

Statistical Theory of Equations of State and Phase Transitions. II. Lattice Gas and Ising Model

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The problems of an Ising model in a magnetic field and a lattice gas are proved mathematically equivalent. From this equivalence an example of a two-dimensional lattice gas is given for which the phase transition regions in the $p-v$ diagram is exactly calculated.

A theorem is proved which states that under a class of general conditions the roots of the grand partition function always lie on a circle. Consequences of this theorem and its relation with practical approximation methods are discussed. All the known exact results about the two-dimensional square Ising lattice are summarized, and some new results are quoted.

INTRODUCTION

IN paper I¹ we have seen that the problem of a statistical theory of phase transitions and equations of state is closely connected with the distribution of roots of the grand partition function. It was shown there that the distribution of roots determines completely the equation of state, and in particular its behavior near the positive real axis prescribes the properties of the system in relation to phase transitions. It was also shown there that the equation of state of the condensed phases as well as the gas phase can be correctly obtained from a knowledge of the distribution of roots. While this general and abstract theory clarifies the problems underlying the statistical theory of phase transitions and condensed phases, it is natural to ask whether it also provides us with a means of obtaining practical approximation methods for calculating properties pertaining to phase transitions and condensed phases.

The problem is clearly that of seeking for the properties of the distribution of roots of the grand partition function. At first sight this appears to be a formidable problem, as the roots are in general complex and would naturally be expected to spread themselves for an infinite sample in the entire complex plane, or at least regions of the complex plane, and make it very difficult to calculate their distribution. We were quite surprised, therefore, to find that for a large class of problems of practical interest, the roots behave remarkably well in that they distribute themselves not all over the complex plane, but only on a fixed circle. This fact will be stated

TABLE I. Identification of corresponding quantities in Ising model and lattice gas.^a

Ising model		Lattice gas
No. of spins	=	volume
No. of \downarrow spins	=	No. of atoms
$2/(1-I)$	=	specific volume v
$-F-H$	=	pressure p

^a I , H , and F are respectively the intensity of magnetization, the magnetic field, and the free energy per spin in the Ising model problem.

¹ C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952).

as a theorem in Sec. IV of the present paper and proved in the appendix. Implications of the theorem are discussed in Sec. V.

Also in this paper we shall give a proof (Sec. II) that the problem of an Ising model with a magnetic field is mathematically identical with that of a "lattice gas." From this identification we were able to trace exactly the transition region in the $p-v$ diagram of a two-dimensional lattice gas in detail. This will be presented in Sec. III and forms a clear illustration of the discussions of paper I and of Sec. V of the present paper.

At the end of Sec. V we give a summary of all the exact knowledge known to us about the two-dimensional Ising model in a magnetic field and its relationship with the distribution of roots of the partition function.

II. ISING MODEL AND LATTICE GAS

We shall in this section show that the problems of an Ising model in a magnetic field and of a lattice gas are mathematically equivalent. In the former problem one considers a lattice of interacting spins each of which can assume two possible positions: \uparrow and \downarrow . In the latter, one considers a corresponding lattice with each lattice point either vacant or occupied by an atom.² To each configuration of the lattice of spins there corresponds a configuration of the lattice gas in which a lattice point is vacant or occupied according as whether the corresponding spin is \uparrow or \downarrow . Using this geometrical correspondence, one could establish the mathematical equivalence of the two problems.

For clarity of presentation we shall take as an example a simple cubic lattice and consider first the Ising model problem with nearest neighbor interaction. The same treatment can be applied to any lattice with arbitrary interaction between the spins. Denote by $[\uparrow\uparrow]$, $[\downarrow\downarrow]$, and $[\uparrow\downarrow]$ the total number of nearest neighboring spins that are respectively parallel and upward, parallel and downward, and antiparallel to each other. Also denote by $[\uparrow]$ and $[\downarrow]$ the total numbers of upward and downward spins in the lattice.

² Similar ideas have been used in the "hole theory of liquids." See, e.g., J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A169**, 317 (1939); **A170**, 464 (1939). F. Cernuschi and H. Eyring, J. Chem. Phys. **7**, 547 (1939).

Counting the number of nearest neighbors of all the upward spins, one arrives at the following identity:

$$2[\uparrow\uparrow] + [\uparrow\downarrow] = 6[\uparrow]. \quad (1)$$

Similarly

$$2[\downarrow\downarrow] + [\uparrow\downarrow] = 6[\downarrow]. \quad (2)$$

Evidently

$$\mathfrak{N} = [\uparrow] + [\downarrow] \quad (3)$$

is the total number of spins in the lattice.

The interaction energy of all the spins can be written as $[\uparrow\downarrow]\epsilon$ if the interaction energy between parallel spins is taken to be zero. Here ϵ is a constant and is positive for ferromagnetic interactions and negative for anti-ferromagnetic interactions. In an external magnetic field H (measured in proper units), there is an additional magnetic energy so that the total energy of the Ising lattice is

$$U_I = H([\downarrow] - [\uparrow]) + [\uparrow\downarrow]\epsilon. \quad (4)$$

The partition function is therefore

$$\exp(-\mathfrak{N}F/kT) = \sum \exp(-U_I/kT), \quad (5)$$

where F is the free energy per spin and the summation extends over all arrangements of the spins. F as a function of the magnetic field H and the temperature T defines completely the thermodynamic behavior of the lattice. Its derivative with respect to H gives the intensity of magnetization I ,

$$\partial F/\partial H = -I, \quad (6)$$

where I is defined to be

$$I = \mathfrak{N}^{-1}([\uparrow] - [\downarrow]). \quad (7)$$

Now consider a lattice gas on the same simple cubic lattice. According to the geometrical correspondence discussed before, each downward spin \downarrow corresponds to one gas atom, hence $[\downarrow]$ is equal to the number of atoms in the gas. Also the "volume" of the gas (in proper units) is simply \mathfrak{N} . The specific volume v per atom is, by Eqs. (3) and (7), related to the intensity of magnetization I by

$$v = 2/(1 - I). \quad (8)$$

To prevent more than one atom from occupying the same lattice site and to correspond to the case of nearest neighbor interaction in the Ising model problem, we consider here the following potential energy u between two atoms:

$$\begin{aligned} u &= +\infty && \text{if the two atoms occupy the same lattice site,} \\ u &= -2\epsilon && \text{if the two atoms are nearest neighbors,} \end{aligned} \quad (9)$$

and

$$u = 0 \text{ otherwise.}$$

It should be remarked that this interaction closely simulates the actual interaction between atoms of an atomic gas. For $\epsilon > 0$ (ferromagnetic case), the gas atoms attract each other at intermediate distances and

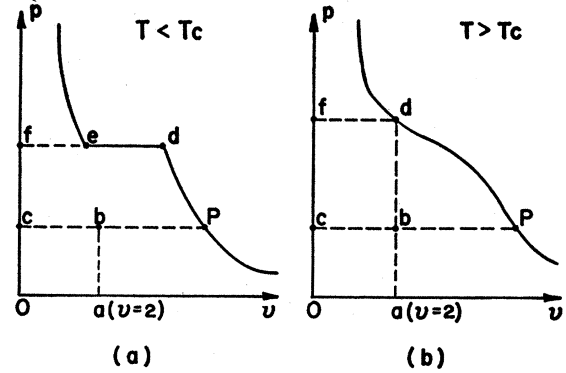


FIG. 1. Geometrical construction of the thermodynamic functions of the Ising model from the $p-v$ diagram of the corresponding lattice gas. Solid curves are isotherms. Given a point P the corresponding Ising model has a magnetic field $H = \frac{1}{2}$ (area $cPdf$), a free energy per spin $F = -\frac{1}{2}$ (area $OabPdf$).

for $\epsilon < 0$ (antiferromagnetic case) they repel each other. Since $[\downarrow\downarrow]$ is by the geometrical correspondence the number of nearest neighboring pairs of atoms the energy of the gas is

$$U_G = -2[\downarrow\downarrow]\epsilon.$$

The grand partition function of the gas is

$$\exp(p\mathfrak{N}/kT) = \sum y^{[\downarrow]} \exp(2[\downarrow\downarrow]\epsilon/kT), \quad (10)$$

where p is the pressure of the gas and y the fugacity given by Eq. (3) in paper I. Now on using (2), (3), and (4), one can write Eq. (5) in the form

$$\begin{aligned} \exp\{-\mathfrak{N}(F+H)/kT\} \\ = \sum \exp\{(-2H[\downarrow] - 6\epsilon[\downarrow] + 2\epsilon[\downarrow\downarrow])/kT\}. \end{aligned}$$

Upon comparing this with Eq. (10), one concludes that for a value of the fugacity given by

$$y = \exp\{(-2H - 6\epsilon)/kT\}, \quad (11)$$

the pressure p of the lattice gas is related to the free energy F per spin of the Ising lattice by

$$p = -F - H. \quad (12)$$

The same treatment can be easily applied to *any general lattice with arbitrary interactions, yielding results identical with Eqs. (8) and (12)*. These results are compiled in Table I which lists the corresponding quantities for the problems of an Ising model with a magnetic field and of a lattice gas. The two problems are completely equivalent; the thermodynamical properties of one system can be derived with the aid of Table I from those of the other and vice versa. In particular, the isotherms in the $I-H$ and $p-v$ diagrams bear a very close relationship to each other. We mention specifically that a discontinuity in I corresponds to a discontinuity in v . In the case of ferromagnetism, below the Curie temperature T_c , I has a discontinuity, and this corresponds to a phase transition at the same temperature in the lattice gas. Above T_c the isotherms in

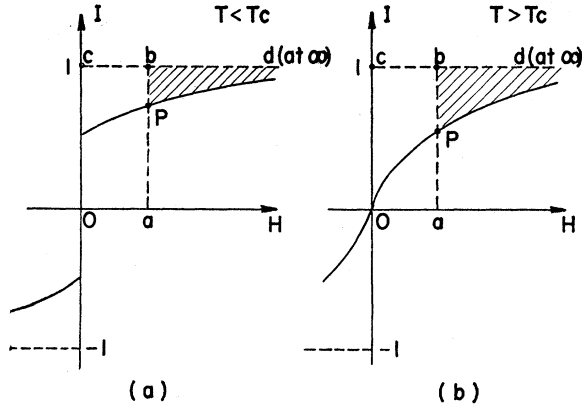


FIG. 2. Geometrical construction of the thermodynamic functions of the lattice gas from the $I-H$ diagram of the corresponding Ising model. Solid curves are isotherms. Given a point P the corresponding lattice gas had a density $\rho = \frac{1}{2}$ (length bP), a pressure $p = \text{area } Pdb$. p can be obtained from the free energy of the Ising model which is $F = -\text{area } OaPdc$.

both of the two diagrams become smooth, and we therefore identify the Curie temperature with the critical temperature of the lattice gas.

From the $p-v$ diagram one can construct the thermodynamic properties of the Ising model in a simple geometric manner and vice versa. These are illustrated in Figs. 1 and 2.

III. AN EXAMPLE OF A TWO-DIMENSIONAL LATTICE GAS

The question naturally arises as to the relationship between a lattice gas and a real gas in which the atoms are not confined to move on lattice points. If one replaces the configurational integral in the partition function of the real gas by a summation over lattice sites, one would obtain the partition function of the lattice gas. Theoretically speaking, by making the lattice constant smaller and smaller one could obtain successively better approximations to the partition function of the real gas.³ In practice this is a very difficult procedure. However, referring back to the simple example discussed in detail in Sec. II one sees that if $\epsilon > 0$ the interaction u there has all the characteristics of the interaction between gas atoms that are usually considered responsible for the phenomenon of condensation, namely, an attractive force with a finite range outside of a strongly repulsive core. Thus one would expect that the main features of the phenomenon of condensation should be revealed even in this simple example.

It happens fortunately that in two dimensions this example can be solved exactly in the transition region. To be more specific, the problem is that of a two-dimensional lattice gas with the interaction u specified in (9). (A square lattice is considered.) ϵ is assumed to be positive so that the gas atoms attract each other. The corresponding Ising model problem has been studied

³ See Appendix I for a simple illustration on this point.

extensively. It is known that the model exhibits ferromagnetism so that according to the discussion of Sec. II the lattice gas has a phase transition. In the Ising model, for temperatures lower than the Curie temperature T_c which is given by

$$\exp(-\epsilon/kT_c) = \sqrt{2} - 1, \quad (13)$$

the intensity of magnetization has a discontinuity at $H=0$. The corresponding phase transition of the lattice gas occurs at a value of the fugacity⁴

$$y = x^4,$$

where

$$x = \exp(-\epsilon/kT).$$

Since the free energy⁵ and the spontaneous magnetization⁶ of the Ising model problem are known exactly at zero magnetic field, the transition region in the $p-v$ diagram of the lattice gas can be mapped out completely with the aid of Table I. We list here the formulas used for the vapor pressure p and specific volumes v_g and v_l of the equilibrium gas and liquid phases:

$$\frac{p}{kT} = \log(1+x^2) + \frac{1}{2\pi} \int_0^\pi \log\left\{\frac{1}{2}[1+(1-k_1^2 \sin^2 \varphi)^{\frac{1}{2}}]\right\} d\varphi, \quad (14)$$

$$v_g^{-1} = \frac{1}{2} - \frac{1}{2}[(1+x^2)(1-6x^2+x^4)^{\frac{1}{2}}/(1-x^2)^2]^{\frac{1}{2}}, \quad (15)$$

and

$$v_g^{-1} + v_l^{-1} = 1, \quad (16)$$

where

$$k_1 = 4x(1-x^2)(1+x^2)^{-2}. \quad (17)$$

In Fig. 3 the transition region in the $p-v$ diagram is plotted. The isotherms are calculated in the following way:

(1) For small values of the fugacity y , one uses Mayer's series expansion⁷ in powers of y :

$$\frac{p}{kT} = y + y^2 \left(\frac{2}{x^2} - \frac{5}{2} \right) + y^3 \left(\frac{6}{x^4} - \frac{16}{x^2} + \frac{31}{3} \right) + y^4 \left(\frac{1}{x^8} + \dots \right) + \dots, \quad (18)$$

⁴ The relation between the quantity $\exp(-2H/kT)$ of the two-dimensional Ising model in a magnetic field and the fugacity y of the corresponding lattice gas can be easily obtained by using similar reasonings as that used in deriving Eq. (11). One obtains

$$y = x^4 \exp(-2H/kT). \quad (A)$$

The fourth power in x comes from the fact that each lattice point has four nearest neighbors. The corresponding equation for any general lattice with arbitrary interaction can be written as

$$y = \sigma \exp(-2H/kT), \quad (B)$$

where σ is a constant and is determined by the structure of the lattice and the interaction between the atoms.

⁵ L. Onsager, Phys. Rev. **65**, 117 (1944); B. Kaufman, Phys. Rev. **76**, 1232 (1949).

⁶ C. N. Yang, Phys. Rev. **85**, 808 (1952).

⁷ J. E. Mayer, J. Chem. Phys. **5**, 67 (1937); J. E. Mayer and Ph. G. Ackermann, J. Chem. Phys. **5**, 74 (1937); J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87, 101 (1938).

and

$$\frac{1}{v} = y \frac{\partial}{\partial y} \left(\frac{p}{kT} \right). \quad (19)$$

We shall see in the next section that (18) is convergent for all values of y less than x^4 .

(2) When y is equal to x^4 , the gas undergoes a phase transition at temperatures lower than the critical temperature. The vapor pressure and specific volumes of the gas and liquid at this value of y have been given before in Eqs. (14), (15), and (16).

(3) At $y = x^4$, but above the critical temperature, the pressure of the gas is still given by Eq. (14), but the specific volume v now is a constant

$$v = 2. \quad (20)$$

This is so because the corresponding Ising model problem has now, according to Eq. (A),⁴ zero magnetic field and consequently zero intensity of magnetization.

(4) For $y > x^4$, the Ising model problem has, according to Eq. (A),⁴ a negative magnetic field. Changing the sign of the magnetic field corresponds to changing the fugacity to a value y' given by, according to Eq. (A),⁴

$$yy' = x^8. \quad (21)$$

Since the free energy F is even in H and the intensity of magnetization I is odd, one could express with the aid of Table I the pressure and density in terms of their values when the fugacity is equal to y' . But y' is less than x^4 . On using (18) and Table I, one can therefore expand the pressure and density in inverse powers of the fugacity y :

$$\begin{aligned} \frac{p}{kT} = \log \frac{y}{x^4} + y^{-1}x^8 + y^{-2}(2x^{14} - (5/2)x^{16}) \\ + y^{-3}(6x^{20} - 16x^{22} + (31/3)x^{24}) \\ + y^{-4}(x^{24} + \dots) + \dots, \end{aligned} \quad (22)$$

and

$$\frac{1}{v} = y \frac{\partial}{\partial y} \left(\frac{p}{kT} \right).$$

This series is convergent for all $y > x^4$, which holds everywhere in the liquid phase and also in part of the gas phase above the critical temperature.

It is really quite remarkable that a model with so many properties characteristic of a real gas should allow of a complete and exact solution in the transition region where the usual virial expansion does not apply. A complete solution outside of the transition region is related to the solution of an Ising model in a non-vanishing magnetic field, which still remains unknown. However, the problem can be reduced by the results of paper I, to that of the distribution of roots of the grand partition function; and although the complete distribution is not known, many of its properties have been obtained. We shall return to this problem in Sec. V.

Before closing this section we shall make the following remark. Equation (16) shows that the sum of the densities of the vapor and liquid in equilibrium is a constant independent of the temperature.⁸ This closely resembles the behavior of a real gas where a law called "law of rectilinear diameter"⁹ is known to hold. It states that the sum of the densities of the vapor and liquid in equilibrium increases linearly with decreasing temperature. This increment is, however, very slow, being not more than 10 percent for a temperature variation over a factor 2 for He near its critical temperature. Now our model obeys what may be called the "law of constant diameter," which provides no increment of the sum of densities with decreasing temperature and may be considered a first approximation to the law of rectilinear diameter. The difference lies, we believe, in the inadequacy of the lattice model (with a finite lattice constant) as an approximation to a true gas. One can formulate arguments which indicate that the correction to the lattice model is in the right direction (i.e., it tends to make the sum of the densities of the vapor and liquid in equilibrium increase with decreasing temperature).

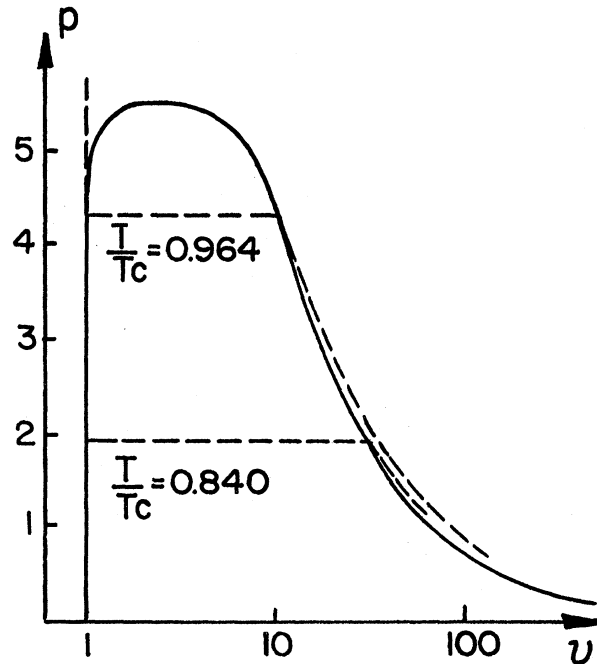


FIG. 3. p - v diagrams for a two-dimensional lattice gas. The solid curve is the exact boundary of the two-phase region. The dotted curves are the isotherms.

⁸ The constancy of the sum of the densities of the vapor and liquid in equilibrium is true even for any general lattice. This can be seen very easily since there exists a one to one correspondence between the configurations of the vapor phase and that of the liquid phase, which is obtained simply by replacing the lattice sites occupied by the atoms in the former by vacant sites in the latter and vice versa. Compare Cernuschi and Eyring's paper quoted in footnote 2.

⁹ Mathias, Onnes, and Crommelin, Proc. Sect. Sci. Amsterdam 15, 960 (1913).

IV. A THEOREM ON THE DISTRIBUTION OF ROOTS OF THE GRAND PARTITION FUNCTION

We shall now return to the general problem of the condensation of gases, and shall in the following apply the results of paper I to the problem of a lattice gas. There is actually no loss of generality in confining our attention to a lattice gas, as a real continuum gas can be considered as the limit of a lattice gas as the lattice constant becomes infinitesimally small.

The equivalence proved in Sec. II states that the problem of a lattice gas is identical with that of an Ising model in a magnetic field, and that the grand partition function in the former problem is proportional to the partition function in the latter problem. It is convenient to introduce in the Ising model problem the variable

$$z = \exp(-2H/kT), \quad (23)$$

which is by Eq. (B),⁴ proportional to the fugacity y of the lattice gas:

$$y = \sigma z, \quad (24)$$

where σ is a constant. In terms of z the partition function $\exp(-\mathcal{N}F/kT)$ of the Ising lattice is equal to $\exp(\mathcal{N}H/kT)$ times a polynomial \mathcal{O} in z of degree \mathcal{N} :

$$\exp(-\mathcal{N}F/kT) = \mathcal{O} \exp(\mathcal{N}H/kT), \quad (25)$$

where

$$\mathcal{O} = \sum P_n z^n, \quad (n=0, 1, \dots, \mathcal{N}). \quad (26)$$

The coefficients P_n are the contribution to the partition function of the Ising lattice in zero external field from configurations with the number of \downarrow spins equal to n . It should be noticed that

$$P_n = P_{n'} \text{ if } n+n' = \mathcal{N}.$$

The P_n 's are, of course, real and positive.

Evidently the roots of the polynomial \mathcal{O} are never on the positive real z axis, and are in general complex.

The results of paper I show that if at a given temperature as \mathcal{N} approaches infinity, the roots of the polynomial \mathcal{O} do not close in onto the positive real axis in the complex z plane, the free energy F is an analytic function of the positive real variable z . Physically this means that the Ising model has a smooth isotherm in the $I-H$ diagram and that the corresponding lattice gas undergoes no phase transition at the given temperature. If, on the other hand, the roots of the polynomial \mathcal{O} do close in onto the positive real z axis at the points $z = t_1, t_2, \dots$, each of these points would correspond to a discontinuity of the isotherm in the $I-H$ diagram of the Ising lattice and to a phase transition of the lattice gas.

To study the problem of phase transitions of the lattice gas (and of an Ising model), one therefore needs only to study the distribution in the complex z plane of the roots of the polynomial \mathcal{O} . The surprising thing is that under quite general conditions this distribution

shows a remarkably simple regularity, which may be stated in the form of the following theorem:

Theorem 3. If the interaction u between two gas atoms is such that

$$u = +\infty \text{ if the two atoms occupy the same lattice} \\ \text{and } u \leq 0 \text{ otherwise,} \quad (27)$$

then all the roots of the polynomial \mathcal{O} lie on the unit circle in the complex z -plane.

This theorem will be proved in Appendix II. It should be noticed that in the theorem no assumptions are made about (1) the range of the interaction u , (2) the dimensionality of the lattice, and (3) the size and structure of the lattice. In fact, even the periodicity property of the lattice plays no part at all in the proof.

For the Ising model problem Eq. (27) means that the interaction between all pairs of spins (not limited to pairs of nearest neighbors) are ferromagnetic.

Some immediate consequences of theorem 3 may be enumerated as follows:

(1) The lattice gas cannot undergo more than one phase transition, which must occur, if at all, at a value of the fugacity equal to σ , which according to Eq. (24), corresponds to $z=1$. The isotherms in the $I-H$ diagram of the corresponding Ising model problem is smooth everywhere except possibly at zero magnetic field (which occurs at $z=1$). This is usually believed to be true but was not proved.

(2) Mayer's series expansions⁷ of the pressure p and density $1/v$ in powers of the fugacity y [see, e.g., Eq. (18)] are convergent for all values of y less than σ . This is easily proved by the argument used in footnote 9 of paper I. On using the symmetry property of the Ising model problem with respect to a reversal of sign of the magnetic field, one obtains, for values of y greater than σ , convergent series expansions of p and $1/v$ in inverse powers of the fugacity [see, e.g., Eq. (22)].

V. DISTRIBUTION OF ROOTS ON THE UNIT CIRCLE

A. Distribution Function $g(\theta)$

We have seen in the last section that for the interaction (27) the roots of \mathcal{O} lie on the unit circle. Its distribution as $\mathcal{N} \rightarrow \infty$ may be described by a density function $g(\theta)$ ¹⁰ so that $\mathcal{N}g(\theta)d\theta$ is the number of roots with z between $e^{i\theta}$ and $e^{i(\theta+d\theta)}$. Evidently one has

$$g(\theta) = g(-\theta), \quad (28)$$

¹⁰ The average density of a finite lattice gas is easily seen to be

$$\sum_k z / [z - \exp(i\theta_k)],$$

where $z = \exp(i\theta_k)$ are the zeros of the grand partition function. The results of paper I show that this average density converges to an analytic function in z both inside and outside of the unit circle as the size of the lattice approaches infinity. It seems intuitively clear from this that the distribution of these roots should also approach a limiting distribution on the unit circle for an infinite lattice. This is indeed the case and a rigorous mathematical proof exists in the literature. See A. Wintner, *Monatsh. Math. Phys.* 4, 1 (1934). We are indebted to Professor Kac for showing us the proof.

and

$$\int_0^\pi g(\theta) d\theta = \frac{1}{2}. \quad (29)$$

Taking the logarithm of (25) and factorizing \mathcal{O} one obtains for the Ising model

$$\begin{aligned} \frac{-F}{kT} &= \frac{H}{kT} + \int_0^{2\pi} g(\theta) \log(z - e^{i\theta}) d\theta \\ &= \frac{H}{kT} + \int_0^\pi g(\theta) \log(z^2 - 2z \cos\theta + 1) d\theta. \end{aligned} \quad (30)$$

The intensity of magnetization is obtained from Eqs. (6) and (30):

$$I = 1 - 4z \int_0^\pi g(\theta) \frac{z - \cos\theta}{z^2 - 2z \cos\theta + 1} d\theta. \quad (31)$$

For the lattice gas one has, on using Table I and Eqs. (30) and (31),

$$\frac{p}{kT} = \int_0^\pi g(\theta) \log(z^2 - 2z \cos\theta + 1) d\theta, \quad (32)$$

and

$$\frac{1}{v} = 2z \int_0^\pi g(\theta) \frac{z - \cos\theta}{z^2 - 2z \cos\theta + 1} d\theta. \quad (33)$$

These equations enable one to calculate the isotherms in the $I-H$ and $p-v$ diagrams from the distribution function $g(\theta)$. The isotherms thus obtained extend to the condensed region, the two-phase region as well as the gas region. They approximate very realistically the isotherms of a real gas even for very simple distribution functions $g(\theta)$.

B. An Electrostatic Analog

A very simple analog of Eqs. (32) and (33) may be found in electrostatics in the following way: Consider a circular cylinder of unit radius perpendicular to the complex z plane discussed above, cutting it at the unit circle. Assume the cylinder to be charged with a surface charge density dependent only on the angle θ and equal to $g(\theta)$ per unit area. Denote the electrostatic potential and the field produced by this charge distribution at any point on the real axis in the z plane by ϕ and E . Since $g(\theta) = g(-\theta)$, the electric field E is evidently parallel to the real z axis. One can easily verify the following equations:

$$-2\phi/kT = \text{electrostatic potential } \phi, \quad (34)$$

$$2/vz = -\partial\phi/\partial z = \text{electric field } E. \quad (35)$$

If $g(\theta)$ vanishes in the neighborhood of $\theta=0$, the sheet of charge has the shape "C" and the electric potential and electric field are well behaved for all real positive values of z . Consequently the pressure and density of

the lattice gas are analytic in the fugacity and the system undergoes no phase transition. If, on the other hand, $g(0)$ does not vanish, the electric field has a discontinuity at $z=1$ as one goes along the positive real z axis through the sheet of surface charge distribution. Evidently

$$E(z=1+) - E(z=1-) = 4\pi g(0). \quad (36)$$

This means of course that the specific volume v of the lattice gas has a discontinuity at $z=1$, showing that the system undergoes a phase transition. The specific volumes v_g and v_l of the gas and liquid phases in equilibrium are related to $g(0)$ by

$$1/v_l - 1/v_g = 2\pi g(0). \quad (37)$$

Another relation between v_l and v_g is given by the "law of constant diameter" discussed in Sec. 3 (see especially footnote 8).

Equation (37) asserts that the value of the distribution function g at the transition point ($\theta=0$) is equal to $(2\pi)^{-1}$ times the difference of the densities of the liquid and gas phases in equilibrium, which is a directly physically observable quantity.

It should be emphasized that this relationship has actually a much wider range of validity and holds even when the roots are not necessarily on the unit circle.

It is evident that the variation of the pressure and density near the point $z=1$ depends very sensitively on the behavior of $g(\theta)$ near $\theta=0$. One would for example expect that the derivatives of $g(\theta)$ near $\theta=0$ should determine the derivatives of the isotherm in the $p-v$ diagram near the region of condensation. This is indeed the case, as can be seen in the example: If for small values of θ ,

$$g(\theta) = g(0) + a|\theta|^n + \dots, \quad (n > 0)$$

the $g(0)$ term, (if nonvanishing), will give rise to a flat horizontal portion on the $p-v$ diagram. The next term will give rise to a discontinuity in the n th derivative of v with respect to p for integral values of n . If n is a fraction between the integers, say, m and $m-1$ then the m th derivative of v with respect to p is discontinuous.

For the Ising model problem, the relation corresponding to Eq. (37) can be obtained by using Table I. The intensity of spontaneous magnetization I is thus expressible in terms of $g(0)$:

$$I = 2\pi g(0). \quad (38)$$

C. Relationship between the Cluster Integrals and $g(0)$

If one expands (32) in powers of z and identifies the coefficient with Mayer's expansion,⁷

$$\frac{p}{kT} = \sum_{l=1}^{\infty} b_l y^l = \sum_{l=1}^{\infty} b_l \sigma^l z^l,$$

where σ is given by (24), one obtains the following expression for the cluster integrals b_l :

$$b_l = \frac{-1}{l\sigma^l} \int_0^{2\pi} g(\theta) \cos l\theta d\theta, \quad l \geq 1. \quad (39)$$

In other words the b_l 's are the Fourier coefficients of the distribution function $g(\theta)$. One has, of course, the inverse relation,

$$g(\theta) = \frac{1}{2\pi} - \frac{1}{\pi} \sum_{l=1}^{\infty} l\sigma^l b_l \cos l\theta, \quad (40)$$

which expresses the distribution function $g(\theta)$ in terms of the cluster integrals b_l , which in turn are themselves calculable from the virial coefficients.

Equations (40) and (37) enable one to make practical approximate calculations of the distribution function $g(\theta)$ from the virial coefficients and the change in specific volume in the phase transition, both of which are experimentally observable quantities.

D. $g(\theta)$ and the Analytical Behavior of the Specific Volume

The density $1/v$ of the lattice gas is evidently an analytic function of z both inside and outside of the unit circle in the complex z plane. Its value is equal to 1 at $z = \infty$ where it is also analytic. All its singularities lie on the unit circle. The values of $1/v$ on the two sides of the unit circle are related to the distribution function $g(\theta)$ by

$$\lim_{r \rightarrow 1+} \frac{1}{v} \Big|_{z=r e^{i\theta}} - \lim_{r \rightarrow 1-} \frac{1}{v} \Big|_{z=r e^{i\theta}} = 2\pi g(\theta). \quad (41)$$

This equation can be proved by extending the reasoning that led to Eq. (37) in the following way: Consider the electric field at a point not necessarily on the real z axis produced by the charge distribution discussed in subsection B. Let E_x and E_y be the components of the electric field \parallel and \perp to the real z axis. Defining

$$\mathcal{E} = E_x + iE_y, \quad \mathcal{E}^* = E_x - iE_y,$$

one can easily verify the identity

$$2/vz = \mathcal{E}^* \quad (42)$$

at every point in the complex z plane. The discontinuity of \mathcal{E} across the unit circle at any point $z = e^{i\theta}$ is related to the charge density $g(\theta)$ by

$$\mathcal{E}|_{\text{outside}} - \mathcal{E}|_{\text{inside}} = 4\pi g(\theta)z.$$

Taking the complex conjugate of this equation and using (42) one obtains Eq. (41).

The corresponding equation for the Ising model problem is

$$\lim_{r \rightarrow 1+} I \Big|_{z=r e^{i\theta}} - \lim_{r \rightarrow 1-} I \Big|_{z=r e^{i\theta}} = -4\pi g(\theta). \quad (41a)$$

E. Example of One- and Two-Dimensional Ferromagnetic Ising Model

We shall illustrate the above discussion with the problem of a one-dimensional ferromagnetic Ising model with nearest neighbor interaction in an external magnetic field. This problem can be rigorously solved by the matrix method.¹¹ We quote here only the results. For a closed chain of \mathfrak{N} spins denote the roots of the partition function by $e^{\pm i\theta_1}, e^{\pm i\theta_2}, \dots$. These roots are given by

$$\cos \theta_j = -x^2 + (1-x^2) \cos[\pi(2j-1)/\mathfrak{N}], \quad (43)$$

where x is defined to be $\exp(-\epsilon/kT)$ and j runs through all integers 1, 2, ... less than or equal to $\frac{1}{2}(\mathfrak{N}+1)$. As $\mathfrak{N} \rightarrow \infty$ these roots distribute themselves continuously on an arc of the unit circle lying to the left of the points

$$z = (1-2x^2) \pm i2x(1-x^2)^{\frac{1}{2}}. \quad (44)$$

For all values of $x > 0$, the roots therefore do not close in onto the positive real axis, confirming the well-established fact that a one-dimensional Ising model does not exhibit ferromagnetism. The density of roots is given by the distribution function

$$g(\theta) = \frac{1}{2\pi} \frac{\sin \frac{1}{2}\theta}{(\sin^2 \frac{1}{2}\theta - x^2)^{\frac{1}{2}}}, \quad \text{for } \cos \theta < 1-2x^2, \\ g(\theta) = 0, \quad \text{for } \cos \theta > 1-2x^2. \quad (45)$$

On substituting this into Eq. (30), one obtains the correct free energy. The intensity of magnetization is given by

$$I = \left[\frac{z^2 - 2z + 1}{z^2 - 2z(1-2x^2) + 1} \right]^{\frac{1}{2}}.$$

This is analytic everywhere except at the two points given in Eq. (44). The cut between these two points should be made along the unit circle toward the left of the two points. One easily verifies that the discontinuity across the cut is exactly $4\pi g(\theta)$, as given by Eq. (41a).

For a two-dimensional ferromagnetic Ising square lattice the problem with a finite magnetic field, to our knowledge, has not been solved. However, the following exact knowledge is available about the problem:

(1) The free energy F at zero magnetic field (i.e., $z = 1$) was obtained by Onsager⁵ as

$$F(z=1) = \frac{-kT}{2\pi^2} \int_0^\pi \int_0^\pi \log[1 + 2x(\cos\omega + \cos\omega') \\ + 2x^2 - 2x^3(\cos\omega + \cos\omega') + x^4] d\omega d\omega'. \quad (46)$$

(2) The intensity of spontaneous magnetization at

¹¹ H. A. Kramers and G. H. Wannier, Phys. Rev. **60**, 252, 263 (1941).

zero magnetic field was obtained by one of us⁶ as

$$I(z=1) = \begin{cases} \left[\frac{1+x^2}{(1-x^2)^2} (1-6x^2+x^4)^{\frac{1}{2}} \right]^{\frac{1}{2}} & \text{for } x \leq \sqrt{2}-1, \\ I(z=1) = 0 & \text{for } x > \sqrt{2}-1. \end{cases} \quad (47)$$

(3) By an extension of a method due to Kac and Ward¹² for obtaining a combinatorial solution of the free energy of the Ising model problem in the absence of a magnetic field, one could obtain¹³ the free energy at $z = -1$ which corresponds to a pure imaginary magnetic field equal to $i\pi/2$:

$$F(z=-1) = -\frac{i\pi}{2} - \frac{kT}{4\pi^2} \int_0^\pi \int_0^\pi \log\{(1-x^2)^2 \times [1 + (6-4\cos^2\omega - 4\cos^2\omega')x^2 + x^4]\} d\omega d\omega'. \quad (48)$$

(4) The intensity of magnetization at this imaginary value¹³ of the magnetic field is

$$I(z=-1) = \left[\frac{(1+x^2)^2}{1-x^2} (1+6x^2+x^4)^{-\frac{1}{2}} \right]^{\frac{1}{2}}. \quad (49)$$

This can be verified by series expansion of both sides in powers of x .

The results quoted above have direct bearing on the distribution function $g(\theta)$ of the zeros of the partition function on the unit circle. In particular (47) and (49) are precisely the value of $g(\theta)/2\pi$ at $\theta=0$ and $\theta=\pi$. It is interesting to notice that $g(0)/2\pi$ is always less than unity while $g(\pi)/2\pi$ is always greater than unity. Also $g(0)$ increases with decreasing temperature while $g(\pi)$ decreases with decreasing temperature. This shows the motion of the roots toward the right along the unit circle as the temperature decreases.

On the other hand, (46) and (48) give through Eq. (30) certain averages with respect to the distribution function $g(\theta)$. The form of these averages are extremely suggestive and we have tried to construct the distribution function from them, but without success.

VI. CONCLUDING REMARKS

The relation between the distribution of roots of a polynomial and its coefficients is mathematically a very complicated problem. It is therefore very surprising that the distribution should exhibit such simple regularities as proved in theorem 3 which applies, as remarked before, under very general conditions. One cannot escape the feeling that there is a very simple basis underlying the theorem, with much wider application, which still has to be discovered.

It is a great pleasure to thank Professor M. Kac for many stimulating and very pleasant discussions from which we learned much in mathematics.

¹² M. Kac and J. C. Ward (to be published).

¹³ We hope to publish in a future communication the details of the steps that led to (48) and (49).

APPENDIX I. ONE-DIMENSIONAL HARD RODS AND LATTICE GAS

A simple example that illustrates clearly the relationship between a continuum gas and a lattice gas is the problem of one-dimensional hard rods and the corresponding problem of a one-dimensional lattice gas, as the problem can be exactly solved in both cases. To be specific, let us consider a lattice gas of n atoms distributed on a one-dimensional lattice of total length L and lattice constant δ . The total number of lattice sites is clearly

$$\mathfrak{N} = L/\delta. \quad (50)$$

The interaction potential $u(r)$ between the gas atoms is

$$u(r) = +\infty \text{ for } r < m\delta, \quad u(r) = 0 \text{ for } r \geq m\delta, \quad (51)$$

where r is the distance between atoms and m is a positive integer. Evidently, r can only be $0, \delta, 2\delta$, etc.

The evaluation of the spatial partition function Q can be reduced to that of a simple combinatorial problem of distribution $(\mathfrak{N}-mn)$ identical pieces into $(n+1)$ different bags. One easily obtains

$$Q/n! = [\mathfrak{N} - (m-1)n]! / (\mathfrak{N} - mn)! n!. \quad (52)$$

The pressure p of the gas is related to Q through the relation

$$\frac{p}{kT} = \frac{\partial}{\partial L} \log \left(\frac{Q}{n!} \right). \quad (53)$$

On using (50) and differentiating (52) one obtains

$$\frac{p}{kT} = \frac{1}{\delta} \log \left(1 + \frac{n\delta}{L - mn\delta} \right). \quad (54)$$

In the limit of an infinitesimal lattice constant δ but a finite value D for $m\delta$, the pressure approaches a limit given by

$$\lim_{\substack{\delta \rightarrow 0 \\ m\delta = D}} \frac{p}{kT} = \frac{n}{L - nD}, \quad (55)$$

which is precisely the expression for the pressure of a system of n hard rods each of length D , enclosed in a one-dimensional box of total length L . Thus one sees that when the lattice constant δ approaches zero the thermodynamic functions of a lattice gas indeed approach that of a continuum gas.

APPENDIX II. PROOF OF THEOREM 3

Theorem 3 is a special case of the following more general theorem:

Theorem: Let $x_{\alpha\beta} = x_{\beta\alpha}$ ($\alpha \neq \beta$, $\alpha, \beta = 1, 2, \dots, n$) be real numbers whose absolute values are less than or equal to 1. Divide the integers $1, 2, \dots, n$ into two groups a and b so that there are γ integers in group a and $(n-\gamma)$ in group b . Consider the product of all $x_{\alpha\beta}$ where α belongs to group a and β to group b . We shall denote by P_γ the sum of all such products over all the

$n! / [\gamma!(n-\gamma)!]$ possible ways of dividing the n integers. In other words

$$P_\gamma = \sum [\gamma!(n-\gamma)!]^{-1} \prod_{j=1}^{n-\gamma} \prod_{i=1}^{\gamma} x_{a_i b_j}, \quad (56)$$

where $a_1 \cdots a_\gamma, b_1 \cdots b_{n-\gamma}$ is any permutation of the integers $1, 2, \dots, n$ and the summation extends over all such permutations; e.g.,

$$P_0 = P_n = 1, \quad P_1 = P_{n-1} = x_{12}x_{13} \cdots x_{1n} + x_{21}x_{23} \cdots x_{2n} + \cdots + x_{n1}x_{n2} \cdots x_{n(n-1)}.$$

It is easy to verify that $P_\alpha = P_{n-\alpha}$. Consider the polynomial

$$\mathcal{P}(z) = 1 + P_1 z + P_2 z^2 + \cdots + P_{n-1} z^{n-1} + z^n. \quad (57)$$

The theorem asserts that all the roots of the equation

$$\mathcal{P} = 0$$

are on the unit circle.

To prove this theorem it is convenient to introduce the following polynomials \mathfrak{P} of the variables z_1, z_2, \dots, z_n :

$$\mathfrak{P}(z_1, \dots, z_n) = \sum \left\{ [\gamma!(n-\gamma)!]^{-1} \left(\prod_{j=1}^{n-\gamma} \prod_{i=1}^{\gamma} x_{a_i b_j} \right) \prod_{i=1}^{\gamma} z_{a_i} \right\}, \quad (58)$$

where, as in the definition of $P_\gamma, a_1, a_2, \dots, a_\gamma, b_1, \dots, b_{n-\gamma}$ is any permutation of the integers $1, 2, \dots, n$ and the summation extends over all such permutations and over all γ . It is clear that

$$\mathfrak{P}(z, z, z, \dots, z) = \mathcal{P}(z). \quad (58a)$$

To prove the theorem it is only necessary to prove that there are no roots of $\mathcal{P} = 0$ that have an absolute value > 1 . Equation (58a) therefore shows that the theorem is an immediate consequence of the following lemma:

Lemma: If $\mathfrak{P}(z_1, z_2, \dots, z_n) = 0$ and none of the z 's has an absolute value less than one, then

$$1 = |z_1| = |z_2| = \cdots = |z_n|.$$

Proof: (1) We shall assume throughout the proof that all the x 's are different from zero and ± 1 . The proof can then be easily generalized to include the case when one or more of the x 's either vanish or are equal to ± 1 .

The lemma is clearly true when $n=1$, for which $\mathfrak{P}_1 = 1 + z_1$. For $n=2$,

$$\mathfrak{P}_2 = 1 + x_{12}(z_1 + z_2) + z_1 z_2.$$

$\mathfrak{P}_2 = 0$ therefore implies

$$z_1 = -(1 + x_{12} z_2) / (z_2 + x_{12}).$$

It is easy to prove that for $|z_2| > 1$ the right-hand side of this equation always has an absolute magnitude < 1 . Hence if $|z_1| \geq 1, |z_2| \geq 1$, they must both be equal to 1, proving the lemma for the case $n=2$.

(2) We shall prove the lemma for general values of n by induction. Assume it is true for $n=m-2$ and $n=m-1$, but not true for $n=m$. We shall call this assumption hypothesis A and prove that it is self-contradictory. Under hypothesis A there exists a set of z 's equal to z_1, z_2, \dots, z_m such that

$$\mathfrak{P}_m(z_1, z_2, \dots, z_m) = 0 \quad (59a)$$

and

$$|z_1| > 1, \quad \text{and} \quad |z_2|, |z_3|, \dots, |z_m| \text{ all } \geq 1. \quad (59b)$$

The subscript m in \mathfrak{P}_m is to indicate that it has m independent variables z .

(3) We now prove in this paragraph that keeping z_3, z_4, \dots, z_m fixed and regarding z_2 as a function of z_1 defined by (59a) one obtains a limit \mathfrak{z}_2 for z_2 as $z_1 \rightarrow \infty$ and that $|\mathfrak{z}_2| < 1$. To prove this we take, say, $m=3$ and notice that

$$\mathfrak{P}_3 = 1 + z_1 x_{12} x_{13} + z_2 x_{21} x_{23} + z_3 x_{31} x_{32} + z_1 z_2 x_{13} x_{23} + z_2 z_3 x_{21} x_{31} + z_3 z_1 x_{32} x_{12} + z_1 z_2 z_3. \quad (61)$$

As $z_1 \rightarrow \infty, \mathfrak{P}_3 = 0$ gives

$$x_{12} x_{13} + \mathfrak{z}_2 x_{13} x_{23} + z_3 x_{32} x_{12} + \mathfrak{z}_2 z_3 = 0, \quad (62)$$

i.e.,

$$\mathfrak{z}_2 = -(x_{12} x_{13} + z_3 x_{32} x_{12}) / (z_3 + x_{13} x_{23}). \quad (63)$$

It is easy to prove that unless the denominator vanishes this does give the correct limit for z_2 . But the denominator cannot vanish, as will be seen later. Hence the limit \mathfrak{z}_2 is correctly given by (62). Now write

$$\mathfrak{z}_2 x_{12}^{-1} = \zeta_2, \quad z_3 x_{13}^{-1} = \zeta_3. \quad (64)$$

Equation (62) reduces to

$$1 + \zeta_2 x_{23} + \zeta_3 x_{23} + \zeta_2 \zeta_3 = 0.$$

But this is exactly an equation of the form

$$\mathfrak{P}_2(\zeta_2 \zeta_3) = 0,$$

where \mathfrak{P}_2 is a polynomial of the general form (58) with $n=2$. Now by condition (59b)

$$|\zeta_3| > |z_3| \geq 1.$$

Hence hypothesis A asserts that $|\zeta_2| < 1$. Hence

$$|\mathfrak{z}_2| < |\zeta_2| < 1.$$

We need now only prove that the denominator in (63) does not vanish. This is evident in the present case of $m=3$. We shall, however, give a formal proof which holds in general for any value of m . The denominator in (63) is clearly the coefficient of $z_2 z_1$ in \mathfrak{P}_3 given in (61), just as the left-hand side of (62) is the coefficient of z_1 in \mathfrak{P}_3 . We therefore make a similar transformation as (64):

$$z_3 x_{13}^{-1} x_{23}^{-1} = \zeta_3',$$

and reduce the denominator in (63) into the form

$$x_{13} x_{23} \mathfrak{P}_1(\zeta_3'). \quad (65)$$

Clearly $|\zeta'_2| > 1$ so that hypothesis *A* implies that (65) does not vanish. The above arguments evidently hold for any general value of m and this completes the proof that as $z_1 \rightarrow \infty$, z_2 approaches a limit smaller than unity in absolute value.

(4) Keeping $z_3, z_4 \dots z_m$ fixed one can increase $|z_1|$ and define z_2 as a continuous function of z_1 . Since by (59b), $|z_2|$ starts to be ≥ 1 in absolute magnitude and tends to a limit < 1 in absolute magnitude as $z_1 \rightarrow \infty$, there must be a value of z_1 equal to z_1' so that z_2 assumes a value z_2' equal to 1 in absolute magnitude, i.e.,

$$\mathfrak{P}_m(z_1', z_2', z_3, \dots z_m) = 0 \tag{66a}$$

and

$$|z_1'| > 1, \quad |z_2'| = 1, \quad |z_3|, \dots |z_m| \geq 1. \tag{66b}$$

We can fix $z_2', z_4, z_6, \dots z_m$ and regard z_3 as a function of z_1' and follow the same procedure by increasing $|z_1'|$ till z_3 assumes a value equal to 1 in absolute magnitude.

Continuing this way we finally get a set of values $z_1'', z_2'', \dots z_m''$ such that

$$\mathfrak{P}_m(z_1'', z_2'', \dots z_m'') = 0, \tag{67a}$$

and

$$|z_1''| > 1, \quad |z_2''| = |z_3''| = \dots = |z_m''| = 1. \tag{67b}$$

But \mathfrak{P}_m is linear in z_1'' . Writing $\mathfrak{P}_m = Bz_1'' + C$ where B and C are independent of z_1'' one verifies easily that

$$B = z_2'' z_3'' \dots z_m'' \mathfrak{C},$$

where \mathfrak{C} is the complex conjugate of C under the condition (67b). Hence

$$|z_1''| = |C|/|B| = 1, \tag{68}$$

which contradicts (67b). (It is easy to show that B does not vanish by making a transformation similar to (64) and reduce B to products of some x 's with \mathfrak{P}_{m-1} .)

This completes the proof by induction.

High Frequency Electrical Breakdown of Gases*

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Previous theoretical treatments of high frequency electrical breakdown in gases based on the Boltzmann transport equation were applied to specific gases and met with mathematical difficulties when applied to higher pressures. We now present a simpler solution applicable to any gas and to a wide pressure range. Agreement between theory and experiment with hydrogen gives confidence that the energy distribution function is correct and the distribution function is therefore used to compute other quantities of physical interest.

I. INTRODUCTION

IN a recent series of papers, the electrical breakdown of helium and hydrogen in a microwave cavity has been predicted from the measured probability of collision P_c and the corresponding probabilities of excitation P_x and ionization P_i . The only processes assumed to take place are acceleration of electrons by the field, elastic and inelastic collisions with the gas, and diffusion to the walls, which in turn have no effect other than to absorb the electrons and ions. Mathematical difficulties arose in the method used in these papers when applied to higher pressures. The simpler solution given in this paper is applicable to any gas and to a wide pressure range.

II. BOLTZMANN EQUATION

When a high frequency electric field $E = E_0 \exp(j\omega t)$ is applied to a gas, the velocity distribution $F(\mathbf{v})$ of the

free electrons is determined by the Boltzmann equation:

$$(\partial F / \partial t) = C - \nabla_r \cdot \mathbf{v} F + \nabla_v \cdot \mathbf{e} E F / m. \tag{1}$$

C represents the effect of collisions and ∇_r and ∇_v are the gradient operators in configuration and velocity space. This equation is solved by expanding the distribution function in spherical harmonics in velocity space and in Fourier series in time,

$$F = \sum_l \sum_k F_k^l P_l(\cos\theta) \exp(jk\omega t) = F_0^0 + \mathbf{v} \cdot [\mathbf{F}_0^1 + \mathbf{F}_1^1 \exp(j\omega t)] / v. \tag{2}$$

All terms except the three indicated may be dropped when the geometry, pressure, and frequency fall within certain limits which have been discussed by Brown and MacDonald.¹ These limits require that the mean free path be less than any dimension of the cavity, that the frequency be sufficiently high so that the electrons do not lose appreciable energy between cycles, and that the average motion of the electrons resulting from the action of the field and of collisions be sufficiently small

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¹ S. C. Brown and A. D. MacDonald, Phys. Rev. **76**, 1629 (1949).