Homogeneous and heterogeneous nucleation in the three–state Blume–Capel model

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Marseille

3-7 April 2023

1. The model
2. Heuristic results and main differences with BC-model with periodic-boundary conditions
3. Main results in the region $\lambda > h > 0$

The model

$\Lambda = \{1, \ldots, L\}^2 \subset \mathbb{Z}^2$.

Configuration space $\mathcal{X} := \{-1, 0, +1\}^\Lambda$.

Zero-boundary conditions.

BC-Hamiltonian function with zero-boundary conditions:

$$H(\eta) = \frac{J}{2} \sum_{\substack{i,j \in \Lambda: \\ |i-j|=1}} [\eta(i) - \eta(j)]^2 + J \sum_{i \in \partial^- \Lambda} \sum_{\substack{j \in \mathbb{Z}^2 \setminus \Lambda: \\ |i-j|=1}} [\eta(i)]^2 - \lambda \sum_{i \in \Lambda} \eta(i)^2 - h \sum_{i \in \Lambda} \eta(i)$$

We choose $J >> \lambda, h > 0$: the system exhibits a metastable behavior, where the chemical potential term equally favors minus and plus spins with respect to zeroes and the external magnetic field favors pluses and disadvantages minuses with respect to the zeroes.

Let $(X_t)_{t\in\mathbb{N}}$ be a Markov chain (Metropolis Algorithm) with transition probabilities:

$$p(\sigma,\eta) = q(\sigma,\eta)e^{-\beta[H(\eta)-H(\sigma)]_+}, \qquad \text{for all } \sigma \neq \eta,$$
$$p(\sigma,\sigma) = 1 - \sum_{\eta\neq\sigma} p(\sigma,\eta)$$

where β is the inverse of the temperature and

$$q(\sigma,\eta) = \begin{cases} \frac{1}{2|\Lambda|} & \text{if } \exists\, x \in \Lambda : \sigma^{(x)} = \eta \\ 0 & \text{otherwise} \end{cases}$$

$$\sigma^{(x)}(z) = \begin{cases} \sigma(z) & \text{if } z \neq x \\ -\sigma(x) & \text{if } z = x \end{cases}$$

Gibbs measure:

$$\mu(\sigma) = \frac{e^{-\beta H(\sigma)}}{\sum_{\eta \in \mathcal{X}} e^{-\beta H(\eta)}}.$$

Reversibility with zero-boundary condition BC-Hamiltonian

The Markov chain defined above is reversible with respect to the Gibbs measure, i.e., the detailed balance condition

$$\mu_\beta(\eta) p_\beta(\eta, \eta') = \mu_\beta(\eta') p_\beta(\eta', \eta)$$

is satisfied for any $\eta, \eta' \in \mathcal{X}$.

Heuristic results

Ground states

Under Condition $J >> \lambda, h > 0$, the homogeneous state $\mathbf{+1}$ is the ground state of the system.

Local minima of the Hamiltonian

- For $h > \lambda$, the homogeneous state $\mathbf{0}$ is a local minimum,
- For $h < \lambda$ the homogeneous states $\mathbf{0}$ and -$\mathbf{1}$ are local minima.

Region $h > \lambda > 0$

We are interested in the structures that give rise to local minima with zero background, since $\mathbf{0}$ is a local minimum of the Hamiltonian.

If a configuration contains a rectangle of plus spins in a sea of zeroes, then it is a local minimum.

Moreover, if the shape of the plus region is not a rectangle, then the configuration is not a local minimum.

Region $h > \lambda > 0$

The energy of a square plus droplet of side length ℓ plunged in a sea of zeroes σ_+ with respect to the energy of $\mathbf{0}$ is

$$H(\sigma_+^\ell) - H(\mathbf{0}) = 4JL - (\lambda + h)\ell^2.$$

Since its maximum is attained at

$$\ell_c = 2J/(\lambda + h),$$

we can infer that this is the critical length:
the droplets with side length smaller than $2J/(\lambda + h)$ *tend to shrink, otherwise they tend to grow.*
Moreover, we compute the energy difference between the critical droplet and the configuration $\mathbf{0}$:

$$H(\sigma_+^{\ell_c}) - H(\mathbf{0}) = 4J^2/(\lambda + h)$$

.

Region $h > \lambda > 0$

At the level of our very rough heuristic discussion, we can conclude that:

- the metastable state is the configuration $\mathbf{0}$,
- the transition to the stable state is performed via the nucleation of a square droplet of pluses with side length $2J/(\lambda + h)$ at any site of the lattice Λ: ***homogeneous nucleation***,
- the exit time is of order $\exp\{\beta 4J^2/(\lambda + h)\}$.

Region $\lambda > h > 0$

We are interested in the structures that give rise to local minima with zero background or minus background, since **0** and -**1** are local minima of the Hamiltonian.

In the case of zero background, the system can exit the state **0** by overcoming the energy barrier $4J^2/(\lambda + h)$ and reaching the stable state $+\mathbf{1}$ via the formation of a critical square droplet of pluses with side length $2J/(\lambda + h)$.

But also the possibility that the system abandons **0** reaching -**1** must be explored: a configuration in which the sites with minus spin form a rectangle plunged in a sea of zeroes is a local minimum.

Region $\lambda > h > 0$

The energy of a square minus droplet of side length ℓ plunged in a sea of zeroes σ_-^ℓ with respect to the energy of $\mathbf{0}$ is

$$H(\sigma_-^\ell) - H(\mathbf{0}) = 4JL - (\lambda - h)\ell^2.$$

Since its maximum is attained at

$$\ell_c = 2J/(\lambda - h),$$

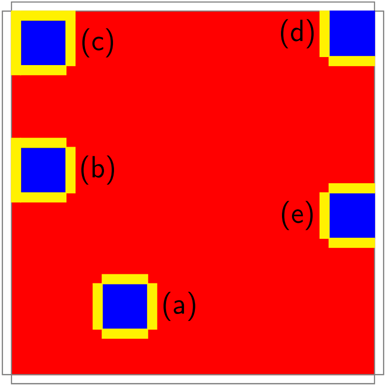
we can infer that this is the critical length:
the droplets with side length smaller than $2J/(\lambda - h)$ tend to shrink, otherwise they tend to grow.
Moreover, we compute the energy difference between the critical droplet and the configuration $\mathbf{0}$:

$$H(\sigma_-^{\ell_c}) - H(\mathbf{0}) = 4J^2/(\lambda - h).$$

Since in this parameter region $4J^2/(\lambda - h) > 4J^2/(\lambda + h)$ we can conclude that the system, starting from $\mathbf{0}$, will perform a direct transition to the stable state $+\mathbf{1}$ paying the energy cost $4J^2/(\lambda + h)$.

Region $\lambda > h > 0$

For what concerns the minus background case, we note that a rectangle of pluses in a sea of minuses is not a local minimum.
Some relevant structures that are local minima are reported in figure below.



Region $\lambda > h > 0$

For each structure we compute its energy with respect to -**1** as a function of the side length ℓ of the internal plus square:

$$
\begin{aligned}
H(\sigma_a^\ell) - H(\text{-}\mathbf{1}) &= -2h\ell^2 + 4J\ell + 4J(\ell+2) + 4\ell(\lambda - h),\\
H(\sigma_b^\ell) - H(\text{-}\mathbf{1}) &= -2h\ell^2 + 4J\ell + 2J(\ell+2) + (4\ell+2)(\lambda - h),\\
H(\sigma_c^\ell) - H(\text{-}\mathbf{1}) &= -2h\ell^2 + 4J\ell + (4\ell+3)(\lambda - h),\\
H(\sigma_d^\ell) - H(\text{-}\mathbf{1}) &= -2h\ell^2 + 2J\ell + 2J(\ell+1) - 2J + 2\ell(\lambda - h),\\
H(\sigma_e^\ell) - H(\text{-}\mathbf{1}) &= -2h\ell^2 + 3J\ell + J(3\ell+2) + 3\ell(\lambda - h).
\end{aligned}
$$

We can conclude that the mechanism providing the transition from -**1** to +**1** is the formation and growth of a chopped corner droplet.

Region $\lambda > h > 0$

The energy of a chopped corner frame with side length ℓ plunged in a sea of minuses σ_F^ℓ with respect to the energy of $\mathbf{-1}$ is

$$H(\sigma_F^\ell) - H(\mathbf{-1}) = -2h\ell^2 + 2J\ell + 2J(\ell+1) - 2J + 2\ell(\lambda - h).$$

Since its maximum is attained at

$$\ell_c = [2J + (\lambda - h)]/(2h),$$

we can infer that this is the critical length:
the droplets with side length smaller than $[2J + (\lambda - h)]/(2h)$ *tend to shrink, otherwise they tend to grow.*
Moreover, we compute the energy difference between the critical droplet and the configuration $\mathbf{-1}$:

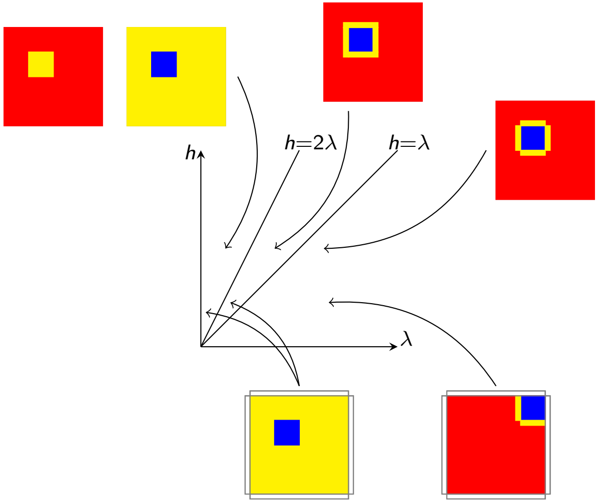
$$H(\sigma_F^{\ell_c}) - H(\mathbf{-1}) \sim 2J^2/h.$$

Region $\lambda > h > 0$

At the level of our very rough heuristic discussion, we can conclude that:

- the metastable state is the configuration **-1**, since $4J^2/(\lambda + h) < 2J^2/h$,
- the transition to the stable state is performed via the nucleation of a chopped corner frame with side length $[2J + (\lambda - h)]/(2h)$: ***heterogeneous nucleation***,
- the exit time is of order $\exp\{\beta 2J^2/h\}$.

Differences between our model and the Blume-Capel model with periodic boundary condition



Main results for the parameter region $\lambda > h > 0$

Let $\Gamma^{BCG} = 4Jl_c + 2\lambda l_c - 2h2l_c^2 - 2h$, where $l_c = \lfloor \frac{2J+\lambda-h}{2h} \rfloor + 1$.

Proposition I

Let $\eta \in \mathcal{X}$ be a configuration such that $\eta \notin \{\textbf{-1}, \textbf{+1}\}$, then $V_\eta < \Gamma^{BCG}$.

Theorem I: Recurrence property

For any $\epsilon > 0$ and sufficiently large β, the function

$$\beta \to \sup_{\eta \in \mathcal{X}} \mathbb{P}_\eta(\tau_{\{\textbf{-1},\textbf{+1}\}} > e^{\beta(\Gamma^{BCG}+\epsilon)})$$

is SES (super exponentially small).

Main results for the parameter region $\lambda > h > 0$

Theorem II: Identification of metastable states

In the region $\lambda > h > 0$, the unique metastable state is $\mathbf{-1}$ and $\Gamma = \Gamma^{BCG}$.

Theorem III: Asymptotic behavior of $\tau_{\mathbf{+1}}$ in probability

For any $\epsilon > 0$, we have

$$\lim_{\beta \to \infty} \mathbb{P}_{\mathbf{-1}}\left(e^{\beta(\Gamma^{BCG}-\epsilon)} < \tau_{\mathbf{+1}} < e^{\beta(\Gamma^{BCG}+\epsilon)}\right) = 1.$$

THANKS FOR YOUR ATTENTION!

Motivation

- Study the role of microscopic impurities (or boundaries): the presence of defects generates a heterogeneous nucleation. Indeed, starting from a single fixed spin, this nucleation is more than four orders of magnitude faster than homogeneous nucleation. Moreover, small microscopic impurities strongly promote nucleation, making very difficult to purify a sample sufficiently in order to observe homogeneous nucleation. See for example *Nucleation at contact lines where fluid-fluid interfaces meet solid surfaces* or *Formation of a metastable phase due to the presence of impurities*, Richard P. Sear.
- Heterogeneous nucleation plays also a pivotal role in the process of *crystallization of proteins* on surfaces: by tuning the geometrical properties of the surface (porosity, pore size, roughness), heterogeneous nucleation can be activated, enhancing the probability of obtaining crystals with appropriate size.

See for Ising model with free boundary conditions: *Metastability in the Two-Dimensional Ising Model with Free Boundary Conditions*, E.N.M. Cirillo and J.L. Lebowitz