

205

FREE ENERGY AND CORRELATION FUNCTIONS OF COULOMB SYSTEMS^{†*}

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I. INTRODUCTION

These notes, like my lectures in Erice consist of several parts which are loosely related by the fact that they all deal with some aspects of statistical mechanics of Coulomb systems. In some sense of course all of statistical mechanics, which is the microscopic theory of macroscopic matter, deals with Coulomb systems. The properties of the materials we see and touch are almost entirely determined by the nature of the Coulomb force as it manifests itself in the collective behavior of interacting electrons and nuclei. In most applications of statistical mechanics however this fact is not explicit at all. One starts with an "effective" short range microscopic Hamiltonian appropriate to the problem at hand. For example, to discuss the superfluidity of He^4 we describe the fluid as a collection of neutral atoms represented by point masses interacting via Lennard-Jones pair potentials. This description seems very adequate. Statistical mechanics of Coulomb systems therefore usually refers to those investigations in which the Coulomb potential is explicitly considered as a part of the starting microscopic Hamiltonian. (Appropriate quantum statistics are always assumed).

There are two reasons for considering explicitly systems with such Hamiltonians. The first is primarily a theoretical one - we would like to understand in a more precise way how the Coulomb forces give rise to the effective interactions. The second reason is more practical. There are many systems, e.g. plasmas, molten salts, ionic crystals, etc. where bare Coulomb interactions are part of the appropriate effective Hamiltonian. We shall review here, very briefly, the status of some selected topics in both of these categories.

Since the aim of the two types of studies mentioned above are different, precise vs. pragmatic understanding of macroscopic behavior, their methods are also different. Workers in the first vineyard state their results as mathematical theorems while those in the second make and exploit various physically reasonable approximations. Of course the good work in either category, such as that reported by Aizenman, Brydges, Fröhlich, Lieb, Seiler, Thirring and other speakers on this subject here, is relevant to both areas. They are the interpid brave explorers leading the attack against ignorance and sloth.

II. THERMODYNAMIC LIMIT FOR COULOMB SYSTEMS (LIEB-LEBOWITZ)

The rigorous derivation of effective Hamiltonians from first principles is at the present time mostly beyond the reach of our mathematical abilities. I simply have no ideas of how to show that the Lennard-Jones description of He⁴ is a good approximation, in certain ranges of temperature and density, to an overall neutral system of α -particles and electrons interacting via the Coulomb potential and satisfying the proper statistics, Bose for the α -nuclei, Fermi for the electrons with spins (see however Remarks later). We have therefore to be satisfied at present with much more modest goals : Prove that the most basic fact of macroscopic thermodynamics, extensivity and stability of the free energy of neutral systems, follows from the prescriptions of statistical mechanics for computing this free energy, $-\beta a(\beta, \rho)$

$$a(\beta, \rho) = \lim_{|\Lambda| \nearrow \mathbb{R}^3} |\Lambda|^{-1} \ln[\text{tr exp}[-\beta H(\underline{N}; \Lambda)]] \tag{2.1}$$

Here $H(\underline{N}; \Lambda)$ is the Coulomb Hamiltonian of k species of charged particles, with charges e_α and numbers N_α , $\alpha = 1, \dots, k$ contained in a box Λ , $\Lambda \subset \mathbb{R}^3$ with volume $|\Lambda|$. The thermodynamic limit $\Lambda \nearrow \mathbb{R}^3$ is taken along a "reasonable" sequence of boxes Λ_j and particle numbers \underline{N}_j such that

$$\underline{N}_j \cdot \underline{E} \equiv \sum_{\alpha=1}^k N_j^\alpha e_\alpha = 0, \quad N_j^\alpha \geq 0, \quad (\text{neutrality}) \tag{2.2}$$

and

$$N_j^\alpha / |\Lambda_j| = \rho_j^\alpha \rightarrow \rho^\alpha \tag{2.3}$$

The existence and thermodynamic stability of the limit function $a(\beta, \rho)$ was proven by Elliott Lieb and myself [1,2] under the assumption that at least one type of charge, the positive or negative ones, obey Fermi statistics - as indeed electrons do. This condition

was proven by Dyson and Lenard [3] to be both sufficient and necessary for the extensivity of the ground state energy of the system, H-stability,

$$\text{Min } H(\underline{N}; \Lambda) \geq -bN, \quad b < \infty \quad (2.4)$$

$N = \sum_{\alpha=1}^k N^{\alpha}$. A simple elegant derivation of (2.4) with a greatly improved constant b was later given by Lieb and Thirring; see lectures by these authors in this volume.

The actual Hamiltonian for which (2.1) was proven in [1] is

$$H(\underline{N}) = \sum_{i=1}^N p_i^2/2m_i + \frac{1}{2} \sum_{i \neq j} e_i e_j / |x_i - x_j| + U(x_1, \dots, x_N) \quad (2.5)$$

where $e_i = e_{\alpha}$ and $m_i = m_{\alpha}$ when particle i is of species α . Dirichlet boundary conditions are used for the wave functions on $\partial\Lambda$ and the negative charges are Fermions. U is any "standard" short range ℓ -body interaction, $\ell = 2, 3, \dots$ finite, which satisfies classical H-stability [4]

$$\text{Min}_{\{x_i\}} U(x_1, \dots, x_N) \geq -bN \quad (2.6)$$

U is essentially such that if $e_{\alpha} = 0 \quad \forall \alpha$, then the thermodynamic limit in (2.1) would exist $^{\alpha}$ without any restrictions on the statistics (superstability is not required when $e_{\alpha} \neq 0$) - in fact the system could be treated by classical statistical mechanics with the trace in (2.1) replaced by the appropriate symmetrized integrals. In fact if U contains a hard core, i.e. $U(x_1, \dots, x_N) = \infty$ whenever $|x_i - x_j| < d$, $d > 0$, then classical and hence also quantum mechanical H-stability for $H(N)$ in (2.5) was proven by Onsager [5] in 1939. The results in [1] then hold also for such classical systems (a suitable representation in many cases).

Onsager's proof is based on the fact that in the presence of hard cores the charge on each particle can be considered (as far as the interactions are concerned) to be smeared out on the surface of a sphere of radius d . This has a self energy $\epsilon(d)$. It is then a basic fact of electrostatics that

$$\begin{aligned} \frac{1}{2} \sum_{i \neq j} e_i e_j / |x_i - x_j| &= \frac{1}{2} \int_{\mathbb{R}^3} E^2(x) d^3 x - \sum \text{self energy} \\ &\geq -N\epsilon(d), \quad |x_i - x_j| \geq d. \end{aligned} \quad (2.7)$$

Here $\underline{E}(x)$ is the electric field at the point x and the integral is obviously non-negative.

To the best of my knowledge, Onsager was the first one to consider the problem of H -stability. This expresses the "saturation" of the interactions between a particle and the "rest of the universe". This is an absolute necessity for the existence and extensivity of the free energy in macroscopic matter. Onsager's proof is not conceptually satisfactory because it requires the existence of a hard core. Even if such a hard core (or something equivalent to it) were to be true in nature as a consequence of other non-Coulombic (strong, weak) interactions, the lower bound $\varepsilon(d)$ in (2.7) would be, for any reasonable d , orders of magnitude larger than the actually observed energies: see article by Thirring. Thus Fermi statistics of electrons are a central ingredient in the stability of matter.

Once we have H -stability there still remains the problem of how to deal with the long range nature of the Coulomb potential: if all the charges were of the same sign then clearly the energy would be non-negative but the system would "explode" - all particles going to the surface of Λ . The reason this does not happen for neutral systems is of course screening. Just because the Coulomb forces are long range they are also very strong (their integral diverges at infinity) and cause the system to be locally neutral. The "effective" interaction between different regions of a macroscopic system is therefore greatly attenuated. This idea was turned (with some effort) into a formal proof of (2.1) for neutral systems. Since I have nothing to add on this point to what is already described in references [1,2] I shall not discuss this further here. Instead, I shall turn, after a few remarks, to the situation in which the system is not strictly neutral. Elliott Lieb has discovered a flaw in one point of our reasonings in [1] regarding some charged systems which leaves a (small) gap in our proof there. The question raised also concerns general mixtures in which the interactions are short range. I hope that this will soon be resolved.

Remarks : (i) We note that the results described above are for the three dimensional Coulomb system specified by the non-relativistic Hamiltonian (2.5). For results in two dimensions we refer the reader to the article by Fröhlich and Spencer in this volume [6]. For the one dimensional Coulomb system see the article by Aizenman (see also remark iii).

It is not clear at present how to deal with inclusion of relativistic effects. H -stability is the basic problem here - magnetic dipolar forces behave as $|x|^{-3}$ and their inclusion makes even the hydrogen atom unstable against collapse. Until this is resolved - which might involve getting a good theory of all the forces in nature - there seems little incentive to consider the thermodynamic

limit problem for relativistic Hamiltonians. This is also the only answer I know to a question raised by E. Wigner in one seminar - if the Coulomb ground state energy per particle for a neutral collection of $2N$ bosons, with charges $\pm e$, is unbounded below,

$E_0(N) \sim -N^{7/5}$ according to Dyson [3], then why is there not spontaneous generation of positive and negative π -mesons.

I believe, on the other hand, that the problem of deriving effective (e.g. Lennard-Jones) interactions between neutral atoms from the Coulomb Hamiltonian (2.5) while very difficult, may not be entirely hopeless. I regard the work described by Fröhlich and Spencer on the two dimensional charged lattice gas as having (despite its being two-dimensional and entirely classical) the right flavor for this problem. They show, in a precise way, that in a certain range of temperature and density the weight of the Gibbs measure is concentrated entirely on "neutral molecules of finite extent". We don't expect this to happen in three dimensions where the Coulomb force is weaker and there should always be a finite density of loose charges (electrons and ions) around - we do expect that these play a negligible role at low temperatures and moderate densities. (At very very low densities the system will always be almost completely ionised.)

(ii) The Hamiltonian (2.5) corresponds to the box Λ having insulating boundaries. The existence of the thermodynamic limit for a Coulomb system in three dimensions with super-conducting boundary conditions was proven by Penrose and Smith [7]. It is not known whether the free energy is the same in both cases.

(iii) A model often used by physicists to describe certain kinds of plasmas or solids is the so-called jellium system. In this model one of the charges, say electrons, are assumed to form a uniform background of constant negative charge density in which the ions move. We shall not go into the justification of this model, which neglects fluctuations in the density of one of the species; or into any details of its properties referring the reader to the excellent recent review by Baus and Hansen [8]. The Hamiltonian for this model is obtained from (2.5) by adding there the potential produced by the uniform background of charge density ρ_B

$$H'(\underline{N}, \Lambda) = H(\underline{N}, \Lambda) + \sum_{i=1}^N e_i \rho_B v_{\Lambda}(x_i) + \frac{1}{2} \rho_B^2 \int_{\Lambda} v(x) d^3x \quad (2.8)$$

with

$$v_{\Lambda}(x) = \int_{\Lambda} d^3y / |x-y| \quad .$$

Charge neutrality is now given by the relation

$$\sum_{\alpha=1}^k N^{\alpha} e_{\alpha} + \rho_B |\Lambda| = 0 \quad (2.9)$$

Lieb and Narnhoffer [9] proved the existence of the thermodynamic limit for the free energy of this system in three dimensions. In two dimensions the electrostatic potential is, of course, $\ln|x|$ rather than $|x|^{-1}$ and the proof needs changing [9b].

In one dimension the Jellium model with electrostatic potential $|x|$ and one moving component, the so-called OCP (One component plasma) can be solved exactly classically as can the two component (no background) charged system: see article by Aizenman. The Jellium system is known to form a crystal, periodic state with spacing $-e_1/\rho_B$ ($k = 1$ here) [10] at all temperatures $\beta > 0$. This is true in both the classical and quantum description and is the only system with translation invariant forces (in the thermodynamic limit or periodic b.c.) for which a crystalline Gibbs state is known to exist. There is strong theoretical and numerical (computer simulation) evidence that in three (and two) dimensions the OCP forms a crystal at low temperatures (Wigner crystal) which melts as the temperature is raised [8].

This system is in some sense both simple and interesting - since its interactions are exact rather than approximate or modeled - and therefore presents a worthwhile challenge to the theorist. It would be particularly interesting to know whether its behavior in three dimensions is "physical" despite of the suppression of fluctuations in one component. As already noted the behaviour in one-dimension is artificial. In two dimensions the system is exactly solvable at one temperature, $\beta e_1 = 2$, where the truncated correlation functions are found to be Gaussian [11] a much faster than typical decay.

It may also be worth mentioning here another problem in this area which is a challenge to theorists. There is some evidence [12] that when there is more than one species of positively charged ions in a uniform negative background, say protons and α -particles, then the system will segregate into a "hydrogen" and "helium" phase at low temperatures. This can be understood to be a consequence of the systems attempt to stay locally neutral which, since the background is assumed at a uniform density, requires a larger spacing between the more highly charged species. If this is true and persists also in real plasmas it may be of great relevance in astro-physics where it might cause the highly charged heavy ions, e.g. iron, in a star to clump together - rather than be uniformly distributed. This might even help explain the apparent deficiency in the number of observed solar neutrinos [12]. (The calculated rate assumes a homogeneous distribution of the heavy ions.)

Finally I want to mention here the question of the existence of the thermodynamic limit of "real" jellium, that is of a regular Coulomb system, confined to a two dimensional layer, i.e. the particles move in \mathbb{R}^2 (and ρ_B is a surface charge density) but the interaction potential is $|x|^{-1}$, $x \in \mathbb{R}^2$. Such systems are used [13] as models for layers of electrons on the surface of fluids like helium. The methods used in [1] make essential use of the harmonic nature of the Coulomb potential and do not therefore apply here. The requirement on the regularity of domain shapes Λ_j in [1] rules out the consideration of this case as a limit.

(iv) As mentioned earlier classical H-stability, Eq. (2.6), can be proven for more or less all potentials commonly used to describe the interactions between neutral molecules. There is a little known simple proof of this fact in a very complicated paper by Morrey [14] for pair potentials $v(r)$ satisfying the inequalities

$$v(\underline{r}) \geq C_1 r^{-(\nu+\epsilon)}, \quad r < r_0 \tag{2.10}$$

$$v(\underline{r}) \geq -C_2 r^{-(\nu+\epsilon)}, \quad r > r_0$$

where $\underline{r} \in \mathbb{R}^\nu$, $r = |\underline{r}|$, and $0 < C_1$, $\epsilon < \infty$. It seems worthwhile presenting his argument here.

Consider a configuration $\{x_1, \dots, x_N\}$ with $x_i \in \mathbb{R}^\nu$. Let λ be the smallest distance between any pair, $\lambda = \text{Min} |x_i - x_j|$, $i \neq j$. Call the pair for which this minimum is achieved x_1 and x_2 . Write then

$$U(x_1, \dots, x_N) = \frac{1}{2} \sum_{i \neq j} v(x_i - x_j) = [v(x_1 - x_2) + \sum_{j=3}^N v(x_1 - x_j)] + U(x_2, \dots, x_N) \tag{2.11}$$

Since the spacing between x_i and x_j is at least λ we have by (2.10) that

$$V_1 = v(x_1 - x_2) + \sum_{j=3}^N v(x_1 - x_j) \geq A_1/\lambda^{\nu+\epsilon} - A_2/\lambda^\nu = G(\lambda)$$

where $0 < A_1 < \infty$. Let now $-b = \text{Min}_\lambda G(\lambda) > -\infty$ and repeat the procedure on the interaction between the $N-1$ particles $\{x_2, \dots, x_N\}$ to obtain (2.6). N.B. The theorem does not give a lower bound for the interaction energy of any particle with the rest of the system. This is clearly impossible if $v(r) < 0$ for some \underline{r} and there is no hard core, e.g. for the Lennard-Jones

potential.

The paper by Morrey sets out to prove that in a certain limit the Liouville equation leads to the Euler equations of hydrodynamics. It is not clear whether the paper ever achieves this goal (I doubt it) but it does prove on the way the convergence of the Mayer expansion for the pressure at small fugacities for potentials satisfying (2.10). This is a remarkable achievement since the author had apparently never heard of the Mayer expansion before, so he derives it as an aside (in fifty pages). His proof ante-dates by many years the proofs of Groeneveld, Ruelle, and Penrose [4] .

III. SYSTEMS WITH NET CHARGE.

it is intuitively clear that the condition of strict charge neutrality, $\underline{N}_j \cdot \underline{E} = 0$, is unnecessarily restrictive. We expect that a "small" amount of uncompensated charge will have no effect on the free energy density in the thermodynamic limit while a "large" amount of uncompensated charge will lead to a divergent free energy density in that limit. The dividing line between "small" and "large" occurs when the excess charge Q_j , in a domain Λ_j , increases in proportion to the "surface area" of Λ_j as $j \rightarrow \infty$. In this case we expect the thermodynamic limit of the free energy density to exist but that its value depends also on the limiting shape of the domains Λ_j .

These expectations come from macroscopic electrostatic theory [15] which shows that the lowest energy configuration for any net charge Q confined to a domain Λ is obtained when Q is concentrated at the boundary of Λ . This configuration of the charge is described in electrostatics by a two dimensional charge density $\sigma(\underline{x})$, $\underline{x} \in S_\Lambda$, where S_Λ is the surface of Λ . This surface charge density will be such as to make the electrostatic potential constant in the interior of Λ , i.e., there will be no electric field in Λ . The electrostatic energy of this surface layer is equal to $\frac{1}{2} Q^2/C(\Lambda)$ where $C(\Lambda)$ is the capacitance of Λ .

For a given domain shape, $C(\Lambda)$ is proportional to $[V(\Lambda)]^{1/3}$ ($V(\Lambda) = |\Lambda|$) and the electrostatic energy per unit volume will thus be proportional to $[Q/V^{2/3}]^2$, the square of the "average surface charge density". Hence for sequence of domains $\{\Lambda_j\}$ with volumes $\{V_j\}$ and capacitances $\{C_j\}$ each containing a net charge Q_j such that as $j \rightarrow \infty$, $V_j \rightarrow \infty$, $C_j/V_j^{1/3} \rightarrow c$, the minimum electrostatic energy per unit volume \tilde{e}_j will also approach a limit $\frac{1}{2} \sigma^2/c$.

We therefore considered in [1] a sequence of domains Λ_j (ellipsoidal for technical reasons) with particle numbers $\underline{N}_j + \underline{n}_j$ such that $\underline{N}_j \cdot \underline{E} = 0$, $\underline{n}_j \cdot \underline{E} = Q_j$. It was then claimed that as $j \rightarrow \infty$ the free energy density

$$a_j(\beta, \underline{\rho}_j, \underline{n}_j) \rightarrow a(\beta, \underline{\rho}) - \frac{1}{2} \sigma^2 / c, \quad \underline{\rho} = \lim \underline{N}_j / V_j. \quad (3.1)$$

where $a(\beta, \underline{\rho})$ is given in (2.1) and c is shape dependent. In the proof of (3.1), for arbitrary \underline{n}_j , we used the continuity of the neutral free energy density $a(\beta, \underline{\rho})$ in each ρ_α . The argument used for this was the standard one - concavity of $a(\beta, \underline{\rho})$.

The difficulty discovered by Lieb in the proof of (3.1) is that, as is well known, concavity does not guarantee continuity at the boundary of the domain of the function, i.e. at $\rho^\alpha = 0$ for some α . This is taken care of in the usual considerations for one component systems [4] by showing explicitly that $a(\rho) \sim \rho \log \rho$ near $\rho \sim 0$. A similar form is true for multi-component systems, including Coulomb ones [1,6] in the neighborhood of $\underline{\rho} = 0$. We have however been unable to come up with a proof of continuity at a general point of the boundary of the positive cone $\rho^\alpha \geq 0$. This requires that we add some conditions on the sequences \underline{n}_j for which (3.1) can be shown to hold rigorously (at the present time). Namely we need to assume that there exists $\underline{m}_j^\alpha \geq 0$ such that

a) $(\underline{n}_j + \underline{m}_j) \cdot \underline{E} = 0$ and b) $\rho^\alpha > 0$ for all those α , $\alpha = 1 \dots k$ for which $\underline{n}_j^\alpha + \underline{m}_j^\alpha > 0$. In other words we require that the excess charge and what it requires to neutralize it be available inside the system at a non-vanishing density. If a) and b) are not satisfied then (3.1) would still be a lower bound but in the upper bound $a(\beta, \underline{\rho})$ would have to be replaced by $a(\beta, \underline{\rho}^+)$ the limiting value of $a_j(\beta, \underline{\rho}_j, \underline{n}_j + \underline{m}_j)$ (It might be necessary as in [1] to introduce a "new" charged species, $\alpha = 0$, to satisfy the strict neutrality condition $(\underline{n}_j + \underline{m}_j) \cdot \underline{E} = 0$).

As I already mentioned before the difficulty here has really nothing to do with the specifics of the Coulomb interaction. Consider, for example, a classical system of two kinds of "neutral atoms" interacting with Lennard-Jones type potentials, i.e. they satisfy (2.10). It is then a standard (by now so familiar as to be trivial) argument [4] to show that for a sequence of 'regular domains' $\Lambda_j \nearrow \mathbb{R}^3$ and densities $\underline{\rho}_j \rightarrow \underline{\rho}$

$$\lim_{j \rightarrow \infty} a_j(\beta, \rho_j^{(1)}, \rho_j^{(2)}) \rightarrow a(\beta, \rho^{(1)}, \rho^{(2)}) \quad (3.2)$$

exists with $a(\rho^{(1)}, \rho^{(2)})$ defined and concave in the positive quadrant of the $\underline{\rho}$ plane ($\beta > 0$ fixed). It follows from this that $a(\rho^{(1)}, \rho^{(2)})$ is continuous in the open quadrant \mathbb{R}_+^2 . The method of proof also yields,

$$a(\underline{\rho}) \sim -\sum \rho^{(i)} \ln \rho^{(i)} \quad \text{as } \underline{\rho} \rightarrow 0 \quad (3.3)$$

and the chemical potentials $\mu_i = -\partial a / \partial \rho^{(i)}$ exist and are monotone for almost all $\underline{\rho} \in \mathbb{R}_+^2$. Independent arguments further prove that $a(\underline{\rho}) + \sum \rho^{(i)} \ln \rho^{(i)}$ is analytic in some domain $D \subset \mathbb{C}^2$ around $\underline{\rho} = 0$ (convergence of the density expansion [16] .) What is not known however is whether, outside the region $D_+ = D \cap \mathbb{R}_+^2$,

$$\lim_{\rho^{(2)} \rightarrow 0} a(\rho^{(1)}, \rho^{(2)}) \stackrel{?}{=} a(\rho^{(1)}) \quad (3.4)$$

the free energy density of the one component system. (The same problem arises when one considers the grand canonical pressure as a function of the fugacities z_1 and z_2). Indeed I do not even know how to prove when $N_j^{(2)}$ is fixed, say one, that $a_j(\beta, \rho_j^{(1)}, 1/V_j)$ approaches the same limit as $a_j(\beta, \rho_j^{(1)})$. Help please!

The difficulty here lies entirely with obtaining an upper bound to a_j (lower bound on the free energy). This requires proving (the "obvious" fact) that configurations in which a finite fraction of particles of species one (A particles) which sit in the "minimum" of the potential of the species two (B) particle make a vanishing contribution to a_j as $j \rightarrow \infty$. There is of course no such problem if the particles have hard cores in which case (for interactions decaying faster than $r^{-(\nu+\epsilon)}$) the interaction energy of any specified particle with the rest of the system is uniformly bounded, e.g. lattice systems. A similar situation obtains when the interaction potential is non-negative - but this still leaves open the general case.

To be a bit more specific let the Hamiltonian of the system, in Λ , be written as

$$H(N_A, N_B, \Lambda) = H(N_A, \Lambda) + H(N_B, \Lambda) + W(N_A, N_B, \Lambda) \quad (3.5)$$

The standard techniques [1,4] will then give, for the partition function Z ,

$$Z(N_A, N_B, \Lambda) > Z(N_A, \Lambda_A) Z(N_B, \Lambda_B) \exp[-\beta \langle W \rangle'] \quad (3.6)$$

where Λ_A and Λ_B are non overlapping regions contained in Λ

and $\langle W \rangle'$ is the expectation value of W in the ensemble specified by having all A-particles in Λ_A and all B-particles in Λ_B . Using the decay of the interaction given in (2.10) the "distance" between Λ_A and Λ_B can be increased, as $\Lambda \nearrow \mathbb{R}^V$, in such a way [1,4] that in the limit $j \rightarrow \infty$.

$$a(\beta, \rho_A, \rho_B) \geq \rho_A / \rho'_A a_A(\beta, \rho'_A) + \rho_B / \rho'_B a_B(\beta, \rho'_B) + c \rho'_A \rho'_B \quad (3.7)$$

where ρ'_A and ρ'_B are the (increased) limiting densities in Λ_A and Λ_B and $c < \infty$ is some constant. Letting $\rho'_B \rightarrow 0$ gives $\rho'_B \rightarrow 0$, $\rho'_A \rightarrow \rho_A$ and the right side of (3.7) then approaches $a(\beta, \rho_A)$ by the continuity of $a_A(\beta, \rho)$, $\rho > 0$, and the bound on $a_B(\beta, \rho)$ as $\rho \rightarrow 0$. (When $N_B/V(\Lambda) \rightarrow 0$ as $\Lambda \nearrow \mathbb{R}^V$ the right side is just $a_A(\beta, \rho_A)$). The same kind of argument, suitably modified for Coulomb systems [1,2], yields (3.1) as a lower bound.

The difficulty arises in getting an upper bound on a . A general method frequently used, for doing this is to define a new Hamiltonian $H_0 = H - G$ where H is given in (3.5). For $G = W$, H_0 is just the energy of the A and B particles in Λ without any mutual interaction. It is however possible to make H_0 be the Hamiltonian of quite a different system, e.g. by adding some particles to the system (as was done in [1]). What is important is that Z_0 be somehow "controllable" in the sense that we can split G into two parts, $G = G_1 + G_2$ and then use the Peierls-Bogolyubow inequality

$$Z_0 = Z(N_A, N_B, \Lambda) < \exp \beta G \rangle \geq Z_1 \exp [\langle G_2 \rangle_1] \quad (3.8)$$

to yield a useful bound on Z . Here $\langle \rangle$ is the expectation taken with the Gibbs measure specified by H in Λ while Z_1 and $\langle \rangle_1$ are obtained from $H_1 = H + G_1$. To be useful we will want $\ln Z_1 / V(\Lambda) \rightarrow a(\beta, \rho_A, \rho_B)$ and the lower bound obtained from (3.8) to coincide with $a(\beta, \rho_A)$ when $\rho_B \rightarrow 0$.

In the case where $G = W = G_2$ we find

$$a(\beta, \rho_A, \rho_B) \leq a(\beta, \rho_A) + a(\beta, \rho_B) - \beta \overline{\langle w \rangle}$$

where $w(x)$ is the pair potential between A and B particles and

$$\begin{aligned}
\langle \bar{w} \rangle &= \lim_{j \rightarrow \infty} \int \left[\frac{1}{V_j} \int_{\Lambda_j} \rho_{AB}(x_1, x_1+x; j) d^V x_1 \right] w(x) d^V x \\
&= \lim_{j \rightarrow \infty} \int \bar{\rho}_{AB}(x; j) w(x) d^V x
\end{aligned} \tag{3.9}$$

$\rho_{AB}(x_1, x_2; j)$ is the density of A,B pairs in Λ_j (for particle numbers $N_{A,j}$ and $N_{B,j}$) and the limit may have to be taken along subsequences. Writing $w(x) = w_+(x) - w_-(x)$, $w_+ \geq 0$, $w_- \geq 0$, we find, using (2.10) that to control the r.s. of (3.9) it is certainly sufficient to have a bound on the radial distribution function

$$-\langle \bar{w} \rangle \leq \rho_A \rho_B^K \lim_{j \rightarrow \infty} \left[\sup_x \bar{\rho}_{AB}(x; j) / \rho_A(j) \rho_B(j) \right] \tag{3.10}$$

with $K = \int w_-(x) d^V x < \infty$ and the sup is over the support of w_- . It should certainly be possible to do this in general.

IV. CORRELATION FUNCTIONS AND SUM RULES

So far we have dealt only with the thermodynamic limit of the free energy - which is necessary and sufficient for the description of the macroscopic behavior of bulk matter. Statistical mechanics goes however beyond thermodynamics in that it also gives a prescription for computing results of microscopic experiments on bulk matter - experiments which directly probe the atomic structure of matter as they show themselves in the deviations from "average" behavior, e.g. fluctuations in the local density measured by x-rays and neutrons.

It is part of the basic dogma of statistical mechanics [4], whose validity has been confirmed experimentally beyond any reasonable doubt (despite the lack of completely convincing theoretical arguments), that the results of such microscopic experiments on macroscopic systems can be obtained in thermal equilibrium, from "appropriate" Gibbs ensembles. These are, for finite systems of N-particles, the canonical (micro, macro grand, ...) ensembles. Results of observations are obtained as ensemble averages using the appropriate density matrix or, for classical systems, the measure on the phase space.

The passage to the infinite volume limit, required to obtain unambiguous, surface independent, results for bulk systems is much more delicate, and therefore mathematically more difficult, for these distributions than it is for the free energy. It is particularly so for quantum systems [17] and I shall not discuss these

further here. For classical systems with rapidly decaying interactions between the particles the mathematical theory is based on the existence of infinite volume Gibbs states [4]. These are the generalization, via the Dobrushin, Lanford and Ruelle equations, of the grand canonical ensemble for a system with a given temperature and fugacity in a finite box Λ . They are (modulo some technical restrictions) the infinite volume thermodynamic limit of all the different ensembles, e.g. microcanonical, canonical, etc..., used to describe finite systems in equilibrium. This requires at the very least that the potential be integrable at infinity, e.g. if the particles interact via a pair potential then it should decay as fast as $r^{-(\nu+\epsilon)}$, e.g. the Lennard-Jones potential which decays as r^{-6} .

A problem occurs however when we are dealing with systems in which the very long range Coulomb force is explicitly present (there is also some problems for dipoles). In this case, there is no conceivable way in which distant parts of a system would be sufficiently decoupled for arbitrary configurations. The usual treatment of infinite volumes Gibbs states, e.g. the DLR equations, will therefore not work here. We expect nevertheless as indicated earlier, that for typical configurations distant parts of an overall neutral system will sufficiently decouple, due to screening, to make the passage to the thermodynamic limit well defined. (For non-neutral systems the limit may present some extra problems). More precisely we expect the correlation functions to have well defined infinite volume limits. This holds indeed at sufficiently high temperatures and low densities where, as described by Brydges here [18] the correlation functions cluster exponentially and for "charge symmetric systems" where it follows from the Fröhlich-Park correlation inequalities [19]. These results however still leave open the question of how to characterize directly the infinite volume Gibbs states of general Coulomb systems in the absence of well defined DLR equations ?

In a recent series of papers [20] Gruber, Martin and their associates have explored the consequences of assuming that the equilibrium correlation functions of Coulomb systems satisfy the stationary BBGKY, (Bogolyubov, Born, Green, Kirkwood, Yvon) hierarchy. These equations are obtained from the time dependent BBGKY hierarchy which describes the time evolution of the n -particle spatial and momentum distribution functions of a classical system $f_n(x_1, p_1, \dots, x_n, p_n; t)$. These have the form [21]

$$\frac{\partial f_n}{\partial t} = H_n f_n + C_{n, n+1} f_{n+1}, \quad n = 1, 2, \dots \quad (4.1)$$

where H and C are linear operators. Assuming that f_n

is a product of a Maxwellian momentum part and a purely spatial part and setting $\frac{\partial f_n}{\partial t} = 0$ leads to an integro-differential equation for the f_n . These stationary eqs. are identically satisfied by the finite volume canonical and grand canonical distribution functions. It is also known that for short range potentials these eqs. are essentially equivalent to the DLR eqs. for the Gibbs states [22]. It is thus expected that the infinite volume limit of the correlations for charged systems will also satisfy them; in fact, this can be rigorously shown to hold for Coulomb systems in one dimension [20] and can presumably be established in all cases where the existence of the infinite volume limit has been proven [23]. It is therefore reasonable to expect that this is always true and explore the consequences which are non-trivial. I now describe briefly this work including extensions in which I participated [24].

Description of the system.

We consider as before a system consisting of k species of charged particles which move either in the whole v -dimensional space \mathbb{R}^v , or in a restricted domain \mathcal{D} defined by appropriate walls. The only condition we impose on \mathcal{D} is that it extends to infinity in at least one direction. Typically \mathcal{D} can be the half-space $\{x \in \mathbb{R}^v; x^1 \geq 0\}$ of the electrode problem.

The particles interact by means of a two body force of the form

$$F_{\alpha_1 \alpha_2}^s(x_1 - x_2) + e_{\alpha_1} e_{\alpha_2} F(x_1 - x_2) \quad \text{where} \quad F_{\alpha_1 \alpha_2}^s(x)$$

is short range and $F(x)$ is the Coulomb force,

$$F(x) \sim \frac{x}{|x|^v}, \quad |x| \rightarrow \infty.$$

The thermodynamic equilibrium state of the system at a temperature T is assumed to be described by means of correlation functions $\rho_{\alpha_1}(x_1)$, $\rho_{\alpha_1 \alpha_2}(x_1, x_2)$, ..., which have their usual meaning,

$\rho_{\alpha_1}(x_1)$ being the density of species α_1 at x_1 , etc... We shall write these as $\rho(q_1)$, $\rho(q_1, q_2)$, $\rho(Q)$, using the abbreviated notation $q_i = (\alpha_i, x_i)$, $Q = (q_{i_1}, \dots, q_{i_n})$. These functions are assumed to satisfy the stationary BBGKY equation

$$\begin{aligned} kTV_1 \rho(q_1, Q) &= [e_{\alpha_1} E(x_1) + \sum_{j=2} F(q_1 - q_j)] \rho(q_1, Q) \\ &+ \int_{\mathcal{D}} dq F(q_1 - q) [\rho(q_1, q, Q) - \rho(q_1, Q) \rho(q)] \end{aligned} \quad (4.2)$$

Here $E(x)$ is the electric field due to all the charges, i.e. all the system's and all the external charges, $F(q_1 - q_2) = e_{\alpha_1} e_{\alpha_2} F(x_1 - x_2)$.

In order to understand (4.2) and the structure of $E(x)$, it is useful to consider first the equilibrium distribution of finite systems in bounded regions $\{\Lambda\}$ and then take the thermodynamic limit $\Lambda \rightarrow \mathcal{D}$. It is easily found that the correlation functions of the finite systems satisfy eq. (4.2) with the electric field $E^\Lambda(x)$ given by the sum of an "external" and an "internal" field

$$\begin{aligned} E^\Lambda(x) &= D^\Lambda(x) + \int_\Lambda dy F(x-y) C^\Lambda(y), \\ C^\Lambda(x) &= \sum_\alpha e_\alpha \rho_\alpha^\Lambda(x) \end{aligned} \quad (4.2)$$

being the charge density at x . Let now $\Lambda \rightarrow \mathcal{D}$ and assume that the state of the finite system converges to a state of the infinite system defined by (4.2). We then have

$$\begin{aligned} E(x) &= D(x) + \lim_{\Lambda \rightarrow \mathcal{D}} \int dy F(x-y) C^\Lambda(y) \\ D(x) &= \lim_{\Lambda \rightarrow \mathcal{D}} D^\Lambda(x) \end{aligned} \quad (4.3)$$

Writing

$$\begin{aligned} C(x) &= \lim_{\Lambda \rightarrow \mathcal{D}} C^\Lambda(x) = \sum_\alpha z_\alpha \rho_\alpha(x), \\ E(x) &= G(x) + \lim_{\Lambda \rightarrow \mathcal{D}} \int_\Lambda F(x-y) C(y), \end{aligned} \quad (4.4)$$

defines the effective external field $G(x)$:

$$G(x) = D(x) + \lim_{\Lambda \rightarrow \mathcal{D}} \int_\Lambda dy F(x-y) (C^\Lambda(y) - C(y)) \quad (4.5)$$

Clearly the second term in (4.5) represents the field due to the system's charges located at infinity when Λ becomes \mathcal{D} . Therefore, one must remember that $G(x)$ has its origin both in external and in the system's charges which reside at "infinity" and are thus invisible in $C(x)$ for any x (see Appendix A in [24] for illustrative example).

It turns out that (4.2) together with certain clustering assumptions on the truncated correlation functions $\rho_T(q_1, \dots, q_n)$ imply the absence of non-translation invariant Gibbs states [25] as well as, certain sum rules. I only describe the latter here.

Electrostatic sum rules.

Define the excess charge density at x in presence of charges located in $Q = (q_1, \dots, q_n)$ as :

$$C(x|Q) = \sum_{\alpha} e_{\alpha} \left(\frac{\rho(\alpha x, Q)}{\rho(Q)} + \sum_j^n \delta_{\alpha \alpha_j} \delta(x-x_j) - \rho(\alpha, x) \right) \quad (4.6)$$

and consider the following relations.

0-sum rule : neutrality

$$\int C(x|Q) dx = 0 \quad (4.7)$$

More explicitly,

$$\left(\sum_j^n e_{\alpha_j} \right) \rho(Q) + \int dq e (\rho(qQ) - \rho(q)\rho(Q)) = 0 \quad .$$

1-sum rule : absence of dipolar moment

$$\int x C(x|Q) dx = 0 \quad , \quad (4.8)$$

or

$$\left(\sum_j^n e_{\alpha_j} x_j \right) \rho(Q) + \int dq e x (\rho(qQ) - \rho(q)\rho(Q)) = 0 \quad .$$

2-sum rule : isotropy

$$\int x^r x^s C(x|Q) dx = \delta_{rs} \frac{1}{v} \int |x|^2 C(x|Q) dx \quad (4.9)$$

Proposition.

$$\text{Let } \rho_T^n(\alpha_1 x_1, \alpha_2 x_2, \dots, \alpha_n x_n) = O\left(\frac{1}{|x_1|^{v+\ell+\epsilon}}\right) \quad \epsilon > 0 \quad (4.10)$$

unif. with respect to x_2 when $n \geq 3$. If (4.11) holds with $\ell = 0$, the 0-sum rule follows. If (4.11) holds with $\ell = 1, 2$, the 1-2 sum rules follow respectively, except in one dimensional Coulomb systems.

Sketch of proof of $\ell = 0$ sum rule for $Q = q_2$

Combination of first and second BBGKY equation and definition of truncated functions gives the identity

$$e_{\alpha_1} \rho(q_1) \rho(q_2) \int F(x_1-x) C(x|q_2) dx = \quad (4.11)$$

$$kT \nabla_1 \rho_T(q_1 q_2) - (e_{\alpha_1} E(x_1) + F(q_1 q_2)) \rho_T(q_1 q_2) - \int dq F(q_1 q) \rho_T(q_1 q_2 q)$$

Clustering hypothesis with $l = 0$ implies that the left side of (4.11) has the form

17

$$\int F(x_1 - x) C(x|q_2) dx = \frac{\hat{x}_1}{|x_1|^{\nu-1}} \int C(x|q_2) dx + o\left(\frac{1}{|x_1|^{\nu-1}}\right) \quad (4.12)$$

and that all terms on the right hand side of (4.11) are

$$o\left(\frac{1}{|x_1|^{\nu-1}}\right)$$

It follows therefore that

$$\int C(x|q_2) dx = 0 .$$

The $l = 1, 2$ sum rules are obtained in a similar way—they are trivial for invariant states when only one particle is kept fixed. In the latter case the right side of (4.9) takes the form $\delta_{rs} I_{\alpha} / (\nu \rho_{\alpha})$, where

$$I_{\alpha} = \int dx |x|^2 \left[\sum_{\alpha} e_{\alpha} \rho_{\alpha, \gamma}^T(|x|, 0) \right] \quad (4.13)$$

is the second moment of the spherically symmetric charge density cloud surrounding an ion of type α located at the origin. This quantity was investigated by Stillinger and Lovett [26] who showed, on the basis of certain physically very reasonable assumptions, that for Coulomb systems

$$\sum_{\alpha=1}^k I_{\alpha} = -2 / (\beta \omega_{\nu}) \quad (4.14)$$

is a universal constant, independent of the short range interactions,

$$\omega_1 = 2, \omega_2 = 2\pi, \omega_3 = 4\pi, \text{ see also [27].}$$

Eq. (4.14) is known as the Stillinger-Lovett second moment condition (the first being the corresponding zero moment condition) and can be shown to hold in the high temperature clustering region of Brydges and Federbush but may fail at low temperatures in two dimensions [23]. An interesting open question is whether (4.14) holds at low temperatures (or at critical points) in three dimensions. This may be related to the question of screening of non-integer charges [6, 24].

V. APPROXIMATIONS

In Erice I spent some time describing certain commonly used schemes for calculating the pair correlation functions, and from them the thermodynamic functions, of a charged fluid, i.e. a molten salt. Among these the Mean Spherical Approximation [28] can be solved easily in a closed form. It yields substantial improvements (when compared with computer and real experiments) over the Debye-Huckel theory at not too low concentrations. A more accurate description is given by the Hyper Netted Chain Approximation which can however only be solved numerically. Since that time there have appeared two review articles covering this material, references [8] and [29]. I refer the interested reader to these excellent expositions. (I should also mention here some interesting recent work on the critical region of the two dimensional Coulomb system by Hoye and Olaussen [30].

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