

Kinetic models for phase transition

Asymptotic Methods for Dissipative Particle Systems

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Summary

- Motivations
- Discussion on models
- Model for a binary mixture
- Free-energy functional
- Characterization of minimizers, finite and infinite volume
- Dynamics on the infinite line. Stability properties
- Dynamics on the 1d torus.

Motivations

- Kinetic theory- phase transition.
Non trivial and **non unique equilibrium** states.
- Complex pattern dynamics. **Stability-instability**
- To generate such situations in kinetic theory a **force term** is needed.
- The simplest model is a Vlasov-Fokker-Plank dynamics, modeling a system of particles interacting through a potential U and with a reservoir at given temperature β^{-1}

Kinetic models

f solution of the **Vlasov-Fokker-Plank equation**

$$\frac{\partial}{\partial t} f + v \cdot \nabla f - F \cdot \nabla_v f = Lf$$

L Fokker-Plank operator

$$Lf := \nabla_v \cdot (M_\beta \nabla_v \frac{f}{M_\beta})$$

$$F = - \int dx' dv f(x', v, t) \nabla U(x - x')$$

M_β standard Maxwellian, with temperature $T = \beta^{-1}$

Vlasov-Fokker-Plank

If $\beta\bar{U}$ ($\bar{U} = \int dx U(|x|)$) is **small**, there is only one stationary solution, the homogeneous equilibrium of the form

$$f_\infty(v) = \rho \frac{1}{(2\pi)^{d/2}} e^{-\frac{|v|^2}{2T}}, \quad \rho = e^{-\beta U \rho}$$

Villani proved the convergence and the rate to equilibrium, for the system on the torus.

f_∞ is the unique minimizer of the **free-energy functional**

$$\int dx dv [f \ln f + \beta f v^2] + \beta \int dx dy U(|x - y|) \rho_f(x) \rho_f(y),$$

$$\rho_f(x) := \int dv f(x, v).$$

If $\beta\bar{U}$ is **not small**, possibility of **phase transition**.

Phase transition

$U \leq 0$ (**attractive interaction**):

the model is not suited because of **collapse**.

The stationary states for U large do not exist with finite density.

To avoid it some cut-off at short distance: difficult to implement in a kinetic model.

Add repulsive interactions to stabilize the system:

4 body repulsive [Lebowitz, Mazel, Presutti \(1998\)](#)

Vapor-liquid transition. Oscillating interface

Vlasov-Fokker-Plank

$U \geq 0$ (**repulsive**),

If the Fourier transform \hat{U} has a strictly negative minimum, then periodic stationary states are expected

crystallization transition

Gates-Penrose (1969)

If $\hat{U}(k) < 0$ for some k_0 , then, there is k close to k_0 such that the free energy functional computed on $\rho_\varepsilon = n + \varepsilon \sin(kx)$, for ε small enough, is strictly lower than the value on the homogeneous $\rho = n$.

Very little is known even for systems on the lattice.

Vlasov-Fokker-Plank

Kinetic model for binary fluids

Vlasov-Fokker-Plank equations for a system of two species of particles $f_1(x, v, t)$, $f_2(x, v, t)$

$$\partial_\tau f_i + v \cdot \nabla_x f_i + F_i \cdot \nabla_v f_i = L f_i$$

Interaction between the two species repulsive.

$$F_i = -\nabla_x \int dy U(|x - y|) \int dv f_j(y, v, t), \quad i \neq j$$

$U \geq 0$ smooth, compact support.

Conservation of masses. First order **phase transition** with coexistence of two states: **segregation**.

Particle models

Mean-field limit $N \rightarrow \infty, \gamma^d N = 1$

Two species of Ornstein-Uhlenbeck processes red and blue,
 $N = N_r + N_b$ interacting by a Kac potential $U^\gamma(r) = \gamma^d U(\gamma r)$

$$q_i^r(t) = v_i^r(t)dt$$

$$v_i^r(t) = - \sum_{j=1}^{N_b} \nabla U^\gamma(q_j^b(t) - q_i^r(t))dt - \beta v_i^r + dw_i^r$$

$$q_i^b(t) = v_i^b(t)dt$$

$$v_i^b(t) = - \sum_{j=1}^{N_r} \nabla U^\gamma(q_j^r(t) - q_i^b(t))dt - \beta v_i^b + dw_i^b$$

Large deviation functional

Large deviation functional for observing a mesoscopic density

Free energy functional $\mathcal{F}(\rho_1, \rho_2)$ determines the probability P_{Λ_γ} of configurations on $\Lambda_\gamma = (\gamma^{-1}L)^d$ whose mesoscopic densities $\rho_i^\gamma = \rho_i(\gamma^{-1}x)$ are close to n_i :

$$P(\rho_1^\gamma, \rho_2^\gamma) \approx \exp\{-\gamma^{-d}(\mathcal{F}(\rho_1, \rho_2) - f_L(n))\}.$$

The *only configurations that we are at all likely to see* are those that minimize \mathcal{F} under the constraint on the total masses

$$f_L(n) = \inf_{\rho_1, \rho_2} \left\{ \mathcal{F}(\rho_1, \rho_2) : \frac{1}{L^d} \int_{\mathcal{I}_L} \rho_i(x) dx = n_i \right\}$$

Equilibrium

■ **Liapunov** functional $\mathcal{G}(f_1, f_2)$:

$$\int dx dv (f_1 \ln f_1 + f_2 \ln f_2) + \frac{\beta}{2} \int dx dv (f_1 + f_2) v^2 \\ + \beta \int dx dy U(|x - y|) \int dv f_1(x, v) \int dv f_2(y, v)$$

■ **Decreasing in time**

$$\frac{d}{dt} \mathcal{G}(f_1, f_2) = - \sum_{i=1,2} \int_{\Omega \times \mathbb{R}^3} dx dv \frac{M^2}{f_i} \left[\nabla_v \frac{f_i}{M} \right]^2 \leq 0$$

Equilibrium

■ Equilibrium distributions: $f_i(x, v) = \rho_i(x) \frac{e^{-v^2/2T}}{(2\pi T)^{3/2}}$

$$T \log \rho_i(x) + \int dy U(|x - y|) \rho_j(y) = C_i, \quad i \neq j$$

■ Spatial *free energy* functional

$$\mathcal{F}(\rho_1, \rho_2) = \sum_{i=1}^2 \int_{\Lambda} \rho_i \log \rho_i + \beta \int dx dy U(|x - y|) \rho_1(x) \rho_2(y)$$

Variational characterization of “**stable**” equilibria

Non convex functional

$$\int_{\Lambda} dx f(\rho_1, \rho_2) + \frac{\beta}{2} \int_{\Lambda \times \Lambda} dx dy U(|x-y|) [\rho_1(x) - \rho_1(y)] [\rho_2(y) - \rho_2(x)]$$

$$f(\rho_1, \rho_2) = \rho_1 \log \rho_1 + \rho_2 \log \rho_2 + \beta \rho_1 \rho_2$$

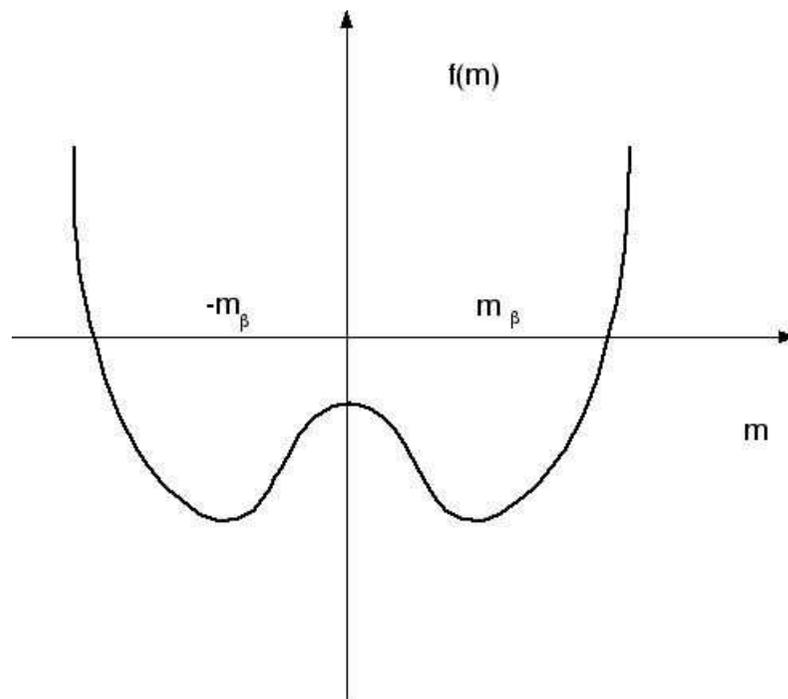
$f(\rho_1, \rho_2)$ is the **thermodynamic free energy**, entropy + internal energy, it is **not convex** at low T , with two symmetric minimizers (under exchange $1 \rightarrow 2$): (ρ^{\pm}, ρ^{\mp})

Non local term positive (Rearrangement inequalities). If the total masses $\frac{1}{\Lambda} \int_{\Lambda} \rho_i(x) dx = n_i$ are minimizers, homogenous profiles. In between, expect **non homogeneous**

Double well.

$$\rho = \rho_1 + \rho_2, m = \frac{\rho_1 - \rho_2}{\rho}; \quad f(\rho_1, \rho_2) = \rho \log \rho + \frac{\rho^2 \beta}{4} + \rho^2 f(m)$$

$$f(m) = -\frac{\beta}{2} \frac{m^2}{2} + \frac{1-m}{2} \log \frac{1-m}{2} + \frac{1+m}{2} \log \frac{1+m}{2}$$

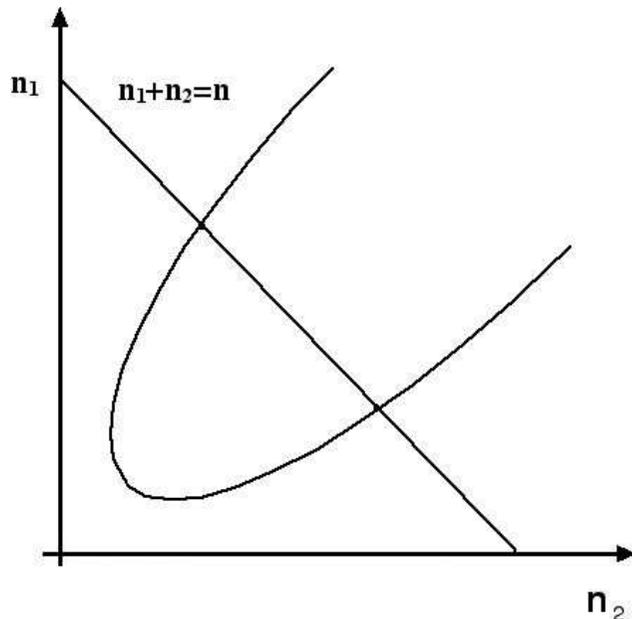


Segregation

If the total density $n = n_1 + n_2$: $n\beta > 2$

Coexistence of two phases, one richer in species 1 and the other richer in species 2.

Phase diagram



In the two phases:

Same density $n = n_1 + n_2$

Concentration $m = \frac{n_1 - n_2}{n}$

changes sign

Variational approach

1) Finite volume

Minimize the **free-energy** in Λ under the mass constraint

$$\frac{1}{\Lambda} \int_{\Lambda} \rho_i(x) dx = n_i$$

Fix n_i so to rule out the absolute minima corresponding to the pure phases

2) Infinite line. (Interface stability).

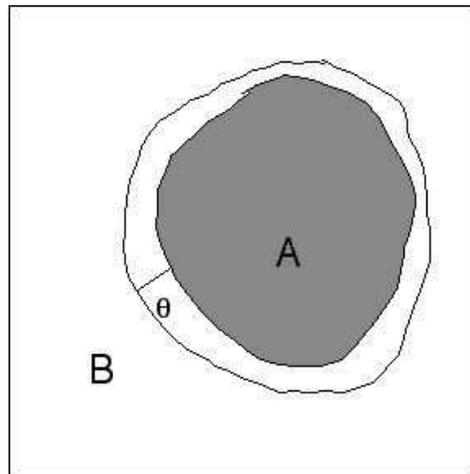
Minimize the **excess free-energy**

$$\hat{\mathcal{F}}(\rho_1, \rho_2) = \mathcal{F}(\rho_1, \rho_2) - \mathcal{F}(\rho^+, \rho^-)$$

with fixed asymptotic values $\lim_{x \rightarrow \pm\infty} \rho_1(x) = \rho^{\pm}, \lim_{x \rightarrow \pm\infty} \rho_2 = \rho^{\mp}$

Large volume

Region A such that $m(x) \approx m_\beta$ in A , and $m(x) \approx -m_\beta$ outside.
Interpolation across the boundary, in a region Δ , of width proportional to the range of the interaction



droplet of + phase (at A) in a sea of - phase.

Profile across the interface is given by the solution of problem 2)

Competing interactions

Attractive+ long range repulsive interaction

Giuliani-Lebowitz-Lieb : Cahn-Hilliard+ repulsive non local

Potential kernel: Laplace transform of a positive measure

Reflection positivity: existence of periodic minimizers

Lebowitz-Penrose: system of particles

Short range + Kac repulsive potential of range γ^{-1}

In the infinite volume limit, for $\gamma \rightarrow 0$, the repulsive term

destroys the coexistence of phases

the surface tension is lowered by the repulsive interaction

For γ finite one expects the formation of a "**froth**", on an

intermediate scale $\gamma^{-\alpha}$

Competing interactions

Kinetic model with competing interactions for a binary mixture

Add a **repulsive interaction between the same species**

$$\begin{aligned} & \int dx dv (f_1 \ln f_1 + f_2 \ln f_2) + \frac{\beta}{2} \int dx dv (f_1 + f_2) v^2 \\ & + \beta \int dx dy U(|x - y|) \int dv f_1(x, v) \int dv f_2(y, v) \\ & + \beta \sum_{i=1,2} \int dx dy U^\lambda(|x - y|) \int dv f_i(x, v) \int dv f_i(y, v) \end{aligned}$$

$$U^\lambda(r) = \lambda^d U(\lambda r), \quad \text{froth for } 1 \ll \lambda?$$

Applications

Lattice Boltzmann algorithms with self consistent potentials.

Phase transition

Nanotubes. Liquid-vapour coexistence.

Gas layer close to the surface change the behaviour in the bulk.

Competing interactions

Binary mixture with self consistent attractive and repulsive potentials

Models of emulsions, many interesting behaviours: ageing, long-time relaxation...

Benzi- Succi Phys. Rev. Lett. 2009

Results

- Existence and characterization of the minimizers on the **infinite line** and on a **d-dimensional finite large volume**

R. M., E. Carlen, M. Carvalho, R. Esposito, J.L.Lebowitz, 2003, 2008

- Infinite line: R. M., L. Esposito, Y. Guo 2009

Asymptotic stability of the non homogeneous minimizer (front solution) in the phase transition region.

Rate of convergence.

- **Asymptotic stability** of the constant minimizer out of the phase transition region

Instability of the constant solution ?

Finite domain

Minimization of **free energy** functional in a torus Λ under the constraints on the total masses

$$n_i = \frac{1}{\Lambda} \int dx \rho_i(x)$$

Results for Λ large: Carvalho, Carlen, R.M., Esposito, Lebowitz, (2003)

$U(x)$ is even non negative and **decreasing**

Homogeneous solution unique for $\beta n \leq 2$.

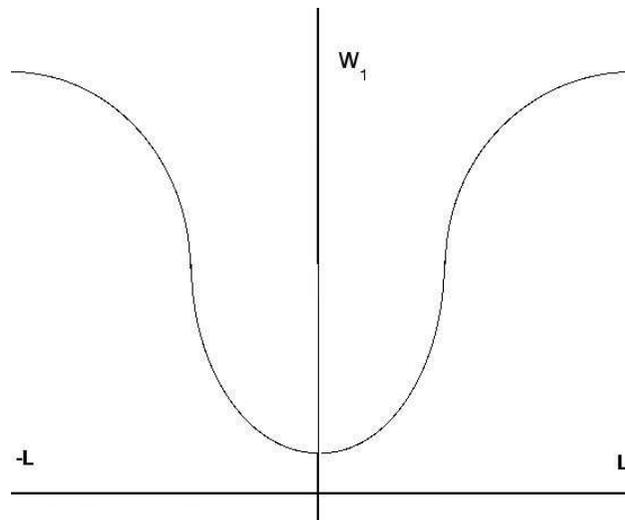
Otherwise, **non homogeneous minimizers**. Regularity.

They are **symmetric monotone**.

Drop

Symmetric monotone minimizer in 1d

Density profile w_1 on the interval $[-L, L]$ centered with the minimum in 0



1d. Infinite line

Results for the excess free-energy

Theorem. (Existence and uniqueness)

If $U(x)$ is even non negative and **decreasing**, then the minimizer of $\hat{\mathcal{F}}(\rho_1, \rho_2)$ is unique (up to translations) and monotone in the sense that ρ_1 is increasing and ρ_2 is decreasing.

Proof: Rearrangement inequality + displacement convexity

C.Carvalho, E.Carlen, R.Esposito, J.L.Lebowitz, R.M. 2007

Front

Front $w = (w_1, w_2)$: centered $w_1(0) = w_2(0)$,
positive and symmetric in the sense that $w_2(x) = w_1(-x)$

Theorem

The front is in $C^\infty(\mathbb{R})$ and converges to its asymptotic values exponentially fast, in the sense that there is $\alpha > 0$ such that

$$(w_1(x) - \rho_{\mp})e^{\alpha|x|} \rightarrow 0 \text{ as } x \rightarrow \mp\infty,$$

$$(w_2(x) - \rho_{\pm})e^{\alpha|x|} \rightarrow 0 \text{ as } x \rightarrow \mp\infty.$$

Dynamical stability

Result: the front is asymptotically stable for the Vlasov-Fokker-Plank dynamics under small symmetric initial perturbation.

R. Esposito, Y. Guo, R.M., Arc. Rat. Mec. 2008,

$$\text{Perturbation } f_i = w_i M + h_i$$

Assume for $h = (h_1, h_2)$ at time zero the symmetry property

$$h_1(z, v_x, v_y, v_z, 0) = h_2(-z, v_x, v_y, -v_z, 0)$$

Theorem

Inner product and L^2 -norms $\|\cdot\|_0$

$$(f, g)_0 = \sum_{i=1,2} \int_{\mathbb{R} \times \mathbb{R}^3} dz dv \frac{1}{w_i M} f_i g_i,$$

$$\|g\|_D^2 = \|(I - P)g\|_0^2 + \|\nabla_v(I - P)g\|_0^2,$$

P is the L^2 -projection on the null space of L : $\{cM, c \in \mathbb{R}^2\}$

In an infinite domain the problem is to control the **tails**, one needs decay at infinite.

Weighted norm: $\|g\|_\gamma = \|\{1 + z^2\}^\gamma g\|_0$

Theorem

Theorem. Global Existence

If for δ_0 small enough,

$$\|h(0)\|_0 + \|\partial_t h(0)\|_0 + \|\partial_z h(0)\|_0 \leq \delta_0$$

then there is a unique global solution of VFP such that for some $K > 0$

$$\begin{aligned} & \frac{d}{dt} \left(K (\|h(t)\|_0^2 + \|\partial_t h(t)\|_0^2) + \|\partial_z h(t)\|_0^2 \right) \\ & + K \nu_0 (\|h(t)\|_D^2 + \|\partial_t h(t)\|_D^2) + \nu_0 \|\partial_z h(t)\|_D^2 \leq 0 \end{aligned}$$

Theorem

Theorem. Asymptotic stability and Decay rate

■ If for δ_0 and γ small enough,

$$\|h(0)\|_\gamma + \|\partial_t h(0)\|_{\frac{1}{2}+\gamma} + \|\partial_z h(0)\|_{\frac{1}{2}+\gamma} \leq \delta_0,$$

then

$$\sup_{0 \leq t \leq \infty} \|h(t)\|_\gamma + \|\partial_t h(t)\|_{\frac{1}{2}+\gamma} + \|\partial_z h(t)\|_{\frac{1}{2}+\gamma} \leq C\delta_0$$

■ Moreover,

$$\|h(t)\|_0 + \|\partial_t h(t)\|_0 + \|\partial_z h(t)\|_0 < C\delta_0 \left[1 + \frac{t}{2\gamma}\right]^{-2\gamma}$$

Proof

Energy estimates. Norms based on the free energy functional.

- **spectral gap** for the Fokker-Planck operator L to control $(I - P)h$, the part of h orthogonal to the null space of L ,
- Equations for Ph , the component of h in the null space of L . They are not close, depend on $(I - P)h$
- **spectral gap** for an operator A , related to the spatial free energy, to control Ph , in terms of $(I - P)h$.

Operator A

Norm involving the **operator A** , the second variation of the **spatial** free energy $\hat{\mathcal{F}}$ at the front w , given by

$$(g, Ag) := \sum_{i=1}^2 \int_{\mathbb{R}} dz g_i(z) (Ag)_i(z) = \frac{d^2}{ds^2} \mathcal{F}(w + sg) \Big|_{s=0}$$

$$(Ag)_1 = \frac{g_1}{w_1} + \beta U * g_2, \quad (Ag)_2 = \frac{g_2}{w_2} + \beta U * g_1$$

Since w is a minimizer of $\hat{\mathcal{F}}$ the quadratic form on the left hand side is nonnegative

Operator A

The first variation gives the Euler-Lagrange equations

$$\frac{\delta \hat{\mathcal{F}}}{\delta \rho_i}(w) = \log w_i + \beta U * w_j - C_i = 0, \quad i \neq j,$$

Differentiating with respect to z

$$(Aw')_i = \frac{w'_1}{w_1} + \beta U * w'_j = 0, \quad i \neq j,$$

w' spans the null space of A and (**spectral gap**)

$$(g, Ag) \geq \lambda \sum_{i=1}^2 \int_{\mathbb{R}} dz \frac{1}{w_i} |(I - \mathcal{P})g_i|^2 = \lambda((I - \mathcal{P})g, (I - \mathcal{P})g)$$

where \mathcal{P} is the projector on the null space of A .

Operator A

Non trivial null space for A . Degeneracy of the stationary state.
Invariance by translation.

The spectral gap for A controls the component of Ph on the orthogonal to the null space of A , but not the component on the null space of A . $Ph = M(v)a(z, t)$ and $a = \alpha w' + (I - \mathcal{P})a$.

$$\alpha(t) = \int_{\mathbb{R} \times \mathbb{R}^3} dz dv Ph(z, v, t) w'(z)$$

The Liapunov functional forces the system to relax to one of the stationary points for the functional, which are of the form Mw^x , with w^x any translate by x of the symmetric front w^0 .

Operator A

The **conservation law**, in the form

$$\int_{\mathbb{R} \times \mathbb{R}^3} dz dv [f(z, v, t) - M(v)w^0] = 0$$

selects the front the solution has to converge to.

But this is a condition on the L_1 norm of the solution while the energy estimates control some L_2 norm. Our weighted norms are not enough to control the L_1 norm.

E. Carlen- C. Carvalho-E. Orlandi (2000) (dissipation on z)

Symmetry

We assume that h is **symmetric** at initial time.

This property is conserved by the dynamics so that h is symmetric at any later time.

Also wM is symmetric while w' is antisymmetric in the z variable. ($w'_1(z) = w'_2(-z)$)

This implies the **vanishing** of

$$\alpha(t) = \sum_{i=1}^2 \int_{\mathbb{R} \times \mathbb{R}^3} dz dv h_i(z, v, t) M(v) w'_i(z)$$

Perturbation

Equation for the perturbation $h_i = a_i M + (I - P)h_i$

$$M[\partial_t a_i + v_z w_i \partial_z (Aa)_i] = B((I - P)h) - F(h_i) \partial_{v_z} h_i + L(I - P)h_i.$$

$$M v_z w_i \partial_z (Aa)_i = v_z M w_i \partial_z a_i - F(w_i M) \partial_{v_z} (a_i M) + F(a_i M) \partial_{v_z} (w_i M)$$

Force term not small

We need a control of the $\|\partial_z (Aa)\|_0$

$$\|(Au)'\|_0^2 \geq k \|Qu'\|_0^2$$

where Q is the projection on the orthogonal complement of w'' .

Decay

In an infinite domain the problem is to control the **tails**, one needs decay at infinite.

We consider weighted L_2 -norms

$$\| \{1 + z^2\}^\gamma g \|_M = \int_{\mathbb{R} \times \mathbb{R}^3} dx dv (1 + z^2)^{2\gamma} |g|^2 M(v)$$

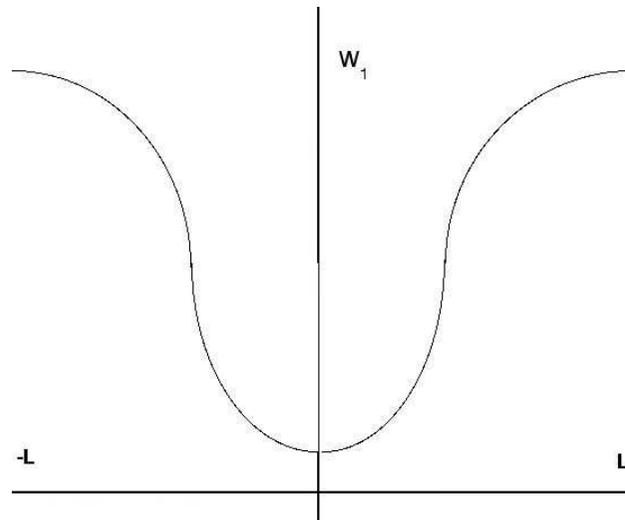
$$0 < \gamma \leq \frac{1}{8}.$$

Enough to get polynomial decay (in space and time)

Not enough for the control of the L_1 norm

Work in progress

- finite volume, **1d torus** (with Esposito and Guo)
Stability of the non constant minimizer ("double front")



- Operator A on T_L , the 1-d torus of size L . Derivative of the front is in the null. **Null space? Spectral gap?**

Spectral gap

A has a **negative eigenvalue**. Vector $\tilde{w} = (|w'_1|, -|w'_2|)$

$$(\tilde{w}, A\tilde{w})_w = \int_{T_L} |w'_1| \left(\frac{|w'_1|}{w_1} - U * |w'_2| \right) + |w'_2| \left(\frac{|w'_2|}{w_2} - U * |w'_1| \right)$$

$$= -2 \int_0^L w'_1 U * (|w'_2| + w'_2) - 2 \int_{-L}^0 w'_2 U * (|w'_1| + w'_1) < 0$$

We have used the EL equations

$$\frac{w'_1}{w_1} = -U * w'_2, \quad x \geq 0; \quad \frac{w'_2}{w_2} = -U * w'_1, \quad x \leq 0$$

Show that the **mass constraint** kills the negative eigenvalue.

Neumann b.c.

Spectral gap true for **anti symmetric** (by reflection) functions.

Problem on the torus for **symmetric** functions reduced to the case of **Neumann boundary conditions on $[0, L]$**

$$(\hat{A}g)_1 = \frac{g_1}{w_1} + \beta \hat{U} * g_2, \quad (\hat{A}g)_2 = \frac{g_2}{w_2} + \beta \hat{U} * g_1$$

$$\hat{U}(z, z') = U(z, z') + U(z, R_0 z') + U(z, R_L z')$$

R_0 reflection around zero and R_L reflection around L .

$\lambda < 0$ minimum eigenvalue and \hat{e} its eigenfunction

Spectral gap

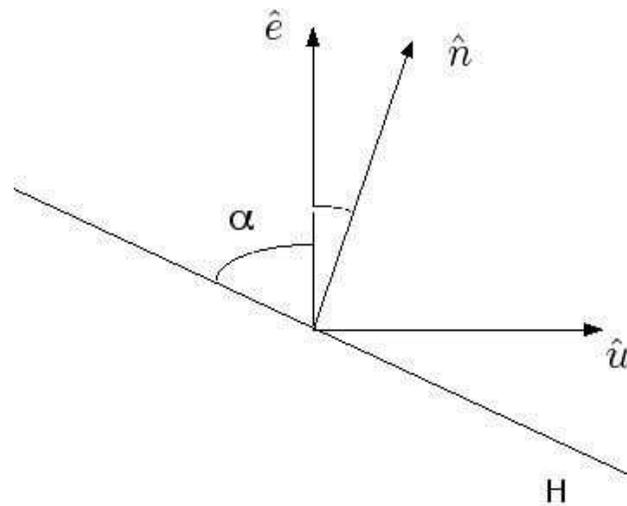
We need spectral gap for functions in the hyperplane

$$H = (h : \int_0^L h = 0).$$

We have spectral gap for functions in the orthogonal to \hat{e}

$$(u, \hat{A}u) \geq \delta(u, u), \quad (u, \hat{e}) = 0$$

If the angle α between \hat{e} and H is too small we are in trouble



Spectral gap

Decompose h as $a\hat{e} + b\hat{u}$ with \hat{u} orthogonal to \hat{e}

$$(h, \hat{A}h) = a^2 \lambda_L + b^2 (\hat{u}, \hat{A}\hat{u})$$

$$a = \cos \alpha, b^2 = \sin^2 \alpha. \sin \alpha = \frac{1}{\sqrt{L}} \int_0^L \hat{e}.$$

If \hat{e} decays fast enough $b^2 \approx \frac{1}{L}$. λ_L is negative

Competition $(h, \hat{A}h) \geq -|\lambda_L| + \frac{c}{L}\delta$

If λ_L decays faster than $\frac{1}{L}$ we can prove spectral gap for **L large**

$$(h, \hat{A}h) > d(h, h)$$

G. Manzi (2007)

Spectrum

Analysis of the spectrum using **Markov chains**. Generalize method by De Masi, Olivieri, Presutti (1998), Ising case.

- bound on the minimum eigenvalue λ_L

$$-c_1 e^{-\gamma L} \leq \lambda_L \leq c_2 e^{-\gamma L}$$

- exponential bound on the minimum eigenfunction \hat{e}

$$-c e^{-\gamma|L-x|} \leq \hat{e} < 0$$

- **spectral gap** in a suitable weighted L_∞ for functions u in the orthogonal to \hat{e} . Implies spectral gap in L_2 .

Spectral gap

Operator S $(Su)_i = w_i \hat{U} * u_j, \quad i \neq j, i = 1, 2$

$$(u, \hat{A}u)_w = \sum_i \int dx w_i u_i (\hat{A}u)_i = (u, u) + (u, Su)$$

$$(u, S^2u) = \sum_i \int u_i w_i \hat{U} * (w_j \hat{U} * u_i) = (u, Tu)$$

Negative eigenvalue for \hat{A} means eigenvalue for S greater than 1

We will study the operators

$$T_1 h = w_1 \hat{U} * (w_2 \hat{U} * h), \quad T_2 h = w_2 \hat{U} * (w_1 \hat{U} * h)$$

Markov chain

$$\hat{J}(x, x') = \int dz \hat{U}(x - z) \frac{w_2(z)}{w_2(x)} \int dy \hat{U}(z - x')$$

$$M(x, x') = p(x) \hat{J}(x, x'); \quad p(x) = w_1(x) w_2(x)$$

For $\lambda_0 > 0$ and $\psi(x)$ positive define the Markov chain

$$K(x, y) = \frac{M(x, y) \psi(y)}{\lambda_0 \psi(x)}$$