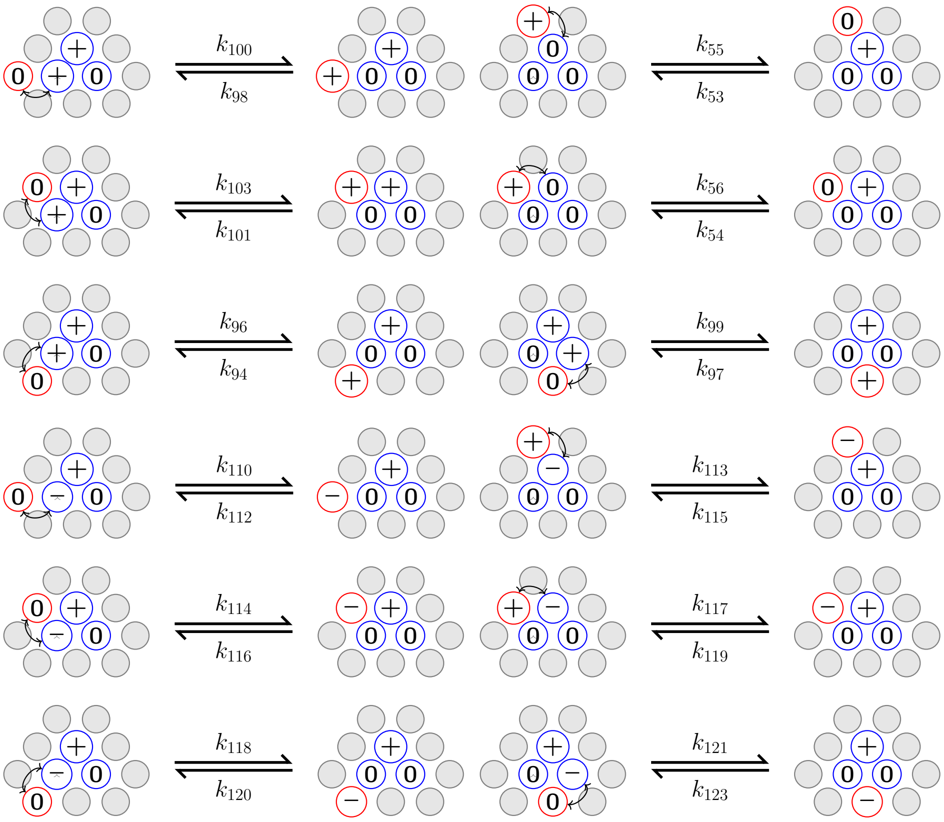


Figure 3.13: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\oplus}{\circledcirc\circledcirc})$ cluster.

We can write the rate equation for the $\left(\overset{\oplus}{\circledcirc\circledcirc}\right)$ cluster by considering the reversible reactions in figure 3.13. Again, each term in the rate equation has a coefficient of 2 corresponding to its spatial translational symmetries

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{0+0})} = {} & 2k_{100}C_{(\dot{0}\widehat{++0})} + 2k_{55}C_{(\dot{+}\widehat{000})} - 2k_{98}C_{(\dot{+}\widehat{0+0})} - 2k_{53}C_{(\dot{0}\widehat{+00})} \\ & +2k_{103}C_{(\ddot{0}\widehat{++0})} + 2k_{56}C_{(\ddot{+}\widehat{000})} - 2k_{101}C_{(\ddot{+}\widehat{0+0})} - 2k_{54}C_{(\ddot{0}\widehat{+00})} \\ & +2k_{96}C_{(\dot{0}\widehat{+0+})} + 2k_{99}C_{(\ddot{0}\widehat{+0+})} - 2k_{94}C_{(\dot{+}\widehat{00+})} - 2k_{97}C_{(\ddot{+}\widehat{00+})} \\ & +2k_{110}C_{(\dot{0}\widehat{-+0})} + 2k_{113}C_{(\dot{+}\widehat{-00})} - 2k_{112}C_{(\dot{-}\widehat{0+0})} - 2k_{115}C_{(\dot{-}\widehat{+00})} \\ & +2k_{114}C_{(\ddot{0}\widehat{-+0})} + 2k_{117}C_{(\ddot{+}\widehat{0-0})} - 2k_{116}C_{(\ddot{-}\widehat{0+0})} - 2k_{119}C_{(\ddot{-}\widehat{+00})} \\ & +2k_{118}C_{(\dot{0}\widehat{-0+})} + 2k_{121}C_{(\ddot{0}\widehat{-0+})} - 2k_{120}C_{(\dot{-}\widehat{00+})} - 2k_{123}C_{(\ddot{-}\widehat{00+})}.\end{aligned} \tag{3.18}$$

3.2.8 Production and Destruction of $\left(\overset{\textcircled{o}}{\ominus\ominus}\right)$ Cluster

Following the same procedure for the $\left(\overset{\textcircled{o}}{\ominus\ominus}\right)$ cluster, its rate of change of concentration can be deduced by investigating all possible elements swaps that involve this cluster. Figure 3.14 displays all possible unique reactions after considering translational symmetries to produce or destroy this cluster. Note that some of the reactions might be similar to previous ones.

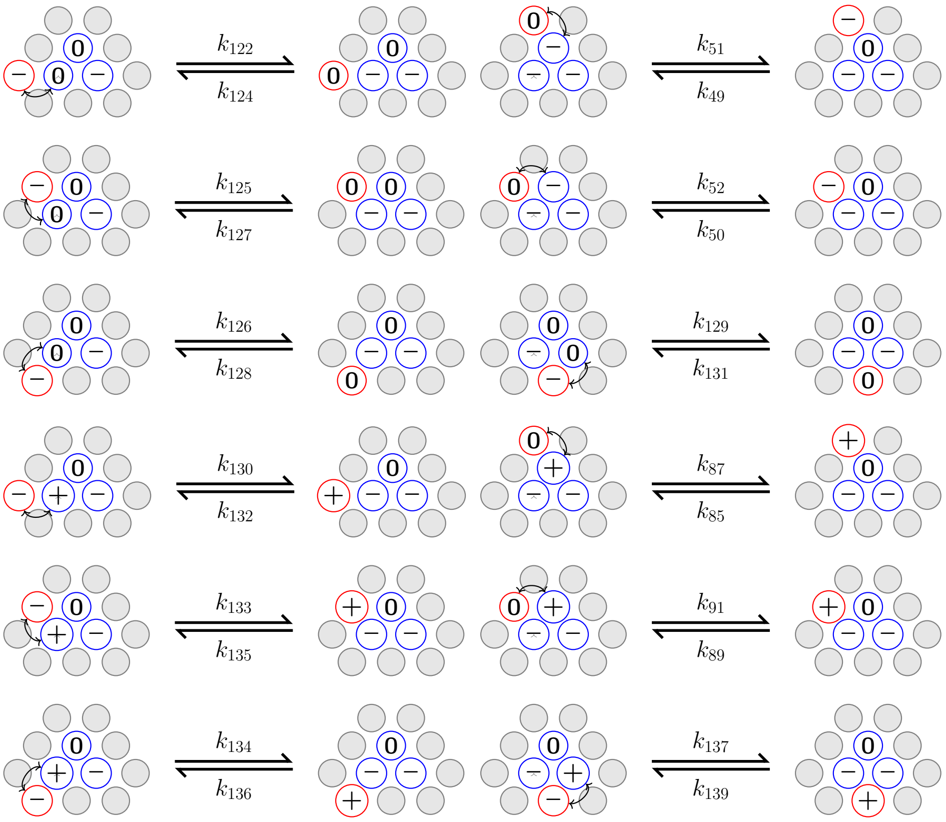


Figure 3.14: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $\left(\overset{\textcircled{o}}{\ominus\ominus}\right)$ cluster.

The rate equation for the $\left(\overset{\textcircled{o}}{\ominus\ominus}\right)$ cluster will be obtained based on the reversible reactions in figure 3.14. Again, each term in the rate equation has a coefficient of 2 due to translation invariance of the system

$$\begin{aligned}\frac{d}{dt}C_{(\widehat{-0-})} = 2k_{122}C_{(\dot{-}\widehat{00-})} + 2k_{51}C_{(\dot{0}\widehat{---})} - 2k_{124}C_{(\dot{0}\widehat{-0-})} - 2k_{49}C_{(\dot{-}\widehat{0--})}\\ +2k_{125}C_{(\ddot{-}\widehat{00-})} + 2k_{52}C_{(\ddot{0}\widehat{---})} - 2k_{127}C_{(\ddot{0}\widehat{-0-})} - 2k_{50}C_{(\ddot{-}\widehat{0--})}\\ +2k_{126}C_{(\dot{-}\widehat{0-0})} + 2k_{129}C_{(\ddot{-}\widehat{0-0})} - 2k_{128}C_{(\dot{0}\widehat{--0})} - 2k_{131}C_{(\ddot{0}\widehat{--0})}\\ +2k_{130}C_{(\dot{-}\widehat{+0-})} + 2k_{87}C_{(\dot{0}\widehat{+--})} - 2k_{132}C_{(\dot{+}\widehat{-0-})} - 2k_{85}C_{(\dot{+}\widehat{0--})}\\ +2k_{133}C_{(\ddot{-}\widehat{+0-})} + 2k_{91}C_{(\ddot{0}\widehat{-+-})} - 2k_{135}C_{(\ddot{+}\widehat{-0-})} - 2k_{89}C_{(\ddot{+}\widehat{0--})}\\ +2k_{134}C_{(\dot{-}\widehat{+-0})} + 2k_{137}C_{(\ddot{-}\widehat{+-0})} - 2k_{136}C_{(\dot{+}\widehat{--0})} - 2k_{139}C_{(\ddot{+}\widehat{--0})}.\end{aligned} \tag{3.19}$$

3.2.9 Production and Destruction of $\left(\overset{\ominus}{\textcircled{o}\textcircled{o}}\right)$ Cluster

Similarly, the reactions leading in producing or destroying the $\left(\overset{\ominus}{\textcircled{o}\textcircled{o}}\right)$ cluster are obtained by investigating the element swaps between nearest neighbors to the elements of the blue window. Figure 3.15 highlights the aforementioned reactions.

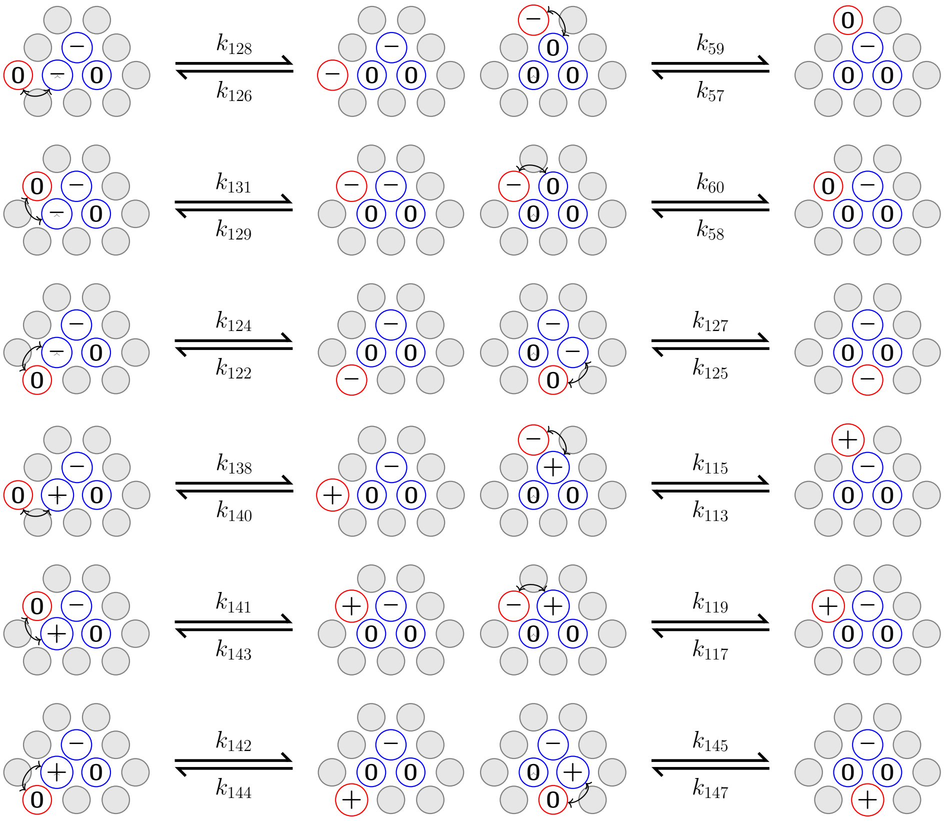


Figure 3.15: Unique reversible reactions, after considering translational symmetries, to produce or destroy a $(\overset{\ominus}{\text{⓪⓪}})$ cluster.

Considering the number of spatial translations for each reversible reaction, the following rate equation will be derived

$$\begin{aligned}
\frac{d}{dt}C_{(\widehat{0-0})} = {}& 2k_{128}C_{(\dot{0}\widehat{--0})} + 2k_{59}C_{(\dot{-}\widehat{000})} - 2k_{126}C_{(\dot{-}\widehat{0-0})} - 2k_{57}C_{(\dot{0}\widehat{-00})} \\
& +2k_{131}C_{(\ddot{0}\widehat{--0})} + 2k_{60}C_{(\ddot{-}\widehat{000})} - 2k_{129}C_{(\ddot{-}\widehat{0-0})} - 2k_{58}C_{(\ddot{0}\widehat{-00})} \\
& +2k_{124}C_{(\dot{0}\widehat{-0-})} + 2k_{127}C_{(\ddot{0}\widehat{-0-})} - 2k_{122}C_{(\dot{-}\widehat{00-})} - 2k_{125}C_{(\ddot{-}\widehat{00-})} \\
& +2k_{138}C_{(\dot{0}\widehat{+-0})} + 2k_{115}C_{(\dot{-}\widehat{+00})} - 2k_{140}C_{(\dot{+}\widehat{0-0})} - 2k_{113}C_{(\dot{+}\widehat{-00})} \\
& +2k_{141}C_{(\ddot{0}\widehat{+-0})} + 2k_{119}C_{(\ddot{-}\widehat{0+0})} - 2k_{143}C_{(\ddot{+}\widehat{0-0})} - 2k_{117}C_{(\ddot{+}\widehat{-00})} \\
& +2k_{142}C_{(\dot{0}\widehat{+0-})} + 2k_{145}C_{(\ddot{0}\widehat{+0-})} - 2k_{144}C_{(\dot{+}\widehat{00-})} - 2k_{147}C_{(\ddot{+}\widehat{00-})}.
\end{aligned} \tag{3.20}$$

3.2.10 Production and Destruction of $(\overset{\textcircled{o}}{\oplus\ominus})$ Cluster

Deriving the rate equation for the $\left(\overset{\textcircled{o}}{\oplus\ominus}\right)$ cluster is performed by considering all possible reactions that involve 3 types of elements. It is notable that all of the rate constants introduced here have been already introduced in the previous sections. Hence, there will not be any new rate constants specific to this type of cluster. Here, we skip the representation of the reversible reactions, as they have been constructed earlier in this section. Each of the reversible reactions for this cluster has only one translation. Totally, there are 24 different element swaps that can happen to destroy a cluster of this form and produce a new cluster. All of the translational symmetries of this cluster will be accounted for in the normalization condition of the system. The following rate equation can be deduced

$$
\begin{aligned}
\frac{d}{dt}C_{(\widehat{+0-})} = {} & -k_{69}C_{(\dot{+}\widehat{0-+})} + k_{71}C_{(\dot{0}\widehat{+-+})} - k_{73}C_{(\ddot{+}\widehat{0-+})} + k_{75}C_{(\ddot{0}\widehat{+-+})} \\
& -k_{77}C_{(\dot{+}\widehat{0+-})} - k_{78}C_{(\ddot{+}\widehat{+0-})} + k_{79}C_{(\dot{0}\widehat{++-})} + k_{80}C_{(\ddot{0}\widehat{++-})} \\
& -k_{82}C_{(\dot{-}\widehat{0+-})} + k_{84}C_{(\dot{0}\widehat{-+-})} - k_{86}C_{(\ddot{-}\widehat{0+-})} + k_{88}C_{(\ddot{0}\widehat{-+-})} \\
& -k_{90}C_{(\dot{-}\widehat{0-+})} - k_{93}C_{(\ddot{-}\widehat{0-+})} + k_{92}C_{(\dot{0}\widehat{--+})} + k_{95}C_{(\ddot{0}\widehat{--+})} \\
& -k_{102}C_{(\dot{+}\widehat{-0+})} + k_{104}C_{(\dot{-}\widehat{+0+})} - k_{105}C_{(\ddot{+}\widehat{-0+})} + k_{107}C_{(\ddot{-}\widehat{+0+})} \\
& -k_{106}C_{(\dot{+}\widehat{-+0})} - k_{109}C_{(\ddot{+}\widehat{+-0})} + k_{108}C_{(\dot{-}\widehat{++0})} + k_{111}C_{(\ddot{-}\widehat{++0})} \\
& -k_{110}C_{(\dot{0}\widehat{-+0})} + k_{112}C_{(\dot{-}\widehat{0+0})} - k_{114}C_{(\ddot{0}\widehat{-+0})} + k_{116}C_{(\ddot{-}\widehat{0+0})} \\
& -k_{118}C_{(\dot{0}\widehat{-0+})} - k_{121}C_{(\ddot{0}\widehat{-0+})} + k_{120}C_{(\dot{-}\widehat{00+})} + k_{123}C_{(\ddot{-}\widehat{00+})} \\
& -k_{130}C_{(\dot{-}\widehat{+0-})} + k_{132}C_{(\dot{+}\widehat{-0-})} - k_{133}C_{(\ddot{-}\widehat{+0-})} + k_{135}C_{(\ddot{+}\widehat{-0-})} \\
& -k_{134}C_{(\dot{-}\widehat{+-0})} - k_{137}C_{(\ddot{-}\widehat{+-0})} + k_{136}C_{(\dot{+}\widehat{--0})} + k_{139}C(\ddot{+}\widehat{--0}) \\
& -k_{138}C_{(\dot{0}\widehat{+-0})} + k_{140}C_{(\dot{+}\widehat{0-0})} - k_{141}C_{(\ddot{0}\widehat{+-0})} + k_{143}C_{(\ddot{+}\widehat{0-0})} \\
& -k_{142}C_{(\dot{0}\widehat{+0-})} - k_{145}C_{(\ddot{0}\widehat{+0-})} + k_{144}C_{(\dot{+}\widehat{00-})} + k_{147}C_{(\ddot{+}\widehat{00-})}.
\end{aligned}
\tag{3.21}
$$

All in all, the triangular cluster model produces a system of ODEs for the rate of change of concentrations of different cluster types. In this case, considering 3 types of elements in the model, the triangular model consists of 10 ODEs, along with 109 unique rate constants for each reaction type. The system is not closed and cannot be solved without further simplification. Additionally, the system of equations is hierarchical, in the sense that the rate of change of concentration of 3-clusters is calculated from 4-cluster concentrations. In the following section, we will investigate how the moment closure model will truncate the hierarchy at the level of 3-clusters and make it a closed system of equations.

3.3 Moment Closure Approximation

3.3.1 Three-Element Two-Cluster Model

In order to solve system of equations eq. (3.9), one must truncate the hierarchical dynamical system. Hierarchical system of ODEs arise when the rate of change of the concentrations of n clusters are written in terms of the concentrations of $n+1$ clusters, where n denotes the size of the cluster. Truncation of this hierarchy by some approximations will allow us to solve the system in a desired closed form. As introduced in section 2.3, the pair approximation model will be used for truncating the system of equations. Eq. (2.31) is used to write triplets' concentrations in terms of the concentrations of pairs and singlets. Applying the moment closure scheme to eq. (3.9) will produce following closed dynamical system

$$\begin{aligned}\frac{d}{dt}C_{++} = &\frac{2}{5}4k_1\frac{C_{+-}^2}{C_-} + \frac{1}{5}2k_2\frac{C_{+-}^2}{C_-} - \frac{2}{5}4k_3\frac{C_{++}C_{+-}}{C_+} - \frac{1}{5}2k_4\frac{C_{++}C_{+-}}{C_+}\\ &+\frac{2}{5}4k_5\frac{C_{+0}^2}{C_0} + \frac{1}{5}2k_6\frac{C_{+0}^2}{C_0} - \frac{2}{5}4k_7\frac{C_{++}C_{+0}}{C_+} - \frac{1}{5}2k_8\frac{C_{++}C_{+0}}{C_+},\end{aligned} \tag{3.22.1}$$

$$\begin{aligned}\frac{d}{dt}C_{--} = &\frac{2}{5}4k_9\frac{C_{+-}^2}{C_+} + \frac{1}{5}2k_{10}\frac{C_{+-}^2}{C_+} - \frac{2}{5}4k_{11}\frac{C_{--}C_{+-}}{C_-} - \frac{1}{5}2k_{12}\frac{C_{--}C_{+-}}{C_-}\\ &+\frac{2}{5}4k_{13}\frac{C_{-0}^2}{C_0} + \frac{1}{5}2k_{14}\frac{C_{-0}^2}{C_0} - \frac{2}{5}4k_{15}\frac{C_{--}C_{-0}}{C_-} - \frac{1}{5}2k_{16}\frac{C_{--}C_{-0}}{C_-},\end{aligned} \tag{3.22.2}$$

$$\begin{aligned}\frac{d}{dt}C_{00} = {} & \frac{2}{5}4k_{17}\frac{C_{+0}^2}{C_+} + \frac{1}{5}2k_{18}\frac{C_{+0}^2}{C_+} - \frac{2}{5}4k_{19}\frac{C_{00}C_{+0}}{C_0} - \frac{1}{5}2k_{20}\frac{C_{00}C_{+0}}{C_0} \\ & + \frac{2}{5}4k_{21}\frac{C_{-0}^2}{C_-} + \frac{1}{5}2k_{22}\frac{C_{-0}^2}{C_-} - \frac{2}{5}4k_{23}\frac{C_{00}C_{-0}}{C_0} - \frac{1}{5}2k_{24}\frac{C_{00}C_{-0}}{C_0},\end{aligned} \tag{3.22.3}$$

$$\begin{aligned}\frac{d}{dt}C_{+-} = {} & \frac{2}{5}2k_{3}\frac{C_{++}C_{+-}}{C_+} + \frac{2}{5}2k_{11}\frac{C_{--}C_{+-}}{C_-} - \frac{2}{5}2k_{1}\frac{C_{+-}^2}{C_-} - \frac{2}{5}2k_{9}\frac{C_{+-}^2}{C_+} \\ & + \frac{1}{5}k_{4}\frac{C_{++}C_{+-}}{C_+} + \frac{1}{5}k_{12}\frac{C_{--}C_{+-}}{C_-} - \frac{1}{5}k_{2}\frac{C_{+-}^2}{C_-} - \frac{1}{5}k_{10}\frac{C_{+-}^2}{C_+} \\ & + \frac{2}{5}2k_{25}\frac{C_{+0}C_{-0}}{C_0} + \frac{2}{5}2k_{26}\frac{C_{+0}C_{-0}}{C_0} - \frac{2}{5}2k_{27}\frac{C_{+-}C_{-0}}{C_-} - \frac{2}{5}2k_{28}\frac{C_{+-}C_{+0}}{C_+} \\ & + \frac{1}{5}k_{29}\frac{C_{+0}C_{-0}}{C_0} + \frac{1}{5}k_{30}\frac{C_{+0}C_{-0}}{C_0} - \frac{1}{5}k_{31}\frac{C_{+-}C_{-0}}{C_-} - \frac{1}{5}k_{32}\frac{C_{+-}C_{+0}}{C_+},\end{aligned} \tag{3.22.4}$$

$$\begin{aligned}\frac{d}{dt}C_{+0} = {} & \frac{2}{5}2k_{7}\frac{C_{++}C_{+0}}{C_+} + \frac{2}{5}2k_{19}\frac{C_{00}C_{+0}}{C_0} - \frac{2}{5}2k_{5}\frac{C_{+0}^2}{C_0} - \frac{2}{5}2k_{17}\frac{C_{+0}^2}{C_+} \\ & + \frac{1}{5}k_{8}\frac{C_{++}C_{+0}}{C_+} + \frac{1}{5}k_{20}\frac{C_{00}C_{+0}}{C_0} - \frac{1}{5}k_{6}\frac{C_{+0}^2}{C_0} - \frac{1}{5}k_{18}\frac{C_{+0}^2}{C_+} \\ & + \frac{2}{5}2k_{27}\frac{C_{+-}C_{-0}}{C_-} + \frac{2}{5}2k_{33}\frac{C_{+-}C_{-0}}{C_-} - \frac{2}{5}2k_{25}\frac{C_{+0}C_{-0}}{C_0} - \frac{2}{5}2k_{35}\frac{C_{+-}C_{+0}}{C_+} \\ & + \frac{1}{5}k_{31}\frac{C_{+-}C_{-0}}{C_-} + \frac{1}{5}k_{34}\frac{C_{+-}C_{-0}}{C_-} - \frac{1}{5}k_{29}\frac{C_{+0}C_{-0}}{C_0} - \frac{1}{5}k_{36}\frac{C_{+-}C_{+0}}{C_+},\end{aligned} \tag{3.22.5}$$

$$\begin{aligned}\frac{d}{dt}C_{-0} = {} & \frac{2}{5}2k_{15}\frac{C_{--}C_{-0}}{C_-} + \frac{2}{5}2k_{23}\frac{C_{00}C_{-0}}{C_0} - \frac{2}{5}2k_{13}\frac{C_{-0}^2}{C_0} - \frac{2}{5}2k_{21}\frac{C_{-0}^2}{C_-} \\ & + \frac{1}{5}k_{16}\frac{C_{--}C_{-0}}{C_-} + \frac{1}{5}k_{24}\frac{C_{00}C_{-0}}{C_0} - \frac{1}{5}k_{14}\frac{C_{-0}^2}{C_0} - \frac{1}{5}k_{22}\frac{C_{-0}^2}{C_-} \\ & + \frac{2}{5}2k_{28}\frac{C_{+-}C_{+0}}{C_+} + \frac{2}{5}2k_{35}\frac{C_{+-}C_{+0}}{C_+} - \frac{2}{5}2k_{26}\frac{C_{+0}C_{-0}}{C_0} - \frac{2}{5}2k_{33}\frac{C_{+-}C_{-0}}{C_-} \\ & + \frac{1}{5}k_{32}\frac{C_{+-}C_{+0}}{C_+} + \frac{1}{5}k_{36}\frac{C_{+-}C_{+0}}{C_+} - \frac{1}{5}k_{30}\frac{C_{+0}C_{-0}}{C_0} - \frac{1}{5}k_{34}\frac{C_{+-}C_{-0}}{C_-}.\end{aligned} \tag{3.22.6}$$

As we are interested in the equilibrium state of the system, the rate of change of the concentrations for each specific cluster will be equal to zero, as the rates of the forward and backward reactions will be the same. Hence, the right hand sides of the ODE system in eq. (3.22) will be equal to zero, resulting in a system of algebraic equations

$$\begin{aligned} &4k_1\frac{C_{+-}^2}{C_-} + k_2\frac{C_{+-}^2}{C_-} - 4k_3\frac{C_{++}C_{+-}}{C_+} - k_4\frac{C_{++}C_{+-}}{C_+} \\ &+4k_5\frac{C_{+0}^2}{C_0} + k_6\frac{C_{+0}^2}{C_0} - 4k_7\frac{C_{++}C_{+0}}{C_+} - k_8\frac{C_{++}C_{+0}}{C_+} = 0, \end{aligned} \tag{3.23.1}$$

$$\begin{aligned} &4k_9\frac{C_{+-}^2}{C_+} + k_{10}\frac{C_{+-}^2}{C_+} - 4k_{11}\frac{C_{--}C_{+-}}{C_-} - k_{12}\frac{C_{--}C_{+-}}{C_-} \\ &+4k_{13}\frac{C_{-0}^2}{C_0} + k_{14}\frac{C_{-0}^2}{C_0} - 4k_{15}\frac{C_{--}C_{-0}}{C_-} - k_{16}\frac{C_{--}C_{-0}}{C_-} = 0, \end{aligned} \tag{3.23.2}$$

$$\begin{aligned} &4k_{17}\frac{C_{+0}^2}{C_+} + k_{18}\frac{C_{+0}^2}{C_+} - 4k_{19}\frac{C_{00}C_{+0}}{C_0} - k_{20}\frac{C_{00}C_{+0}}{C_0} \\ &+4k_{21}\frac{C_{-0}^2}{C_-} + k_{22}\frac{C_{-0}^2}{C_-} - 4k_{23}\frac{C_{00}C_{-0}}{C_0} - k_{24}\frac{C_{00}C_{-0}}{C_0} = 0, \end{aligned} \tag{3.23.3}$$

$$\begin{aligned} &4k_3\frac{C_{++}C_{+-}}{C_+} + 4k_{11}\frac{C_{--}C_{+-}}{C_-} - 4k_1\frac{C_{+-}^2}{C_-} - 4k_9\frac{C_{+-}^2}{C_+} \\ &+k_4\frac{C_{++}C_{+-}}{C_+} + k_{12}\frac{C_{--}C_{+-}}{C_-} - k_2\frac{C_{+-}^2}{C_-} - k_{10}\frac{C_{+-}^2}{C_+} \\ &+4k_{25}\frac{C_{+0}C_{-0}}{C_0} + 4k_{26}\frac{C_{+0}C_{-0}}{C_0} - 4k_{27}\frac{C_{+-}C_{-0}}{C_-} - 4k_{28}\frac{C_{+-}C_{+0}}{C_+} \\ &+k_{29}\frac{C_{+0}C_{-0}}{C_0} + k_{30}\frac{C_{+0}C_{-0}}{C_0} - k_{31}\frac{C_{+-}C_{-0}}{C_-} - k_{32}\frac{C_{+-}C_{+0}}{C_+} = 0, \end{aligned} \tag{3.23.4}$$

$$\begin{aligned} &4k_7\frac{C_{++}C_{+0}}{C_+} + 4k_{19}\frac{C_{00}C_{+0}}{C_0} - 4k_5\frac{C_{+0}^2}{C_0} - 4k_{17}\frac{C_{+0}^2}{C_+} \\ &+k_8\frac{C_{++}C_{+0}}{C_+} + k_{20}\frac{C_{00}C_{+0}}{C_0} - k_6\frac{C_{+0}^2}{C_0} - k_{18}\frac{C_{+0}^2}{C_+} \\ &+4k_{27}\frac{C_{+-}C_{-0}}{C_-} + 4k_{33}\frac{C_{+-}C_{-0}}{C_-} - 4k_{25}\frac{C_{+0}C_{-0}}{C_0} - 4k_{35}\frac{C_{+-}C_{+0}}{C_+} \\ &+k_{31}\frac{C_{+-}C_{-0}}{C_-} + k_{34}\frac{C_{+-}C_{-0}}{C_-} - k_{29}\frac{C_{+0}C_{-0}}{C_0} - k_{36}\frac{C_{+-}C_{+0}}{C_+} = 0, \end{aligned} \tag{3.23.5}$$

$$\begin{aligned}4k_{15}\frac{C_{--}C_{-0}}{C_-}+4k_{23}\frac{C_{00}C_{-0}}{C_0}-4k_{13}\frac{C_{-0}^2}{C_0}-4k_{21}\frac{C_{-0}^2}{C_-}\\+k_{16}\frac{C_{--}C_{-0}}{C_-}+k_{24}\frac{C_{00}C_{-0}}{C_0}-k_{14}\frac{C_{-0}^2}{C_0}-k_{22}\frac{C_{-0}^2}{C_-}\\+4k_{28}\frac{C_{+-}C_{+0}}{C_+}+4k_{35}\frac{C_{+-}C_{+0}}{C_+}-4k_{26}\frac{C_{+0}C_{-0}}{C_0}-4k_{33}\frac{C_{+-}C_{-0}}{C_-}\\+k_{32}\frac{C_{+-}C_{+0}}{C_+}+k_{36}\frac{C_{+-}C_{+0}}{C_+}-k_{30}\frac{C_{+0}C_{-0}}{C_0}-k_{34}\frac{C_{+-}C_{-0}}{C_-}=0.\end{aligned}\tag{3.23.6}$$

Also, in the equilibrium state, the reversible reactions will have equal forward and backward reaction rates. All unique reversible reactions in the two-cluster model with three elements can be found in figures 3.1, 3.2, 3.3, 3.4 and 3.5. Hence, the equilibrium constants can be deduced from these reversible reactions in equilibrium. These constants can be used to reduce the number of the degrees of freedom in the system of equations. In addition, pair approximation is used to break down the triplet concentrations and write them in terms of smaller clusters

$$k_1C_{\widehat{+-+}}=k_3C_{\widehat{++-}}\Rightarrow Q_1=\frac{k_1}{k_3}=\frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}}=\frac{C_{++}C_-}{C_{+-}C_+},\tag{3.24.1}$$

$$k_2C_{(\overline{+-+})}=k_4C_{(\overline{++-})}\Rightarrow Q_2=\frac{k_2}{k_4}=\frac{C_{(\overline{++-})}}{C_{(\overline{+-+})}}=\frac{C_{++}C_-}{C_{+-}C_+},\tag{3.24.2}$$

$$k_5C_{\widehat{+0+}}=k_7C_{\widehat{++0}}\Rightarrow Q_3=\frac{k_5}{k_7}=\frac{C_{\widehat{++0}}}{C_{\widehat{+0+}}}=\frac{C_{++}C_0}{C_{+0}C_+},\tag{3.24.3}$$

$$k_6C_{\overline{+0+}}=k_8C_{\overline{++0}}\Rightarrow Q_4=\frac{k_6}{k_8}=\frac{C_{\overline{++0}}}{C_{\overline{+0+}}}=\frac{C_{++}C_0}{C_{+0}C_+},\tag{3.24.4}$$

$$k_9C_{\widehat{-+-}}=k_{11}C_{\widehat{--+}}\Rightarrow Q_5=\frac{k_9}{k_{11}}=\frac{C_{\widehat{--+}}}{C_{\widehat{-+-}}}=\frac{C_{--}C_+}{C_{+-}C_-},\tag{3.24.5}$$

$$k_{10}C_{(\overline{-+-})}=k_{12}C_{(\overline{--+})}\Rightarrow Q_6=\frac{k_{10}}{k_{12}}=\frac{C_{(\overline{--+})}}{C_{(\overline{-+-})}}=\frac{C_{--}C_+}{C_{+-}C_-}\tag{3.24.6}$$

$$k_{13}C_{\widehat{-0-}}=k_{15}C_{\widehat{--0}}\Rightarrow Q_7=\frac{k_{13}}{k_{15}}=\frac{C_{\widehat{--0}}}{C_{\widehat{-0-}}}=\frac{C_{--}C_0}{C_{-0}C_-},\tag{3.24.7}$$

$$k_{14}C_{(\overline{-0-})}=k_{16}C_{(\overline{--0})}\Rightarrow Q_8=\frac{k_{14}}{k_{16}}=\frac{C_{(\overline{--0})}}{C_{(\overline{-0-})}}=\frac{C_{--}C_0}{C_{0-}C_-}\tag{3.24.8}$$

$$k_{17}C_{\widehat{0+-0}} = k_{19}C_{\widehat{00+}} \Rightarrow Q_9 = \frac{k_{17}}{k_{19}} = \frac{C_{\widehat{00+}}}{C_{\widehat{0+0}}} = \frac{C_{00}C_+}{C_{+0}C_0}, \tag{3.24.9}$$

$$k_{18}C_{(\overline{0+0})} = k_{20}C_{(\overline{00+})} \Rightarrow Q_{10} = \frac{k_{18}}{k_{20}} = \frac{C_{(\overline{00+})}}{C_{(\overline{0+0})}} = \frac{C_{00}C_+}{C_{+0}C_0} \tag{3.24.10}$$

$$k_{21}C_{\widehat{0-0}} = k_{23}C_{\widehat{00-}} \Rightarrow Q_{11} = \frac{k_{21}}{k_{23}} = \frac{C_{\widehat{00-}}}{C_{\widehat{0-0}}} = \frac{C_{00}C_-}{C_{-0}C_0}, \tag{3.24.11}$$

$$k_{22}C_{\overline{0-0}} = k_{24}C_{\overline{00-}} \Rightarrow Q_{12} = \frac{k_{22}}{k_{24}} = \frac{C_{\overline{00-}}}{C_{\overline{0-0}}} = \frac{C_{00}C_-}{C_{-0}C_0}, \tag{3.24.12}$$

$$k_{25}C_{\widehat{+0-}} = k_{27}C_{\widehat{+-0}} \Rightarrow Q_{13} = \frac{k_{25}}{k_{27}} = \frac{C_{\widehat{+-0}}}{C_{\widehat{+0-}}} = \frac{C_{+-}C_0}{C_{+0}C_-}, \tag{3.24.13}$$

$$k_{26}C_{\widehat{-0+}} = k_{28}C_{\widehat{-+0}} \Rightarrow Q_{14} = \frac{k_{26}}{k_{28}} = \frac{C_{\widehat{-+0}}}{C_{\widehat{-0+}}} = \frac{C_{+-}C_0}{C_{-0}C_+}, \tag{3.24.14}$$

$$k_{29}C_{\overline{+0-}} = k_{31}C_{\overline{+-0}} \Rightarrow Q_{15} = \frac{k_{29}}{k_{31}} = \frac{C_{\overline{+-0}}}{C_{\overline{+0-}}} = \frac{C_{+-}C_0}{C_{+0}C_-}, \tag{3.24.15}$$

$$k_{30}C_{\overline{-0+}} = k_{32}C_{\overline{-+0}} \Rightarrow Q_{16} = \frac{k_{30}}{k_{32}} = \frac{C_{\overline{-+0}}}{C_{\overline{-0+}}} = \frac{C_{+-}C_0}{C_{-0}C_+}, \tag{3.24.16}$$

$$k_{33}C_{\widehat{0-+}} = k_{35}C_{\widehat{0+-}} \Rightarrow Q_{17} = \frac{k_{33}}{k_{35}} = \frac{C_{\widehat{0+-}}}{C_{\widehat{0-+}}} = \frac{C_{+0}C_-}{C_{-0}C_+}, \tag{3.24.17}$$

$$k_{34}C_{\overline{0-+}} = k_{36}C_{\overline{0+-}} \Rightarrow Q_{18} = \frac{k_{34}}{k_{36}} = \frac{C_{\overline{0+-}}}{C_{\overline{0-+}}} = \frac{C_{+0}C_-}{C_{-0}C_+}. \tag{3.24.18}$$

As can be observed, after applying the moment closure approximations, the following equilibrium constants will be equal and will further reduce the number of the degrees of freedom of the system: $Q_1 = Q_2$, $Q_3 = Q_4$, $Q_5 = Q_6$, $Q_7 = Q_8$, $Q_9 = Q_{10}$, $Q_{11} = Q_{12}$, $Q_{13} = Q_{15}$, $Q_{14} = Q_{16}$ and $Q_{17} = Q_{18}$. The next step is to write eq. (3.23) in terms of equilibrium constants, Q_1 to Q_{18}. Appendix 7.5 demonstrates the full derivation of the resulting equations. First, equilibrium constants will be substituted into the equations in place of the rate constants, then some extra ratios will be introduced. For this reason, the number of unknowns will diminish significantly. As a result, the system (3.23) takes the following form

$$\begin{aligned}(4\beta_1+\beta_2)Q_1\frac{C_{+-}^2}{C_-}-(4\beta_1+\beta_2)\frac{C_{++}C_{+-}}{C_+}\\ +(4\beta_3+1)Q_3\frac{C_{+0}^2}{C_0}-(4\beta_3+1)\frac{C_{++}C_{+0}}{C_+}=0,\end{aligned}\tag{3.25.1}$$

$$\begin{aligned}(4\beta_4+\beta_5)Q_5\frac{C_{+-}^2}{C_+}-(4\beta_4+\beta_5)\frac{C_{--}C_{+-}}{C_-}\\ +(4\beta_6+1)Q_7\frac{C_{-0}^2}{C_0}-(4\beta_6+1)\frac{C_{--}C_{-0}}{C_-}=0,\end{aligned}\tag{3.25.2}$$

$$\begin{aligned}(4\beta_7+\beta_8)Q_9\frac{C_{+0}^2}{C_+}-(4\beta_7+\beta_8)\frac{C_{00}C_{+0}}{C_0}\\ +(4\beta_9+1)Q_{11}\frac{C_{-0}^2}{C_-}-(4\beta_9+1)\frac{C_{00}C_{-0}}{C_0}=0,\end{aligned}\tag{3.25.3}$$

$$\begin{aligned}(4\beta_{10}+\beta_{11})\frac{C_{++}C_{+-}}{C_+}-(4\beta_{10}+\beta_{11})Q_1\frac{C_{+-}^2}{C_-}\\ -(4\beta_{12}+\beta_{13})Q_5\frac{C_{+-}^2}{C_+}+(4\beta_{12}+\beta_{13})\frac{C_{--}C_{+-}}{C_-}\\ +(4\beta_{14}+\beta_{16})Q_{13}\frac{C_{+0}C_{-0}}{C_0}-(4\beta_{14}+\beta_{16})\frac{C_{+-}C_{-0}}{C_-}\\ +(4\beta_{15}+1)Q_{14}\frac{C_{+0}C_{-0}}{C_0}-(4\beta_{15}+1)\frac{C_{+-}C_{+0}}{C_+}=0,\end{aligned}\tag{3.25.4}$$

$$\begin{aligned}(4\beta_{17}+\beta_{18})\frac{C_{++}C_{+0}}{C_+}-(4\beta_{17}+\beta_{18})Q_3\frac{C_{+0}^2}{C_0}\\ +(4\beta_{19}+\beta_{20})\frac{C_{00}C_{+0}}{C_0}-(4\beta_{19}+\beta_{20})Q_9\frac{C_{+0}^2}{C_+}\\ +(4\beta_{21}+\beta_{22})\frac{C_{+-}C_{-0}}{C_-}-(4\beta_{21}-\beta_{22})Q_{13}\frac{C_{+0}C_{-0}}{C_0}\\ +(4\beta_{23}+1)Q_{17}\frac{C_{+-}C_{-0}}{C_-}-(4\beta_{23}-1)\frac{C_{+-}C_{+0}}{C_+}=0,\end{aligned}\tag{3.25.5}$$

$$\begin{aligned}
(4\beta_{24}+\beta_{25})\frac{C_{--}C_{-0}}{C_{-}}-(4\beta_{24}+\beta_{25})Q_{7}\frac{C_{-0}^{2}}{C_{0}}\\
+(4\beta_{26}+\beta_{27})\frac{C_{00}C_{-0}}{C_{0}}-(4\beta_{26}+\beta_{27})Q_{11}\frac{C_{-0}^{2}}{C_{-}}\\
+(4\beta_{28}+\beta_{29})\frac{C_{+-}C_{+0}}{C_{+}}-(4\beta_{28}+\beta_{29})Q_{14}\frac{C_{+0}C_{-0}}{C_{0}}\\
+(4\beta_{30}+1)\frac{C_{+-}C_{+0}}{C_{+}}-(4\beta_{30}+1)Q_{17}\frac{C_{+-}C_{-0}}{C_{-}}=0.
\end{aligned} \tag{3.25.6}$$

As can be observed, this model contains 18 equilibrium constants Q_1-Q_{18} and 30 additional ratios β_1-β_{30}. As noted before, equilibrium constants are calculated based on the unique reversible reactions in equilibrium and further broken down in terms of pairs and singlets concentrations. Each of the extra parameters, namely β_1 to β_{30}, is the ratio of the rate constants which do not correspond to the same reversible reaction. The parameters are chosen arbitrarily without influencing the equilibrium phase of the system. Nonetheless, the choice of these arbitrary parameters might influence the intermediate states of the system. In other words, as long as the equilibrium constants are not changing, the system will reach the same equilibrium phase regardless of the choice of additional parameters. However, changing these arbitrary parameters from one experiment to another might affect the intermediate states of the system when converging to the same equilibrium.

3.3.2 Three-Element Triangular-Cluster Model

In section 3.2, we derived the rate equations for each triangular cluster type. The system of equations is significantly under-determined and with a hierarchy that needs to be truncated. The moment closure model introduced earlier will be used to truncate the hierarchy of the system at the level of 3-clusters. Additionally, we are interested in the equilibrium phase of the system, where the rate of change of concentrations for different clusters remains constant as the forward reaction rate will be equal to the backward reaction rate. Adding the assumption of equilibrium will assist us in reducing the number of parameters in the model by calculating the equilibrium constants of the model.

The ODE system of equations in equilibrium will then become an algebraic system of equations. The following equations will be derived for equilibrium after applying the moment closure scheme on ODE equations

$$\begin{aligned} &k_{37}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2} + \frac{1}{5}k_{38}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2} - k_{39}\frac{C_{++}^3C_{+-}}{C_+^4} - \frac{1}{5}k_{40}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-} \\ &+k_{41}\frac{C_{++}C_{+0}^3}{C_+^2C_0^2} + \frac{1}{5}k_{42}\frac{C_{++}^2C_{+0}^3}{C_+^4C_0^2} - k_{43}\frac{C_{++}^3C_{+0}}{C_+^4} - \frac{1}{5}k_{44}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0} = 0, \end{aligned} \tag{3.26.1}$$

$$\begin{aligned} &k_{45}\frac{C_{--}C_{+-}^3}{C_+^2C_-^2} + \frac{1}{5}k_{46}\frac{C_{--}^2C_{+-}^3}{C_-^4C_+^2} - k_{47}\frac{C_{--}^3C_{+-}}{C_-^4} - \frac{1}{5}k_{48}\frac{C_{--}^3C_{+-}^2}{C_-^5C_+} \\ &+k_{49}\frac{C_{--}C_{-0}^3}{C_0^2C_-^2} + \frac{1}{5}k_{50}\frac{C_{--}^2C_{-0}^3}{C_-^4C_0^2} - k_{51}\frac{C_{--}^3C_{-0}}{C_-^4} - \frac{1}{5}k_{52}\frac{C_{--}^3C_{0-}^2}{C_-^5C_0} = 0, \end{aligned} \tag{3.26.2}$$

$$\begin{aligned} &k_{53}\frac{C_{00}C_{+0}^3}{C_+^2C_0^2} + \frac{1}{5}k_{54}\frac{C_{00}^2C_{+0}^3}{C_0^4C_+^2} - k_{55}\frac{C_{00}^3C_{+0}}{C_0^4} - \frac{1}{5}k_{56}\frac{C_{00}^3C_{+0}^2}{C_0^5C_+} \\ &+k_{57}\frac{C_{00}C_{-0}^3}{C_-^2C_0^2} + \frac{1}{5}k_{58}\frac{C_{00}^2C_{-0}^3}{C_0^4C_-^2} - k_{59}\frac{C_{00}^3C_{-0}}{C_0^4} - \frac{1}{5}k_{60}\frac{C_{00}^3C_{-0}^2}{C_0^5C_-} = 0, \end{aligned} \tag{3.26.3}$$

$$\begin{aligned} &k_{61}\frac{C_{--}C_{+-}^3}{C_+C_-^3} + k_{39}\frac{C_{++}^3C_{+-}}{C_+^4} - k_{63}\frac{C_{++}C_{+-}^3}{C_+^3C_-} \\ &-k_{37}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2} + \frac{1}{5}k_{62}\frac{C_{--}C_{+-}^4}{C_+^2C_-^4} + \frac{1}{5}k_{40}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-} \\ &-\frac{1}{5}k_{64}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3} - \frac{1}{5}k_{38}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2} + k_{65}\frac{C_{--}C_{+-}^3}{C_+C_-^3} \\ &+\frac{1}{5}k_{66}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3} - k_{67}\frac{C_{++}C_{+-}^3}{C_+^3C_-} - \frac{1}{5}k_{68}\frac{C_{++}C_{+-}^4}{C_+^4C_-^2} \\ &+k_{69}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2} + k_{70}\frac{C_{++}C_{+0}^2C_{-0}}{C_+^2C_0^2} - k_{71}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-} \\ &-k_{72}\frac{C_{++}C_{+-}^2C_{-0}}{C_+^2C_-^2} + \frac{1}{5}k_{73}\frac{C_{+-}^2C_{+0}^2C_{-0}}{C_+^2C_-^2C_0^2} + \frac{1}{5}k_{74}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2} \\ &-\frac{1}{5}k_{75}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0} - \frac{1}{5}k_{76}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0} + k_{77}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2} \\ &+\frac{1}{5}k_{78}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2} - k_{79}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-} - \frac{1}{5}k_{80}\frac{C_{++}C_{+-}^2C_{+0}^2}{C_+^4C_-C_0} = 0, \end{aligned} \tag{3.26.4}$$

$$\begin{aligned}
& k_{67}\frac{C_{++}C_{+-}^3}{C_+^3C_-} + k_{47}\frac{C_{--}^3C_{+-}}{C_-^4} - k_{65}\frac{C_{--}C_{+-}^3}{C_+C_-^3} \\
& -k_{45}\frac{C_{--}C_{+-}^3}{C_+^2C_-^2} + \frac{1}{5}k_{68}\frac{C_{++}C_{+-}^4}{C_+^4C_-^2} + \frac{1}{5}k_{48}\frac{C_{--}^3C_{+-}^2}{C_-^5C_+} \\
& -\frac{1}{5}k_{66}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3} - \frac{1}{5}k_{46}\frac{C_{--}^2C_{+-}^3}{C_-^4C_+^2} + k_{63}\frac{C_{++}C_{+-}^3}{C_+^3C_-} \\
& +\frac{1}{5}k_{64}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3} - k_{61}\frac{C_{--}C_{+-}^3}{C_+C_-^3} - \frac{1}{5}k_{62}\frac{C_{--}C_{+-}^4}{C_+^2C_-^4} \\
& +k_{82}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-C_0^2} + k_{85}\frac{C_{--}C_{+0}C_{-0}^2}{C_-^2C_0^2} - k_{84}\frac{C_{--}C_{+-}^2C_{-0}}{C_+C_-^3} \\
& -k_{87}\frac{C_{--}C_{+-}^2C_{+0}}{C_+^2C_-^2} + \frac{1}{5}k_{86}\frac{C_{+-}^2C_{+0}C_{-0}^2}{C_+^2C_-^2C_0^2} + \frac{1}{5}k_{89}\frac{C_{--}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^3C_0^2} \\
& -\frac{1}{5}k_{88}\frac{C_{--}C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-^3C_0} - \frac{1}{5}k_{91}\frac{C_{--}C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-^3C_0} + k_{90}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-C_0^2} \\
& +\frac{1}{5}k_{93}\frac{C_{--}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^3C_0^2} - k_{92}\frac{C_{--}C_{+-}^2C_{-0}}{C_+C_-^3} - \frac{1}{5}k_{95}\frac{C_{--}C_{+-}^2C_{-0}^2}{C_+C_-^4C_0} = 0,
\end{aligned} \tag{3.26.5}$$

$$\begin{aligned}
& k_{94}\frac{C_{00}C_{+0}^3}{C_+C_0^3} + k_{43}\frac{C_{++}^3C_{+0}}{C_+^4} - k_{96}\frac{C_{++}C_{+0}^3}{C_+^3C_0} \\
& -k_{41}\frac{C_{++}C_{+0}^3}{C_+^2C_0^2} + \frac{1}{5}k_{97}\frac{C_{00}C_{+0}^4}{C_+^2C_0^4} + \frac{1}{5}k_{44}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0} \\
& -\frac{1}{5}k_{99}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3} - \frac{1}{5}k_{42}\frac{C_{++}^2C_{+0}^3}{C_+^4C_0^2} + k_{98}\frac{C_{00}C_{+0}^3}{C_+C_0^3} \\
& +\frac{1}{5}k_{101}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3} - k_{100}\frac{C_{++}C_{+0}^3}{C_+^3C_0} - \frac{1}{5}k_{103}\frac{C_{++}C_{+0}^4}{C_+^4C_0^2} \\
& +k_{102}\frac{C_{+-}^2C_{+0}C_{-0}}{C_+C_-^2C_0} + k_{72}\frac{C_{++}C_{+-}^2C_{-0}}{C_+^2C_-^2} - k_{104}\frac{C_{++}C_{+0}^2C_{+-}}{C_+^3C_0} \\
& -k_{70}\frac{C_{++}C_{+0}^2C_{-0}}{C_+^2C_0^2} + \frac{1}{5}k_{105}\frac{C_{+-}^2C_{+0}^2C_{-0}}{C_+^2C_-^2C_0^2} + \frac{1}{5}k_{76}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0} \\
& -\frac{1}{5}k_{107}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2} - \frac{1}{5}k_{74}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2} + k_{106}\frac{C_{+-}^2C_{+0}C_{-0}}{C_+C_-^2C_0} \\
& +\frac{1}{5}k_{109}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0} - k_{108}\frac{C_{++}C_{+-}C_{+0}^2}{C_+^3C_0} - \frac{1}{5}k_{111}\frac{C_{++}C_{+-}^2C_{+0}^2}{C_+^4C_-C_0} = 0,
\end{aligned} \tag{3.26.6}$$

$$\begin{aligned}
k_{100}\frac{C_{++}C_{+0}^3}{C_+^3C_0} + k_{55}\frac{C_{00}^3C_{+0}}{C_0^4} - k_{98}\frac{C_{00}C_{+0}^3}{C_+C_0^3}\\
-k_{53}\frac{C_{00}C_{+0}^3}{C_+^2C_0^2} + \frac{1}{5}k_{103}\frac{C_{++}C_{+0}^4}{C_+^4C_0^2} + \frac{1}{5}k_{56}\frac{C_{00}^3C_{+0}^2}{C_0^5C_+}\\
-\frac{1}{5}k_{101}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3} - \frac{1}{5}k_{54}\frac{C_{00}^2C_{+0}^3}{C_0^4C_+^2} + k_{96}\frac{C_{++}C_{+0}^3}{C_+^3C_0}\\
+\frac{1}{5}k_{99}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3} - k_{94}\frac{C_{00}C_{+0}^3}{C_+C_0^3} - \frac{1}{5}k_{97}\frac{C_{00}C_{+0}^4}{C_+^2C_0^4}\\
+k_{110}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0} + k_{113}\frac{C_{00}C_{+-}C_{-0}^2}{C_-^2C_0^2} - k_{112}\frac{C_{00}C_{+0}^2C_{-0}}{C_+C_0^3}\\
-k_{115}\frac{C_{00}C_{+-}C_{+0}^2}{C_+^2C_0^2} + \frac{1}{5}k_{114}\frac{C_{+-}C_{+0}^2C_{-0}^2}{C_+^2C_-^2C_0^2} + \frac{1}{5}k_{117}\frac{C_{00}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0^3}\\
-\frac{1}{5}k_{116}\frac{C_{00}C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0^3} - \frac{1}{5}k_{119}\frac{C_{00}C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0^3} + k_{118}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0}\\
+\frac{1}{5}k_{121}\frac{C_{00}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0^3} - k_{120}\frac{C_{00}C_{+0}^2C_{-0}}{C_+C_0^3} - \frac{1}{5}k_{123}\frac{C_{00}C_{+0}^2C_{-0}^2}{C_+C_-C_0^4} = 0,
\end{aligned}\tag{3.26.7}$$

$$\begin{aligned}
k_{122}\frac{C_{00}C_{-0}^3}{C_-C_0^3} + k_{51}\frac{C_{--}^3C_{-0}}{C_-^4} - k_{124}\frac{C_{--}C_{-0}^3}{C_-^3C_0}\\
-k_{49}\frac{C_{--}C_{-0}^3}{C_0^2C_-^2} + \frac{1}{5}k_{125}\frac{C_{00}C_{-0}^4}{C_0^4C_-^2} + \frac{1}{5}k_{52}\frac{C_{--}^3C_{-0}^2}{C_-^5C_0}\\
-\frac{1}{5}k_{127}\frac{C_{--}C_{00}C_{-0}^3}{C_-^3C_0^3} - \frac{1}{5}k_{50}\frac{C_{--}^2C_{-0}^3}{C_-^4C_0^2} + k_{126}\frac{C_{00}C_{-0}^3}{C_-C_0^3}\\
+\frac{1}{5}k_{129}\frac{C_{--}C_{00}C_{-0}^3}{C_-^3C_0^3} - k_{128}\frac{C_{--}C_{-0}^3}{C_-^3C_0} - \frac{1}{5}k_{131}\frac{C_{--}C_{-0}^4}{C_-^4C_0^2}\\
+k_{130}\frac{C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-C_0} + k_{87}\frac{C_{--}C_{+-}^2C_{+0}}{C_+^2C_-^2} - k_{132}\frac{C_{--}C_{+-}C_{-0}^2}{C_-^3C_0}\\
-k_{85}\frac{C_{--}C_{+0}C_{-0}^2}{C_-^2C_0^2} + \frac{1}{5}k_{133}\frac{C_{+-}^2C_{+0}C_{-0}^2}{C_+^2C_-^2C_0^2} + \frac{1}{5}k_{91}\frac{C_{--}C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-^3C_0}\\
-\frac{1}{5}k_{135}\frac{C_{--}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^3C_0^2} - \frac{1}{5}k_{89}\frac{C_{--}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^3C_0^2} + k_{134}\frac{C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-C_0}\\
+\frac{1}{5}k_{137}\frac{C_{--}C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-^3C_0} - k_{136}\frac{C_{--}C_{+-}C_{-0}^2}{C_-^3C_0} - \frac{1}{5}k_{139}\frac{C_{--}C_{+-}^2C_{-0}^2}{C_+C_-^4C_0} = 0,
\end{aligned}\tag{3.26.8}$$

$$\begin{aligned}
&k_{128}\frac{C_{--}C_{-0}^3}{C_-^3C_0}+k_{59}\frac{C_{00}^3C_{-0}}{C_0^4}-k_{126}\frac{C_{00}C_{-0}^3}{C_-C_0^3}\\
&-k_{57}\frac{C_{00}C_{-0}^3}{C_-^2C_0^2}+\frac{1}{5}k_{131}\frac{C_{--}C_{-0}^4}{C_-^4C_0^2}+\frac{1}{5}k_{60}\frac{C_{00}^3C_{-0}^2}{C_0^5C_-}\\
&-\frac{1}{5}k_{129}\frac{C_{--}C_{00}C_{-0}^3}{C_-^3C_0^3}-\frac{1}{5}k_{58}\frac{C_{00}^2C_{-0}^3}{C_0^4C_-^2}+k_{124}\frac{C_{--}C_{-0}^3}{C_-^3C_0}\\
&+\frac{1}{5}k_{127}\frac{C_{--}C_{00}C_{-0}^3}{C_-^3C_0^3}-k_{122}\frac{C_{00}C_{-0}^3}{C_-C_0^3}-\frac{1}{5}k_{125}\frac{C_{00}C_{-0}^4}{C_0^4C_-^2}\\
&+k_{138}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0}+k_{115}\frac{C_{00}C_{+-}C_{+0}^2}{C_+^2C_0^2}-k_{140}\frac{C_{00}C_{+0}C_{-0}^2}{C_-C_0^3}\\
&-k_{113}\frac{C_{00}C_{+-}C_{-0}^2}{C_-^2C_0^2}+\frac{1}{5}k_{141}\frac{C_{+-}C_{+0}^2C_{-0}^2}{C_+^2C_-^2C_0^2}+\frac{1}{5}k_{119}\frac{C_{00}C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0^3}\\
&-\frac{1}{5}k_{143}\frac{C_{00}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0^3}-\frac{1}{5}k_{117}\frac{C_{00}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0^3}+k_{142}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0}\\
&+\frac{1}{5}k_{145}\frac{C_{00}C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0^3}-k_{144}\frac{C_{00}C_{+0}C_{-0}^2}{C_-C_0^3}-\frac{1}{5}k_{147}\frac{C_{00}C_{+0}^2C_{-0}^2}{C_+C_-C_0^4}=0.
\end{aligned}\tag{3.26.9}$$

Same for the two-element model, the rate of forward reactions and backward reactions will be equal for reversible reactions in equilibrium. The following equilibrium constants can be introduced based on reversible reactions in equilibrium. Each one of them is broken down by applying the moment closure approximations.

$$Q_{19}=\frac{k_{37}}{k_{39}}=\frac{C_{(\dot{-}\widehat{+++})}}{C_{(\dot{+}\widehat{-++})}}=\frac{C_{\widehat{+++}}C_-}{C_{\widehat{-++}}C_+}=\frac{C_{++}^2C_-^2}{C_{+-}^2C_+^2},\tag{3.27.1}$$

$$Q_{20}=\frac{k_{38}}{k_{40}}=\frac{C_{(\ddot{-}\widehat{+++})}}{C_{(\ddot{+}\widehat{-++})}}=\frac{C_{\widehat{+++}}C_{+-}}{C_{\widehat{-++}}C_{++}}=\frac{C_{++}C_-}{C_{+-}C_+},\tag{3.27.2}$$

$$Q_{21}=\frac{k_{41}}{k_{43}}=\frac{C_{(\dot{0}\widehat{+++})}}{C_{(\dot{+}\widehat{0++})}}=\frac{C_{\widehat{+++}}C_0}{C_{\widehat{0++}}C_+}=\frac{C_{++}^2C_0^2}{C_{+0}^2C_+^2},\tag{3.27.3}$$

$$Q_{22}=\frac{k_{42}}{k_{44}}=\frac{C_{(\ddot{0}\widehat{+++})}}{C_{(\ddot{+}\widehat{0++})}}=\frac{C_{\widehat{+++}}C_{+0}}{C_{\widehat{0++}}C_{++}}=\frac{C_{++}C_0}{C_{+0}C_+},\tag{3.27.4}$$

$$Q_{23}=\frac{k_{45}}{k_{47}}=\frac{C_{(\dot{+}\widehat{---})}}{C_{(\dot{-}\widehat{+--})}}=\frac{C_{\widehat{---}}C_+}{C_{\widehat{+--}}C_-}=\frac{C_{--}^2C_+^2}{C_{+-}^2C_-^2},\tag{3.27.5}$$

$$Q_{24}=\frac{k_{46}}{k_{48}}=\frac{C_{(\ddot{+}\widehat{---})}}{C_{(\ddot{-}\widehat{+--})}}=\frac{C_{\widehat{---}}C_{+-}}{C_{\widehat{+--}}C_{--}}=\frac{C_{--}C_+}{C_{+-}C_-},\tag{3.27.6}$$

$$Q_{25} = \frac{k_{49}}{k_{51}} = \frac{C_{(\dot{0}\widehat{---})}}{C_{(\dot{-}\widehat{0--})}} = \frac{C_{\widehat{---}}C_0}{C_{\widehat{0--}}C_-} = \frac{C^2_{--}C^2_0}{C^2_{0-}C^2_-}, \tag{3.27.7}$$

$$Q_{26} = \frac{k_{50}}{k_{52}} = \frac{C_{(\ddot{0}\widehat{---})}}{C_{(\ddot{-}\widehat{0--})}} = \frac{C_{\widehat{---}}C_{0-}}{C_{\widehat{0--}}C_{--}} = \frac{C_{--}C_0}{C_{0-}C_-}, \tag{3.27.8}$$

$$Q_{27} = \frac{k_{53}}{k_{55}} = \frac{C_{(\dot{+}\widehat{000})}}{C_{(\dot{0}\widehat{+00})}} = \frac{C_{\widehat{000}}C_+}{C_{\widehat{+00}}C_0} = \frac{C^2_{00}C^2_+}{C^2_{+0}C^2_0}, \tag{3.27.9}$$

$$Q_{28} = \frac{k_{54}}{k_{56}} = \frac{C_{(\ddot{+}\widehat{000})}}{C_{(\ddot{0}\widehat{+00})}} = \frac{C_{\widehat{000}}C_{+0}}{C_{\widehat{+00}}C_{00}} = \frac{C_{00}C_+}{C_{+0}C_0}, \tag{3.27.10}$$

$$Q_{29} = \frac{k_{57}}{k_{59}} = \frac{C_{(\dot{-}\widehat{000})}}{C_{(\dot{0}\widehat{-00})}} = \frac{C_{\widehat{000}}C_-}{C_{\widehat{-00}}C_0} = \frac{C^2_{00}C^2_-}{C^2_{-0}C^2_0}, \tag{3.27.11}$$

$$Q_{30} = \frac{k_{58}}{k_{60}} = \frac{C_{(\ddot{-}\widehat{000})}}{C_{(\ddot{0}\widehat{-00})}} = \frac{C_{\widehat{000}}C_{-0}}{C_{\widehat{-00}}C_{00}} = \frac{C_{00}C_-}{C_{-0}C_0}, \tag{3.27.12}$$

$$Q_{31} = \frac{k_{61}}{k_{63}} = \frac{C_{(\dot{-}\widehat{+-+})}}{C_{(\dot{+}\widehat{--+})}} = \frac{C_{\widehat{+-+}}C_-}{C_{\widehat{--+}}C_+} = \frac{C_{++}C^2_-}{C_{--}C^2_+}, \tag{3.27.13}$$

$$Q_{32} = \frac{k_{62}}{k_{64}} = \frac{C_{(\ddot{-}\widehat{+-+})}}{C_{(\ddot{+}\widehat{--+})}} = \frac{C_{\widehat{+-+}}C_{--}}{C_{\widehat{--+}}C_{+-}} = \frac{C_{++}C_-}{C_{+-}C_+}, \tag{3.27.14}$$

$$Q_{33} = \frac{k_{65}}{k_{67}} = \frac{C_{(\dot{-}\widehat{++-})}}{C_{(\dot{+}\widehat{-+-})}} = \frac{C_{\widehat{++-}}C_-}{C_{\widehat{-+-}}C_+} = \frac{C_{++}C^2_-}{C_{--}C^2_+}, \tag{3.27.15}$$

$$Q_{34} = \frac{k_{66}}{k_{68}} = \frac{C_{(\ddot{-}\widehat{++-})}}{C_{(\ddot{+}\widehat{-+-})}} = \frac{C_{\widehat{++-}}C_{+-}}{C_{\widehat{-+-}}C_{++}} = \frac{C_{+-}C_-}{C_{--}C_+}, \tag{3.27.16}$$

$$Q_{35} = \frac{k_{69}}{k_{71}} = \frac{C_{(\dot{0}\widehat{+-+})}}{C_{(\dot{+}\widehat{0-+})}} = \frac{C_{\widehat{+-+}}C_0}{C_{\widehat{0-+}}C_+} = \frac{C_{++}C_{+-}C^2_0}{C_{+0}C_{-0}C^2_+}, \tag{3.27.17}$$

$$Q_{36} = \frac{k_{70}}{k_{72}} = \frac{C_{(\dot{0}\widehat{-++})}}{C_{(\dot{-}\widehat{0++})}} = \frac{C_{\widehat{-++}}C_0}{C_{\widehat{0++}}C_-} = \frac{C^2_{+-}C^2_0}{C^2_{+0}C^2_-}, \tag{3.27.18}$$

$$Q_{37} = \frac{k_{73}}{k_{75}} = \frac{C_{(\ddot{0}\widehat{+-+})}}{C_{(\ddot{+}\widehat{0-+})}} = \frac{C_{\widehat{+-+}}C_{-0}}{C_{\widehat{0-+}}C_{+-}} = \frac{C_{++}C_0}{C_{+0}C_+}, \tag{3.27.19}$$

$$Q_{38} = \frac{k_{74}}{k_{76}} = \frac{C_{(\ddot{0}\widehat{+-+})}}{C_{(\ddot{-}\widehat{+0+})}} = \frac{C_{\widehat{+-+}}C_{+0}}{C_{\widehat{+0+}}C_{+-}} = \frac{C_{+-}C_0}{C_{+0}C_-}, \tag{3.27.20}$$

$$Q_{39} = \frac{k_{77}}{k_{79}} = \frac{C_{(\dot{0}\widehat{++-})}}{C_{(\dot{+}\widehat{0+-})}} = \frac{C_{\widehat{++-}}C_0}{C_{\widehat{0+-}}C_+} = \frac{C_{++}C_{+-}C^2_0}{C_{+0}C_{-0}C^2_+}, \tag{3.27.21}$$

$$Q_{40} = \frac{k_{78}}{k_{80}} = \frac{C_{(\ddot{0}\widehat{++-})}}{C_{(\ddot{+}\widehat{0+-})}} = \frac{C_{\widehat{++-}}C_{+0}}{C_{\widehat{0+-}}C_{++}} = \frac{C_{+-}C_{0}}{C_{-0}C_{+}}, \tag{3.27.22}$$

$$Q_{41} = \frac{k_{82}}{k_{84}} = \frac{C_{(\dot{0}\widehat{-+-})}}{C_{(\dot{-}\widehat{0+-})}} = \frac{C_{\widehat{-+-}}C_{0}}{C_{\widehat{0+-}}C_{-}} = \frac{C_{--}C_{+-}C_{0}^{2}}{C_{+0}C_{-0}C_{-}^{2}}, \tag{3.27.23}$$

$$Q_{42} = \frac{k_{85}}{k_{87}} = \frac{C_{(\dot{0}\widehat{+--})}}{C_{(\dot{+}\widehat{0--})}} = \frac{C_{\widehat{+--}}C_{0}}{C_{\widehat{0--}}C_{+}} = \frac{C_{+-}^{2}C_{0}^{2}}{C_{-0}^{2}C_{+}^{2}}, \tag{3.27.24}$$

$$Q_{43} = \frac{k_{86}}{k_{88}} = \frac{C_{(\ddot{0}\widehat{-+-})}}{C_{(\ddot{-}\widehat{0+-})}} = \frac{C_{\widehat{-+-}}C_{+0}}{C_{\widehat{0+-}}C_{+-}} = \frac{C_{--}C_{0}}{C_{-0}C_{-}}, \tag{3.27.25}$$

$$Q_{44} = \frac{k_{89}}{k_{91}} = \frac{C_{(\ddot{0}\widehat{-+-})}}{C_{(\ddot{+}\widehat{-0-})}} = \frac{C_{\widehat{-+-}}C_{-0}}{C_{\widehat{-0-}}C_{+-}} = \frac{C_{+-}C_{0}}{C_{-0}C_{+}}, \tag{3.27.26}$$

$$Q_{45} = \frac{k_{90}}{k_{92}} = \frac{C_{(\dot{0}\widehat{--+})}}{C_{(\dot{-}\widehat{0-+})}} = \frac{C_{\widehat{--+}}C_{0}}{C_{\widehat{0-+}}C_{-}} = \frac{C_{--}C_{+-}C_{0}^{2}}{C_{+0}C_{-0}C_{-}^{2}}, \tag{3.27.27}$$

$$Q_{46} = \frac{k_{93}}{k_{95}} = \frac{C_{(\ddot{0}\widehat{--+})}}{C_{(\ddot{-}\widehat{0-+})}} = \frac{C_{\widehat{--+}}C_{-0}}{C_{\widehat{0-+}}C_{--}} = \frac{C_{+-}C_{0}}{C_{+0}C_{-}}, \tag{3.27.28}$$

$$Q_{47} = \frac{k_{94}}{k_{96}} = \frac{C_{(\dot{0}\widehat{+0+})}}{C_{(\dot{+}\widehat{00+})}} = \frac{C_{\widehat{+0+}}C_{0}}{C_{\widehat{00+}}C_{+}} = \frac{C_{++}C_{0}^{2}}{C_{00}C_{+}^{2}}, \tag{3.27.29}$$

$$Q_{48} = \frac{k_{97}}{k_{99}} = \frac{C_{(\ddot{0}\widehat{+0+})}}{C_{(\ddot{+}\widehat{00+})}} = \frac{C_{\widehat{+0+}}C_{00}}{C_{\widehat{00+}}C_{+0}} = \frac{C_{++}C_{0}}{C_{+0}C_{+}}, \tag{3.27.30}$$

$$Q_{49} = \frac{k_{98}}{k_{100}} = \frac{C_{(\dot{0}\widehat{++0})}}{C_{(\dot{+}\widehat{0+0})}} = \frac{C_{\widehat{++0}}C_{0}}{C_{\widehat{0+0}}C_{+}} = \frac{C_{++}C_{0}^{2}}{C_{00}C_{+}^{2}}, \tag{3.27.31}$$

$$Q_{50} = \frac{k_{101}}{k_{103}} = \frac{C_{(\ddot{0}\widehat{++0})}}{C_{(\ddot{+}\widehat{0+0})}} = \frac{C_{\widehat{++0}}C_{+0}}{C_{\widehat{0+0}}C_{++}} = \frac{C_{+0}C_{0}}{C_{00}C_{+}}, \tag{3.27.32}$$

$$Q_{51} = \frac{k_{102}}{k_{104}} = \frac{C_{(\dot{-}\widehat{+0+})}}{C_{(\dot{+}\widehat{-0+})}} = \frac{C_{\widehat{+0+}}C_{-}}{C_{\widehat{-0+}}C_{+}} = \frac{C_{++}C_{+0}C_{-}^{2}}{C_{+-}C_{-0}C_{+}^{2}}, \tag{3.27.33}$$

$$Q_{52} = \frac{k_{105}}{k_{107}} = \frac{C_{(\ddot{-}\widehat{+0+})}}{C_{(\ddot{+}\widehat{-0+})}} = \frac{C_{\widehat{+0+}}C_{-0}}{C_{\widehat{-0+}}C_{+0}} = \frac{C_{++}C_{-}}{C_{+-}C_{+}}, \tag{3.27.34}$$

$$Q_{53} = \frac{k_{106}}{k_{108}} = \frac{C_{(\dot{-}\widehat{++0})}}{C_{(\dot{+}\widehat{-+0})}} = \frac{C_{\widehat{++0}}C_{-}}{C_{\widehat{-+0}}C_{+}} = \frac{C_{++}C_{+0}C_{-}^{2}}{C_{+-}C_{-0}C_{+}^{2}}, \tag{3.27.35}$$

$$Q_{54} = \frac{k_{109}}{k_{111}} = \frac{C_{(\ddot{-}\widehat{++0})}}{C_{(\ddot{+}\widehat{-+0})}} = \frac{C_{\widehat{++0}}C_{+-}}{C_{\widehat{-+0}}C_{++}} = \frac{C_{+0}C_{-}}{C_{-0}C_{+}}, \tag{3.27.36}$$

$$Q_{55} = \frac{k_{110}}{k_{112}} = \frac{C_{(\dot{-}\widehat{0+0})}}{C_{(\dot{0}\widehat{-+0})}} = \frac{C_{\widehat{0+0}}C_{-}}{C_{\widehat{-+0}}C_{0}} = \frac{C_{00}C_{+0}C_{-}^{2}}{C_{+-}C_{-0}C_{0}^{2}}, \tag{3.27.37}$$

$$Q_{56} = \frac{k_{113}}{k_{115}} = \frac{C_{(\dot{-}\widehat{+00})}}{C_{(\dot{+}\widehat{-00})}} = \frac{C_{\widehat{+00}}C_{-}}{C_{\widehat{-00}}C_{+}} = \frac{C_{+0}^{2}C_{-}^{2}}{C_{-0}^{2}C_{+}^{2}}, \tag{3.27.38}$$

$$Q_{57} = \frac{k_{114}}{k_{116}} = \frac{C_{(\ddot{-}\widehat{0+0})}}{C_{(\ddot{0}\widehat{-+0})}} = \frac{C_{\widehat{0+0}}C_{+-}}{C_{\widehat{-+0}}C_{+0}} = \frac{C_{00}C_{-}}{C_{-0}C_{0}}, \tag{3.27.39}$$

$$Q_{58} = \frac{k_{117}}{k_{119}} = \frac{C_{(\ddot{-}\widehat{0+0})}}{C_{(\ddot{+}\widehat{0-0})}} = \frac{C_{\widehat{0+0}}C_{-0}}{C_{\widehat{0-0}}C_{+0}} = \frac{C_{+0}C_{-}}{C_{-0}C_{+}}, \tag{3.27.40}$$

$$Q_{59} = \frac{k_{118}}{k_{120}} = \frac{C_{(\dot{-}\widehat{00+})}}{C_{(\dot{0}\widehat{-0+})}} = \frac{C_{\widehat{00+}}C_{-}}{C_{\widehat{-0+}}C_{0}} = \frac{C_{00}C_{+0}C_{-}^{2}}{C_{+-}C_{-0}C_{0}^{2}}, \tag{3.27.41}$$

$$Q_{60} = \frac{k_{121}}{k_{123}} = \frac{C_{(\ddot{-}\widehat{00+})}}{C_{(\ddot{0}\widehat{0-+})}} = \frac{C_{\widehat{00+}}C_{-0}}{C_{\widehat{0-+}}C_{00}} = \frac{C_{+0}C_{-}}{C_{+-}C_{0}}, \tag{3.27.42}$$

$$Q_{61} = \frac{k_{122}}{k_{124}} = \frac{C_{(\dot{0}\widehat{-0-})}}{C_{(\dot{-}\widehat{00-})}} = \frac{C_{\widehat{-0-}}C_{0}}{C_{\widehat{00-}}C_{-}} = \frac{C_{--}C_{0}^{2}}{C_{00}C_{-}^{2}}, \tag{3.27.43}$$

$$Q_{62} = \frac{k_{125}}{k_{127}} = \frac{C_{(\ddot{0}\widehat{-0-})}}{C_{(\ddot{-}\widehat{00-})}} = \frac{C_{\widehat{-0-}}C_{00}}{C_{\widehat{00-}}C_{-0}} = \frac{C_{--}C_{0}}{C_{-0}C_{-}}, \tag{3.27.44}$$

$$Q_{63} = \frac{k_{126}}{k_{128}} = \frac{C_{(\dot{0}\widehat{--0})}}{C_{(\dot{-}\widehat{0-0})}} = \frac{C_{\widehat{--0}}C_{0}}{C_{\widehat{0-0}}C_{-}} = \frac{C_{--}C_{0}^{2}}{C_{00}C_{-}^{2}}, \tag{3.27.45}$$

$$Q_{64} = \frac{k_{129}}{k_{131}} = \frac{C_{(\ddot{0}\widehat{--0})}}{C_{(\ddot{-}\widehat{0-0})}} = \frac{C_{\widehat{--0}}C_{-0}}{C_{\widehat{0-0}}C_{--}} = \frac{C_{-0}C_{0}}{C_{00}C_{-}}, \tag{3.27.46}$$

$$Q_{65} = \frac{k_{130}}{k_{132}} = \frac{C_{(\dot{+}\widehat{-0-})}}{C_{(\dot{-}\widehat{+0-})}} = \frac{C_{\widehat{-0-}}C_{+}}{C_{\widehat{+0-}}C_{-}} = \frac{C_{--}C_{-0}C_{+}^{2}}{C_{+0}C_{+-}C_{-}^{2}}, \tag{3.27.47}$$

$$Q_{66} = \frac{k_{133}}{k_{135}} = \frac{C_{(\ddot{+}\widehat{-0-})}}{C_{(\ddot{-}\widehat{+0-})}} = \frac{C_{\widehat{-0-}}C_{+0}}{C_{\widehat{+0-}}C_{-0}} = \frac{C_{--}C_{+}}{C_{+-}C_{-}}, \tag{3.27.48}$$

$$Q_{67} = \frac{k_{134}}{k_{136}} = \frac{C_{(\dot{+}\widehat{--0})}}{C_{(\dot{-}\widehat{+-0})}} = \frac{C_{\widehat{--0}}C_{+}}{C_{\widehat{+-0}}C_{-}} = \frac{C_{--}C_{-0}C_{+}^{2}}{C_{+0}C_{+-}C_{-}^{2}}, \tag{3.27.49}$$

$$Q_{68} = \frac{k_{137}}{k_{139}} = \frac{C_{(\ddot{+}\widehat{--0})}}{C_{(\ddot{-}\widehat{+-0})}} = \frac{C_{\widehat{--0}}C_{+-}}{C_{\widehat{+-0}}C_{--}} = \frac{C_{-0}C_{+}}{C_{+0}C_{-}}, \tag{3.27.50}$$

$$Q_{69} = \frac{k_{138}}{k_{140}} = \frac{C_{(\dot{+}\widehat{0-0})}}{C_{(\dot{0}\widehat{+-0})}} = \frac{C_{\widehat{0-0}}C_{+}}{C_{\widehat{+-0}}C_{0}} = \frac{C_{00}C_{-0}C_{+}^{2}}{C_{+-}C_{+0}C_{0}^{2}}, \tag{3.27.51}$$

$$Q_{70} = \frac{k_{141}}{k_{143}} = \frac{C_{(\ddot{+}\widehat{0-0})}}{C_{(\ddot{0}\widehat{+-0})}} = \frac{C_{\widehat{0-0}}C_{+-}}{C_{\widehat{+-0}}C_{-0}} = \frac{C_{00}C_{+}}{C_{+0}C_{0}}, \tag{3.27.52}$$

$$Q_{71} = \frac{k_{142}}{k_{144}} = \frac{C_{(\dot{+}\widehat{00-})}}{C_{(\dot{0}\widehat{+0-})}} = \frac{C_{\widehat{00-}}C_{+}}{C_{\widehat{+0-}}C_{0}} = \frac{C_{00}C_{-0}C_{+}^{2}}{C_{+-}C_{+0}C_{0}^{2}}, \tag{3.27.53}$$

$$Q_{72} = \frac{k_{145}}{k_{147}} = \frac{C_{(\ddot{+}\widehat{00-})}}{C_{(\ddot{0}\widehat{+0-})}} = \frac{C_{\widehat{00-}}C_{+0}}{C_{\widehat{+0-}}C_{00}} = \frac{C_{-0}C_{+}}{C_{+-}C_{0}}. \tag{3.27.54}$$

As can be observed, after applying the moment closure scheme, some of the equilibrium constants are equal to each other. The rate equations derived in eq. (3.26) will be written in terms of equilibrium constants and will be closed by moment closure scheme in terms of 2-clusters. Appendix 7.6 provides the full derivation of these new equations. Note that one of the rate equations is redundant as it can be deduced by imposing the normalization condition

$$\begin{aligned} &Q_{19}\beta_{31}\frac{C_{++}C_{+-}^{3}}{C_{+}^{2}C_{-}^{2}} + \frac{1}{5}Q_{20}\beta_{32}\frac{C_{++}^{2}C_{+-}^{3}}{C_{+}^{4}C_{-}^{2}} - \beta_{31}\frac{C_{++}^{3}C_{+-}}{C_{+}^{4}} - \frac{1}{5}\beta_{32}\frac{C_{++}^{3}C_{+-}^{2}}{C_{+}^{5}C_{-}} \\ &+Q_{21}\beta_{33}\frac{C_{++}C_{+0}^{3}}{C_{+}^{2}C_{0}^{2}} + \frac{1}{5}Q_{22}\frac{C_{++}^{2}C_{+0}^{3}}{C_{+}^{4}C_{0}^{2}} - \beta_{33}\frac{C_{++}^{3}C_{+0}}{C_{+}^{4}} - \frac{1}{5}\frac{C_{++}^{3}C_{+0}^{2}}{C_{+}^{5}C_{0}} = 0, \end{aligned} \tag{3.28.1}$$

$$\begin{aligned} &Q_{23}\beta_{34}\frac{C_{--}C_{+-}^{3}}{C_{+}^{2}C_{-}^{2}} + \frac{1}{5}Q_{24}\beta_{35}\frac{C_{--}^{2}C_{+-}^{3}}{C_{-}^{4}C_{+}^{2}} - \beta_{34}\frac{C_{--}^{3}C_{+-}}{C_{-}^{4}} - \frac{1}{5}\beta_{35}\frac{C_{--}^{3}C_{+-}^{2}}{C_{-}^{5}C_{+}} \\ &+Q_{25}\beta_{36}\frac{C_{--}C_{-0}^{3}}{C_{0}^{2}C_{-}^{2}} + \frac{1}{5}Q_{26}\frac{C_{--}^{2}C_{-0}^{3}}{C_{-}^{4}C_{0}^{2}} - \beta_{36}\frac{C_{--}^{3}C_{-0}}{C_{-}^{4}} - \frac{1}{5}\frac{C_{--}^{3}C_{0-}^{2}}{C_{-}^{5}C_{0}} = 0, \end{aligned} \tag{3.28.2}$$

$$\begin{aligned} Q_{27}\beta_{37}\frac{C_{00}C_{+0}^3}{C_+^2C_0^2}+\frac{1}{5}Q_{28}\beta_{38}\frac{C_{00}^2C_{+0}^3}{C_0^4C_+^2}-\beta_{37}\frac{C_{00}^3C_{+0}}{C_0^4}-\frac{1}{5}\beta_{38}\frac{C_{00}^3C_{+0}^2}{C_0^5C_+}\\ +Q_{29}\beta_{39}\frac{C_{00}C_{-0}^3}{C_-^2C_0^2}+\frac{1}{5}Q_{30}\frac{C_{00}^2C_{-0}^3}{C_0^4C_-^2}-\beta_{39}\frac{C_{00}^3C_{-0}}{C_0^4}-\frac{1}{5}\frac{C_{00}^3C_{-0}^2}{C_0^5C_-}=0,\end{aligned} \tag{3.28.3}$$

$$\begin{aligned} Q_{31}\beta_{40}\frac{C_{--}C_{+-}^3}{C_+C_-^3}-\beta_{40}\frac{C_{++}C_{+-}^3}{C_+^3C_-}+\frac{1}{5}Q_{32}\beta_{41}\frac{C_{--}C_{+-}^4}{C_+^2C_-^4}\\ -\frac{1}{5}\beta_{41}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}+Q_{33}\beta_{42}\frac{C_{--}C_{+-}^3}{C_+C_-^3}+\frac{1}{5}Q_{34}\beta_{43}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}\\ -\beta_{42}\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\frac{1}{5}\beta_{43}\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}+Q_{35}\beta_{44}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2}\\ +Q_{36}\beta_{45}\frac{C_{++}C_{+0}^2C_{-0}}{C_+^2C_0^2}-\beta_{44}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-}-\beta_{45}\frac{C_{++}C_{+-}^2C_{-0}}{C_+^2C_-^2}\\ +\frac{1}{5}Q_{37}\beta_{46}\frac{C_{+-}^2C_{+0}^2C_{-0}}{C_+^2C_-^2C_0^2}+\frac{1}{5}Q_{38}\beta_{47}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}-\frac{1}{5}\beta_{46}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}\\ -\frac{1}{5}\beta_{47}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}+Q_{39}\beta_{48}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2}+\frac{1}{5}Q_{40}k_{80}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}\\ -\beta_{48}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-}-\frac{1}{5}k_{80}\frac{C_{++}C_{+-}^2C_{+0}^2}{C_+^4C_-C_0}=0,\end{aligned} \tag{3.28.4}$$

$$\begin{aligned} \beta_{49}\frac{C_{++}C_{+-}^3}{C_+^3C_-}-Q_{33}\beta_{49}\frac{C_{--}C_{+-}^3}{C_+C_-^3}+\frac{1}{5}\beta_{50}\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}\\ -\frac{1}{5}Q_{34}\beta_{50}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}+\beta_{51}\frac{C_{++}C_{+-}^3}{C_+^3C_-}+\frac{1}{5}\beta_{52}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}\\ -Q_{31}\beta_{51}\frac{C_{--}C_{+-}^3}{C_+C_-^3}-\frac{1}{5}Q_{32}\beta_{52}\frac{C_{--}C_{+-}^4}{C_+^2C_-^4}+Q_{41}\beta_{53}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-C_0^2}\\ +Q_{42}\beta_{54}\frac{C_{--}C_{+0}C_{-0}^2}{C_-^2C_0^2}-\beta_{53}\frac{C_{--}C_{+-}^2C_{-0}}{C_+C_-^3}-\beta_{54}\frac{C_{--}C_{+-}^2C_{+0}}{C_+^2C_-^2}\\ +\frac{1}{5}Q_{43}\beta_{55}\frac{C_{+-}^2C_{+0}C_{-0}^2}{C_+^2C_-^2C_0^2}+\frac{1}{5}Q_{44}\beta_{56}\frac{C_{--}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^3C_0^2}-\frac{1}{5}\beta_{55}\frac{C_{--}C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-^3C_0}\\ -\frac{1}{5}\beta_{56}\frac{C_{--}C_{+-}^2C_{+0}C_{-0}}{C_+^2C_-^3C_0}+Q_{45}\beta_{57}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-C_0^2}+\frac{1}{5}Q_{46}\frac{C_{--}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^3C_0^2}\\ -\beta_{57}\frac{C_{--}C_{+-}^2C_{-0}}{C_+C_-^3}-\frac{1}{5}\frac{C_{--}C_{+-}^2C_{-0}^2}{C_+C_-^4C_0}=0,\end{aligned} \tag{3.28.5}$$

$$\begin{aligned}
Q_{47}\beta_{58}\frac{C_{00}C_{+0}^3}{C_+C_0^3}-\beta_{58}\frac{C_{++}C_{+0}^3}{C_+^3C_0}+\frac{1}{5}Q_{48}\beta_{59}\frac{C_{00}C_{+0}^4}{C_+^2C_0^4}\\
-\frac{1}{5}\beta_{59}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3}+Q_{49}\beta_{60}\frac{C_{00}C_{+0}^3}{C_+C_0^3}+\frac{1}{5}Q_{50}\beta_{61}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3}\\
-\beta_{60}\frac{C_{++}C_{+0}^3}{C_+^3C_0}-\frac{1}{5}\beta_{61}\frac{C_{++}C_{+0}^4}{C_+^4C_0^2}+Q_{51}\beta_{62}\frac{C_{+-}^2C_{+0}C_{-0}}{C_+C_-^2C_0}\\
+\beta_{63}\frac{C_{++}C_{+-}^2C_{-0}}{C_+^2C_-^2}-\beta_{62}\frac{C_{++}C_{+0}^2C_{+-}}{C_+^3C_0}-Q_{36}\beta_{63}\frac{C_{++}C_{+0}^2C_{-0}}{C_+^2C_0^2}\\
+\frac{1}{5}Q_{52}\beta_{64}\frac{C_{+-}^2C_{+0}^2C_{-0}}{C_+^2C_-^2C_0^2}+\frac{1}{5}\beta_{65}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}-\frac{1}{5}\beta_{64}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}\\
-\frac{1}{5}Q_{38}\beta_{65}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}+Q_{53}\beta_{66}\frac{C_{+-}^2C_{+0}C_{-0}}{C_+C_-^2C_0}+\frac{1}{5}Q_{54}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}\\
-\beta_{66}\frac{C_{++}C_{+-}C_{+0}^2}{C_+^3C_0}-\frac{1}{5}\frac{C_{++}C_{+-}^2C_{+0}^2}{C_+^4C_-C_0}=0,
\end{aligned}\tag{3.28.6}$$

$$\begin{aligned}
\beta_{67}\frac{C_{++}C_{+0}^3}{C_+^3C_0}-Q_{49}\beta_{67}\frac{C_{00}C_{+0}^3}{C_+C_0^3}+\frac{1}{5}\beta_{68}\frac{C_{++}C_{+0}^4}{C_+^4C_0^2}\\
-\frac{1}{5}Q_{50}\beta_{68}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3}+\beta_{69}\frac{C_{++}C_{+0}^3}{C_+^3C_0}+\frac{1}{5}\beta_{70}\frac{C_{++}C_{00}C_{+0}^3}{C_+^3C_0^3}\\
-Q_{47}\beta_{69}\frac{C_{00}C_{+0}^3}{C_+C_0^3}-\frac{1}{5}Q_{48}\beta_{70}\frac{C_{00}C_{+0}^4}{C_+^2C_0^4}+Q_{55}\beta_{71}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0}\\
+Q_{56}\beta_{72}\frac{C_{00}C_{+-}C_{-0}^2}{C_-^2C_0^2}-\beta_{71}\frac{C_{00}C_{+0}^2C_{-0}}{C_+C_0^3}-\beta_{72}\frac{C_{00}C_{+-}C_{+0}^2}{C_+^2C_0^2}\\
+\frac{1}{5}Q_{57}\beta_{73}\frac{C_{+-}C_{+0}^2C_{-0}^2}{C_+^2C_-^2C_0^2}+\frac{1}{5}Q_{58}\beta_{74}\frac{C_{00}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0^3}-\frac{1}{5}\beta_{73}\frac{C_{00}C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0^3}\\
-\frac{1}{5}\beta_{74}\frac{C_{00}C_{+-}C_{+0}^2C_{-0}}{C_+^2C_-C_0^3}+Q_{59}\beta_{75}\frac{C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0}+\frac{1}{5}Q_{60}\frac{C_{00}C_{+-}C_{+0}C_{-0}^2}{C_+C_-^2C_0^3}\\
-\beta_{75}\frac{C_{00}C_{+0}^2C_{-0}}{C_+C_0^3}-\frac{1}{5}\frac{C_{00}C_{+0}^2C_{-0}^2}{C_+C_-C_0^4}=0,
\end{aligned}\tag{3.28.7}$$

$$\begin{aligned}
&Q_{61}\beta_{76}\frac{C_{00}C_{-0}^{3}}{C_{-}C_{0}^{3}} - \beta_{76}\frac{C_{--}C_{-0}^{3}}{C_{-}^{3}C_{0}} + \frac{1}{5}Q_{62}\beta_{77}\frac{C_{00}C_{-0}^{4}}{C_{0}^{4}C_{-}^{2}} \\
&-\frac{1}{5}\beta_{77}\frac{C_{--}C_{00}C_{-0}^{3}}{C_{-}^{3}C_{0}^{3}} + Q_{63}\beta_{78}\frac{C_{00}C_{-0}^{3}}{C_{-}C_{0}^{3}} + \frac{1}{5}Q_{64}\beta_{79}\frac{C_{--}C_{00}C_{-0}^{3}}{C_{-}^{3}C_{0}^{3}} \\
&-\beta_{78}\frac{C_{--}C_{-0}^{3}}{C_{-}^{3}C_{0}} - \frac{1}{5}\beta_{79}\frac{C_{--}C_{-0}^{4}}{C_{-}^{4}C_{0}^{2}} + Q_{65}\beta_{80}\frac{C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{2}C_{-}C_{0}} \\
&+\beta_{81}\frac{C_{--}C_{+-}^{2}C_{+0}}{C_{+}^{2}C_{-}^{2}} - \beta_{80}\frac{C_{--}C_{+-}C_{-0}^{2}}{C_{-}^{3}C_{0}} - Q_{42}\beta_{81}\frac{C_{--}C_{+0}C_{-0}^{2}}{C_{-}^{2}C_{0}^{2}} \\
&+\frac{1}{5}Q_{66}\beta_{82}\frac{C_{+-}^{2}C_{+0}C_{-0}^{2}}{C_{+}^{2}C_{-}^{2}C_{0}^{2}} + \frac{1}{5}\beta_{83}\frac{C_{--}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{2}C_{-}^{3}C_{0}} - \frac{1}{5}\beta_{82}\frac{C_{--}C_{+-}C_{+0}C_{-0}^{2}}{C_{+}C_{-}^{3}C_{0}^{2}} \\
&-\frac{1}{5}Q_{44}\beta_{83}\frac{C_{--}C_{+-}C_{+0}C_{-0}^{2}}{C_{+}C_{-}^{3}C_{0}^{2}} + Q_{67}\beta_{84}\frac{C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{2}C_{-}C_{0}} + \frac{1}{5}Q_{68}\frac{C_{--}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{2}C_{-}^{3}C_{0}} \\
&-\beta_{84}\frac{C_{--}C_{+-}C_{-0}^{2}}{C_{-}^{3}C_{0}} - \frac{1}{5}\frac{C_{--}C_{+-}^{2}C_{-0}^{2}}{C_{+}C_{-}^{4}C_{0}} = 0,
\end{aligned} \tag{3.28.8}$$

$$\begin{aligned}
&\beta_{85}\frac{C_{--}C_{-0}^{3}}{C_{-}^{3}C_{0}} - Q_{63}\beta_{85}\frac{C_{00}C_{-0}^{3}}{C_{-}C_{0}^{3}} + \frac{1}{5}\beta_{86}\frac{C_{--}C_{-0}^{4}}{C_{-}^{4}C_{0}^{2}} \\
&-\frac{1}{5}Q_{64}\beta_{86}\frac{C_{--}C_{00}C_{-0}^{3}}{C_{-}^{3}C_{0}^{3}} + \beta_{87}\frac{C_{--}C_{-0}^{3}}{C_{-}^{3}C_{0}} + \frac{1}{5}\beta_{88}\frac{C_{--}C_{00}C_{-0}^{3}}{C_{-}^{3}C_{0}^{3}} \\
&-Q_{61}\beta_{87}\frac{C_{00}C_{-0}^{3}}{C_{-}C_{0}^{3}} - \frac{1}{5}Q_{62}\beta_{88}\frac{C_{00}C_{-0}^{4}}{C_{0}^{4}C_{-}^{2}} + Q_{69}\beta_{89}\frac{C_{+-}C_{+0}^{2}C_{-0}}{C_{+}^{2}C_{-}C_{0}} \\
&+\beta_{90}\frac{C_{00}C_{+-}C_{+0}^{2}}{C_{+}^{2}C_{0}^{2}} - \beta_{89}\frac{C_{00}C_{+0}C_{-0}^{2}}{C_{-}C_{0}^{3}} - Q_{56}\beta_{90}\frac{C_{00}C_{+-}C_{-0}^{2}}{C_{-}^{2}C_{0}^{2}} \\
&+\frac{1}{5}Q_{70}\beta_{91}\frac{C_{+-}C_{+0}^{2}C_{-0}^{2}}{C_{+}^{2}C_{-}^{2}C_{0}^{2}} + \frac{1}{5}\beta_{92}\frac{C_{00}C_{+-}C_{+0}^{2}C_{-0}}{C_{+}^{2}C_{-}C_{0}^{3}} - \frac{1}{5}\beta_{91}\frac{C_{00}C_{+-}C_{+0}C_{-0}^{2}}{C_{+}C_{-}^{2}C_{0}^{3}} \\
&-\frac{1}{5}Q_{58}\beta_{92}\frac{C_{00}C_{+-}C_{+0}C_{-0}^{2}}{C_{+}C_{-}^{2}C_{0}^{3}} + Q_{71}\beta_{93}\frac{C_{+-}C_{+0}^{2}C_{-0}}{C_{+}^{2}C_{-}C_{0}} + \frac{1}{5}Q_{72}\frac{C_{00}C_{+-}C_{+0}^{2}C_{-0}}{C_{+}^{2}C_{-}C_{0}^{3}} \\
&-\beta_{93}\frac{C_{00}C_{+0}C_{-0}^{2}}{C_{-}C_{0}^{3}} - \frac{1}{5}\frac{C_{00}C_{+0}^{2}C_{-0}^{2}}{C_{+}C_{-}C_{0}^{4}} = 0.
\end{aligned} \tag{3.28.9}$$

Note that expressions for the ratios β_{31}-β_{93} of the rate constants are provided in Appendinx 7.6. Each of these parameters is defined as the ratios of the rate constants that do not correspond to the same reversible reaction. These parameters cannot be calculated by looking at reversible reactions in the system. However, these parameters can be chosen arbitrarily without altering the equilibrium phase of the system. Having system of equations (3.28), and determining the equilibrium constants from the experimental results, one will be able to solve the forward problem to calculate concentrations of micro-states of the system.

All in all, dynamical systems were built for the concentrations of 2-clusters and 3-clusters based on higher order cluster concentrations. The pair-approximation truncation scheme is utilized to truncate the hierarchy of equations. Rate constants were replaced by their ratios to reduce the number of unknowns in the equations in equilibrium. Consequently, the resulting algebraic system of equations is solvable analytically using equilibrium constants and some additional arbitrary parameters. In order to determine the rate constants in the dynamical system, we propose a different computational framework in the next chapter based on inverse modeling approach.

Chapter 4

Computational Framework for Inverse Modeling

In the previous chapters we developed a system of evolution equations for the two-element and three-element systems. Two different, yet interconnected models were developed for describing the evolution of the concentrations of the clusters at different levels, namely, two-cluster model and triangular-cluster model, in which the evolution of 2-clusters and 3-clusters are considered respectively. An analytic solution of the dynamical system was developed at equilibrium and equilibrium constants were calculated explicitly from concentrations for each reversible reaction. In this chapter we will present computational frameworks for proposing a new closure approximation model and also calculating the rate constants. First, the pair approximation truncation scheme, which was based on neglecting the non-nearest-neighbor correlations of elements, is improved in order to produce more accurate results. Also, we will propose a computational framework for deriving the rate constants of each unique reaction. These parameters are considered to be constant in this formulation. However, temperature-dependent rate constants will also be investigated in a more general setting. Section 4.1 proposes a novel truncation scheme to close the dynamical system and will be subsequently compared to the pair approximation scheme. Section 4.2 discusses the computational framework used for deriving the parameters of the model via an inverse modeling approach. Finally, section 4.3 suggests a framework for calculating the temperature-dependent rate constants.

4.1 Optimal Moment Closure Approximation

The pair approximation scheme introduced in eq. (2.31), (2.36) and (2.37) can be used to close the hierarchy of the evolution equations. However, the accuracy of this scheme is questionable as the results are shown in section 5.4. Some analyses have been performed using this scheme which are presented in chapter 5. In order to enhance the accuracy of the truncation scheme, here we propose a new approach based on a non-linear regression analysis in order to truncate the hierarchical system of equations more accurately. The pair approximation scheme attempts to predict the concentrations of the higher order clusters in terms of lower order ones with a specific functional form. In the new approach, we attempt to give more degree of freedom to the functional forms to make them more flexible. The new closure model depends on the same concentrations as before but the functional relation is more general. Table 4.1 demonstrates the functional forms for each particular triplet using the pair approximation and optimal closure schemes. PA stands for the pair approximation scheme and OA refers to the optimal approximation scheme. Note that eq. (2.31) can be expanded for each particular cluster as shown in Table 4.1. It is notable that the new functional forms are the generalizations of the original ones obtained by adding more degree of freedom to the functions and involving more cluster concentrations. The numerators of the functions involve the nearest-neighbor 2-clusters such that the effect of non-nearest neighbor ones are neglected. The denominators, on the other hand, involve the singlet concentrations that are present in the triplet. The later makes the functional form different from the pair approximation in some of the cases. Also, the exponents of the concentrations in the new model are to be determined using nonlinear regression techniques.

Triplet Type	PA	OA	Cost Functional (F)	$\mathbf{\Gamma}$
$C_{\overline{+++}}$	$\frac{1}{5}\frac{C_{++}^2}{C_+}$	$\frac{1}{5}\frac{C_{++}^{\gamma_1}}{C_+^{\gamma_2}}$	$F_1 = \frac{1}{2}\int_0^T [C_{\overline{+++}}(t,\mathbf{\Gamma}) - \tilde{C}_{\overline{+++}}(t)]^2 dt$	$\mathbf{\Gamma}_1 = [\gamma_1\ \gamma_2]$
$C_{\overline{---}}$	$\frac{1}{5}\frac{C_{--}^2}{C_-}$	$\frac{1}{5}\frac{C_{--}^{\gamma_1}}{C_-^{\gamma_2}}$	$F_2 = \frac{1}{2}\int_0^T [C_{\overline{---}}(t,\mathbf{\Gamma}) - \tilde{C}_{\overline{---}}(t)]^2 dt$	$\mathbf{\Gamma}_2 = [\gamma_1\ \gamma_2]$
$C_{\overline{+-+}}$	$\frac{1}{5}\frac{C_{+-}^2}{C_-}$	$\frac{1}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	$F_3 = \frac{1}{2}\int_0^T [C_{\overline{+-+}}(t,\mathbf{\Gamma}) - \tilde{C}_{\overline{+-+}}(t)]^2 dt$	$\mathbf{\Gamma}_3 = [\gamma_1\ \gamma_2\ \gamma_3]$
$C_{\overline{-+-}}$	$\frac{1}{5}\frac{C_{+-}^2}{C_+}$	$\frac{1}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	$F_4 = \frac{1}{2}\int_0^T [C_{\overline{-+-}}(t,\mathbf{\Gamma}) - \tilde{C}_{\overline{-+-}}(t)]^2 dt$	$\mathbf{\Gamma}_4 = [\gamma_1\ \gamma_2\ \gamma_3]$
$C_{\overline{++-}}$	$\frac{1}{5}\frac{C_{++}C_{+-}}{C_+}$	$\frac{1}{5}\frac{C_{++}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	$F_5 = \frac{1}{2}\int_0^T [C_{\overline{++-}}(t,\mathbf{\Gamma}) - \tilde{C}_{\overline{++-}}(t)]^2 dt$	$\mathbf{\Gamma}_5 = [\gamma_1\ \gamma_2\ \gamma_3\ \gamma_4]$
$C_{\overline{--+}}$	$\frac{1}{5}\frac{C_{--}C_{+-}}{C_-}$	$\frac{1}{5}\frac{C_{--}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	$F_6 = \frac{1}{2}\int_0^T [C_{\overline{--+}}(t,\mathbf{\Gamma}) - \tilde{C}_{\overline{--+}}(t)]^2 dt$	$\mathbf{\Gamma}_6 = [\gamma_1\ \gamma_2\ \gamma_3\ \gamma_4]$
$C_{\widehat{+++}}$	$\frac{2}{5}\frac{C_{++}^2}{C_+}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}}{C_+^{\gamma_2}}$	$F_7 = \frac{1}{2}\int_0^T [C_{\widehat{+++}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{+++}}(t)]^2 dt$	$\mathbf{\Gamma}_7 = [\gamma_1\ \gamma_2]$
$C_{\widehat{---}}$	$\frac{2}{5}\frac{C_{--}^2}{C_-}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}}{C_-^{\gamma_2}}$	$F_8 = \frac{1}{2}\int_0^T [C_{\widehat{---}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{---}}(t)]^2 dt$	$\mathbf{\Gamma}_8 = [\gamma_1\ \gamma_2]$
$C_{\widehat{+-+}}$	$\frac{2}{5}\frac{C_{+-}^2}{C_-}$	$\frac{2}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	$F_9 = \frac{1}{2}\int_0^T [C_{\widehat{+-+}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{+-+}}(t)]^2 dt$	$\mathbf{\Gamma}_9 = [\gamma_1\ \gamma_2\ \gamma_3]$
$C_{\widehat{-+-}}$	$\frac{2}{5}\frac{C_{+-}^2}{C_+}$	$\frac{2}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	$F_{10} = \frac{1}{2}\int_0^T [C_{\widehat{-+-}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{-+-}}(t)]^2 dt$	$\mathbf{\Gamma}_{10} = [\gamma_1\ \gamma_2\ \gamma_3]$
$C_{\widehat{++-}}$	$\frac{2}{5}\frac{C_{++}C_{+-}}{C_+}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	$F_{11} = \frac{1}{2}\int_0^T [C_{\widehat{++-}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{++-}}(t)]^2 dt$	$\mathbf{\Gamma}_{11} = [\gamma_1\ \gamma_2\ \gamma_3\ \gamma_4]$
$C_{\widehat{--+}}$	$\frac{2}{5}\frac{C_{--}C_{+-}}{C_-}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	$F_{12} = \frac{1}{2}\int_0^T [C_{\widehat{--+}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{--+}}(t)]^2 dt$	$\mathbf{\Gamma}_{12} = [\gamma_1\ \gamma_2\ \gamma_3\ \gamma_4]$
$C_{\widehat{\overline{+++}}}$	$\frac{2}{5}\frac{C_{++}^3}{C_+^3}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}}{C_+^{\gamma_2}}$	$F_{13} = \frac{1}{2}\int_0^T [C_{\widehat{\overline{+++}}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{\overline{+++}}}(t)]^2 dt$	$\mathbf{\Gamma}_{13} = [\gamma_1\ \gamma_2]$
$C_{\widehat{\overline{---}}}$	$\frac{2}{5}\frac{C_{--}^3}{C_-^3}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}}{C_-^{\gamma_2}}$	$F_{14} = \frac{1}{2}\int_0^T [C_{\widehat{\overline{---}}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{\overline{---}}}(t)]^2 dt$	$\mathbf{\Gamma}_{14} = [\gamma_1\ \gamma_2]$
$C_{\widehat{\overline{++-}}}$	$\frac{2}{5}\frac{C_{++}C_{+-}^2}{C_+^2C_-}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	$F_{15} = \frac{1}{2}\int_0^T [C_{\widehat{\overline{++-}}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{\overline{++-}}}(t)]^2 dt$	$\mathbf{\Gamma}_{15} = [\gamma_1\ \gamma_2\ \gamma_3\ \gamma_4]$
$C_{\widehat{\overline{--+}}}$	$\frac{2}{5}\frac{C_{--}C_{+-}^2}{C_+C_-^2}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	$F_{16} = \frac{1}{2}\int_0^T [C_{\widehat{\overline{--+}}}(t,\mathbf{\Gamma}) - \tilde{C}_{\widehat{\overline{--+}}}(t)]^2 dt$	$\mathbf{\Gamma}_{16} = [\gamma_1\ \gamma_2\ \gamma_3\ \gamma_4]$

Table 4.1: The functional forms of pair approximation scheme vs. optimal closure scheme for each triplet type.

We will try to find the parameters of these models by minimizing the residuals between the experimental data and the model output data points for different times [17–19]. In this formulation the concept of time refers to the iterations of the simulated annealing experiment as time is not an independent variable for this simulation. Each time step corresponds to number of iterations of the simulated annealing experiment, as the data is sampled here. The functional forms for the pair approximation and the optimal approximation are proposed in Table 4.1. Also, the error functional to be minimized is presented for each triplet type. C and $\tilde{C}$ correspond to the model output concentrations and the experimental concentrations respectively. T is the final time of the process. Notice that for each specific triplet, a separate regression analysis will be performed individually. Γ is the vector of exponents in the new functional forms which is different for each triplet type. Note that the triple concentrations are written in terms of lower order concentrations and hence, the new functional forms have to preserve the unit of concentration. Thus, for each functional form, the exponents have to add up to one to maintain the concentration unit. To do so, we present three distinct formulations for different triplet types based on the number of exponents that they have. The following nonlinear regression problem needs to be solved

$$\begin{aligned} \min_{\mathbf{\Gamma}_i} \ & F_i(\mathbf{\Gamma}_i) \quad i = 1, 2, 7, 8, 13, 14 \\ \text{such that} \ & \begin{cases} \gamma_1 > 0, \\ \gamma_1 - \gamma_2 = 1, \end{cases} \end{aligned} \tag{4.1}$$

where F_i is the cost functional to be minimized as stated in Table 4.1 and $\mathbf{\Gamma}$ is the vector of exponent (parameters) of the model. However, this formulation takes another form for some other cases, namely,

$$\begin{aligned} &\min_{\mathbf{\Gamma}_i} \ F_i(\mathbf{\Gamma}_i) \quad i = 3, 4, 9, 10 \\ &\text{such that} \ \begin{cases} \gamma_1 > 0, \\ \gamma_1 - \gamma_2 - \gamma_3 = 1. \end{cases} \end{aligned} \tag{4.2}$$

The rest of the cases are analyzed via the following formulation:

$$\begin{aligned} &\min_{\mathbf{\Gamma}_i} \ F_i(\mathbf{\Gamma}_i) \quad i = 5, 6, 11, 12, 15, 16 \\ &\text{such that} \ \begin{cases} \gamma_1, \gamma_2 > 0, \\ \gamma_1 + \gamma_2 - \gamma_3 - \gamma_4 = 1. \end{cases} \end{aligned} \tag{4.3}$$

The reason for making the exponents strictly positive in the numerator is that the negative exponents can cause the system of ODEs to blow up for concentrations between 0 and 1. In other words, the concentrations are defined for values in $[0, 1]$ and the negative exponents of the pair concentrations will, in some cases, produce unbounded terms in the equations, which further leads to the blow up of the ODE system. Note that some of the functions have two factors on the numerator, however, others preserve one factor in the numerator. Notably, the exponents on the factors in the denominator are concentrations of singlets, which are constants throughout the process and have no contribution to the blow up of the ODEs. Optimal closure model presents the new functional forms which can be used to predict the 3-cluster concentrations from lower order ones. The unconstrained optimization problem can be solved using standard solvers.

4.2 An Inverse Modeling Approach for Parameter Estimation

As we discussed in the previous chapters, the dynamical system at equilibrium becomes an algebraic system of equations which is solved analytically using the expressions of equilibrium constants and moment closure approximation truncation scheme. Nonetheless, the main goal is to calculate the rate constants from concentrations throughout the process. The parameters are reconstructed by minimizing the mismatch between the computational and experimental cluster concentrations [20, 21]. The "experimental" concentrations are obtained by simulating a Monte-Carlo experiment using Metropolis-Hastings algorithm as shown in chapter 5. Temperature is one of the factors changing with time in this simulation. One simplifying assumption is that the parameters (rate constants) of the model are not changing with temperature throughout the process. The goal is to fit experimental data to model outputs via assuming constant parameters. However, in a real physical system, the reaction rate constants are changing with temperature. This assumption will be relaxed in the next section. Also, each of the ratios of the rate constants corresponding to each of the reversible reactions have to be equal to their equilibrium constants throughout the evolution of the cluster concentrations (for instance, $Q_1 = \frac{k_1}{k_3} = \frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}} = \frac{C_{++}C_{-}}{C_{+-}C_{+}}$) as stated in eq. (2.33) and eq. (2.40). It is noteworthy that the ratios of concentrations corresponding to a reversible reaction, as stated in eq. (2.9) and eq. (2.17), are equal to the ratios of the rate constants corresponding to the same reversible reaction, as the forward and backward rates are equal in equilibrium ($\frac{k_1}{k_3} = \frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}}$ at equilibrium). This statement is not true during the process as the forward and backward rates of each reversible reactions are not equal. The ratios of concentrations corresponding to a reversible reaction ($\frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}}$) are changing during the process and are referred to as rate quotients. The rate quotient is equal to the equilibrium constant only at the equilibrium phase of the system. However, the ratios of the rate constants (and not rate quotients) corresponding to a reversible reaction are equal to the equilibrium constants during the process and in equilibrium. For instance, $Q_1 = \frac{k_1}{k_3}$ at all times of the process, however, $Q_1 = \frac{k_1}{k_3} = \frac{C_{\widehat{++-}}}{C_{\widehat{+-+}}}$ only at equilibrium. In order to find the parameters of the two-cluster model, the following formulation is used

$$\min_{\mathbf{K}} \; J(\mathbf{K}) = \frac{1}{2}\int_0^T \big[\mathbf{C}(t,\mathbf{K}) - \widetilde{\mathbf{C}}(t)\big]^2 dt$$
$$\text{such that} \quad \begin{cases} \begin{cases} \frac{d\mathbf{C}}{dt} = f(\mathbf{C};\mathbf{K}) \;\; on \;\; \big(0,T\big], \\ \mathbf{C} = \mathbf{C}_i \;\; on \;\; t=0, \\ C_{++} + C_{--} + 2C_{+-} = 1, \end{cases} \\ \mathbf{Q}(\mathbf{K}) = \widetilde{\mathbf{Q}}, \end{cases} \tag{4.4}$$

where $\mathbf{K}$ is the vector of rate constants, $\mathbf{C}$ is the vector of concentrations from the model, $\widetilde{\mathbf{C}}$ is the vector of concentration from the experimental results, $\mathbf{C}_i$ is the vector of initial concentrations at the start of the process, $\mathbf{Q}$ is the vector of equilibrium constants which are written as ratios of the rate constants, $\widetilde{\mathbf{Q}}$ is the vector of equilibrium constants calculated from the simulated annealing results at equilibrium and T is the final time of the process. The objective function is defined as the discrepancy between the experimental concentrations and concentrations obtained from the evolutionary system of equations, both as functions of time. This objective function is calculated for the entire time evolution of the process. Note that the system of differential algebraic equations used as the constraint satisfies the normalization condition by itself. Hence, the normalization condition becomes redundant and one can solve the system of equations in time by an ODE solver. Also, the concentration of $(+-)$ cluster can be written in terms of concentrations of the $(++)$ and $(--)$ clusters based on the normalization condition. Note that in our approach the vector of concentrations are

$$\begin{aligned} \mathbf{C} &= \big[C_{++} \; C_{--}\big], \\ \widetilde{\mathbf{C}} &= \big[\widetilde{C}_{++} \; \widetilde{C}_{--}\big]. \end{aligned} \tag{4.5}$$

The system of ODEs is solved for the concentrations using an ODE solver. The evolutionary system of equations for the two-cluster two-element model is

$$\frac{dC_{++}}{dt} = 4k_1 C_{(\widehat{+-+})} + 2k_2 C_{(\overline{+-+})} - 4k_3 C_{(\widehat{++-})} - 2k_4 C_{(\overline{++-})}, \tag{4.6.1}$$

$$\frac{dC_{--}}{dt} = 4k_5 C_{(\widehat{-+-})} + 2k_6 C_{(\overline{-+-})} - 4k_7 C_{(\widehat{--+})} - 2k_8 C_{(\overline{--+})}, \tag{4.6.2}$$

where $k_i,\ i = 1, ..., 8$ are the unique rate constants of the model which need to be determined. Equation (4.6) is the hierarchical form of the equation which needs to be truncated via the pair approximation closure scheme or an alternative one, which is discussed in the previous section. Chapter 5 demonstrates the results of this analysis.

4.3 Temperature Dependent Rate Constants

Rate constants in chemical processes are generally temperature dependent. Section 4.2 proposes an inverse modeling approach for estimating the rate constants which are constant during the process. In this section, we will neglect this assumption by making the parameters temperature dependent. To do so, the experimental data which is evolved in time (and temperature), is divided into a number of sub-intervals. The temperature is decreased monotonously with time. Each sub-interval covers a range of the temperature decrease. By increasing the number of sub-intervals we can make our grid finer and obtain rate constants that resolve finer variations with temperature. This can be performed by introducing a cost functional for minimizing the mismatch between the experimental concentrations and the model outputs which is evaluated in time for n

equal sub-intervals

$$\min_{\mathbf{K}} \; J(\mathbf{K}) = \frac{1}{2}\int_0^T \big[\mathbf{C}(t,\mathbf{K}) - \widetilde{\mathbf{C}}(t)\big]^2 dt$$

$$\text{such that} \begin{cases} \begin{cases} \frac{d\mathbf{C}}{dt} = f(\mathbf{C};\mathbf{K}) \;\; on \;\; \big(0,T\big], \\ \mathbf{C} = \mathbf{C}_i \;\; at \;\; t=0, \\ C_{++} + C_{--} + 2C_{+-} = 1, \\ \mathbf{K} = \big[\mathbf{K}_1, \mathbf{K}_2, \cdots, \mathbf{K}_n\big], \\ \mathbf{K}_j \in \mathbb{R}^8 \;\text{ for }\; t \in \big((j-1)\Delta T, j\Delta T\big], \;\; j = 1,2,\cdots,n, \end{cases} \\ \mathbf{Q}(\mathbf{K}) = \widetilde{\mathbf{Q}}, \end{cases} \tag{4.7}$$

where $\mathbf{K}_j$ is the vector of rate constants for each subinterval of the simulation introduced in $\mathbb{R}^8$, ΔT is the time duration for each subinterval, T is the final time which is divided into n equal sub-intervals, t is simulation time, J is the cost functional to be minimized, C is the vector of concentrations and C_i is the initial concentration at time zero. In calculation of the cost functional, the system of ODEs is solved for each sub-interval depending on their specific rate constants. The ratios of the rate constants (**Q**) is equal to the corresponding equilibrium constants throughout the process. This optimization problem will be solved with standard solvers and the results are presented in chapter 5.

4.4 Computational Tools

In order to solve the constrained optimization problems in eq. (4.4) and (4.7) the "`fmincon`" solver in MATLAB is used. This solver is designed for optimizing non-linear multivariable functions subject to nonlinear constraints. The "`SQP`" algorithm is used for optimizing the cost functional as an iterative approach. This algorithm respects the bounds of the decision variables at all iterations and is able to handle NaN or Inf values referenced to by the objective function. The reader can refer to [14] and [15] for further details regarding this algorithm.

The system introduced in eq. (4.1) to (4.3) is a least square curve-fitting problem. "`lsqcurvefit`" solver in MATLAB is used which is a nonlinear curve-fitting solver allowing for bounded decision variables. The optimization problem is solved via iterative methods due to the nonlinear dependencies. The "trust-region-reflective" algorithm is used for this optimization problem. The reader can refer to [16] for the details of this algorithm.

Each iteration of the optimization problem in eq. (4.4) and (4.7) is constrained to the solutions of a system of ODEs. "`ode15s`" in MATLAB is used for solving the initial value problem. The solver is used for solving stiff differential equations and differential algebraic equations.

Chapter 5

Results

In the previous chapter we proposed a computational framework for calculating the constant and temperature-dependent parameters in a more general setting from the results of a simulated annealing experiment. Also, the optimal closure model was proposed for improving the performance of the moment closure approximation model. The results of the simulated annealing experiment were introduced in the first chapter of this document and will be used as "experimental" data in our formulations. In this chapter, first, the equilibrium constants will be calculated at equilibrium based on the simulated annealing results. These equilibrium constants will be used later in the calculation of rate constants. The results of the optimal closure approximation will be presented and compared to the pair approximation model. The rate constants will be calculated based on both closure approximation models by assuming both constant and temperature-dependent parameters. Finally, the accuracy of both models will be investigated by reconstructing higher order concentrations and comparing them to the concentrations obtained from the simulated annealing experiment.

5.1 Calculation of Equilibrium Constants

Two different models were developed for describing the evolution of various clusters, namely, the two-cluster model and the triangular-cluster model. The former predicts the evolution of 2-clusters from 3-clusters and the latter describes the evolution of triangular-clusters in terms of 4-clusters. As mentioned in the previous chapters, the equilibrium state of the system is a matter of interest since the rate of forward and reverse reactions are equivalent. The equilibrium constants are defined as the ratios of the rate constants corresponding to the same reversible reaction. These constants can be calculated based on the concentrations of different clusters in equilibrium as stated in eq. (2.33) and (2.40) for the two-cluster model and the triangular-cluster model, respectively. There are 2 unique equilibrium constants involved in the two-cluster model and 8 unique equilibrium constants in the triangular-cluster model that require to be calculated. The results are presented for the $Li_{1/3}Mn_{2/3}$ system in Table 5.1. In the ordered system, some of the equilibrium constants become zero or infinity. We emphasize that the equilibrium constants are calculated based on concentrations at equilibrium as in (2.33) and (2.40).

Constant	Formula	Approximated Value by Two-Cluster Model
$Q_1 = Q_2$	$\frac{C_{++}C_{-}}{C_{+-}C_{+}}$	0.4980
$Q_3 = Q_4$	$\frac{C_{--}C_{+}}{C_{+-}C_{-}}$	0.0000

Constant	Formula	Approximated Value by Triangular-Cluster Model
Q_5	$\frac{C_{++}^2C_{-}^2}{C_{+-}^2C_{+}^2}$	0.0827
Q_6	$\frac{C_{++}C_{-}}{C_{+-}C_{+}}$	0.4980
Q_7	$\frac{C_{--}^2C_{+}^2}{C_{+-}^2C_{-}^2}$	0.0000
Q_8	$\frac{C_{--}C_{+}}{C_{+-}C_{-}}$	0.0000
Q_9	$\frac{C_{++}C_{-}^2}{C_{--}C_{+}^2}$	∞
Q_{10}	$\frac{C_{++}C_{-}}{C_{+-}C_{+}}$	0.4995
Q_{11}	$\frac{C_{++}C_{-}^2}{C_{--}C_{+}^2}$	∞
Q_{12}	$\frac{C_{+-}C_{-}}{C_{--}C_{+}}$	∞

Table 5.1: Equilibrium constants calculated for the $Li_{1/3}Mn_{2/3}$ system using pair approximation truncation scheme.

As can be observed, there are some infinite and zero equilibrium constants in the equilibrium state of this system. The reason is that all equilibrium constants are written in terms of pair and singlet concentrations and the concentration of $Li - Li$ cluster is zero in the final state of this regular system as shown in figure 1.3. Substituting these parameters into eq. (2.40), we notice that eqs. (2.40.1) and (2.40.2) are satisfied. However, eq. (2.40.3) becomes degenerate in this case as C_{--} is equal to zero and some parameters are infinite. In other words, in the limiting case of pair concentrations equal to zero, the system of algebraic equations can be re-written by eliminating the pair concentrations that are zero, as in Appendix 7.4.

Moreover, the equilibrium constants have to satisfy equilibrium conditions, specifically the ones presented in figures 2.4 and 2.10. In the chemical equilibrium, the rate of forward reaction has to be equal to the rate of reverse reaction. In other words, while the forward reaction produces a specific cluster, the backward reaction will destroy it with the same rate. The equilibrium constant can be written as the ratio of concentration of products in the reversible reaction over the concentration of reactants. In the final state of the $Li_{1/3}Mn_{2/3}$ system, some of the reversible reactions are satisfied even without the utilization of moment closure approximation. However, the following constants are not satisfied without the approximation: $Q_1 = \frac{k_1}{k_3}$, $Q_2 = \frac{k_2}{k_4}$, $Q_5 = \frac{k_9}{k_{11}}$, $Q_6 = \frac{k_{10}}{k_{12}}$. Considering Q_5 and figure 2.10, this constant can be calculated as $Q_5 = \frac{k_9}{k_{11}} = \frac{C_{(\dot{-}\widehat{+++})}}{C_{(\dot{+}\widehat{-++})}}$ before applying the moment closure approximation. By looking at figure 1.3 at equilibrium, we notice that $C_{\dot{-}\widehat{+++}}$ as the product of the reaction of k_9, is equal to zero at equilibrium, however, $C_{\dot{+}\widehat{-++}}$ as the reactant of the same reaction is not zero. In other words, Q_5 should be zero at equilibrium. However, it takes the value of 0.0827 which has been obtained by considering moment closure approximation for the higher order clusters. This discrepancy is being generated as the result of using moment closure approximation to make them consistent with other equations. Likewise, the original equilibrium constant values for Q_1, Q_2 and Q_6 will be different from their approximations. Consequently, all of the reversible reactions will satisfy the equilibrium constants as long as the higher order concentrations are written in terms of pairs or singlets.

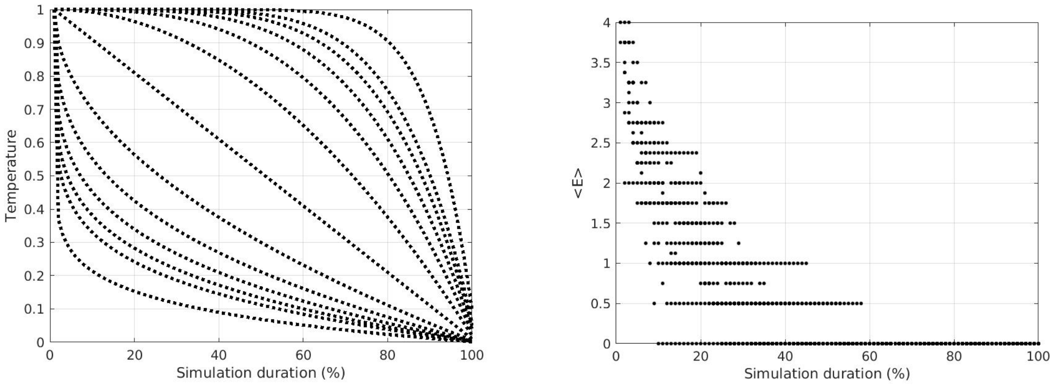
5.2 Optimal Moment Closure

As discussed in the previous chapters, the evolutionary system of equations is hierarchical, meaning that the rates of change of concentrations of lower order clusters are described in terms of higher order ones. Pair approximation truncation scheme was introduced in section 2.3 in order to close the dynamical system. In order to enhance the performance of the model, one needs to increase the accuracy of the pair approximation model. Previously, in the pair approximation model, the functional form was fixed for all 3-clusters or 4-clusters and it was only dependent on the shape of the triplet as stated in eqs. (2.31), (2.36) and (2.37). Section 4.1 proposes new functional forms for each triplet type to be approximated by the nearest-neighbor pairs inside the triplet. However, the new formulation suggests the functional forms according to the triplet type. The coefficients of this new model are determined using a nonlinear regression technique. In order to find the parameters of this model, the triplet and pair concentrations are obtained as functions of time (temperature) from the results of the simulated annealing approach. The unknown parameters of the new functional forms are calculated by fitting the outputs of the nonlinear model to the simulated annealing data.

It is noteworthy that the simulated annealing algorithm is an stochastic optimization method with judiciously selected updates at each iteration. Due to the stochastic nature of this method, it does not have repeatability on successive runs of the algorithm with the same initial condition. Moreover, the temperature profile can be chosen arbitrarily as long as the simulation converges to the equilibrium state at the end. These two conditions, namely, repeatability of the simulation and arbitrariness in the choice of temperature profile, forces us to consider an ensemble of simulated annealing data sets collected from different experiments with different temperature profiles. This can result in the system visiting a larger number of states. Different simulated annealing experiments are performed for the $Li_{1/3}Mn_{2/3}$ system by altering the temperature profile. The temperature profiles are generated based on the following equation:

$$T = 1 - \left(\frac{t}{N}\right)^{\alpha}, \quad \alpha \in \left\{10, 6, 5, 4, 3, 2, 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}, \frac{1}{6}, \frac{1}{10}\right\}, \tag{5.1}$$

where N is the total number of iterations in the simulated annealing experiment and t is the iteration index. Figure 5.1 demonstrates all different temperature profiles with simulation duration. Also, the energy of the lattice for the ensemble of all the experiments is demonstrated in this figure. As can be observed, all experiments have reached the equilibrium state after about 60% of the simulation duration.



(a) (b)

Figure 5.1: (a) Temperature profiles and (b) energy of the lattice for the ensemble of 13 different simulated annealing experiments in $Li_{1/3}Mn_{2/3}$ system, with the temperature profiles given in Eq. (5.1)

10^5 iterations were used for each of the simulated annealing experiments and 100 equally spaced samples are taken from simulated annealing data for each experiment. The reason is to mitigate the noise of the data and obtain a close to monotonic behaviour from the data. An ensemble of the data corresponding to different temperature profiles is used to perform regression analysis for each triplet type. Table 5.2 presents the results of this analysis.

Triplet Type	PA	OA	γ_1	γ_2	γ_3	γ_4
$C_{\overline{+++}}$	$\frac{1}{5}\frac{C_{++}^2}{C_+}$	$\frac{1}{5}\frac{C_{++}^{\gamma_1}}{C_+^{\gamma_2}}$	2.75	1.75	-	-
$C_{\overline{---}}$	$\frac{1}{5}\frac{C_{--}^2}{C_-}$	$\frac{1}{5}\frac{C_{--}^{\gamma_1}}{C_-^{\gamma_2}}$	1.41	0.41	-	-
$C_{\overline{+-+}}$	$\frac{1}{5}\frac{C_{+-}^2}{C_-}$	$\frac{1}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	2.01	-2.32	3.33	-
$C_{\overline{-+-}}$	$\frac{1}{5}\frac{C_{+-}^2}{C_+}$	$\frac{1}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	0	2.72	-3.72	-
$C_{\overline{++-}}$	$\frac{1}{5}\frac{C_{++}C_{+-}}{C_+}$	$\frac{1}{5}\frac{C_{++}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	2.51	5.83	-2.32	9.67
$C_{\overline{--+}}$	$\frac{1}{5}\frac{C_{--}C_{+-}}{C_-}$	$\frac{1}{5}\frac{C_{--}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	1.06	1.80	-2.67	4.53
$C_{\widehat{+++}}$	$\frac{2}{5}\frac{C_{++}^2}{C_+}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}}{C_+^{\gamma_2}}$	0	-1	-	-
$C_{\widehat{---}}$	$\frac{2}{5}\frac{C_{--}^2}{C_-}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}}{C_-^{\gamma_2}}$	1.47	0.47	-	-
$C_{\widehat{+-+}}$	$\frac{2}{5}\frac{C_{+-}^2}{C_-}$	$\frac{2}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	1.94	-1.32	2.26	-
$C_{\widehat{-+-}}$	$\frac{2}{5}\frac{C_{+-}^2}{C_+}$	$\frac{2}{5}\frac{C_{+-}^{\gamma_1}}{C_+^{\gamma_2}C_-^{\gamma_3}}$	4.29	-1.33	4.62	-
$C_{\widehat{++-}}$	$\frac{2}{5}\frac{C_{++}C_{+-}}{C_+}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	20.94	0	3.75	16.19
$C_{\widehat{--+}}$	$\frac{2}{5}\frac{C_{--}C_{+-}}{C_-}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	1.23	2.95	-2.35	5.53
$C_{\overset{\triangle}{+++}}$	$\frac{2}{5}\frac{C_{++}^3}{C_+^3}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}}{C_+^{\gamma_2}}$	4.18	3.18	-	-
$C_{\overset{\triangle}{---}}$	$\frac{2}{5}\frac{C_{--}^3}{C_-^3}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}}{C_-^{\gamma_2}}$	2.06	1.06	-	-
$C_{\overset{\triangle}{++-}}$	$\frac{2}{5}\frac{C_{++}C_{+-}^2}{C_+^2C_-}$	$\frac{2}{5}\frac{C_{++}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	1.31	3.25	-1.32	4.89
$C_{\overset{\triangle}{--+}}$	$\frac{2}{5}\frac{C_{--}C_{+-}^2}{C_+C_-^2}$	$\frac{2}{5}\frac{C_{--}^{\gamma_1}C_{+-}^{\gamma_2}}{C_+^{\gamma_3}C_-^{\gamma_4}}$	1.02	0.60	-1.43	2.05

Table 5.2: Exponents of the optimal closure approximation scheme for each triplet type. PA stands for pair approximation and OA refers to the optimal approximation model.

In order to assess the accuracy of the optimal closure model as compared to the pair approximation the triplet concentrations are plotted against the pair concentrations for each specific triplet type in figures 5.2, 5.3 and 5.4. Black dots represent the results of the ensemble of simulated annealing experiments which serve as the "true data". The predictions of the triplet concentrations from the pair concentrations have been investigated by both pair approximation and the optimal approximation models. Note that some of the triple concentrations are written as functions of two different pair concentrations (such as $C_{\overline{++-}}$), hence, surface plots are presented instead of line plots.

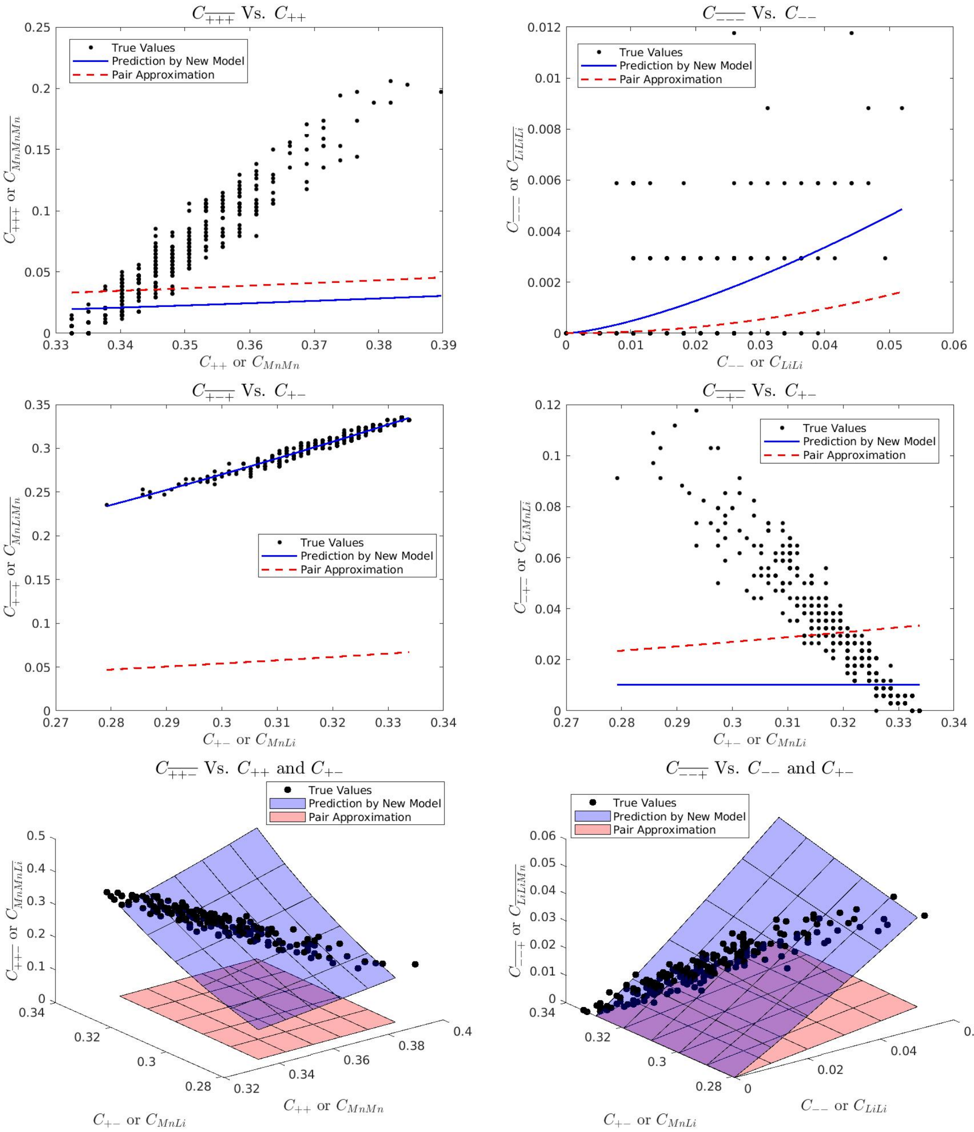


Figure 5.2: Experimental data (black dots) and linear triplet concentration predictions from pair concentrations via pair approximation (red) and optimal approximation (blue) schemes for the $Li_{1/3}Mn_{2/3}$ system.

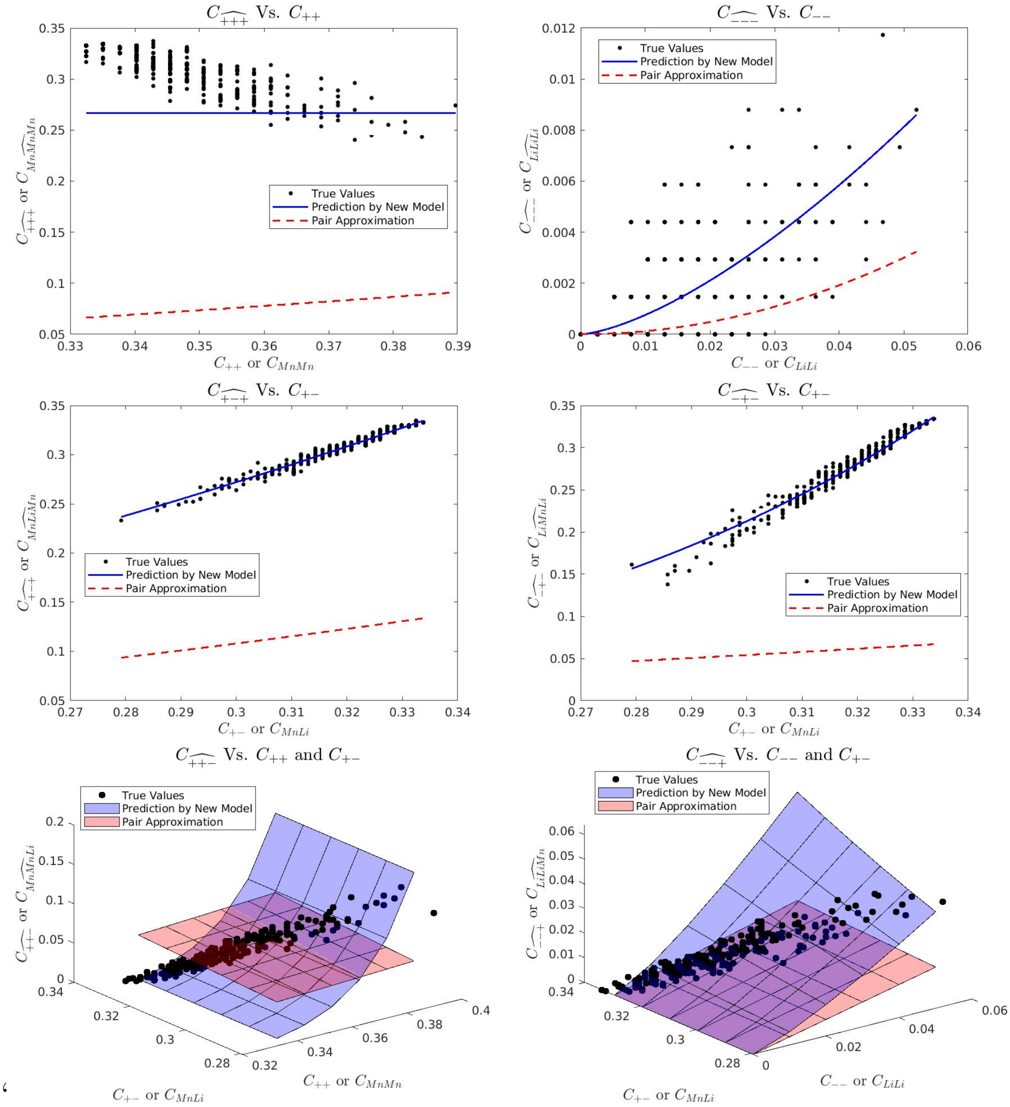


Figure 5.3: Experimental data (black dots) and open triplet concentration predictions from pair concentrations via pair approximation (red) and optimal approximation (blue) schemes for the $Li_{1/3}Mn_{2/3}$ system.

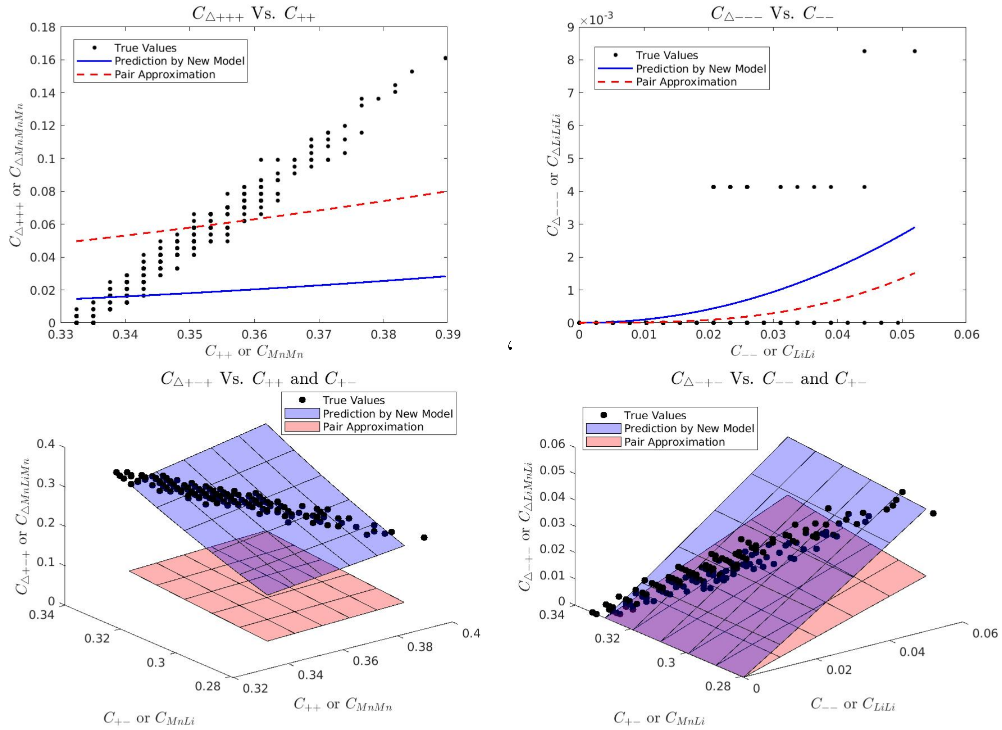


Figure 5.4: Experimental data (black dots) and closed triplet concentration predictions from pair concentrations via pair approximation (red) and optimal approximation (blue) schemes for the $Li_{1/3}Mn_{2/3}$ system.

As can be observed, the prediction accuracy using the optimal closure model is significantly improved in almost all of the cases in comparison to the pair approximation model. The mean-square errors of the non-linear regression analysis for each triplet type is also presented in figure 5.5.

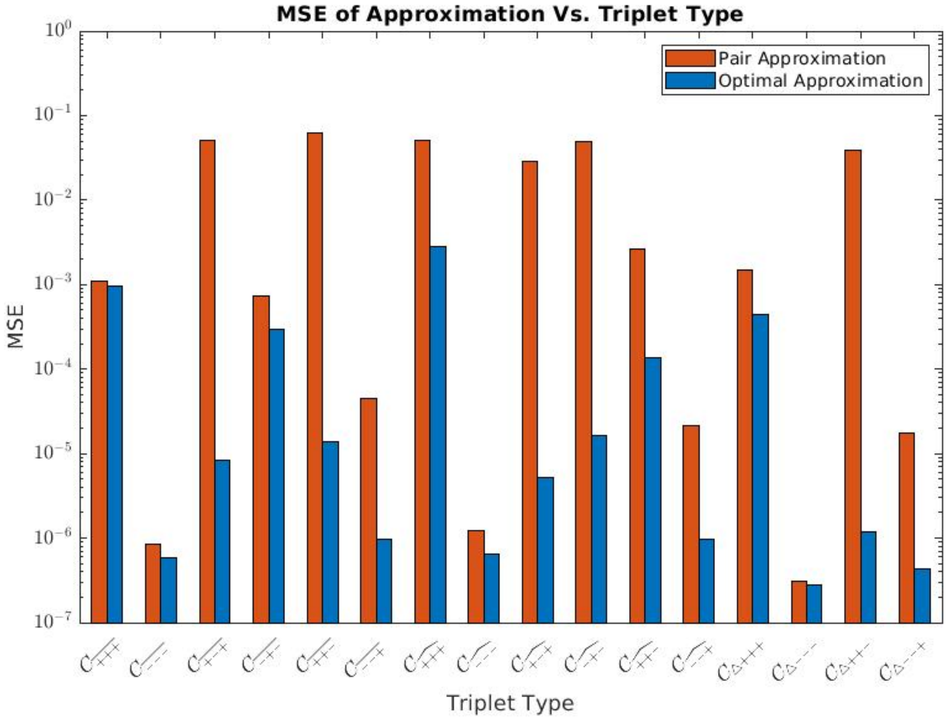


Figure 5.5: Mean-square errors of the regression analysis using PA (red bars) and OA (blue bars) schemes for each triplet type in comparison to the true data for the $Li_{1/3}Mn_{2/3}$ system.

As can be observed, the optimal closure model outperforms the pair approximation model by a few orders of magnitude in most cases. These two truncation schemes will be used for solving the inverse modeling problem in order to calculate the rate constants of the model as described in the next section.

5.3 Inverse Problem for Calculation of Rate Constants

In this section we will be calculating the rate constants of the cluster approximation model by minimizing the mismatch between the experimental data and the model outputs. The rate constants will be calculated by assuming that they are either constant or temperature-dependent in sections 5.3.1 and 5.3.2.

5.3.1 Constant Parameters

Considering constant parameters in the cluster approximation model, the inverse modeling approach will be used to calculate these parameters by minimizing the discrepancy between simulated annealing results and the model outputs. The simulated annealing experiment used here is described in chapter 1. The temperature will be decreased linearly during the process. The initial and final temperatures are chosen to be one and zero, respectively. In order to truncate the hierarchy of the system of ODEs, the pair approximation and optimal truncation schemes are used. The optimization problem starts with a random initial guess and converges to a local minimum. In order to probe different local minimums this optimization problem is solved 100 times independently and the results are collected. Table 5.3 presents 10 best results of solving the inverse problem using the pair approximation scheme where the lowest values of the error functional were obtained at the end of iterations. The results are sorted based on their error functional values. 8 unique parameters, k_1 to k_8, are involved in the two-element two-cluster model for the $Li_{1/3}Mn_{2/3}$ system.

k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	Function Value
5.07999332e-04	1.01786072e-01	1.01996740e-03	2.04367348e-01	0	0	4.56008251e-02	1.94582406e-02	1.13322747e-03
3.51388596e-03	8.97602673e-02	7.05522416e-03	1.80221786e-01	0	0	3.63248872e-02	5.65610343e-02	1.13322748e-03
6.50987820e-04	1.01211647e-01	1.30706148e-03	2.03214010e-01	0	0	7.91509741e-03	1.70196579e-01	1.13322748e-03
2.57437202e-02	8.36746510e-04	5.16885632e-02	1.68003013e-03	0	0	1.16382089e-03	1.97214229e-01	1.13322751e-03
2.44660734e-02	5.93709763e-03	4.91232880e-02	1.19205788e-02	0	0	1.34488380e-02	1.48073551e-01	1.13322765e-03
8.51382014e-04	1.00409558e-01	1.70940900e-03	2.01603569e-01	0	0	8.61264635e-03	1.67319037e-01	1.13322871e-03
1.96907011e-02	2.49682472e-02	3.95352351e-02	5.01315631e-02	0	0	5.41535284e-03	1.80438140e-01	1.13323439e-03
7.33479572e-05	1.04372869e-01	1.47304016e-04	2.09561151e-01	0	0	5.07526120e-02	6.64693891e-04	1.13370810e-03
2.64111722e-02	4.94505491e-03	5.30286824e-02	9.92873927e-03	0	0	7.33035082e-03	1.80143597e-01	1.15449423e-03
5.46541687e-04	9.95803073e-02	1.09735298e-03	1.99938586e-01	0	0	1.00260496e-01	7.28701238e-01	3.04122211e-03

Table 5.3: 10 best results of solving the inverse problem in (4.4) using the pair approximation truncation scheme.

As can be observed, different trials are converging to different local minima. Some of the parameters such as k_5 and k_6 remain the same for all of these trials, however, the others are changing by few orders of magnitude. This indicates varying sensitivity of the model to different parameters. In order to assess the performance of the cluster approximation model using these parameters, the system of ODEs is solved numerically as a forward problem using the best results of the inverse modeling approach. More specifically, the 3 best results of the calculation of parameters (with the lowest error function values) are selected and the system of ODEs is solved numerically as an initial value problem. Figure 5.6 demonstrates the pair concentrations evolved in time using the cluster approximation model compared to the experimental data.

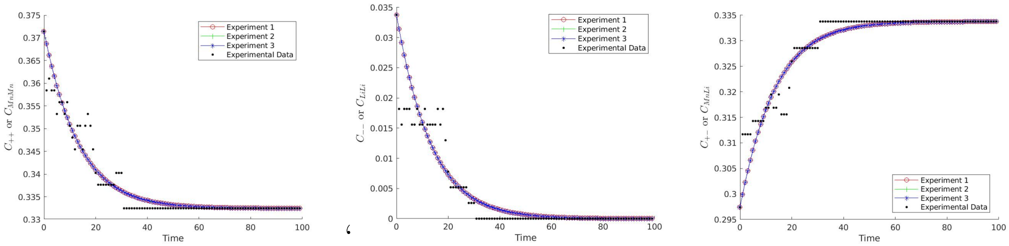


Figure 5.6: The evolutionary trajectory of pair concentrations using the cluster approximation model truncated by the pair approximation scheme. Black dots correspond to the experimental data. Experiments 1, 2 and 3 are obtained as the solution of the forward problem using the best parameters of the inverse problem.

As can be seen, the difference between the results are negligible for 3 different set of parameters even though some of their rate constants are different by few orders of magnitude.

The same analysis is performed by using the optimal approximation truncation scheme. The inverse problem is again solved 100 independent trials. Note that due to the new closure scheme, the equilibrium constants are different from Table 5.1. The new equilibrium constants are presented in Table 5.4. These new equilibrium constants are used as the constraint of the inverse modeling approach. The 10 best results of solving this problem are presented in Table 5.5.

Constant	Formula	Approximated Value by Two-Cluster Model
Q_1	$\frac{C_{++}^{20.94}C_{-}^{-13.93}}{C_{+-}^{1.94}C_{+}^{5.07}}$	0.0281
Q_2	$\frac{C_{++}^{2.51}C_{-}^{-6.34}}{C_{+-}^{-3.82}C_{+}^{0}}$	1.0095
Q_3	$\frac{C_{--}^{1.23}C_{+}^{1.02}}{C_{+-}^{1.34}C_{-}^{0.91}}$	0
Q_4	$\frac{C_{--}^{1.06}C_{+}^{5.39}}{C_{+-}^{-1.8}C_{-}^{8.25}}$	0

Table 5.4: Equilibrium constants calculated for $Li_{1/3}Mn_{2/3}$ system using optimal approximation truncation scheme.

k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	Function Value
1.17200538e-02	9.21985714e-01	4.16770535e-01	9.14415115e-01	0	0	7.00308010e-16	4.19054317e-02	9.18351205e-04
2.75342644e-02	2.19483359e+00	9.79131181e-01	2.17426407e+00	0	0	2.73545836e-08	4.18370670e-02	9.31666648e-04
1.00207681e-02	7.83872314e-01	3.56343176e-01	7.76526029e-01	0	0	4.64664075e-16	4.18994411e-02	9.32743512e-04
1.00011892e-02	7.82881400e-01	3.55646917e-01	7.75544400e-01	0	0	1.18135128e-05	4.19431264e-02	9.32757084e-04
3.66990299e-02	2.98789522e+00	1.30503448e+00	2.95998814e+00	0	0	1.29445702e-15	4.20500621e-02	9.33357848e-04
2.14109117e-02	1.59780412e+00	7.61381926e-01	1.58282983e+00	0	0	2.80246554e-11	4.10202393e-02	9.33454679e-04
2.74975316e-02	2.19895426e+00	9.77824948e-01	2.17834613e+00	0	0	7.53164713e-06	4.22289328e-02	9.33721094e-04
1.94615625e-02	1.47971229e+00	6.92062167e-01	1.46584474e+00	0	0	6.20284780e-07	4.13432321e-02	9.34553059e-04
1.57181800e-02	1.21423278e+00	5.58945752e-01	1.20285325e+00	0	0	7.51773325e-07	4.15682069e-02	9.34597982e-04
1.16306491e-02	9.13472126e-01	4.13591263e-01	9.04911257e-01	0	0	1.78329504e-15	4.18890802e-02	9.34685820e-04

Table 5.5: 10 best results of solving the inverse modeling problem in (4.4) using the optimal approximation truncation scheme.

As can be observed, the objective function values using the optimal closure truncation scheme are slightly smaller than those of pair approximation model. Also, some of the parameters such as k_5 and k_6 are always the same. However, the rest of the parameters are changing slightly in different trials. It is noteworthy that the order of magnitude of parameters is remaining the same in most of the trials which is an important improvement comparing to the pair approximation model results as in Table 5.3. The optimal closure model is converging to local minima that are producing more accurate fits than in the pair approximation case. In order to evaluate the performance of the cluster approximation model using the calculated parameters, the system of ODEs is solved numerically as an initial value problem. The parameters of the 3 best results of the inverse modeling problem is used along with the optimal closure approximation scheme. The results are demonstrated in figure 5.7. As can be observed, different parameters result in approximately identical evolutionary trajectories of pair concentrations, indicating the low sensitivity of the cluster approximation model to the variation of the parameters.

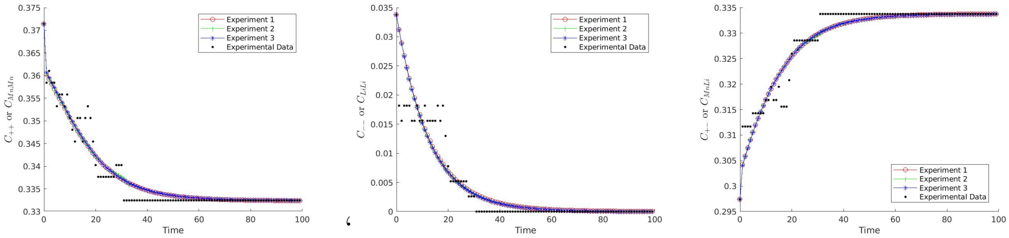


Figure 5.7: The evolutionary trajectory of pair concentrations using the cluster approximation model truncated by the optimal approximation scheme. Black dots represent the experimental data. Experiments 1, 2 and 3 are the solutions of the forward problem using the best parameters obtained from the inverse problem.

5.3.2 Temperature-Dependent Parameters

In this section we consider the parameters that are temperature-dependent, giving the model more flexibility to fit the experimental data. The formulation used here is presented in section 4.3. We try to minimize the discrepancy between the experimental data and the model outputs by assuming parameters (rate constants) that can change with time. In a step-like manner, the simulation window is divided into a few subintervals, allowing different vectors of parameters to fit the data in each subinterval. Note that in the case of constant parameters the optimization initiates with an initial guess of parameters and is solved 100 times. The best result of the inverse problem (corresponding to the lowest error functional value) is used as the initial guess for solving the inverse problem with 2 subintervals. In other words, the vector of parameters with lowest error functional value is used as the vector of parameters for each subinterval. This optimization problem again is solved 100 times, using the result of each trial as the initial guess of the next trial. Solving them 100 times ensures that the error functional values converge to each other in the subsequent trials. Similarly, the best results for 2 subintervals is used as the initial guess of 4 subintervals. Note that the first and second subintervals out of 4 subintervals are getting the vector of parameters for the first subinterval out of 2 subintervals. Similarly this process continues for 8 subintervals. The best results of each problem are chosen and their error function values are presented in Table 5.6 using both pair approximation and optimal approximation truncation schemes.

Objective Function Value via Pair Approximation			
1 subinterval	2 subintervals	4 subintervals	8 subintervals
1.13322747826335e-03	1.09716778134897e-03	9.84297621794587e-04	9.41550238311428e-04
Objective Function Value via Optimal Approximation			
1 subinterval	2 subintervals	4 subintervals	8 subintervals
9.18351205546793e-04	8.58598052208305e-04	7.93552785604102e-04	7.90988553261657e-04

Table 5.6: Error function values obtained by solving the inverse problem using pair approximation and optimal approximation schemes and different number of subdivisions of the time window.

As can be observed, the error function values are decreasing as the number of subintervals increases, giving the model more flexibility on fitting the experimental data. Also, for each case of the number of subintervals, the optimal approximation scheme outperforms the pair approximation scheme in terms of the accuracy of the fits.

Note that this inverse modeling problem is ill-posed, meaning that no unique solution can be found in different trials. In other words, small changes in the initial guesses of the parameters can lead to a significantly different parameters. It is noteworthy that we are interested in a vector of parameters such that the resulting time-dependent concentrations can match the experimental data. There might be more than one solution to this problem with slighly different performances. The piecewise-constant rate constants inferred using different numbers of subintervals are presented in figures 5.8 and 5.9.

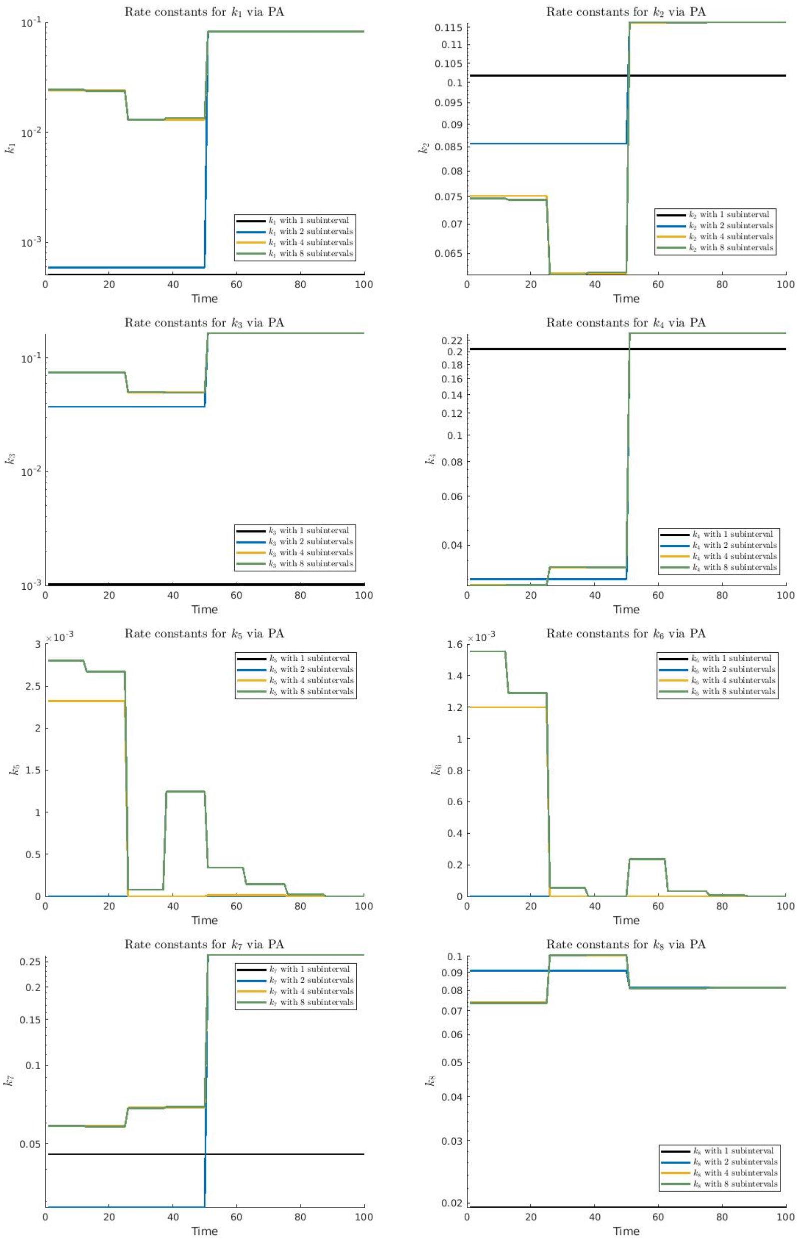


Figure 5.8: Rate constants obtained by solving the inverse modeling problem as constant or temperature-dependent parameters via pair approximation scheme using different numbers of subintervals.

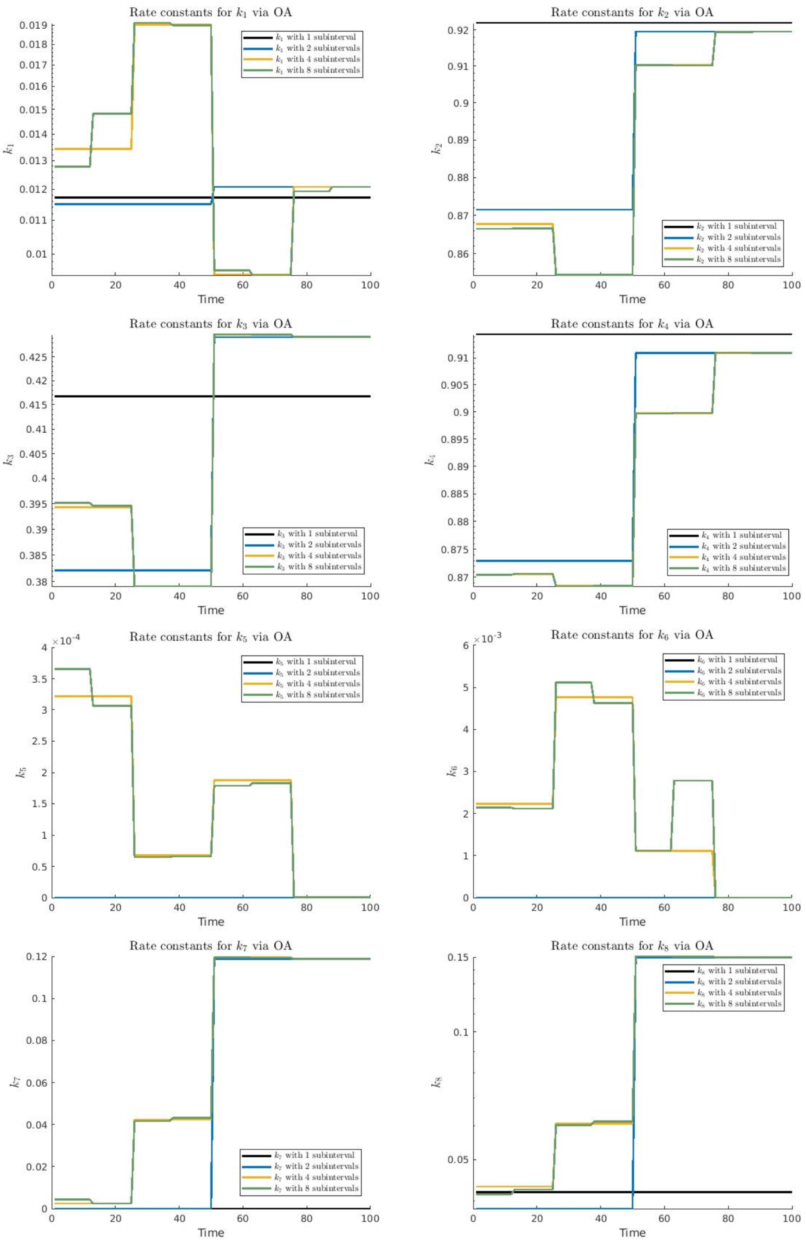


Figure 5.9: Rate constants obtained by solving the inverse modeling problem as constant or temperature-dependent parameters via optimal approximation scheme using different numbers of subintervals.

As can be observed, in most of the cases the parameters obtained using 2, 4 and 8 subintervals are close to each other. However, in some cases the constant parameter is different from the temperature dependent ones. Normally, when an interval is split into 2 subintervals, it is plausible to expect that the rate constant will get higher values in one subinterval and lower values for the other one. Most of the cases are in accordance with this statement, however, some of them do not follow this trend. This behaviour can be justified by the sensitivity of the model to parameters. The model is less sensitive to some of the parameters, allowing them to change significantly from one trial to another. Hence, the results for different number of subintervals might vary significantly.

5.4 Model Accuracy

In this section, we present the results as regards the accuracy of the two-cluster model in terms of quantities not matched in the inverse problem. Two types of approximations has been used here, the pair approximation and the optimal closure. The performance of these two methods will be investigated by reconstructing the triple concentrations and comparing them to the experimental data. There are three types of triplets: triangular clusters, open triplets with 120 deg bonds and open triplets with 180 deg bonds as shown in figure 2.1. In these approximations, each triplet has been written in terms of pair and singlet concentrations. Also the true triple concentrations are generated from the simulated annealing results. Figures 5.10, 5.11 and 5.12 demonstrate the sampled simulated annealing data, along with reconstruction of triple concentrations from pair and singlet concentrations. The inverse problem was solved in order to generate the rate constants of the model as constant parameters. The initial value problem for the ODE system was then solved using the best vector of parameters for both pair approximation and optimal approximation schemes. The time evolution of pair concentrations are used to reconstruct the concentrations of triplets based on the formulas presented in Table 5.2. Note that the reconstructed triple concentrations can be obtained in two ways. First, we can use the simulated annealing data in time for pair concentrations and reconstruct the triple concentrations using the pair approximation and optimal approximation formulas. However, as another approach, the time evolution of pair concentrations obtained by solving the system of ODEs can be used to reconstruct the triple concentrations. Figures 5.10, 5.11 and 5.12 present the results using both approaches and both truncation schemes. Note that in some figures the experimental data (black dots) are not visible as they are getting zero values and logarithmic scale is used.

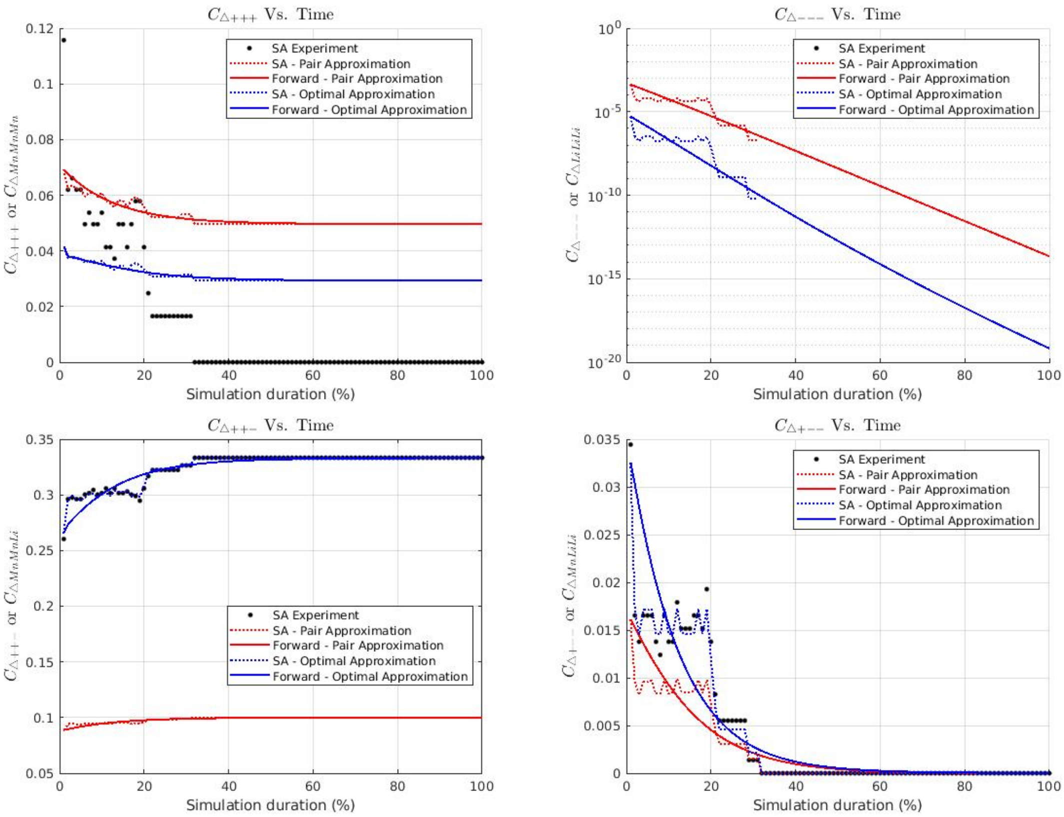


Figure 5.10: Reconstruction of closed triple concentrations using pair approximation and optimal approximation truncation schemes. Black dots represent the simulated annealing data. Blue and red lines represent the reconstructions by using the optimal approximation and pair approximation truncation schemes respectively. Solid lines refer to triple concentration reconstructions by using pair concentrations resulted from solving the system of ODEs. However, the dotted lines refer to reconstructions resulted from using pair concentrations from the simulated annealing data.

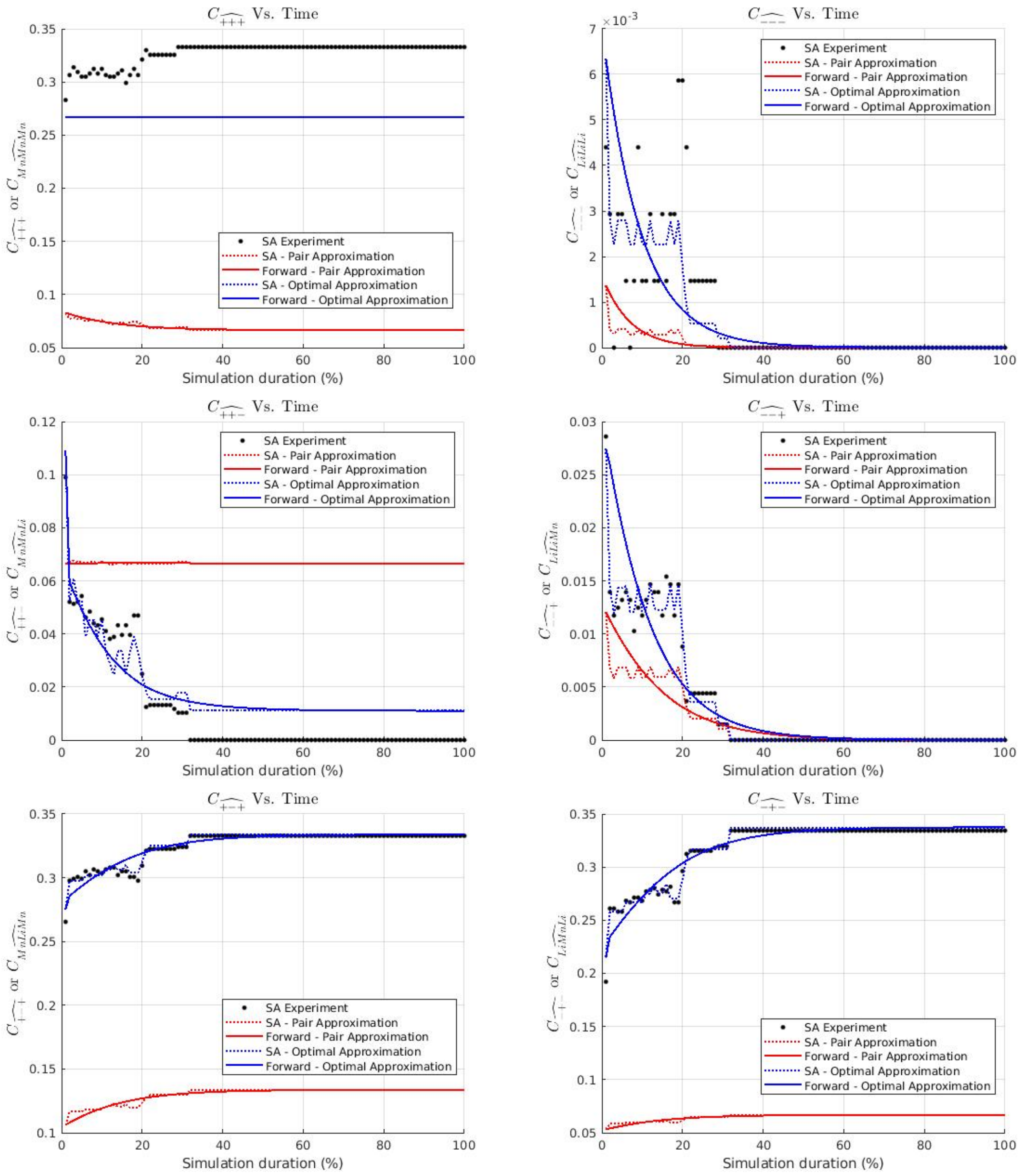


Figure 5.11: Reconstruction of open triple concentrations using pair approximation and optimal approximation truncation schemes. Black dots represent the simulated annealing data. Blue and red lines represent the reconstructions by using the optimal approximation and pair approximation truncation schemes respectively. Solid lines refer to triple concentration reconstructions by using pair concentrations resulted from solving the system of ODEs. However, the dotted lines refer to reconstructions resulted from using pair concentrations from the simulated annealing data.

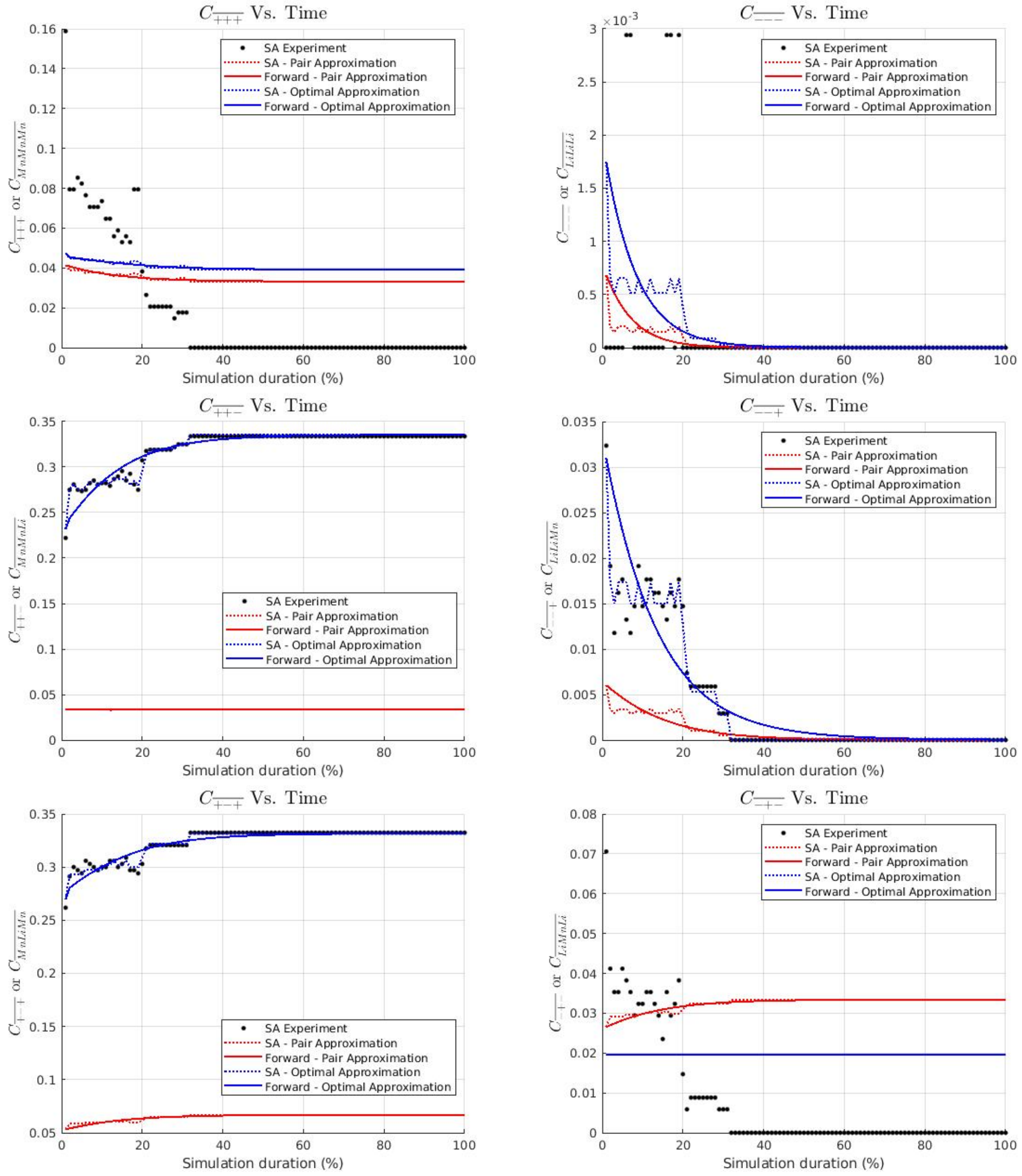


Figure 5.12: Reconstruction of linear triple concentrations using pair approximation and optimal approximation truncation schemes. Black dots represent the simulated annealing data. Blue and red lines represent the reconstructions by using the optimal approximation and pair approximation truncation schemes respectively. Solid lines refer to triple concentration reconstructions by using pair concentrations resulted from solving the system of ODEs. However, the dotted lines refer to reconstructions resulted from using pair concentrations from the simulated annealing data.

As can be observed, in almost all cases, the reconstructed triple concentrations are more accurate by using the optimal closure model than when the pair approximation is used. The reason is the use of triple concentrations in performing the regression analysis and building the optimal closure model. Note that in reconstruction of $(\widehat{+++})$ cluster in figure 5.11, both models are performing poorly. The reason is that the exponents of the functional forms in building the optimal closure approximation model are forced to be positive as show in figure 5.3, in order to prevent the system of ODEs from blowing up. This restricts the optimal closure model to predict the triple concentrations in some cases and decreases the accuracy of the model.

Chapter 6

Summary and Conclusions

In this study, we were interested in discovering the micro-structure concentrations of the NMC layer of the cathode of Li-ion batteries. Different dynamical systems are proposed for describing the evolution of micro-structure concentrations in time. Here is a summary of key steps we performed.

- A 2D triangular lattice with two or three types of elements has been assumed in our model which is a representative of the NMC layer of Li-ion batteries' cathodes.
- Simulated annealing approach was used to obtain the structure of the lattice. However, this approach is computationally heavy and provides unnecessary information for comparison to the NMR spectroscopy data.
- Alternatively, a dynamical system for obtaining the micro-structure concentrations is developed. Two different cluster approximation models are built based on the order of the clusters, namely, two-cluster model and triangular-cluster model.

The former describes the evolution of the concentrations of 2-clusters in terms of concentrations of 3-clusters. The latter relates the concentrations of 3-clusters to the concentrations of 4-clusters.

- The hierarchical dynamical systems for the evolution of concentrations are closed using standard moment closure schemes. Also, an algorithm for an optimal closure of the hierarchical systems is proposed and validated.

- An algorithm is used based on the inverse modeling approach to derive the parameters of the model by minimizing the mismatch between the experimental data and the model outputs.

- The parameters of the model, which control the evolution of different clusters in the lattice, are considered to be either constant or temperature-dependent.

The following conclusions can be drawn from this study.

- No global minima is found by the solution of the inverse problem. Different trials of solving the inverse problem with different initial guesses converge to a different local minima. Therefore, the inverse problem is ill-posed.

- The sensitivity of the model to some of its parameters is low, hence allowing them to change significantly from one trial to another. However, some of the parameters remain essentially unchanged between different trials, suggesting higher sensitivity of the model to the small changes of these parameters.

- The optimal approximation model results are more accurate, as the resulting parameters mostly remain in the same order of magnitude between different trials of solving the inverse problem. However, the precision of the results are lower in reconstructing the parameters of the model using the pair approximation scheme.

- The performance of the two-element two-cluster model using both truncation schemes is investigated by solving the system of ODEs using the reconstructed parameters. The pair concentrations obtained by both truncation schemes are following the trajectory of the experimental data, with slightly better results for the optimal approximation model.

- The prediction capability of both closure models is tested by reconstructing the concentrations of different 3-clusters in time. The optimal approximation closure scheme is outperforming the pair approximation one by producing far more accurate predictions for all triplet types. This shows that the optimal closure approximation better represents the intrinsic dynamics of the system than the nearest-neighbor approximation.

Overall, these findings result in a better prediction of micro-structure concentrations by using optimal closure truncation scheme. However, many other questions remain unanswered. The following points highlight some of the possible future avenues of this study.

- Exploring the prediction accuracy of the reconstructed triple concentrations for the different systems with different composition of materials.
- Exploring the inverse modeling problem based on the triangular-clusters for reconstructing the concentrations of triangular clusters and comparing the performance of the model with the predictions of the two-cluster model.
- Building cluster approximation models that can match to the NMR spectroscopy experimental data directly by eliminating the need for the simulated annealing data.
- Quantifying the uncertainty in the parameters of the model, obtaining the distribution of each one of the parameters and their corresponding confidence intervals using statistical inference techniques.

Chapter 7

Appendix

7.1 Theorems

Theorem 7.1.1. *Assuming 2-clusters in a 2D triangular lattice, each site can have 6 nearest neighbors which are positioned in equal angles around the site in the middle. Every rotation of the 2-cluster in the form of* ($\oplus\ominus$) *will have the same concentration.*

Proof. Assuming one site with positive element, the concentration of the positive element can be obtained by summing over concentrations of 2-clusters, in which the second site can be occupied by all possible elements of the system. Note that

($\bullet$) states an unspecified state in the lattice.

$$\begin{aligned}
C\left(\oplus\right) &= C\left(\oplus\bullet\right) = C\left(\oplus\oplus\right) + C\left(\oplus\ominus\right)\\
&= C\left(\bullet\oplus\right) = C\left(\oplus\oplus\right) + C\left(\ominus\oplus\right)\\
&= C\left(\oplus^{\bullet}\right) = C\left(\oplus^{\oplus}\right) + C\left(\oplus^{\ominus}\right)\\
&= C\left({}^{\bullet}\oplus\right) = C\left({}^{\oplus}\oplus\right) + C\left({}^{\ominus}\oplus\right)\\
&= C\left(\oplus_{\bullet}\right) = C\left(\oplus_{\oplus}\right) + C\left(\oplus_{\ominus}\right)\\
&= C\left({}_{\bullet}\oplus\right) = C\left({}_{\oplus}\oplus\right) + C\left({}_{\ominus}\oplus\right)\\
\Rightarrow C\left(\oplus\ominus\right) &= C\left(\ominus\oplus\right) = C\left(\oplus^{\ominus}\right) = C\left({}^{\ominus}\oplus\right) = C\left(\oplus_{\ominus}\right) = C\left({}_{\ominus}\oplus\right)
\end{aligned} \tag{7.1}$$

□

Theorem 7.1.2. *Assuming linear clusters in a 2D lattice with straight angle between the bonds, 3-clusters in the form of* ($\oplus\oplus\ominus$) *and* ($\ominus\oplus\oplus$) *have equal concentrations. This, also, can be understood via translational symmetry of the lattice. Likewise, linear 3-clusters in the form of* ($\ominus\ominus\oplus$) *and* ($\oplus\ominus\ominus$) *have equal concentrations.*

Proof. Assuming 2-clusters with same elements on both sites (both positive or both negative elements), the concentration of the 2-cluster can be calculated by summing over concentrations of linear 3-clusters, in which the third site can be occupied by all possible elements of the system. Note that ($\bullet$) states an unspecified state in the lattice.

$$\begin{aligned}
C\left(\oplus\oplus\right) &= C\left(\oplus\oplus\bullet\right) = C\left(\oplus\oplus\ominus\right) + C\left(\oplus\oplus\oplus\right)\\
&= C\left(\bullet\oplus\oplus\right) = C\left(\ominus\oplus\oplus\right) + C\left(\oplus\oplus\oplus\right)\\
&\Rightarrow C\left(\oplus\oplus\ominus\right) = C\left(\ominus\oplus\oplus\right)
\end{aligned} \tag{7.2}$$

$$\begin{aligned} C(\ominus\ominus) &= C(\ominus\ominus\bullet) = C(\ominus\ominus\ominus) + C(\ominus\ominus\oplus) \\ &= C(\bullet\ominus\ominus) = C(\ominus\ominus\ominus) + C(\oplus\ominus\ominus) \\ &\Rightarrow C(\ominus\ominus\oplus) = C(\oplus\ominus\ominus) \end{aligned} \tag{7.3}$$

□

Theorem 7.1.3. *Assuming angled clusters in a triangular 2D lattice with obtuse angles between the bonds (120 degrees angle), all angled 3-clusters containing a* ($\ominus\ominus$) *cluster and a positive element occupying the third site, have equal concentrations. The third site has to be in a position to hold an obtuse angle with the other two elements. Four different configurations can be found for the aforementioned cluster; Each of which can be obtained by rotating or flipping the others, supporting the translational symmetry of the lattice. Likewise, angled 3-clusters containing a* ($\oplus\oplus$) *cluster and a third negative element are also translations of each other.*

Proof. Assuming 2-clusters with same elements on both sites (both positive or both negative elements), the concentration of the 2-cluster can be calculated by summing over concentrations of obtuse-angled 3-clusters, in which the third site can be occupied by all possible elements of the system. Note that ($\bullet$) states an unspecified state in the lattice.

$$\begin{aligned} C\left(\oplus\oplus\right) &= C\left({}^{\bullet}\oplus\oplus\right) = C\left({}^{\oplus}\oplus\oplus\right) + C\left({}^{\ominus}\oplus\oplus\right) \\ &= C\left(\oplus\oplus^{\bullet}\right) = C\left(\oplus\oplus^{\oplus}\right) + C\left(\oplus\oplus^{\ominus}\right) \\ &= C\left({}_{\bullet}\oplus\oplus\right) = C\left({}_{\oplus}\oplus\oplus\right) + C\left({}_{\ominus}\oplus\oplus\right) \\ &= C\left(\oplus\oplus_{\bullet}\right) = C\left(\oplus\oplus_{\oplus}\right) + C\left(\oplus\oplus_{\ominus}\right) \\ \Rightarrow C\left({}^{\ominus}\oplus\oplus\right) &= C\left(\oplus\oplus^{\ominus}\right) = C\left({}_{\ominus}\oplus\oplus\right) = C\left(\oplus\oplus_{\ominus}\right) \end{aligned} \tag{7.4}$$

$$\begin{aligned} C\left(\ominus\ominus\right) &= C\left({}^{\bullet}\ominus\ominus\ \right) = C\left({}^{\ominus}\ominus\ominus\ \right) + C\left({}^{\oplus}\ominus\ominus\ \right) \\ &= C\left(\ \ominus\ominus^{\bullet}\right) = C\left(\ \ominus\ominus^{\ominus}\right) + C\left(\ \ominus\ominus^{\oplus}\right) \\ &= C\left({}_{\bullet}\ominus\ominus\ \right) = C\left({}_{\ominus}\ominus\ominus\ \right) + C\left({}_{\oplus}\ominus\ominus\ \right) \\ &= C\left(\ \ominus\ominus_{\bullet}\right) = C\left(\ \ominus\ominus_{\ominus}\right) + C\left(\ \ominus\ominus_{\oplus}\right) \\ \Rightarrow C\left({}^{\oplus}\ominus\ominus\ \right) &= C\left(\ \ominus\ominus^{\oplus}\right) = C\left({}_{\oplus}\ominus\ominus\ \right) = C\left(\ \ominus\ominus_{\oplus}\right) \end{aligned} \tag{7.5}$$

Note that the concentration of angled $(\widehat{---})$ will be the same regardless of its orientation, due to the symmetry of the system. Same happens for angled $(\widehat{+++})$ cluster. ☐

Theorem 7.1.4. *Assuming angled clusters in a triangular 2D lattice with acute angle between the bonds (60 degrees angle), all angled 3-clusters containing a* $(\ominus\ominus)$ *cluster and a positive element occupying the third site, have equal concentrations. The third site have to be in a position to hold an acute angle with the other two elements. Each one the configurations of this form can be obtained by rotating or flipping the others, supporting the translational symmetry of the lattice. Likewise, angled 3-clusters containing a* $(\oplus\oplus)$ *cluster and a third negative element, have also same concentrations.*

Proof. Assuming 2-clusters with same elements on both sites (both positive or both negative elements), the concentration of the 2-cluster can be calculated by summing over concentrations of acute-angled 3-clusters, in which the third site can be occupied by all possible elements of the system. Note that $(\bullet)$ states an unspecified state in the lattice.

$$\begin{aligned}
C\left(\oplus\oplus\right) &= C\left(\oplus\overset{\bullet}{}\oplus\right) = C\left(\overset{\oplus}{\oplus\oplus}\right) + C\left(\overset{\ominus}{\oplus\oplus}\right)\\
&= C\left(\underset{\bullet}{\oplus\oplus}\right) = C\left(\underset{\oplus}{\oplus\oplus}\right) + C\left(\underset{\ominus}{\oplus\oplus}\right)\\
&= C\left(\overset{\oplus}{\oplus\,\bullet}\right) = C\left(\overset{\oplus}{\oplus\oplus}\right) + C\left(\overset{\oplus}{\oplus\ominus}\right)\\
&= C\left(\overset{\oplus}{\bullet\,\oplus}\right) = C\left(\overset{\oplus}{\oplus\oplus}\right) + C\left(\overset{\oplus}{\ominus\oplus}\right)\\
\Rightarrow C\left(\overset{\ominus}{\oplus\oplus}\right) &= C\left(\underset{\ominus}{\oplus\oplus}\right) = C\left(\overset{\oplus}{\oplus\ominus}\right) = C\left(\overset{\oplus}{\ominus\oplus}\right)
\end{aligned} \tag{7.6}$$

$$\begin{aligned}
C\left(\ominus\ominus\right) &= C\left(\ominus\overset{\bullet}{}\ominus\right) = C\left(\overset{\ominus}{\ominus\ominus}\right) + C\left(\overset{\oplus}{\ominus\ominus}\right)\\
&= C\left(\underset{\bullet}{\ominus\ominus}\right) = C\left(\underset{\ominus}{\ominus\ominus}\right) + C\left(\underset{\oplus}{\ominus\ominus}\right)\\
C\left(\overset{\ominus}{\ominus\,\bullet}\right) &= C\left(\overset{\ominus}{\ominus\ominus}\right) + C\left(\overset{\ominus}{\ominus\oplus}\right)\\
&= C\left(\overset{\ominus}{\bullet\,\ominus}\right) = C\left(\overset{\ominus}{\ominus\ominus}\right) + C\left(\overset{\ominus}{\oplus\ominus}\right)\\
\Rightarrow C\left(\overset{\oplus}{\ominus\ominus}\right) &= C\left(\underset{\oplus}{\ominus\ominus}\right) = C\left(\overset{\ominus}{\ominus\oplus}\right) = C\left(\overset{\ominus}{\oplus\ominus}\right)
\end{aligned} \tag{7.7}$$

□

Similar derivations can also be concluded for 4-clusters.

Theorem 7.1.5. *Assuming 4-clusters containing a triangular 3-cluster (with all positive or all negative elements in the triangle), the fourth site could be occupied by a different element. All rotations of such clusters have equal concentrations.*

Proof. Assuming 3-clusters of the form $\left(\overset{\ominus}{\ominus\ominus}\right)$, the concentration of the 3-cluster can be calculated by summing over concentrations of 4-clusters, in which the fourth site can be occupied by all possible elements of the system. Same consideration can be taken into account for $\left(\overset{\oplus}{\oplus\oplus}\right)$ Note that ($\bullet$) states an unspecified state in the lattice.

$$\begin{aligned}
C\left(\begin{smallmatrix} & \oplus & \\ \oplus & & \oplus \end{smallmatrix}\right) &= C\left(\begin{smallmatrix} & \oplus & & \bullet \\ \oplus & & \oplus & \end{smallmatrix}\right) = C\left(\begin{smallmatrix} & \oplus & & \oplus \\ \oplus & & \oplus & \end{smallmatrix}\right) + C\left(\begin{smallmatrix} & \oplus & & \ominus \\ \oplus & & \oplus & \end{smallmatrix}\right) \\
&= C\left(\begin{smallmatrix} \bullet & & \oplus & \\ & \oplus & & \oplus \end{smallmatrix}\right) = C\left(\begin{smallmatrix} \oplus & & \oplus & \\ & \oplus & & \oplus \end{smallmatrix}\right) + C\left(\begin{smallmatrix} \ominus & & \oplus & \\ & \oplus & & \oplus \end{smallmatrix}\right) \\
&= C\left(\begin{smallmatrix} & \oplus & \\ \oplus & & \oplus \\ & \bullet & \end{smallmatrix}\right) = C\left(\begin{smallmatrix} & \oplus & \\ \oplus & & \oplus \\ & \oplus & \end{smallmatrix}\right) + C\left(\begin{smallmatrix} & \oplus & \\ \oplus & & \oplus \\ & \ominus & \end{smallmatrix}\right) \\
\Rightarrow C\left(\begin{smallmatrix} & \oplus & & \ominus \\ \oplus & & \oplus & \end{smallmatrix}\right) &= C\left(\begin{smallmatrix} \ominus & & \oplus & \\ & \oplus & & \oplus \end{smallmatrix}\right) = C\left(\begin{smallmatrix} & \oplus & \\ \oplus & & \oplus \\ & \ominus & \end{smallmatrix}\right)
\end{aligned} \tag{7.8}$$

$$\begin{aligned}
C\left(\begin{smallmatrix} & \ominus & \\ \ominus & & \ominus \end{smallmatrix}\right) &= C\left(\begin{smallmatrix} & \ominus & & \bullet \\ \ominus & & \ominus & \end{smallmatrix}\right) = C\left(\begin{smallmatrix} & \ominus & & \ominus \\ \ominus & & \ominus & \end{smallmatrix}\right) + C\left(\begin{smallmatrix} & \ominus & & \oplus \\ \ominus & & \ominus & \end{smallmatrix}\right) \\
&= C\left(\begin{smallmatrix} \bullet & & \ominus & \\ & \ominus & & \ominus \end{smallmatrix}\right) = C\left(\begin{smallmatrix} \ominus & & \ominus & \\ & \ominus & & \ominus \end{smallmatrix}\right) + C\left(\begin{smallmatrix} \oplus & & \ominus & \\ & \ominus & & \ominus \end{smallmatrix}\right) \\
&= C\left(\begin{smallmatrix} & \ominus & \\ \ominus & & \ominus \\ & \bullet & \end{smallmatrix}\right) = C\left(\begin{smallmatrix} & \ominus & \\ \ominus & & \ominus \\ & \ominus & \end{smallmatrix}\right) + C\left(\begin{smallmatrix} & \ominus & \\ \ominus & & \ominus \\ & \oplus & \end{smallmatrix}\right) \\
\Rightarrow C\left(\begin{smallmatrix} & \ominus & & \oplus \\ \ominus & & \ominus & \end{smallmatrix}\right) &= C\left(\begin{smallmatrix} \oplus & & \ominus & \\ & \ominus & & \ominus \end{smallmatrix}\right) = C\left(\begin{smallmatrix} & \ominus & \\ \ominus & & \ominus \\ & \oplus & \end{smallmatrix}\right)
\end{aligned} \tag{7.9}$$

□

All in all, any cluster with an arbitrary size and shape can be rotated in at most 6 different states and the resulting clusters will preserve the concentration of the original one. This feature can be utilized in order to simplify rate equations.

7.2 Derivations of Two-Element Two-Cluster Model

System of equations in (2.33) represent the rate equations in equilibrium plus the formulas for concentrations of equilibrium constants. In order to solve the system of equations, they need to be simplified by writing higher order clusters in terms of 2-clusters and substituting the rate constants with equilibrium constants. Here, the derivations of simplified equations are presented.

$$4k_1\frac{C_{+-}^2}{C_-}+k_2\frac{C_{+-}^2}{C_-}-4k_3\frac{C_{++}C_{+-}}{C_+}-k_4\frac{C_{++}C_{+-}}{C_+}=0, \tag{7.10.1}$$

$$4k_5\frac{C_{+-}^2}{C_+}+k_6\frac{C_{+-}^2}{C_+}-4k_7\frac{C_{--}C_{+-}}{C_-}-k_8\frac{C_{--}C_{+-}}{C_-}=0, \tag{7.10.2}$$

$$\begin{aligned} Q_1=\frac{k_1}{k_3}=\frac{C_{++}C_-}{C_{+-}C_+},\ Q_2=\frac{k_2}{k_4}=\frac{C_{++}C_-}{C_{+-}C_+},\\ Q_3=\frac{k_5}{k_7}=\frac{C_{--}C_+}{C_{+-}C_-},\ Q_4=\frac{k_6}{k_8}=\frac{C_{--}C_+}{C_{+-}C_-}. \end{aligned} \tag{7.10.3}$$

Equation $(7.10.1)$ can be simplified as follows:

$$\begin{aligned} 4k_1\frac{C_{+-}^2}{C_-}+k_2\frac{C_{+-}^2}{C_-}-4k_3\frac{C_{++}C_{+-}}{C_+}-k_4\frac{C_{++}C_{+-}}{C_+}&=0\Rightarrow\\ 4Q_1k_3\frac{C_{+-}^2}{C_-}+Q_2k_4\frac{C_{+-}^2}{C_-}-4k_3\frac{C_{++}C_{+-}}{C_+}-k_4\frac{C_{++}C_{+-}}{C_+}&=0\Rightarrow\\ 4Q_1\beta_1\frac{C_{+-}^2}{C_-}+Q_2\frac{C_{+-}^2}{C_-}-4\beta_1\frac{C_{++}C_{+-}}{C_+}-\frac{C_{++}C_{+-}}{C_+}&=0,\ \beta_1=\frac{k_3}{k_4}\Rightarrow\\ (4Q_1\beta_1+Q_2)\frac{C_{+-}^2}{C_-}-(4\beta_1+1)\frac{C_{++}C_{+-}}{C_+}&=0\Rightarrow\\ Q_1(4\beta_1+1)\frac{C_{+-}^2}{C_-}-(4\beta_1+1)\frac{C_{++}C_{+-}}{C_+}&=0\Rightarrow\\ (4\beta_1+1)\frac{C_{++}C_-}{C_{+-}C_+}\frac{C_{+-}^2}{C_-}-(4\beta_1+1)\frac{C_{++}C_{+-}}{C_+}&=0\Rightarrow\\ (4\beta_1+1)\frac{C_{++}C_{+-}}{C_+}-(4\beta_1+1)\frac{C_{++}C_{+-}}{C_+}&=0\Rightarrow\\ 0&=0. \end{aligned} \tag{7.11}$$

Equation $(7.10.2)$ can be simplified as follows:

$$\begin{aligned}
4k_5\frac{C_{+-}^2}{C_+} + k_6\frac{C_{+-}^2}{C_+} - 4k_7\frac{C_{--}C_{+-}}{C_-} - k_8\frac{C_{--}C_{+-}}{C_-} &= 0 \Rightarrow \\
4Q_3k_7\frac{C_{+-}^2}{C_+} + Q_4k_8\frac{C_{+-}^2}{C_+} - 4k_7\frac{C_{--}C_{+-}}{C_-} - k_8\frac{C_{--}C_{+-}}{C_-} &= 0 \Rightarrow \\
4Q_3\beta_2\frac{C_{+-}^2}{C_+} + Q_4\frac{C_{+-}^2}{C_+} - 4\beta_2\frac{C_{--}C_{+-}}{C_-} - \frac{C_{--}C_{+-}}{C_-} &= 0,\ \beta_2 = \frac{k_7}{k_8} \Rightarrow \\
(4Q_3\beta_2 + Q_4)\frac{C_{+-}^2}{C_+} - (4\beta_2+1)\frac{C_{--}C_{+-}}{C_-} &= 0 \Rightarrow \qquad (7.12) \\
(4\beta_2+1)\frac{C_{--}C_+}{C_{+-}C_-}\frac{C_{+-}^2}{C_+} - (4\beta_2+1)\frac{C_{--}C_{+-}}{C_-} &= 0 \Rightarrow \\
(4\beta_2+1)\frac{C_{--}C_{+-}}{C_-} - (4\beta_2+1)\frac{C_{--}C_{+-}}{C_-} &= 0 \Rightarrow \\
0 &= 0.
\end{aligned}$$

7.3 Derivations of Two-Element Triangular-Cluster Model

System of equations in (2.39) in equilibrium can be solved by substituting rate constants with equilibrium constants to make the system of equations determined. The following equations govern the system in equilibrium after applying moment closure approximations.

$$\begin{aligned}
&6k_9\frac{2}{3}C_{\widehat{\overline{++-}}}\frac{C_{(+-)}}{C_-} + 6k_{10}\frac{1}{3}C_{\widehat{\overline{++-}}}\frac{C_{\widehat{\overline{++-}}}}{C_{+-}} \\
&-6k_{11}\frac{2}{3}C_{\widehat{\overline{+++}}}\frac{C_{(+-)}}{C_+} - 6k_{12}\frac{1}{3}C_{\widehat{\overline{+++}}}\frac{C_{\widehat{\overline{++-}}}}{C_{++}} = 0,
\end{aligned} \qquad (7.13.1)$$

$$\begin{aligned} & 6k_{13}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_{+}} + 6k_{14}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{+-}} \\ & -6k_{15}\frac{2}{3}C_{\widehat{---}}\frac{C_{(+-)}}{C_{-}} - 6k_{16}\frac{1}{3}C_{\widehat{---}}\frac{C_{\widehat{--+}}}{C_{--}} = 0, \end{aligned} \tag{7.13.2}$$

$$\begin{aligned} & 2k_{17}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_{-}} + 2k_{11}\frac{2}{3}C_{\widehat{+++}}\frac{C_{(+-)}}{C_{+}} + 2k_{18}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}} \\ & +2k_{12}\frac{1}{3}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} + 2k_{19}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_{-}} + 2k_{20}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}} \\ & -2k_{21}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_{+}} - 2k_{9}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_{-}} - 2k_{22}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}} \\ & -2k_{10}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} - 2k_{23}\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_{+}} - 2k_{24}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}} = 0, \end{aligned} \tag{7.13.3}$$

$$\begin{aligned} & Q_5 = \frac{k_9}{k_{11}} = \frac{C_{++}^2 C_{-}^2}{C_{+-}^2 C_{+}^2},\ Q_6 = \frac{k_{10}}{k_{12}} = \frac{C_{++}C_{-}}{C_{+-}C_{+}},\ Q_7 = \frac{k_{13}}{k_{15}} = \frac{C_{--}^2 C_{+}^2}{C_{+-}^2 C_{-}^2}, \\ & Q_8 = \frac{k_{14}}{k_{16}} = \frac{C_{--}C_{+}}{C_{+-}C_{-}},\ Q_9 = \frac{k_{17}}{k_{21}} = \frac{C_{++}C_{-}^2}{C_{--}C_{+}^2},\ Q_{10} = \frac{k_{18}}{k_{22}} = \frac{C_{++}C_{-}}{C_{+-}C_{+}}, \\ & Q_{11} = \frac{k_{19}}{k_{23}} = \frac{C_{++}C_{-}^2}{C_{--}C_{+}^2},\ Q_{12} = \frac{k_{20}}{k_{24}} = \frac{C_{+-}C_{-}}{C_{--}C_{+}}. \end{aligned} \tag{7.13.4}$$

Equation $(7.13.1)$ can be simplified as follows:

$$
\begin{aligned}
6k_9\frac{2}{3}C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} + 6k_{10}\frac{1}{3}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} \\
-6k_{11}\frac{2}{3}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} - 6k_{12}\frac{1}{3}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} = 0 \Rightarrow \\
\\
2k_9C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} + k_{10}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} \\
-2k_{11}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} - k_{12}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} = 0 \Rightarrow \\
\\
2Q_5k_{11}C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} + Q_6k_{12}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} \\
-2k_{11}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} - k_{12}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} = 0 \Rightarrow \\
\\
2Q_5\beta_3C_{\widehat{++-}}\frac{C_{(+-)}}{C_-} + Q_6C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}} \\
-2\beta_3C_{\widehat{+++}}\frac{C_{(+-)}}{C_+} - C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}} = 0, \beta_3 = \frac{k_{11}}{k_{12}} \Rightarrow \\
\\
2Q_5\beta_3\frac{C_{++}C_{+-}^2}{C_+^2C_-}\frac{C_{(+-)}}{C_-} + Q_6\frac{C_{++}^2C_{+-}^4}{C_+^4C_-^2}\frac{1}{C_{+-}} \\
-2\beta_3\frac{C_{++}^3}{C_+^3}\frac{C_{(+-)}}{C_+} - \frac{C_{++}^3}{C_+^3}\frac{C_{++}C_{+-}^2}{C_+^2C_-}\frac{1}{C_{++}} = 0 \Rightarrow \\
\\
2Q_5\beta_3\frac{C_{++}C_{+-}^3}{C_+^2C_-^2} + Q_6\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2} \\
-2\beta_3\frac{C_{++}^3C_{+-}}{C_+^4} - \frac{C_{++}^3C_{+-}^2}{C_+^5C_-} = 0 \Rightarrow \\
\\
2\beta_3\frac{C_{++}^2C_-^2}{C_{+-}^2C_+^2}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2} + \frac{C_{++}C_-}{C_{+-}C_+}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2} \\
-2\beta_3\frac{C_{++}^3C_{+-}}{C_+^4} - \frac{C_{++}^3C_{+-}^2}{C_+^5C_-} = 0 \Rightarrow \\
\\
2\beta_3\frac{C_{++}^3C_{+-}}{C_+^4} + \frac{C_{++}^3C_{+-}^2}{C_+^5C_-} \\
-2\beta_3\frac{C_{++}^3C_{+-}}{C_+^4} - \frac{C_{++}^3C_{+-}^2}{C_+^5C_-} = 0 \Rightarrow 0 = 0.
\end{aligned}
\tag{7.14}
$$

Hence, for all values of β_3 the expression is true. Also, eq. (7.13.2) can be simplified as follows:

$$\begin{aligned}
&6k_{13}\frac{2}{3}C_{\widehat{--+}}\frac{C_{(+-)}}{C_{+}}+6k_{14}\frac{1}{3}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{+-}}\\
&-6k_{15}\frac{2}{3}C_{\widehat{---}}\frac{C_{(+-)}}{C_{-}}-6k_{16}\frac{1}{3}C_{\widehat{---}}\frac{C_{\widehat{--+}}}{C_{--}}=0\Rightarrow\\[2ex]
&2k_{13}C_{\widehat{--+}}\frac{C_{(+-)}}{C_{+}}+k_{14}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{+-}}\\
&-2k_{15}C_{\widehat{---}}\frac{C_{(+-)}}{C_{-}}-k_{16}C_{\widehat{---}}\frac{C_{\widehat{--+}}}{C_{--}}=0\Rightarrow\\[2ex]
&2Q_7k_{15}\frac{C_{--}C_{+-}^2}{C_-^2C_+}\frac{C_{(+-)}}{C_+}+Q_8k_{16}\frac{C_{--}^2C_{+-}^4}{C_-^4C_+^2}\frac{1}{C_{+-}}\\
&-2k_{15}\frac{C_{--}^3}{C_-^3}\frac{C_{(+-)}}{C_-}-k_{16}\frac{C_{--}^3}{C_-^3}\frac{C_{--}C_{+-}^2}{C_-^2C_+}\frac{1}{C_{--}}=0\Rightarrow\\[2ex]
&2Q_7\beta_4\frac{C_{--}C_{+-}^3}{C_-^2C_+^2}+Q_8\frac{C_{--}^2C_{+-}^3}{C_-^4C_+^2}\\
&-2\beta_4\frac{C_{--}^3C_{+-}}{C_-^4}-\frac{C_{--}^3C_{+-}^2}{C_-^5C_+}=0,\ \beta_4=\frac{k_{15}}{k_{16}}\Rightarrow\\[2ex]
&2\beta_4\frac{C_{--}^2C_+^2}{C_{+-}^2C_-^2}\frac{C_{--}C_{+-}^3}{C_-^2C_+^2}+\frac{C_{--}C_+}{C_{+-}C_-}\frac{C_{--}^2C_{+-}^3}{C_-^4C_+^2}\\
&-2\beta_4\frac{C_{--}^3C_{+-}}{C_-^4}-\frac{C_{--}^3C_{+-}^2}{C_-^5C_+}=0\Rightarrow\\[2ex]
&2\beta_4\frac{C_{--}^3C_{+-}}{C_-^4}+\frac{C_{--}^3C_{+-}^2}{C_-^5C_+}\\
&-2\beta_4\frac{C_{--}^3C_{+-}}{C_-^4}-\frac{C_{--}^3C_{+-}^2}{C_-^5C_+}=0\Rightarrow 0=0.
\end{aligned}\tag{7.15}$$

As can be seen, all values of β_4 will satisfy this equation. Also, eq. $(7.13.3)$ can be simplified as follows:

$$\begin{aligned}
&2k_{17}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+2k_{11}C_{\widehat{+++}}\frac{C_{(+-)}}{C_+}+k_{18}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}+k_{12}C_{\widehat{+++}}\frac{C_{\widehat{++-}}}{C_{++}}\\
&+2k_{19}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+k_{20}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}-2k_{21}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-2k_9C_{\widehat{++-}}\frac{C_{(+-)}}{C_-}\\
&-k_{22}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}-k_{10}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{+-}}-2k_{23}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{24}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}}=0\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&2k_{17}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+k_{18}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}+2k_{19}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+k_{20}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}\\
&-2k_{21}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{22}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}-2k_{23}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{24}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}}=0\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&2Q_9k_{21}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+Q_{10}k_{22}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}+2Q_{11}k_{23}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+Q_{12}k_{24}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}\\
&-2k_{21}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{22}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}-2k_{23}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{24}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}}=0\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&2Q_9\beta_5k_{22}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+Q_{10}k_{22}C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}+2Q_{11}\beta_6k_{24}C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+Q_{12}k_{24}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}\\
&-2\beta_5k_{22}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{22}C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}-2\beta_6k_{24}C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-k_{24}C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}}=0,\\
&\beta_5=\frac{k_{21}}{k_{22}},\ \beta_6=\frac{k_{23}}{k_{24}}\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&2Q_9\beta_5\beta_7C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+Q_{10}\beta_7C_{\widehat{--+}}\frac{C_{\widehat{--+}}}{C_{--}}+2Q_{11}\beta_6C_{\widehat{--+}}\frac{C_{(+-)}}{C_-}+Q_{12}C_{\widehat{--+}}\frac{C_{\widehat{++-}}}{C_{+-}}\\
&-2\beta_5\beta_7C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-\beta_7C_{\widehat{++-}}\frac{C_{\widehat{--+}}}{C_{+-}}-2\beta_6C_{\widehat{++-}}\frac{C_{(+-)}}{C_+}-C_{\widehat{++-}}\frac{C_{\widehat{++-}}}{C_{++}}=0,\beta_7=\frac{k_{22}}{k_{24}}\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&2\beta_5\beta_7\frac{C_{++}C_-^2}{C_{--}C_+^2}\frac{C_{--}C_{+-}^2}{C_-^2C_+}\frac{C_{(+-)}}{C_-}+\beta_7\frac{C_{++}C_-}{C_{+-}C_+}\frac{C_{--}^2C_{+-}^4}{C_-^4C_+^2}\frac{1}{C_{--}}+2\beta_6\frac{C_{++}C_-^2}{C_{--}C_+^2}\frac{C_{--}C_{+-}^2}{C_-^2C_+}\frac{C_{(+-)}}{C_-}\\
&+\frac{C_{+-}C_-}{C_{--}C_+}\frac{C_{--}C_{+-}^2}{C_-^2C_+}\frac{C_{++}C_{+-}^2}{C_+^2C_-}\frac{1}{C_{+-}}-2\beta_5\beta_7\frac{C_{++}C_{+-}^2}{C_+^2C_-}\frac{C_{(+-)}}{C_+}-\beta_7\frac{C_{++}C_{+-}^2}{C_+^2C_-}\frac{C_{--}C_{+-}^2}{C_-^2C_+}\frac{1}{C_{+-}}\\
&-2\beta_6\frac{C_{++}C_{+-}^2}{C_+^2C_-}\frac{C_{(+-)}}{C_+}-\frac{C_{++}^2C_{+-}^4}{C_+^4C_-^2}\frac{1}{C_{++}}=0\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&2\beta_5\beta_7\frac{C_{++}C_{+-}^3}{C_+^3C_-}+\beta_5\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}+2\beta_6\frac{C_{++}C_{+-}^3}{C_+^3C_-}+\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}\\
&-2\beta_5\beta_7\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\beta_7\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}-2\beta_6\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}=0\Rightarrow
\end{aligned}$$

$$0=0. \tag{7.16}$$

Note that the terms containing k_9, k_{10}, k_{11} and k_{12} are cancelling out as in eq. (7.13.1). These are the terms associated with producing or reducing $(+++)$ triangle, which simultaneously will produce or destroy $(++-)$ triangles. Hence, these terms will be removed from this equation for simplicity. Likewise, the equation will be satisfied for all values of β_5, β_6 and β_7.

7.4 Equations of Two-Element Triangular-Cluster Model for the Regular Case

In this section, I will propose the equations for the triangular-cluster model, in the limiting case of pair concentrations being equal to zero. In the $Li_{1/3}Mn_{2/3}$ system of elements, The final state, which corresponds to the minimal energy of the lattice, will be completely regular. The lattice will be filled with $\widehat{Mn - Li - Mn}$ clusters, in which the concentration of $Li - Li$ pair is equal to zero. In this limiting case, the eq. (2.40.3) becomes degenerate and has to be re-written in the following format.

$$2Q_5\beta_3\frac{C_{++}C_{+-}^3}{C_+^2C_-^2} + Q_6\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2} - 2\beta_3\frac{C_{++}^3C_{+-}}{C_+^4} - \frac{C_{++}^3C_{+-}^2}{C_+^5C_-} = 0, \tag{7.17.1}$$

$$2Q_7\beta_4\frac{C_{--}C_{+-}^3}{C_-^2C_+^2} + Q_8\frac{C_{--}^2C_{+-}^3}{C_-^4C_+^2} - 2\beta_4\frac{C_{--}^3C_{+-}}{C_-^4} - \frac{C_{--}^3C_{+-}^2}{C_-^5C_+} = 0, \tag{7.17.2}$$

$$\begin{aligned} 2\beta_5\beta_7\frac{C_{++}C_{+-}^3}{C_+^3C_-} + \beta_7\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3} + 2\beta_6\frac{C_{++}C_{+-}^3}{C_+^3C_-} + \frac{C_{++}C_{+-}^4}{C_+^4C_-^2} \\ -2\beta_5\beta_7\frac{C_{++}C_{+-}^3}{C_+^3C_-} - \beta_7\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3} - 2\beta_6\frac{C_{++}C_{+-}^3}{C_+^3C_-} - \frac{C_{++}C_{+-}^4}{C_+^4C_-^2} = 0, \end{aligned} \tag{7.17.3}$$

$$\begin{gathered}
Q_5 = \frac{k_9}{k_{11}} = \frac{C_{++}^2 C_-^2}{C_{+-}^2 C_+^2},\ Q_6 = \frac{k_{10}}{k_{12}} = \frac{C_{++} C_-}{C_{+-} C_+},\ Q_7 = \frac{k_{13}}{k_{15}} = \frac{C_{--}^2 C_+^2}{C_{+-}^2 C_-^2}, \\
Q_8 = \frac{k_{14}}{k_{16}} = \frac{C_{--} C_+}{C_{+-} C_-},\ Q_9 = \frac{k_{17}}{k_{21}} = \frac{C_{++} C_-^2}{C_{--} C_+^2},\ Q_{10} = \frac{k_{18}}{k_{22}} = \frac{C_{++} C_-}{C_{+-} C_+}, \\
Q_{11} = \frac{k_{19}}{k_{23}} = \frac{C_{++} C_-^2}{C_{--} C_+^2},\ Q_{12} = \frac{k_{20}}{k_{24}} = \frac{C_{+-} C_-}{C_{--} C_+},\ \beta_3 = \frac{k_{11}}{k_{12}}, \\
\beta_4 = \frac{k_{15}}{k_{16}},\ \beta_5 = \frac{k_{21}}{k_{22}},\ \beta_6 = \frac{k_{23}}{k_{24}},\ \beta_7 = \frac{k_{22}}{k_{24}}.
\end{gathered} \tag{7.17.4}$$

In this formulation, the terms containing $(0 * \infty)$ is eliminated by simplifying the equations and eliminating the C_{--} from calculations.

7.5 Derivations of Three-Element Two-Cluster Model

The three-element two-cluster model produces a set of equations for the rate of change in concentrations of different 2-clusters in the system. Equations $(3.23.1)$ to $(3.23.6)$ will govern the physical system in equilibrium by considering the moment closure approximations to truncate the hierarchy of the equations. These equations will be simplified in the equations (7.18) - (7.23) respectively by introducing equilibrium constants and extra ratios into the model.

$$
\begin{aligned}
&4k_1\frac{C_{+-}^2}{C_-}+k_2\frac{C_{+-}^2}{C_-}-4k_3\frac{C_{++}C_{+-}}{C_+}-k_4\frac{C_{++}C_{+-}}{C_+}\\
&+4k_5\frac{C_{+0}^2}{C_0}+k_6\frac{C_{+0}^2}{C_0}-4k_7\frac{C_{++}C_{+0}}{C_+}-k_8\frac{C_{++}C_{+0}}{C_+}=0\Rightarrow\\[1em]
&4Q_1k_3\frac{C_{+-}^2}{C_-}+Q_2k_4\frac{C_{+-}^2}{C_-}-4k_3\frac{C_{++}C_{+-}}{C_+}-k_4\frac{C_{++}C_{+-}}{C_+}\\
&+4Q_3k_7\frac{C_{+0}^2}{C_0}+Q_4k_8\frac{C_{+0}^2}{C_0}-4k_7\frac{C_{++}C_{+0}}{C_+}-k_8\frac{C_{++}C_{+0}}{C_+}=0\Rightarrow\\[1em]
&4Q_1\beta_1\frac{C_{+-}^2}{C_-}+Q_2\beta_2\frac{C_{+-}^2}{C_-}-4\beta_1\frac{C_{++}C_{+-}}{C_+}-\beta_2\frac{C_{++}C_{+-}}{C_+}+4Q_3\beta_3\frac{C_{+0}^2}{C_0}\\
&+Q_4\frac{C_{+0}^2}{C_0}-4\beta_3\frac{C_{++}C_{+0}}{C_+}-\frac{C_{++}C_{+0}}{C_+}=0,\ \frac{k_3}{k_8}=\beta_1,\ \frac{k_4}{k_8}=\beta_2,\ \frac{k_7}{k_8}=\beta_3\Rightarrow\\[1em]
&(4\beta_1+\beta_2)Q_1\frac{C_{+-}^2}{C_-}-(4\beta_1+\beta_2)\frac{C_{++}C_{+-}}{C_+}\\
&+(4\beta_3+1)Q_3\frac{C_{+0}^2}{C_0}-(4\beta_3+1)\frac{C_{++}C_{+0}}{C_+}=0\Rightarrow\\[1em]
&(4\beta_1+\beta_2)\frac{C_{++}C_-}{C_{+-}C_+}\frac{C_{+-}^2}{C_-}-(4\beta_1+\beta_2)\frac{C_{++}C_{+-}}{C_+}\\
&+(4\beta_3+1)\frac{C_{++}C_0}{C_{+0}C_+}\frac{C_{+0}^2}{C_0}-(4\beta_3+1)\frac{C_{++}C_{+0}}{C_+}=0\Rightarrow\\[1em]
&(4\beta_1+\beta_2)\frac{C_{++}C_{+-}}{C_+}-(4\beta_1+\beta_2)\frac{C_{++}C_{+-}}{C_+}\\
&+(4\beta_3+1)\frac{C_{++}C_{+0}}{C_+}-(4\beta_3+1)\frac{C_{++}C_{+0}}{C_+}=0\Rightarrow 0=0.
\end{aligned}
\tag{7.18}
$$

Eq. $(3.23.2)$ can be simplified as follows:

$$\begin{aligned}4k_9\frac{C_{+-}^2}{C_+}+k_{10}\frac{C_{+-}^2}{C_+}-4k_{11}\frac{C_{--}C_{+-}}{C_-}-k_{12}\frac{C_{--}C_{+-}}{C_-}\\+4k_{13}\frac{C_{-0}^2}{C_0}+k_{14}\frac{C_{-0}^2}{C_0}-4k_{15}\frac{C_{--}C_{-0}}{C_-}-k_{16}\frac{C_{--}C_{-0}}{C_-}=0\Rightarrow\end{aligned}$$

$$\begin{aligned}4Q_5\beta_4\frac{C_{+-}^2}{C_+}+Q_6\beta_5\frac{C_{+-}^2}{C_+}-4\beta_4\frac{C_{--}C_{+-}}{C_-}-\beta_5\frac{C_{--}C_{+-}}{C_-}\\+4Q_7\beta_6\frac{C_{-0}^2}{C_0}+Q_8\frac{C_{-0}^2}{C_0}-4\beta_6\frac{C_{--}C_{-0}}{C_-}-\frac{C_{--}C_{-0}}{C_-}=0,\\\frac{k_{11}}{k_{16}}=\beta_4,\ \frac{k_{12}}{k_{16}}=\beta_5,\ \frac{k_{15}}{k_{16}}=\beta_6\Rightarrow\end{aligned}\tag{7.19}$$

$$\begin{aligned}(4\beta_4+\beta_5)Q_5\frac{C_{+-}^2}{C_+}-(4\beta_4+\beta_5)\frac{C_{--}C_{+-}}{C_-}\\+(4\beta_6+1)Q_7\frac{C_{-0}^2}{C_0}-(4\beta_6+1)\frac{C_{--}C_{-0}}{C_-}=0\Rightarrow 0=0.\end{aligned}$$

Eq. $(3.23.3)$ can be simplifies as follows:

$$\begin{aligned}4k_{17}\frac{C_{+0}^2}{C_+}+k_{18}\frac{C_{+0}^2}{C_+}-4k_{19}\frac{C_{00}C_{+0}}{C_0}-k_{20}\frac{C_{00}C_{+0}}{C_0}\\+4k_{21}\frac{C_{-0}^2}{C_-}+k_{22}\frac{C_{-0}^2}{C_-}-4k_{23}\frac{C_{00}C_{-0}}{C_0}-k_{24}\frac{C_{00}C_{-0}}{C_0}=0\Rightarrow\end{aligned}$$

$$\begin{aligned}4Q_9\beta_7\frac{C_{+0}^2}{C_+}+Q_{10}\beta_8\frac{C_{+0}^2}{C_+}-4\beta_7\frac{C_{00}C_{+0}}{C_0}-\beta_8\frac{C_{00}C_{+0}}{C_0}+4Q_{11}\beta_9\frac{C_{-0}^2}{C_-}\\+Q_{12}\frac{C_{-0}^2}{C_-}-4\beta_9\frac{C_{00}C_{-0}}{C_0}-\frac{C_{00}C_{-0}}{C_0}=0,\ \frac{k_{19}}{k_{24}}=\beta_7,\ \frac{k_{20}}{k_{24}}=\beta_8,\ \frac{k_{23}}{k_{24}}=\beta_9\Rightarrow\end{aligned}\tag{7.20}$$

$$\begin{aligned}(4\beta_7+\beta_8)Q_9\frac{C_{+0}^2}{C_+}-(4\beta_7+\beta_8)\frac{C_{00}C_{+0}}{C_0}\\+(4\beta_9+1)Q_{11}\frac{C_{-0}^2}{C_-}-(4\beta_9+1)\frac{C_{00}C_{-0}}{C_0}=0\Rightarrow 0=0.\end{aligned}$$

Eq. (3.23.4) can be simplifies as follows:

$$
\begin{aligned}
&4k_3\frac{C_{++}C_{+-}}{C_+} + 4k_{11}\frac{C_{--}C_{+-}}{C_-} - 4k_1\frac{C_{+-}^2}{C_-} - 4k_9\frac{C_{+-}^2}{C_+}\\
&+k_4\frac{C_{++}C_{+-}}{C_+} + k_{12}\frac{C_{--}C_{+-}}{C_-} - k_2\frac{C_{+-}^2}{C_-} - k_{10}\frac{C_{+-}^2}{C_+}\\
&+4k_{25}\frac{C_{+0}C_{-0}}{C_0} + 4k_{26}\frac{C_{+0}C_{-0}}{C_0} - 4k_{27}\frac{C_{+-}C_{-0}}{C_-} - 4k_{28}\frac{C_{+-}C_{+0}}{C_+}\\
&+k_{29}\frac{C_{+0}C_{-0}}{C_0} + k_{30}\frac{C_{+0}C_{-0}}{C_0} - k_{31}\frac{C_{+-}C_{-0}}{C_-} - k_{32}\frac{C_{+-}C_{+0}}{C_+} = 0 \Rightarrow\\
\\
&4k_3\frac{C_{++}C_{+-}}{C_+} + k_4\frac{C_{++}C_{+-}}{C_+} - 4Q_1k_3\frac{C_{+-}^2}{C_-} - Q_2k_4\frac{C_{+-}^2}{C_-}\\
&-4Q_5k_{11}\frac{C_{+-}^2}{C_+} - Q_6k_{12}\frac{C_{+-}^2}{C_+} + 4k_{11}\frac{C_{--}C_{+-}}{C_-} + k_{12}\frac{C_{--}C_{+-}}{C_-}\\
&+4Q_{13}k_{27}\frac{C_{+0}C_{-0}}{C_0} + 4Q_{14}k_{28}\frac{C_{+0}C_{-0}}{C_0} - 4k_{27}\frac{C_{+-}C_{-0}}{C_-} - 4k_{28}\frac{C_{+-}C_{+0}}{C_+}\\
&+Q_{15}k_{31}\frac{C_{+0}C_{-0}}{C_0} + Q_{16}k_{32}\frac{C_{+0}C_{-0}}{C_0} - k_{31}\frac{C_{+-}C_{-0}}{C_-} - k_{32}\frac{C_{+-}C_{+0}}{C_+} = 0 \Rightarrow\\
\\
&4\beta_{10}\frac{C_{++}C_{+-}}{C_+} + \beta_{11}\frac{C_{++}C_{+-}}{C_+} - 4Q_1\beta_{10}\frac{C_{+-}^2}{C_-} - Q_2\beta_{11}\frac{C_{+-}^2}{C_-}\\
&-4Q_5\beta_{12}\frac{C_{+-}^2}{C_+} - Q_6\beta_{13}\frac{C_{+-}^2}{C_+} + 4\beta_{12}\frac{C_{--}C_{+-}}{C_-} + \beta_{13}\frac{C_{--}C_{+-}}{C_-}\\
&+4Q_{13}\beta_{14}\frac{C_{+0}C_{-0}}{C_0} + 4Q_{14}\beta_{15}\frac{C_{+0}C_{-0}}{C_0} - 4\beta_{14}\frac{C_{+-}C_{-0}}{C_-} - 4\beta_{15}\frac{C_{+-}C_{+0}}{C_+}\\
&+Q_{15}\beta_{16}\frac{C_{+0}C_{-0}}{C_0} + Q_{16}\frac{C_{+0}C_{-0}}{C_0} - \beta_{16}\frac{C_{+-}C_{-0}}{C_-} - \frac{C_{+-}C_{+0}}{C_+} = 0,\\
&\frac{k_3}{k_{32}} = \beta_{10},\ \frac{k_4}{k_{32}} = \beta_{11},\ \frac{k_{11}}{k_{32}} = \beta_{12},\ \frac{k_{12}}{k_{32}} = \beta_{13},\\
&\frac{k_{27}}{k_{32}} = \beta_{14},\ \frac{k_{28}}{k_{32}} = \beta_{15},\ \frac{k_{31}}{k_{32}} = \beta_{16} \Rightarrow\\
\\
&(4\beta_{10}+\beta_{11})\frac{C_{++}C_{+-}}{C_+} - (4\beta_{10}+\beta_{11})Q_1\frac{C_{+-}^2}{C_-}\\
&-(4\beta_{12}+\beta_{13})Q_5\frac{C_{+-}^2}{C_+} + (4\beta_{12}+\beta_{13})\frac{C_{--}C_{+-}}{C_-}\\
&+(4\beta_{14}+\beta_{16})Q_{13}\frac{C_{+0}C_{-0}}{C_0} - (4\beta_{14}+\beta_{16})\frac{C_{+-}C_{-0}}{C_-}\\
&+(4\beta_{15}+1)Q_{14}\frac{C_{+0}C_{-0}}{C_0} - (4\beta_{15}+1)\frac{C_{+-}C_{+0}}{C_+} = 0 \Rightarrow\\
\\
&0 = 0.
\end{aligned}
\tag{7.21}
$$

Eq. $(3.23.5)$ can be simplifies as follows:

$$
\begin{aligned}
4k_7\frac{C_{++}C_{+0}}{C_+} + k_8\frac{C_{++}C_{+0}}{C_+} - 4k_5\frac{C_{+0}^2}{C_0} - k_6\frac{C_{+0}^2}{C_0} \\
+4k_{19}\frac{C_{00}C_{+0}}{C_0} + k_{20}\frac{C_{00}C_{+0}}{C_0} - 4k_{17}\frac{C_{+0}^2}{C_+} - k_{18}\frac{C_{+0}^2}{C_+} \\
+4k_{27}\frac{C_{+-}C_{-0}}{C_-} + k_{31}\frac{C_{+-}C_{-0}}{C_-} - 4k_{25}\frac{C_{+0}C_{-0}}{C_0} - k_{29}\frac{C_{+0}C_{-0}}{C_0} \\
+4k_{33}\frac{C_{+-}C_{-0}}{C_-} + k_{34}\frac{C_{+-}C_{-0}}{C_-} - 4k_{35}\frac{C_{+-}C_{+0}}{C_+} - k_{36}\frac{C_{+-}C_{+0}}{C_+} = 0 \Rightarrow \\
\\
4\beta_{17}\frac{C_{++}C_{+0}}{C_+} + \beta_{18}\frac{C_{++}C_{+0}}{C_+} - 4Q_3\beta_{17}\frac{C_{+0}^2}{C_0} - Q_4\beta_{18}\frac{C_{+0}^2}{C_0} \\
+4\beta_{19}\frac{C_{00}C_{+0}}{C_0} + \beta_{20}\frac{C_{00}C_{+0}}{C_0} - 4Q_9\beta_{19}\frac{C_{+0}^2}{C_+} - Q_{10}\beta_{20}\frac{C_{+0}^2}{C_+} \\
+4\beta_{21}\frac{C_{+-}C_{-0}}{C_-} + \beta_{22}\frac{C_{+-}C_{-0}}{C_-} - 4Q_{13}\beta_{21}\frac{C_{+0}C_{-0}}{C_0} - Q_{15}\beta_{22}\frac{C_{+0}C_{-0}}{C_0} \\
+4Q_{17}\beta_{23}\frac{C_{+-}C_{-0}}{C_-} + Q_{18}\frac{C_{+-}C_{-0}}{C_-} - 4\beta_{23}\frac{C_{+-}C_{+0}}{C_+} - \frac{C_{+-}C_{+0}}{C_+} = 0, \\
\frac{k_7}{k_{36}} = \beta_{17},\ \frac{k_8}{k_{36}} = \beta_{18},\ \frac{k_{19}}{k_{36}} = \beta_{19},\ \frac{k_{20}}{k_{36}} = \beta_{20}, \\
\frac{k_{27}}{k_{36}} = \beta_{21},\ \frac{k_{31}}{k_{36}} = \beta_{22},\ \frac{k_{35}}{k_{36}} = \beta_{23} \Rightarrow \\
\\
(4\beta_{17}+\beta_{18})\frac{C_{++}C_{+0}}{C_+} - (4\beta_{17}+\beta_{18})Q_3\frac{C_{+0}^2}{C_0} \\
+(4\beta_{19}+\beta_{20})\frac{C_{00}C_{+0}}{C_0} - (4\beta_{19}+\beta_{20})Q_9\frac{C_{+0}^2}{C_+} \\
+(4\beta_{21}+\beta_{22})\frac{C_{+-}C_{-0}}{C_-} - (4\beta_{21}-\beta_{22})Q_{13}\frac{C_{+0}C_{-0}}{C_0} \\
+(4\beta_{23}+1)Q_{17}\frac{C_{+-}C_{-0}}{C_-} - (4\beta_{23}-1)\frac{C_{+-}C_{+0}}{C_+} = 0, \Rightarrow \\
0 = 0.
\end{aligned}
\tag{7.22}
$$

Eq. $(3.23.6)$ can be simplifies as follows:

$$\begin{aligned}
&4k_{15}\frac{C_{--}C_{-0}}{C_{-}}+k_{16}\frac{C_{--}C_{-0}}{C_{-}}-4k_{13}\frac{C_{-0}^{2}}{C_{0}}-k_{14}\frac{C_{-0}^{2}}{C_{0}}\\
&+4k_{23}\frac{C_{00}C_{-0}}{C_{0}}+k_{24}\frac{C_{00}C_{-0}}{C_{0}}-4k_{21}\frac{C_{-0}^{2}}{C_{-}}-k_{22}\frac{C_{-0}^{2}}{C_{-}}\\
&+4k_{28}\frac{C_{+-}C_{+0}}{C_{+}}+k_{32}\frac{C_{+-}C_{+0}}{C_{+}}-4k_{26}\frac{C_{+0}C_{-0}}{C_{0}}-k_{30}\frac{C_{+0}C_{-0}}{C_{0}}\\
&+4k_{35}\frac{C_{+-}C_{+0}}{C_{+}}+k_{36}\frac{C_{+-}C_{+0}}{C_{+}}-4k_{33}\frac{C_{+-}C_{-0}}{C_{-}}-k_{34}\frac{C_{+-}C_{-0}}{C_{-}}=0\Rightarrow
\end{aligned}$$

$$\begin{aligned}
&4\beta_{24}\frac{C_{--}C_{-0}}{C_{-}}+\beta_{25}\frac{C_{--}C_{-0}}{C_{-}}-4Q_{7}\beta_{24}\frac{C_{-0}^{2}}{C_{0}}-Q_{8}\beta_{25}\frac{C_{-0}^{2}}{C_{0}}\\
&+4\beta_{26}\frac{C_{00}C_{-0}}{C_{0}}+\beta_{27}\frac{C_{00}C_{-0}}{C_{0}}-4Q_{11}\beta_{26}\frac{C_{-0}^{2}}{C_{-}}-Q_{12}\beta_{27}\frac{C_{-0}^{2}}{C_{-}}\\
&+4\beta_{28}\frac{C_{+-}C_{+0}}{C_{+}}+\beta_{29}\frac{C_{+-}C_{+0}}{C_{+}}-4Q_{14}\beta_{28}\frac{C_{+0}C_{-0}}{C_{0}}-Q_{16}\beta_{29}\frac{C_{+0}C_{-0}}{C_{0}}\\
&+4\beta_{30}\frac{C_{+-}C_{+0}}{C_{+}}+\frac{C_{+-}C_{+0}}{C_{+}}-4Q_{17}\beta_{30}\frac{C_{+-}C_{-0}}{C_{-}}-Q_{18}\frac{C_{+-}C_{-0}}{C_{-}}=0,\\
&\frac{k_{15}}{k_{36}}=\beta_{24},\ \frac{k_{16}}{k_{36}}=\beta_{25},\ \frac{k_{23}}{k_{36}}=\beta_{26},\ \frac{k_{24}}{k_{36}}=\beta_{27},\\
&\frac{k_{28}}{k_{36}}=\beta_{28},\ \frac{k_{32}}{k_{36}}=\beta_{29},\ \frac{k_{35}}{k_{36}}=\beta_{30}\Rightarrow
\end{aligned}\tag{7.23}$$

$$\begin{aligned}
&(4\beta_{24}+\beta_{25})\frac{C_{--}C_{-0}}{C_{-}}-(4\beta_{24}+\beta_{25})Q_{7}\frac{C_{-0}^{2}}{C_{0}}\\
&+(4\beta_{26}+\beta_{27})\frac{C_{00}C_{-0}}{C_{0}}-(4\beta_{26}+\beta_{27})Q_{11}\frac{C_{-0}^{2}}{C_{-}}\\
&+(4\beta_{28}+\beta_{29})\frac{C_{+-}C_{+0}}{C_{+}}-(4\beta_{28}+\beta_{29})Q_{14}\frac{C_{+0}C_{-0}}{C_{0}}\\
&+(4\beta_{30}+1)\frac{C_{+-}C_{+0}}{C_{+}}-(4\beta_{30}+1)Q_{17}\frac{C_{+-}C_{-0}}{C_{-}}=0,\Rightarrow\\
&0=0.
\end{aligned}$$

The extra ratios that has been introduced into the model in eqs. (7.18) - (7.23), namely, β_1 to β_{30}, are chosen arbitrarily and the equations will be satisfied for all values of these parameters. In other words, the calculation of equilibrium constants based on eq. (3.24) is enough to solve the dynamical system in equilibrium. The rest of the ratios can be chosen arbitrarily without affecting the equilibrium phase of the model.

7.6 Derivations of Three-Element Triangular-Cluster Model

The system of algebraic equations in (3.26) will be solved analytically by substituting rate constants with equilibrium constants and ratios of rate constants. This way, degree of freedom of the system will diminish significantly. Equation (3.26.1) will be simplified as follows:

$$
\begin{aligned}
&k_{37}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2}+\frac{1}{5}k_{38}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2}-k_{39}\frac{C_{++}^3C_{+-}}{C_+^4}-\frac{1}{5}k_{40}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}\\
&+k_{41}\frac{C_{++}C_{+0}^3}{C_+^2C_0^2}+\frac{1}{5}k_{42}\frac{C_{++}^2C_{+0}^3}{C_+^4C_0^2}-k_{43}\frac{C_{++}^3C_{+0}}{C_+^4}-\frac{1}{5}k_{44}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0}=0\Rightarrow\\
&Q_{19}\beta_{31}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2}+\frac{1}{5}Q_{20}\beta_{32}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2}-\beta_{31}\frac{C_{++}^3C_{+-}}{C_+^4}-\frac{1}{5}\beta_{32}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}\\
&+Q_{21}\beta_{33}\frac{C_{++}C_{+0}^3}{C_+^2C_0^2}+\frac{1}{5}Q_{22}\frac{C_{++}^2C_{+0}^3}{C_+^4C_0^2}-\beta_{33}\frac{C_{++}^3C_{+0}}{C_+^4}-\frac{1}{5}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0}=0,\\
&\frac{k_{39}}{k_{44}}=\beta_{31},\ \frac{k_{40}}{k_{44}}=\beta_{32},\ \frac{k_{43}}{k_{44}}=\beta_{33}\Rightarrow\\
&\beta_{31}\frac{C_{++}^2C_-^2}{C_{+-}^2C_+^2}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2}+\beta_{32}\frac{1}{5}\frac{C_{++}C_-}{C_{+-}C_+}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2}-\beta_{31}\frac{C_{++}^3C_{+-}}{C_+^4}-\frac{1}{5}\beta_{32}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}\\
&+\beta_{33}\frac{C_{++}^2C_0^2}{C_{+0}^2C_+^2}\frac{C_{++}C_{+0}^3}{C_+^2C_0^2}+\frac{1}{5}\frac{C_{++}C_0}{C_{+0}C_+}\frac{C_{++}^2C_{+0}^3}{C_+^4C_0^2}-\beta_{33}\frac{C_{++}^3C_{+0}}{C_+^4}-\frac{1}{5}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0}=0\Rightarrow\\
&\beta_{31}\frac{C_{++}^3C_{+-}}{C_+^4}+\beta_{32}\frac{1}{5}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}-\beta_{31}\frac{C_{++}^3C_{+-}}{C_+^4}-\frac{1}{5}\beta_{32}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}\\
&+\beta_{33}\frac{C_{++}^3C_{+0}}{C_+^4}+\frac{1}{5}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0}-\beta_{33}\frac{C_{++}^3C_{+0}}{C_+^4}-\frac{1}{5}\frac{C_{++}^3C_{+0}^2}{C_+^5C_0}=0,\\
&0=0.
\end{aligned}
\tag{7.24}
$$

Following the same procedure, eqs. $(3.26.2)$ and $(3.26.3)$ will be satisfied by our choice of equilibrium constants. Eq. $(3.26.4)$ can be written in following format.

$$\begin{aligned}
k_{61}\frac{C_{--}C_{+-}^3}{C_+C_-^3}+k_{39}\frac{C_{++}^3C_{+-}}{C_+^4}-k_{63}\frac{C_{++}C_{+-}^3}{C_+^3C_-}\\
-k_{37}\frac{C_{++}C_{+-}^3}{C_+^2C_-^2}+\frac{1}{5}k_{62}\frac{C_{--}C_{+-}^4}{C_+^2C_-^4}+\frac{1}{5}k_{40}\frac{C_{++}^3C_{+-}^2}{C_+^5C_-}\\
-\frac{1}{5}k_{64}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}-\frac{1}{5}k_{38}\frac{C_{++}^2C_{+-}^3}{C_+^4C_-^2}+k_{65}\frac{C_{--}C_{+-}^3}{C_+C_-^3}\\
+\frac{1}{5}k_{66}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}-k_{67}\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\frac{1}{5}k_{68}\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}\\
+k_{69}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2}+k_{70}\frac{C_{++}C_{+0}^2C_{-0}}{C_+^2C_0^2}-k_{71}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-}\\
-k_{72}\frac{C_{++}C_{+-}^2C_{-0}}{C_+^2C_-^2}+\frac{1}{5}k_{73}\frac{C_{+-}^2C_{+0}^2C_{-0}}{C_+^2C_-^2C_0^2}+\frac{1}{5}k_{74}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}\\
-\frac{1}{5}k_{75}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}-\frac{1}{5}k_{76}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}+k_{77}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2}\\
+\frac{1}{5}k_{78}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}-k_{79}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-}-\frac{1}{5}k_{80}\frac{C_{++}C_{+-}^2C_{+0}^2}{C_+^4C_-C_0}=0\Rightarrow
\end{aligned}\tag{7.25.1}$$

$$\begin{aligned}
Q_{31}\beta_{40}\frac{C_{--}C_{+-}^3}{C_+C_-^3}-\beta_{40}\frac{C_{++}C_{+-}^3}{C_+^3C_-}+\frac{1}{5}Q_{32}\beta_{41}\frac{C_{--}C_{+-}^4}{C_+^2C_-^4}\\
-\frac{1}{5}\beta_{41}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}+Q_{33}\beta_{42}\frac{C_{--}C_{+-}^3}{C_+C_-^3}+\frac{1}{5}Q_{34}\beta_{43}\frac{C_{++}C_{--}C_{+-}^3}{C_+^3C_-^3}\\
-\beta_{42}\frac{C_{++}C_{+-}^3}{C_+^3C_-}-\frac{1}{5}\beta_{43}\frac{C_{++}C_{+-}^4}{C_+^4C_-^2}+Q_{35}\beta_{44}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2}\\
+Q_{36}\beta_{45}\frac{C_{++}C_{+0}^2C_{-0}}{C_+^2C_0^2}-\beta_{44}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-}-\beta_{45}\frac{C_{++}C_{+-}^2C_{-0}}{C_+^2C_-^2}\\
+\frac{1}{5}Q_{37}\beta_{46}\frac{C_{+-}^2C_{+0}^2C_{-0}}{C_+^2C_-^2C_0^2}+\frac{1}{5}Q_{38}\beta_{47}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}\\
-\frac{1}{5}\beta_{46}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}-\frac{1}{5}\beta_{47}\frac{C_{++}C_{+-}^2C_{+0}C_{-0}}{C_+^3C_-^2C_0}\\
+Q_{39}\beta_{48}\frac{C_{+-}C_{+0}^2C_{-0}}{C_+C_-C_0^2}+\frac{1}{5}Q_{40}k_{80}\frac{C_{++}C_{+-}C_{+0}^2C_{-0}}{C_+^3C_-C_0^2}\\
-\beta_{48}\frac{C_{++}C_{+-}^2C_{+0}}{C_+^3C_-}-\frac{1}{5}k_{80}\frac{C_{++}C_{+-}^2C_{+0}^2}{C_+^4C_-C_0}=0,\\
\frac{k_{63}}{k_{80}}=\beta_{40},\ \frac{k_{64}}{k_{80}}=\beta_{41},\ \frac{k_{67}}{k_{80}}=\beta_{42},\ \frac{k_{68}}{k_{80}}=\beta_{43},\ \frac{k_{71}}{k_{80}}=\beta_{44}\\
,\ \frac{k_{72}}{k_{80}}=\beta_{45},\ \frac{k_{75}}{k_{80}}=\beta_{46},\ \frac{k_{76}}{k_{80}}=\beta_{47},\ \frac{k_{79}}{k_{80}}=\beta_{48}\Rightarrow
\end{aligned}\tag{7.25.2}$$

$$\begin{aligned}
&\beta_{40}\frac{C_{++}C_{-}^{2}}{C_{--}C_{+}^{2}}\frac{C_{--}C_{+-}^{3}}{C_{+}C_{-}^{3}} - \beta_{40}\frac{C_{++}C_{+-}^{3}}{C_{+}^{3}C_{-}} + \frac{1}{5}\beta_{41}\frac{C_{++}C_{-}}{C_{+-}C_{+}}\frac{C_{--}C_{+-}^{4}}{C_{+}^{2}C_{-}^{4}} \\
&-\frac{1}{5}\beta_{41}\frac{C_{++}C_{--}C_{+-}^{3}}{C_{+}^{3}C_{-}^{3}} + \beta_{42}\frac{C_{++}C_{-}^{2}}{C_{--}C_{+}^{2}}\frac{C_{--}C_{+-}^{3}}{C_{+}C_{-}^{3}} + \frac{1}{5}\beta_{43}\frac{C_{+-}C_{-}}{C_{--}C_{+}}\frac{C_{++}C_{--}C_{+-}^{3}}{C_{+}^{3}C_{-}^{3}} \\
&-\beta_{42}\frac{C_{++}C_{+-}^{3}}{C_{+}^{3}C_{-}} - \frac{1}{5}\beta_{43}\frac{C_{++}C_{+-}^{4}}{C_{+}^{4}C_{-}^{2}} + \beta_{44}\frac{C_{++}C_{+-}C_{0}}{C_{+0}C_{-0}C_{+}^{2}}\frac{C_{+-}C_{+0}^{2}C_{-0}^{2}}{C_{+}C_{-}C_{0}^{2}} \\
&+\beta_{45}\frac{C_{+-}^{2}C_{0}^{2}}{C_{+0}^{2}C_{-}^{2}}\frac{C_{++}C_{+0}^{2}C_{-0}}{C_{+}^{2}C_{0}^{2}} - \beta_{44}\frac{C_{++}C_{+-}^{2}C_{+0}}{C_{+}^{3}C_{-}} - \beta_{45}\frac{C_{++}C_{+-}^{2}C_{-0}}{C_{+}^{2}C_{-}^{2}} \\
&+\frac{1}{5}\beta_{46}\frac{C_{++}C_{0}}{C_{+0}C_{+}}\frac{C_{+-}^{2}C_{+0}^{2}C_{-0}}{C_{+}^{2}C_{-}^{2}C_{0}^{2}} + \frac{1}{5}\beta_{47}\frac{C_{+-}C_{0}}{C_{+0}C_{-}}\frac{C_{++}C_{+-}C_{+0}^{2}C_{-0}}{C_{+}^{3}C_{-}C_{0}^{2}} \\
&-\frac{1}{5}\beta_{46}\frac{C_{++}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{3}C_{-}^{2}C_{0}} - \frac{1}{5}\beta_{47}\frac{C_{++}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{3}C_{-}^{2}C_{0}} \\
&+\beta_{48}\frac{C_{++}C_{+-}C_{0}^{2}}{C_{+0}C_{-0}C_{+}^{2}}\frac{C_{+-}C_{+0}^{2}C_{-0}}{C_{+}C_{-}C_{0}^{2}} + \frac{1}{5}\frac{C_{+-}C_{0}}{C_{-0}C_{+}}\frac{C_{++}C_{+-}C_{+0}^{2}C_{-0}}{C_{+}^{3}C_{-}C_{0}^{2}} \\
&-\beta_{48}\frac{C_{++}C_{+-}^{2}C_{+0}}{C_{+}^{3}C_{-}} - \frac{1}{5}\frac{C_{++}C_{+-}^{2}C_{+0}^{2}}{C_{+}^{4}C_{-}C_{0}} = 0, \Rightarrow
\end{aligned} \tag{7.25.3}$$

$$\begin{aligned}
&\beta_{40}\frac{C_{++}C_{+-}^{3}}{C_{+}^{3}C_{-}} - \beta_{40}\frac{C_{++}C_{+-}^{3}}{C_{+}^{3}C_{-}} + \frac{1}{5}\beta_{41}\frac{C_{++}C_{--}C_{+-}^{3}}{C_{+}^{3}C_{-}^{3}} \\
&-\frac{1}{5}\beta_{41}\frac{C_{++}C_{--}C_{+-}^{3}}{C_{+}^{3}C_{-}^{3}} + \beta_{42}\frac{C_{++}C_{+-}^{3}}{C_{+}^{3}C_{-}} + \frac{1}{5}\beta_{43}\frac{C_{++}C_{+-}^{4}}{C_{+}^{4}C_{-}^{2}} \\
&-\beta_{42}\frac{C_{++}C_{+-}^{3}}{C_{+}^{3}C_{-}} - \frac{1}{5}\beta_{43}\frac{C_{++}C_{+-}^{4}}{C_{+}^{4}C_{-}^{2}} + \beta_{44}\frac{C_{++}C_{+-}^{2}C_{+0}}{C_{+}^{3}C_{-}} \\
&+\beta_{45}\frac{C_{++}C_{+-}^{2}C_{-0}}{C_{+}^{2}C_{-}^{2}} - \beta_{44}\frac{C_{++}C_{+-}^{2}C_{+0}}{C_{+}^{3}C_{-}} - \beta_{45}\frac{C_{++}C_{+-}^{2}C_{-0}}{C_{+}^{2}C_{-}^{2}} \\
&+\frac{1}{5}\beta_{46}\frac{C_{++}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{3}C_{-}^{2}C_{0}} + \frac{1}{5}\beta_{47}\frac{C_{++}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{3}C_{-}^{2}C_{0}} \\
&-\frac{1}{5}\beta_{46}\frac{C_{++}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{3}C_{-}^{2}C_{0}} - \frac{1}{5}\beta_{47}\frac{C_{++}C_{+-}^{2}C_{+0}C_{-0}}{C_{+}^{3}C_{-}^{2}C_{0}} \\
&+\beta_{48}\frac{C_{++}C_{+-}^{2}C_{+0}}{C_{+}^{3}C_{-}} + \frac{1}{5}\frac{C_{++}C_{+-}^{2}C_{+0}^{2}}{C_{+}^{4}C_{-}C_{0}} \\
&-\beta_{48}\frac{C_{++}C_{+-}^{2}C_{+0}}{C_{+}^{3}C_{-}} - \frac{1}{5}\frac{C_{++}C_{+-}^{2}C_{+0}^{2}}{C_{+}^{4}C_{-}C_{0}} = 0, 0 = 0.
\end{aligned} \tag{7.25.4}$$

As can be seen, the rate equation will be satisfied by using equilibrium constants, which are written in terms of pair and singlet concentrations. Some extra ratios are defined in the model ($\beta_{40} - \beta_{48}$) which can take any arbitrary value without changing the equilibrium phase of the model. Equations (3.26.5) to (3.26.9) can be simplified by following the same procedures.

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