Mayer's theory about the relation between the phase transitions and the singular points has been criticized. The matrix method is connected with Mayer's cluster theory applied to regular solutions. It is shown that the following two cases are possible. They are
i) that the density of atoms is a single analytic function of the active number density, at least, on the positive real axis, and the first singularity of this function is an essential singular point and the phase transition occurs at this point,
ii) that the density of atoms may consist of different analytic functions of the active number density, and the phase transition may occur at the point which is not analytic singular point of the function.

The same is true of continuous aggregate systems such as imperfect gases. In the continuous case the partition function may be obtained as the smallest eigenvalue of Fredholm's integral equation.

§ 1. Introduction

The existing theories, which deal with the systems composed of strongly interacting particles, such as imperfect gases, liquids and crystalline solids, are classified into three types, except very simple ones. The first of them is the integral equation method developed by Kirkwood\(^1\), Yvon\(^2\) and Born and Green\(^3\). This method is only approximative, and we can place trust in not all of quantitative results of it, since the Kirkwood approximation is utilized in this method. The same is true of the customary approximate theories applied to crystal statistics, such as Bethe's theory. The next is the matrix method elaborated by Krammers and Wannier\(^4\), Montroll\(^5\), Lassette and Howe\(^6\), Onsager\(^7\) and others. This method is strict, but applicable only to the case of crystal statistics. The last one is the method of cluster integrals of Mayer\(^8\), which is considered as the most general one. This method is, however, not so useful for practical calculations and some of its important conclusions have been drawn without complete proof, as pointed out by Katsura and Fujita\(^9\).

The purposes of the present paper are to criticize the results of Mayer's theory about the relation between the phase transitions and the singular points, to investigate properties of the singularities in detail, and to give the proper statistical interpretation of the phase transition. Since the matrix method seems to give more definitive conclusion, we may make clear the ambiguous points of Mayer's theory if we connect the matrix method with Mayer's method of series developments. Since the matrix method is established only for the case of crystal statistics, we shall, at first, study the connection between these two methods for this case. And an attempt to extend the eigenvalue method to continuous aggregate systems will be discussed in the last portion of this paper.
§ 2. Phase change and singularity

In this paper we shall consider a single-component system. If we denote by \( \Xi(T, z, V) \) the grand partition function of it as a function of the absolute temperature \( T \), the active number density* \( z \), and the volume \( V \), the pressure is written as

\[
pV = kT \ln \Xi(T, z, V),
\]

\( k \) being Boltzmann's constant. And if the classical laws of mechanics are applied to the system, the grand partition function \( \Xi(T, z, V) \) is given by

\[
\Xi(T, z, V) = \sum_{r=0}^{\infty} \frac{z^r}{r!} \mathcal{Q}_r(T, V),
\]

where \( \mathcal{Q}_r(T, V) \) is the configurational partition function of the system composed of the \( r \) molecules contained in the volume \( V \). Here we assume that \( \rho \) is expressible as a power series in \( z \) as follows:

\[
pV = kTV \sum_{s=1}^{\infty} b_s(T, V) z^s.
\]

Then from the above relations, we see that the relation between \( \mathcal{Q}_r(T, V) \) and \( \mathcal{V}_s \) \( b_s(T, V) \) is the same as that between the \( r' \)th moment and the \( s' \)th Thiele semi-invariant in mathematical statistics\(^{(1)}\)

\[
V b_s(T, V) = \sum \left[ \sum i r_i = s \right] (-1)^{r_i-1} (\sum r_i - 1)! \prod_{i=1}^{r_i} \left( \frac{Q_{i}(T, V)}{i!} \right)^{r_i} \frac{1}{r_i!},
\]

where the sum extends over all sets of \( r_i \) such that \( \sum i r_i = s \). If the potential energy is expressible as a sum of that between all pairs, \( b_s(T, V) \) given by (4) agrees with Mayer's expression for the \( s' \)th cluster integral. This method is applicable also to the case of quantum statistics, and will give the result same as that Kahn and Uhlenbeck\(^{(2)}\) have deduced.

If the volume is finite, and if two molecules cannot approach beyond a certain limit, a finite volume can contain only finite number of molecules. So \( \mathcal{Q}_r(T, V) \) vanishes for \( r \) larger than a certain value. And the \( \Xi(T, z, V) \) is regular for all finite \( z \) of the complex plane, since it becomes polynomial in \( z \). And (3) also is regular except at the zeros of (2).

If the intermolecular force is sufficiently short-ranged, \( b_s(T, V) \) for every \( s \) is asymptotically independent of the volume. And it will approach a certain limiting value \( b_s(T) \), if we let the volume be infinite:

\[
b_s(T) = \lim_{V \to \infty} b_s(T, V).
\]

Mayer considered the series

\[
p = kT \sum_{s=1}^{\infty} b_s(T) z^s,
\]

\( \ast \) The parameter, \( z \), has been referred by Mayer as the fugacity.
which may correspond to (3): By means of (6), one may define the function $p(z)$ for complex values of $z$. And Mayer suggested that the singularities of the analytic function obtained from (6) by the process of continuation correspond to the values of the fugacity characteristic of the phase transitions. But Mayer has neither justified the above conclusion, nor has spoken of the properties of these singularities. And he has not shown which branch of the analytic function may express the true pressure if this function is many-valued.

Katsura and Fujita pointed out that the phase transitions correspond to the singularities of the function

$$p = \lim_{r \to \infty} kT \sum_{i=1}^{\infty} b_i(T, V) z^i,$$

rather than those of (6). Although Mayer's theory on the relation between the phase transitions and the singularities is not based on any complete proof, it seems not to have been proved by Katsura and Fujita that the first singularities of (6) and (7) do differ.

Green and Rodriguez have shown that the first singularity is not the point of condensation but is the point separating super-saturated vapor from liquid, but it may be plausible that this result follows from the Kirkwood approximation employed in these theories.

§ 3. The series-development method in crystal statistics

Let us consider a binary solid solution consisting of two types of atoms, $A$ and $B$, of which the total potential energy is represented by the sum of the interactions of each atom with its contact neighbors. As shown in Fig. 1, let us divide the system into $l \times m \times u$ cells, each containing an $A$ or $B$ atom. Then, we shall denote the interactions between an $AA$-contact, a $BB$-contact, and an $AB$-contact by $\varepsilon_{AA}$, $\varepsilon_{BB}$, and $\varepsilon_{AB}$, respectively. Then the configurational partition function of the system containing $r$ $A$-atoms is of the form

$$Q_r(T; l, mu) = r! \sum g(r, X; l, mu) \times \exp \{ -X \Delta \varepsilon / kT \},$$

where $g(r, X; l, mu)$ is the number of configurations for which the number of $AB$-contacts is $X$, and $\Delta \varepsilon$ is given by

$$\Delta \varepsilon = \varepsilon_{AB} - \frac{1}{2} (\varepsilon_{AA} + \varepsilon_{BB}).$$

* Strictly speaking, the configurational partition function is given by $Q_r(T; l, mu) \exp \{ -lmu \varepsilon_{BB} - r(\varepsilon_{AA} - \varepsilon_{BB}) \}$, the form of the grand partition function being independent of this additional factor if the active number densities, $z_A$ and $z_B$ are replaced by their respective effective values, $\overline{z}_A$ and $\overline{z}_B$. 
The arrangements produced by only interchange between the same type of atoms are regarded as the same configuration. Denoting the effective active number densities of $A$ and $B$ atoms by $\varphi_A$ and $\varphi_B$, respectively, we express the grand partition function in the form

$$\Xi(T; \varphi_A, \varphi_B; l, mn) = \Xi_l^{mn}(T, \varphi_A, \varphi_B; l, mn),$$

where

$$\Xi(T, \varphi; l, mn) = \sum_{r=0}^{mn} \frac{\varphi^r}{r!} Q_r(T; l, mn),$$

and

$$\varphi = \frac{\varphi_A}{\varphi_B}.$$  \hspace{1cm} (11)

As shown by Lassettre and Howe, if one interchanges the roles of $A$ and $B$, one obtains

$$\Xi(T, \varphi; l, mn) = \Xi_l^{mn}(T, 1/\varphi; l, mn).$$

Since (10) is of the same form as (2), we obtain, as in the case of (4),

$$\ln mu b_s(T; l, mn) = \sum \left[ \sum (\varphi_i) (-)^{\sum r_i-1} (\sum r_i-1) ! \prod_{i=1}^{\sum r_i} \frac{Q_r(T; l, mn)}{r_i !} \right].$$

Then, as with (3), we have the relation

$$\ln \Xi(T, \varphi; l, mn) = \sum_{s=1}^{\infty} b_s(T, l, mn) \varphi^s.$$  \hspace{1cm} (14)

And if we introduce the function defined as

$$\exp \chi(T, \varphi; l, mn) = \Xi(T, \varphi; l, mn)^{1/\ln m},$$

we obtain

$$\chi(T, \varphi; l, mn) = \sum_{s=1}^{\infty} b_s(T, l, mn) \varphi^s,$$  \hspace{1cm} (16)

for $\varphi$ in the circle of convergence. $b_s(T; l, mn)$ is the cluster sum introduced by Fuchs and Muto in applying Mayer's method of cluster integrals to regular solutions. In this case the cluster sums for small values of $\varphi$ do not depend on $l$, $m$, $n$. On the other hand, Tanaka and Ogura, Oguchi and Wakefield calculated $Q_r(T; l, mn)$ for small $r$ by the direct counting of complexions. Because $Q_r$ and $b_s$ are related each other through (13), this method is entirely equivalent to Fuchs and Muto's one.

As in the theory of condensation, we may write, corresponding to (16),

$$\chi(T, \varphi) = \sum_{s=1}^{\infty} b_s(T) \varphi^s,$$  \hspace{1cm} (17)

where

$$b_s(T) = \lim_{m,n \to \infty} \lim_{l \to \infty} b_s(T; l, mn).$$  \hspace{1cm} (18)

Furthermore, we define the following functions:

$$\chi(T, \varphi; \infty, \infty) = \lim_{m,n \to \infty} \lim_{l \to \infty} \chi(T, \varphi; l, mn),$$  \hspace{1cm} (19)
\[
\chi(T, \varepsilon; \infty, mn) = \lim_{l \to \infty} \chi(T, \varepsilon; l, mn),
\]
and
\[
\chi(T, \varepsilon; \infty, mn) = \sum_{l=1}^{m} b_l(T, mn) \varepsilon^l,
\]
where
\[
b_l(T, mn) = \lim_{l \to \infty} b_l(T; l, mn).
\]

Since we may not proceed to the limit term by term, as pointed out by Katsura and Fujita\textsuperscript{10}, (17) is not necessarily equal to (19). The same is true of (20) and (21).

According to Mayer's standpoint of view, the active number density at which the phase transition occurs is given as the singularity of the function (17).

§ 4. The matrix method

The system described in the previous section consists of \( l \) layers each composed of \( m \times n \) cells. Let us denote a configuration of the \( i \)'th layer by \( s_i \). In the case of solid solution, \( s_i \) corresponds to a distribution of the two types of atoms in the \( i \)'th layer, and every \( s \) assumes \( 2^{mn} \) values. Suppose the \( j \)'th and \( j+1 \)'th layers have the distribution \( s_j \) and \( s_{j+1} \) respectively, and we denote the number of contacts of unlike atoms in the \( j \)'th layer by \( \chi(s_j) \) and the number of contacts of unlike atoms between the \( j \)'th and \( j+1 \)'th by \( \chi(s_j, s_{j+1}) \). Then the total number of contacts of unlike atoms is given by

\[
\chi = \sum_{j=1}^{l} \chi(s_j) + \sum_{j=1}^{l} \chi(s_j, s_{j+1}).
\]

Here we assume that the Born von Kármán boundary condition is imposed upon the system: \( s_{l+1} = s_1 \). And let \( r(s_j) \) be the number of \( A \) atom in the \( j \)'th layer at the distribution \( s_j \). Then \( \tilde{\mathcal{E}}(T, \varepsilon; l, mn) \) given by (10) may be, according to (7) and (23), rewritten in the form

\[
\tilde{\mathcal{E}}(T, \varepsilon; l, mn) = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_l} \mathcal{K}(s_1, s_{l+1}),
\]

where

\[
\mathcal{K}(s_j, s_{j+1}) = \exp \left\{ \{r(s_j) + r(s_{j+1}) \} \ln \varepsilon / 2 - \chi(s_j) - \chi(s_{j+1}) \} \lambda \varepsilon / kT \right\}
\times \exp \left\{ - \chi(s_j, s_{j+1}) \lambda \varepsilon / kT \right\}.
\]

Lassettre and Howe\textsuperscript{6}, and Montroll\textsuperscript{5} have shown that \( \tilde{\mathcal{E}}(T, \varepsilon; l, mn) \) is written as

\[
\tilde{\mathcal{E}}(T, \varepsilon; l, mn) = \sum_{s_1}^{2^{mn}} \mathcal{A}_s(T, \varepsilon; mn) \lambda^s,
\]

where \( \mathcal{A}_s(T, \varepsilon; mn) \)'s are \( 2^{mn} \) roots of the secular equation

\[
\det [\mathcal{K}(u, \beta) - \lambda \mathcal{A}_s] = 0.
\]

If the largest root is simple, \( \chi(T, \varepsilon; \infty, mn) \) defined by (15) and (20) becomes

\[
\chi(T, \varepsilon; \infty, mn) = (1/mn) \ln \mathcal{A}^*(T, \varepsilon; mn),
\]

where

\[
\mathcal{A}^*(T, \varepsilon; mn) = \lim_{l \to \infty} \mathcal{A}_s(T; l, mn).
\]
where $A^*(T, z; mn)$ is the largest of $A_i(T, z; mn)$.

(27) is a polynomial of degree $2^{\infty \times \infty}$ in $A$. The coefficients of this polynomial are polynomials in $z$, since we can apply a suitable transformation to the matrix produced from (25), so that each element becomes a polynomial in $z$. Thus $A_1(T, z; mn), A_2(T, z; mn), \ldots$ form an algebraic function or a set of algebraic functions of $z$ according as (27) is irreducible or reducible.

Since the algebraic functions cannot possess essential singular points, the largest root of (27) must be degenerate at the active number density at which the phase transition occurs. And according to the theorem due to Frobenius, the largest root is simple and positive as far as $mn$ is finite, because the matrix elements given by (25) are always positive, $\delta e/kT$ being assumed to be finite. Thus Montroll(8) concluded that phase transitions cannot occur in the crystals infinite in only one direction.

§ 5. Singularities and degeneracy of eigenvalues

Since the coefficient of $A^{\infty \times \infty}$ in (27) is unity, any analytic function obtained from (27) has no pole, except the one at infinity, in the complex plane. Then all the singular points of the function $A(z)$ are branch-points. On the other hand, when $z=0$, the largest root of (27) is obviously simple and is equal to unity. Hence the branch of $A(z)$ which becomes unity at the origin is expressible as a power series in $z$ about $z=0$. Let $A_i(T, z; mn)$ be the analytic function obtained from this series by the process of continuation along the positive real axis. For sufficiently small $z$, $A_i(T, z; mn)$ is evidently equal to $A^{*}(T, z; mn)$. And let $z^*$ be the nearest singularity of $A_i(T, z; mn)$ on the positive real axis, $z^*$ being not necessarily finite. If $z^*$ is finite, $A_i(T, z; mn)$ has a branch-point at $z=z^*$. And, if $A^{*}(T, z^*; mn)=A_i(T, z^*; mn)$, the largest root is no longer simple at $z^*$, in contradiction with Frobenius' theorem. Then, the lower limit of the positive real $z$ at which $A_i(T, z; mn)$ is smaller than $A^{*}(T, z; mn)$ must exist and smaller than $z^*$, and let $z_1$ be the value of this lower limit. This implies that $A_i(T, z; mn)$ becomes equal to other branch of the same function or some branch of other analytic function at $z=z_1<z^*$, and also contradicts with Frobenius' theorem. Hence neither $z_1$ nor $z^*$ can be finite, and consequently $A^{*}(T, z; mn)=A_i(T, z; mn)$ for all real $z \geq 0$.

And then we see from (28) that $\mathcal{l}(T, z; \infty, mn)$ represents a branch of a function which has no pole on the whole positive real axis—other branch of this function might have singularities on the positive real axis—and equal to (21) for sufficiently small $z$. Hence we have

$$\mathcal{l}(T, z; mn)=\lim_{l \to \infty} \mathcal{l}(T, z; l, mn),$$

if $mn$ is finite. Here $\mathcal{l}(T, z; mn)$ in the left-hand side should be understood to be the analytic function obtained from $\mathcal{l}(T, z; mn)$ defined within the circle of convergence by the process of continuation along the positive real axis. Thus it has been proved that the transition from (20) to (21) is correct as far as $mn$ is finite.

In the case of the linear chain, the equation (27) reduces to
of which the largest root is given by

$$A^*(T, z; 1) = A_1(T, z, 1) = \frac{1}{2} \left[ 1 + z + \left( 1 - z^2 + 4z^2 \exp(-2z\Delta\varepsilon/kT) \right)^{\frac{1}{3}} \right].$$  \hspace{1cm} (30)

If $\Delta\varepsilon > 0$, $A_1(T, z; 1)$ has no zero and has a pair of branch-points at

$$z = \left[ 1 - 2 \exp(-2\Delta\varepsilon/kT) \right] \pm 2i \exp(-\Delta\varepsilon/kT) \{1 - \exp(-2\Delta\varepsilon/kT)\}^{\frac{1}{3}}. \hspace{1cm} (31)$$

Then $\chi(T, z; 1)$ defined by (22) is regular within the unit circle, and the radius of the circle of convergence is unity.

In the case of the two-phase separation, where $\Delta\varepsilon$ is positive, it is plausible that the radius of convergence of the series (21) may be unity as far as $mn$ is finite. And the two-phase separation must occur at $z = 1$, if it occurs, as seen from (12). If $mn$ is sufficiently large, as in a macroscopic crystal, the change of $d\chi/dz = \chi/z$ at $z = 1$ becomes so abrupt as experimenter observes a sharp separation into two phases. This implies that the one of the singularities on the circumference of the unit circle appears in the immediate neighborhood of the point $z = 1$ on the positive real axis as $mn$ increases.

As $mn$ is increased, this branch-point will approach the real axis without limit. In this case, the function $A_1(z)$, obtained as the largest root of (27) and the function $A_2(z)$, which becomes the next largest root of (27) at $z = 1$ may be such that as shown in Fig. 2a. Letting $mn$ be infinite, we obtain, from (19) and (29),

$$\chi(T, z; \infty, \infty) = \lim_{mn \to \infty} \chi(T, z; mn),$$  \hspace{1cm} (32)

from which the thermodynamical behavior of the system of infinite extent may be derived. For the limiting function the following two cases are possible.

i) $\chi(T, z; \infty, \infty)$ consists of a single analytic function, at least, on the whole real axis, which has an analytic singularity at $z = 1$, as shown in Fig. 2b.

ii) $\chi(T, z; \infty, \infty)$ consists of two different analytic functions which cross each
other at $z=1$ as shown in Fig. 2c.

In the first case, $\chi(T, z; \infty, \infty)$ is identical with $\chi(T, z)$, defined as (17), at least, on the positive real axis, since both functions coincide for sufficiently small values of $z$. Then the first singularity of (17) is same as that of (32) on the positive real axis. And the active number density characteristic of the two-phase separation is given as the first singularity of $\chi(T, z)$ defined as (17), agreeing with Mayer's theory of condensation. And the singularity of $\chi(T, z)$ at $z=1$ must be an essential singular point, since the first derivative of $\chi$ with respect to $z$ is finite and discontinuous at $z=1$. An example of such a function is as follows:

$$\chi(z) = z^2 \{ \exp(-1/z) + 1 \}^{-1}. \quad (33)$$

On the other hand, if ii) is the case, $\chi(T, z; \infty, \infty)$ coincides with $\chi(T, z)$ on the positive real axis only up to $z=1$. And it is possible that the first singularity of (17) and (19) may differ, as pointed out by Katsura and Fujita for the case of continuous aggregate systems.

Since the relative concentration, $x$, is given by $z(\partial \chi/\partial z)$, the above two cases are possible for the density of each component in binary solid solutions as a function of the active number density.

§ 6. The eigenvalue method for continuous aggregate systems

In usual form, the variables which appear in crystal statistics assume only two discrete values. In the case where molecules in each lattice site have a continuum of a possible configurations, the partition function per molecule may be calculated from one of the eigenvalues of the homogeneous integral equation instead of that of the matrix. Such a method was first applied to problems arising in statistical mechanics of linear chains of molecules by Montroll and Kubo.

In the present paper, we shall treat the phase transition in the continuous aggregate systems, such as condensation, by means of the reduction of the problem to an eigenvalue problem of a linear integral equation. This method may be considered as a generalization of the method used by van Hove in statistical mechanics of one-dimensional systems.

* These two functions may be different branch of such an analytic function that $z=1$ is not a branch-point. And the reducibility of the equation (27) plays no essential role in the present theory. In this point the author is indebted to Mr. K. Ikeda.
Let us consider the system in the shape of a rectangular parallelepiped with the volume $V$ and the base of the area $D$. And let us divide this system into $l$ layers, whose thickness is $\delta$, and denote these layers by $A_1, A_2, \ldots, A_l$ as shown in Fig. 3. The grand partition function (2) is written as

$$
\Xi(T, z) = \sum_{n=0}^{\infty} \left( \frac{z^n}{n!} \right) \int \cdots \int \exp \left\{ -\frac{U_n\{n\}}{kT} \right\} d\{n\},
$$

(34)

where $\{n\}$ is a set of coordinates of $n$ molecules, $U_n\{n\}$ is the potential energy of $n$ molecules at the configuration $\{n\}$, and $d\{n\}$ is the set of the volume elements of $n$ molecules. In the configurational integral, integrals over the coordinates may be considered as a sum of integrals over each of layers

$$
\Xi(T, z) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_l=0}^{\infty} \frac{s_1^{n_1}}{n_1!} \frac{s_2^{n_2}}{n_2!} \cdots \frac{s_l^{n_l}}{n_l!} \int d\{n_1\} \int d\{n_2\} \cdots \int d\{n_l\} \exp \left\{ -\frac{U_n\{n\}}{kT} \right\},
$$

(35)

in which $\int d\{n\}$ for $n=0$ may be regarded as the simple multiplication by unity.

Suppose that the thickness of each layer, $\delta$, is larger than the maximum range of intermolecular forces. Then intermolecular forces do not extend beyond immediately adjacent layers. The potential energy of the system is

$$
U_n\{n\} = \frac{1}{2} \sum_{i=1}^{l} (U\{n_i\} + U\{n_{i+1}\}) + \sum_{i=1}^{l-1} V\{n_i, n_{i+1}\},
$$

(36)

where

$$
V\{n_i, n_{i+1}\} = \frac{1}{2} U\{n_i\} + U\{n_{i+1}\} - \frac{1}{2} U\{n_{i+1}\},
$$

(37)

$U\{n_i\}$ is the potential energy of $n_i$ molecules contained in the $i$'th layer and $U\{n_i, n_{i+1}\}$ is the interaction between the molecules in the $i$'th layer and the molecules in the $i+1$'th layer. (35) may be rewritten in the form

$$
\Xi(T, z) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_l=0}^{\infty} \int d\{n_1\} \int d\{n_2\} \cdots \int d\{n_l\} \times (n_1! n_{l+1})^{\frac{-1}{2} s_2(n_i+n_{i+1})} \exp \left\{ -\frac{U\{n_i\} + U\{n_{i+1}\}}{kT} \right\} \prod_{i=1}^{l-1} K(\{n_i\}, \{n_{i+1}\}),
$$

(38)

where

$$
K(\{n_i\}, \{n_{i+1}\}) = (n_i! n_{i+1})^{\frac{-1}{2} s_2(n_i+n_{i+1})} \exp \left\{ -V(\{n_i\}, \{n_{i+1}\})/kT \right\}.
$$

(39)

If one expresses the coordinates of the molecules in $A_i$ by the coordinate system with origin at the center of the $i$'th cell, the values of coordinates assume the same range of the values $A$. Here we introduce the notation

$$
K^{(p)}(\{\lambda\}, \{\mu\}) = \sum_{n=0}^{\infty} K^{(p-1)}(\{\mu\}, \{\nu\}) K(\{\nu\}, \{\mu\}) d\{\nu\},
$$

(40)

and

$$
K^{(0)}(\{\lambda\}, \{\mu\}) = K(\{\lambda\}, \{\mu\}).
$$

(41)
From (38), (40), and (41), we have

\[
\mathcal{E}(T, z) = \sum_{n_1 \geq 0} \sum_{n_1' \geq 0} \int_{\Delta} K^{(a-1)}(\{n_1\}, \{n_1'\})(n_1 \, n_1')^{-1/2} e^{(a_1 + n_1')/2} \times \exp\left\{-(U\{n_1\} + U\{n_1'\})/kT\right\} d\{n_1\} d\{n_1'\}.
\]

(42)

\(K^{(p)}(\{i\}, \{\mu\})\) resembles the \(p\)'th iterated kernel obtained from \(K(\{i\}, \{\mu\})\), but somewhat different from ordinary iterated kernel in the theory of linear integral equations. It may be, however, brought into the ordinary form in the manner to be described below.

If the volume of \(\Delta\) is finite, the number of molecules contained in each layer cannot exceed a certain limit, say \(N\), due to the diameter of incompressibility of molecules. And let us consider the functions, defined in \(\Delta\), \(\mathcal{F}\{N\}, \mathcal{F}\{N-1\}, \ldots, \mathcal{F}\{N-k\}, \ldots, 1\).

Now we definite the function \(\Phi(\{N\}, \tau)\), defined in the domains \(\Delta\) and \(\tau\), by

\[
\Phi(\{N\}, \tau) = \prod_{a=1}^{N} (1 - \varepsilon_i(\alpha)) \mathcal{F}\{N\} + \varepsilon_i(1/\tau) \prod_{a=2}^{N} (1 - \varepsilon_i(\alpha)) \mathcal{F}\{N-1\} + \cdots + \prod_{a=1}^{N-1} \varepsilon_i(\alpha)/\tau \cdot (1 - \varepsilon_i(N)) \mathcal{F}(1) + \prod_{a=1}^{N} \varepsilon_i(\alpha)/\tau,
\]

(43)

where \(\varepsilon_i(\alpha)\) is a characteristic function of the domain \(\tau\) such that

\[
\varepsilon_i(\alpha) = \begin{cases} 1 & \text{if } \alpha\text{'th molecule in } \tau, \\ 0 & \text{otherwise}, \end{cases}
\]

(44)

\(\tau\) being the normalization constant equal to the volume of this domain. If \(\mathcal{F}\{n\}\) is symmetric in permutations of molecules, we have

\[
\int_{\Delta} \Phi(\{N\}, \tau) \, d\{N\} = \sum_{n=0}^{N} \int_{\Delta} \mathcal{F}\{n\} \, d\{n\}.
\]

(45)

Similarly for \(K(\{i\}, \{\mu\})\) we obtain

\[
K(\{N\}, \{N'\}, \tau) = \prod_{k=0}^{N-1} \sum_{\alpha \in N-k} \prod_{a=1}^{\alpha} \varepsilon_i(\alpha)/\tau \cdot \prod_{a=2}^{\alpha} (1 - \varepsilon_i(\alpha)) \mathcal{F}(1) + \prod_{a=1}^{N} \varepsilon_i(\alpha)/\tau \cdot (1 - \varepsilon_i(N)) \mathcal{F}\{N-1\} + \cdots + \prod_{a=1}^{N-1} \varepsilon_i(\alpha)/\tau \cdot (1 - \varepsilon_i(N)) \mathcal{F}\{N-1\} + \cdots + \prod_{a=1}^{1} \varepsilon_i(\alpha)/\tau \cdot (1 - \varepsilon_i(N)) \mathcal{F}\{N\},
\]

(46)

where \(\{N'\}\) expresses other set of \(N\) molecules than \(\{N\}\), \(\alpha'\) being the molecules of \(\{N'\}\). The convention

\[
K(0, 0) = 1
\]

is used, and \(\prod_{a=1}^{k} \varepsilon_i(\alpha)/\tau\) should be regarded as unity for \(k=0\). If (46) is utilized, (42), (43) and (44) are respectively expressed in the forms

\[
K^{(p)}(\{N\}, \{N'\}, \tau) = \int_{\Delta} K^{(p-1)}(\{N\}, \{N''\}, \tau) K(\{N''\}, \{N'\}, \tau) \, d\{N''\},
\]

(47)

\[
K^{(1)}(\{N\}, \{N'\}, \tau) = K(\{N\}, \{N'\}, \tau),
\]

(48)

and
\[
\mathcal{E}(T, z) = \int_{\Delta+\tau} K^{(l-1)}(\{N\}, \{N'\}, \tau) U(\{N'\}, \{N\}, \tau) d\{N\} d\{N'\},
\]

(49)

where \( U(\{N\}, \{N'\}, \tau) \) is the one defined by the equation like (46), in which \((\lambda ! \mu!)^{-1/2} z^{(\lambda+\mu)/2} \exp\{-(U(\lambda)+U(\mu))/2\} \) appears instead of \( K(\lambda, \mu) \).

Since \( K^{(l-1)}(\{N\}, \{N'\}, \tau) \) increases with \( l \), and \( U(\{N\}, \{N'\}, \tau) \) becomes asymptotically independent of \( \{N\}, \{N'\} \), one obtains, in the limit of increasing \( l \), from (49)

\[
A(T, z; D) = \lim_{l \to \infty} [\mathcal{E}(T, z)]^l = \lim_{l \to \infty} [K^{(l-1)}(\{N\}, \{N'\}, \tau)]^l,
\]

(50)
in which \( A(T, z; D) \) corresponds to \( A^*(T, z; mn) \) in (29), as seen from (15), (20) and (29).

Now let us consider the power series in \( A \) defined by

\[
k(\{N\}, \{N'\}, \tau) = \sum_{p=1}^{\infty} K^{(p)}(\{N\}, \{N'\}, \tau) A^p,
\]

(51)

the radius of the circle of convergence of this series is \( A(T, z; D) \) given by (50) according to Cauchy and Hadamard's theorem\(^{20}\). On the other hand, (51) is Neumann's series in the theory of Fredholm's integral equation. And according to Fredholm's theorem\(^{20}\), the radius of the circle of convergence of (51) is equal to the eigenvalues with the minimum absolute value of the equation. This eigenvalue is given as the root with minimum absolute value of the equation

\[
D(\lambda) = 0,
\]

(52)

where \( D(\lambda) \) is

\[
D(\lambda) = -\lambda \int_{\Delta+\tau} K(\{N\}, \{N\}, \tau) d\{N\}
\]

\[
+ \frac{\lambda^2}{2} \int_{\Delta+\tau} \int_{\Delta+\tau} K(\{N\}, \{N\}, \tau) K(\{N'\}, \{N\}, \tau) K(\{N'\}, \{N'\}, \tau) d\{N\} d\{N'\} \cdots .
\]

(53)

A set of the roots of (52) may be represented by an analytic function or a set of analytic functions of \( z \), as in the case of the set of roots of (27). The phase transition in continuous aggregate system may corresponds to the degeneracy of the smallest root of (52). And this root, \( A^*(T, z; D) \), may be expressed in the power series in \( z \). And one sees from (1), (50), and (51) that the pressure is given by

\[
p/kT = \lim_{n \to \infty} A^*(T, z; D)/\partial D.
\]

(54)

And for sufficiently small values of \( z \) (54) may agree with (6). Hence the same discussion as in the case of crystal statistics is applied to the continuous case. And Mayer's theory is correct if the value of the active number density for which the smallest root of (52) degenerates is the analytic singular point of the function \( A^*(T, z; D) \), and otherwise the first singularity of (6) may differ from that of (7), as stated in the objection proposed by Katsura and Fujita.

The above theory is somewhat like Mayer's simplified caricature of phase transition\(^{25}\),
though in Mayer's treatment the value of the active number density characteristic of phase transition appears as the smallest eigenvalue of the integral equation.

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Note added in proof. Recently C. N. Yang and T. D. Lee (private communications to the author) have shown that all zeros of (10) are on the unit circle with the centre at the origin, and the series (16) converges uniformly at every interior point of this circle, if $\delta s$ is positive. Consequently, in the two-phase-separation case of crystal statistics, (32) is certainly regular in the half-open interval $0 \leq \delta s < 1$ on the positive real axis, as considered in the present paper.