RDS II, Bielefeld

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Kawasaki Dynamics in Large Volumes

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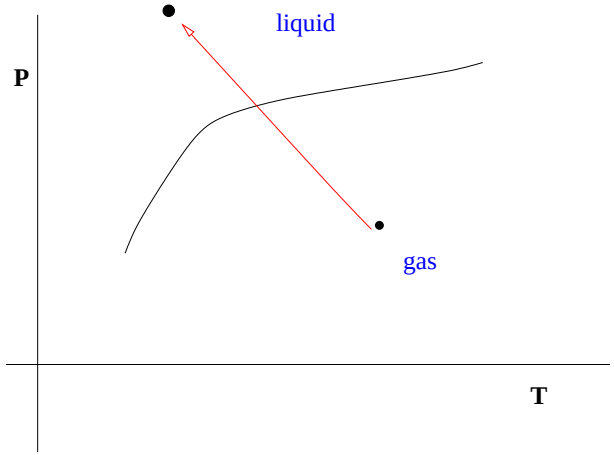
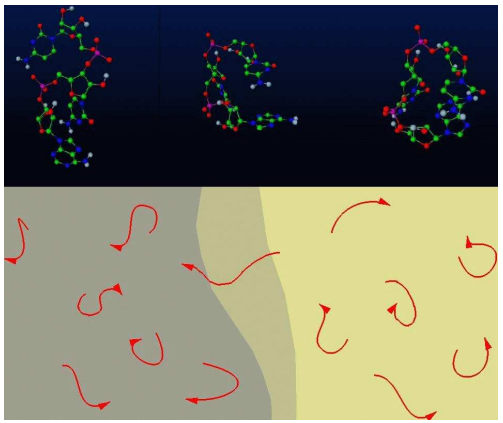
Motivation

Metastability is a common phenomenon related to the dynamics of first order phase transitions:





Thermally activated transitions between comformations

If the parameters of a systems are changed rapidly across the line of a first order phase transition, the system will persist for a long time in a metastable state before transiting rapidly to the new equilibrium state under the influence of random fluctuations.

The most standard example is the vapour-liquid transition from oversaturated vapour through nucleation.

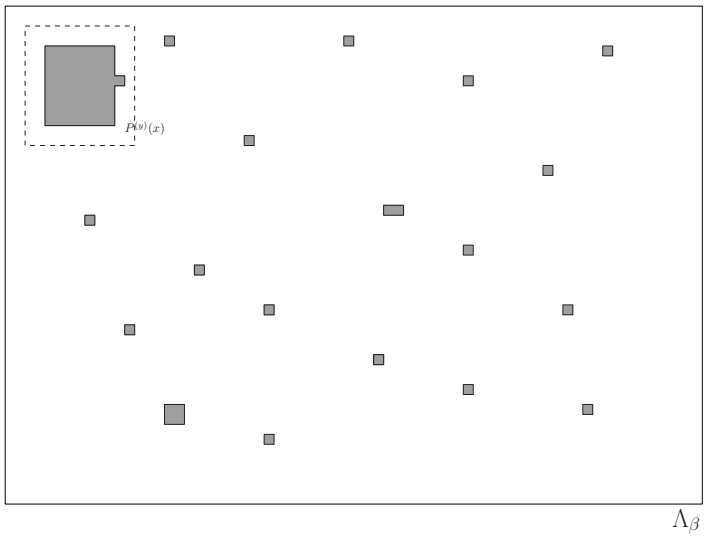
Surprisingly, this is still a rather unsettled problem. In this talk I will present some partial results in a reasonable context.

Conservative dynamics of lattice gas: $\Lambda_\beta \subset \mathbb{Z}^d$, $\eta \in \{0,1\}^{\Lambda_\beta}$.
Canonical ensemble

$$\mathcal{X}_\beta^{n_\beta} \equiv \{\eta : \sum_{x \in \Lambda_\beta} \eta_x = n_\beta\}$$

Interaction:

$$H_{\Lambda_\beta}(\eta) = -U \sum_{x \sim y \in \Lambda_\beta} \eta_x \eta_y$$



Dynamics: Change a configuration η to η' at rate

$$\exp(-\beta[H(\eta') - H(\eta)]_+)$$

for all η' obtainable from η via

exchange of the values of occupation numbers between two neighboring sites.

This model mimics the behaviour of a gas in the canonical ensemble. We consider the asymptotic situation where

- the temperature, β^{-1}, is a small parameter,
- the box Λ_β is exponentially large in β, and
- the density of the gas is $\rho_\beta = \exp(-\beta\Delta)$.

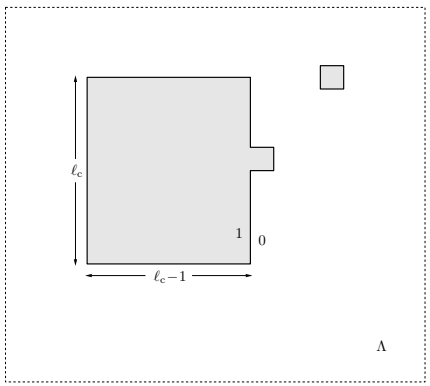
We are interested in the regime when the canonical Gibbs measure is concentrated on configurations with a single solid droplet of particles in a sea of density $\exp(-\beta 2U) \ll \rho_\beta$. We call this state ■.

The metastable set, ■, will be configurations that contain no large droplets of particles. This occurs when $\Delta \in (U, dU)$. We call this the metastable regime. We would be interested in understanding on how the system goes from an initial configuration ■ to a final configuration ■.

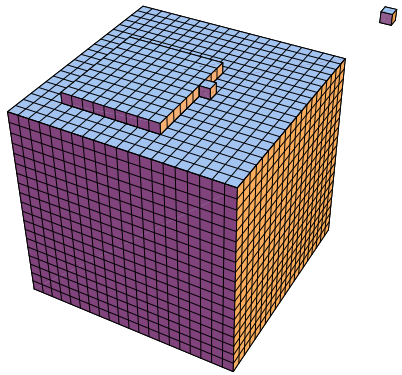
Heuristically, the metastable behaviour is the result of the competition between evaporation and adsorption:

- ▷ Small droplets typically evaporate before additional particles from the reservoir attach to them;
- ▷ Large droplets grow rapidly by condensation;
- ▷ Nucleation is triggered by the first, random, appearance of a critical droplet.

In $d = 2$:



In $d = 3$:



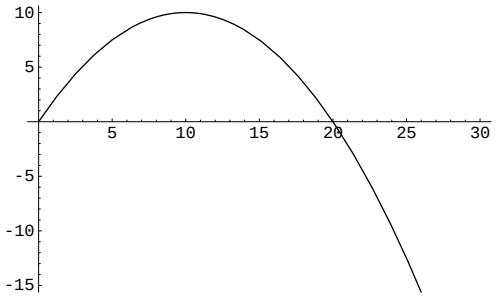
The analysis of the nucleation dynamics of this system requires three basic ingredients:

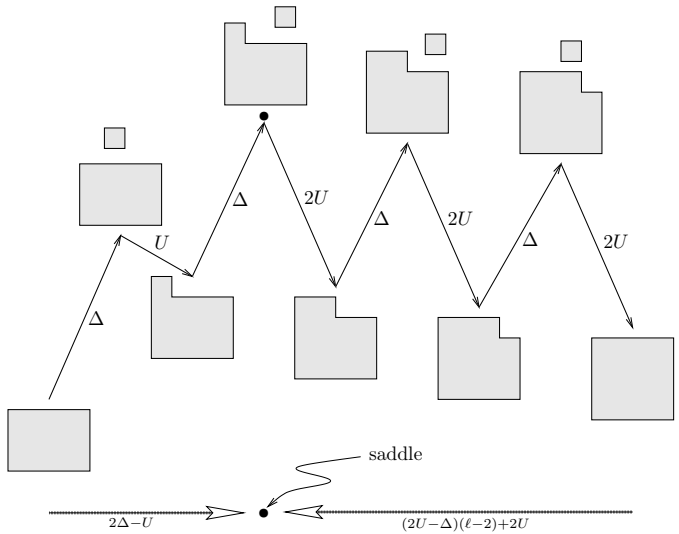
- The analysis of the rather complex energy landscape and the connectivity graph of the dynamics. In particular, one needs to identify the critical droplets and the local structure of the graph around them.
- Understanding of the dynamical production of entropy, which in contrast to earlier work on local Kawasaki dynamics is crucial.
- Probabilistic techniques that allow to derive from these information in nucleation times and their probability distributions.

Critical droplets ($d = 2$)

We need to identify the minimal saddle points that a process ■ → ■ must cross. For this we need to take entropy into account:

Clustering k particles together generates a loss of entropy of $k\beta\Delta$. The maximal energy gain is achieved by forming a square. The free energy of squares of side-length ℓ has a maximum at $\ell_c = \left[\frac{2U}{2U-\Delta}\right]$ and is given by $\Gamma_2^* = 2U(\ell_c + 1) - (2U - \Delta)(\ell_c(\ell_c - 1) + 2)$.



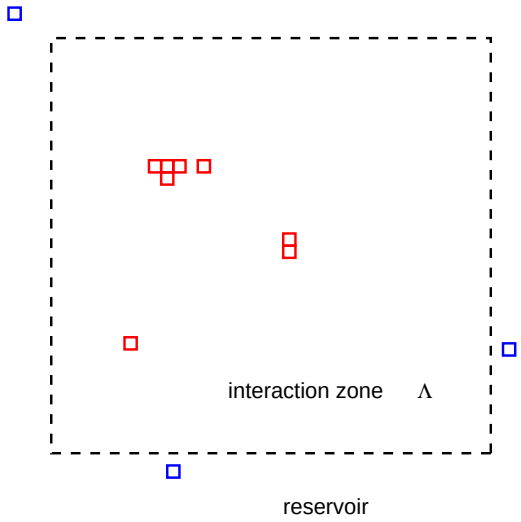


Earlier results: dynamics in finite open boxes

First rigorous results on Kawasaki dyanamics concern a simplified model where:

- ▷ The volume Λ is finite and *indepent* of β;
- ▷ particles enter the box with rate $\exp(-\Delta\beta)$ at the boundary of Λ, and leave there with rate 1;

This corresponds to approximating the dynamics in a finite box by replacing the gas outside of it by an ideal gas.



Here one is interested in the time the dynamics takes to move from an empty box, □ to a full box, ■.

This problem was studied by den Hollander, Nardi, Olivieri, and Scoppola using large deviation methods, and by B, den Hollander, and Nardi via potential theory.

THEOREM. (den Hollander, Olivieri, and Scoppola 2000, den Hollander, Nardi, Olivieri, Scoppola, 2002)

(i)

$$\lim_{\beta\to\infty} \mathbb{P}_{\square}\big(e^{(\Gamma^*-\delta)\beta} < \tau_{\blacksquare} < e^{(\Gamma^*+\delta)\beta}\big) = 1 \qquad \forall\, \delta > 0.$$

(ii)

$$\lim_{\beta\to\infty} \mathbb{P}_{\square}\big(\tau_{\mathcal{C}^*} < \tau_{\blacksquare} \mid \tau_{\blacksquare} < \tau_{\square}\big) = 1.$$

Assertion (i) identifies the nucleation time to exponential order in β, with exponent Γ^*. Assertion (ii) states that $\mathcal{C}^*$ is a *gate for the nucleation*.

Results via potential theory

Theorem:(B, den Hollander, Nardi, '06)

(i) In $d = 2$,

$$\mathbb{E}_{\square}\tau_{\blacksquare} = K_2 \exp\left(\beta\Gamma_2^*\right)\left(1 + O(e^{-O(\beta)})\right)$$

and

$$K_2 = \frac{1}{4\pi N(\ell_c)}\frac{\ln|\Lambda|}{\Lambda}$$

where

$$N(\ell_c) = \frac{1}{3}(\ell_c - 1)\ell_c^2(\ell_c + 1)$$

(ii) In $d = 3$,

$$\mathbb{E}_{\square}\tau_{\blacksquare} = K_3 \exp\left(\beta\Gamma_3^*\right)\left(1 + O(e^{-(\beta)})\right)$$

where

$$K_3 = \frac{1}{M(\ell_c, \Lambda)N})\frac{1}{|\Lambda|}$$

N: cardinality of $\mathcal{D}$ modulo shifts, and

$M(\ell_c, \Lambda)$: $\sim$ capacity of a ℓ_c-cube in $\mathbb{Z}^d$, ($\Lambda \uparrow \mathbb{Z}^d$, and $\ell_c \uparrow \infty$).

Moreover,

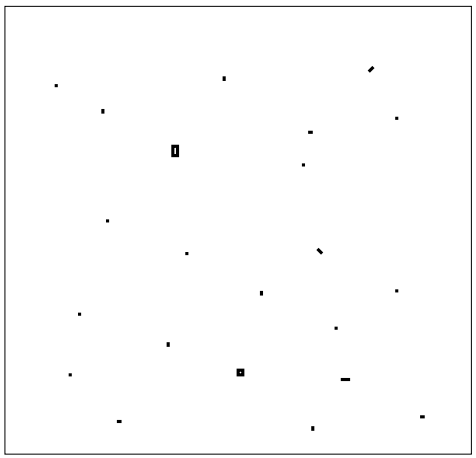
$$\mathbb{P}_{\square}[\tau_{\blacksquare} > t\mathbb{E}_{\square}\tau_{\blacksquare}] \to e^{-t}$$

Define

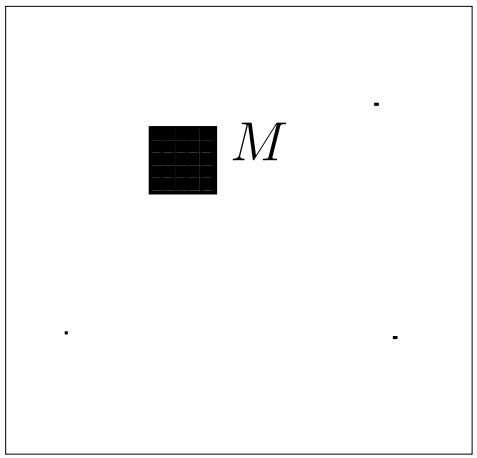
$\mathcal{S}_L = \{\sigma \in \mathcal{S}$: no box of size L_β contains more than L particles in $\Lambda_\beta\}$

and

$\mathcal{D}_M = \{\sigma \in \mathcal{S}$: $\exists$ a full $M \times M$-square in $\Lambda_\beta\}$



$\mathcal{S}_L$



$\mathcal{D}_M$

Theorem. (B, den Hollander, Spitoni '08) Let $d = 2$. Assume that

- $U < \Delta < 2\Delta$ and
- $\lim_{\beta\to\infty} |\Lambda_\beta|\, \rho_\beta = \infty, \qquad \lim_{\beta\to\infty} |\Lambda_\beta|\, e^{-\beta\Gamma_2^*} = 0.$

Then, for $\ell_c \le M \le 2\ell_c - 1$,

$$\lim_{\beta\to\infty} |\Lambda_\beta| \frac{4\pi}{\beta\Delta} e^{-\beta\Gamma_2^*} \mathbb{E}_{\nu_{\mathcal{S}_L}} \left(\tau_{\mathcal{D}_M}\right) = \frac{1}{N}$$

Here:

- Γ_2^*:free energy of a critical droplet;
- $N = \frac{1}{3}\ell_c^2(\ell_c^2 - 1)$: number of critical droplets with fixed lower left corner.
- $\frac{4\pi}{\beta\Delta}$: escape probability of a particle from a critical droplet to a distance $e^{\beta\Delta}$.

Equilibrium potential for $A \cap B = \emptyset$, $-L = P - 1$ generator, solution of

$$(Lh_{B,A})(\sigma) = 0, \quad \sigma \notin A \cup B,$$

with boundary conditions $h_{B,A}(\sigma) = 1$, if $\sigma \in B$, $\quad h_{B,A}(\sigma) = 0$, if $\sigma \in A$.

Equilibrium measure $e_{B,A}(\sigma) \equiv -(Lh_{B,A})(\sigma)$.

Capacity: $\sum_{\sigma \in B} \mu(\sigma) e_{B,A}(\sigma) \equiv \mathrm{cap}(B, A)$.

Equilibrium potentials and equilibrium measures also determine the Green's function:

$$h_{B,A}(\sigma) = \sum_{\sigma' \in B} G_{S_N \setminus A}(\sigma, \sigma') e_{A,B}(\sigma')$$

Mean hitting times:

$$\sum_{\sigma \in B} \mu(\sigma) e_{A,B}(\sigma) \mathbb{E}_\sigma \tau_A = \sum_{\sigma' \in S_N} \mu(\sigma') h_{A,B}(\sigma'),$$

or

$$\sum_{\sigma \in B} \nu_{B,A}(\sigma) \mathbb{E}_\sigma \tau_A = \frac{1}{\mathsf{cap}(B,A)} \sum_{\sigma' \in S_N} \mu(\sigma') h_{B,A}(\sigma').$$

Thus we need

- precise control of capacities and some
- rough control of equilibrium potential.

Computation of capacities

Variational principle for capacities offers a two convenient options for upper and lower bounds:

Dirichlet principle:

$$\mathrm{cap}(A,B) = \inf_{h \in \mathcal{H}_{A,B}} \frac{1}{2} \sum_{x,y} \mathbb{Q}(x) p(x,y) [h(x - h(y)]^2$$

$\mathcal{H}_{A,B}$ space of functions with boundary constraints; minimizer harmonic function.

Berman-Konsowa principle:

$$\mathrm{cap}(A,B) = \sup_{f \in \mathbb{U}_{A,B}} \mathbb{E}^f \left[\sum_{e \in \mathcal{X}} \frac{f(e)}{\mathbb{Q}(e_a) p(e)} \right]^{-1}$$

$\mathbb{U}_{A,B}$ space of unit flows; maximizer harmonic flow. $\mathbb{E}^f$: law of a directed Markov chain with transition probabilities proportional to to flow.

Conclusion and Future Challenges

We have shown that it is possible to compute very precisely the nucleation times in exponentially large volumes. In the regime we treat, there is typically at most one droplet (and occasionally an extra particle) in the reaction zone.
This ignores all effects of competition between several droplets.

Major challenges:

- Detailled treatment of the growth phase of the supercritical droplet.
- Extension of the general theory to infinite volumes, allowing multiple nucleation points.
- Extension to higher temperatures.