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PIERRE-LOUIS LIONS (*)

Lattices and Mean Energy

ABSTRACT. — We discuss here some notions of stationary stochastic lattices introduced in collaboration with X. Blanc and C. Lebris. These notions allow to derive a mean energy (or energy per unit volume) and an electronic density in the context of various Quantum Physics or Quantum Chemistry models such as Thomas-Fermi-Von Weiszâcker models (for instance).

1. - INTRODUCTION

In a series of works [9]-[11] (see also the announcements [7], [8]), the so-called thermodynamic limit problem was investigated for a variety of models used in Quantum Mechanics and Quantum Chemistry, in an attempt to derive rigorously some models describing solid matter at the microscopic scale. These studies postulate a periodic organisation of nuclei (for instance) as is the case for a perfect crystal. It is expected (at least in some general cases ...) that periodicity should not be an assumption but should be consequence of the full definition of the ground-state energy in terms of minimization over geometric configurations. This is essentially an open problem with a few recent contributions [1], [12].

Another step of this long-term research program "from Quantum Mechanics to Continuum Mechanics" was carried out in [3] (see also the announcement [2] where we investigated the so-called macroscopic limit, deriving some explicit formula for the stored energy function of the material from the energy of a microscopic periodic lattice.

There are various reasons to go beyond periodic lattices in general and to address stochastic lattices in particular, the simplest of which simply being the fact that a perfect crystal does not exist. This is why we briefly studied in [9] the case of almost periodic lattices and we derived in [4] necessary and sufficient conditions on the geometry of a lattice for the definition of the mean energy. Finally, we introduce and study in [5] (see

(*) Indirizzo dell'Autore: Collège de France 3, rue d'Ulm F-75005 Paris and Ceremade - UMR CNRS 7534; Université Paris-Dauphine, Place de Lattre de Tassigny F-75775 Paris Cedex 16

[6] for the corresponding macroscopic limit) some general classes of stationary stochastic lattices. Our motivations are the following : i) there are natural extensions of almost periodic lattices, ii) a stochastic stationary setting is consistent with many realistic materials, iii) one can test the "crystal problem" using stochastic perturbations of the equilibrium periodic lattice (if it exists ...) and iv) a stochastic lattice may be viewed as a naive representation (or model) for temperature effects.

We report here on the approach and results of [5] and we do so in the case of the simplest possible model for the energy namely a 2-body or pair potential. Given a finite set of points x_i in $\boldsymbol{R}^3$ namely $\ell_N = \{x_i \in \boldsymbol{R}^3 / -N \leq i \leq N\}$, we define the energy of ℓ_N by

$$\mathcal{E}(\ell_N) = \frac{1}{2N+1} \sum_{i \neq j = -N}^{+N} V(x_i - x_j) \tag{1}$$

where V is a given spherically symmetric potential $V \in L^1_{loc}(\boldsymbol{R}^3)$ and V is assumed to be (at least) continuous on $\boldsymbol{R}^3 - \{0\}$ and to go to 0 at infinity ($V(z) \to 0$ as $|z| \to +\infty$) "fast enough" (in a way we shall make precise later on). The problem of defining and deriving the mean energy of a lattice ℓ i.e. of a set of points $\ell = \{x_i / i \in \boldsymbol{Z}^3\}$ is to understand under which conditions upon ℓ do we obtain a limit as N goes to $+\infty$ for $\mathcal{E}(\ell_N)$ with ℓ_N defined as above or by another type of finite sampling of the lattice ℓ ...

If ℓ is a periodic lattice i.e. $\ell = A\boldsymbol{Z}^3$ (where $\det A \neq 0$), then the answer is straightforward and we obtain

$$\mathcal{E}(\ell_N) \xrightarrow[N \to +\infty]{} \mathcal{E}(\ell) = \sum_{k \neq 0 \in \boldsymbol{R}^3} V(-Ak) \tag{2}$$

provided V satisfies (for instance) for some $C \geq 0$

$$|V(z)| \leq \frac{C}{(1+|z|^2)^{m/2}} \quad \text{for} \quad |z| \geq 1 \ , \ \text{for some} \quad m > 3 \ . \tag{3}$$

And this is still the case if ℓ is almost periodic instead of periodic. Note that the almost periodic case is physically extremely relevant since it contains as a particular case the case of quasi-crystals.

Obviously, periodicity or almost periodicity is a structural condition on the organization of the charges which is only "needed at infinity" if we are simply interested in the mean energy (in the context of the simplistic 2-Body models !). Extensions in that direction are considered in [4] and we shall not detail them here.

It is thus natural to investigate whether there are other assumptions on the global organization of the lattice or of the charges which allow to define in a meaningful way the mean energy. This is precisely what we achieved in [5] by the introduction of appropriate notions of stochastic lattices for which not only the mean energy is defined almost surely (i.e. for almost all realization of the lattice) but it is deterministic (i.e. independent of the realization).

2. - Stationary lattices and measures

Several settings are possible (see [5] for more details). The first one is the following. Let $(\Omega, \mathcal{F}, P)$ be a probability space endowed with a commutative group $(\tau_k)_{k \in \boldsymbol{Z}^3}$ of measure invariant (unitary) transforms on Ω, which is assumed to be ergodic

(4) $$A \in \mathcal{F}\ ,\ \tau_k\, A = A \quad \text{for all} \quad k \in \boldsymbol{Z}^3 \Longrightarrow P(A) = 0 \quad \text{or} \quad 1\,.$$

We then view a stationary lattice as a random variable on Ω with values in $(\boldsymbol{R}^3)^{\boldsymbol{Z}^3}$ i.e. $\ell(\omega) = \{x_i(\omega)/i \in \boldsymbol{Z}^3\}$ which is stationary i.e.

(5) $$\ell(\tau_k\, \omega) = \ell(\omega) - k\ ,\ \forall\, k \in \boldsymbol{Z}^3\,.$$

A typical example consists of stationary perturbations of $\boldsymbol{Z}^3$ i.e.

(6) $$\ell(\omega) = \{\tilde{x}_k(\omega)/k \in \boldsymbol{Z}^3\}\,.$$

where $\tilde{x}_k(\omega) = k + x_k(\omega), x_k(\omega) = x_0(\tau_k\omega), x_0 \in L^p(\Omega)$, with $p > 3$ (for example) and $E[x_0] = 0$.

The main result in [5] is the following

Theorem 1: *We assume that V satisfies*

(7) $$\sum_{x_i \in \ell \cap Q}\ \sum_{x_j \in \ell \setminus \{x_i\}} |V(x_i - x_j)|\ \in L^1(\Omega)\ ,$$

where Q is the unit cube. We then define ℓ_N by $\ell \cap (2N+1)Q$ and

$$\mathcal{E}(\ell_N) = \frac{1}{(2N+1)^3} \sum_{x_i \in \ell_N}\ \sum_{x_j \in \ell_N \setminus \{x_i\}} V(x_i - x_j)\,.$$

Then, we have almost surely on Ω

(8) $$\mathcal{E}[\ell_N] \xrightarrow[N \to +\infty]{} E\Bigg(\sum_{x_i \in \ell \cap Q}\ \sum_{x_j \in \ell \setminus \{x_i\}} V(x_i - x_j)\Bigg)\,.$$

Remark: The condition (7) is slightly technical but obviously necessary (in general) in order for (8) to hold (indeed, take $V \geq 0 \ldots$). It is satisfied when V is bounded as soon as $\#(\ell \cap Q) \in L^2(\Omega)$ (which amounts to control the size of the random number of charges concentrated in the unit cube ...).

In the particular case of the example (6), (7) is implied by simpler conditions and the limit $\mathcal{E}(\ell_N)$ may be made more explicit as explained in the following

Corollary 2: *We assume that V is bounded or that the law μ_k of $k + x_k$, satisfies*

(9) $$\sum_{k \in \boldsymbol{Z}^d \setminus \{0\}} \| \mu_k \|_{L^\infty(B_\varepsilon)} < \infty \quad \textit{for some} \quad \varepsilon > 0 \quad \textit{with} \quad B_\varepsilon = \varepsilon B$$

and B is the unit ball. Then $\mathcal{E}(\ell_N)$ converges as on Ω, as N goes to $+\infty$, to

$$E\left[\sum_{k\in\boldsymbol{Z}^d\setminus\{0\}} V(k+x_k-x_0)\right].$$

REMARK: An even more natural setting consists in stochastic lattices with stationary increments. In order to simplify the presentation, we explain the idea in one dimension. Let y_k be a stationary sequence ($y_k(\omega)=y_0(\tau_k\omega)$ a.s.) such that $E[|y_0|]<\infty$, $E[y_0]>0$. We then set $x_0=0$, $x_k=\sum_{j=0}^{k-1} y_j$ if $k>0, x_k=-\sum_{j=k}^{-1} y_j$ if $k<0$. With this construction, one can check, under natural conditions on y_0 and V that we do not wish to detail here that $\mathcal{E}_N=\dfrac{1}{2N+1}\sum_{i\neq j=-N}^{N} V(x_i-x_j)$ converges a.s. on Ω, as N goes to $+\infty$, to $2\sum_{k\geq 1} E\,V\left(\sum_{-k}^{-1} y_k\right)$. At least heuristically, this result is clear: indeed $\mathcal{E}_N=\dfrac{1}{2N+1}\sum_{i\leq j<i\leq N}^{N} V\left(\sum_{j}^{i-1} y_\ell\right)$ and introducing $k=i-j$, we see that under appropriate conditions on the decay of V, $\mathcal{E}_N$ is close to

$$2\frac{1}{2N+1}\sum_{i=-N}^{+N}\left\{\sum_{k\geq 1}\left[V\left(\sum_{i-k}^{i-1} y_\ell\right)\right]\right\}.$$

Next, we observe that $\sum_{k\geq 1} V\left(\sum_{i-k}^{i-1} y_\ell\right)$ is a stationary random variable since we have

$$\sum_{k\geq 1} V\left(\sum_{i-k}^{i-1} y_\ell(\tau_m\,\omega)\right)=\sum_{k\geq 1} V\left(\sum_{i-k}^{i-1} y_{\ell+m}(\omega)\right)=\sum_{k\geq 1} V\left(\sum_{i+m-k}^{i+m-1} y_\ell(\omega)\right).$$

And the conclusion follows (at least formally) from the ergodic theorem.

We conclude with a different setting for stationary lattices and their distributions of charges. We now consider a probability space $(\Omega,\mathcal{F},P)$ endowed with a commutative group $(\tau_x)_{x\in\boldsymbol{R}^3}$ of measure preserving (unitary) transforms on Ω, which is assumed to be ergodic

(10) $$A\in\mathcal{F}\;,\;\tau_x\,A=A\quad\text{for all}\quad x\in\boldsymbol{R}^3\Rightarrow P(A)=0\cap 1\,.$$

The only modification with respect to the preceding setting is that we replace now (5) by

(11) $$\ell(\tau_x\omega)=\ell(\omega)-x\,.$$

We then observe that the lattice comes into the definition of the energy only through the distribution of charges namely

$$m(x,\omega) = \sum_{k \in \boldsymbol{Z}^3} \rho_0(x - x_k(\omega)) \tag{12}$$

and the stationary condition becomes the usual stationary condition

$$m(x, \tau_y\, \omega) = m(x + y, \omega) \quad \forall\, y \in \boldsymbol{R}^3. \tag{13}$$

We may then consider only a non negative measure m satisfying (3) and $E\left[\sup_{z \in \boldsymbol{R}^3} \int_{z+Q} dm\right] < \infty$, and we do not recall anymore the fact that m is or may be defined through a lattice ℓ. We then consider the "truncated" energy

$$\mathcal{E}_R = \frac{1}{|B_R|} \int_{B_R} \int_{B_R} V(x-y)\; m(x,\omega)\; m(y,\omega)\; dxdy$$

where $|B_R|$ denotes the volume of B_R and $R \in (0,\infty)$. Once more in order to simplify the presentation, we only consider here the case when V is continuous bounded on $\boldsymbol{R}^3$ and we introduce the potential (which is easily shown to exist in view of the assumptions made upon V)

$$U(x,\omega) = \int V(x-y)\; m(y,\omega)\; dx\,.$$

Then, U is stationary since we have for all $k \in \boldsymbol{R}^3$

$$U(x, \tau_k\, \omega) = \int_{\boldsymbol{R}^3} V(x-y)\, m(y, \tau_k \omega)\, dy = \int V(x-y)\; m(y+k, \omega)\, dy = \int V(x+k-y)\; m(y,\omega)\, dy$$

and this observation allows to show that, by the ergodic theorem, $\mathcal{E}_R$ converges a.s. on Ω, as R goes to $\mp\infty$, to a deterministic quantity that one can write formally as $E[U(0,\omega)\; m(0,\omega)] = E \int V(-y)\; m(0,\omega)\; m(y,\omega) dy$;

And we refer the reader to [5] for more details (and in particular for the precise statements and the complete proofs).

REFERENCES

[1] X. Blanc - C. Le Bris, *Periodicity of the infinite-volume ground-state of a one-dimensional quantum model*, Nonlin. Anal. T.M.A., 48 (2002), 791-883.

[2] X. Blanc - C. Le Bris - P.-L. Lions, *Convergence de modèles moléculaires vers des modèles de mécanique des milieux continus*, C.R. Acad. Sci. Paris, 332 (2001), 949-956.

[3] X. Blanc - C. Le Bris - P.-L. Lions, *From molecular models to continuum mechanics*, Arch. Rat. Mech. Anal., 164 (2002), 341-381.

[4] X. Blanc - C. Le Bris - P.-L. Lions, *A definition of the ground state energy for systems composed of infinitely many particles*, Comm. P.D.E., 28 (2003), 439-475.

[5] X. Blanc - C. Le Bris - P.-L. Lions, *On the energy of some microscopic stochastic lattices*, Preprint.

[6] X. Blanc - C. Le Bris - P.-L. Lions, *Macroscopic limit of the energy of some microscopic stochastic lattices*, Preprint.

[7] I. Catto - C. Le Bris - P.-L. Lions, *Limite thermodynamique pour des modèles de type Thomas-Fermi*, C.R. Acad. Sci. Paris, 322 (1996), 357-364.

[8] I. Catto - C. Le Bris - P.-L. Lions, *Sur la limite thermodynamique pour des modèles de type Hartree et Hartree-Fock*, C.R. Acad. Sci. Paris, 327 (1998), 259-266.

[9] I. Catto - C. Le Bris - P.-L. Lions, *Mathematical theory of thermodynamic limits: Thomas-Fermi type models*, Oxford University Press (1998).

[10] I. Catto - C. Le Bris - P.-L. Lions, *On the thermodynamic limit for Hartree-Fock type models*, Ann. I.H.P. Anal. Non Lin., 18 (2001), 687-760.

[11] I. Catto - C. Le Bris - P.-L. Lions, *On some periodic Hartree-type models for crystals*, Ann. I.H.P. Anal. Non Lin., 19 (2002), 143-190.

[12] F. Theil, *A proof of crystallization in two dimensions*, preprint of the University of Warwick (2005).

Direttore responsabile: Prof. A. Ballio - Autorizz. Trib. di Roma n. 7269 dell'8-12-1959
«Monograf» - Via Collamarini, 5 - Bologna