Applied Stochastic Analysis Final Project:

Kinetic Monte Carlo (KMC) Simulations on Falicov-Kimball Model

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Abstract

This documentation illustrates the study on the paper *Anomalous phase separation in a correlated electron system: Machine-learning–enabled large-scale kinetic Monte Carlo simulations* (▷ https://www.pnas.org/doi/epdf/10.1073/pnas.2119957119)[**1**], and its connections with applied stochastic processes. In the paper, the authors investigate the dynamics of phase separation in correlated electron systems, a fundamental phenomenon in condensed matter physics with implications for material properties. Utilizing stochastic analysis techniques, specifically large-scale kinetic Monte Carlo simulations, they explore the phase-ordering processes in the Falicov-Kimball model, a canonical model for strongly correlated electron systems. In their findings, they uncover complex, multi-scale dynamics including unusual relaxation behaviors and spatial pattern formations like checkerboard and superclusters, providing new insights into the mechanisms driving phase separation in non-equilibrium electron systems. Here, we implemented a similar method (Kinetic Monte Carlo (kMC) simulations) and reproduced a few figures from the paper with some variations. In addition, we also provided some extra insights, in terms of the system change with temperature variations and different materials properties. There are also two interesting movies generated. Moreover, Hamiltonian Monte Carlo (HMC) and Quantum Monte Carlo (QMC) were also briefly mentioned.

1 Mathematical Background

1.1 Kinetic Monte Carlo (kMC) simulations

Kinetic Monte Carlo (KMC) can be seen as an extension of the Metropolis class of algorithms, which are designed to sample from a complex target probability distribution. Denote $\boldsymbol{\pi}$ as the target probability distribution, and $\mathbf{P}$ as the transition matrix of the corresponding Markov chain. Then we have $\boldsymbol{\pi}\mathbf{P} = \boldsymbol{\pi}$. This means that $\boldsymbol{\pi}$ is a stationary distribution of the Markov chain, which ensures that the chain, if run indefinitely, converges to $\boldsymbol{\pi}$. A fundamental aspect of Monte Carlo methods is to approximate integrals using the law of large numbers. Specifically, we aim for the empirical mean of a function f evaluated at the states of the Markov chain to converge to the expected value under $\boldsymbol{\pi}$, formally given by:

$$\frac{1}{N}\sum_{k=1}^{N} f(X^k) \to \int f(x)\pi(dx) \quad \text{as } N \to \infty \tag{1}$$

In order to achieve this goal, we can use Metropolis-Hastings Algorithm.

Definition 1.1 (Metropolis-Hastings Algorithm)**.** The Metropolis-Hastings Algorithm involves selecting a transition density $q(y|x)$. The algorithm operates under two scenarios:

1. If $\int q(y \mid x)\pi(dx) = \pi(y)$, then the transition density q is said to preserve π, maintaining the target distribution π unchanged.
2. Otherwise, the algorithm proceeds with generating a new state in the following manner:
   - Generate $Y^{k+1} \sim q(y \mid X^{(k)})$, where Y^{k+1} is the proposed next state in the Markov chain from the current state $X^{(k)}$.

- Accept Y^{k+1} as the new state X^{k+1} with the acceptance probability:

$$\text{pacc} = \min\left\{1, \frac{\pi(Y^{(k+1)})q(X^{(k)} \mid Y^{(k+1)})}{\pi(X^{(k)})q(Y^{(k+1)} \mid X^{(k)})}\right\} \tag{2}$$

If not accepted, set $X^{(k+1)} = X^{(k)}$. Otherwise, set $X^{(k+1)} = Y^{(k+1)}$.

▷▷ **Detailed Balance in Metropolis-Hastings Algorithm**

The detailed balance condition can be demonstrated for the Metropolis-Hastings (M-H) algorithm as follows:

$$q(y \mid x)\text{pacc}(x, y)\pi(x) = q(y \mid x)\min\left\{1, \frac{\pi(y)q(x \mid y)}{\pi(x)q(y \mid x)}\right\}\pi(x) \tag{3}$$

$$= \min\{q(y \mid x)\pi(x), \pi(y)q(x \mid y)\} \tag{4}$$

$$= q(x \mid y)\text{pacc}(y \mid x)\pi(y) \tag{5}$$

This ensures that q is in detailed balance with the stationary distribution π.

▷▷ **Transition Operation**

Consider the transition operation T defined as:

$$Tf(x) = \mathbb{E}[f(X^{(1)} \mid X^{(0)} = x)] \tag{6}$$

$$= f(x)P_{\text{rej}}(x) + \int f(y)\text{pacc}(x, y)q(y \mid x)\, dy \tag{7}$$

where $P_{\text{rej}}(x) = \int(1 - \text{pacc}(x, z))q(z \mid x)\, dz$. The transition probability density $p(y \mid x)$ is then:

$$p(y \mid x) = \delta(y - x)P_{\text{rej}}(x) + \text{pacc}(x, y)q(y \mid x) \tag{8}$$

and the operation T can be expressed as:

$$Tf(x) = \int f(y)p(y \mid x)\, dx \tag{9}$$

▷▷ **Validation of Detailed Balance via Transition Operator**

Detailed balance in terms of the transition operator requires that:

$$\int q(x)Tf(x)\pi(dx) = \int f(x)Tg(x)\pi(dx), \quad \forall g, f \tag{10}$$

This is verified as follows:

$$\int g(x)Tf(x)\pi(dx) = \int g(x)f(x)P_{\text{rej}}(x)\pi(dx) + \iint f(y)q(y \mid x)\text{pacc}(x, y)g(x)\pi(x)\, dx\, dy \tag{11}$$

$$= \int f(y)\int g(x)q(x \mid y)\text{pacc}(y, x)\, dx\pi(y)\, dy \tag{12}$$

$$= \int f(x)Tg(x)\pi(dx) \tag{13}$$

▷▷ **Choice of Transition Density** $q(y \mid x)$

For the transition density $q(y \mid x)$, we can consider a Gaussian proposal:

$$q(y \mid x) = \frac{e^{-(y-x)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} = q(x \mid y) \tag{14}$$

where $y = x + N(0, \sigma^2)$, or alternatively, define $q(y \mid x)$ in a manner consistent with the energy levels of a transition state in a physical system, potentially expressed in a Hamiltonian formulation.

1.2 Hamiltonian Monte Carlo (HMC) simulations

Hamiltonian Monte Carlo (HMC) uses Hamiltonian dynamics to propose transitions in a Markov chain. The Hamiltonian $H(x, p)$, combining potential energy $U(x)$ and kinetic energy $K(p)$, governs the dynamics. The transition density in HMC is derived from simulating the trajectory under Hamilton's equations:

$$\frac{dx}{dt} = \frac{\partial H}{\partial p}, \qquad \frac{dp}{dt} = -\frac{\partial H}{\partial x} \tag{15}$$

The acceptance of transitions is based on the change in the Hamiltonian:

$$\text{Acceptance Probability} = \min\left(1, e^{-[H(x',p')-H(x,p)]}\right) \tag{16}$$

where (x, p) is the current state and (x', p') is the proposed state **[2]**. As we know, any physical systems can be presented in terms of kinetic and potential energies in a form of a Hamiltonian, but there is a transition between a classical system and quantum system, which relates to the potential energy level.

1.3 Quantum Monte Carlo (QMC) simulations

▷▷ Calculation of Chemical Potential

The chemical potential μ in a semiconductor can be estimated by solving the electron density equation:

$$n = \int_0^\infty D(E) \left(\frac{1}{e^{(E-\mu)/k_B T} + 1}\right) dE \tag{17}$$

where $D(E)$ is the density of states, K_B is the Boltzmann constant and T is the temperature.

Given specific values for n, $D(E)$, T, and assuming a particular form for $D(E)$, we would typically use numerical methods to solve for μ. This involves iterative techniques to find μ such that the total number of electrons matches the expected electron density.

▷▷ Integration of Fermi-Dirac Statistics in Quantum Monte Carlo Simulations

Quantum Monte Carlo (QMC) methods are essential for addressing complex quantum systems. They are particularly useful in simulations of fermionic systems, such as electrons, where Fermi-Dirac statistics and the Pauli exclusion principle play critical roles. During simulations, the chemical potential μ is adjusted to maintain the correct particle density, utilizing the Fermi-Dirac distribution within the Metropolis algorithm to manage state transition probabilities **[3]**. In this documentation, we are specifically interested in one quantum system - Falicov-Kimball Model.

1.4 Falicov-Kimball Model

▷▷ The basic model

The spinless Falicov-Kimball model (as mentioned in the paper) is crucial in condensed matter physics for studying interactions between localized and itinerant electron species. It features a Hamiltonian:

$$\mathcal{H} = -t_{\text{nn}} \sum_{\langle i,j \rangle} c_i^\dagger c_j + U \sum_i c_i^\dagger c_i n_i^f \tag{18}$$

where $c_i^\dagger$ and c_i are the creation and annihilation operators for itinerant c-electrons at each lattice site i. The model sums over nearest-neighbor pairs $\langle i, j \rangle$ to reflect spatial interactions through hopping, with $n_i^c = c_i^\dagger c_i$ and n_i^f representing the number operators for itinerant and localized electrons, respectively. The Hamiltonian incorporates t_{nn} as the hopping constant and energy unit for kinetic movements, and U for the Coulomb interaction between itinerant and localized electrons at the same site.

▷▷ Dynamics of Electron Movement

The motion of localized f-electrons is influenced by the quasi-equilibrium states of itinerant c-electrons. Updates in the configuration, especially moves between nearest-neighbor sites, are governed by the acceptance probability:

$$p_{i\to j} = 1/4 \min\left(1, e^{-\Delta E_{i\to j}/k_B T}\right) \tag{19}$$

Here, $\Delta E_{i\to j}$ is the energy change, with k_B as the Boltzmann constant and T the system temperature. This setup promotes energy minimization, aligning with the principles of statistical mechanics **[1]**.

2 Simulation Integration

In the referenced paper [**1**], the authors employed machine learning-enhanced large-scale kinetic Monte Carlo (KMC) simulations to explore the Falicov-Kimball model. Owing to the unavailability of the original machine learning datasets, our study concentrates solely on KMC simulations. We have also introduced additional analyses, including temperature effects and the relationship between effective potential and cluster formation, which were not covered in the original paper.

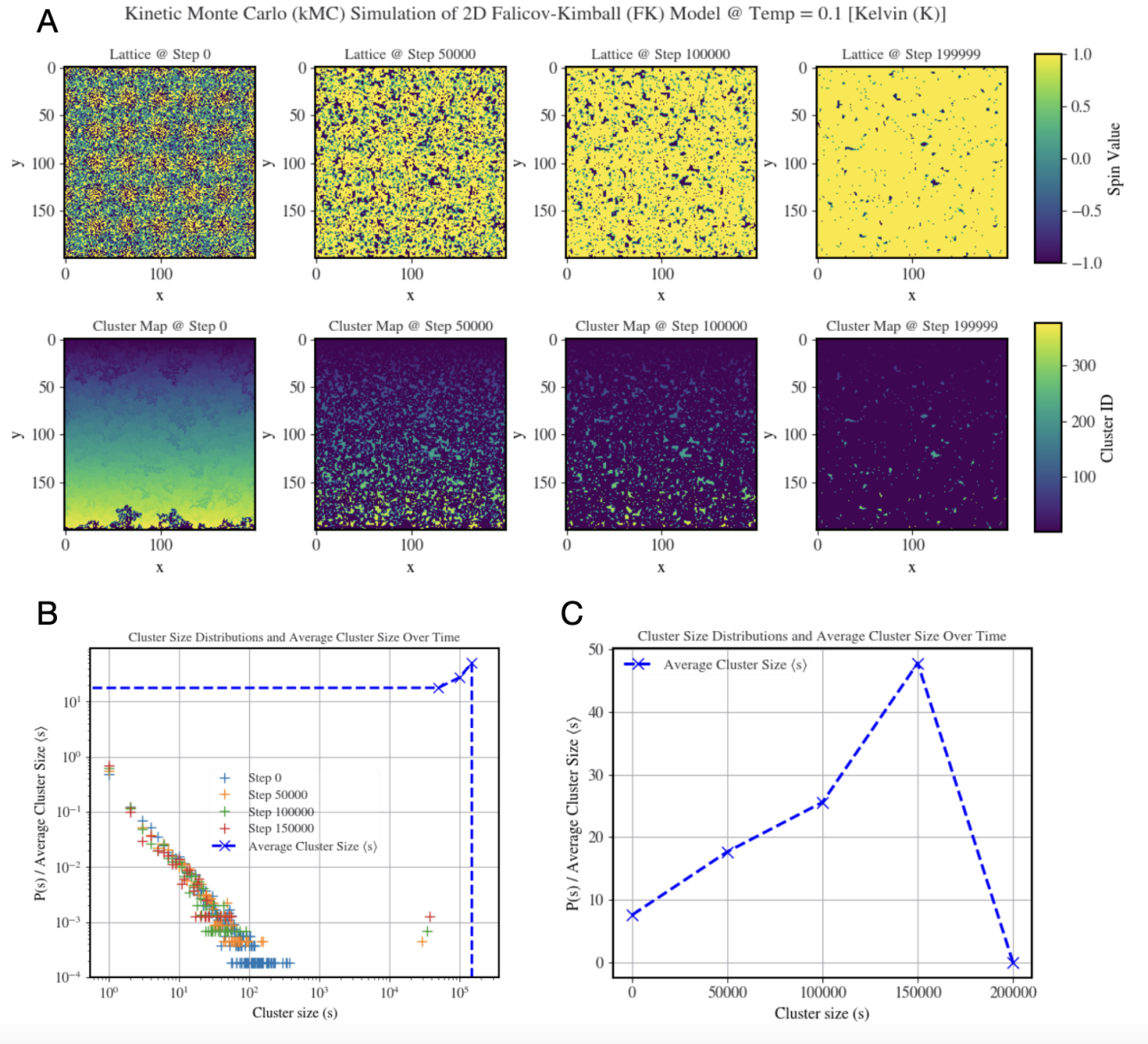

Figure 1: Kinetic Monte Carlo (kMC) simulations on the Falicov-Kimball model at 1K (using scaled units where Boltzmann's constant kB=1) are depicted. **Panel A** illustrates the dynamics of spin motions across kMC steps: the first row shows spin migrations, while the second row details cluster formation dynamics. **Panel B** examines cluster sizes and formation probabilities at various kMC steps. **Panel C** enhances understanding of cluster growth probabilities under these conditions.

In subplot **A** of our 200×200 grid, as the kMC steps approach the 200,000 mark, the spin map shifts toward a unified heterogeneous state where each electron likely exhibits spin up in their degenerate orbitals. This alignment, consistent with Hund's rule, leads to a stable configuration. The lower row in **A** shows phase separation and the formation of checkerboard clusters, as discussed in the original paper. Subplots **B** and **C** detail the sizes and growth probabilities of these clusters, and their correlation with time steps. Notably, after 50,000 steps in **B**, super-clusters ranging from 10^4 to 10^5 in size begin to appear, with the most common size around 1.5×10^5, as indicated in **C**. Upcoming sections will further explore the critical role of temperature in influencing these physical systems.

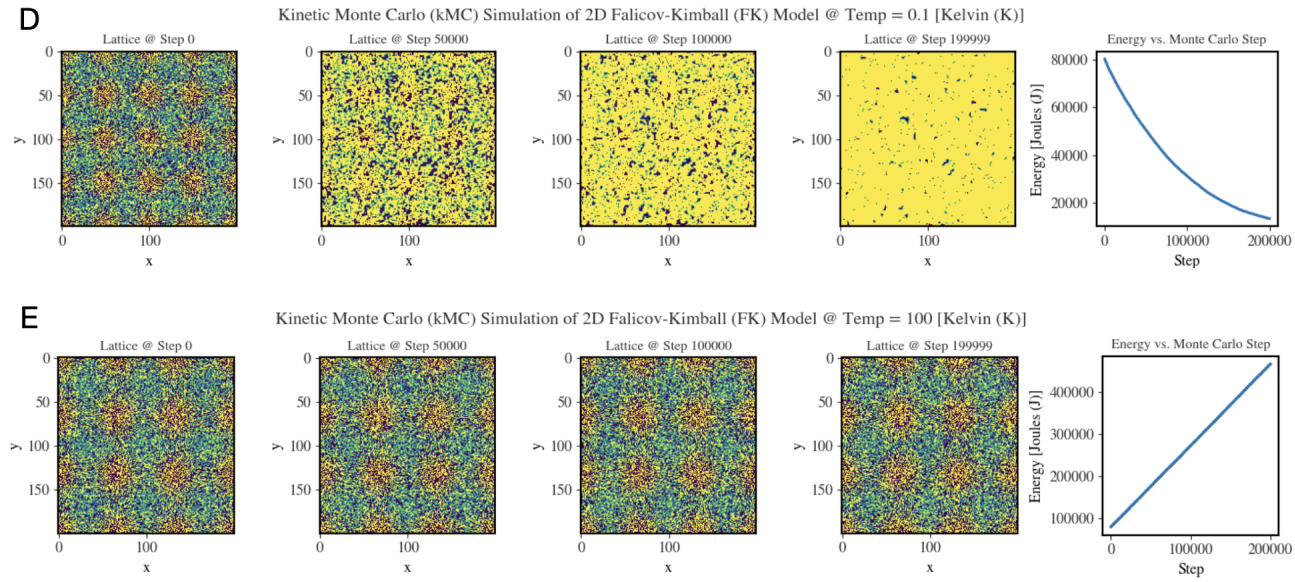

Figure 2: Kinetic Monte Carlo (kMC) simulations on the Falicov-Kimball model examine the influence of different temperatures on energy dynamics. Subplot **D** explores the dynamics at a temperature of 0.1K, while subplot **E** investigates the same under conditions at 100K.

The dynamics vary significantly with temperature changes while other conditions remain constant. In subplot **D**, as previously mentioned in Figure 1, low temperatures support the formation of stable clusters. The energy decreases as the simulation progresses, leading to a more stabilized state due to the spin co-alignment conducive to proper quantum interactions at these temperatures. Conversely, subplot **E** illustrates a scenario at 100K where a stable state is not achieved; instead, the energy continues to rise, signifying a randomized system disrupted by high temperatures. This increase in energy reflects the thermal agitation's overpowering effect on the spin interactions, hindering the formation of stable clusters or aligned domains. In such high-temperature conditions, the lattice remains dynamically unstable with frequent spin flips and minimal long-term order, highlighting the detrimental impact of high thermal energy on quantum mechanical interactions that typically aid in system stabilization. This phenomenon is further evidenced by the correlation between lattice dynamics and potential changes observed in the simulations.

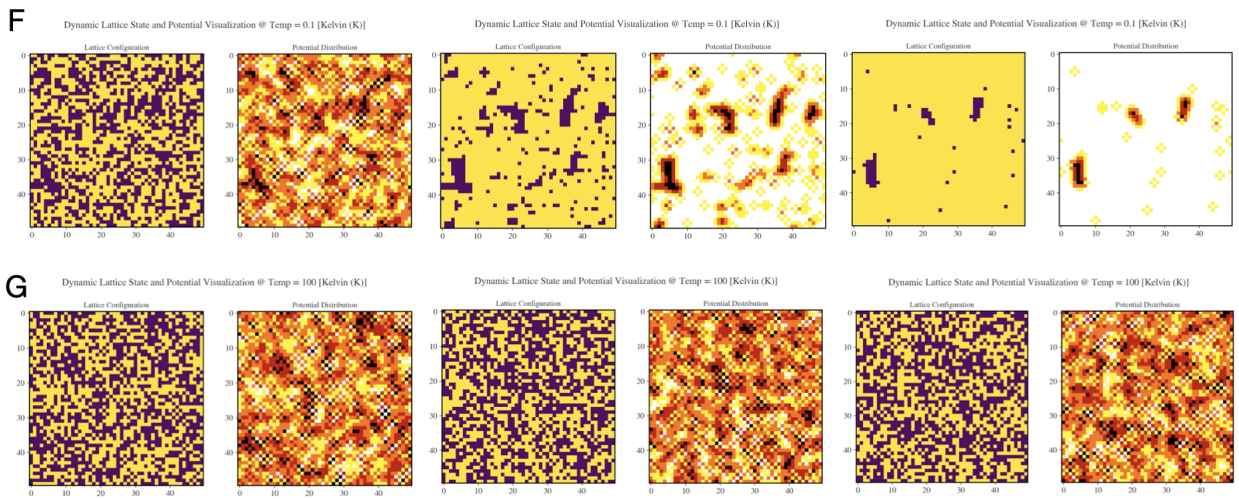

Figure 3: Movie screenshots compare the lattice dynamics and the effective potential changes at various temperatures for a grid size of 50×50. Subplot **F** details the dynamics at a temperature of 0.1K, and subplot **G** examines the same parameters at 100K.

As evident, there is a strong correlation between the lattice dynamics (checkerboard cluster domains) and the effective potential energy changes. According to the paper, f electrons tend to cluster on the same sublattice within these domains, promoting supercluster growth. Over time, these clusters expand to encompass the entire lattice, fostering a stable and ordered state. Conversely, at higher temperatures, this stability is disrupted as the system remains in a constantly changing, unstable state. Further details and movie visuals can be accessed on the Github site mentioned in the conclusion section, as well as in the code packag uploaded in gradescope.

3 Conclusion

In this document, we have illustrated a simplified Kinetic Monte Carlo (kMC) simulation on the Falicov-Kimball model, extending the study mentioned at the beginning. We have demonstrated that at low temperatures, the spin system exhibits non-equilibrium phase-separation dynamics, which lowers the energy and facilitates the formation of checkerboard clusters that enhance material insulation properties. The simulations were performed using Python, and the source code is available at https://github.com/cw0508/asa_final_project. Notably, the calculations in this study are simplified; for instance, Boltzmann's constant is maintained at 1, as opposed to the actual value of 1.38×10^{-23} J/K. Similarly, the hopping constant t_{nn} is set to 1 and the Coulomb interaction U at 2, although these parameters may vary with different material properties. While this model offers a general framework, it is important to remember that its applications and results are specific to the physical systems and scenarios being studied.

▷▷ **Some useful links to check for possible future work:**

- The general Falicov-Kimball model: https://arxiv.org/pdf/math-ph/0502041
- Exact solution of the Falicov-Kimball model with dynamical mean-field theory (with some real materials investigations): https://arxiv.org/pdf/math-ph/0502041
- The materials project (to see different materials properties): https://next-gen.materialsproject.org
- The Staggered Mesh Method or Fock exchange energy in periodic lattice systems (with some real materials investigations): https://arxiv.org/pdf/2402.13538v1

References

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[3] Wikipedia contributors. (2024, April 30). Hamiltonian Monte Carlo. Wikipedia. https://en.wikipedia.org/wiki/Hamiltonian_Monte_Carlo