

## Low density form of the free energy for real matter\*

Joel L. Lebowitz and Rafael E. Pena

Belfer Graduate School of Science, Yeshiva University, New York, New York 10033

(Received 22 March 1973)

We prove that the thermodynamic free energy per unit volume of an over-all neutral system, composed of electrons and nuclei interacting via Coulomb forces, has the low density asymptotic form  $kT \sum_{\alpha=0}^s \rho^\alpha \ln \rho^\alpha$ . Here  $\rho^0$  is the over-all number density of electrons and  $\rho^\alpha$ ,  $\alpha = 1, \dots, s$  the number density of nuclei of species  $\alpha$ . This indicates that, as expected on the basis of nonrigorous arguments, any real physical system will become completely ionized as the density approaches zero (at a fixed nonzero temperature).

### I. INTRODUCTION

We consider a system consisting of electrons and  $s$  different nuclear species all contained in a three-dimensional region  $\Lambda$  of volume  $V(\Lambda)$ . Choosing units in which the electron charge is  $-1$ , each nuclear species will have a positive integer charge  $e_\alpha$ . Let  $N^0$  be the number of electrons and  $N^\alpha$  the number of nuclei of species  $\alpha$ ,  $\alpha = 1, \dots, s$ . Define  $\mathbf{N} = (N^0, N^1, \dots, N^s)$  to be the particle number vector with  $N = \sum_{\alpha=0}^s N^\alpha$ . Neutrality is guaranteed by imposing upon the  $N^\alpha$  the condition that  $\sum_{\alpha=1}^s N^\alpha e_\alpha = N^0$ .

The Hamiltonian of the system will consist of a kinetic term  $T$  and a Coulomb interaction term  $U$ . The canonical partition function of the system will be designated by  $Z(\mathbf{N}; \Lambda)$  and the Helmholtz free energy per unit volume by  $a(\rho; \Lambda) = -\ln Z(\mathbf{N}, \Lambda)/V(\Lambda)$  where  $\rho = \mathbf{N}/V$  is the density vector, and we are using units in which  $kT = 1$ ,  $k$  being Boltzmann's constant.

It has been shown recently<sup>1</sup> that the limit of the free energy density when the size of the domain  $V(\Lambda) \rightarrow \infty$  (the thermodynamic limit) exists. Formally one considers a sequence of "reasonably-shaped" domains  $\Lambda_j$  and particle number vectors  $\mathbf{N}_j$  so that  $V_j \rightarrow \infty$  and  $\rho_j = \mathbf{N}_j/V_j \rightarrow \rho$ . It is then shown that when  $\sum_{\alpha=0}^s N_j^\alpha e_\alpha = 0$ , then  $\lim_{j \rightarrow \infty} a(\rho_j; \Lambda_j) = a(\rho)$  exists and is independent of the "shapes" of the domains  $\Lambda_j$ . (For other results see Ref. 1.)

In this paper we shall be concerned exclusively with the "low density" behavior of the free energy density. Setting  $\rho^\alpha = y_\alpha \rho$ , where  $\rho = \sum_{\alpha=0}^s \rho^\alpha$  is the overall density and the  $y_\alpha$  are independent of  $\rho$  we shall show that at low densities,  $\rho \leq \bar{\rho}$ , (with  $\bar{\rho}$  some fixed and for our purposes irrelevant density)

$$\left| a(\rho) - \sum_{\alpha=0}^s \rho^\alpha \ln \rho^\alpha \right| \leq K\rho, \quad (1.1)$$

where  $K$  is some finite constant. Physically (1.1) corresponds to the system being entirely "ionized" at low enough densities. Taking the "neutral

atoms" to be the basic units the low density behavior of  $a(\rho)$  would be expected to be  $\sum_{\alpha=1}^s \rho^\alpha \ln \rho^\alpha$  since  $\rho^\alpha$ ,  $\alpha \geq 1$ , is the density of the atoms of species  $\alpha$ . (Partial ionization would give similar incorrect results.)

The proof of (1.1) will be accomplished by establishing upper and lower bounds on  $a(\rho)$ . The arguments are similar to those used frequently in Ref. 1 and we will therefore be very brief. Also for the sake of brevity we consider only purely Coulombic interactions. The addition of "tempered interactions" presents no difficulty and does not change the results.

### II. LOWER BOUND FOR $a(\rho)$

The Hamiltonian of the system has the form

$$H(\mathbf{N}; \Lambda) = T(\mathbf{N}; \Lambda) + U(\mathbf{N}) \quad (2.1)$$

with  $T(\mathbf{N}; \Lambda)$  the kinetic energy operator and  $U$  the Coulomb potential energy:

$$U(\mathbf{N}) = \sum_{1 \leq i \leq j \leq N} e^i e^j / |\mathbf{x}_i - \mathbf{x}_j|, \quad (2.2)$$

where  $e^i$  is the charge of the  $i$ th particle (which depends on the species) and  $\mathbf{x}_i$  is the position vector of the  $i$ th particle in  $\Lambda \subset R^3$ . The electrons are Fermions and the nuclei may be either Fermions or Bosons. (We do not include the spin explicitly since that would not change the result.)

The Hamiltonian may be written as

$$H(\mathbf{N}; \Lambda) = H^*(\mathbf{N}; \Lambda) + \left(\frac{1}{2}\right) T(\mathbf{N}; \Lambda), \quad (2.3)$$

where  $H^*$  is just the Hamiltonian for the system under consideration in which all masses  $m_\alpha$  have been doubled.

Using the Dyson-Lenard theorem to obtain a lower bound for  $H^*$  it is readily shown<sup>1</sup> that

$$Z(\mathbf{N}; \Lambda) = \text{Tr} \{e^{-H}\} \leq \exp[NB] \prod_{\alpha=0}^s Z_{0\alpha}(N^\alpha; \Lambda), \quad (2.4)$$

where  $B$  is a constant, independent of  $\mathbf{N}$  or  $\Lambda$ , and  $Z_{0\alpha}$  is the ideal gas partition function for  $N^\alpha$  parti-

cles with masses  $2m_\alpha$  and appropriate statistics. The partition function for an ideal Fermi gas is readily bounded by that of an ideal Boltzmann gas which can be evaluated explicitly for large  $\Lambda$  (since  $a(\rho)$  is shape independent we can use cubical boxes for  $\Lambda$ ). For the Bose ideal gas there is an upper bound of the form,<sup>2</sup>

$$Z_{0\alpha}(N^\alpha; \Lambda) \leq \exp(N^\alpha \{1 - \ln[1 - \exp(-\rho^\alpha \lambda_\alpha^3)]\}), \quad (2.5)$$

where  $\lambda_\alpha = (\hbar^2/4\pi m_\alpha)^{1/2}$ .

Taking logs in (2.4) dividing by  $V(\Lambda)$  and going to the thermodynamic limit we readily find in all cases

$$a(\rho) \geq \sum_{\alpha=0}^s \rho^\alpha \ln \rho^\alpha + K_1 \rho + K_2 \rho, \quad \rho \leq \bar{\rho}, \quad (2.6)$$

where  $K_1$  is some constant independent of  $\rho$  and  $\bar{\rho}$  is some fixed finite density. (The restriction to low densities  $\rho \leq \bar{\rho}$  is needed only when some species are Bosons.)

### III. UPPER BOUND FOR $a(\rho)$

To get an upper bound for  $a(\rho)$  we make use of the basic inequality used in Ref. 1. It is proven there (cf. 1b sec. II) that

$$Z(\mathbf{N}; \Lambda) \geq \prod_{i=1}^J Z(\mathbf{N}_{(i)}; \Lambda_{(i)}) \exp[-\langle W \rangle], \quad (3.1)$$

where  $Z(\mathbf{N}_{(i)}; \Lambda_{(i)})$  is the partition function of a group of  $\mathbf{N}_{(i)}$  particles in a domain  $\Lambda_{(i)}$ . The  $\Lambda_{(i)}$ ,  $i = 1, \dots, J$  are disjoint subdomains of  $\Lambda$  and the  $\mathbf{N}_{(i)}$  are disjoint subsets of  $\mathbf{N} = \sum_{i=1}^J \mathbf{N}_{(i)}$ .  $W$  is the interdomain interaction energy, here purely Coulombic:

$$W = \sum_{1 \leq i < j \leq J} W_{ij},$$

with  $W_{ij}$  the Coulomb interaction energy between particles in domain  $\Lambda_{(i)}$  with particles in domain  $\Lambda_{(j)}$ . The expectation value  $\langle W \rangle$  is to be taken with respect to an ensemble in which each subdomain is independent of the others, i. e., as if there were no interaction between particles in different domains. A particular consequence of (3.1) is that when the domains  $\Lambda_{(i)}$  are spheres, say  $S_i$ , then  $\langle W_{ij} \rangle = Q_i Q_j / R_{ij}$ , where  $Q_k$ ,  $k = 1, \dots, J$  is the total charge in  $S_k$ ,  $Q_k = \sum_{\alpha=0}^s N_{(k)}^\alpha e_\alpha$ , and  $R_{ij}$  is the distance between the centers of the spheres  $S_i$  and  $S_j$ . In particular  $\langle W_{ij} \rangle$  will be zero if either  $Q_i$  or  $Q_j$  (or both) are zero, i. e., if either  $S_i$  or  $S_j$  is neutral over-all.

We now make the following construction. We divide  $\Lambda$  into  $M$  cubes of side  $D$ ;  $D^3 = V(\Lambda)/M$ , where  $M = \sum_{\alpha=1}^s N^\alpha$  is the number of nuclei in the system. (Since  $a(\rho)$  is shape independent no harm is done by

assuming that  $\Lambda$  has a shape in which  $M$  cubes fit perfectly.) Inside each such cube we now inscribe a sphere  $S_i$ ,  $i = 1, \dots, M$  of diameter  $D$  and place inside each  $S_i$  one nucleus and a number of electrons equal to  $e_\alpha$  the charge of that nucleus. Thus each  $S_i$  will contain a neutral atom of some species  $\alpha$ . Let us denote by  $M_i^\alpha$  the "atom" of species  $\alpha$  in  $S_i$ . Then by (3.1)

$$Z(\mathbf{N}; \Lambda) \geq \prod_{i=1}^M Z(M_i^\alpha; S_i) = \prod_{\alpha=1}^s [Z(M^\alpha; S)]^{N^\alpha}, \quad (3.2)$$

where in the second equality we have used the fact that there are  $N^\alpha$  atoms of type  $\alpha$  and that  $Z(M_i^\alpha; S_i)$  is the same for all  $i$ .

We now place into each sphere  $S_i$ , which contains an atom of species  $\alpha$  (and thus  $e_\alpha + 1$  particles),  $e_\alpha + 1$  spheres  $C^\alpha$  of diameter  $R_\alpha$ . ( $R_\alpha$  is made as large as will make the  $C^\alpha$  fit in  $S$ .)

Using (3.1) again,

$$Z(M^\alpha; S) \geq Z(\alpha; C^\alpha) [Z(e; C^\alpha)]^{e_\alpha} \exp[-\langle W_\alpha \rangle], \quad (3.3)$$

where  $Z(\alpha; C^\alpha)$  is the partition function of a single nucleus of type  $\alpha$  in a sphere of diameter  $R_\alpha$  and  $Z(e; C^\alpha)$  is the partition function of a single electron in such a sphere. The interaction  $\langle W_\alpha \rangle$  can now be explicitly evaluated or readily bounded.  $|\langle W_\alpha \rangle| \leq (3/2) e_\alpha^2 R_\alpha^{-1}$ , where  $R_\alpha$  is proportional to  $D = (V(\Lambda)/M)^{1/3}$ . The important point now is that there is a bound on this interaction energy  $\langle W_\alpha \rangle$  which is independent of the size of the system when  $\mathbf{N}(\Lambda)/V(\Lambda) \rightarrow \rho$ . Hence its contribution to  $a(\rho)$  will be bounded by a term of  $\theta(\rho^{4/3})$ .

We are finally left with the problem of finding a lower bound for the partition function of a single particle in a sphere  $C$  of diameter  $R$ . This can be readily done by inscribing in  $C$  a cube of side  $R' = R/\sqrt{3}$  restricting the particle to be inside the cube and using (3.1). Since the energy levels of a single particle in such a cube are simply  $(\hbar^2 \pi^2 / 2mR'^2) \times (n_x^2 + n_y^2 + n_z^2)$  with  $n_x, n_y, n_z$  integers,

$$Z(\alpha; C^\alpha) \geq \sum_{n=0}^{\infty} (q_\alpha^{n^2})^3 - 1 \geq (\pi m_\alpha / 2\hbar^2)^{3/2} R_\alpha'^3 - 1, \quad (3.4)$$

where  $q = \exp[-\hbar^2 \pi^2 / 2m_\alpha R_\alpha'^2]$  and we have used the inequality

$$\sum_{n=0}^{\infty} q^{n^2} \geq \int_0^{\infty} dn q^{n^2}$$

for  $q < 1$ . A similar relation with  $m_\alpha$  replaced by  $m_0$  holds for  $Z(e; C^\alpha)$ .

By our construction  $R_\alpha = A_\alpha \rho^{-1/3}$ ,  $A_\alpha$  a constant independent of  $\mathbf{N}$  or  $\Lambda$ . Hence for  $\rho < \bar{\rho}$ ,  $\bar{\rho}$  some

constant, (3.3) may be written as

$$Z(M^\alpha; S) \geq K_\alpha a^{-(e_\alpha+1)}, \quad (3.5)$$

where  $K_\alpha$  is a constant independent of  $N$  and  $\Lambda$  for  $N/V(\Lambda) \rightarrow \rho$ ,  $\rho^\alpha \rightarrow y_\alpha \rho$ . Combining (3.2), (3.3), and (3.5) yields the desired result

$$a(\rho) \leq \sum_{\alpha=0}^s \rho^\alpha \ln \rho^\alpha + K_2 \rho, \quad \rho \leq \bar{\rho}. \quad (3.6)$$

Combining (3.6) and (3.5) yields (1.1).

#### ACKNOWLEDGMENT

We would like to thank Dr. Elliott Lieb for valuable discussions.

\*Research supported by USAFOSR grant No. AFOSR-73-2430.

<sup>1</sup>J. L. Lebowitz and E. H. Lieb, Phys. Rev. Lett. **22**, 631 (1969); E. H. Lieb and J. L. Lebowitz, Adv. Math. **9**, 317 (1972).

<sup>2</sup>M. E. Fisher, Arch. Ration. Mech. Anal. **17**, 377 (1964), cf. also errata.