

not be stressed unduly. Nevertheless, while maintaining strong reservations of judgement because of our very literal application of the nearly free electron model, we are inclined to view the results of Klee and Witte as providing an experimental demonstration of the great strength of band-band interaction in influencing the magnetic properties of electrons in metals.

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<sup>1</sup> H. Klee and H. Witte, *Z. Phys. Chem.* **202**, 352 (1954).

<sup>2</sup> E. N. Adams, II, *Phys. Rev.* **89**, 633 (1953).

<sup>3</sup> R. Peierls, *Z. Physik.* **80**, 763 (1933).

## Quantum Statistics of Closed and Open Systems

F. ANSBACHER AND P. T. LANDSBERG

*Department of Natural Philosophy, University of Aberdeen, Scotland*

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THE exact mean occupation numbers for an ideal Fermi-Dirac or Bose-Einstein gas on the basis of a canonical ensemble are respectively given by<sup>1,2</sup>

$$n(N, j) = 1 / \left\{ \frac{Z_{N+1}}{Z_N} \frac{n(N+1, j)}{n(N, j)} \exp \eta(j) \pm 1 \right\} \quad (\text{all } j, \text{ all } N, T > 0). \quad (1)$$

$\eta(j)$  is the energy divided by  $nT$  of the  $j$ th quantum state and  $Z_N$  is the partition function if  $N$  particles are in the volume  $V$ . It has been shown<sup>3,4</sup> that these expressions go over into those which are obtained on the basis of a grand canonical ensemble under those limiting conditions for which

$$n(N+1, j)/n(N, j) \sim 1 \quad (\text{all } j, T > 0), \quad (2)$$

where  $\sim$  denotes an equality for the limiting case. It has been pointed out<sup>3,4</sup> that condition (2) should hold if the system is infinitely large, but has a finite and nonzero volume density of particles (the "limit  $L$ "). The proof of this statement was made to depend on the inequalities

$$n(N+1, j)/n(N, j) > 1 \quad (\text{all } j, \text{ finite } N, T > 0), \quad (3)$$

which hold for Fermi-Dirac<sup>3</sup> and Bose-Einstein<sup>5</sup> systems. But the argument employed was not rigorous.<sup>6</sup>

In fact, let

$$n(N+1, j)/n(N, j) = 1 + \alpha(N, j), \quad \alpha(N, j) > 0 \quad (\text{all } j, \text{ all } N); \quad (4)$$

then

$$\sum_j \alpha(N, j) n(N, j) = 1. \quad (5)$$

It is easy to see from (5) that  $\alpha \leq 1/N$  for some (or possibly all) quantum states, so that (2) may hold as  $N \rightarrow \infty$ , whatever the volume  $V$  of the system. However,

(5) does not ensure that (2) holds for *all* quantum states, though this now becomes a reasonable conjecture. The argument which was previously used fails now because the inequality  $n(N+1, j)/n(N, j) \geq \sum_k n(N+1, k)/\sum_k n(N, k)$  does not necessarily hold for all states  $j$ .

We therefore consider it worth while to give an independent and rigorous argument which leads to (2) in the limit  $L$ . In the Fermi-Dirac case we use (3) and the result<sup>2</sup>

$$n(N+1, j) = (Z_N/Z_{N+1}) [1 - n(N, j)] \exp[-\eta(j)]. \quad (6)$$

Replacing first  $n(N+1, j)$  by  $n(N, j)$  on the left, and then  $n(N, j)$  by  $n(N+1, j)$  on the right, we find

$$\dots > n(N+1, j) > \mu(N, j) > n(N, j) > \mu(N-1, j) > \dots, \quad (7)$$

where

$$\mu(N, j) \equiv 1/[1 + (Z_{N+1}/Z_N) \exp \eta(j)]. \quad (8)$$

For all limiting processes for which  $Z_{N+1}/Z_N \sim Z_N/Z_{N-1}$  we must have  $n(N, j) \sim \mu(N, j)$ . Comparison of (8) and (1) shows then that (2) holds.

In the Bose-Einstein case no relation of type (7) can be found which has equal generality, and one must proceed in a different way. The basic recurrence relation is in this case<sup>5</sup>

$$x_{N+1} a_{N+1} = a_N + 1 - (1/x_N), \quad (9)$$

where  $x_N \equiv n(N, j)/n(N-1, j)$ ,  $a_N \equiv (Z_N/Z_{N-1}) \exp \eta(j)$ . For all limiting processes for which  $a_{N+1} \sim a_N$  ( $\sim a$  say) and  $x_{N+1} \sim x_N$  ( $\sim x$  say), one finds that  $x$  must be a solution of  $ax^2 - (a+1)x + 1 \sim 0$ , whence  $x \sim 1$  or  $1/a$ . The last possibility is ruled out since  $x_N > 1$ ,  $a_N > 1$  for all  $j$  and finite  $N$ . Hence (2) must hold again in these cases. It remains to discuss the various limiting relations whose existence has been assumed in the above argument.

For Fermi-Dirac systems the relation  $Z_{N+1}/Z_N \sim Z_N/Z_{N-1}$  is valid in the limit  $L$  (and possibly for other limiting processes). Let

$$P \equiv V^{-1} \sum_j \mu(N, j), \quad Q \equiv V^{-1} \sum_j \mu(N-1, j),$$

$$\epsilon \equiv 1 - \frac{Z_{N+1}/Z_N}{Z_N/Z_{N-1}}, \quad 0 \leq \epsilon \leq 1,$$

$$c_j \equiv \frac{\epsilon (Z_N/Z_{N-1}) \exp \eta(j)}{1 + (Z_N/Z_{N-1}) \exp \eta(j)}.$$

Then

$$VP = \sum_j [1 + (Z_N/Z_{N-1}) \exp \eta(j)]^{-1} [1 - c_j]^{-1},$$

and

$$\frac{1}{1 - c_j} \geq 1 + \frac{\epsilon Z_N/Z_{N-1}}{1 + (1 - \epsilon) Z_N/Z_{N-1}}.$$

Now by (7),  $(N+1)/V > P > N/V > Q > (N-1)/V$ , so that  $Q = (N-\alpha)/V$ ,  $0 < \alpha < 1$ . These relations give rise to

$$\frac{N+1}{V} > Q + \left( \frac{N-\alpha}{V} \right) \frac{\epsilon Z_N/Z_{N-1}}{1 + (1-\epsilon)Z_N/Z_{N-1}} > Q > \frac{N-1}{V}. \quad (10)$$

It follows that in the limit  $L$ ,  $\epsilon Z_N/Z_{N-1} \rightarrow 0$ . This proves our statement.

For Bose-Einstein systems, we use<sup>5</sup>

$$(1+1/N)(Z_{N+1}/Z_N) > Z_N/Z_{N-1} > Z_{N+1}/Z_N. \quad (11)$$

Thus for all limiting processes for which  $N$  tends to infinity  $Z_{N+1}/Z_N \sim Z_N/Z_{N-1}$ , and therefore relations  $a_{N+1} \sim a_N$  hold.

To establish relations of the type  $x_{N+1} \sim x_N$  for Bose-Einstein systems, one can use an argument of the type given in Sec. 4 of Fraser's paper. If  $M$  be a positive integer smaller than  $N$ , one first notes that

$$R(N, M) \equiv \sum_{r=M+1}^{\infty} a_N^{-r} - \sum_{r=M+1}^N \frac{Z_{N-r}}{Z_N} \exp(-r\eta_j) < a_N^{-M}(a_N - 1). \quad (12)$$

Hence

$$n(N, j) > b_M(1 - a_N^{-M})/(a_N - 1),$$

where  $b_M \equiv (N-1)(N-2) \cdots (N-M+1)N^{-r+1}$ . Since  $x_{N+1} = (1/a_{N+1})\{1 + [1/n(N, j)]\}$ , it follows that

$$a_N/a_{N+1} < x_{N+1} < \frac{1}{a_{N+1}} \left[ 1 + \frac{1}{b_M} \frac{a_N - 1}{1 - a_N^{-M}} \right]. \quad (13)$$

The first inequality follows immediately from (9). Let  $M$  go to infinity with  $N$ , but more slowly than  $\sqrt{N}$ , so that<sup>5</sup>  $b_M \rightarrow 1$ . It now follows from (13) that for all limiting processes for which  $N \rightarrow \infty$ ,  $x_{N+1} \rightarrow a_N/a_{N+1}$  whether  $a_N \rightarrow 1$  or  $a_N \rightarrow a > 1$ . By (11),  $a_N/a_{N+1} = 1 + \gamma/N$  where  $0 < \gamma < 1$ . Hence relations  $x_N \sim x_{N+1}$  hold for all limiting processes of this type, and, in particular, for the limit  $L$ . Fraser's restrictions on the nature of the single-particle energy spectrum are not required.

For  $T=0$  the mean occupation numbers can be calculated exactly from (1) by evaluating  $(Z_{N+1}/Z_N) \times \exp(\eta_j)$  directly. The results agree with those obtained from the grand canonical ensemble.

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<sup>3</sup> P. T. Landsberg, Proc. Cambridge Phil. Soc. **50**, 65 (1954).

<sup>4</sup> P. T. Landsberg, Phys. Rev. **93**, 1170 (1954).

<sup>5</sup> A. R. Fraser, Phil. Mag. **42**, 165 (1951).

<sup>6</sup> We are grateful to Dr. R. Nozawa of the Tokyo Institute of Technology for drawing our attention to this fact.

## Use of *p-n* Junctions for Solar Energy Conversion

E. S. RITTNER

Philips Laboratories, Irvington-on-Hudson, New York

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THE recent discovery<sup>1</sup> that silicon *p-n* junction photovoltaic cells possess a nearly tenfold higher efficiency for solar energy conversion than photo-cells previously available has reawakened interest in this type of device. Cummrow<sup>2</sup> has presented a theory of the photovoltaic effect in a *p-n* junction cell with monochromatic radiation incident in a direction normal to the plane of the junction and has also made as estimate of the efficiency to be expected from the use of a silicon cell in solar energy conversion.<sup>3</sup> Similar calculations by the writer<sup>4</sup> lead to conclusions substantially identical to those arrived at by Cummrow with one exception. For maximum power conversion efficiency we propose the use of a semiconductor with an energy separation in the neighborhood of 1.5–1.6 ev in preference to Cummrow's choice of a "gap energy somewhere near the photon energy characteristic of the peak of the solar spectrum, i.e., 2 ev."

The basis for this conclusion may be found in Fig. 1 which shows a plot of conversion efficiency (neglecting surface reflection losses and ohmic losses within the cell, and assuming that the depth of the junction below the illuminated surface is small compared to a diffusion length) as a function of band separation for several values of donor and acceptor densities ( $N_d = N_a = 10^{15}$ ,  $10^{17}$ ,  $10^{19}/\text{cm}^3$ ). The plot is based upon computations performed for germanium ( $\Delta E = 0.7$  ev), silicon (1.0 ev), aluminum antimonide (1.6 ev) and for a hypothetical substance with a band separation of 2.0 ev. The values taken for the diffusion constants and lifetimes in germanium and silicon are the same as those employed by Cummrow<sup>2,3</sup> and values equal to those of silicon have been assumed for the remaining substances. Fortunately

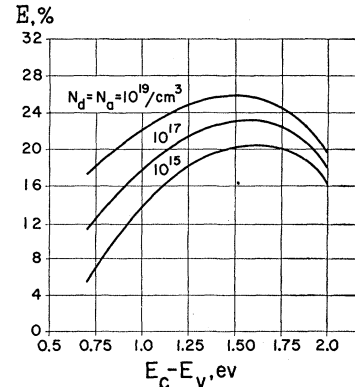


Fig. 1. Computed conversion efficiency vs band separation for several values of donor and acceptor density. Load resistance chosen for maximum power output.