Phase transitions and coarse graining for a system of particles in the continuum

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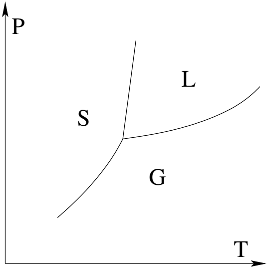
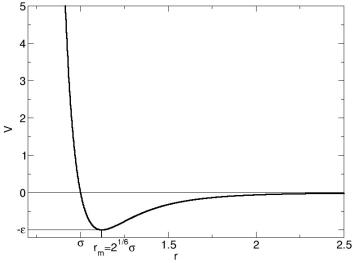
Problem: derivation of phase diagrams of fluids.



Phase transition (1st order, order parameter ρ): there is a *forbidden interval* $[\rho', \rho'']$ of density values, namely: if we put a mass $\rho|\Lambda|$, $\rho \in (\rho', \rho'')$, T small enough, then we see ρ' in a set $\Lambda' \subset \Lambda$ and ρ'' in $\Lambda \setminus \Lambda'$

We want to study the liquid-vapour coexistence line

Model: identical point particles which interact pairwise via a potential repulsive at the origin and with an attractive tail at large distances (the prototype is the Lennard-Jones potential)



Conjecture: fluids interacting via a Lennard-Jones potential behave according to the phase diagram.

... but no rigorous proof of this conjecture!

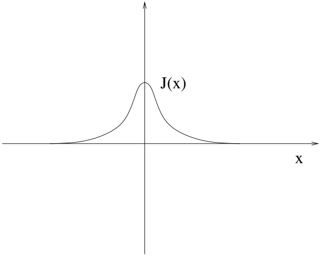
State of the art:

- In the discrete: first proof of liquid-vapor type phase transitions was given for lattice systems as the Ising model (argument of Peierls).
- In the continuum:
  - Widom-Rowlinson model of two component fluids (Ruelle, '71)
  - 1d with long range interaction (Johansson, '95)
  - Lebowitz, Mazel and Presutti (LMP) in '99 prove liquid-vapor phase transition for a model of **particles in the continuum** $d \geq 2$ interacting via a 2-body attractive plus a 4-body repulsive interaction (both long range).

Microscopic model

Local mean field: local energy density $e(\cdot)$ is a function of local particle density

$$\rho_\gamma(r;\mathbf{q}) := \sum_{q_i \in \mathbf{q}} J_\gamma(r, q_i)$$ local particle density at $r \in \mathbb{R}^d$



Kac potentials

$$J_\gamma(r, r') = \gamma^d J(\gamma r, \gamma r')$$

$\gamma > 0$: Kac scaling parameter
($\gamma \to 0$ mean field limit)

$$\int dr J(r, r') = 1$$

$$H_\gamma(\mathbf{q}) = \int_{\mathbb{R}^d} e(\rho_\gamma(r;\mathbf{q}))\, dr$$

LMP model (Lebowitz, Mazel, Presutti): Take the energy density

$$e(\rho) = -\frac{\rho^2}{2} + \frac{\rho^4}{4!} \qquad H_\gamma^{\mathsf{LMP}}(\mathbf{q}) = \int_{\mathbb{R}^d} e(\rho_\gamma(r;\mathbf{q}))\,dr,$$

$$H_\gamma^{\mathsf{LMP}}(\mathbf{q}) = \underbrace{-\frac{1}{2!}\sum_{i\neq j} J_\gamma^{(2)}(q_i,q_j)}_{\text{2-body}} + \underbrace{\frac{1}{4!}\sum_{i_1\neq\ldots\neq i_4} J_\gamma^{(4)}(q_{i_1},\ldots,q_{i_4})}_{\text{4-body}}$$

$$J_\gamma^{(2)}(q_i,q_j) := J_\gamma * J_\gamma(q_i,q_j) = \int J_\gamma(r,q_i)J_\gamma(r,q_j)\,dr$$

Towards our model

Theorem (LMP): There are $\beta_c > 0, \beta^* > \beta_c$ such that for $\beta \in (\beta_c, \beta^*)$ for any γ small enough there is a "forbidden interval" $(\rho'_{\beta,\gamma}, \rho''_{\beta,\gamma})$.

Drawbacks:
• scale attraction $\sim$ scale repulsion
• towards crystal structures and solid phase...need repulsion on scale 1

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LMP + h.c. model:
add the interaction given by $H^{\text{hc}}(\mathbf{q}) := \sum_{i<j} V^{\text{hc}}(q_i, q_j)$ where $V^{\text{hc}} : \mathbb{R}^d \to \mathbb{R}$

$$V^{\text{hc}}(q_i, q_j) = \begin{cases} +\infty & \text{if } |q_i - q_j| \leq R \\ 0 & \text{if } |q_i - q_j| > R \end{cases}$$

with R the radius of the hard spheres and $\epsilon = |B_0(R)|$ their volume.

Our goal: to extend this result to: LMP + hard core (perturbation theory for small values of the radius R) (...work in progress)

Statistical mechanics formulation

Grand canonical measure in the region $\Lambda \subset \mathbb{R}^d$ and b. c. $\bar{q}$ in Λ^c is:

$$\mu^{\Lambda}_{\gamma,\beta,R,\lambda}(d\mathbf{q}|\bar{q}) = Z^{-1}_{\gamma,\beta,R,\lambda}(\Lambda|\bar{q})e^{-\beta H_{\gamma,R,\lambda}(\mathbf{q}|\bar{q})}\nu^{\Lambda}(d\mathbf{q})$$

First order phase transition $\Longleftrightarrow$ if β is large enough, the limiting ($\Lambda \nearrow \mathbb{R}^d$) Gibbs state is **not unique**, i.e. we have instability with respect to boundary conditions

Diluted Gibbs measure:

$$\mu^{\pm}_{\Lambda,\beta,\gamma,R} = \mu^{\Lambda}_{\gamma,\beta,R}\mathbb{1}_{\{\text{on the boundary of } \Lambda \text{ we fix a frame with the phase } \pm\}}$$

Result

R: radius of the hard spheres, γ: Kac scaling parameter

Theorem (Liquid-vapor phase transition for LMP+hc)

Consider the LMP+hc model in dimensions $d \geq 2$.
For: $0 < R \leq R_0$, $\beta \in (\beta_{c,R}, \beta_{0,R})$, $\gamma \leq \gamma_{\beta,R}$,
there is $\lambda_{\beta,\gamma,R}$ such that:

There are two distinct infinite volume measures $\mu^{\pm}_{\beta,\gamma,R}$ with chemical potential $\lambda_{\beta,\gamma,R}$ and inverse temperature β and two different densities: $0 < \rho_{\beta,\gamma,R,-} < \rho_{\beta,\gamma,R,+}$.

Remark 1.

$$\lim_{\gamma\to 0}\rho_{\beta,\gamma,R,\pm}=\rho_{\beta,R,\pm},\qquad \lim_{\gamma\to 0}\lambda_{\beta,\gamma,R}=\lambda_{\beta,R}$$

with are respectively densities and chemical potential for which there is a phase transition in the LMP + h.c. mean field model. $\rho_{\beta,R,-}<\rho_{\beta,R,+}$.

Remark 2.

$$\beta_{c,R}=\beta_c^{\mathsf{LMP}}-\epsilon\,(\beta_c^{\mathsf{LMP}})^{2/3}+O(\epsilon^2)$$

$$\beta_c^{\mathsf{LMP}}=\frac{3}{2}^{\frac{3}{2}},\qquad \epsilon=|B_0(R)|$$

Contour method approach and Pirogov-Sinai theory

Idea (for Ising): to look at configurations at small T as of perturbations of the two ground states ($+$ and $-$)
Instead: perturb mean field ($\gamma \to 0$), where two g.s. are ρ_+, ρ_-

Analogy:

T small $\Longleftrightarrow$ γ small

spin-flip symmetry $\Longleftrightarrow$ no symmetry

... towards an abstract contour model!

Abstract contour model

Scaling parameters:

$$\ell_- = \gamma^{-(1-\alpha)}, \quad \ell_+ = \gamma^{-(1+\alpha)}, \quad \zeta = \gamma^a, \qquad 1 \gg \alpha \gg a > 0$$

Two partitions with cubes $C^{(\ell_-)}, C^{(\ell_+)}$

- $$\eta^{(\zeta,\ell_-)}(q;r) = \begin{cases} \pm 1 & \text{if } \left|\rho^{(\ell_-)}(q;r) - \rho_{\beta,R,\pm}\right| \leq \zeta \\ 0 & \text{otherwise} \end{cases}$$
- $$\theta^{(\zeta,\ell_-,\ell_+)}(q;r) = \begin{cases} \pm 1 & \text{if } \eta^{(\zeta,\ell_-)}(q;r') = \pm 1 \quad \forall r' \in C_r^{(\ell_+)} \\ 0 & \text{otherwise} \end{cases}$$

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which are the phase indicators!

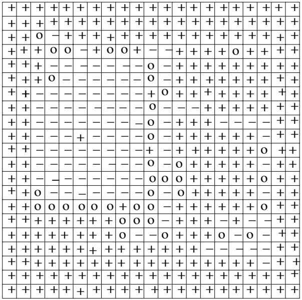


Figure: Values of $\theta^{(\ell_-,\ell_+,\zeta)}$

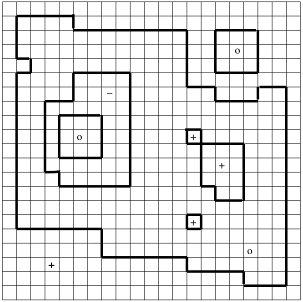
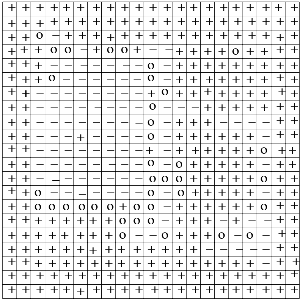


Figure: Discontinuity lines of $\Theta^{(\ell_-,\ell_+,\zeta)}$ and regions where it is $+$, $-$ and 0.

Abstract contour model



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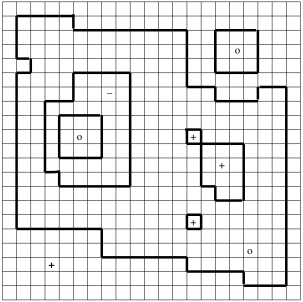

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Definition (Contour)

A contour is a pair $\Gamma = \big(\text{sp}(\Gamma), \eta_\Gamma\big)$, where $\text{sp}(\Gamma)$ is a maximal connected component of the "incorrect set" $\{r \in \mathbb{R}^d : \Theta^{(\zeta,\ell_-,\ell_+)}(q;r) = 0\}$ and η_Γ is the restriction to $\text{sp}(\Gamma)$ of $\eta^{(\zeta,\ell_-)}(q;\cdot)$.

Abstract contour model

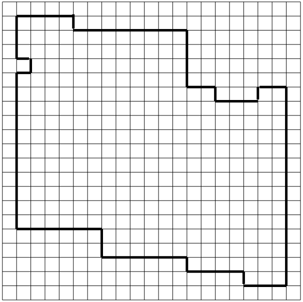

Figure: The set $c(\Gamma)$

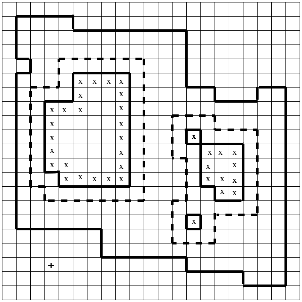

Figure: $A_i(\Gamma)$ are the regions made of the x marked squares contained in $\mathrm{int}_i(\Gamma)$

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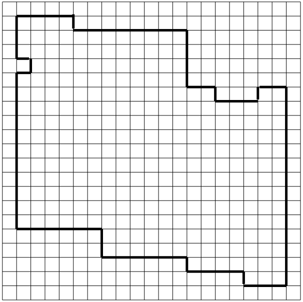

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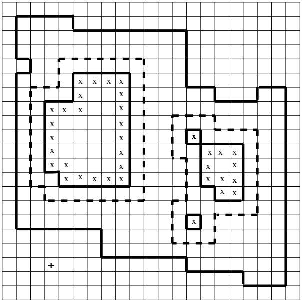

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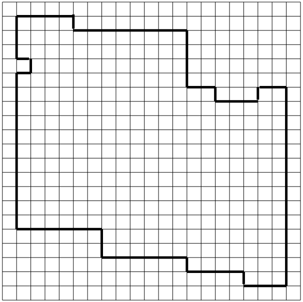
$\Gamma = \big(\mathrm{sp}(\Gamma), \eta_\Gamma\big)$ is called $+$ (or $-$) contour if $\Theta(q; r) = +1$ (or -1) on the frame of width ℓ^+ around the set $c(\Gamma)$.

Abstract contour model



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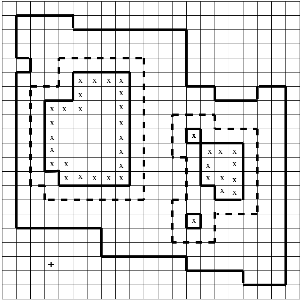

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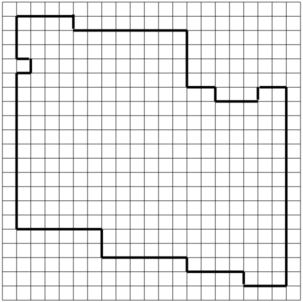
The weight $W^{+}_{\gamma,R,\lambda}(\Gamma;\bar{q})$ of a $+$ contour Γ is

$$\frac{\text{Prob. of having a } + \text{ contour}}{\text{Prob. of having the } + \text{ phase}}$$

Abstract contour model



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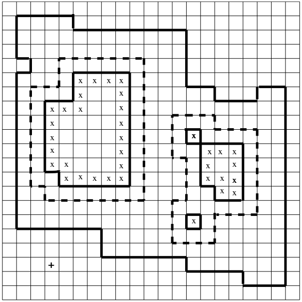

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The weight $W^{+}_{\gamma,R,\lambda}(\Gamma;\bar{q})$ of a $+$ contour Γ is

$$\frac{\mu_{q^+}^{c(\Gamma)}\Big(\eta(q_{c(\Gamma)};r)=\eta_\Gamma(r), r\in \mathrm{sp}(\Gamma);\ \Theta(q_{c(\Gamma)};r)=\pm 1, r\in A^{\pm}(\Gamma)\Big)}{\mu_{q^+}^{c(\Gamma)}\Big(\eta(q_{c(\Gamma)};r)=1, r\in \mathrm{sp}(\Gamma);\ \Theta(q_{c(\Gamma)};r)=1, r\in A^{\pm}(\Gamma)\Big)}$$

Peierls bounds

The main technical point is to prove that contours are improbable, i.e. Peierls estimates:

Theorem

For: $0 < R \le R_0,\qquad \beta \in (\beta_{c,R}, \beta_{0,R}),\qquad \gamma \le \gamma_{\beta,R},$
there is $\lambda_{\beta,\gamma,R}$ *so that:*
for any $\pm$ *contour* Γ *and any* $\pm$ *boundary condition* $q^{\pm}$ *outside* Γ*,*

$$W^{\pm}_{\gamma,R,\lambda}(\Gamma; q^{\pm}) \le \exp\Big\{ -\beta c\,(\zeta^2 \ell_-^d)\, N_\Gamma \Big\}, \qquad N_\Gamma = \frac{|\mathrm{sp}(\Gamma)|}{\ell_+^d}$$

Corollary

...then for any bounded, simply connected, $\mathcal{D}^{(\ell_+)}$*-measurable region* Λ*,*
any $\pm$ *boundary condition* $q^{\pm}$ *and any* $r \in \Lambda$*,*

$$\mu^{\Lambda,\pm}_{q^{\pm}}(\{\Theta(q;r) = \pm 1\}) \ge 1 - \exp\Big\{ -\beta \frac{c}{2}\,(\zeta^2 \ell_-^d) \Big\}.$$

Problems:

- both numerator and denominator in the weight defined in terms of expressions which involve not only the support of Γ but also its whole interior (bulk quantities!).
- the desired bound involves only the volume of the support of Γ which is a surface quantity!
- Cancellation of bulk terms difficult when there is no simmetry between phases (as for Ising).

Three steps

Step one:
Equality of pressures
For any $\lambda \in [\lambda(\beta, R) - 1, \lambda(\beta, R) + 1]$ the following holds

$$\lim_{n\to\infty} \frac{1}{\beta|\Lambda_n|} \log Z^{\pm}_{\lambda}(\Lambda_n | q^{\pm}_n) = P^{\pm}_{\lambda}$$

moreover, for all γ small enough there is $\lambda^* := \lambda_{\beta,\gamma,R}$ such that

$$P^{+}_{\lambda^*} = P^{-}_{\lambda^*}, \qquad |\lambda^* - \lambda(\beta, R)| \leq c\gamma^{1/2}$$

(coarse graining argument a la Lebowitz-Penrose, closeness of the pressures to their mean field values $p^{\pm;\mathsf{mf}}_{R,\lambda}$)

Step two:
Energy estimates
Given γ small and $R < R_0$:

$$\frac{N^{+}_{\lambda^*}(\Gamma, q^{+})}{D^{+}_{\lambda^*}(\Gamma, q^{+})} \leq e^{-\beta(c\zeta^2 - c'\gamma^{1/2-2\alpha d})\ell_-^d N_\Gamma} \frac{e^{\beta I^{-}(\mathrm{int}^{-}(\Gamma))}\, Z^{-}_{\lambda^*}(\mathrm{int}^{-}(\Gamma)|\chi^{-})}{e^{\beta I^{+}(\mathrm{int}^{-}(\Gamma))}\, Z^{+}_{\lambda^*}(\mathrm{int}^{-}(\Gamma)|\chi^{+})}$$

where:

- $I^{\pm}(\mathrm{int}^{-}(\Gamma))$ is a surface term
- $\chi^{\pm}_{\Delta}(r) = \rho_{\beta,\pm} \mathbb{1}_{r\in\Delta}, \quad \chi^{\pm} = \chi^{\pm}_{\mathbb{R}^d}$
- $\exp\Big\{ -\beta c\, \zeta^2 \ell_-^d N_\Gamma \Big\}$ is Peierls' gain term
- $\exp\Big\{ \beta c \gamma^{1/2-2\alpha d} \ell_-^d N_\Gamma \Big\}$ small error

Step three:
Surface correction to the pressure
For any γ small enough and all plus contours Γ:

$$\left| \log \left\{ \frac{e^{\beta I^{\pm}(\mathrm{int}^{-}(\Gamma))} \, Z^{\pm}_{\lambda^*}(\mathrm{int}^{-}(\Gamma)|\chi^{\pm})}{e^{\beta|\mathrm{int}^{-}(\Gamma)|P^{\pm}_{\lambda^*}}} \right\} \right| \leq c' \gamma^{1/2} \ell_{+}^{d} N_{\Gamma}$$

Let x_i be the centers of the cubes $C^{(\ell_-)} \in \mathcal{D}^{(\ell_-)}$.

$$f_{x_1,x_2} = \frac{1}{2!} \sum_{q_{i_1} \in C^{(\ell_-)}_{x_1}, q_{i_2} \in C^{(\ell_-)}_{x_2}} J^{(2)}_{\gamma}(q_{i_1}, q_{i_2})$$

Theorem (Exponential decay of correlations)

There are positive constants δ, c' and c so that for all $f_{x_1,..,x_n}$

$$\Rightarrow \left| E_{\mu^1}\left(f_{x_1,..,x_n}\right) - E_{\mu^2}\left(f_{x_1,..,x_n}\right) \right| \le c' e^{-c[\gamma^{-\delta} \ell_+^{-1} dist(C^{(\ell_-)}_{x_1}, \Lambda^c)]}$$

where μ^1 is the Gibbs measure in the volume Λ with b.c. $\bar{q}$ and μ^2 is the Gibbs measure on a torus $\mathcal{T}$ much larger than Λ, both referring to the hamiltonian $H_{\gamma,R}$.

Eventually take the limit $\mathcal{T} \to \mathbb{R}^d$...

Exponential decay of correlations

To prove exponential decay of correlations we need two ingredients:

1. Cluster expansion
2. Dobrushin condition

Restricted ensembles

A central point in P-S theory is a change of measure.

The diluted partition function in a region Λ can be written as a partition function in $\mathcal{Q}_+^\Lambda = \{q \in \mathcal{Q}_\Lambda : \eta(q,r) = 1, r \in \Lambda\}$ (*restricted ensemble*).

Let us consider Λ bounded and $\mathcal{D}^{(\ell_+)}$ measurable and $\bar{q}$ + b.c.

$$Z^+_{\gamma,R,\lambda}(\Lambda|\bar{q}) = \sum_{\underline{\Gamma}:\mathrm{sp}(\Gamma)\subset\Lambda} \int_{\mathcal{Q}_+^\Lambda} \nu^\Lambda(dq) e^{-\beta H_{\gamma,R}(q|\bar{q})} \prod_{\Gamma\in\underline{\Gamma}} W^+_{\gamma,R,\lambda}(\Gamma, q)$$

Coarse graining

Coarse graining: fix the number of particles in each cube $C^{(\ell_-)}$
$\rightarrow$ density configuration $\rho = \{\rho_x\}_{x \in X_\Lambda^{(\ell_-)}}$. Hence:

$$Z^+_{\gamma,R,\lambda}(\Lambda|\bar{q}) = \sum_{\rho} e^{-h(\rho|\bar{q})}$$

where h is finite volume **effective hamiltonian** (function only of the cell variables).
... cluster expansion to find h, multi-canonical constraint ...

Cluster expansion

Why it works:

- **Kac**: Because we can confuse H_γ with its coarse grained version $H_\gamma^{(\ell-)}$ making a small error ΔH_γ, $\Rightarrow e^{-\beta \Delta H_\gamma}$ is ok for cl. exp.!
- **Hard core**: ... "Cluster expansion in the canonical ensemble" (E. P., D. Tsagkarogiannis) Commun. Math. Phys. (2012)

Cluster expansion in the canonical ensemble

Model with *stable* and *tempered* pair potential:

Theorem

$\exists c_0$, indep. of N and Λ, s.t. if $\rho C(\beta) < c_0$:

$$\frac{1}{|\Lambda|} \log Z_{\beta,\Lambda,N} = \frac{1}{|\Lambda|} \log \frac{|\Lambda|^N}{N!} + \frac{N}{|\Lambda|} \sum_{n \geq 1} F_{\beta,\Lambda,N}(n)$$

with $N = \lfloor \rho |\Lambda| \rfloor$ and $|F_{\beta,\Lambda,N}(n)| \leq C e^{-cn}$.

Furthermore in the thermodynamic limit:

$$\lim_{N,|\Lambda| \to \infty,\, N = \lfloor \rho |\Lambda| \rfloor} F_{\beta,N,\Lambda}(n) = \frac{1}{n+1} \beta_n \rho^{n+1}, \qquad \forall n \geq 1$$

where β_n are the Mayer's coefficients.

Remark: $C(\beta)$ is equal to the volume of hard spheres ϵ.

Dobrushin condition

Weak dependence on the boundaries $\rightarrow$ decay of correlations
Space for spin block model:

$$\mathcal{X}^{\Lambda} = \Big\{ \underline{n} = (n_x)_{x \in X_\Lambda} \in \mathbb{N}^{X_\Lambda} : |\ell_-^{-d} n_x - \rho_{\beta,R,+}| \le \zeta, \text{ for all } x \in X_\Lambda \Big\}$$

p^1, p^2 conditional Gibbs measures on $\mathcal{X}^x$:

$$p^i(n_x) := p(n_x | \rho^i, \bar{q}^i) = \frac{1}{Z_x(\rho^i, \bar{q}^i)} \exp\big\{ -h(\rho_x | \rho^i, \bar{q}^i) \big\} \qquad i = 1, 2$$

Vaserstein distance is

$$R\Big(p^1(\cdot), p^2(\cdot)\Big) := \inf_Q \sum_{n_x^1, n_x^2} Q(n_x^1, n_x^2) d(n_x^1, n_x^2)$$

where Q are joint representations of p^1 and p^2

Dobrushin condition

Theorem

There are $u, c_1, c_2 > 0$ *s.t.* $\forall x \in \Lambda$

$$R\Big(p^1(\cdot), p^2(\cdot)\Big) \le \sum_{z \in X_\Lambda, z \neq x} r_{\gamma,R}(x,z) d(n_z^1, n_z^2) + \sum_{z \in X_{\Lambda^c}} r_{\gamma,R}(x,z) D_z(\bar{q}^1, \bar{q}^2)$$

with

$$\sum_z r_{\gamma,R}(x,z) \le u < 1$$

$$r_{\gamma,R}(x,z) \le c_1 e^{-c_2 \gamma |z-x|}, \quad |z-x| \ge \ell_+$$

Then: "local bounds can be made global"
if μ^1, μ^2 Gibbs measures on $\mathcal{X}^\Lambda$, there exists a joint repr. $\mathcal{P}(\underline{n}^1, \underline{n}^2 | \bar{q}^1, \bar{q}^2)$ s.t.

$$\mathcal{E}\big[(d(n_x^1, n_x^2)\big] := \sum_{\underline{n}^1, \underline{n}^2} d(n_x^1, n_x^2) \mathcal{P}(\underline{n}^1, \underline{n}^2)$$
$$\le c \exp\Big\{ - c' \gamma^{-\delta} \ell_+^{-1} \mathsf{dist}(x, \Lambda^c) \Big\}$$

Conclusions and open problems

- **Phase transitions in the canonical ensemble**
- **Cluster expansion in the canonical ensemble**
  - compute correlations (work in progress...)
  - get a better radius of convergence
  - finite volume corrections to the free energy (work in progress...)
- **Quantum models**
  - Cluster expansion (Ginibre)
  - Phase transitions for systems of bosons (Kuna-Merola-Presutti, for quantum gas with Boltzmann statistics)