Metastability for the Widom - Rowlinson model

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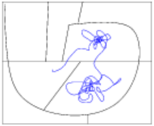
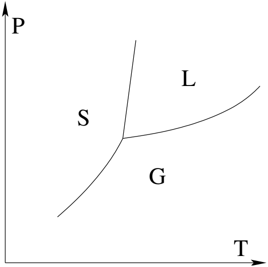
What is metastability?

Metastability is a phenomenon where a system, under the influence of a stochastic dynamics, moves between different regions of its state space on different time scales.



- Fast time scale: quasi-equilibrium within single subregion
- Slow time scale: transitions between different subregions

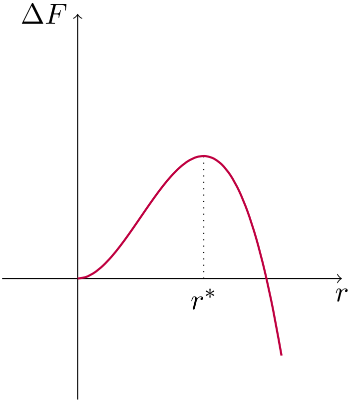
Metastable behaviour is the dynamical manifestation of a first-order phase transition, for instance: condensation.



When vapour is cooled rapidly below the critical temperature, we see that the system will persist for long time in a metastable vapour state (supersaturated gas) before transiting (rapidly) to the new stable liquid state under some random fluctuations.

Why?

Metastable behaviour is the dynamical manifestation of a first-order phase transition, for instance: condensation.



The system has to form a critical droplet of liquid to trigger the crossover, which then will grow and invade the whole space.

But many unsuccessful attempts because forming small droplets results in an increasing of free energy...

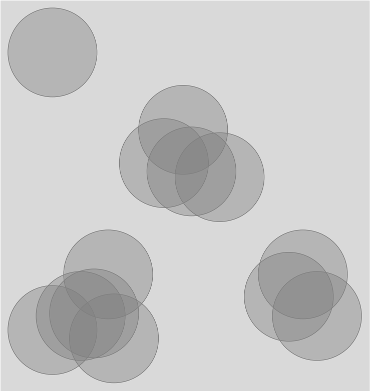
Models in the continuum

- Several results for metastable behaviour of stochastic models on the lattice
- Continuum systems modelling fluids are very difficult to study. Rigorous proof of the presence of phase transitions has been achieved only for few models:
  - Widom-Rowlinson model (Ruelle, '71)
  - Kac models with 2-body attraction and 4-body repulsion (Lebowitz, Mazel and Presutti, '99)
- Metastability for continuum systems:
  - Crystalisation of 2-dimensional particles interacting via a soft-disk potential (Jansen and den Hollander, in preparation)
  - We will focus on the Widom-Rowlinson model, adapting what has been done in the discrete. This is very challenging!

The static Widom-Rowlinson model

$\Lambda \subset \mathbb{R}^2$ with periodic boundary conditions, Γ set of particle configurations with

$$\Gamma = \{\gamma \subset \Lambda\colon\ N(\gamma) \in \mathbb{N}_0\}, \quad N(\gamma):\ \text{cardinality of } \gamma$$



halo of a configuration

$$h(\gamma) = \bigcup_{x \in \gamma} B_2(x)$$

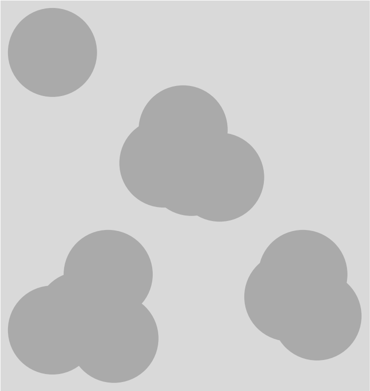
$$V_0 := |B_2(0)|$$

$|\cdot|$: Leb. measure

The static Widom-Rowlinson model

Hamiltonian

$$H(\gamma) = |h(\gamma)| - N(\gamma)V_0 \quad \Rightarrow \quad -(N(\gamma)-1)V_0 \le H(\gamma) \le 0 \quad \text{(attractive)}$$



halo of a configuration

$$h(\gamma) = \bigcup_{x\in\gamma} B_2(x)$$

$$V_0 := |B_2(0)|$$

$|\cdot|$: Leb. measure

$$\mu(\mathrm{d}\gamma) = \frac{z^{N(\gamma)}}{\Xi}\, e^{-\beta H(\gamma)}\mathbb{Q}(\mathrm{d}\gamma),$$

Grand-canonical Gibbs measure

The static Widom-Rowlinson model

Hamiltonian

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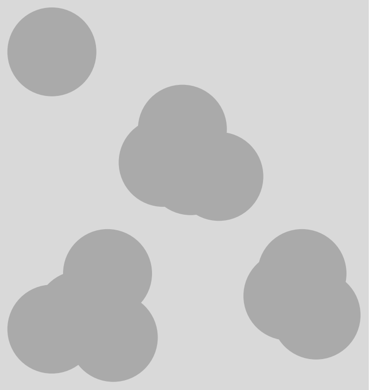
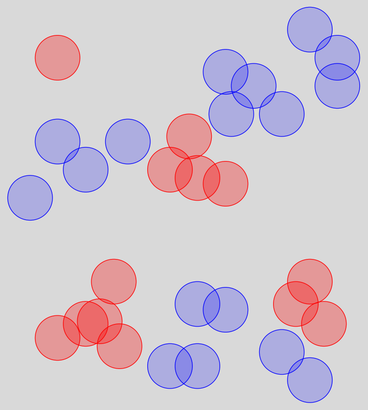


- $\mathbb{Q}$: Poisson point process with intensity 1
- $z \in (0,\infty)$: activity
- $\beta \in (0,\infty)$: inverse temperature
- Ξ: grand-canonical partition function
- notation: $V(\gamma) = |h(\gamma)|$

$$\mu(\mathrm{d}\gamma) = \frac{z^{N(\gamma)}}{\Xi} e^{-\beta H(\gamma)} \mathbb{Q}(\mathrm{d}\gamma), \qquad \text{Grand-canonical Gibbs measure}$$

The 2-species Widom-Rowlinson model

Two type of particles (blue, red) with configurations γ^B, γ^R



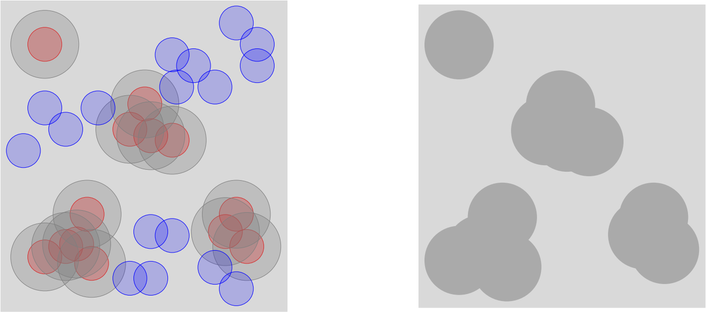
Interaction:
Hard-core with radius 2 between particles with different color (imagine particles as disks of radius 1)

Grand-canonical Gibbs measure:

$$\tilde{\mu}(\mathrm{d}\gamma^R, \mathrm{d}\gamma^B) = \frac{1}{\tilde{\Xi}} \mathbf{1}_{\{\text{red-blue hard-core}\}}\, {z_R}^{N(\gamma^R)} {z_B}^{N(\gamma^B)} \mathbb{Q}(\mathrm{d}\gamma^R)\, \mathbb{Q}(\mathrm{d}\gamma^B)$$

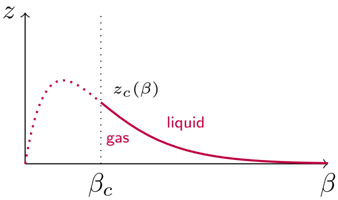
Fix the red and integrate over the blue:

$$\frac{1}{\tilde{\Xi}} \int \mathbb{Q}(\mathrm{d}\gamma^B) \mathbf{1}_{\{\text{red-blue hard-core}\}}\, z_R^{N(\gamma^R)} z_B^{N(\gamma^B)} = const. \frac{z^{N(\gamma^R)}}{\Xi} e^{-\beta H(\gamma^R)}$$



$$(z_B, z_R) \to (\beta, z\, e^{\beta V_0})$$

Phase transition



Coexistence line: ($z_R = z_B$ in the 2-species model)

$$z_c(\beta) = \beta e^{-V_0 \beta}$$

$\beta < \beta_c$ single phase

$\beta > \beta_c$ two phases: gas/liquid

Phase transition at the thermodynamic limit, i.e. $\Lambda \to \mathbb{R}^d$.
(D. Ruelle, '71; J.T. Chayes, L. Chayes and R. Kotecký, '95)

Heat bath dynamics

Particle configuration is a continuous-time Markov process $(\gamma_t)_{t\geq 0}$ with state space Γ and with generator

$$(Lf)(\gamma) = \int_\Lambda \mathrm{d}x\; b(x,\gamma)\,[f(\gamma\cup x) - f(\gamma)] + \sum_{x\in\gamma} d(x,\gamma)\,[f(\gamma\backslash x) - f(\gamma)]$$

where particles are added at rate b and removed at rate d

$$b(x,\gamma) = z\, e^{-\beta[H(\gamma\cup x) - H(\gamma)]}, \quad x\notin\gamma, \qquad d(x,\gamma) = 1, \quad x\in\gamma.$$

The grand-canonical Gibbs measure is reversible, i.e.

$$b(x,\gamma)\, e^{-\beta H(\gamma)} = d(x,\gamma\cup x)\, e^{-\beta H(\gamma\cup x)}, \qquad x\notin\gamma, \quad \gamma\in\Gamma.$$

Metastability for the WR model

- Start with **empty box** $\square = \emptyset$ (preparation in vapour state)
- Choose $z = \kappa\, z_c(\beta)$, $z_c(\beta) = \beta\, \mathrm{e}^{-\beta V_0}$, $\kappa \in (1, \infty)$, (reservoir is supersaturated vapour),
- Wait for the first time the system reaches the **full box** $\blacksquare = \{\gamma \in \Gamma : h(\gamma) = \Lambda\}$ (condensation to liquid state)

Question: In the regime

$$\beta \to \infty$$

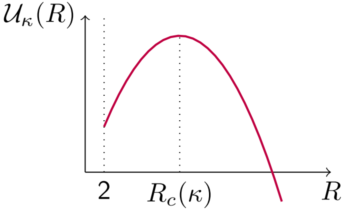
$$\Lambda \quad \text{fixed}$$

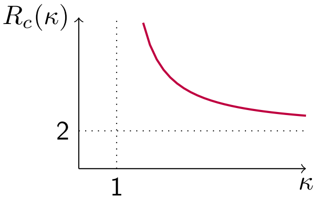
what is the law of

$$\tau_{\blacksquare} = \inf\{t > 0 \colon\ \gamma_t = \blacksquare\}?$$

Results

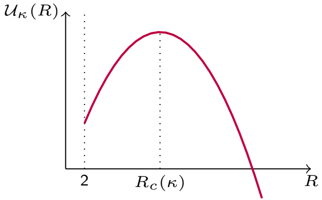
$$R \in [2, \infty), \qquad \mathcal{U}_\kappa : [2, \infty) \to \mathbb{R}, \qquad \mathcal{U}_\kappa(R) = \pi R^2 - \kappa\pi(R-2)^2$$

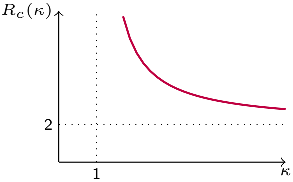




$$R_c(\kappa) = \frac{2\kappa}{\kappa - 1}$$

Results





Theorem 1 [Arrhenius formula]
For every $\kappa \in (1, \infty)$,

$$E_\square(\tau_\blacksquare) = \exp\left[\beta\,\mathcal{U}(\kappa) - \beta^{1/3}\mathcal{S}(\kappa) + o(\beta^{1/3})\right], \quad \beta \to \infty$$

with

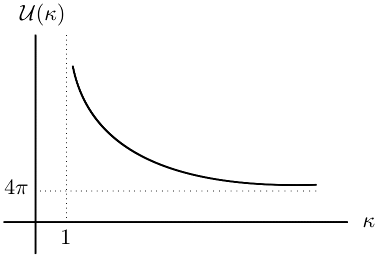
$$\mathcal{U}(\kappa) := \mathcal{U}_\kappa(R_c(\kappa)) = \frac{4\pi\kappa}{\kappa - 1}$$

$$\mathcal{S}(\kappa) = \frac{s}{6^{1/3}} \frac{\kappa^{2/3}}{\kappa - 1}$$

where $s \in (0, \infty)$ is the unique solution of a certain integral equation.

Results

Plots of the key quantities $\mathcal{U}(\kappa)$ and $\mathcal{S}(\kappa)$ in the Arrhenius formula



- $\mathcal{U}(\kappa)$ is the volume free energy of the critical droplet
- $\mathcal{S}(\kappa)$ is the surface free energy of the critical droplet (associated with the surface fluctuations)

Results

Theorem 2 [Exponential law]
For every $\kappa \in (1, \infty)$,

$$\lim_{\beta \to \infty} P_{\square}\big(\tau_{\blacksquare} / E_{\square}(\tau_{\blacksquare}) > t\big) = e^{-t} \qquad \forall\, t \geq 0.$$

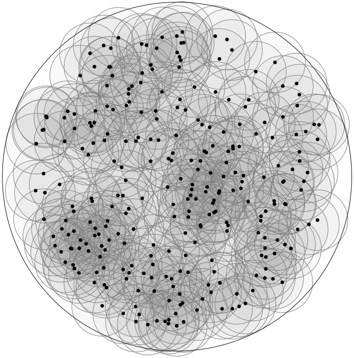
Theorem 3 [Critical droplet]
For every $\kappa \in (1, \infty)$ and $\delta > 0$,

$$\lim_{\beta \to \infty} P_{\square}\big(\tau_{\mathcal{C}_{\delta}(\kappa)} < \tau_{\blacksquare} \mid \tau_{\square} > \tau_{\blacksquare}\big) = 1$$

where

$$\mathcal{C}_{\delta}(\kappa) = \Big\{\gamma \in \Gamma \colon\ \exists x \in \Lambda,\ B_{R_c(\kappa)-\delta}(x) \subset h(\gamma) \subset B_{R_c(\kappa)+\delta}(x)\Big\}$$

Heuristics



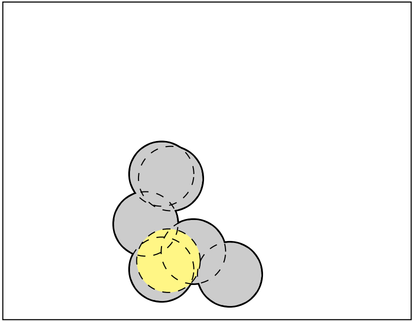
A droplet of radius R filled with 2-disks: $\asymp \beta$ disks in the interior, $\asymp \beta^{1/3}$ disks on the boundary

Heuristics for volume free energy

The birth rate is

$$b(x,\gamma) = z\, e^{-\beta[H(\gamma\cup x)-H(\gamma)]} = z\, e^{V_0\beta}\, e^{-\beta[V(\gamma\cup x)-V(\gamma)]}$$

particles inside a cluster are created at a rate $ze^{V_0\beta} \sim \kappa\beta$ (remember $z = \kappa z_c(\beta)$, $z_c(\beta) = \beta e^{-V_0\beta}$)



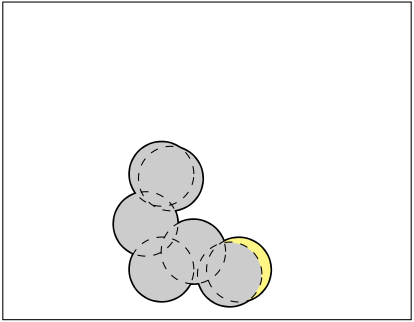
Inside a droplet Poisson process with intensity $\kappa\beta \gg 1$!!

Heuristics for surface free energy

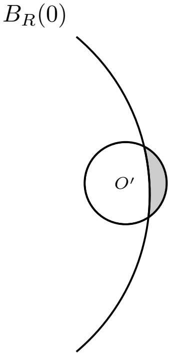
The birth rate is

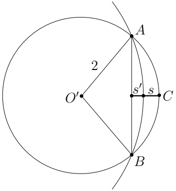
$$b(x, \gamma) = z\, e^{V_0 \beta}\, e^{-\beta[V(\gamma \cup x) - V(\gamma)]}$$

particles sticking out are created at a rate exp small in "sticking out" area (yellow area), which is function of the local curvature!



Heuristics for surface free energy





When adding a new particle to a locally disk-like halo, with s protruding distance

$$\Delta V(s) = C(R)\, s^{3/2}\, [1 + O(s)], \quad \text{dist}(A, B) \sim s^{1/2}, \quad s \downarrow 0$$

For $e^{-\beta \Delta V(s)}$ not to be negligible we have $\Delta V(s) \sim \beta^{-1}$ and $s \sim \beta^{-2/3}$,

$$\Rightarrow \text{dist}(A, B) \sim \beta^{-1/3} \qquad \text{(width of a bump)}$$

number of boundary circles $\sim \beta^{1/3}$

Potential theoretic approach

Bovier, Eckhoff, Gayrard and Klein, 2001
Bovier and den Hollander, 2015

Translates the problem of understanding the metastable behaviour of Markov processes to the study of capacities of electric networks. Link between **mean metastable crossover time** and **capacity**

$$E_{\square}(\tau_{\blacksquare}) = [1 + o(1)]\,\frac{\mu(\square)}{\mathrm{cap}(\square, \blacksquare)}, \qquad \beta \to \infty$$

where the *capacity* of $\square, \blacksquare \subset \Gamma$ is defined as

$$\mathrm{cap}(\square, \blacksquare) = \int_{\square} \mu(\mathrm{d}\gamma)\, P_{\gamma}(\tau_{\blacksquare} < \tau_{\square})$$

and $\tau_C = \inf\{t > 0\colon\ X_t \in C,\ X_{t-} \notin C\}$ is the first return time to $C \subset \Gamma$.
So instead of computing $\tau_{\blacksquare}$, estimate $\mathrm{cap}(\square, \blacksquare)$ ...

Potential theoretic approach

Estimate capacity via the Dirichlet principle

$$\mathrm{cap}(\square, \blacksquare) = \inf_{\substack{f:\ \Gamma \to [0,1] \\ f|_{\square}=1,\ f|_{\blacksquare}=0}} \mathcal{E}(f,f), \quad \text{where}$$

$$\begin{aligned}\mathcal{E}(f,f) &= \int_\Gamma f(\gamma)(-Lf)(\gamma)\,\mu(\mathrm{d}\gamma) \\ &= \frac{1}{\Xi}\int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\int_\Lambda \mathrm{d}x\, z^{N(\gamma\cup x)}\, e^{-\beta H(\gamma \cup x)}\, \big[f(\gamma\cup x) - f(\gamma)\big]^2.\end{aligned}$$

- Upper bound: Estimate $\mathrm{cap}(\square, \blacksquare) \le \mathcal{E}(f,f)$, for a test function f that is guessed via physical insight.

- Lower bound: Use the Thomson principle

$$\mathrm{cap}(\square, \blacksquare) = \sup_{\substack{f:\ \Gamma \to [0,1] \\ Lf \le 0 \text{ on } \Gamma \setminus (\square, \blacksquare)}} \frac{\mathcal{E}(\mathbf{1}_{\square}, f)^2}{\mathcal{E}(f,f)}$$

Upper bound for the capacity

Choose test function

$$\mathrm{cap}(\square,\blacksquare) \leq \frac{1}{\Xi}\int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\int_\Lambda \mathrm{d}x\,(\kappa\beta)^{N(\gamma\cup x)}\,\mathrm{e}^{-\beta V(\gamma\cup x)}\left[f(\gamma\cup x)-f(\gamma)\right]^2$$

...and get an upper bound for the capacity.

$$\mathrm{cap}(\square,\blacksquare) \leq O(\beta) I_1(\kappa,\beta;\eta) + \text{smaller orders}$$

$$I_1(\kappa,\beta;\eta) = \int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\,(\kappa\beta)^{N(\gamma)}\,\mathrm{e}^{-\beta V(\gamma)}\,\mathbf{1}_{\{V(\gamma)\in\pi R_c^2+[-\eta,\eta]\}}$$

The biggest contribution to the capacity comes from the configurations where the volume of the halo is close to the volume of the critical disk.

Upper bound for the capacity

The asymptotics of I_1 gives the asymptotics of the capacity. We choose $\eta = C\beta^{-2/3}$ and we want to prove

$$I_1(\kappa,\beta;C\beta^{-2/3}) = \int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\,(\kappa\beta)^{N(\gamma)}\,\mathrm{e}^{-\beta V(\gamma)}\,\mathbf{1}_{\{V(\gamma)\in\pi R_c^2+[-C,C]\beta^{-2/3}\}}$$
$$= \exp\Big[-\beta\,\mathcal{U}(\kappa)+\beta^{1/3}\,\mathcal{S}(\kappa)+o(\beta^{1/3})\Big], \qquad \beta\to\infty.$$

Upper bound for the capacity

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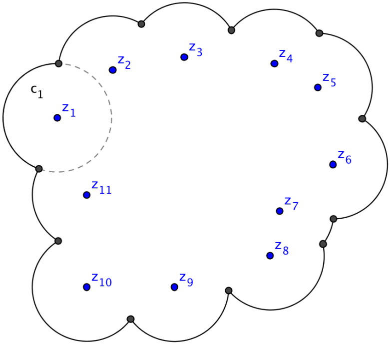
$$= \exp\Big[-\beta\, \mathcal{U}(\kappa) + \beta^{1/3}\, \mathcal{S}(\kappa) + o(\beta^{1/3}) \Big], \qquad \beta \to \infty.$$

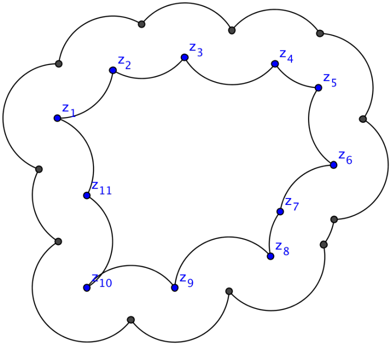
- $\mathcal{U}(\kappa)$ comes from LDP plus isoperimetric inequality
- $\mathcal{S}(\kappa)$ comes from MDP after reparametrizing every halo through its $O(\beta^{1/3})$ boundary points

Let S be a halo shape.



LDP and volume free energy

Let $S^- = \{x \in S\colon\ B_2(x) \subset S\}$ be the 2-interior of S



and $\mathcal{S}_\Lambda$ be the set of "admissible" halo shapes.

LDP and volume free energy

Let $S^- = \{x \in S\colon\ B_2(x) \subset S\}$ the 2-interior of S and $\mathcal{S}_\Lambda$ be the set of "admissible" halo shapes.

Proposition [LDP for halo volume]

The family of probability measures $(\mathbb{P}_\beta)_{\beta \geq 1}$ on $[0, \infty)$ defined by

$$\mathbb{P}_\beta(\mathcal{C}) = \frac{1}{\Xi} \int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\, (\kappa\beta)^{N(\gamma)}\, \mathrm{e}^{-\beta V(\gamma)}\, \mathbf{1}_{\{V(\gamma) \in \mathcal{C}\}}, \qquad \mathcal{C} \subseteq [0, \infty) \text{ Borel},$$

satisfies the large deviation principle with rate β and rate function $\mathcal{I}$ given by

$$\mathcal{I} = \sup_{[0,\infty)} J - J,$$

$$J(x) = \inf \big\{ |S| - \kappa |S^-|\colon\ S \in \mathcal{S}_\Lambda,\ |S| = x \big\}, \qquad x \in [0, \infty).$$

LDP for volume comes as a corollary from an LPD for halo shapes and particle positions.
[ideas from T. Schreiber, 2003]

Isoperimetric inequality

Let $S^- = \{x \in S\colon\ B_2(x) \subset S\}$ the 2-interior of S and $\mathcal{S}_\Lambda$ be the set of "admissible" halo shapes.

Proposition [Isoperimetric inequality]

For every $R \in (2, \frac{1}{2}L)$,

$$\min\left\{|S| - \kappa|S^-|\colon\ S \in \mathcal{S}_\Lambda, |S| = \pi R^2\right\} = \pi R^2 - \kappa\pi(R-2)^2 = \mathcal{U}_\kappa(R)$$

and the minimisers are the disks of radius R. Moreover, for every $S \in \mathcal{S}_\Lambda$ and $\epsilon > 0$,

$$\left.\begin{array}{l} |S| - \kappa|S^-| - \mathcal{U}_\kappa(R) \leq 2\pi\kappa\epsilon \\ |S| = \pi R^2 \end{array}\right\} \quad \Longrightarrow \quad d_H(B_R, S) \leq \sqrt{(2R+\epsilon)^2 - (2R)^2},$$

where d_H denotes the Hausdorff distance.

[standard isoperimetric inequality and Bonnesen's strong isoperimetric inequality]

Moderate deviation and surface term

We want to prove

$$I_1(\kappa,\beta;C\beta^{-2/3}) = \int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\,(\kappa\beta)^{N(\gamma)}\,\mathrm{e}^{-\beta V(\gamma)}\,\mathbf{1}_{\{V(\gamma)\in\pi R_c^2+[-C,C]\beta^{-2/3}\}}$$
$$= \exp\Big[-\beta\,\mathcal{U}(\kappa) + \beta^{1/3}\,\mathcal{S}(\kappa) + o(\beta^{1/3})\Big], \qquad \beta\to\infty.$$

Via LD for the volume of droplet and isoperimetric we prove (roughly)

$$\int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\,(\kappa\beta)^{N(\gamma)}\,\mathrm{e}^{-\beta V(\gamma)}\,\mathbf{1}_{\{V(\gamma)\approx\pi R^2\}} \approx \mathrm{e}^{-\beta\,\mathcal{U}_\kappa(R)}, \qquad \beta\to\infty$$

(remember $\mathcal{U}_\kappa(R_c)=\mathcal{U}(\kappa)$).

For the next term, we need control at a more refined level → moderate deviations for the surface free energy of the droplet!

Moderate deviation and surface term

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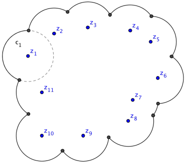
(remember $\mathcal{U}_\kappa(R_c)=\mathcal{U}(\kappa)$).
Very roughly, we want to compute

$$\frac{1}{\beta^{1/3}}\log\Big\{\mathrm{e}^{\beta\,\mathcal{U}(\kappa)}\int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\,(\kappa\beta)^{N(\gamma)}\,\mathrm{e}^{-\beta V(\gamma)}\,\mathbf{1}_{\{V(\gamma)\approx\pi R_c^2\}}\Big\}\approx ? \qquad \beta\to\infty$$



Parametrize the halo's boundary points by polar coordinates: $\{\rho_i, \theta_i\}$, $i = 1, ..., n$, with $\rho_{n+1} = \rho_1$, $\sum_{i=1}^{n} \theta_i = 2\pi$.

Conjecture:

$$\rho_i = W_{t_i}, \qquad t_i = \sum_{j=1}^{i-1} \theta_j, \qquad i = 1, \dots, n,$$

$$W_t = \big(R_c(\kappa) - 2\big) + \sqrt{\big(R_c(\kappa) - 2\big)/2\beta}\; V_t,$$

where $(V_t)_{t\in[0,2\pi]}$ is standard Brownian motion conditioned on being periodic and have $\int_0^{2\pi} V_t \,\mathrm{d}t = 0$

Concluding remarks

- W-R is a very "simple" model for fluids, but displays a rich behavior (geometric interaction, continuum symmetries, Wulff shape...)
- The details of the computation are rather delicate and need to be precise enough in order to produce the surface free energy factor in the Arrhenius formula.
- There are many challenges in understanding metastability of continuum particle systems!

Open problems...

Thank you for your attention!