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THERMODYNAMIC LIMIT FOR COULOMB SYSTEMS

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RESUME

On montre qu'un système de particules chargées avec interactions coulombiennes (et éventuellement en outre des interactions tempérées) à une limite thermodynamique bien définie pour l'énergie libre par unité de volume : celle-ci peut dépendre de la forme pour un système qui n'est pas électriquement neutre. Cela prouve que la mécanique statistique, développée par Gibbs, conduit bien à la thermodynamique pour des systèmes macroscopiques, au moins quand les effets relativistes peuvent être négligés.

ABSTRACT

It is shown that a system of charged particles interacting with coulomb forces (and possibly also with other tempered interactions) has a well defined statistical-mechanically computed, free energy/unit volume in the thermodynamic (bulk) limit : which may be shape dependent when the system is not electrically neutral. This proves that statistical mechanics, as developed by Gibbs, really leads to a proper thermodynamics for macroscopic systems, at least in situations when relativistic effects are not important.

There has grown up in recent years a large body of exact results in statistical mechanics. The most fundamental of these results concern the proof that the equilibrium statistical mechanics developed by Gibbs and Einstein with its later generalization to quantum systems can really yield equilibrium thermodynamics. To be more precise, given our present understanding of the microscopic laws, e.g. Hamiltonian, relevant to the behabior of macroscopic matter in "ordinary circumstances" it is desired to show that the free energy derived from the partition function $Z = \mathrm{tr}\,(e^{-\beta H})$ has the properties postulated by equilibrium thermodynamics, a theory based on macroscopic experiments, i.e., starting from the appropriate partition function, is it true that the resulting properties of matter will be extensive and otherwise the same as those postulated in the science of thermodynamics? In particular, does the thermodynamic, or bulk, limit exist for the free energy derived from the partition function and if so does it have the appropriate convexity, i.e. stability, properties ?

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To be precise, if N_j are an unbounded, increasing sequence of particle numbers, and Ω_j a sequence of reasonable domains (or "boxes") of volume V_j such that $N_j/V_j \longrightarrow$ constant $= \rho$, does the free energy/unit volume

$$f_j = -\beta^{-1}(V_j)^{-1} \ln Z(\beta, N_j, \Omega_j) \quad : \quad Z = [\Sigma_\alpha e^{-\beta E_\alpha(N_j, \Omega_j)}] \qquad (1)$$

approach a limit (called $f(\beta, \rho)$) as $j \longrightarrow \infty$ and is this limit independent of the particular sequence and shape of the domains? If so, is f convex in the density ρ and concave in the temperature, β^{-1}. Convexity is the same as *thermodynamic stability* (non-negative compressibility and specific heat). Here $E_\alpha(N, \Omega)$ is the α th energy level of the N particle system obtained from the solution of the Schroedinger Equation with the requirement that the wave function vanish on the "boundary" of Ω. (There is not a full proof for the existence of the thermodynamic limit for different types of boundary conditions, e.g. periodic or normal derivative vanishing on the boundary).

Various authors have evolved a technique for proving the above [1], but always with one severe drawback. It had to be assumed that the interparticle potentials were short range (in a manner to be described precisely later), thereby excluding the Coulomb potential which is the true potential relevant for real matter. (Actually, Griffiths [2], using the Dyson-Lenard theorem, below, found a way to extend the "canonical" proof [1] to electrically neutral systems with Coulomb forces under the restrictive assumption of complete charge symmetry, i.e. that positive and negative particles have the same mass, spin, etc. but this is clearly insufficient for nuclei and electrons. Similarly Penrose [2] was able to prove the above for the case of a system enclosed by a very special, unphysical, container). That a nice thermodynamic limit exists for neutral systems with Coulomb forces is a fact of common experience, but the proof that it does so is a much more subtle matter than for short range forces. It is screening, brought about by the Coulomb force itself, that causes the Coulomb force to behave as if it were short range.

In this note we will indicate the lines along which a proof for Coulomb forces can be, and has been constructed. The proof itself, which is quite long, will be given elsewhere [3]. We will also list here some additional results for charged systems that go beyond the existence and convexity of $f(\beta, \rho)$.

To begin, with, a *sine qua non* for thermodynamics is the *stability* criterion on the N body Hamiltonian, H = K.E. + V. It is that there exists a constant $B \geqslant 0$ such that for all N

$$V(r_1, \ldots, r_N) \geqslant -BN \quad \text{(classical mechanics)}, \qquad (2)$$

$$E_0 \geqslant -BN \quad \text{(quantum mechanics)} \qquad (3)$$

where E_0 is the ground state energy in infinite space. (Classical stability implies quantum mechanical stability, but not conversely). Heuristically, stability insures against collapse. From the mathematical point of view, it provides a lower bound to f_l in (1). We wish to emphasize that stability of the Hamiltonian (H-stability), while necessary, is insufficient for assuring the existence of thermodynamics. Indeed, the concept of H-stability has very little to do with thermodynamic stability discussed above : (1) H-stability refers to infinite space in which the concept of density does not enter ; (2) No considerations of limit enters the definition ; (3) H-stability does not in itself imply a thermodynamic limit. As an example, it is trivial to prove H-stability for charged particles all of one sign, and it is equally obvious that the thermodynamic limit does not exist in this case.

It is not too difficult to prove classical and thus also quantum H-stability for a wide variety of short range potentials or for charged particles having a hard core [2,4]. But real charged particles require quantum mechanics and the recent proof of H-stability by Dyson and Lenard [5] is as difficult as it is elegant. They show that stability will hold for any set of charges and masses provided that the negative particles and/or the positive ones are fermions. (It is curious that although stability of a small number of charged particles, say an atom, comes about mainly through the uncertainty principle, which keeps the oppositely charged particles apart, to obtain (3) it is also necessary to keep the negative particles apart from each other through the Pauli principle). Dyson and Lennard did not include spin-spin dipolar forces because relativistic considerations are then necessary to keep the binding energies finite (private communication). If the particles have hard cores then Onsager's proof of stability holds also for dipolar interactions and our proof of the thermodynamic limit would automatically apply also to the general case. The magnetic interactions between moving charges, treated to lowest order in v/c, can also be taken into account in our proof.

The second requirement in the canonical proofs [1] is that the potential be *tempered* which is to say that there exists a fixed r_0 and constants $C \geqslant 0$ and $\epsilon > 0$ such that if two groups of N_a and N_b particles are separated by a distance $r > r_0$ their interparticle energy is bounded by

$$V(N_a \oplus N_b) - V(N_a) - V(N_b) \leqslant C r^{-(3+\epsilon)} N_a N_b \tag{4}$$

Tempering is roughly the antithesis of stability because the requirements that the forces are not too repulsive at infinity insures against "explosion". Coulomb forces are obviously not tempered and for this reason the canonical proofs have to be altered. Our proof, however, is valid for a mixture of Coulomb and tempered potentials and this will always be understood in the theorems below. It is not altogether useless to include tempered potentials along with the true Coulomb potentials because one might wish to consider model systems in which ionized molecules are the elementary particles.

Prior to explaining how to overcome the lack of tempering we list the main theorems we are able to prove. These are true classically as well as quantum mechanically. But first three definitions are needed :

D1 : We consider s species of particles with charges e_i, particle numbers $N^{(i)}$ and densities $\rho^{(i)}$. In the following N and ρ are a shorthand notation for s fold multiplets of numbers. The conditions for H-stability (see above) are assumed to hold.

D2 : A neutral system is one for which $\sum_i^s N^{(i)} e_i = 0$, alternatively

$$\sum_i^s \rho^{(i)} e_i = 0 \ .$$

This requires the fundamental charges to be rational multiples of some unit charge.

D3 : The ordinary s species grand canonical partition function is

$$\sum_{N^{(s)}=0}^{\infty} \cdots \sum_{N^{(1)}=0}^{\infty} \left[\prod_i^s e^{\beta \mu_i N^{(i)}} \right] Z(N, \Omega) \tag{5}$$

with μ_i the chemical potential of the i th species.

The neutral grand canonical partition function is the same as (5) except that only neutral systems enter the sum. The theorems are :

T1 : The canonical thermodynamic limiting free energy/unit volume, $f(\beta, \rho)$ exists for a neutral system and is independent of the shape of the domain for reasonable domains. Furthermore, $f(\beta, \rho^{(1)}, \rho^{(2)}, \ldots)$ is concave in β^{-1} and jointly convex in the s variables $(\rho^{(1)}, \ldots \rho^{(s)})$.

T2 : The thermodynamic limiting microcanonical [6] entropy/unit volume exists for a neutral system and is a concave function of the energy/unit volume. It is also independent of domain shape for reasonable shapes, and is equal to the entropy computed from the canonical free energy.

T3 : The thermodynamic limiting free energy/unit volume exist for both the ordinary and the neutral grand canonical ensembles and are independent of domain shape for reasonable domains. Moreover, they are equal to each other and equal to the canonical pressure.

Theorem 3 states that systems which are not charge neutral make a vanishingly small contribution to the grand canonical free energy. While this is quite reasonable physically, it does raise an interesting point about non-uniform convergence because the ordinary and neutral partition functions are definitely not equal if we switch off the charge before passing to the thermodynamic limit, whereas they are equal if the limits are taken in the reverse order.

An interesting question is how much can charge neutrality be violated before the free energy/unit volume deviates appreciably from its neutral value ? This is answered by

T4 : Consider the canonical free energy with a surplus (i.e. imbalance) of charge Q and take the thermodynamic limit in either of three ways :

(a) $QV^{-2/3} \longrightarrow 0$; (b) $QV^{-2/3} \longrightarrow \infty$; (c) $QV^{-2/3} \longrightarrow$ constant.

In case (a) the limit is the same as for the neutral system while in case (b) the limit does not exist, i.e. $f \longrightarrow \infty$. In case (c) the free energy approaches a limit equal to the neutral system free energy plus the energy of a surface layer of charge Q as given by elementary electrostatics. This energy is of course shape dependent and the existence of the thermodynamic limit for non-neutral systems requires, at the minimum, that shapes of domains Ω_l approach some reasonable limiting shape. For a sequence of spherical domains the excess free energy/per unit volume is equal to $6\pi\sigma^2$ where $\sigma = \lim_{R \to \infty} [Q/4\pi R^2]$.

We turn now to a sketch of the method of proof and will restrict ourselves here to the neutral canonical ensemble. As usual, one first proves the existence of the limit for a standard sequence of domains. The limit for an arbitrary domain is then easily arrived at by packing that domain with the standard ones. The basic inequality that is needed is that if a domain Ω containing N particles is partitioned into D domains $\Omega_1, \Omega_2, \ldots, \Omega_D$ containing $N_1, N_2, \ldots, N_D$ particles respectively and if the inter-domain interaction be neglected then

$$Z(N, \Omega) \geq \prod_1^D Z(N_l, \Omega_l)\,, \tag{6}$$

(Classically, this inequality comes from restricting the configuration space integral. Quantum mechanically, it stems from the observation that the artificial introduction of nodes into the wave functions raises all the energy levels [1]). If Ω is partitioned into sub-domains as above plus "corridors" of thickness $> r_0$ which are devoid of particles, one can use (4) to obtain a useful bound on the tempered part of the omitted inter-domain interaction energy. We will refer to these energies as surface terms.

The normal choice [1] for the standard domains are cubes, C_l, containing N_l particles with C_{l+1} being composed of eight copies of C_l, together with corridors and $N_{l+1} = 8N_l$. Neglecting surface terms one would have from (6) and (1)

$$f_{l+1} \leq f_l \,. \tag{7}$$

Since f_j is bounded below by H-stability, (7) implies the existence of a limit. To justify neglect of the surface terms one makes the corridors increase in thickness with increasing j although V_j^c, the corridor volume, approaches ∞ one makes $V_j^c/V_j \longrightarrow 0$ in order that the limiting density not vanish. The positive ϵ of (4) allows one to accomplish these desiderta.

Obviously, such a strategy will fail with Coulomb forces, but fortunately there is another way to bound the inter-domain energy. The essential point is that it is not necessary to bound this energy for all possible states of the systems in the sub domains; it is only necessary to bound the "average" interaction between domains which is much easier. This is expressed mathematically by using the Peierls-Bogoliubov inequality to show that

$$Z(N, \Omega) \geqslant e^{-\beta U} \prod_{i}^{D} Z(N_i, \Omega_i) \tag{8}$$

where U is the *average* inter-domain energy in an ensemble where each domain is independent. U consists of a coulomb part, U_c, and a tempered part U_t, which can be readily bounded [1]. (Griffiths' result [2], referred to above, follows from (8) by noting that if each sub-domain were charge neutral U_c would vanish *provided* the particles were charge symmetric. In the absence of external fields, the spin dipole-dipole interaction would vanish for the same reason). We now make the observation, which is one of the crucial steps in our proof, that independently of charge symmetry U_c will vanish if the sub-domains are spheres and are *overall* neutral. The rotational invariance of the Hamiltonian will produce a spherically symmetric charge distribution in each sphere and, as Newton [7] observed, two such spheres would then interact as though their total charges (which are zero) were concentrated at their centers.

With this in mind we choose spheres for our standard domains. Sphere S_j will have radius $R_j = p^j$ with p an integer. The price we pay for using spheres instead of cubes is that a given one, S_k, cannot be packed arbitrarily full with spheres S_{k-1} only. We prove, however, that it can be packed arbitrarily closely (as $k \longrightarrow \infty$) if we use *all* the previous spheres $S_{k-1}, S_{k-2}, \ldots S_0$. Indeed for the sequence of integers

$$n_1, n_2, \ldots, n_j = (p-1)^{(j-1)} p^{2j}$$

we can show that we can simultaneously pack n_j spheres S_{k-j} into S_k for $1 \leqslant j \leqslant k$. The fractional volume of S_k occupied by the S_{k-j} spheres is $\varphi_j = p^{-3j} n_j$ and from (8) we then have

$$f_k \leqslant \varphi_1 f_{k-1} + \varphi_2 f_{k-2} + \cdots + \varphi_k f_0 \tag{9}$$

and

$$\sum_{1}^{\infty} \varphi_j = 1 \tag{10}$$

(Note : (6) is correct as it stands for pure Coulomb forces because U_c in (8) is identically zero. If short range potentials are included there will also be surface terms, as in the cube construction, but these present only a technical complication that can be handled in the same manner as before [1]). While Eq. (9) is more complicated than (7) it is readily proven explicitly that f_k approaches a limit as $k \longrightarrow \infty$. [Indeed, it follows from the theory of the renewal equation [8] that (9) will have a limit if $\sum_1^\infty j\varphi_j < \infty$].

The possibility of packing spheres this way is provided by the following geometrical theorem which plays the key role in our analysis. We state it without proof, but we do so in d-dimensions generally. The notation is : σ_d = volume of a unit d-dimensional sphere = $4\pi/3$ in 3 dimensions ; $\alpha_d = (2^d - 1)\, 2d^{1/2}$.

T5 : Let $p \geqslant \alpha_d + 2^d \sigma_d^{-1}$ be a positive integer. For all positive integers, j, define radii $r_j = p^{-j}$ and integers $n_j = (p-1)^{j-1} p^{j(d-1)}$. Then it is possible to place simultaneously U_j (n_j spheres of radius r_j) into a unit d-dimensional sphere so that none of them overlap.

The minimum allowed value of p is 27 in 3 dimensions.

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