The Thermodynamic Limit of Quantum Coulomb Systems: a New Approach

Mathieu LEWIN

Mathieu.Lewin@math.cnrs.fr

(CNRS & University of Cergy-Pontoise)

Joint work with C. Hainzl (Birmingham, USA)
& J.P. Solovej (Copenhagen, Denmark)

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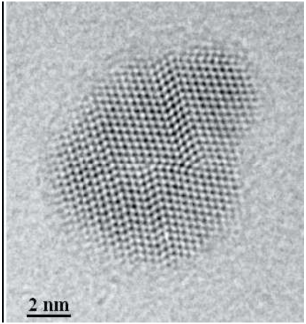
Coulomb forces

Goal: describe macroscopic systems using Quantum Mechanics.



Picture of CdSe Crystal (CEA-SP2M-NPSC)

Ordinary matter is composed of electrons and nuclei interacting via Coulomb forces.

The Coulomb potential between two charges z and z' located at $x, x' \in \mathbb{R}^3$ is

$$\frac{zz'}{4\pi\epsilon_0|x - x'|}.$$

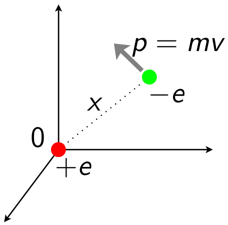
Two different issues related to stability:

- the singularity at 0 of $1/|x|$;
- the "slow" decay at infinity of $1/|x|$.

Stability of the first kind

Singularity at zero of $1/|x|$: need to explain why a particle does not rush to a particle of the opposite sign.

Example: Hydrogen atom. • *Classical* energy of the electron at $x \in \mathbb{R}^3$ with momentum $p \in \mathbb{R}^3$:



$$E(x,p) = \frac{|p|^2}{2m} - \frac{e^2}{4\pi\epsilon_0|x|} = \frac{|p|^2}{2} - \frac{1}{|x|}.$$

Atomic units: $m = e = 1/(4\pi\epsilon_0) = 1.$

Instability: $\inf_{(x,p)\in\mathbb{R}^3\times\mathbb{R}^3} E(x,p) = -\infty.$

• *Quantum mechanics:* Kato's inequality $= \forall\epsilon > 0,\quad \dfrac{1}{|x|} \leq \epsilon(-\Delta) + \dfrac{C}{\epsilon}$

$$\Longrightarrow \text{stability of the first kind: } -\frac{\Delta}{2} - \frac{1}{|x|} \geq -C$$

Macroscopic behavior

• **Slow decay of $1/|x|$ at infinity:** explain how a very large number of particles can stay bounded together to form macroscopic systems, although each particle interacts with many other charged particles.

Let $E(N)$ be the ground state energy of a system (to be defined) of N quantum particles, interacting via Coulomb forces.

$$\text{Stability of the first kind: } E(N) > -\infty.$$

Goal: prove the following physical macroscopic behavior:

$$E(N) \sim_{N\to\infty} CN.$$

Rmk. If $E(N) \sim CN^p$ with $p \neq 1$, then $|E(2N) - 2E(N)|$ can be very big as $N \gg 1$: a very large amount of energy will be necessary (or released) to put two identical systems together.
Occupied volume is usually proportional to $N \Longrightarrow$ this is the same as

$$E(\Omega) \sim_{|\Omega|\to\infty} C|\Omega|$$

where $E(\Omega) =$ ground state energy of the system in the domain Ω.

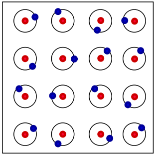
Screening

• Consider classical identical particles on the lattice $\mathbb{Z}^3$, interacting via the potential $1/|x|^p$, $p < 3$.

$$E(L) = \sum_{x,y\in\mathbb{Z}^3\cap(-L/2;L/2]^3} \frac{1}{|x-y|^p} \sim CL^{6-p} = CN^{5/3} \text{ if } p = 1.$$

For Coulomb, a thermodynamic limit will exist only when particles have different charges ! $\rightarrow$ **screening**

• Nuclei (charge 1) on $\mathbb{Z}^3$. An electron (charge -1) at a fixed distance δ of each nucleus. They interact through the Coulomb potential.



Let $E(L)$ be the ground state energy (optimize the position of the electrons) in a box of size L. It can be proved that $E(L) \sim CL^3$.

$\rightarrow$ In quantum mechanics, screening is a subtle effect because particles are delocalized.

Historical overview

- **Ruelle** (HPA '63) and **Fisher** (ARMA '64) first raised the question of stability of matter (=of the second kind) for quantum systems: $E(\Omega) \geq -C|\Omega|$ or $E(N) \geq -CN$. Proof for short-range potentials.
Dyson-Lenard (JMP '66): proof for Coulomb.
Lieb-Thirring (PRL '75): new proof based on a functional inequality.
- **Dyson** (JMP '67): bosonic matter is unstable. Proof by **Conlon, Lieb, Yau, Solovej** (CMP '88, '04 & '06).
- **Lieb-Lebowitz** (Adv. Math. '72): proof that $E(\Omega_n) \sim \bar{e}|\Omega_n|$ for 'regular' sequences $|\Omega_n| \to \infty$. System composed of quantum electrons and quantum nuclei. Important use of the invariance by rotation.
- **Lieb-Simon** (Adv. Math. '77), **Catto-Le Bris-Lions** (AHP '98) Study of the thermo. limit of the crystal for approximate models (TF, HF).
- **Fefferman** (CMP '85) : proof that $E(\Omega_n) \sim \bar{e}|\Omega_n|$ for the many-body Schrödinger model of the crystal.
- **Graf-Schenker** (CMP '95): an electrostatic inequality inspired by **Conlon-Lieb-Yau** (CMP '89) = starting point of our new approach.

The quantum crystal

For simplicity, we put identical nuclei of charge $+1$ on each site of $\mathbb{Z}^3$.
Let Ω be a bounded open set of $\mathbb{R}^3$ and define:

$$H_\Omega^N := \sum_{i=1}^N -\frac{\Delta_{x_i}}{2} + V_\Omega(x_1, ..., x_N),$$

$$V_\Omega(x) = \sum_{i=1}^N \sum_{R\in\mathbb{Z}^3\cap\Omega} \frac{-1}{|R-x_i|} + \frac{1}{2}\sum_{1\leq i\neq j\leq N} \frac{1}{|x_i-x_j|} + \frac{1}{2}\sum_{R\neq R'\in\mathbb{Z}^3\cap\Omega} \frac{1}{|R-R'|}.$$

$-\Delta=$**Dirichlet Laplacian on** Ω. H_Ω^N acts on N-body fermionic wavefunctions $\Psi(x_1, .., x_N) \in \bigwedge_1^N L^2(\Omega)$.

Stability of the first kind:

$$E_\Omega^N = \inf\left\{\left\langle \Psi, H_\Omega^N \Psi\right\rangle,\ \Psi\in\bigwedge_1^N H_0^1(\Omega),\ \|\Psi\|_{L^2}=1\right\} > -\infty.$$

Define: $\boxed{E(\Omega) := \inf_{N\geq 0} E_\Omega^N = \inf_{N\geq 0} \inf \sigma_{\bigwedge_1^N L^2(\Omega)}(H_\Omega^N).}$

Grand canonical formalism

Fock space:

$$\mathcal{F}_\Omega := \mathbb{C} \oplus \bigoplus_{N\geq 1} \bigwedge_1^N L^2(\Omega), \qquad H_\Omega := \bigoplus_{N\geq 0} H_\Omega^N \quad \text{and} \quad \mathcal{N} := \bigoplus_{N\geq 0} N.$$

$$\Longrightarrow \qquad E(\Omega) = \inf \sigma(H_\Omega) = \inf_{\substack{\Gamma\in\mathcal{B}(\mathcal{F}_\Omega),\ \Gamma^*=\Gamma,\\ 0\leq\Gamma\leq 1,\ \mathrm{tr}_{\mathcal{F}_\Omega}(\Gamma)=1.}} \mathrm{tr}_{\mathcal{F}_\Omega}\left(H_\Omega\Gamma\right).$$

Free Energy at temperature $T = 1/\beta$ and chemical potential $\mu \in \mathbb{R}$:

$$\begin{aligned} F(\Omega,\beta,\mu) &:= \inf_{\substack{\Gamma\in\mathcal{B}(\mathcal{F}_\Omega),\ \Gamma^*=\Gamma,\\ 0\leq\Gamma\leq 1,\ \mathrm{tr}_{\mathcal{F}_\Omega}(\Gamma)=1.}} \left(\mathrm{tr}_{\mathcal{F}_\Omega}((H_\Omega - \mu\mathcal{N})\Gamma) + \frac{1}{\beta}\mathrm{tr}_{\mathcal{F}_\Omega}(\Gamma\log\Gamma)\right). \\ &= -\frac{1}{\beta}\log \mathrm{tr}_{\mathcal{F}_\Omega}\left[e^{-\beta(H_\Omega-\mu\mathcal{N})}\right]. \end{aligned}$$

We shall mainly consider the energy for simplicity.

Stability of matter

Theorem (Stability of Matter)

There exists a constant C such that the following holds:

$$E(\Omega) \geq -C|\Omega|, \qquad F(\Omega,\beta,\mu) \geq -C\left(1+\beta^{-5/2}+\mu_+^{5/2}\right)|\Omega|$$

for any bounded open set $\Omega \subset \mathbb{R}^3$ and any $\beta > 0$, $\mu \in \mathbb{R}$.

A proof (energy): 1) Inequality of Baxter (1980) / Lieb-Yau (1988):

$$V(x_1, ..., x_N) \geq -\sum_{i=1}^N \frac{3/2+\sqrt{2}}{\delta(x_i)}$$

where $\delta(x) = \inf_{R\in\mathbb{Z}^3} |x-R|$ is the distance to the closest nucleus. Hence:

$$H^N_\Omega \geq \sum_{i=1}^N \left(-\frac{\Delta_{x_i}}{2} - \frac{c}{\delta(x_i)}\right)$$

Stability of matter

2) Stability of the first kind (Sobolev inequality):

$$-\frac{\Delta}{4} - \frac{c}{\delta(x)} \geq C, \qquad \text{even on } L^2(\mathbb{R}^3).$$

3) Lieb-Thirring inequality for a fermionic wavefunction $\Psi \in \bigwedge_1^N L^2(\Omega)$:

$$\left\langle \left(\sum_{i=1}^N -\frac{\Delta_{x_i}}{4} \right) \Psi, \Psi \right\rangle \geq C \int_\Omega \rho_\Psi^{5/3} \geq C \left(\int_\Omega 1 \right)^{-2/3} \left(\int_\Omega \rho_\Psi \right)^{5/3}$$
$$= C|\Omega|^{-2/3} N^{5/3}.$$

Here $\rho_\Psi \in L^1(\Omega)$ is the density of charge which satisfies $\int_\Omega \rho_\Psi = N$:

$$\rho_\Psi(x) = N \int_{\Omega^{3(N-1)}} dx' |\Psi(x, x')|^2 dx'.$$

4) Conclusion:

$$H_\Omega^N \geq C|\Omega|^{-2/3} N^{5/3} - CN \geq C'|\Omega|.$$

Regular domains

Definition (Regular domains)

Let be $a > 0$ and $\epsilon > 0$.

1) We say that a bounded open set $\Omega \subseteq \mathbb{R}^3$ has *an a-regular boundary in the sense of Fisher* if

$$\forall t \leq 1, \qquad \left|\left\{x \in \mathbb{R}^3 \mid \mathrm{d}(x, \partial\Omega) \leq |\Omega|^{1/3} t\right\}\right| \leq |\Omega|\, a|t|,$$

where $\partial\Omega = \overline{\Omega} \setminus \Omega$ is the boundary of Ω.

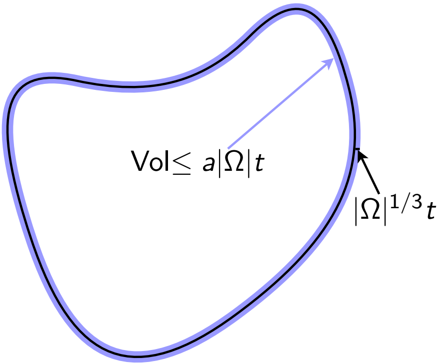
2) We say that a bounded open set $\Omega \subseteq \mathbb{R}^3$ satisfies the *ε-cone property* if for any $x \in \Omega$ there is a unit vector $a_x \in \mathbb{R}^3$ such that

$$\{y \in \mathbb{R}^3 \mid (x - y) \cdot a_x > (1 - \varepsilon^2)|x - y|,\ |x - y| < \varepsilon\} \subseteq \Omega.$$

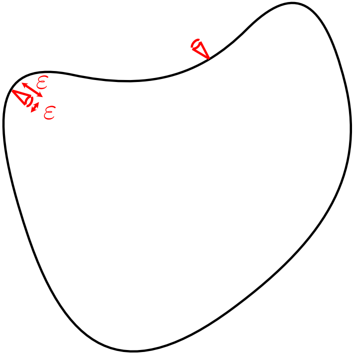
We denote by $\mathcal{R}_{a,\varepsilon}$ the set of all $\Omega \subseteq \mathbb{R}^3$ which have an a-regular boundary and such that both Ω and $\mathbb{R}^3 \setminus \Omega$ satisfy the ε-cone property.

Rmk. any open convex set is in $\mathcal{R}_{a,\varepsilon}$ for some $a > 0$ large enough and $\varepsilon > 0$ small enough.

Regular domains



Regular boundary



Cone property

The thermodynamic limit

Theorem (Existence of the Thermodynamic Limit for the Crystal)

There exist $\bar{e} \in \mathbb{R}$ *and a function* $\bar{f} : (0, \infty) \times \mathbb{R} \to \mathbb{R}$ *such that the following holds: for any sequence* $\{\Omega_n\}_{n\geq 1} \subseteq \mathcal{R}_{a,\epsilon}$ *of connected domains with* $|\Omega_n| \to \infty$, $a \geq a_0 > 0$ *and* $0 < \varepsilon \leq \varepsilon_0$,

$$\lim_{n\to\infty} \frac{E(\Omega_n)}{|\Omega_n|} = \bar{e}, \qquad \lim_{n\to\infty} \frac{F(\Omega_n, \beta, \mu)}{|\Omega_n|} = \bar{f}(\beta, \mu). \tag{1}$$

By definition $p(\beta, \mu) = -\beta \bar{f}(\beta, \mu)$ is the pressure.

Remarks. a) The same theorem was proved by Fefferman (CMP '85) assuming $\Omega_n = \ell_n(\Omega + x_n)$ with $\{x_n\} \subseteq \mathbb{R}^3$ and $\ell_n \to \infty$, Ω being a fixed convex set with a non-empty interior.

b) One can perturb a bit the crystal and obtain the same limit.

c) A similar result can be proved in the Hartree-Fock approximation.

Other models

Our proof is general and can be applied to other models.

- **Quantum nuclei and electrons in a periodic magnetic field.**

$T(A) = (-i\nabla + A(x))^2$ where $B = \nabla \times A$ is periodic and $A \in L^2_{\rm loc}(\mathbb{R}^3)$.

$$H_\Omega^{N,K} := \sum_{i=1}^N T(A)_{x_i} + \sum_{k=1}^K T(A)_{R_k} + V(x,R)$$

$$V(x,R) = \sum_{i,k} \frac{-1}{|R_k - x_i|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|x_i - x_j|} + \frac{1}{2}\sum_{k\neq k'} \frac{1}{|R_k - R_{k'}|}$$

$$E(\Omega) := \inf_{N,K\geq 0} \inf \sigma_{\bigotimes_1^K L^2(\Omega)\otimes \bigwedge_1^N L^2(\Omega)} \left(H_\Omega^{N,K}\right).$$

Lieb-Lebowitz '72 when $A \equiv 0$ (rotation-inv. used to obtain screening).

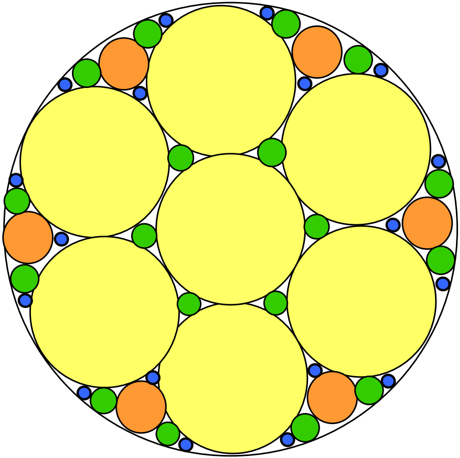
- **Classical nuclei with optimized position.** $\forall R \subset \Omega$, $\# R < \infty$, define

$$H_\Omega^{N,R} := \sum_{i=1}^N -\frac{\Delta_{x_i}}{2} + V(x,R)$$

$$E(\Omega) := \inf_{N\geq 0} \inf_{\substack{R\subset\Omega,\\ \#R<\infty}} \inf \sigma_{\bigwedge_1^N L^2(\mathbb{R}^3)} \left(H_\Omega^{N,R}\right).$$

The Lieb-Lebowitz proof

Idea: pack a big ball with small balls (swiss cheese).



- Put the neutral ground state in each little ball.
- Average over rotations of states in each little ball to find one such that the interaction between all the subsystems cancel.

$\Rightarrow E(B) \leq \sum_i E(B_i)$.

- This is used to prove the existence of the limit for balls in the neutral case.

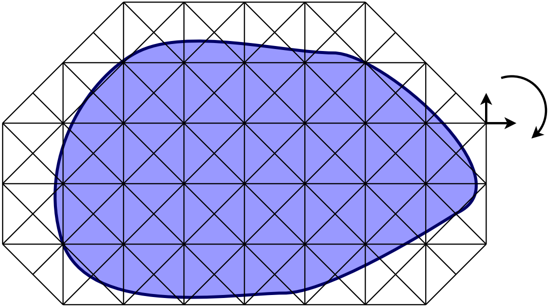
$\rightarrow$ fixed decomposition of the big domain into small pieces.
Average over states in the little balls (only rotation-invariant model !).

The Graf-Schenker inequality

A tiling of simplices instead of packing by balls. Based on ideas of Conlon, Lieb and Yau (CMP '89).

$\rightarrow$ fixed state in the big domain.

Average over the different decompositions in small domains.



$\Rightarrow$ an inequality of the form $E(\Omega) \geq \sum_i E(\triangle_i) + \text{errors}$.

$\rightarrow$ First prove the existence of the thermodynamic limit for simplices.

The Graf-Schenker inequality

Let $G = \mathbb{R}^3 \rtimes SO_3(\mathbb{R})$ be the group of translations and rotations acting on $\mathbb{R}^3$, and denote by $d\lambda(g)$ its Haar measure.

Theorem (Graf-Schenker - CMP '95)

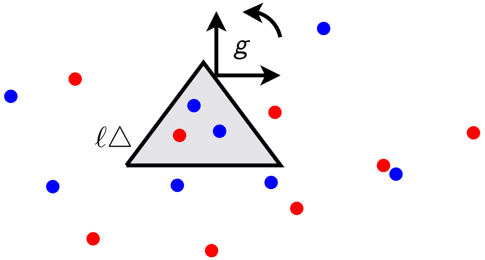
Let $\triangle$ be a simplex in $\mathbb{R}^3$. There exists a constant C such that for any $N \in \mathbb{N}$, $z_1, ..., z_N \in \mathbb{R}$, $x_i \in \mathbb{R}^3$ and any $\ell > 0$,

$$\sum_{1\leq i<j\leq N} \frac{z_i z_j}{|x_i - x_j|} \geq \frac{1}{|\ell\triangle|} \int_G d\lambda(g) \sum_{1\leq i<j\leq N} \frac{z_i z_j \mathbb{1}_{g\ell\triangle}(x_i) \mathbb{1}_{g\ell\triangle}(x_j)}{|x_i - x_j|} - \frac{C}{\ell} \sum_{i=1}^N z_i^2.$$

Remark. Similar result proved for the Yukawa potential and cubes by Conlon, Lieb and Yau (CMP '89). But only translations were considered ($G = \mathbb{R}^3$).

The Graf-Schenker inequality

$$\sum_{1\leq i<j\leq N} \frac{z_iz_j}{|x_i-x_j|} \geq \frac{1}{|\ell\triangle|}\int_G d\lambda(g) \sum_{1\leq i<j\leq N} \frac{z_iz_j\mathbb{1}_{g\ell\triangle}(x_i)\mathbb{1}_{g\ell\triangle}(x_j)}{|x_i-x_j|} - \frac{C}{\ell}\sum_{i=1}^N z_i^2.$$



Rmk. (i) The inequality can be used to prove stability of matter (Graf, HPA '96).

(ii) Generalizations ? As such, only seems to hold for Coulomb, with simplices and in 3D.

Hints on the Graf-Schenker inequality

Proof. 1) If $\widehat{f} \geq 0$, then $\sum_{k\neq\ell=1}^N z_k z_\ell f(x_k - x_\ell) + f(0)\sum_{k=1}^N z_k^2 \geq 0$.

2) The idea is to show that $\widehat{f} \geq 0$ with

$$f(x-y) = \frac{1}{|x-y|} - \frac{1}{|\ell\triangle|}\int_G d\lambda(g)\frac{\mathbb{1}_{g\ell\triangle}(x)\mathbb{1}_{g\ell\triangle}(y)}{|x-y|} := \frac{1-h(|x-y|)}{|x-y|}$$

and

$$h(|x-y|) = \int_G d\lambda(g)\frac{\mathbb{1}_{g\ell\triangle}(x)\mathbb{1}_{g\ell\triangle}(y)}{|\ell\triangle|} = \int_{SO_3} du\frac{|\ell\triangle \cap (\ell\triangle - u(x-y))|}{|\ell\triangle|}.$$

Notice $h(0) = 1$. Graf and Schenker proved that $h \in C^2([0,\infty))$ (in particular $f(0)$ is well-defined) and that $\widehat{f} \geq 0$ by an explicit computation.

General framework

Let $\mathcal{M} = \{\Omega \subset \mathbb{R}^3 \text{ open and bounded}\}$ and consider $E : \mathcal{M} \to \mathbb{R}$. Assume $\exists \triangle \in \mathcal{R}_{a,\epsilon}$, α with $\lim_{\ell\to\infty} \alpha(\ell) = 0$ and κ, δ such that

(A1) *(Normalization).* $E(\emptyset) = 0$.

(A2) *(Stability).* $\forall \Omega \in \mathcal{M}$, $E(\Omega) \geq -\kappa|\Omega|$.

(A3) *(Translation Invariance).* $\forall \Omega \in \mathcal{R}_{a,\epsilon}$, $\forall z \in \mathbb{Z}^3$, $E(\Omega + z) = E(\Omega)$.

(A4) *(Continuity).* $\forall \Omega \in \mathcal{R}_{a,\epsilon}$, $\forall \Omega' \in \mathcal{R}_{a',\epsilon'}$ with $\Omega' \subseteq \Omega$ and $\mathrm{d}(\partial\Omega, \partial\Omega') > \delta$,

$$E(\Omega) \leq E(\Omega') + \kappa|\Omega \setminus \Omega'| + |\Omega|\alpha(|\Omega|).$$

(A5) *(Subaverage Property).* For all $\Omega \in \mathcal{M}$, we have

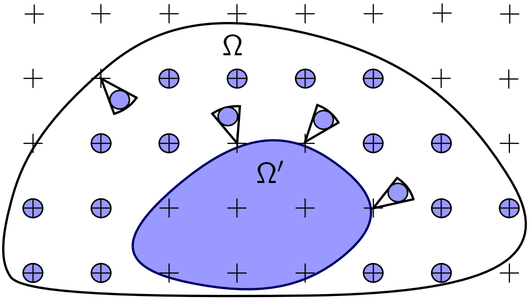
$$E(\Omega) \geq \frac{1}{|\ell\triangle|} \int_G E\big(\Omega \cap g \cdot (\ell\triangle)\big)\, d\lambda(g) - |\Omega|_{\mathrm{r}}\, \alpha(\ell) \qquad (2)$$

where $|\Omega|_{\mathrm{r}} := \inf\{|\tilde{\Omega}|, \quad \Omega \subseteq \tilde{\Omega}, \quad \tilde{\Omega} \in \mathcal{R}_{a,\epsilon}\}$ = regularized volume of Ω.

Proof of (A1)–(A5) for the crystal

- **(A1)** and **(A3)** are obvious. **(A2)** is stability of matter.
- **(A5)** is the Graf-Schenker inequality + localization of the kinetic energy.
- **(A4)** $\Omega' \subset \Omega$ regular sets $\Rightarrow E(\Omega) \leq E(\Omega') + \kappa|\Omega \setminus \Omega'| + o(|\Omega|)$.

Dipole argument:



Need to show that the interaction between the dipoles and the ground state in Ω' is $o(|\Omega|)$.

Thermodynamic limit for the reference set $\triangle$

Assumption **(A3)** can be replaced by a much weaker one.

Theorem (In preparation)

Assume $E : \mathcal{M} \to \mathbb{R}$ satisfies the above properties **(A1)–(A5)** *for some convex set $\triangle \in \mathcal{R}_{a,\epsilon}$ with $0 \in \triangle$. There exists $\bar{e} \in \mathbb{R}$ such that $e_\ell(g) = |\ell\triangle|^{-1} E\big(g\ell\triangle\big)$ converges uniformly towards $\bar{e}$ for $g \in G = \mathbb{R}^3 \rtimes SO(3)$ and as $\ell \to \infty$.*
Additionally, the limit $\bar{e}$ does not depend on the set $\triangle$.

Idea of the proof. a) By **(A1)**, **(A2)** and **(A4)**, e_ℓ is unif. bounded on G.

b) **(A5)**, **(A2)** and **(A3)** can be used to prove that

$$\forall g' \in G, \quad e_L(g') \geq \int_{g \in SO3 \times [0,1]^3} e_\ell(g) d\lambda(g) - C\ell/L - \alpha(L^3).$$

c) $\inf_G e_\ell$ and $\int_{g \in SO3 \times [0,1]^3} e_\ell$ have the same limit $\bar{e}$.

d) $e_\ell \to \bar{e}$ in $L^1(SO3 \times [0,1]^3)$.

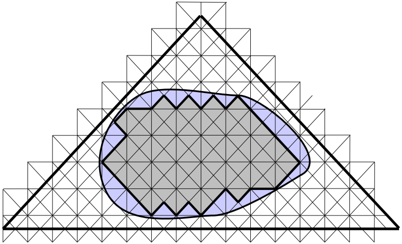
e) **(A4)** implies that the limit is uniform.

Proof for general domains

For all regular domain sequences we can only get

$$\liminf_{n\to\infty} \frac{E(\Omega_n)}{|\Omega_n|} \geq \bar{e}.$$

To get an upper bound, we need to add some assumptions. We assume that $\triangle$ yields a tiling of $\mathbb{R}^3$ and that the interaction is "two-body" (or more generally finite-body).



Upper bound: we use the state in a large reference set $L\triangle$ to build a trial state for A_n, which is itself an approximation of Ω_n, constructed as a union of small $\ell\triangle$'s.

An important ingredient is the strong subadditivity of the entropy. It was proved for quantum systems by Lieb & Ruskai '73.

The two-body assumption

Γ subgroup of G. $\cup_{\mu\in\Gamma}\mu\triangle=\mathbb{R}^3$, $\mu\triangle\cap\nu\triangle=\emptyset$ for $\mu\neq\nu$.

(A6) *(Two-body decomposition).* For all L and ℓ we can find $g\in G$ and maps $E_g:\Gamma\to\mathbb{R}$, $I_g:\Gamma\times\Gamma\to\mathbb{R}$, $s_g:\{\mathcal{P}:\mathcal{P}\subseteq\Gamma\}\to\mathbb{R}$ such that

- $$E(L\triangle)\geq\sum_{\mu\in\Gamma}E_g(\mu)+\frac{1}{2}\sum_{\substack{\mu,\nu\in\Gamma\\ \mu\neq\nu}}I_g(\mu,\nu)-s_g(\Gamma)-|L\triangle|\alpha(\ell)$$
- For all $\mathcal{P}\subseteq\Gamma$ and $A_{\mathcal{P}}=L\triangle\cap\bigcup_{\mu\in\mathcal{P}}\ell g\mu\triangle$
$$E(A_{\mathcal{P}})\leq\sum_{\mu\in\mathcal{P}}E_g(\mu)+\frac{1}{2}\sum_{\substack{\mu,\nu\in\mathcal{P}\\ \mu\neq\nu}}I_g(\mu,\nu)-s_g(\mathcal{P})+|A_{\mathcal{P}}|\alpha(\ell),$$
- *(Strong subadditivity).* For any disjoint subsets $\mathcal{P}_1$, $\mathcal{P}_2$, $\mathcal{P}_3\subseteq\Gamma$
$$s_g(\mathcal{P}_1\cup\mathcal{P}_2\cup\mathcal{P}_3)+s_g(\mathcal{P}_2)\leq s_g(\mathcal{P}_1\cup\mathcal{P}_2)+s_g(\mathcal{P}_2\cup\mathcal{P}_3)$$
- *(Subaverage property).* $\displaystyle\int_{G/\Gamma}dg\sum_{\substack{\mu,\nu\in\Gamma\\ \mu\neq\nu}}I_g(\mu,\nu)\geq-|L\triangle|\alpha(\ell).$

Open problems

• (i) Convergence of the energy is not enough, one would like to prove **convergence of states**.

• (ii) If a local potential V is added to the crystal (modelling a defect and/or deplacement of some nuclei), then the thermodynamic limit is the same. Open problem: prove that

$$E^V(\Omega_n) = E^0(\Omega_n) + f(V) + o(1) \quad \text{as} \quad |\Omega_n| \to \infty.$$

For some approximate models of the crystal, (i) was solved by Lieb-Simon (Thomas-Fermi '77), Catto-Le Bris-Lions (TFW + reduced HF '98).

Proof of (ii) with identification of $f(V)$ done by

- Cancès-Deleurence-L. (preprint) for the reduced-HF model of the crystal ;
- Hainzl-L.-Solovej (CPAM '07) for the Hartree-Fock approximation of no-photon QED.