

served following a Penning reaction. The polarization of the ion should not be disturbed by radiative processes^{7,8}; consequently, a large polarization of the ion ground-state atoms can be obtained. This technique should be applicable to a wide variety of ions and provide a useful source of beams of highly polarized ions. We finally wish to point out that the electron that comes off in the reaction should also be polarized. The method of producing a polarized electron beam introduced by Walters and his colleagues⁹ could be improved by several orders of magnitude by the addition of an impurity such as Cd to the optical-pumping cell.

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EXISTENCE OF THERMODYNAMICS FOR REAL MATTER WITH COULOMB FORCES

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It is shown that a system made up of nuclei and electrons, the constituents of ordinary matter, has a well-defined statistical-mechanically computed free energy per unit volume in the thermodynamic (bulk) limit. This proves that statistical mechanics, as developed by Gibbs, really leads to a proper thermodynamics for macroscopic systems.

In this note we wish to report the solution to a classic problem lying at the foundations of statistical mechanics.

Ever since the daring hypothesis of Gibbs and others that the equilibrium properties of matter could be completely described in terms of a phase-space average, or partition function, $Z = \text{Tr} e^{-\beta H}$, it was realized that there were grave difficulties in justifying this assumption in terms of basic microscopic dynamics and that such delicate matters as the ergodic conjecture stood in the way. These questions have still not been satisfactorily resolved, but more recently still another problem about Z began to receive attention: Assuming the validity of the 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?

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 $N_j/V_j \rightarrow \text{constant} = \rho$, does the free energy per unit volume

$$f_j = -kT(V_j)^{-1} \ln Z(\beta, N_j, \Omega_j) \quad (1)$$

approach a limit [called $f(\beta, \rho)$] as $j \rightarrow \infty$, 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).

Various authors have evolved a technique for proving the above,^{1,2} 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. 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 the limiting free energy.

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

$$V(r_1, \dots, r_N) > -BN \quad (\text{classical mechanics}), \quad (2)$$

$$E_0 > -BN \quad (\text{quantum mechanics}), \quad (3)$$

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_j in (1). We wish to emphasize that stability of the Hamiltonian (H stability), while necessary, is insufficient for assuring the existence of thermodynamics. For 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-mechanical 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 Lenard⁵ 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.

The second requirement in the canonical proofs¹ is that the potential be tempered, which is to say that there exist a fixed r_0 and constants $C \geq 0$ 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

$$V(N_a \oplus N_b) - V(N_a) - V(N_b) \leq Cr^{-(3+\epsilon)} N_a N_b. \quad (4)$$

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 $\sum_1^s N^{(i)} \times e_i = 0$, alternatively $\sum_1^s \rho^{(i)} e_i = 0$.

(D3) The ordinary s -species grand canonical partition function is

$$\sum_{N^{(s)}=0}^{\infty} \cdots \sum_{N^{(1)}=0}^{\infty} \prod_i^s z_i^{N^{(i)}} Z(N, \Omega). \quad (5)$$

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

The theorems are the following:

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

(T2) The thermodynamic limiting microcanonical⁶ entropy per unit volume exists for a neutral system and is a concave function of the energy per unit volume. It is also independent of domain shape for reasonable shapes and it is equal to the entropy computed from the canonical free energy.

(T3) The thermodynamic limiting free energy per unit volume exists 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 to the neutral canonical free energy per unit volume.

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 nonuniform 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 nonconserved before the free energy per unit volume deviates appreciably from its neutral value? The answer is in theorem 4.

(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) $QV^{-2/3} \rightarrow 0$; (b) $QV^{-2/3} \rightarrow \infty$; (c) $QV^{-2/3} \rightarrow \text{const.}$ In case (a) the limit is the same as for the neutral system while in case (b) the limit does not exist, i.e., $f \rightarrow \infty$. 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.

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 $\Omega_1, \Omega_2, \dots, \Omega_D$ containing N_1, N_2, \dots, N_D particles, respectively, and if the interdomain interaction be neglected, then

$$Z(N, \Omega) \geq \prod_1^D Z(N_i, \Omega_i). \quad (6)$$

If Ω is partitioned into subdomains, 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 interdomain interaction energy. We will refer to these energies as surface terms.

The normal choice¹ for the standard domains are cubes C_j containing N_j particles, with C_{j+1} being composed of eight copies of C_j together with corridors, and with $N_{j+1} = 8N_j$. Neglecting surface terms one would have from (6) and (1)

$$f_{j+1} \leq f_j. \quad (7)$$

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 $V_j^C/V_j \rightarrow 0$ in order that the limiting density not vanish. The positive ϵ of (4) allows one to accomplish these desiderata.

Obviously, such a strategy will fail with Coulomb forces, but fortunately there is another way to bound the interdomain energy. The essential point is that it is not necessary to bound this energy for all possible states of the systems in the subdomains; it is only necessary to bound the "average" interaction between domains, which is much easier. This is expressed mathematically by using the Peierls-Bogoliubov inequality⁷ to show that

$$Z(N, \Omega) \geq e^{-\beta U} \prod_1^D Z(N_i, \Omega_i), \quad (8)$$

where U is the average interdomain 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

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 subdomains are spheres and are overall neutral. The rotation invariance of the Hamiltonian will produce a spherically symmetric charge distribution in each sphere and, as Newton⁸ 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 $k \rightarrow \infty$) if we use all the previous spheres $S_{k-1}, S_{k-2}, \dots, S_0$. Indeed for the sequence of integers $n_1, n_2, \dots, n_j = (p-1)^{j-1} p^{2j}$ we can show that we can simultaneously pack n_j spheres S_{k-j} into S_k for $1 \leq j \leq k$. 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

$$f_k \leq \varphi_1 f_{k-1} + \varphi_2 f_{k-2} + \dots + \varphi_k f_0, \quad (9)$$

and

$$\sum_1^\infty \varphi_j = 1. \quad (10)$$

[Note that the inequality (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 $k \rightarrow \infty$. [Indeed, it follows from the theory of the renewal equation⁹ that (9) will have a limit if $\sum_1^\infty j\psi_j < \infty$.]

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 and use the following notation: σ_d = volume of a unit d -dimensional sphere = $\frac{4}{3}\pi$ in three dimensions and $\alpha_d = (2^d - 1)2^{d/2}$.

(T5) Let $p \geq \alpha_d + 2^d \sigma_d^{-1}$ 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 $\bigcup_j (n_j \text{ spheres of radius } r_j)$ into a unit d -dimensional sphere so that none of them overlap.

The minimum value of p required by the theorem in three dimensions is 27.

Many of the ideas presented here had their genesis at the Symposium on Exact Results in Statistical Mechanics at Irvine, California, in 1968, and we should like to thank our colleagues for their encouragement and stimulation: M. E.

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SUPERCONDUCTIVITY OF BARIUM UNDER PRESSURE*

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Superconductivity of barium is observed under high volume compression. The high-pressure phase, Ba II, has a T_C somewhat lower than 1.3°K at 55 kbar, T_C sharply rising with increase of pressure. A second solid phase above 140 kbar has a T_C of approximately 5°K.

Since the discovery of superconductivity in cerium,¹ barium was also thought to become superconducting under pressure. If there is a common origin of superconductivity in neighboring lanthanum and cerium it seemed worthwhile to look at barium, naively assuming similar electronic properties might exist if it were compressed to the same density.² The abnormal pressure dependence of the electrical resistivity³ (cf. Fig. 1) as well as the highly abnormal P - T phase diagram

showing two maxima of the melting temperature⁴ indicate fundamental changes of electronic structure with pressure.

The apparatus and procedure have been described in a recent publication.⁵ Difficulties of sample preparation and cell loading caused by the chemical reactivity of barium as previously mentioned⁵ were overcome by covering the thin (20- μ) metal strip with a film of petrolatum. Two disks of Mylar foil (thickness 6 μ) provide protection