

Report 99-053
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ISSN 1389-2355

Nucleation in fluids: some rigorous results

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November 24, 1999

Abstract

In this paper we review some recent results obtained in [4] on metastability and nucleation for the two-dimensional lattice gas with Kawasaki dynamics at low temperature and low density. We also present some new results on the typical path of nucleation and discuss some open problems. The conservation of particles makes the analysis much harder than for Glauber dynamics.

AMS 1991 subject classifications. 60K35, 82C26.

Key words and phrases. Lattice gas, Kawasaki dynamics, critical droplet, dynamical phase transition.

Acknowledgment. Research partially supported by MURST-grant Cofinanziamento 1998 Scienze Fisiche/21.

* This paper is dedicated to Joel Lebowitz on the occasion of his 70-th birthday. His pioneering work with Oliver Penrose in the early 1970's on metastability in van der Waals theory has opened up a new area in mathematical physics.

1 Recent results on metastability and nucleation

1.1. Introduction. Metastability is a dynamic phenomenon taking place in the vicinity of a first-order phase transition. Typical examples are supersaturated vapours and magnetic materials with a magnetization opposite to the external field. We may prepare the system in a pure equilibrium phase, characterized by thermodynamic parameters close to a phase transition curve, and change one of the parameters so as to move to the opposite side of the curve. We may then observe that the system, instead of undergoing a phase transition, persists in

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the old unstable phase, called *metastable state*, until it tunnels to a new stable phase. The escape from this metastable state is driven by the formation of a “critical nucleus” of the new phase.

The activation energy necessary to nucleate a large enough droplet of the new phase can be very high, so that the life-time of the metastable state can be very long. Before the escape, which itself takes place in a relatively short time, the system behaves in a stationary way (in some sort of temporary equilibrium) characterized by many unsuccessful attempts to nucleate.

The above two examples share the main features of metastability, but they exhibit some physically relevant differences. The supersaturated vapour is *conservative*: expansion and contraction of a liquid droplet inside the supersaturated vapour take place via absorption and evaporation, which preserve the number of particles. A possible model is provided by the Kawasaki lattice gas dynamics, where the elementary process is an exchange between occupation numbers of neighbouring sites. The equilibrium in this case is naturally described by the *canonical* Gibbs ensemble. The magnetic materials, on the other hand, are *non-conservative*: expansion and contraction of the droplet take place via spin flips at the boundary of the droplet, which do not preserve the magnetization. A possible model is provided by the Glauber Ising spin dynamics, where the elementary process is a flipping of individual spins. The equilibrium in this case is the *grand-canonical* Gibbs ensemble.

Let us compare these two types of dynamics. To fix ideas, we choose in both cases a Metropolis algorithm and adopt the lattice gas language, i.e., the plus sites in the Ising spin version correspond to the occupied sites in the lattice gas version. The magnetization then corresponds to the particle density. In the Kawasaki dynamics, when we analyze a small subsystem, both this subsystem and the “reservoir” given by the rest of the system have to be simultaneously taken into consideration, as they both take part in the dynamics. In particular, if we want to describe the growth of a nucleus of liquid inside the supersaturated vapour, then we are forced to analyze the surrounding gas and its interaction with the nucleus through an exchange of particles. In contrast, such an exchange does not occur in the Glauber dynamics, since particles can be created or annihilated. We may formally think of the Glauber dynamics as a lattice gas dynamics with an “omnipresent reservoir” of particles. But we do not need to include this reservoir into our description, since it does not participate in the dynamics. We refer to [10] for relevant references.

1.2. A simplified model. In [4] we considered a local version of the Kawasaki lattice gas model defined as follows. Let $\Lambda_\beta \subset \mathbb{Z}^2$ be a large finite box centered at the origin, with periodic boundary conditions. Let $\bar{\Lambda} \subset \Lambda_\beta$ be a smaller box centered at the origin. We think of Λ_β as our full system and of $\bar{\Lambda}$ as our “observation window”. With each $x \in \Lambda_\beta$ we associate an occupation variable $\eta(x)$, assuming the values 0 or 1 for $x \in \bar{\Lambda}$ and any non-negative integer for $x \in \Lambda_\beta \setminus \bar{\Lambda}$. A lattice gas configuration is denoted by

$$\eta \in \mathcal{X} = \{0, 1\}^{\bar{\Lambda}} \times \mathbb{N}_0^{\Lambda_\beta \setminus \bar{\Lambda}}. \quad (1.1)$$

We take the interaction to be defined by the following Hamiltonian:

$$H(\eta) = -U \sum_{(x,y) \in \bar{\Lambda}_0^*} \eta(x)\eta(y), \quad (1.2)$$

where $\bar{\Lambda}_0^*$ is the set of bonds in $\bar{\Lambda}_0 = \bar{\Lambda} \setminus \partial^- \bar{\Lambda}$ with $\partial^- \bar{\Lambda}$ the interior boundary of $\bar{\Lambda}$. Thus, there is a binding energy $U > 0$ between neighboring occupied sites in $\bar{\Lambda}_0$. The interaction only acts inside $\bar{\Lambda}_0$. Outside $\bar{\Lambda}_0$ there is no interaction, outside $\bar{\Lambda}$ there is even no exclusion.

We fix the particle density in Λ_β at $\rho = e^{-\Delta\beta}$ with $\Delta > 0$. This corresponds to a total number of particles

$$N_{\Lambda_\beta}(\eta) = \sum_{x \in \Lambda_\beta} \eta(x) = \rho |\Lambda_\beta| = N. \quad (1.3)$$

On the set of configurations with N particles

$$\mathcal{N}_N = \{\eta \in \mathcal{X}: N_{\Lambda_\beta}(\eta) = N\} \quad (1.4)$$

we define the *canonical Gibbs measure*

$$\nu_N(\eta) = \frac{e^{-\beta H(\eta)} 1_{\mathcal{N}_N}(\eta)}{Z_N} \quad (\eta \in \mathcal{X}) \quad (1.5)$$

with $Z_N = \sum_{\eta \in \mathcal{N}_N} e^{-\beta H(\eta)}$.

We will consider a stochastic dynamics on the state space \mathcal{N}_N given by independent random walks outside $\bar{\Lambda}$ and Kawasaki dynamics inside $\bar{\Lambda}$. The latter means that inside $\bar{\Lambda}$ two nearest-neighbor sites x and y exchange their occupation numbers, leading from the configuration η to the configuration η^{xy} , at a rate given by $e^{-\beta[H(\eta^{xy}) - H(\eta)]_+}$, where $[\cdot]_+$ denotes the positive part. Clearly, ν_N is the equilibrium measure of this dynamics.

We see from the choice of the density ρ that, in order to have particles at all, we must pick $|\Lambda_\beta|$ at least exponentially large in β . This means that the regime where Λ_β is fixed, typically considered in the Glauber dynamics, has no relevance here. We are in fact interested in the regime

$$\Delta \in (U, 2U), \quad \beta \rightarrow \infty, \quad \lim_{\beta \rightarrow \infty} \frac{1}{\beta} \log |\Lambda_\beta| = \infty, \quad (1.6)$$

corresponding to a low temperature and low density limit. The restriction on Δ arises as follows. The density $\rho_g = \rho_g(\beta)$ of the saturated vapour is related to the spontaneous magnetization $m^* = m^*(\beta)$ in the spin language by the formula $\rho_g = \frac{1+(-m^*)}{2}$. Since $m^* = 1 - e^{-2U\beta + o(\beta)}$ for large β in the lattice gas language, a supersaturated vapour with $\rho \gg \rho_g$ corresponds to $\Delta < 2U$. On the other hand, in order to have a metastable regime at all, we need $\Delta > U$, since otherwise even a minimal cluster of two particles would have a tendency to grow. This is because $e^{U\beta}$ is the typical time for the two particles to break up under the Kawasaki dynamics, while $e^{\Delta\beta}$ is the typical time needed for the gas to send in a third particle.

1.3. Notation. Let

$$\begin{aligned} \blacksquare &= \{\eta \in \mathcal{X}: \eta(x) = 1 \ \forall x \in \bar{\Lambda}_0\} \\ \square &= \{\eta \in \mathcal{X}: \eta(x) = 0 \ \forall x \in \bar{\Lambda}\}. \end{aligned} \quad (1.7)$$

For $\bar{\eta} \in \bar{\mathcal{X}} = \{0, 1\}^{\bar{\Lambda}}$, let $\nu_{\bar{\eta}}$ denote the canonical Gibbs measure on \mathcal{X} conditioned on the configuration inside $\bar{\Lambda}$ being $\bar{\eta}$, i.e.,

$$\nu_{\bar{\eta}}(\eta) = \frac{\nu(\eta) 1_{I_{\bar{\eta}}}(\eta)}{\nu(I_{\bar{\eta}})} \quad (\eta \in \mathcal{X}), \quad (1.8)$$

where $I_{\bar{\eta}} = \{\eta \in \mathcal{X}: \eta|_{\bar{\Lambda}} = \bar{\eta}\}$, $\eta|_{\bar{\Lambda}}$ is the restriction of η to $\bar{\Lambda}$, and $\nu = \nu_N$ is the canonical Gibbs measure defined in (1.5). For $\bar{\eta} \in \bar{\mathcal{X}}$, write $\mathbb{P}_{\nu_{\bar{\eta}}}$ to denote the probability law of the Markov process $(\eta_t)_{t \geq 0}$ on \mathcal{X} following the above stochastic dynamics when η_0 is chosen according to $\nu_{\bar{\eta}}$. For $\mathcal{A} \subset \mathcal{X}$, let

$$\tau_{\mathcal{A}} = \min\{t \geq 0: \eta_t \in \mathcal{A}\} \quad (1.9)$$

be the first hitting time of the set \mathcal{A} .

Let

$$\bar{H}(\bar{\eta}) = H(\bar{\eta}) + \Delta N_{\bar{\Lambda}}(\bar{\eta}) \quad (\bar{\eta} \in \bar{\mathcal{X}}) \quad (1.10)$$

be the *local grand-canonical* Hamiltonian associated with $\bar{\Lambda}$, i.e., $-\Delta$ plays the role of a chemical potential. For $\bar{\eta}, \bar{\eta}' \in \bar{\mathcal{X}}$, let $\bar{H}(\bar{\eta}, \bar{\eta}')$ be the solution of the minimax problem between $\bar{\eta}$ and $\bar{\eta}'$, i.e.,

$$\bar{H}(\bar{\eta}, \bar{\eta}') = \min_{\bar{\phi} = (\bar{\phi}_t): \bar{\eta} \rightarrow \bar{\eta}'} \max_t \bar{H}(\bar{\phi}_t) \quad (1.11)$$

with the minimum running over all paths from $\bar{\eta}$ to $\bar{\eta}'$.

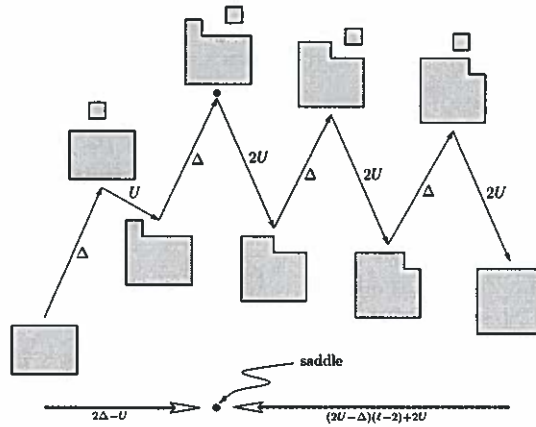


FIG. 1. Local saddles of \bar{H}

The energy barriers for adding resp. removing a row or column of length l on a rectangular droplet are given in terms of the local saddles of \bar{H} (see Fig. 1):

$$\begin{aligned} \text{energy barrier for adding} &= 2\Delta - U \\ \text{energy barrier for removing} &= (2U - \Delta)(l-2) + 2U. \end{aligned} \quad (1.12)$$

The balance of the two barriers gives the *critical droplet size*:

$$\ell_c = \left\lceil \frac{U}{2U - \Delta} \right\rceil. \quad (1.13)$$

It is possible to evaluate $\bar{H}(\bar{\square}, \bar{\blacksquare})$ and to identify the set $\bar{\mathcal{C}}^*$ of saddle point configurations where the minimax between $\bar{\square}$ and $\bar{\blacksquare}$ is achieved. Indeed, let $\bar{\mathcal{R}}^* \subset \bar{\mathcal{X}}$ be the set of configurations inside $\bar{\Lambda}$ where the particles form a quasi-square with side lengths $\ell_c - 1$ and ℓ_c , with a protuberance attached anywhere to one of the sides of length ℓ_c , and with a free particle anywhere else, all contained in $\bar{\Lambda}_0$ (see Fig. 2). Then it turns out that $\bar{\mathcal{C}}^* \supset \bar{\mathcal{R}}^*$ is the set of those configurations that are U -equivalent to some configuration in $\bar{\mathcal{R}}^*$, i.e., can be connected to that configuration via a path with a maximal saddle U .

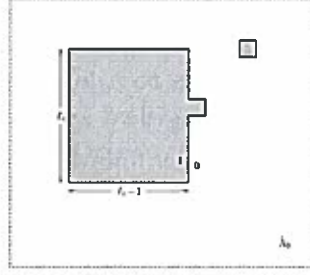


FIG. 2. A critical droplet configuration

1.4. Main theorem on metastability and nucleation. We are now ready to formulate the main result in [4].

Theorem 1 ([4]) *Let $\Delta \in (\frac{3}{2}U, 2U)$ and suppose that $\frac{U}{2U - \Delta}$ is not integer. (a) Let $\bar{\mathcal{R}} \subset \bar{\mathcal{X}}$ be the set of configurations inside $\bar{\Lambda}$ where the particles form a square or quasi-square contained in $\bar{\Lambda}_0$. For $\bar{\eta} \in \bar{\mathcal{R}}$, let $\ell_1(\bar{\eta}) \times \ell_2(\bar{\eta})$ with $|\ell_1(\bar{\eta}) - \ell_2(\bar{\eta})| \leq 1$ be the square or quasi-square of particles in $\bar{\eta}$, and let $\ell(\bar{\eta}) = \min\{\ell_1(\bar{\eta}), \ell_2(\bar{\eta})\}$. Then, for any $\bar{\eta} \in \bar{\mathcal{R}}$,*

$$\begin{aligned} \ell(\bar{\eta}) < \ell_c &: \lim_{\beta \rightarrow \infty} \mathbb{P}_{\nu_{\bar{\eta}}}(\tau_{\square} < \tau_{\blacksquare}) = 1 \\ \ell(\bar{\eta}) \geq \ell_c &: \lim_{\beta \rightarrow \infty} \mathbb{P}_{\nu_{\bar{\eta}}}(\tau_{\blacksquare} < \tau_{\square}) = 1. \end{aligned} \quad (1.14)$$

(b) Let $\theta_{\square, \blacksquare} = \max\{t < \tau_{\blacksquare}: \eta_t \in \square\}$ and $\tau_{\square, \bar{\mathcal{C}}^*, \blacksquare} = \min\{t > \theta_{\square, \blacksquare}: \eta_t \in \bar{\mathcal{C}}^*\}$. Then

$$\lim_{\beta \rightarrow \infty} \mathbb{P}_{\nu_{\square}}(\tau_{\square, \bar{\mathcal{C}}^*, \blacksquare} < \tau_{\blacksquare}) = 1. \quad (1.15)$$

(c) Let $\Gamma = \Gamma(U, \Delta) = -U(2\ell_c^2 - 4\ell_c + 2) + \Delta(\ell_c^2 - \ell_c + 2)$. Then

$$\lim_{\beta \rightarrow \infty} \mathbb{P}_{\nu_{\square}}\left(e^{(\Gamma - \delta)\beta} < \tau_{\blacksquare} < e^{(\Gamma + \delta)\beta}\right) = 1 \quad \forall \delta > 0. \quad (1.16)$$

Theorem 1 not only identifies the size and shape of the critical droplet (see Fig. 2), it also shows that the critical droplet is the “gate” of the transition from \square to \blacksquare , and it identifies the transition time up to logarithmic equivalence in β . Note that $\Gamma(U, \Delta)$ is the energy of the critical droplet under the local grand-canonical Hamiltonian in (1.10).

A result similar to Theorem 1 under the Glauber dynamics has been derived in [6], [7].

There are important differences in the way clusters evolve under the Kawasaki dynamics and the Glauber dynamics. In particular, under the Kawasaki dynamics there is a movement of particles *along the border* of a rectangular droplet, leading to a (more stable) square or quasi-square droplet on a time scale much shorter than the one needed to grow or shrink (namely $e^{\Delta\beta}$). It turns out that the geometry of this movement has its own peculiarities.

Our simplified model is a *local* version of a lattice gas. The removal of the interaction outside $\bar{\Lambda}_0$ and the exclusion outside $\bar{\Lambda}$ allows us to mathematically control the gas. From a physical point of view this approximation seems very reasonable, because $\beta \rightarrow \infty$ corresponds to a low density limit ($\rho = e^{-\Delta\beta}$) in which the gas essentially behaves like an ideal gas.

The rest of this paper is organized as follows. In Section 2 we sketch the main ideas behind the proof of Theorem 1 (the full proof in [4] is long and technically complicated). The key ingredient is Proposition 2 below, which gives bounds on some of the transition probabilities in a “reduced dynamics”. In Section 3 we formulate a sharpening of the latter (Proposition 3 below). Under a certain conjecture (Conjecture 4 below), this sharpening is used to extend Theorem 1 to a statement about the “typical trajectory” followed by the reduced dynamics during the nucleation (Theorem 5 below). In Section 4 we close by formulating some open problems.

2 Sketch of the proof of Theorem 1

The main ingredients in the proof of Theorem 1 are the following:

1. Control of the gas particles outside $\bar{\Lambda}$ over long time intervals via random walk estimates.
2. Study of a local Markov chain on $\bar{\Lambda}$ in which the effect of the gas outside $\bar{\Lambda}$ is simulated by creation of particles on $\partial^- \bar{\Lambda}$ at rate $e^{-\Delta\beta}$ and annihilation of particles when they attempt to leave $\bar{\Lambda}$.
3. Control of the interaction between the gas outside $\bar{\Lambda}$ and the configuration inside $\bar{\Lambda}$ by means of a comparison of the full Markov chain and the local Markov chain.

We comment on each of these ingredients in some more detail.

1. Starting from equilibrium, we can obtain a priori estimates on the density of the gas particles in large boxes around $\bar{\Lambda}$ in terms of large deviation estimates

away from the equilibrium measure. These estimates turn out to be superexponentially sharp in β up to times that are exponentially large in β . These density estimates can be combined with standard random walk estimates in order to control the behavior of the gas particles over long time intervals. For instance, we can prove that the probability that a gas particle arrives at a given site $x \in \partial^- \bar{\Lambda}$ at a given time t is of order $e^{-\Delta\beta}$, provided t is at least of order $e^{\Delta\beta}$ itself. This estimate shows that the arrival of gas particles can be described by a creation process on $\partial^- \bar{\Lambda}$ at rate $e^{-\Delta\beta}$. Similarly, since a random walk in two dimensions is almost transient, once a particle leaves $\bar{\Lambda}$ it will typically need a very long time to return. Hence, an annihilation process for such particles is a good approximation.

2. We define the *local Markov chain* $(\bar{\eta}_t)$ on $\bar{\mathcal{X}}$ by considering the Metropolis algorithm with Hamiltonian \bar{H} defined in (1.10). This dynamics precisely corresponds to the Kawasaki dynamics inside $\bar{\Lambda}$, to creation of particles on $\partial^- \bar{\Lambda}$ at rate $e^{-\Delta\beta}$, and to annihilation of particles when they attempt to leave $\bar{\Lambda}$. This dynamics is in the Freidlin-Wentzell regime (see [3]) and thus its analysis can be carried out rather easily.

We can classify the configurations in $\bar{\mathcal{X}}$ into subsets of increasing geometric “regularity”:

$$\bar{\mathcal{X}} \supset \bar{\mathcal{X}}_1 \supset \bar{\mathcal{X}}_2 \supset \bar{\mathcal{X}}_3. \quad (2.1)$$

We can prove that the local Markov chain $(\bar{\eta}_t)$ visits the set $\bar{\mathcal{X}}_i$ within a time $T_i e^{\delta_0 \beta}$ with a probability that is close to one superexponentially in β , where $\delta_0 > 0$ is arbitrary and

$$T_1 = 1 \ll T_2 = e^{U\beta} \ll T_3 = e^{\Delta\beta} \quad (2.2)$$

are the basic time scales of the dynamics. This behavior is referred to as the “recurrence property”.

The set $\bar{\mathcal{X}}_1$ is chosen to consist of those configurations that are local minima of \bar{H} , i.e., those $\bar{\eta}$ such that there is no path from $\bar{\eta}$ to any $\bar{\eta}'$ with $\bar{H}(\bar{\eta}') < \bar{H}(\bar{\eta})$ along which the energy \bar{H} does not increase. Following the ideas developed in the Freidlin-Wentzell scenario, we choose the set $\bar{\mathcal{X}}_2 \subset \bar{\mathcal{X}}_1$ to consist of those configurations $\bar{\eta}$ such that there is no path from $\bar{\eta}$ to any $\bar{\eta}'$ with $\bar{H}(\bar{\eta}') < \bar{H}(\bar{\eta})$, this time allowing paths that contain segments in which the energy \bar{H} increases but not more than U , i.e., we replace the concept of a non-increasing path by a “downhill cascade in which a sequence of lakes of depth at most U can be present”. Replacing U by Δ , we obtain an even smaller set $\bar{\mathcal{X}}_3 \subset \bar{\mathcal{X}}_2$.

With this iterative procedure, we are selecting configurations that are ever more “regular” from a geometric point of view. For instance, configurations in $\bar{\mathcal{X}}_1$ have no free particles, configurations in $\bar{\mathcal{X}}_2$ have no protuberances. The configurations in $\bar{\mathcal{X}}_3$ can be characterized as follows. For $0 \leq \ell_2 - \ell_1 \leq 1$, let $\mathcal{R}_{\ell_1, \ell_2}$ denote the set of all configurations inside $\bar{\Lambda}$ where the occupied sites form an $\ell_1 \times \ell_2$ rectangle, including all possible translations and rotations. These are called squares or quasi-squares. Let \mathcal{L} denote the set of all configurations where the occupied sites form a square or quasi-square with minimal side length $\ell_1 > \frac{\ell_0}{3}$ (ℓ_0 is the side length of $\bar{\Lambda}$) with “holes” inside that have a sufficiently

regular shape. These are called lacunary squares or quasi-squares. It turns out that $\bar{\mathcal{X}}_3 = (\cup_{0 \leq \ell_2 - \ell_1 \leq 1} \mathcal{R}_{\ell_1, \ell_2}) \cup \mathcal{L}$.

3. We now come to the difficult part of the proof. Namely, we have to compare the local Markov chain and the full Markov chain by studying the interaction of the gas particles outside $\bar{\Lambda}$ with the configuration inside $\bar{\Lambda}$.

The first step here is to prove that also for the full Markov chain (η_t) the recurrence property holds for suitably regular sets:

$$\begin{aligned} \mathcal{X}_1 &= \{\eta \in \mathcal{X}: \bar{\eta}|_{\bar{\Lambda}} \in \bar{\mathcal{X}}_1\} \\ \mathcal{X}_2 &= \{\eta \in \mathcal{X}: \bar{\eta}|_{\bar{\Lambda}} \in \bar{\mathcal{X}}_2\} \\ \mathcal{X}_3 &= \{\eta \in \mathcal{X}: \bar{\eta}|_{\bar{\Lambda}} \in \bar{\mathcal{X}}_3, N_{\Lambda_{\ell_-} \setminus \bar{\Lambda}}(\eta) = 0\}. \end{aligned} \quad (2.3)$$

Here, $\ell_- = e^{\frac{\Delta - \gamma_0}{2}\beta}$ with $\gamma_0 > 0$ arbitrary is a space scale slightly below the typical inter-particle distance $1/\sqrt{\rho}$, and the recurrence to \mathcal{X}_i occurs within time $T_i e^{\delta_0 \beta}$, just as in the case of the local Markov chain, for a suitable $\delta_0 = \delta_0(\gamma_0)$ satisfying $\lim_{\gamma_0 \downarrow 0} \delta_0(\gamma_0) = 0$. This recurrence property suggests that we look at (η_t) only when it visits the regular configurations in \mathcal{X}_3 . Indeed, by using the fact that configurations in \mathcal{X}_3 have no particles in $\Lambda_{\ell_-} \setminus \bar{\Lambda}$, we can apply the results proved in Step 1, because gas particles need a time of order $e^{\Delta \beta}$ to arrive in $\bar{\Lambda}$.

The *reduced Markov chain* (η_i^R) is defined as follows. For $\bar{\eta} \in \bar{\mathcal{X}}_3$, consider the set of configurations that are reachable from $\bar{\eta}$ within energy Δ , i.e.,

$$\bar{\mathcal{C}}_{\bar{\eta}}^{\Delta} = \{\bar{\eta}' \in \bar{\mathcal{X}}: \bar{H}(\bar{\eta}', \bar{\eta}) - \bar{H}(\bar{\eta}) < \Delta\}. \quad (2.4)$$

Extend this definition to the configurations in \mathcal{X} in the obvious way: for $\eta \in \mathcal{X}_3$, consider the set

$$\mathcal{C}_{\eta}^{\Delta} = \{\eta' \in \mathcal{X}: \eta'|_{\bar{\Lambda}} \in \bar{\mathcal{C}}_{\eta|_{\bar{\Lambda}}}^{\Delta}\}. \quad (2.5)$$

Now put

$$\begin{aligned} \tau_0 &= 0 \\ \sigma_0 &= \min\{t \geq 0: \eta_t \notin \mathcal{C}_{\eta_0}^{\Delta}\} \end{aligned} \quad (2.6)$$

and, for $i \in \mathbb{N}$, put

$$\begin{aligned} \tau_i &= \min\{t > \sigma_{i-1}: \eta_t \in \mathcal{X}_3\} \\ \sigma_i &= \min\{t > \tau_i: \eta_t \notin \mathcal{C}_{\eta_{\tau_i}}^{\Delta}\}. \end{aligned} \quad (2.7)$$

Then

$$\eta_i^R = \eta_{\tau_i}, \quad i \in \mathbb{N}_0, \quad (2.8)$$

defines a (discrete-time) Markov chain $(\eta_i^R)_{i \in \mathbb{N}_0}$ on \mathcal{X}_3 with transition probabilities

$$P^R(\eta, \eta') = \mathbb{P}_{\eta}(\eta_{\tau_1} = \eta'). \quad (2.9)$$

For $\eta \in \mathcal{X}_3$ and $\bar{\eta}' \in \bar{\mathcal{X}}_3$, let

$$P^R(\eta, I_{\bar{\eta}'}) = \sum_{\eta'' \in I_{\bar{\eta}'} \cap \mathcal{X}_3} P^R(\eta, \eta''). \quad (2.10)$$

The key estimate in Step 3 is the following proposition:

Proposition 2 ([4]) *There exists $\delta = \delta(\delta_0, \gamma_0)$, satisfying $\lim_{\delta_0, \gamma_0 \downarrow 0} \delta(\delta_0, \gamma_0) = 0$, and $\beta_0 > 0$ such that for all $\beta > \beta_0$:*

(i) *If $\bar{\eta} \in \mathcal{R}_{\ell_1, \ell_2}$, $\bar{\eta}' \in \mathcal{R}_{\ell_1+1, \ell_2}$, then*

$$\min_{\eta \in I_{\bar{\eta}} \cap \mathcal{X}_3} P^R(\eta, I_{\bar{\eta}'}) \geq e^{-(\Delta-U)\beta} e^{-\delta\beta}. \quad (2.11)$$

(ii) *If $\bar{\eta} \in \mathcal{R}_{\ell_1, \ell_2}$, $\bar{\eta}' \in \mathcal{R}_{\ell_1, \ell_2-1}$, then*

$$\min_{\eta \in I_{\bar{\eta}} \cap \mathcal{X}_3} P^R(\eta, I_{\bar{\eta}'}) \geq e^{-(2U-\Delta)(\ell_1-1)\beta} e^{-\delta\beta}. \quad (2.12)$$

(iii) *If $\bar{\eta} \in \mathcal{L}$, then there exists a sequence $\bar{\eta}_0, \bar{\eta}_1, \dots, \bar{\eta}_n$, satisfying $\bar{\eta}_0 = \bar{\eta}$, $\bar{\eta}_i \in \mathcal{L}$ for $i = 1, \dots, n-1$, $\bar{\eta}_n \in \bar{\mathcal{X}}_3 \setminus \mathcal{L}$, and $|\bar{\eta}_i| \geq |\bar{\eta}_{i-1}|$ for $i = 1, \dots, n$, such that*

$$\min_{i=0,1,\dots,n-1} \min_{\eta_i \in I_{\bar{\eta}_i}} P^R(\eta_i, I_{\bar{\eta}_{i+1}}) \geq e^{-(2U-\Delta)\beta} e^{-\delta\beta}. \quad (2.13)$$

(iv) *Let*

$$\begin{aligned} r(\bar{\eta}) &= \Delta - U && \text{if } \bar{\eta} \in \mathcal{R}_{\ell_1, \ell_2} \text{ with } \ell_1 \geq \ell_c \\ r(\bar{\eta}) &= (2U - \Delta)(\ell_1 - 1) && \text{if } \bar{\eta} \in \mathcal{R}_{\ell_1, \ell_2} \text{ with } \ell_1 < \ell_c \\ r(\bar{\eta}) &= 2U - \Delta && \text{if } \bar{\eta} \in \mathcal{L}. \end{aligned} \quad (2.14)$$

Then

$$\max_{\eta \in I_{\bar{\eta}}} \max_{\bar{\eta}' \in \bar{\mathcal{X}}_3: \bar{\eta}' \notin \mathcal{E}_3(\bar{\eta})} P^R(\eta, I_{\bar{\eta}'}) \leq e^{-r(\bar{\eta})\beta} e^{\delta\beta}, \quad (2.15)$$

where $\mathcal{E}_3(\bar{\eta})$ is the set of configurations in $\bar{\mathcal{X}}_3$ that are Δ -equivalent to $\bar{\eta}$, i.e., can be connected to $\bar{\eta}$ via a path with maximal saddle Δ .

The estimates in Proposition 2 can be used to study the behavior of (η_t) over long time intervals. Indeed, the trajectory of (η_i^R) corresponding to a given trajectory of (η_t) contains all the relevant information on the behavior of (η_t) in terms of the sequence of squares or quasi-squares visited by (η_t) , while the details of the trajectory of (η_t) corresponding to time intervals shorter than $e^{\Delta\beta}$ are neglected in (η_i^R) .

The definition of the reduced Markov chain can obviously be adapted to construct a local reduced chain $(\bar{\eta}_i^R)$, starting from $(\bar{\eta}_t)$ instead of (η_t) . It is immediate that the estimates in Proposition 2 are logarithmically equivalent to the corresponding transition probabilities of $(\bar{\eta}_i^R)$, thus providing a comparison between the full Markov chain and the local Markov chain.

The proof of Proposition 2 is quite complicated, especially part (iv). Indeed, for the latter we have introduced in [4] a coloring of particles: particles inside $\bar{\Lambda}$ are “white”, particles outside Λ_{ℓ_-} or inside $\Lambda_{\ell_-} \setminus \bar{\Lambda}$ but coming from $\Lambda_{\beta} \setminus \Lambda_{\ell_-}$ are “green”, while particles inside $\Lambda_{\ell_-} \setminus \bar{\Lambda}$ but coming from $\bar{\Lambda}$ are “red”. It is not difficult to show that the results of Step 1 are sufficient to control the effect of the green particles. The difficult part is to control the effect of the red particles. The main idea here is to control at the same time the regularity of the configuration inside $\bar{\Lambda}$, in terms of the sets $\bar{\mathcal{X}}_i$, and the behavior of the random walks describing the red particles. It is possible to show that the

interaction between the red particles and the white particles can take place only during time intervals in which the local configuration is not in $\bar{\mathcal{X}}_2$. Cutting out these interaction time intervals, we find that red particles behave essentially as independent random walks. Following this idea, we are able to control the interaction between the red particles and the white particles via the recurrence property to \mathcal{X}_i of (η_t) .

3 New results on the typical path of nucleation

In the proof of Theorem 1 reviewed in Section 2, we have used the idea that the full Markov chain (η_t) behaves like the local Markov chain $(\bar{\eta}_t)$. Namely, we have shown that they have similar recurrence properties, and even that there is a partial equivalence by means of Proposition 2.

A first natural question therefore is the following: Is it possible to prove a complete equivalence between (η_t) and $(\bar{\eta}_t)$? More precisely: Is it possible to improve Proposition 2 in the sense of controlling *all* transition probabilities from above and from below by quantities that are logarithmically equivalent to the corresponding transition probabilities of $(\bar{\eta}_t^R)$? Such an equivalence would represent a *canonical vs. grand-canonical equivalence from a dynamic point of view*.

A second natural question, weaker than this equivalence, is the following: What is the typical path followed by the dynamics when going from \square to \blacksquare ? For Markov chains with a finite state space the problem of the first exit from a suitable set of states has been completely solved in the Freidlin-Wentzel scenario (see [11], [9], [1]). In particular, for a reversible finite Markov chain like $(\bar{\eta}_t)$ the identification of the exiting path is easy (see [8], [11]). However, for our dynamics with $|\Lambda_\beta| \rightarrow \infty$ as $\beta \rightarrow \infty$ the lack of a complete equivalence between (η_t) and $(\bar{\eta}_t)$ causes that we cannot take advantage of these finite-volume results. Still, we can define the typical paths of (η_t) in terms of the typical paths of (η_t^R) , which are restricted to $\bar{\Lambda}$. Indeed, due to the recurrence property to the set \mathcal{X}_3 , the typical paths of (η_t^R) define the typical paths of (η_t) directly. Again, the solution of the problem is related to an improvement of Proposition 2. In particular, we need more detailed upper bounds on the various transition probabilities (uniform in the gas configuration outside $\bar{\Lambda}$).

From the sketch of the proof of Proposition 2 in Section 2 it is clear that upper bounds are the more difficult estimates. For this reason improvements of Proposition 2 are far from trivial. By using the ideas developed in [4] we are able to prove the following:

Proposition 3 *There exists $\beta_0 > 0$ such that, for all $\beta > \beta_0$ and $\bar{\eta}, \bar{\eta}' \in \bar{\mathcal{X}}_3$,*

$$\max_{\eta \in I_{\bar{\eta}} \cap \mathcal{X}_3} P^R(\eta, I_{\bar{\eta}'}) \leq e^{-[\hat{H}(\bar{\eta}, \bar{\eta}') - \hat{H}(\bar{\eta}) - \Delta]\beta}. \quad (3.1)$$

Moreover, we believe that we can prove that the reduced Markov chain typically makes transitions only between nearest-neighbor squares or quasi-squares:

Conjecture 4 For $\bar{\eta} \in \mathcal{R}_{\ell_1, \ell_2} \subset \bar{\mathcal{X}}_3$, let $\bar{\eta}^- = \mathcal{R}_{\ell_1, \ell_2 - 1}$ and $\bar{\eta}^+ = \mathcal{R}_{\ell_1 + 1, \ell_2}$. Then there exist $\beta_0 > 0$ and $\kappa > 0$ such that, for all $\beta > \beta_0$ and $\bar{\eta}' \neq \bar{\eta}^-, \bar{\eta}^+$,

$$\max_{\eta \in I_{\bar{\eta}} \cap \mathcal{X}_3} P^R(\eta, I_{\bar{\eta}'}) \leq e^{-[\bar{H}(\bar{\eta}', \bar{\eta}') - \bar{H}(\bar{\eta}) - \Delta + \kappa]\beta}. \quad (3.2)$$

Proposition 3 and Conjecture 4 provide the answer to our first question on the equivalence of the full Markov chain and the local Markov chain. Indeed, combining Propositions 2 and 3, we have the logarithmic equivalence for all the nearest-neighbor transition probabilities of (η_i^R) and $(\bar{\eta}_i^R)$, and from Conjecture 4 we conclude that these are the only relevant transitions.

By using the ideas developed in [4] in combination with Proposition 3 and Conjecture 4, we are now able to prove the following result identifying the typical path of nucleation:

Theorem 5 Suppose that Conjecture 4 is true. Then for all $\kappa, \epsilon > 0$ there exists $\beta_0 = \beta_0(\kappa, \epsilon)$ such that, for all $\beta > \beta_0$,

$$\mathbb{P}_{\nu_{\square}} \left((\eta_t)_{t \in [\theta_{\square, \blacksquare}, \tau_{\blacksquare}]} \in \mathbb{T}_{\epsilon, \beta} \mid \theta_{\square, \blacksquare} = 0 \right) > 1 - e^{-\kappa\beta}, \quad (3.3)$$

where $\mathbb{T}_{\epsilon, \beta}$ is the set of all trajectories $\phi = (\phi_t)$ such that its reduced trajectory (ϕ_i^R) , when changing state, follows the sequence

$$\square, \mathcal{R}_{2,2}, \mathcal{R}_{2,3}, \mathcal{R}_{3,3}, \dots, \blacksquare, \quad (3.4)$$

and ϕ spends in each $C_{\phi_i^R}$ a time that falls in the interval

$$[e^{[r(\phi_i^R) + \Delta - \epsilon]\beta}, e^{[r(\phi_i^R) + \Delta + \epsilon]\beta}]. \quad (3.5)$$

Here, r is given by (2.14), while

$$\begin{aligned} C_{\bar{\eta}} &= \{\eta' \in \mathcal{X}: \eta' \upharpoonright_{\bar{\Lambda}} \in \bar{C}_{\bar{\eta}}\} \\ \bar{C}_{\bar{\eta}} &= \{\bar{\eta}' \in \bar{\mathcal{X}}: \bar{H}(\bar{\eta}', \bar{\eta}) - \bar{H}(\bar{\eta}) < r(\bar{\eta}) + \Delta\} \end{aligned} \quad (3.6)$$

are the analogues of (2.4) and (2.5).

4 Open problems

The main challenge is to prove the analogues of Theorems 1 and 5 in the case of a Hamiltonian with interaction everywhere in Λ_β , i.e., the complete Kawasaki dynamics. We believe that a first step in this direction should be done by considering an intermediate model with energy interaction only in $\bar{\Lambda}_0$ but with exclusion everywhere in Λ_β . By using coupling methods, such a model can be compared with our simplified model.

Our simplified model in fact focusses on the *local* aspects of metastability and nucleation: the removal of the interaction outside $\bar{\Lambda}_0$ forces the critical droplet to appear inside $\bar{\Lambda}_0$. In the full model with interaction and exclusion throughout Λ_β , if $\liminf_{\beta \rightarrow \infty} \frac{1}{\beta} \log |\Lambda_\beta|$ is large enough, then the decay from

the metastable to the stable state is driven by the formation of many droplets far away from the origin, which subsequently grow and coalesce. This is a much harder problem, which we hope to tackle in the future (see [2] for a description of this behavior for Ising spins under Glauber dynamics). In the full model also the question of the growth of large *supercritical* droplets comes up, which is absent for the simplified model because $\bar{\Lambda}_0$ is finite. For Kawasaki dynamics this poses new problems compared to Glauber dynamics, because large droplets deplete the gas.

But, even when remaining with our simplified model, there are other non-trivial problems to settle. For instance, we can try to study an anisotropic interaction. This means that we replace the Hamiltonian in (1.2) by

$$H(\eta) = -U_h \sum_{(x,y) \in \bar{\Lambda}_0^{*,h}} \eta(x)\eta(y) - U_v \sum_{(x,y) \in \bar{\Lambda}_0^{*,v}} \eta(x)\eta(y), \quad (4.1)$$

where $\bar{\Lambda}_0^{*,h}$ ($\bar{\Lambda}_0^{*,v}$) is the set of horizontal (vertical) bonds in $\bar{\Lambda}_0$ and $U_h \neq U_v$. The interesting question is whether the shapes of the droplets typically visited by the dynamics during the nucleation process coincide with the Wulff shapes at low temperature. This comparison has been done for the Glauber dynamics in [5].

Another interesting problem is to analyze the three-dimensional version of our simplified model. We expect here a non-trivial behavior even for the local Markov chain. The movement of particles along the border of the droplet will produce much more complicated geometric problems.

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