Phase transitions, multi-scale Kac potentials and pattern formation.

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Phase transitions. (Restrict to first order phase transitions with order parameter the mass density)

There is a "forbidden" interval $[\rho', \rho'']$ of density values, namely:

If we put $\rho|\Lambda|$ particles in a region Λ, $\rho \in (\rho', \rho'')$, ("canonical constraint") the state segregates and we see ρ' in a set $\Lambda' \subset \Lambda$ and ρ'' in the complement.

Multi-scale potentials: we shall see examples where the long scale potential acts as a canonical constraint by fixing a local density. If this is "forbidden" by the shorter scale potential we have "local segregation" with the emergence of spatial patterns.

Contents.

Introduction. Zero temperature

Point particles in $\mathbb{R}^2$ with Lennard-Jones interactions

$$V(r) = ar^{-12} - br^{-6}, \quad a, b > 0$$

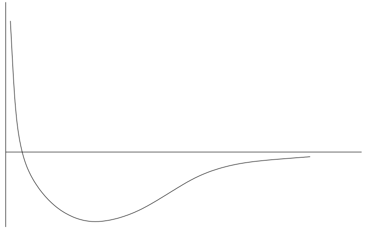

Figure: Lennard-Jones potential

Zero temperature equilibrium states at density ρ: configurations with density ρ which minimize the energy. $e(\rho)$ the minimal energy density.

If we restrict to triangular lattice configurations:

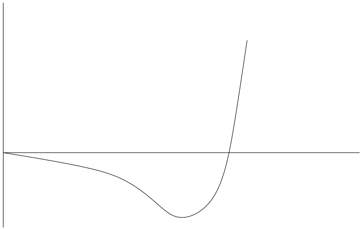

Figure: graph of $e_T(\rho)$, the energy on triangular lattice configurations

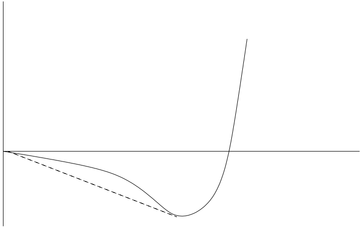

Figure: $e(\rho)$ convex envelope of $e_T(\rho)$, straight in $[0, \rho_c]$

The straight segment is: $e(\rho) = e_T(\rho_c)\dfrac{\rho}{\rho_c}$, $\rho \in (0, \rho_c)$.
Clearly $e(\rho) < e_T(\rho)$ in $(0, \rho_c)$.
$e(\rho)$ is the energy density of a configuration with density ρ made of a triangular configuration with density ρ_c on a fraction $\dfrac{\rho}{\rho_c}$ of the volume and no particles in the complement (the void phase).

By construction $e(\rho) = e_T(\rho_c)\dfrac{\rho}{\rho_c}$ and $e_T(\rho)$ have same slope at ρ_c, then

$$\frac{e_T(\rho_c)}{\rho_c} = e'_T(\rho_c) \quad \Rightarrow \quad \rho_c \;\; \text{minimizes} \;\; \frac{e_T(\rho)}{\rho}$$

F. Theil: rigorous proof that the minimimun of $e(\rho)/\rho$ is attained at ρ_c and realized by a triangular lattice configuration.

Phase segregation and Wulff shape for $\rho < \rho_c$

Positive temperatures, Gibbs measures.

Postulate: equilibrium states are described by Gibbs measures.

Put N particles in a box Λ, then the Gibbs probability of a configuration $\underline{x} = (q_1, .., q_N)$ is

$$\mu(d\underline{x}) = \frac{1}{Z}\{\frac{1}{N!}\, e^{-\beta H(\underline{x})} d\underline{x}\}, \quad \beta = \frac{1}{kT}$$

If $T \to 0$ μ gets supported by ground state configurations.

Conjecture: There is (ρ', ρ'') so that if T is small enough and $N/|\Lambda| \in (\rho', \rho'')$ then the "typical configurations" have density ρ' in $\Lambda' \subset \Lambda$ and ρ'' in the complement.
$(\rho', \rho'') \to (0, \rho_c)$ as $T \to 0$.

Conjecture is proved in the lattice: $\underline{x} \in \{0, 1\}^{\Lambda}$, $\Lambda \subset \mathbb{Z}^d$.

Boltzmann entropy.

Probability density of having energy dE is

$$\frac{1}{Z}\, e^{-\beta E} N(E) dE$$

$N(E)dE$ the phase space volume of configurations with energy dE.
Boltzmann hypothesis identifies entropy: $S(E) = k \log N(E)$,

$$\frac{1}{Z}\, e^{-\beta \left(E - TS(E)\right)} dE$$

Derivation of thermodynamics from statistical mechanics.

$S(E)$ is difficult to handle, (geometry of phase space).

Mean field and van der Waals theory. (Large T, liquid-vapour phases)

Mean field: energy is a function of the particles density.

Van der Waals theory is based on two assumptions:

- $\dfrac{E(\rho)}{|\Lambda|} = -J\rho^2$, $J > 0$, (attractive tail of interaction)
- $S(\rho) = k \log \left\{ \dfrac{1}{N!} |\Lambda - Na|^N \right\}$,

$\rho = \frac{N}{|\Lambda|}$, $a =$ volume occupied by a particle.

Local mean field and Kac potentials.

Local mean field: local energy density $e(\cdot)$ is a function of local particles density $\rho_\gamma(r;\underline{x})$.

- $\rho_\gamma(r;\underline{x}) := \sum_{q_i \in \underline{x}} J_\gamma(q_i - r)$, $J_\gamma(r) = \gamma^d J(\gamma r)$.

$J(r)dr =$ probability density (smooth, compact support).
$\gamma > 0$ Kac scaling parameter

- $H(\underline{x}) = \int_{\mathbb{R}^d} e\big(\rho_\gamma(r;\underline{x})\big)\, dr$

The Kac model.

The Kac energy density is

$$e(\rho) = -\frac{\rho^2}{2}$$

To avoid collapse of matter ($\rho \to \infty$) Kac imposes the hard-core constraint

$$\underline{x} = (q_1, .., q_N)\colon\ |q_i - q_j| \geq R > 0$$

Hard cores (necessary to avoid collapse of matter) make hard the analysis of phase space volumes at large densities.

and phase transitions are only proved after taking $\gamma \to 0$.

The LMP models.

To prove phase transitions at fixed $\gamma > 0$ LMP (Lebowitz, Mazel, Presutti) drop the hard-core constraint and to ensure stability of matter modify the energy density as:

$$e(\rho) = -\frac{\rho^2}{2} + \frac{\rho^4}{4!}$$

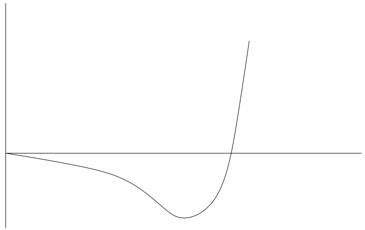

Figure: $e(\rho)$ similar to L-J energy on triangular lattices

Theorem. (Phase transitions for the LMP model)
There are $\beta_c > 0$, $\beta^* > \beta_c$ and for $\beta \in (\beta_c, \beta^*)$ the following holds. For any γ small enough there is a "forbidden interval" $(\rho'_{\beta,\gamma}, \rho''_{\beta,\gamma})$, namely:

for any $\rho \in (\rho'_{\beta,\gamma}, \rho''_{\beta,\gamma})$ the typical confgurations of the Gibbs measure in a large region Λ with periodic boundary conditons and $N = \rho|\Lambda|$ particles have densities $\rho'_{\beta,\gamma}$ and $\rho''_{\beta,\gamma}$ respectively in $\Lambda' \subset \Lambda$ and its complement (approximately, but sharp in the limit $|\Lambda| \to \infty$).

Proof by coarse-graining:

Free energy functionals.

Probability of a density profile $\rho(r)$, $r \in \gamma\Lambda$,

$$Z^{-1} \exp\Big\{ -\gamma^{-d}\beta F_\gamma(\rho)\Big\} d\rho$$

where F_γ is approximately

$$\int \Big(e(J * \rho(r)) - \beta^{-1} s(\rho(r))\Big) dr$$

$$s(\rho) = -\rho(\log\rho - 1)$$

For small γ the Gibbs measure concentrates on a neighborhood of the minimizers of F. Proof based on bounds on the cost of deviations from minimizers.

Drawbacks.

The basic assumption that
"the energy density depends only on the local particles density"
is not reasonable when ρ is large, (the phase space volume of neighborhoods of ground states configurations is far from being equal to $s(\rho) = -\rho(\log \rho - 1)$).

Kac + LMP.
Add to LMP the hard core condition $|q_i - q_j| \geq R > 0$.
The new free energy functional has the entropy term $s(\rho)$ replaced by the entropy density of hard core configurations.

Work in progress: if R is "small" then LMP phase transition persists.

The hard spheres gas.

The only interaction is the hard core condition: $|q_i - q_j| \geq R > 0$. If ρR^d is small the entropy is close to $s(\rho)$, Mayer virial expansion.

Numerical evidence shows that in $d = 3$ the free energy density $f_{hc}(\rho)$ is flat in a interval (ρ_1, ρ_2) (which scales as R^{-d}).

Then the free energy functional of Kac+LMP looks like (after coarse graining on the scale γ^{-1})

$$F(\rho(\cdot)) := \int \Big(e(J * \rho(r)) + f_{hc}(\rho(r)) \Big) dr$$

Spatial patterns

• If R is small enough, the graph of F is flat in (ρ', ρ'') (the LMP phase transition)

• and it is strictly convex in (ρ_1, ρ_2) (the hard-sphere forbidden interval).

• If $\rho \in (\rho_1, \rho_2)$ the local density (on a small scale) is either ρ_1 or ρ_2 hence a pattern formation

Too far for a mathematical analysis !!!

Simplified models.

Hamiltonian is sum of two energies with different scales:

• short scale potential has a phase transition with forbidden interval (ρ_1, ρ_2) (as the hard sphere gas)

• large scale potential is convex in (ρ_1, ρ_2)

LMP only known model which fulfills first request. Possible hamiltonian: ($e(\cdot) =$ LMP energy)

$$H(\underline{x}) = \int e(\rho_\gamma(r;\underline{x})) + \int \Big(\rho_{\gamma^2}(r;\underline{x}) - \lambda\Big)^2$$

$\lambda \in \mathbb{R}$ a parameter (chemical potential)

$$\rho_\delta(r;\underline{x}) = \delta^d \sum_{q_i \in \underline{x}} J(\delta(q_i - r))$$

Free energy functionals with competing interactions.

Many works on free energy functionals of the form

$$F(\rho) = f(\rho) + \int \Big(J_\gamma * \rho - \lambda \Big)^2$$

with $f(\rho)$ (for instance the Ginzburg-Landau functional) having a phase transition in (ρ', ρ'').

Micromagnetism, Coulomb interactions, ground states in lattice systems.

...... A. De Simone, R. V. Kohn, F. Otto, S. Müller, G. Alberti, A. Giuliani, J. L. Lebowitz, E. H. Lieb.....

The analysis does not extend (as far as I know) to particle systems.