Statistical Theory of Equations of State and Phase Transitions. I. Theory of Condensation

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A theory of equations of state and phase transitions is developed that describes the condensed as well as the gas phases and the transition regions. The thermodynamic properties of an infinite sample are studied rigorously and Mayer's theory is re-examined.

I. INTRODUCTION

THIS and a subsequent paper will be concerned with the problem of a statistical theory of equations of state and phase transitions. This problem has always interested physicists both from the practical viewpoint of seeking for a workable theory of properties of matter (such as a theory of liquids) and also from the more academic viewpoint of understanding the occurrence of the discontinuities associated with phase transitions in the thermodynamic functions.

The work reported in this paper is quite general and fairly abstract. We are returning in a subsequent paper to the illustration and application of the methods here outlined. In order to present the work of this present paper in its proper perspective, it may be helpful if we outline briefly the history of our own thinking on the subject.

About a year ago one of us was able to make progress[1] with the problem of the spontaneous magnetization of the Ising model, taking advantage of some special properties of this problem when treated by the Onsager-Kaufman method.[2] We then noted that the solution there obtained was also the solution of another, physically quite different, but formally identical, problem. This is the problem of a lattice gas with attractive interaction between nearest neighbors. We were thus able to follow in detail the behavior of such a lattice gas, which in many ways should reveal the features of an actual gas. In particular, we were able to study and characterize the condensation phenonenon, and to identify the liquid, gas, and transition regions in the $p-v$ diagram. The isotherms thus obtained are flat in the transition region and rise very rapidly with increasing density in the liquid phase. At this point, we were led to compare the specific solution with the well-known work[3] of Mayer on the theory of condensation of gases. In particular we were led to inquire as to why, in Mayer's theory, the isotherms stay flat beyond the condensation point and do not give the equation of state for the liquid phase. It soon became apparent that this

difference lay, not in the difference of the models, but in the inadequacy of Mayer's method for dealing with a condensed phase. This led to a study of the analytical behavior of the grand partition function of an assembly of interacting atoms, and we were able, as in the special case mentioned above, to identify and characterize quite generally the condensation phenomena. These general conclusions will be presented in the present paper.

The problem is approached by allowing the fugacity to take on complex values. Although only real values of the fugacity are of any physical interest, the analytical behavior of the thermodynamic functions can only be completely revealed by going into the complex plane, whereby one is able to obtain a description of the condensed phases as well as the gas phase and the transition regions. This approach is of a very general nature and can be applied to other problems of phase transitions such as ferromagnetism, order disorder transition, etc. It will be emphasized that also this approach can lead to practical approximation methods for the description of systems undergoing transitions. These points will be discussed in paper II.

The physical conclusions of this paper derive from some mathematical results which we shall state in the form of two theorems. Due to the nature of the problem (which involves a double limiting process) it is imperative to have mathematical rigor preserved throughout. The proofs are necessarily of a mathematical nature and will be given in the appendix.

II. INTERACTION

We consider a monatomic gas with the interaction

$$U = \sum u(r_{ij}), \tag{1}$$

where r_{ij} is the distance between the ith and jth atoms. The following assumptions are made about the nature of these interactions:

(1) The atoms have a finite impenetrable core of diameter a, so that $u(r) = +\infty$ for $r \leq a$.

(2) The interaction has a finite range b so that

$$u(r) = 0 \text{ for } r \geq b.$$

(3) $u(r)$ is nowhere minus infinity.

The theory can be easily generalized to include many body forces and forces with a weak long tail such as

[1] C. N. Yang, Phys. Rev. **85**, 808 (1952).
[2] L. Onsager, Phys. Rev. **65**, 117 (1944); B. Kaufman, Phys. Rev. **76**, 1232 (1949).
[3] 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); B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938). M. Born and K. Fuchs, Proc. Roy. Soc. (London) **A166**, 391 (1938).

van der Waals' force. But for clarity we shall first treat only interactions with the properties enumerated above.

Consider a box of volume V kept at a constant temperature T. If it is allowed to exchange atoms with a reservoir at a given chemical potential μ per atom, the relative probability of having N atoms in the box is

$$Q_N y^N / N!,$$

where

$$Q_N = \int \cdots \int_V d\tau_1 \cdots d\tau_N \exp(-U/kT) \qquad (2)$$

is the configurational part of the partition function for N atoms and

$$y = (2\pi mkT/h^2)^{\frac{3}{2}} \exp(\mu/kT). \qquad (3)$$

The quantities m, k, and h have the usual meanings,

The grand partition function of the gas in the volume V is

$$\mathcal{Q}_V = \sum_{N=0}^{M} \frac{Q_N}{N!} y^N, \qquad (4)$$

where M is the maximum number of atoms that can be crammed into V.

III. THE LIMIT OF INFINITE VOLUME

The average pressure and the average density of such a gas in V are calculable in terms of $\mathcal{Q}_V$ by the standard treatment of statistical mechanics, and are evidently dependent on V. In thermodynamics, however, one is only interested in an infinite sample and the thermodynamic functions are limits of these average quantities as $V \to \infty$. The pressure p and density ρ are accordingly given by

$$\frac{p}{kT} = \underset{V \to \infty}{\text{Lim}} \frac{1}{V} \log \mathcal{Q}_V, \qquad (5)$$

$$\rho = \underset{V \to \infty}{\text{Lim}} \frac{\partial}{\partial \log y} \frac{1}{V} \log \mathcal{Q}_V. \qquad (6)$$

The question of whether these limits do exist is usually not discussed.[4] It is, however, generally believed that in the gas phase such limits do exist and that (5) and (6) give the correct equation of state. At the point of condensation and in the liquid phase the situation has been extremely unclear. As a matter of fact doubts have been raised[5] as to whether the equation of state of both the liquid and the gas phase can be obtained

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[4] The behavior of the partition function Q_N as the volume approaches infinite was discussed by L. von Hove, Physica **15**, 951 (1949), where it is proved that $N^{-1} \log Q_N$ approaches a limit as the volume approaches infinity at constant density. His proof is similar to our proof of theorem 1.

[5] There was apparently some discussion on this point at the International Conference held in Amsterdam, 26 November 1937. The doubts can perhaps be formulated in the form of the question: "How can t e gas molecules know when they have to coagulate to form a lic id or solid?" See p. 391 of reference 3 (Born and Fuchs).

from the same interaction (1) through the considerations of statistical mechanics.

We shall try to resolve these problems and prove that (5) and (6) do give a complete description of the equation of state of both the gas and condensed phases. In fact in paper II we shall give a concrete example in which it is seen how the same partition function describes both phases, and in which the two-phase-equilibrium region is exactly known.

We first state the following:

Theorem 1.—(Proved in Appendix I.) For all positive real values of y, $V^{-1} \log \mathcal{Q}_V$ approaches, as $V \to \infty$, a limit which is independent of the shape of V. Furthermore, this limit is a continuous, monotonically increasing function of y.

The assumption is made, of course, that the shape of V is not so queer that its surface area increases faster than $V^{\frac{2}{3}}$.

One might be tempted to conclude from the independence of the limit on the shape of V that the system under consideration exists only in fluid phases (i.e., gas and liquid) with no elastic resistance against shearing strain. It is to be emphasized that this is not the case. The independence of the limit on the shape of V is not due to the lack of elastic resistance against shearing strain, but rather due to the fact that for an infinite sample changing the shape of V does not produce a strain in the interior which might serve to differentiate between a fluid and a solid. This is so because the strain at the boundary only penetrates to a finite depth and is inconsequential for an infinite sample.

To study the limit of $(\partial/\partial \log y) V^{-1} \log \mathcal{Q}_V$ we notice that $\mathcal{Q}_V$ is a polynomial in y of finite degree M. This is a direct consequence of the assumed impenetrable core of the atoms. It is therefore possible to factorize $\mathcal{Q}_V$ and write

$$\mathcal{Q}_V = \prod_{i=1}^{M} \left(1 - \frac{y}{y_i} \right), \qquad (7)$$

where $y_1, \cdots y_M$ are the roots of the algebraic equation

$$\mathcal{Q}_V(y) = 0. \qquad (8)$$

Evidently none of these roots can be real and positive, since all the coefficients in the polynomial $\mathcal{Q}_V$ are positive.

As V increases these roots move about in the complex y plane and their number M increases (essentially) linearly with V. Their distribution in the limit $V \to \infty$ gives the complete analytic behavior of the thermodynamic functions in the y plane. In fact one can prove the following:

Theorem 2.—(Proved in Appendix II.) If in the complex y plane a region R containing a segment of the positive real axis is always free of roots, then in this region as $V \to \infty$ all the quantities:

$$\frac{1}{V} \log \mathcal{Q}_V, \quad \left(\frac{\partial}{\partial \log y} \right) \frac{1}{V} \log \mathcal{Q}_V, \quad \left(\frac{\partial}{\partial \log y} \right)^2 \frac{1}{V} \log \mathcal{Q}_V \cdots,$$

approach limits which are analytic with respect to y. Furthermore the operations $(\partial/\partial \log y)$ and $\text{Lim}_{V\to\infty}$ commute in R so that, e.g.,

$$\underset{V\to\infty}{\text{Lim}}\frac{\partial}{\partial \log y}\frac{1}{V}\log\mathcal{Q}_V=\frac{\partial}{\partial \log y}\underset{V\to\infty}{\text{Lim}}\frac{1}{V}\log\mathcal{Q}_V. \quad (9)$$

This gives, together with (5) and (6),

$$\rho=(\partial/\partial \log y)(p/kT). \quad (10)$$

IV. PHASE TRANSITIONS

The quantity $(\partial/\partial \log y)V^{-1}\log\mathcal{Q}_V$ does not, however, always approach a limit ρ for all values of y. Physically this must evidently be as the density of the system does not assume a single value at the point of condensation. It is clear therefore that the problem of phase transition is intrinsically related to the form of the regions R described in theorem 2. We discuss the following cases:

(1) The roots of $\mathcal{Q}_V(y)=0$ do not close in onto the positive real axis of y as $V\to\infty$, or more exactly, there exists a region R which contains the whole positive real axis and is free of roots.

In this case from the two theorems one concludes that the pressure and density of the system are analytic functions of y (along the positive real axis). They are related by Eq. (10). Furthermore, p is an increasing function of y. We shall show in Appendix III that ρ is also an increasing function of y. Consequently in the $p-\rho$ diagram, on the isotherm p increases analytically
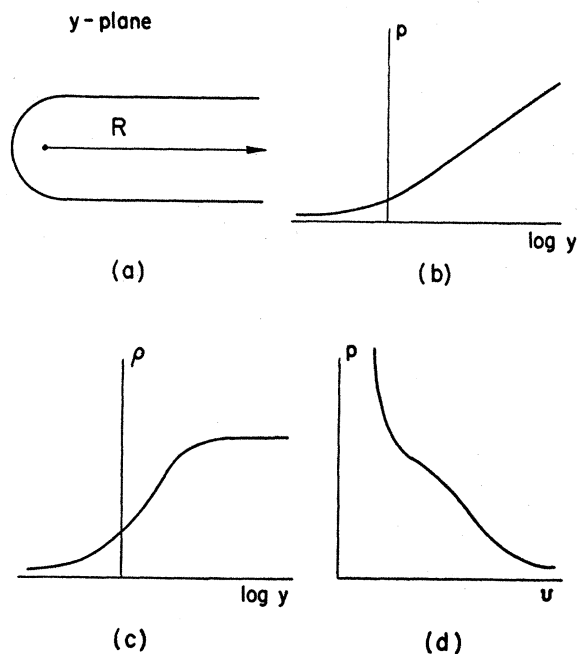

FIG. 1. Analytical behavior at a given temperature of thermodynamic functions for a single phase system. The quantity y is defined by Eq. (3) in the text. The region R is free of roots of Eq. (8). Notice that the density ρ of (c) is proportional to the slope of the $p-\log y$ curve in (b).

as the specific volume v decreases. The system under consideration is thus a single phase system (see Fig. 1).

(2) The roots of $\mathcal{Q}_V(y)=0$ do close in onto the real axis as $V\to\infty$, say at the points $y=t_1$, t_2; and regions R_1, R_2, and R_3 free of roots enclose, respectively, the three segments of the positive real axis as in Fig. 2(a).

By the same reasoning as in the previous case one concludes, within any one of these three segments, that the system exists in a single phase, that p and ρ are analytic and increasing functions of y, that ρ is $(kT)^{-1}(\partial p/\partial \log y)$, and that on the isotherm p increases analytically as v decreases.

At the points $y=t_1$, t_2 the pressure p is continuous (by theorem 1), but its derivative ρ has in general a discontinuity. By Appendix III one shows easily that ρ increases across the discontinuity. The functions p and ρ are schematically plotted in Figs. 2(b) and 2(c) which together give the isotherm in Fig. 2(d).

As the temperature varies the points t_1 and t_2 will in general move along the y axis. If at a certain temperature T_c the roots cease to close in onto one of the points, say t_1, then T_c is the critical temperature for the transition phase 1↔ phase 2. If, on the other hand, t_1 and t_2 merge together at a particular temperature T_0, we would then have a triple point at that temperature.

It may be remarked that at $y=t_1$ or t_2 the density ρ may in some cases be continuous (although its derivative will in general be discontinuous). At the critical temperature this will happen, but not at neighboring temperatures. If, however, this happens over an extended temperature range, one would have a transition of second (or higher) order.

It is clear therefore that phase transitions of the system occur only at the points on the positive real y axis onto which the roots of $\mathcal{Q}(V)=0$ close in as $V\to\infty$. For other values of the fugacity y a single phase system obtains.

As mentioned before, the theory can be easily generalized to include many body forces and forces with a weak long tail. In fact, the generalization does not lead to any alterations of the conclusions reached above.

Generalization can also be made to other kinds of phase transitions such as order-disorder phenomena and ferromagnetism, as will be discussed in paper II. The study of the equations of state and phase transitions can thus be reduced to the investigation of the distribution of roots of the grand partition function. In many cases, as will be seen in paper II, such distributions turn out to have some surprisingly simple regularities.

V. COMPARISON WITH MAYER'S THEORY

We first notice that by expanding in powers of y one obtains from (7)

$$\frac{1}{V}\log\mathcal{Q}_V=\sum_{l=1}^{\infty} b_l(V)y^l, \quad (11)$$

where

$$b_l(V) = \frac{-1}{lV} \sum_{j=1}^{M} \left(\frac{1}{y_j}\right)^l. \qquad (12)$$

Combining (11) and (3) we have

$$\frac{Q_N}{N!} = \text{coefficient of } y^N \text{ in } \exp[V \sum_{l=1}^{\infty} b_l y^l]. \qquad (13)$$

Comparison of this equation with Mayer's theory shows that the b_l's defined by (12) are identical with the reducible cluster integrals defined[6] by Mayer. It is interesting to notice that these reducible cluster integrals are, according to (12), closely related to the moments of the roots y_j of Eq. (8). It should be emphasized that in both (12) and in Mayer's definition the b_l's are functions of the volume V. It is evident from Mayer's definition that they approach definite limits $b_l(\infty)$ as $V \to \infty$.

In Mayer's theory the cluster integrals b_l are replaced from the very beginning by their limiting values $b_l(\infty)$. He then considers the series

$$\chi(y) = \sum_{1}^{\infty} b_l(\infty) y^l \qquad (14)$$

and its analytical continuation along the positive real axis. If one calls the first singularity of $\chi(y)$ along the positive real axis t_1, one shows in Mayer's theory that

(1) for densities ρ less than

$$\rho_1 = \lim_{y \to t_1-} y \chi'(y), \qquad (15)$$

the system exists in a single phase;

(2) for $\rho \geqq \rho_1$, the pressure p (at a given temperature) becomes independent of the density. Consequently, one identifies the density ρ_1 as the density of the gas at condensation.

An essential difficulty of Mayer's theory is that it does not admit of the existence of a liquid phase with finite density, since the isotherm remains horizontal for all specific volume less than ρ_1^{-1}. This is clearly due to the replacement of the volume dependent b_l's by their limiting values. The question is therefore often raised[7] as to exactly at what point on the isotherm Mayer's theory breaks down.

In the present theory by retaining the volume dependence of the partition function $\mathcal{Q}_V$ we do not encounter these difficulties. To clarify the relationship with Mayer's theory, we refer back to Fig. 2(a) and draw a small circle C within R_1 with the center at the origin. The series

$$\sum_{l=1}^{\infty} b_l(V) y^l$$

[6] See for example Eq. (13.5) in J. E. Mayer and Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1946), p. 280.
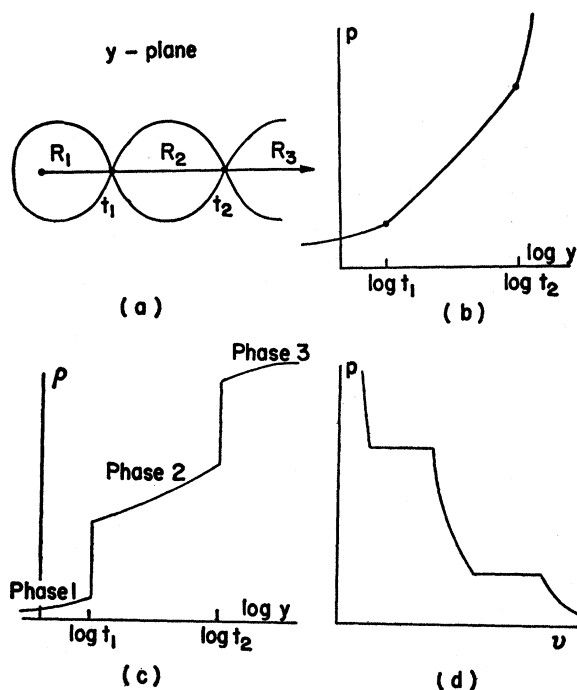[7] See, for example, reference 3 (Kahn and Uhlenbeck), p. 415.

FIG. 2. Analytical behavior at a given temperature of thermodynamic functions for a system that undergoes two phase transitions. The transitions occur at t_1 and t_2 which are the points at which the roots of Eq. (8) close in onto the positive real y axis. The regions R_1, R_2, and R_3 are free of roots. The three phases 1, 2, and 3 are indicated in (c). The horizontal parts of (d) represent two-phase-equilibrium regions.

is easily shown[8] to converge uniformly in the circle C. By a well-known mathematical theorem on double limiting processes one concludes that in C

$$\lim_{V \to \infty} \sum_{1}^{\infty} b_l(V) y^l = \sum_{1}^{\infty} b_l(\infty) y^l. \qquad (16)$$

The left-hand side of this equation is by definition

$$\lim_{V \to \infty} V^{-1} \log \mathcal{Q}_V,$$

and the right-hand side $\chi(y)$. Therefore within C the function $\chi(y)$ in Mayer's theory is indeed $(kT)^{-1}$ times the pressure p as defined by (5). By analytical continuation one concludes that this holds throughout the region R_1.

In the interval $0 \leqq y < t_1$ it is evident that $\rho < \rho_1$ and Mayer's theory is seen to give a correct description of the system.

Beyond the point $y = t_1$ (i.e., $y \geqq t_1$) it is not possible in Mayer's theory to analytically continuate $\chi(y)$. The $p - \log y$ and $\rho - \log y$ diagrams [Figs. 2(b) and 2(c)] therefore exist in his theory only to the left of the first singularity. This explains the nonexistence of the liquid phase in Mayer's theory.

[8] All roots y_j have absolute values larger than the radius σ of the circle C. By Eq. (12) we have $|b_l| \leqq (M/V) l^{-1} \sigma^{-l}$. But M/V is bounded. Hence the statement.

We thus remark:

(1) Throughout the gas phase (i.e., $\rho < \rho_1$) Mayer's theory gives correct results.

(2) For $\rho \geqq \rho_1$ Mayer's conclusion that the $p-v$ diagram becomes horizontal is, as already mentioned, incorrect for high densities due to the existence of the liquid phase. It is not even justified for densities immediately above ρ_1, as for transitions of high order the isotherm does not even have any horizontal part at all.

We are indebted to Professor J. R. Oppenheimer for criticism and comment.

APPENDIX I

To prove theorem 1 we first establish the following:

Lemma 1.—Let V and W be two cubes of linear dimensions L and $L+(b/2)$, respectively. Keeping b fixed one has as $L \to \infty$,

$$\mathrm{Lim} W^{-1}(\log \mathcal{Q}_W - \log \mathcal{Q}_V) = 0. \tag{17}$$

Proof.—Put V completely inside W and write $\mathcal{Q}_W$ as the sum of contributions $A_0, A_1 \cdots$ from configurations with zero, one . . . atoms outside of V. Now (a) since the interaction has finite range, each atom interacts with at most a finite and definite number of other atoms. Also (b) the available volume for the first atom outside of V is $\Delta = W - V$. If the volume of the impenetrable core of an atom is α, the available volume for the second atom outside of V is less than $\Delta - \alpha$, the third, $\Delta - 2\alpha$, etc. Combining (a) and (b) one concludes that

$$A_m \leqq \beta^m [\Delta(\Delta - \alpha)(\Delta - 2\alpha) \cdots (\Delta - m\alpha + \alpha)/m!] \mathcal{Q}_V, \tag{18}$$

where β is a constant. (This inequality is obtained by comparing the contributions to A_m and $\mathcal{Q}_V$ of a distribution of atoms with, say, N atoms inside of V and m atoms outside.) Adding all A's one obtains

$$\mathcal{Q}_W \leqq \mathcal{Q}_V (1 + \beta\alpha)^{\Delta/\alpha}.$$

But $\Delta \sim L^2$, and clearly

$$\mathcal{Q}_V \leqq \mathcal{Q}_W.$$

Hence the lemma.

Lemma 2.—Let W_i be a cube of linear dimension $2^i L$ and $\mathcal{Q}_i$ an abbreviation for $\mathcal{Q}_{W_i}$. Then

$$\mathrm{Lim}_{i \to \infty} W_i^{-1} \log \mathcal{Q}_i = K \text{ exists.}$$

Proof.—Consider W_j to be built up from 8^{j-i} smaller cubes $W_i (j > i)$. Evidently the number of atoms interacting across the boundaries of the small cubes is at most proportional to the area of such boundaries and hence is less than $8^i 2^{-i} \gamma$, ($\gamma =$ constant). Should one neglect these interactions, $\mathcal{Q}_j$ would become $\mathcal{Q}_i$ raised to the power 8^{j-i}. The inclusion of these terms violates this identity by not more than a constant factor β raised to the power $8^j 2^{-i}$, i.e.,

$$\log \mathcal{Q}_j \leqq 8^{j-i} \log \mathcal{Q}_i + 8^j 2^{-i} \gamma \log \beta. \tag{19}$$

Next draw within each small cube W_i a concentric cube V_i with linear dimension $2^i L - (b/2)$. Since b is the range of interaction, clearly atoms in different V_i's do not interact. Hence,

$$8^{j-i} \log \mathcal{Q}_{V_i} \leqq \log \mathcal{Q}_j. \tag{20}$$

Equations (19) and (20) give

$$W_i^{-1} \log \mathcal{Q}_{V_i} \leqq W_j^{-1} \log \mathcal{Q}_j \leqq W_i^{-1} \log \mathcal{Q}_i + 2^{-i} \gamma L^{-3} \log \beta. \tag{21}$$

The last term approaches zero as $i \to \infty$. Also by Lemma 1, $W_i^{-1}(\log \mathcal{Q}_i - \log \mathcal{Q}_{V_i}) \to 0$. Thus as $j > i \to \infty$ $\cdot W_j^{-1} \log \mathcal{Q}_j - W_i^{-1} \log \mathcal{Q}_i \to 0$. Hence the lemma.

Proof of the theorem.—Given any $\epsilon > 0$ there exists by Lemma 2 a large enough box W such that

$$|K - W^{-1} \log \mathcal{Q}_W| < \epsilon.$$

In fact by the same reasoning as used in proving that lemma, one easily sees that this can also be made true of any box Ω which can by adding partitions be divided into cubes of size W:

$$|K - \Omega^{-1} \log \mathcal{Q}_\Omega| < \epsilon.$$

Now consider a volume V of arbitrary shape. For sufficiently large V one can build two Ω-type boxes Ω_1 and Ω_2 such that Ω_1 is contained in V and Ω_2 contains V and that

$$|(\Omega_1/\Omega_2) - 1| < \epsilon.$$

Using

$$\mathcal{Q}_{\Omega_1} \leqq \mathcal{Q}_V \leqq \mathcal{Q}_{\Omega_2},$$

one proves easily that $V^{-1} \log \mathcal{Q}_V$ also approaches K.

That this limit monotonically increases with y follows from the same property of $V^{-1} \log \mathcal{Q}_V$. That it is also continuous follows from the observation that $(\partial/\partial \log y) V^{-1} \log \mathcal{Q}_V$ has a finite and definite upper bound (equal to the density of closest packing).

APPENDIX II

We first prove the following:

Lemma 3.—Consider the series

$$\sum_{l=0}^{\infty} b_l(V) z^l = S_V(z),$$

where

$$|b_l(V)| \leqq A \sigma^{-l},$$

A and σ being positive constants. For all real z between $-\sigma$ and $+\sigma$ assume $\mathrm{Lim} S_V(z)$ to exist as $V \to \infty$. Then (a) $\mathrm{Lim} b_l(V)$ as $V \to \infty$ exists and will be denoted by $b_l(\infty)$. (b) $S_V(z)$ approaches the limit

$$\sum_{l=0}^{\infty} b_l(\infty) z^l, \tag{22}$$

as $V \to \infty$ for all $|z| < \sigma$. The series (22) is convergent for all $|z| < \sigma$.

Proof.—(a) Evidently $\mathfrak{b}_0(\infty)$ exists and is equal to $\text{Lim} S_V(0)$ as $V \to \infty$. To prove the existence of $\text{Lim} \mathfrak{b}_1(V)$: Given any real ϵ between 0 and $\sigma/2$ consider the convergence of $S_V(\epsilon)$ and $\mathfrak{b}_0(V)$ as $V \to \infty$. There exists a volume V_0 such that for any volumes V and W greater than V_0 one has

$$|S_V(\epsilon) - S_W(\epsilon)| < \epsilon^2, \tag{23}$$

$$|\mathfrak{b}_0(V) - \mathfrak{b}_0(W)| < \epsilon^2. \tag{24}$$

But

$$|\sum_{l=2}^{\infty} \mathfrak{b}_l(V)\epsilon^l| \leq \frac{A\epsilon^2}{1 - \epsilon\sigma^{-1}} \leq 2A\epsilon^2. \tag{25}$$

The same is true if one replaces V by W. Using

$$\epsilon \mathfrak{b}_1(V) = S_V(\epsilon) - \mathfrak{b}_0(V) - \sum_{l=2}^{\infty} \mathfrak{b}_l(V)\epsilon_l,$$

one proves easily with the aid of (23), (24), and (25) that

$$\epsilon |\mathfrak{b}_1(V) - \mathfrak{b}_1(W)| < (2+4A)\epsilon^2.$$

Hence $\text{Lim} \mathfrak{b}_1(V)$ exists as $V \to \infty$. Similar proof holds for the other $\mathfrak{b}_l$'s.

(b) The series $\sum \mathfrak{b}_l(V)z^l$ evidently converges uniformly in z for $|z| < \sigma$. The lemma follows from a well-known theorem on double limits.

Proof of theorem 2.—Consider first a circle C, lying inside R, with its center at the point $y = \eta$ along the positive real axis. We shall first prove the theorem inside this circle. Making the displacement $z = y - \eta$ we express (7) in the form

$$\mathcal{Q}_V = \prod_{i=1}^{M} \left(1 - \frac{z}{z_i}\right)\left(\frac{z_i}{y_i}\right), \tag{26}$$

where $z_i = y_i - \eta$ are the roots of $\mathcal{Q}_V$. Expanding $V^{-1} \log \mathcal{Q}_V$ in powers of z one obtains

$$\frac{1}{V} \log \mathcal{Q}_V = \sum_{l=0}^{\infty} \mathfrak{b}_l(V)z^l, \tag{27}$$

where

$$\mathfrak{b}_l(V) = \frac{-1}{Vl} \sum_{i=1}^{M} \left(\frac{1}{z_i}\right)^l \text{ for } l \geq 1, \tag{28}$$

and

$$\mathfrak{b}_0(V) = \frac{1}{V} \sum_{i=1}^{M} \log \frac{z_i}{y_i}. \tag{29}$$

If σ is the radius of C, since C is free of roots we have $|z_i| \geq \sigma$. Hence by (28)

$$|\mathfrak{b}_l(V)| \leq (M/V)l^{-1}\sigma^{-l} \text{ for } l \geq 1.$$

But M/V is bounded; hence we can use Lemma 3 and the theorem is proved in C.

By similar arguments we can extent the theorem into a circle C' lying inside R with its center inside C. One can easily prove the theorem in the whole region R by repeating this process.

APPENDIX III

To prove that ρ is an increasing function of y it is only necessary to show for any finite V the inequality

$$\frac{d^2}{(d \log y)^2} \log \mathcal{Q}_V > 0.$$

Now $\mathcal{Q}_V$ is a polynomial in y with positive coefficients. Regarding the various terms of $\mathcal{Q}_V$ as relative probabilities we have obviously

$$\frac{d}{d \log y} \log \mathcal{Q}_V = \langle N \rangle,$$

where $\langle \ \rangle$ means "average." Also

$$\frac{d^2}{(d \log y)^2} \log \mathcal{Q}_V = \langle N^2 \rangle - \langle N \rangle^2 = \langle (\Delta N)^2 \rangle,$$

which is always positive. Here ΔN is the deviation of N from the average

$$\Delta N = N - \langle N \rangle.$$