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On the invariance of charged systems with respect to external fields

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Abstract. It is shown that the n -sum rule implies that the equilibrium states cannot carry an electric field $\vec{E}_0 = -\nabla\phi_0$, where ϕ_0 is an harmonic polynomial of order $(n-1)$.

1. Introduction

In a series of papers [1, 2, 3], it was shown that equilibrium states of charged systems obey certain ‘sum rules’ which express the perfect screening due to the long range nature of the Coulomb force. More recently it was noticed that these sum rules can be considered as the Ward identities associated with the *local* transformation $z_\alpha \mapsto z_\alpha e^{ie_\alpha y(x)}$ where (z_α, e_α) are the activity and charge of specy α and $y(x)$ is an harmonic function [4]. Formally this symmetry could be understood as the invariance of the plasma phase with respect to external harmonic potentials.

In the following we shall argue that the validity of the k -sum rules for $k = 0, 1, \dots, n$, implies that the system is neutral and cannot carry any electric field $E_0 = -\nabla\phi_0$ with ϕ_0 an harmonic potential of order $n-1$; again this result indicates the relation between the sum rule and the invariance of the state with respect to external field defined by harmonic potentials. Furthermore it is shown that the sum rules will always be satisfied as soon as the clustering is sufficiently fast; therefore a charged system with correlation functions decaying sufficiently rapidly at infinity is a perfect conductor.

2. Finite systems

We consider a system which consists of N species of charged particles and we denote by e_α , $\alpha = 1, \dots, N$, the charge of the specy α . We denote by $q = (x, \alpha) \in \mathbb{R}^v \times \{1, \dots, N\}$ the position and specie of the particle, $\int_\Lambda dq = \int_\Lambda dx \sum_{\alpha=1}^N$, $Q = (q_1, \dots, q_n)$, and $F^c(x) = x/|x|^v$ is the Coulomb force.

The particles interact by means of a two-body force $F(q_1, q_2) = e_{\alpha_1} e_{\alpha_2} F(x_1 - x_2)$, with $F = -\nabla\phi$ where the two-body potential $\phi(x) = \phi(|x|)$ is \mathcal{C}_∞ and $F(x) - F^c(x)$ is short range (i.e. decays faster than any power as $|x| \rightarrow \infty$).

Furthermore, the particles are submitted to an external electric field $E_0 = -\text{grad } \phi_0$ where ϕ_0 is some harmonic potential of order l , i.e.

$$\phi_0(x) = \sum_{k=0}^l \sum_{m=-k}^{+k} A_{km} |x|^k Y_{km}(\hat{x}) \quad (1)$$

To simplify the following discussion we shall take $\nu = 3$; the case of dimension 2 as well as the case of Jellium systems can be analysed in a similar way.

It is well known that the equilibrium correlation functions for a finite system Λ at temperature T satisfy the BBGKY-hierarchy:

$$\begin{aligned} kT \nabla_{\bar{x}} \rho_{\Lambda}(\bar{q}Q) = & \left\{ e_{\bar{\alpha}} [G_{\Lambda}(\bar{x}) + E_{\Lambda}(\bar{x})] + \sum_{q_j \in Q} F(\bar{q}, q_j) \right\} \rho_{\Lambda}(\bar{q}Q) \\ & + \int_{\Lambda} dq F(\bar{q}, q) [\rho_{\Lambda}(q\bar{q}Q) - \rho_{\Lambda}(q)\rho_{\Lambda}(\bar{q}Q)] \end{aligned} \quad (2)$$

where:

$$G_{\Lambda}(\bar{x}) = \int dx [F(\bar{x} - x) - F^c(\bar{x} - x)] c_{\Lambda}(x) \quad (2a)$$

$$c_{\Lambda}(x) = \sum_{\alpha=1}^N e_{\alpha} \rho_{\Lambda}(x, \alpha) \quad (2b)$$

$$E_{\Lambda}(\bar{x}) = E_0(\bar{x}) + \int_{\Lambda} dx F^c(\bar{x} - x) c_{\Lambda}(x)$$

i.e.

$$\text{div } E_{\Lambda}(x) = 4\pi c_{\Lambda}(x) \quad (2c)$$

3. Infinite systems

Let $\phi_0(x)$, equation (1), be the external potential inside the volume Λ due to charges outside of Λ ; if the system is a conductor the density of charges inside the system, $c_{\Lambda}(x)$ equation (2b), will be localized on the boundary of Λ in such a manner that the electric field $E_{\Lambda}(x)$ is zero in the bulk. Therefore, except for the density of particles, the properties in the bulk should be independent of the external electric potential $\phi_0(x)$; in other words, we expect that for a very large system the state in the bulk will be identical to the state of a system without external field but for some other value of the particle density.

As usual to discuss bulk properties one considers an infinite system obtained by means of an appropriate thermodynamic limit. We would like then to investigate whether the equilibrium states of the infinite system are invariant with respect to external harmonic potentials; or whether it is possible to obtain different limiting states associated with different ϕ_0 ; this is analogous to the question whether or not the equilibrium states are invariant with respect to the transformation $z_{\alpha} \mapsto z_{\alpha} \exp [e_{\alpha} \phi_0(x)]$ such as considered in Ref. [4].

The external electric field $E_0 = -\text{grad } \phi_0$ being given once for all by equation (1), it is clear that the thermodynamic limit $\Lambda \rightarrow \mathbb{R}^3$ has to be taken with special

care in order to obtain a well defined equilibrium state of the infinite system. One could for example take a sequence of finite neutral systems Λ_n with a number of particles such that the density of particles around the origin be fixed. Let us note that if Λ_n is a sphere of radius R_n and if E_0 is created by a charge density on this sphere, then this external charge density will be of the order R_n^{l-1} ; therefore, since the system charges will be localized on the boundary of Λ_n , we can expect that $c_{\Lambda_n}(x)$ will be of the order R_n^{l-1} near the boundary and zero inside the system; it seems thus reasonable to assume in the following that $c(x) = O(|x|^{l-1})$. Another way to take the thermodynamic limit would be to consider an external field $E_0^{(n)}$ which varies with Λ_n , such as $E_0^{(n)} = R_n^{-(l-1)} E_0$; in such a case $E_0^{(n)}$ and the charge density would be finite.

The problem of the thermodynamic limit being very difficult, we shall not discuss it and we shall consider directly the infinite system. We assume that the equilibrium states of the infinite system are solution of the following BBGKY-hierarchy:

$$kT \nabla_{\bar{x}} \rho(\bar{q}Q) = \left\{ e_{\bar{\alpha}} [G(\bar{x}) + E(\bar{x})] + \sum_{q_j \in Q} F(\bar{q}, q_j) \right\} \rho(\bar{q}Q) + \int dq F(\bar{q}, q) [\rho(q\bar{q}Q) - \rho(q)\rho(\bar{q}Q)] \quad (3)$$

where:

$$\begin{aligned} \text{div } E(x) &= 4\pi c(x) & c(x) &= \sum_{\alpha=1}^N e_{\alpha} \rho(x, \alpha) \\ G(\bar{x}) &= \int dx [F(\bar{x} - x) - F^c(\bar{x} - x)] c(x) \end{aligned} \quad (4)$$

As usual we also assume that the clustering is such that the truncated correlation function satisfy

$$\begin{aligned} \int dq |\rho^T(qQ)| &< \infty & |Q| &\neq 0 \\ \int dq d\bar{q} |\rho^T(q\bar{q}Q)| &< \infty \end{aligned} \quad (5)$$

Let us note that (3) is the natural extension of (2) for infinite systems; in fact in the absence of external fields, it has been shown that the infinite volume equilibrium state satisfies (3), at least for systems satisfying some weak clustering conditions [4].

The problem we want to investigate is thus whether there can exist solutions of (3) such that

$$E(x) = O(|x|^n) \quad \text{and} \quad |c(x)| = O(|x|^n)$$

where n is a non negative integer.

Introducing

$$\rho(q | Q) = \frac{\rho(qQ)}{\rho(Q)} - \rho(q) + \sum_{q_j \in Q} \delta(q, q_j) \quad (6)$$

our result is given by the following propositions:

Proposition 1. *Let ρ be any solution of the BBGKY-hierarchy such that*

$$E(x) = O(|x|^n) \quad c(x) = O(|x|^n), \quad n \geq 0$$

and

$$[\rho(qQ) - \rho(q)\rho(Q)] = O\left(\frac{1}{|x|^{\nu+n+2+\epsilon}}\right) \quad \text{as} \quad |x| \rightarrow \infty \quad \epsilon > 0 \quad (7)$$

If the following sum rule¹⁾

$$\int dq e_\alpha h(x) \rho(q \mid Q) = 0 \quad (8)$$

holds for any harmonic function $h(x)$ of order $(n+2)$, then the state is invariant under translation, neutral, and the electric field $E(x)$ is zero.

In other words, the validity of the sum rule (8) for harmonic polynomial of order $(n+2)$ implies that the state cannot carry any electric field $\mathcal{E}_0 = -\text{grad } \phi_0$ where ϕ_0 is an harmonic potential of order $(n+1)$. We can thus argue that the validity of the n -sum rule ($n \geq 2$) implies the invariance of the state with respect to external potential which are harmonic polynomials of order $(n-1)$.

The validity of the n -sum rule is then guaranteed by the following result.

Proposition 2. *Let ρ be any solution of the BBGKY-hierarchy such that*

$$E(x) = O(|x|^n) \quad \rho_\alpha(x) = O(|x|^n)$$

and such that the truncated correlation functions satisfy the clustering conditions:

$$|r^{\nu+\delta+\epsilon} \rho^T(Q)| < \text{cte} \quad \text{for some} \quad \epsilon > 0$$

$$r = \sup_{(q_i, q_j)} |x_i - x_j| \quad |Q| \geq 2; \quad \delta = \max \{n+2, 2n+1\}$$

then the sum rule (8) holds for any harmonic function of order $(n+2)$ (for $\nu \geq 2$).

Combining Propositions 1 and 2, we obtain finally:

Proposition 3. *Any solution of the BBGKY-hierarchy such that*

$$E(x) = O(|x|^n) \quad \rho_\alpha(x) = O(|x|^n)$$

and satisfying the clustering condition

$$|r^{\nu+\delta+\epsilon} \rho^T(Q)| < \text{cte} \quad \delta = \max \{n+2, 2n+1\}$$

is translation invariant, neutral and has zero electric field.

Let us note that this last result indicates that equilibrium states with exponential clustering are invariant with respect to harmonic external potentials.

¹⁾ If equation (8) holds for any harmonic functions of order n , we say that the state satisfy the n -sum rule.

Proof of Proposition 1. It follows from equation (3) that:

$$kT \sum_{q_j \in Q} \nabla_j \rho(Q) = \sum_{q_j \in Q} e_{\alpha_j} [G(x_j) + E(x_j)] \rho(Q) + \int d\bar{q} \left[\sum_{q_j \in Q} F(q_j, \bar{q}) \right] [\rho(\bar{q}Q) - \rho(\bar{q})\rho(Q)] \quad (9)$$

and

$$\begin{aligned} kT \nabla_{\bar{x}} [\rho(\bar{q}Q) - \rho(\bar{q})\rho(Q)] &= \left\{ e_{\bar{\alpha}} [G(\bar{x}) + E(\bar{x})] + \sum_{q_j \in Q} F(\bar{q}, q_j) \right\} [\rho(\bar{q}Q) - \rho(\bar{q})\rho(Q)] \\ &+ \left[\sum_{q_j \in Q} F(\bar{q}, q_j) \right] \rho(\bar{q})\rho(Q) \\ &+ \int dq F(\bar{q}, q) [\rho(q\bar{q}Q) - \rho(q)\rho(\bar{q}Q) - \rho^T(q\bar{q})\rho(Q)] \end{aligned} \quad (10)$$

The integrand in (10) can be written as

$$[\dots] = \rho(\bar{q})[\rho(qQ) - \rho(q)\rho(Q)] + \mathcal{R}(q\bar{q}Q)$$

where $\mathcal{R}(q\bar{q}Q)$ is symmetric in (q, \bar{q}) . Furthermore, using the clustering condition (5), \mathcal{R} is integrable in (q, \bar{q}) and

$$\int d\bar{q} \int dq F(\bar{q}, q) \mathcal{R}(q\bar{q}Q) = 0$$

The integral in equation (9) can be transformed by means of equation (10); to do so, we integrate (10) on a ball B_R of radius R and take the limit $R \rightarrow \infty$. Using the conditions (5) and (7), we have:

$$G(\bar{x}) = O(|x|^n) \quad \text{and} \quad \lim_{R \rightarrow \infty} \int_{B_R} d\bar{q} \nabla_{\bar{x}} [\rho(\bar{q}Q) - \rho(\bar{q})\rho(Q)] = 0$$

thus

$$\begin{aligned} kT \sum_{q_j \in Q} \nabla_j \rho(Q) &= \int d\bar{q} [G(\bar{x}) + E(\bar{x})] e_{\bar{\alpha}} \rho(\bar{q} | Q) \rho(Q) \\ &+ \lim_{R \rightarrow \infty} \int_{B_R} d\bar{q} \int dq F(\bar{q}, q) \rho(q | Q) \rho(\bar{q}) \rho(Q) \end{aligned} \quad (11)$$

Let us then define the electric field $\mathcal{E}_0(x)$ by

$$\mathcal{E}_0(x) = E(x) - \int dy \{ [F^c(x - y) - F^c(-y)] c(y) - R_{n+1}(x; y) \tilde{c}(y) \} \quad (12)$$

where

$$R_{n+1}(x; y) = \sum_{k=1}^{n+1} (-1)^k \frac{4\pi}{2k+1} \sum_{m=-k}^{+k} \nabla_y \left(\frac{Y_{km}^*(\hat{y})}{|y|^{k+1}} \right) |x|^k Y_{km}(\hat{x}) \quad (13)$$

and $\tilde{c}(y) = \varphi(y)c(y)$ with $\varphi(y)$ a continuous function such that $\varphi(y) = 1$ for $|y| \geq a$ and $\varphi(y) = O(|y|^{n+2})$ as $|y| \rightarrow 0$.

Note that the function $\varphi(y)$ is introduced in order that the integrand in equation (12) be integrable around $|y| = 0$; note also that by comparison with the external electric field E_0 in the finite system we had to subtract in equation (12) the first terms of the Taylor expansion of $F^c(x - y)$ around y in order that the function be integrable.

Since $c(y) = O(|y|^n)$, then $\{\cdot \cdot \cdot\} = O\left(\frac{1}{|y|^4}\right)$ and thus \mathcal{E}_0 is well defined. Furthermore, the functions $\mathcal{E}_0^i(x)$, $i = 1, 2, 3$, are such that $\Delta \mathcal{E}_0^i = 0$ and $\mathcal{E}_0^i(x) = O(|x|^{n+2})$; indeed decomposing the integral in equation (12) as

$$\int dy = \int_{|y| \geq 2x} dy + \int_{|y| < 2x} dy$$

we can use the rest of the Taylor expansion to bound the first integral and the fact that

$$\int_{\alpha \leq |y| \leq 2x} dy |y|^{-\gamma} = \begin{cases} O(|x|) & \text{if } 2 \leq \gamma < 3 \\ O(\ln |x|) & \text{if } \gamma = 3 \\ O(1) & \text{if } \gamma > 3 \end{cases}$$

to bound the second integral. Furthermore $\int_{B_R} dy \{\cdot \cdot \cdot\} = O(|x|^{n+2})$ uniformly with respect to R . Therefore assuming the validity of the sum rule (8) for any harmonic function of order $(n+1)$ and using the clustering condition (7), we can write the last term of (11) as

$$\begin{aligned} & \lim_{R \rightarrow \infty} \int_{B_R} d\bar{x} \int dx \{[F(\bar{x} - x) - F^c(\bar{x} - x) + F^c(\bar{x} - x) - F^c(\bar{x})]c(\bar{x}) \\ & + R_{n+1}(\bar{x}; x)\tilde{c}(\bar{x})\} \sum_{\alpha} e_{\alpha} \rho(q | Q) \rho(Q) \\ & = - \int dq [G(x) + E(x) - \mathcal{E}_0(x)] e_{\alpha} \rho(q | Q) \rho(Q) \end{aligned} \quad (14)$$

Therefore equations (11) and (14) yield:

$$kT \sum_{q_i \in Q} \nabla_{q_i} \rho(Q) = \int dq e_{\alpha} \mathcal{E}_0(x) \rho(q | Q) \rho(Q) \quad (15)$$

Assuming the sum rule (8) for harmonic functions of order $(n+2)$ it then follows that the state is invariant under translation. Moreover

$$\begin{aligned} kT \nabla_x \rho(q) &= 0 = e_{\alpha} \left\{ [G + E(x)] \rho_{\alpha} \right. \\ & \left. + \int dy F(x - y) \sum_{\bar{\alpha}} e_{\bar{\alpha}} \rho_{\alpha \bar{\alpha}}^T(x - y) \right\} \end{aligned}$$

$$G = c \int dy [F(x - y) - F^c(x - y)] \quad \text{div } E(x) = c$$

imply $E(x) = E$, $c = 0$, $G = 0$; we are therefore in the context of Ref. [5] which gives $E = 0$.

Remark. Let us note that we have used the sum rule at two different places. First to give a meaning to the electric field $\mathcal{E}_0(x)$ and thus obtain (14); then to conclude from (15) that the state is invariant under translation. If we had simply assumed that the density is bounded we would have needed only the $n = 1$ sum rule to obtain (14), but we need the $(n + 2)$ sum rule to conclude from (15) that $E = 0$.

Proof of Proposition 2. It is sufficient to notice that the conditions of Proposition 2 yield for any $\bar{x} = \lambda \hat{u}$,

$$[E(\bar{x}) + G(\bar{x})][\rho(\bar{q}Q) - \rho(\bar{q})\rho(Q)] = O\left(\frac{1}{\lambda^{\nu-1+(n+2)}}\right) \quad \text{as } \lambda \rightarrow \infty$$

we can thus repeat the proof given in [2, 3].

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