Metastability for low-temperature Kawasaki dynamics with two types of particles

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1 Introduction

In this thesis, we consider a low-temperature and low-density lattice gas with particles of two types, describing the condensation of a supersaturated gas mixture. Particles are subject to random hopping with hard-core repulsion, while particles of different types are subject to nearest-neighbor attraction and have different densities. The goal of the thesis is to study the metastable behavior of this system. In Section 1.1 we introduce the concept of metastability, in Section 1.2 we describe the mathematical approaches to metastability and the questions that are of interest. In Section 1.3 we turn to finite systems at low temperature, define Metropolis dynamics, and define the quantities that play a central role in the analysis of metastable behavior. We describe earlier work for Kawasaki dynamics with one type of particle and state our target to extend this work to two types of particles.

1.1 The concept of metastability

Metastability is a phenomenon where a system moves between different region of its state space according to a noisy dynamics. On a *short time scale*, the system explores a limited region of the state space and therefore is in a quasi-equilibrium. On a *long time scale*, the system undergoes rapid transitions between different regions of the state space, where it reaches new quasi-equilibria. The transitions between these different *phases* of the system are typically triggered by the creation of a *critical droplet*, via spontaneous fluctuations or external perturbations. Throughout the sequel, we will concentrate on the case where the transition is from a *metastable state* (a single quasi-equilibrium) to a *stable state* (a single equilibrium).

In thermodynamics, metastability is associated with a *first-order phase transition*. Examples are supercooled liquids, supersaturated gases, as well as ferromagnets in the part of the hysteresis loop where the magnetization is opposite to the external magnetic field. In all these cases the system may remain for a long time in a metastable phase that, for the given thermodynamic parameters such as temperature or magnetic field, is not stable. The appearance of a *nucleus* of the stable phase inside the unstable phase will initiate a rapid crossover.

The occurrence of metastable phenomena is not limited to thermodynamics and plays a key role in various different fields, ranging from biology and chemistry to economics and computer science.

1.2 Mathematical approaches and questions of interest

The mathematical description of metastable systems started in the 1930s and 1940s, with the work of Eyring [Eyr35] and Kramers [Kra40], who studied a one-dimensional diffusion process in a double-well potential in the context of the theory of chemical reactions. The first attempt to formulate a rigorous dynamical theory of metastability goes back to the work of Lebowitz and Penrose [PL71] on metastable states in Van der Waals theory. In the 1980s Freidlin and Wentzell [FW84] used large deviation theory to study the long-term behavior of dynamical systems with small random perturbations. They associated metastable systems with what they called a *Markov Chain with exponentially small transition probabilities*, whose states correspond to the different attractors of the underlying dynamical system. The transition probabilities of this Markov chain are computed by finding the probability of the most likely trajectory between these attractors.

Later it was noted that such Markov chains also arise in other contexts, in particular, in stochastic dynamics of interacting particle systems at low temperature, which have become the subject of intense investigation (Olivieri and Scoppola [OS95], [OS96], Ben Arous and Cerf [BAC96], Catoni and Cerf [CC97]), initially again with the help of large deviation techniques. Since then a vast literature has developed. The different models investigated can be classified according to the "size" of their state space and the "type" of dynamics governing their evolution.

From the point of view of state space, an important distinction is between *finite* and *infinite* state space. In the first case, in the low-temperature regime, the stochastic dynamics is driven by energy only and entropic effects can essentially be neglected. In the second case, however, entropic effects play an important role and must be taken into account when studying the statistical properties of the transition toward global equilibria.

From the point of view of dynamics, an important distinction is between *non-conservative* dynamics and *conservative* dynamics. In the first case, the total number of particles or spins (of a given type) is not conserved. Examples are spin-flip dynamics in magnets, either sequentially (Glauber dynamics) or parallel dynamics (cellular automata). Models of Glauber dynamics in finite volume are

Neves and Schonmann [NS91] and Bovier and Manzo [BM02], and in infinite volume Dehghanpour and Schonmann [DS97] and Schonmann and Shlosman [SS98], while models of cellular automata can be found in Cirillo and Nardi [CN03], Cirillo Nardi and Spitoni [CNS08b] and [CNS08a]. In the second case, the total number of particle or spins stays fixed, which places a severe restriction on the evolution. In general, models with conservative dynamics are more difficult to analyze because of long-range effects introduced by the conservation law. Examples are hopping dynamics in lattice gases, either sequentially (Kawasaki dynamics) or parallel dynamics (cellular automata) Models of Kawasaki dynamics in finite volume are den Hollander Olivieri and Scoppola [dOS00], [dHNOS03] and Bovier den Hollander and Nardi [BdN06], and in infinite volume Gaudillière, den Hollander, Nardi, Olivieri and Scoppola [GdHN$^+$a], [GdHN$^+$b] and Bovier den Hollander and Spitoni [BdHS10]. An example of a parallel conservative dynamics can be found in Gaudillière, Scoppola, Scoppola and Viale [GSSV11]. Typical questions addressed in the context of metastability are: What is the probability distribution of the time it takes to observe the transition from the metastable to the stable state (nucleation time)? What are the critical configurations that trigger the transition (critical droplets)? What are the typical trajectories the dynamics follows in order to realize the transition (tube of trajectories)? Different approaches have been developed to tackle these questions. We will see what are the questions these approaches manage to answer. A unified theory is still lacking, and a detailed analysis of specific models and of model-dependent properties is therefore crucial to make progress on the key issues of interest.

1.2.1 Pathwise approach

The pathwise approach, in essence, exploits the large deviation techniques developed in the theory of Friedlin and Wentzell. This approach was initiated by Cassandro, Galves, Olivieri, Vares [CGOV84] in 1984, who applied large deviation techniques to a dynamics with Metropolis transition probabilities, i.e., probabilities depending on the difference of the energy of the configurations immediately before and after the transition. The equilibrium properties of the system are described by a probability measure that is determined by the Hamiltonian defined on the state space of the Markov chain. In the limit of inverse temperature β tending to ∞, it is hard for trajectories to climb out of wells in the energy landscape, and the local minima of the Hamiltonian correspond to the metastable states.

In the framework of the pathwise approach, it is natural to study the typical trajectories realizing the tunneling between the metastable and the stable configuration. In this description, a central role is played by the optimal paths, i.e., the paths

realizing the minimax between the metastable state and the stable state. The transition time is determined by the largest energy barrier separating these two states. A comprehensive overview of this method can be found in the monograph on large deviations and metastability by Olivieri and Vares [OV05]. The essential features of metastability have been listed in Manzo, Nardi, Olivieri, and Scoppola [MNOS04]. Here, the asymptotic behavior of the transition time is separated from the study of the typical trajectories realizing the transition. Results on the transition times are obtained via control on the depth of the wells of the energy landscape and the saddles connecting them.

1.2.2 Potential-theoretic approach

The potential-theoretic approach has been developed around 2000 in the works of Bovier, Eckhoff, Gayrard and Klein [BEGK01]. It exploits the link between potential theory and Markov processes. The Markov chain is regarded as an electric network, where the nodes of the network represent the configurations the Markov chain can visit and the edges of the network represent the possible transitions. The electric potential corresponds to the hitting probabilities, while the conductances associated with the edges correspond to the transitions rate between the configurations.

The potential-theoretic apporach largely discards the trajectories that play a central role in the theory of Freidlin and Wentzell. Nevertheless, this lack of information is compensated by the capability of computing sharp asymptotic bounds for the transition time. These bounds are obtained via the computation of capacities, which can be estimated with the help of powerful variational principles involving the potential and the current of the electric network associated with the Markov chain. Applications of the potential-theoretic approach can be found in Bovier and Manzo [BM02], Bovier, Eckhoff, Gayrard and Klein [BEGK04], Bovier, den Hollander and Nardi [BdN06], Bovier den Hollander and Spitoni [BdHS10]. For an overview, see Bovier [Bov06] and [Bov09].

1.3 Finite systems at low temperature

In the rest of this introduction we will focus on *Metropolis dynamics* in *finite volume* at *low temperature*. In words, we will take a finite state space, consider the asymptotic regime where the inverse temperature β tends to infinity, and use "updating rules" that only depend on the change in the energy associated with the transition. In this setting, the transition from the metastable to the stable state is

essentially driven by the energy landscape on the configuration space in which the system evolves. Many models in this class have been investigated over the past twenty years. The general setting is the following.

Let $\Lambda \subset \mathbb{Z}^d$, $d \geq 1$, and let S be a finite set. With each site $x \in \Lambda$ we associated a variable $\eta(x) \in S$. A configuration $\eta = \{\eta(x)\colon\ x \in \Lambda\}$ is an element of the state space $\mathcal{X} = S^\Lambda$. With each configuration we associate an energy given by a Hamiltonian $H\colon\ \mathcal{X} \to \mathbb{R}$ depending on one or more parameters. The equilibrium properties of the system are described by the *Gibbs measure*

$$\mu_\beta(\eta) = \frac{e^{-\beta H(\xi)}}{Z_\beta}, \qquad \eta \in \mathcal{X}, \tag{1.1}$$

where $\beta \in (0, \infty)$ is the inverse temperature, and Z_β is the normalizing partition sum. In the limit of low temperature the measure is concentrated on the global minimizer of H.

As dynamics we consider the continuous-time Markov process $(\eta_t)_{t\geq 0}$ with state space $\mathcal{X}$ whose transition rates are given by

$$c_\beta(\eta, \eta') = \begin{cases} e^{-\beta[H(\eta')-H(\eta)]_+}, & \eta, \eta' \in \mathcal{X},\ \eta \neq \eta',\ \eta \sim \eta', \\ 0, & \text{otherwise}, \end{cases} \tag{1.2}$$

where $\eta \sim \eta'$ means that η' can be obtained from η via a single draw from a *set of allowed moves* satisfying the following assumptions:

- $\sim$ is reflective, i.e., the reverse of an allowed move is allowed too.
- $\mathcal{X}$ is connected with respect to $\sim$, i.e., any two configurations are connected by a path of allowed moves.

This dynamics is called the *Metropolis dynamics* with respect to H at inverse temperature β. It is ergodic and reversible with respect to μ_β:

$$\mu_\beta(\eta)c_\beta(\eta, \eta') = \mu_\beta(\eta')c_\beta(\eta', \eta) \qquad \forall\, \eta, \eta' \in \mathcal{X}. \tag{1.3}$$

Choosing a particular model amounts to choosing Λ, S, H, β and $\sim$.

In this setting the following quantities are key for the analysis of the transition from a local minimizer of the Hamiltonian $\mathbf{m}$ to a global minimizer $\mathbf{s}$.

- $\Phi(\eta, \eta')$ is the *communication height* between $\eta, \eta' \in \mathcal{X}$ defined by

$$\Phi(\eta, \eta') = \min_{\omega\colon\ \eta \to \eta'} \max_{\sigma \in \omega} H(\sigma), \tag{1.4}$$

where $\omega\colon\ \eta \to \eta'$ is any path of allowed moves from η to η'. For non-empty sets $\mathcal{A}, \mathcal{B} \subseteq \mathcal{X}$ put

$$\Phi(\mathcal{A}, \mathcal{B}) = \min_{\eta \in \mathcal{A}, \eta' \in \mathcal{B}} \Phi(\eta, \eta'). \tag{1.5}$$

- $\mathcal{S}(\eta, \eta')$ is the *communication level set* between $\eta, \eta' \in \mathcal{X}$ defined by

$$\mathcal{S}(\eta, \eta') = \big\{\chi \in \mathcal{X}\colon\ \exists\, \omega\colon\ \eta \to \eta',\, \omega \ni \chi\colon\ \max_{\zeta \in \omega} H(\zeta) = H(\chi) = \Phi(\eta, \eta')\big\}. \tag{1.6}$$

- V_η is the *stability level* of $\eta \in \mathcal{X}$ defined by

$$V_\eta = \Phi(\eta, I_\eta) - H(\eta), \tag{1.7}$$

  where $I_\eta = \{\zeta \in \mathcal{X}\colon\ H(\zeta) < H(\eta)\}$ is the set of configurations with energy lower than η.

- $(\mathbf{m} \to \mathbf{s})_{\mathrm{opt}}$ is the set of paths realizing the minimax in $\Phi(\mathbf{m}, \mathbf{s})$.

In words, the communication height between configurations η and η' is the minimal energy the path needs to reach in order to achieve the transition between configurations η and η', whereas the stability level of a configuration is the height of the energy barrier separating a configuration η from the set of configurations with lower energy.

If the condition

$$V_\eta < V_{\mathbf{m}} \quad \forall \eta \in \mathcal{X} \setminus \{\mathbf{s}\} \tag{1.8}$$

holds, then the local minimum $\mathbf{m}$ is called a metastable configuration. The energy barrier separating $\mathbf{m}$ and $\mathbf{s}$ is denoted by

$$\Gamma^\star = \Phi(\mathbf{m}, \mathbf{s}) - H(\mathbf{m}). \tag{1.9}$$

If the energy landscape is sufficiently "well behaved" (for instance if $\mathbf{m}$ is metastable in the sense of (1.8)), then

$$\lim_{\beta \to \infty} \frac{1}{\beta} \log \mathbb{E}_{\mathbf{m}}(\tau_{\mathbf{s}}) = \Gamma^\star. \tag{1.10}$$

Furthermore, the probability distribution of the nucleation time divided by its

mean is exponential with mean 1. This is due to the fact that uphill transitions are improbable and each time the dynamics does not manage to climb over the hill it falls back to the bottom of the valley in the energy landscape where it came from and it starts afresh. For a detailed analysis, see [MNOS04].

Applying potential theory in this framework allows us to sharpen the results in (1.10). The key object in the potential-theoretic approach to metastability is the *Dirichlet form*

$$\mathcal{E}_\beta(h) = \tfrac{1}{2} \sum_{\eta,\eta' \in \mathcal{X}} \mu_\beta(\eta) c_\beta(\eta,\eta')[h(\eta) - h(\eta')]^2, \qquad h\colon\ \mathcal{X} \to [0,1], \tag{1.11}$$

where μ_β is the Gibbs measure defined in (1.1) and c_β is the kernel of transition rates defined in (1.2). Given a pair of non-empty disjoint sets $\mathcal{A}, \mathcal{B} \subseteq \mathcal{X}$, the *capacity* of the pair $\mathcal{A}, \mathcal{B}$ is defined by

$$\mathrm{CAP}_\beta(\mathcal{A},\mathcal{B}) = \min_{\substack{h\colon\ \mathcal{X}\to[0,1] \\ h|_{\mathcal{A}} \equiv 1, h|_{\mathcal{B}} \equiv 0}} \mathcal{E}_\beta(h), \tag{1.12}$$

where $h|_{\mathcal{A}} \equiv 1$ means that $h(\eta) = 1$ for all $\eta \in \mathcal{A}$ and $h|_{\mathcal{B}} \equiv 0$ means that $h(\eta) = 0$ for all $\eta \in \mathcal{B}$. The unique minimizer $h^\star_{\mathcal{A},\mathcal{B}}$ of (1.11) is called the *equilibrium potential* of the pair $\mathcal{A}, \mathcal{B}$ and is given by

$$h^\star_{\mathcal{A},\mathcal{B}}(\eta) = P_\eta(\tau_{\mathcal{A}} < \tau_{\mathcal{B}}), \qquad \eta \in \mathcal{X} \backslash (\mathcal{A} \cup \mathcal{B}). \tag{1.13}$$

This is the solution of the equation

$$(c_\beta h)(\eta) = 0, \qquad \eta \in \mathcal{X} \setminus (\mathcal{A} \cup \mathcal{B}), \tag{1.14}$$

$$h(\eta) = 1, \qquad \eta \in \mathcal{A}, \tag{1.15}$$

$$h(\eta) = 0, \qquad \eta \in \mathcal{B}, \tag{1.16}$$

with $(c_\beta h)(\eta) = \sum_{\eta' \in \mathcal{X}} c_\beta(\eta,\eta') h(\eta')$. Moreover,

$$\mathrm{CAP}_\beta(\mathcal{A},\mathcal{B}) = \sum_{\eta \in \mathcal{A}} \mu_\beta(\eta)\, c_\beta(\eta, \mathcal{X} \setminus \{\eta\})\, \mathbb{P}_\eta(\tau_{\mathcal{B}} < \tau_{\mathcal{A}}) \tag{1.17}$$

with $c_\beta(\eta, \mathcal{X}\setminus\{\eta\}) = \sum_{\eta' \in \mathcal{X}\setminus\{\eta\}} c_\beta(\eta,\eta')$ the rate to move out of η. This rate enters because $\tau_{\mathcal{A}}$ is the first hitting time of $\mathcal{A}$ after the initial configuration is left.

As shown in [BEGK02],

$$\mathbb{E}_{\mathbf{m}}(\tau_{\mathbf{s}}) = \frac{\mu_\beta(\mathcal{R}_{\mathbf{m}})}{\mathrm{CAP}_\beta(\mathbf{m},\mathbf{s})}\,[1 + o(1)] \quad \text{as } \beta \to \infty, \tag{1.18}$$

where

$$\mathcal{R}_{\mathbf{m}} = \{\eta \in \mathcal{X} \colon \mathbb{P}_\eta(\tau_{\mathbf{m}} < \tau_{\mathbf{s}}) \geq \mathbb{P}_\eta(\tau_{\mathbf{s}} < \tau_{\mathbf{m}})\} \tag{1.19}$$

is the set of configuration from which it is more likely to reach $\mathbf{m}$ before $\mathbf{s}$. Sharp estimates on the capacity therefore translate into sharp estimates on the nucleation time, provided the states $\mathbf{m}$ and $\mathbf{s}$ satisfy:

$$\lim_{\beta\to\infty} \frac{\max_{\eta\notin\{\mathbf{m},\mathbf{s}\}} \mu_{\beta(\eta)}/\mathrm{CAP}_{\beta(\eta,\{\mathbf{m},\mathbf{s}\})}}{\min_{\eta\in\{\mathbf{m},\mathbf{s}\}} \mu_{\beta(\eta)}/\mathrm{CAP}_{\beta(\eta,\{\mathbf{m},\mathbf{s}\})}} = 0. \tag{1.20}$$

If the previous equality holds, then the pair $(\mathbf{m}, \mathbf{s})$ is called a *metastable pair* according to Bovier, Eckhoff, Gayrard and Klein [BEGK02]. The estimates on the capacity can then be obtained via *variational principles*. In [dHNT11] it is shown that (1.8) indeed implies (1.20). Works where this approach is exploited are Bovier and Manzo [BM02], and Bovier, den Hollander and Nardi [BdN06].

1.3.1 Kawasaki dynamics on a finite box with open boundary for one type of particle

In this section we will explain what results have been obtained with the help of the potential-theoretic approach for the lattice gas subject to Kawasaki dynamics. Since this thesis focusses on Kawasaki dynamics with two types of particles, a review of this work provides the necessary background.

In [BdN06], Kawasaki dynamics on a large finite box $\Lambda \subset \mathbb{Z}^2$ is considered with an *open boundary condition* that mimics the presence of an infinite gas reservoir outside Λ with density $e^{-\beta\Delta}$, $\Delta > 0$. Particles are conserved inside Λ, and are created and annihilated at the boundary. In this sense, the dynamics is *locally conservative*. The set of critical configurations is identified, the expected value of the nucleation time is computed up to a multiplicative factor that tends to one, and it is shown that the nucleation time divied by its mean has exponential probability distribution with mean 1, all in the limit as $\beta \to \infty$. Moreover, sharp bounds are derived for the proportionality constant of the average nucleation time in term of capacities associated with simple random walk, and the asymptotic behavior of this constant is computed as the system size tends to infinity. These results sharpen those obtained by den Hollander, Olivieri and Scoppola [dOS00] on $\mathbb{Z}^2$ and den Hollander, Nardi, Olivieri and Scoppola [dHNOS03] on $\mathbb{Z}^3$ with the help of the pathwise approach.

The results in [BdN06] are comparable with those obtained by Bovier and Manzo

[BM02] for the Ising model on a finite box in two and three dimensions with periodic boundary conditions subject to Glauber dynamics at low temperature. This work, in terms, sharpened the results obtained by Neves and Schonmann [NS92] on $\mathbb{Z}^2$ and by Ben Arous and Cerf [BAC96] on $\mathbb{Z}^3$.

Since inside Λ the number of particles is conserved, controlling the growing and shrinking of a droplet is complicated because particles have to travel between the boundary of the box and the boundary of the droplet. Moreover, it turns out that particles move along the droplet faster than they arrive from the boundary of the box, and this makes the shape of the critical droplets more complicated than those for Ising spins subject to Glauber dynamics.

For the purpose of this introduction, we will only refer to the analysis in the two-dimensional case. Let $\Lambda \subset \mathbb{Z}^2$ be a large finite box. Let

$$\partial^- \Lambda = \{x \in \Lambda \colon\ \exists\, y \notin \Lambda \colon\ |y - x| = 1\}, \tag{1.21}$$

$$\partial^+ \Lambda = \{x \notin \Lambda \colon\ \exists\, y \in \Lambda \colon\ |y - x| = 1\}, \tag{1.22}$$

be the internal boundary, respectively, the external boundary of Λ, and put $\Lambda^- = \Lambda \backslash \partial^- \Lambda$ and $\Lambda^+ = \Lambda \cup \partial^+ \Lambda$. Let $S = \{0, 1\}$. A configuration η is an element of the space $\{0, 1\}^\Lambda$, where $\eta(x) = 1$ and $\eta(x) = 0$ denote, respectively, the presence or the absence of a particle at site x. As Hamiltonian, choose

$$H(\eta) = -U \sum_{x,y \in (\Lambda^-)^\star} \eta(x)\eta(y) + \Delta \sum_{x \in \Lambda} \eta(x), \tag{1.23}$$

where $(\Lambda^-)^\star = \{(x, y) \colon\ x, y \in \Lambda^-, |x - y| = 1\}$ is the set of non-oriented bonds inside Λ^- (with $|\cdot|$ the Euclidean norm), $-U < 0$ is the *binding energy* between neighboring particles Λ^-, and $\Delta \in (U, 2U)$ the *activation energy* for each particle in Λ.

Let $\square \equiv 0$ and $\blacksquare \equiv 1$. These configurations are associated, respectively, to the gas phase and the liquid phase. It is easy to see that $\blacksquare$ is the global minimizer of the Hamiltonian. In [dOS00] it is proven that $\mathbf{m} = \square$ and the value of $\Gamma^\star = \Phi(\square, \blacksquare) - H(\square)$ is determined. Note that, since $H(\square) = 0$, $\Gamma^\star$ coincide with the energy of a critical configuration.

The paradigmatic shape of critical configurations was identified in [dOS00]. It consist of a droplet whose support is quasi-square of side lengths $(\ell_c, \ell_c - 1)$ plus a protuberance on the longest side of the rectangle plus a particle at $\partial^- \Lambda$, where

$$\ell_c = \left\lceil \frac{U}{2U - \Delta} \right\rceil \tag{1.24}$$

(the condition $\frac{U}{2U-\Delta} \notin \mathbb{N}$ is assumed in order to avoid ties). In [BdN06] the full geometry of the set of critical configurations has been determined. It consists of all the configurations obtained by adding a particle in a site in $\partial^- \Lambda$ to a configuration belonging to a set $\mathcal{D}$ defined as $\mathcal{D} = \bar{\mathcal{D}} \cup \widetilde{\mathcal{D}}$ where

– $\bar{\mathcal{D}}$ is the set of configurations with a single cluster anywhere in Λ^- whose support consists of an $(\ell_c - 2) \times (\ell_c - 2)$ square with four bars of lengths $\bar{k}_i$, $i = 1, 2, 3, 4$, attached to its four sides satisfying

$$1 \le \bar{k}_i \le \ell_c - 1, \qquad \sum_i \bar{k}_i = 3\ell_c - 3; \tag{1.25}$$

– $\widetilde{\mathcal{D}}$ is the set of configurations with a single cluster anywhere in Λ^- whose support consists of an $(\ell_c - 3) \times (\ell_c - 1)$ rectangle with four bars of lengths $\widetilde{k}_i$, $i = 1, 2, 3, 4$, attached to its four sides satisfying

$$1 \le \widetilde{k}_i \le \ell_c - 1, \qquad \sum_i \widetilde{k}_i = 3\ell_c - 2. \tag{1.26}$$

Configurations in $\mathcal{D}$ are called protocritical. The set of critical configurations is denoted by $\mathcal{D}^{\rm fp}$. It is proven that the dynamics visits the set of critical configurations with probability 1,

$$\lim_{\beta\to\infty} P_{\square}(\tau_{\mathcal{D}^{\rm fp}} < \tau_{\boxplus} \mid \tau_{\boxplus} < \tau_{\square}) = 1, \tag{1.27}$$

and that all critical configurations are equally likely to be visited,

$$\lim_{\beta\to\infty} P_{\square}(\eta_{\tau_{\mathcal{C}^\star_{\rm bd}}} = \zeta) = 1/|\mathcal{D}^{\rm fp}| \quad \forall\, \zeta \in \mathcal{D}^{\rm fp}, \tag{1.28}$$

when the dynamics reaches for the first time the set $\mathcal{D}^{\rm fp}$.

Application of potential theory to the estimation of the expected nucleation time allows for a proof that there is a constant $K = K(\ell_c, \Lambda)$ such that

$$\mathbb{E}_{\square}(\tau_{\blacksquare}) = K e^{\beta\Gamma^\star}[1 + o(1)] \quad \text{as } \beta \to \infty. \tag{1.29}$$

For the value of K a variational formula is derived whose exact computation is

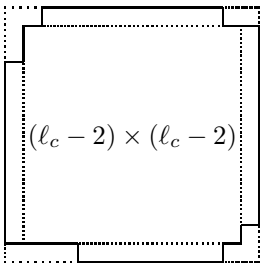

Figure 1.1: A configuration in $\bar{\mathcal{D}}$ with an $(\ell_c - 2) \times (\ell_c - 2)$ square in the center and four bars attached to it. A similar picture applies for $\widetilde{\mathcal{D}}$ with an $(\ell_c - 3) \times (\ell_c - 1)$ rectangle in the center.

highly non-trivial. However, as $\Lambda \to \mathbb{Z}^2$,

$$K \sim \frac{1}{4\pi N(\ell_c)} \frac{\log |\Lambda|}{|\Lambda|} \tag{1.30}$$

with

$$N(\ell_c) = \sum_{k=1,2,3,4} \binom{4}{k} \left[\binom{\ell_c + k - 2}{2k - 1} + 2 \binom{\ell_c + k - 3}{2k - 1} \right] \tag{1.31}$$

being the cardinality of the set $\mathcal{D}$ modulo shifts.

1.3.2 Kawasaki dynamics on a finite box with open boundary for two types of particles

The model studied in this thesis constitutes a first attempt to generalize the results in [BdN06] for two dimensions to *multi-type particles systems*. We take a large finite box $\Lambda \subset \mathbb{Z}^2$. Particles come in two types: type 1 and type 2. Particles hop around subject to hard-core repulsion, and are conserved inside Λ. At the boundary of Λ particles are created and annihilated as in a gas reservoir, where the two types of particles have different densities $e^{-\beta\Delta_1}$ and $e^{-\beta\Delta_2}$. Also in this case the dynamics

is locally conservative. The Hamiltonian is

$$H(\eta) = -U_{12} \sum_{x,y\in(\Lambda^-)^\star} 1_{\eta(x)\eta(y)=2} - U_{11} \sum_{x,y\in(\Lambda^-)^\star} 1_{\eta(x)\eta(y)=1} - U_{22} \sum_{x,y\in(\Lambda^-)^\star} 1_{\eta(x)\eta(y)=4} \tag{1.32}$$

$$+ \Delta_1 \sum_{x\in\Lambda} 1_{\eta(x)=1} + \Delta_2 \sum_{x\in\Lambda} 1_{\eta(x)=2}, \tag{1.33}$$

where $U_{i,j} > 0$ is the binding energy between particles of type i and j and Δ_i is the activation energy of particles of type i. This dynamics can be seen as a conservative analogue of the Blume-Capel model investigated by Cirillo and Olivieri [CO96].

The phase diagram of this model turns out to be very rich: we have to take into account different metastable states. In our analysis, though, we only consider the simplified version of the model obtained by setting $U_{11} = U_{22} = 0$. In order to lighten the notation, we will write $U_{12} = U$. Thus, the Hamiltonian becomes

$$H(\eta) = -U \sum_{x,y\in(\Lambda^-)^\star} 1_{\eta(x)\eta(y)=2} + \Delta_1 \sum_{x\in\Lambda} 1_{\eta(x)=1} + \Delta_2 \sum_{x\in\Lambda} 1_{\eta(x)=2}. \tag{1.34}$$

We will see that for this simplified version of the model the geometry of the local minimizers of the Hamiltonian and saddle points connecting them is already very involved and heavily depends on the values of Δ_1 and Δ_2. The main goal of the thesis is to classify the metastable behavior in different parameter regimes.

1.4 Overview of the main results in the thesis

In Chapter 2 we define the model that is the object of our study. We identify the values of the parameters for which the model properly describes the condensation of a supersaturated gas and exhibits a metastable behavior. Under *three hypotheses*, we determine the distribution and the expectation of the nucleation time, and identify the so-called critical configurations that satisfy a certain "gate property". The first hypothesis assumes that a configuration corresponding to the liquid phase is a minimizer of the Hamiltonian. The second hypothesis requires that the valleys of the energy landscape are not too deep. The third hypothesis requires that the critical configurations have an appropriate geometry. Subject to the three hypotheses, several theorems are derived, for which *three model-dependent quantities* need to be identified as well: (1) the energy barrier $\Gamma^\star$ separating the configuration $\square$ consisting of the empty box and the set $\mathcal{X}_{\text{stab}}$ of global minimizers of the Hamiltonian; (2) the set $\mathcal{C}^\star$ of critical configurations; (3) the cardinality $N^\star$ of the

the set of protocritical configurations. This set can be thought as the "entrance" of $\mathcal{C}^\star$. These quantities are identified in Chapters 3 and 4 via a detailed analysis of the energy landscape that combines combinatorial and geometric techniques.

In Chapter 3 it is shown that the first two hypotheses are satisfied and the first model-dependent quantity is identified.

- In the first part of this chapter we prove that a configuration $\boxplus$, consisting of a large checkerboard filling the volume Λ, minimizes the Hamiltonian, and we identify the energy barrier $\Gamma^\star$ separating the configuration $\square$ from the set $\mathcal{X}_{\text{stab}}$ of global minimizers of the Hamiltonian. To carry out this task, the number of particles of type 2 is identified as a key quantity, and the configurations of minimal energy for a fixed number of particle of type 2 is identified. This is achieved by observing that in configurations of minimal energy, since we will assume that $\Delta_1 < U$, particles of type 2 must be surrounded by particles of type 1. This allows us to look at configurations of minimal energy not as clusters of single particles, but as clusters of "tiles": particles of type 2 surrounded by particles of type 1. To deal with tiles, it is convenient to look at the representation of configurations on a dual lattice. With this dual representation, a tile correspond to a unit square and the configurations of minimal energy are those where these unit squares are arranged in an "optimal" manner. It turns out that for a fixed number of particles of type 2 the quantity over which the optimization must be performed is the number of particles of type 1. This number is linked to the perimeter and the shape of the "polyomino" (union of unit squares) associated with the tiles in a configuration. It turns out that, in order to minimize the energy, the polyomino must be a convex polyomino of minimal perimeter. With this observation, the ground state is easily identified to be a configuration $\boxplus$ consisting of the largest checkerboard configuration fitting inside the box Λ. The prototype shape of critical configurations and the value of $\Gamma^\star$ are then easily derived by considering a foliation of the state space according to the number of particles of type 2 in Λ. Note that all these results only require us to analyze the model from a static point of view.

- In the second part of this chapter we derive an upper bound for the stability level of all the configurations in $\mathcal{X}$, i.e., (loosely speaking) for the depth of the valleys of the energy landscape, and we make sure that close to the phase transition curve the depth of these valleys is smaller than $\Gamma^\star$. Here the particular dynamics that has been chosen plays a crucial role. In order to show that each configuration η other than $\square$ and $\boxplus$ is separated from a configuration with lower energy by a barrier smaller than $\Gamma^\star$, a path leading to $\mathcal{I}_\eta$ is constructed. The complication arises from the fact that particles

can only be created and annihilated at the boundary of Λ, and that the path they follow inside Λ is constrained by the presence of other particles. Furthermore, the fact that only particles of different types feel an attractive interaction poses the problem of parity of clusters: when clusters are close to each other they cannot merge when they have different parity. As a consequence, the transition from one configuration η to a configuration η' that differs from η only at a single site x may require the motion of many particle occupying sites possibly far from x. To achieve this we will make use of a recursive algorithm that, starting from any configuration η, allows us to find a sequence of configurations whose energy is non-increasing that eventually reaches the set $\mathcal{I}_\eta$.

The results derived in Chapter 3 are sufficient to establish the exponential probability distribution of the nucleation time divided by its mean and to determine the mean nucleation time up to a multiplicative factor of order $1+\mathrm{o}(1)$ as $\beta \to \infty$.

In Chapter 4 it is shown that the model satisfies the third hypothesis, and the set of critical configurations is identified. We give a geometric characterization of the configurations $\mathcal{C}^\star$ and compute the value of $N^\star$. A prototype of the critical configuration is already identified in Chapter 3, and consists of a configuration of minimal energy with $\ell^\star(\ell^\star - 1) + 1$ particles of type 2 arranged in a cluster of minimal energy plus a particle of type 2. The difficult task is to characterize the *full* set of critical configurations. Also this part of the analysis uses the specific dynamical aspects of the model, which are investigated in detail in a neighborhood of the saddle configurations $\mathcal{S}(\square, \boxplus)$.

The tiles making up the cluster can travel around the cluster faster than particles of type 2 can appear at the boundary of Λ. This motion of tiles along the border gives the dynamics the opportunity to extend the set of critical configurations. Different mechanism are identified that allow tiles to travel around a cluster. The energy barrier that must be overcome in order to activate these mechanisms is determined, and is compared with the energy barrier the dynamics has to climb in order to let a particle enter Λ. How rich the set of critical configurations is depends on the relative magnitude of these barriers. Consequently, the geometry of this set is highly sensitive to the choice of parameters: the set of critical configurations is indeed very different in different regions of the parameter space.

The problem of computing the value $N^\star$, i.e., the cardinality of the set of protocritical configurations, is reduced to counting the number of polyominoes of minimal perimeter belonging to certain classes of configurations that depend on the values of the parameters Δ_1 and Δ_2. This is a non-trivial problem that is interesting in its own right. With these results we are able to derive the sharp asymptotics

for the nucleation time and to find the entrance distribution of the set of critical configurations.

Results in this chapter are derived using a foliation of the state space according to the number of particles of type 1 in Λ and the fact that configurations in $\mathcal{C}^\star$ must satisfy a "gate property", i.e., they must be visited by all optimal paths. These results allow us to derive appropriate variational formulas for $\mathrm{CAP}(\square, \boxplus)$ and compute sharp asymptotic values for the expected nucleation time.