# On the States of Aggregation

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The problem of investigating systematically the possible states of aggregation has not yet been attacked. It has been approached here in the hope of getting a deeper insight into the nature of the liquid state. After a discussion of the general methods, a simplified one-dimensional model is introduced. It was possible to find the exact equation of state. However, it turned out that in this case a single (gaseous) state exists. This is due to the presence of aggregates of all sizes. It is found that the existence of at least one condensed state is possible only if the change in free energy that occurs when an atom is added to a large aggregate is higher than the change that occurs in the addition of this atom to a small molecule. No progress could be made in the understanding of the liquid state.

## I. INTRODUCTION

IN attempting to obtain some insight into the nature of the liquid phase,[1] we were struck by the absence of a general method of investigating which states of aggregation are possible.

If we know all the properties of an isolated molecule, but had never experienced matter in bulk, we might have predicted theoretically a state of low density and complete disorder, the gas, and also perhaps a state of high density and perfect geometrical order, the crystal.

Historically the van der Waals equation is an attempt to explain the existence of the liquid phase, but gives no account of the solid state.

In this paper, an endeavor was made to deduce exactly the general equation of state under simplified assumptions concerning the molecular interaction.

## II. GENERAL THEORETICAL CONSIDERATIONS

Thermodynamically, the free energy $F$ as a function of volume and temperature determines the properties of the substance. The pressure is obtained from the equation $p = -\partial F/\partial v$. To determine the number of states of aggregation possible at a given temperature, one follows the isotherm $p(V)$ at constant temperature. At transitions between two phases one of two phenomena may occur. Either there are no metastable states, in which case the isotherm should be

horizontal at the transition pressure (vapor pressure or pressure of fusion) between the specific volumes of the two phases; or if there are metastable or unstable phases possible between the two phases (van der Waals equation), the pressure curve should have a maximum and minimum.

The kinetic theory then should provide a method for the deduction of the isotherms in the whole volume-range. Provided we remain in the region of classical physics, the volume-dependent part of the free energy of $N$ identical molecules is given by the phase integral:

$$\Phi = e^{-F/kT}$$

$$= \frac{1}{N!} \int \cdots \int e^{-E/kT} dx_1 dy_1 \cdots dx_N dy_N dz_N. \quad (1)$$

Here $x_n y_n z_n$ are the coordinates of the $n$th molecule, while $E(x_1 \cdots z_N)$ is the mutual potential energy of the molecules in a given position. The integral is to be extended up to the walls of the vessel.

This method, however, seems not to lead to metastable states. The pressure deduced from $\Phi$ is the weighted average for all states possible at a given volume and temperature. Now metastable states are, of course, states that will occur very rarely in the course of events. For example, if we have a vessel almost filled with a liquid, while the rest of the volume is filled with vapor, we have a possible metastable state, in which the whole material is in the liquid state, but the liquid is adhering everywhere to the walls under a nega-

[1] See also J. A. Prins, Naturwiss. **19**, 435 (1931), O. Kratky, Phys. Zeits. **34**, 482 (1933).

tive pressure. Now it is quite clear that the probability of this state is very small, as it will happen exceedingly rarely that the liquid in the almost filled vessel suddenly expands through Brownian motion, and fills the vessel completely. Therefore the average properties given by the phase integral will be the properties of the normal state and we should, from its use, always get curves of the type described in the first alternative. We do not know of any general statistical method that would give us the metastable states. The difficulty consists, of course, in the lack of a sharp definition of a state, except by the external variables, volume and temperature.*

Tammann[2] has adduced reasons against the possibility of a continuity between the liquid and crystalline states. However, from the standpoint of general statistical mechanics, which we have described here, we cannot see any objections against the postulate to find all the possible states, including the crystalline, from a single formula, like formula (1). It might be that Tammann's objections are taken care of by the absence of the metastable states, and their replacement by a sharp break in the isotherm, as described above. We have not succeeded in actually evaluating the phase integral, except in a very simplified case, which will now be treated.

### III. SIMPLIFIED ONE DIMENSIONAL MODEL

We consider $N$ molecules which can move in a straight line over a distance $L$. If each molecule has a diameter $d$, the free space is $L - N d = V$, and everything will behave as if we had point molecules in a line of length $V$. We make the assumption that only neighboring molecules act on each other. Their interaction energy $\epsilon_\nu$ depends on the distance between them. If $x_\nu$ denotes the coordinate of the $\nu$th molecule, and if we further assume that also the origin (the wall at the left) behaves like a molecule and exerts the potential energy $\epsilon(x_1)$ the total energy $E$ becomes

$$E = \epsilon(x_1) + \epsilon(x_2 - x_1) + \epsilon(x_3 - x_2) + \cdots$$
$$+ \epsilon(x_N - x_{N-1}).$$

* *Added in Proof:* The problem has been solved by Professor Otto Stern during a conversation. He pointed out that the portion of the phase space belonging to the metastable state must be surrounded by a potential barrier calculated per molecule high compared with $kT$.

[2] G. Tammann, *Aggregatzustände*, p. 41, Leipzig, 1922.

The integral (1), which takes the form[3]

$$\Phi = \int_0^V dx_1 \int_{x_1}^V dx_2 \cdots \int_{x_{N-1}}^V dx_N e^{-E/kT}$$

can be transformed by introducing the mutual distances

$$\zeta_1 = x_1, \qquad \zeta_2 = x_2 - x_1 \cdots, \qquad \zeta_N = x_N - x_{N-1}$$

into

$$\Phi = \int_0^V e^{-\epsilon_1/kT} d\zeta_1 \int_0^{V-x_1} e^{-\epsilon_2/kT} d\zeta_2$$
$$\cdots \int_0^{V-x_{N-1}} e^{-\epsilon_N/kT} d\zeta_N. \quad (2)$$

It is simpler not to express $x$ by $\zeta$ in the upper limit. We now assume $\epsilon_n$ to have the simplest form; that is

$$\epsilon_n = -\epsilon \qquad \zeta_n < r_0,$$
$$\epsilon_n = 0 \qquad \zeta_n > r_0,$$

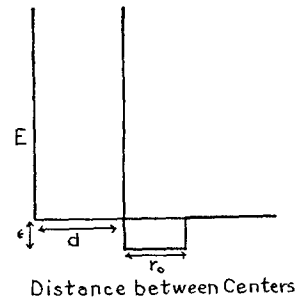so that the total energy curve is given by Fig. 1.



Distance between Centers

FIG. 1. Mutual potential energy of two molecules.

The formula is evaluated in Appendix I. The result is, with the abbreviation $e^{\epsilon/kT} = a$:
For $V > Nr_0$

$$\Phi = \frac{1}{N!} \sum_0^N \binom{N}{\lambda} (1-a)^\lambda a^{N-\lambda} (V - \lambda r_0)^N. \quad (3)$$

For $V < Nr_0$ we define $N'$ through $N'r_0 < V < (N'+1)r_0$ and find

$$\Phi = \frac{1}{N!} \sum_0^{N'} \text{same expression.} \quad (3')$$

[3] $N!$ has been left out in the denominator because there is no exchange of particles possible here.

For $V < r_0$ this becomes

$$\Phi = (aV)^N/N!. \tag{3''}$$

These formulae are exact.

For very large volumes we find of course

$$\Phi = (1/N!) V^N,$$

which is the formula of the ideal gas (with finite molecules). We have the same formula, only with the addition of a potential energy $\epsilon$, also in case $(3'')$.

We might expect equilibrium between gas and a condensed phase in the following region: $T$ a fraction of $(N\epsilon/R)$ ($N\epsilon$ the heat of evaporation), the volume in the interval between the volume of the saturated vapor, that is $V \sim Nr_0 e^{\epsilon/kT}$, down to the volume of the condensed phase.

The formula (3) has been evaluated for this region in which $(1/a) = e^{-\epsilon/kT}$ is small, in Appendix II. The result is: Define $x$ and $y$ through[4]

$$x = (r_0 N/V)a, \tag{4}$$

$$(x/y)(1-y)^2 = 1. \tag{5}$$

Then for large numbers of molecules $N$

$$\Phi^{1/N} = e^{-F/NkT} = (Ve/N)[e^{-y}/(1-y)^2]. \tag{6}$$

To calculate the equation of state, we form

$$\frac{p}{RT} = -\frac{\partial}{\partial V} \frac{F}{NkT} = +\frac{\partial}{\partial V} \ln \Phi^{1/N}$$

$$= \frac{1}{V} - \frac{d}{dy}[y + 2\ln(1-y)]\frac{dy}{dx}\frac{dx}{dV}$$

$$= \frac{1}{V} - \left(1 - \frac{2}{1-y}\right)\frac{dy}{dx}\frac{dx}{dV}$$

$$= \frac{1}{V} + \frac{y}{x}\frac{dx}{dV}\frac{1}{V} = \frac{1}{V}(1-y). \tag{7}$$

Now from (5)

$$1 - y = (1/2x)[(1+4x)^{\frac{1}{2}} - 1]$$

or

$$\frac{p}{RT} = \frac{1}{2ar_0 N}\left[\left(1 + \frac{4ar_0 N}{V}\right)^{\frac{1}{2}} - 1\right]. \tag{7'}$$

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[4] $x$ is essentially the ratio of the saturation volume to the volume $V$.

It is clear that this formula does not show any region where $p$ is independent of $V$ (nor any maxima or minima). Accordingly, there are no transition points, i.e., there exists only a single phase.

Recently N. Fuchs[5] has investigated the adsorption-isotherm assuming that the adsorption occurred on a one dimensional system (edge) and that the adsorbed particles vibrated around fixed points of the adsorbing substance. He found, in agreement with our result, no break in the isotherm, that is, no phase change in the adsorbed substance.

It is possible to get a deeper understanding of this result.

Formula (7) can namely be interpreted in a different manner. Consider a group of $n$ particles where each particle is within the reach of the potential energy of both neighbors (except the end particles which have only one neighbor) as a molecule of $n$ atoms. Then we can consider the whole system according to the formulas which govern in statistical mechanics the chemical equilibrium between $Z_1$ atoms, $Z_2$ diatomic molecules, $Z_n$ $n$-atomic molecules, etc.

We have

$$(Z_n \cdot Z_1)/Z_{n+1} = (V/r_0)e^{-\epsilon/kT}, \tag{8}$$

$$\sum_1^N nZ_n = N. \tag{9}$$

From (8) and (4) one finds

$$Z_n = Z_1^n (e^{\epsilon/kT} r_0/V)^{n-1} = Z_1(Z_1 x/N)^{n-1}. \tag{10}$$

If we insert (10) in (9) we get, with the abbreviation $y' = Z_1 x/N$,

$$\frac{1}{x} y' \frac{1 - N y'^{N-1} + (N-1)y'^N}{(1-y')^2} = 1. \tag{11}$$

This is replaced with sufficient accuracy[6] by

$$y'/x(1-y')^2 = 1. \tag{11'}$$

Comparison of $(11')$ and (5) shows $y = y'$. The

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[5] N. Fuchs, Zeits. f. physik. Chemie B21, 235 (1933).

[6] From (9) and (10) it follows that $y'$ increases with $x$. If $x$ is very small, $y'$ is small, and the transition from (11) to $(11')$ is clear. If $x$ is large, $y'$ is nearly 1, although for very large values of $x$ $(11')$ does not give the very small value $1 - y'$ accurately.

pressure of the mixture of molecules of all sizes is

$$\frac{p}{RT} = \frac{1}{VN}\sum Z_n = \frac{1}{Vx}\sum_1^N y^n = \frac{1}{V}\frac{y}{x}\frac{1-y^N}{1-y} = \frac{1}{V}(1-y)$$

with the help of (5), again neglecting $y^N$ in comparison with (1). But this formula is identical with (7). The reason, therefore, why we do not get a break in the isotherm is as follows: with changing volume the relative numbers of each type of molecule (there are $N$ such types) change in a continuous manner which smoothes out the curve.

## IV. Conditions for the Existence of a Condensed Phase

To get a separate phase it is necessary to make the large aggregates more probable compared with molecules containing only a few atoms.

To investigate that in more detail we can now make use of the usual dissociation formulae since their agreement with the exact calculation has been shown in the previous case.

As the simplest assumption we will permit the existence only of aggregates having at least $m$ atoms, besides free single particles. Let the equations be[7]

$$Z_1{}^m = Z_m K_m{}^{-1},$$

$$Z_1 Z_n / Z_{n+1} = N/x, \qquad N \geqq n > m.$$

Then $Z_n = Z_m(Z_1 x/N)^{n-m} = K_m(N/x)^m (Z_1 x/N)^n$

and

$$Z_1 + K_m\left(\frac{N}{x}\right)^m \sum_m^N n(Z_1 x/N)^n = N$$

or with the abbreviations $K_m(N/x)^{m-1} = A$, $Z_1 x/N = y$.

$$y + A\sum_m^n ny^n = x$$

or

$$y\left[1 + A\frac{my^{m-1} - (m-1)y^m - Ny^{N-1} + (N-1)y^N}{(1-y)^2}\right]$$

$$= x.$$

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[7] See also similar calculations by L. Michaelis, Biochem. Zeits. **103**, 225 (1920).

For small values of $x$, we have simply $y = x$, or $Z_1 = N$ and that is true almost up to $x = 1$, as any appreciable deviation of $y$ from 1 makes $y^{m-1}$ very small for large $m$. For example, for $m = 1000$ $1 - x = 0.02$ still leaves $y = x$ for $A \sim 1$, as before. For large $x$, putting $y = 1 - \delta$, we have $me^{-\delta m}/\delta = x$. The pressure equation is

$$\frac{p}{RT} = \frac{1}{VN}\left(Z_1 + \sum_m^N Z_n\right) = \frac{1}{Vx}\left(y + A\sum_m^N y^n\right)$$

$$= \frac{1}{Vx}y\left(1 + \frac{y^m - y^N}{1-y}\right).$$

Again we have for small values of $x$ the gas equation, for large values

$$\frac{p}{RT} = \frac{1}{Vx}\left(1 + \frac{e^{-\delta m}}{\delta}\right) = \frac{e^{-N\epsilon/RT}}{Nr_0}\left(1 + \frac{x}{m}\right),$$

which is practically independent of $V$ as long as $x \ll m$ or the volume larger than $1/m$ of the volume of the saturated vapor.

The foregoing assumption which forbids the existence of molecules containing more than 1 and less than $m$ atoms is of course not realized in nature. The strong influence of the intermediate molecules in the model discussed in III is due to the fact that the right side of (8) is independent of $n$. That means thermodynamically that the change in free energy when an atom joins a molecule already containing $n$ atoms is independent of $n$. To favor large molecules we must make the change larger for large $n$. This can be accomplished either by a larger change in energy or a smaller change in entropy.

In the model of III the change in energy is independent of $n$ because in a one dimensional system one has to break only one bond to free an atom whatever the size of the molecule to which it is attached. In two or more dimensions that is different. We know experimentally that condensed phases exist in films in spite of the fact that if the molecules of these films vibrate around fixed points on the absorbing substance, the change of entropy is independent of $n$ (see below). But in a two dimensional film the tearing loose of a molecule means the breaking of two bonds, if it is attached to a large mass, but only the breaking of one bond in the case of a small molecule.

In three dimensions the difference is even greater. However, we have not yet succeeded in formulating this statement exactly.

The changes in entropy are essentially determined by the factor occurring in front of the $e$ power in (8). In the model treated under III, the space available to the bound atom is $r_0$ independent of $n$, the number of atoms in the molecule. The same is true if (as in Fuchs' assumption) the vibrations are determined by the adsorbing substance. If we assume, however, that the particles in the aggregate vibrate in respect to each other instead of in respect to a fixed point in space, we get even in the one dimensional case a larger entropy per atom for the larger aggregate, because the average frequencies in a large aggregate are lower than in a small one.

The frequencies of a molecule of $n$ particles are given approximately by $\nu = \nu_0/s$, $1 < s < n-1$. Therefore, in the phase integral of the molecule there appears the factor[8]

$$\prod_s \frac{1}{\nu_s} = \frac{(n-1)!}{\nu_0{}^n}.$$

The dissociation formula takes the form

$$\frac{Z_1 Z_n}{Z_{n+1}} = V \frac{\nu_0}{n} \left(\frac{2\pi m}{kT}\right)^{\frac{1}{2}} e^{-\epsilon/kT}.$$

The essential thing is the $n$ in the denominator

which arises from the fact that the frequency which disappears through the removal of one atom is inversely proportional to the size of the molecule. Therefore, with the abbreviation

$$x' = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{N}{\nu_0 V} e^{\epsilon/kT},$$

we find

$$Z_n = (n-1)! \, Z_1 \left(\frac{Z_1 x'}{N}\right)^{n-1},$$

(9) takes the following form, with $y' = Z_1 x_1'/N$

$$\sum_1^N n! \, y'^n = x'. \tag{9'}$$

Furthermore, the pressure equation

$$pV/RT = \sum Z_n = (y'/x')N\sum (n-1)! \, y'^{n-1}$$
$$= (y'/x')N(1 + x' - N! \, y'^N)$$

with the use of (9'). Now (9') shows for $x' \ll N^{-1}$ $y = x$, $pV = NkT$, ideal gas

$$x' > e/N \qquad y'^N = x'/N!, \qquad y' = e/N.$$

Therefore $pV/RT = e/x'$

$$p = \nu_0 (2\pi m kT)^{\frac{1}{2}} e^{-\epsilon/kT}$$

which is independent of $V$ and is the correct vapor pressure equation for a one dimensional system.

## APPENDIX I

One can easily interpret the integral (2). Consider an $N$-dimensional corner, formed by the positive axes $\zeta_1, \zeta_2 \cdots \zeta_N$ and limited by the plane which cuts the axis at $\zeta_j = V(j = 1 \cdots N)$. That is the domain of integration. The integrand is $\prod e^{-\epsilon_j/kT}$, where $\epsilon_j$ depends only on $\zeta_j$. Call

$$e^{\epsilon/kT} = a > 1. \tag{11}$$

The integrand has then the following property:

It is $=1$, if all the $\zeta > r_0$, that is to say in an inner $N$-dimensional pyramid of edge $V - r_0$.

It is $a$ if one of the $\zeta$ is smaller than $r_0$ and all others larger than $r_0$, $a^2$ if two of the $\zeta$ are smaller than $r_0$ and all others larger, etc., finally the integrand is $a^N$ in the cube of side $r_0$.

To give a better idea, consider a system containing only two particles. The configuration space is there two dimensional and has the form of a right-angle triangle, with sides $= V$. (Fig. 2.) It is divided into four parts: in $A$ both $\zeta_1 = x_1$ and $\zeta_2 = x_2 - x_1$ are larger than $r_0$, both particles are free, the integrand has the value $1(E = 0)$.

In $B$ $\zeta_1$ is smaller than $r_0$, $\zeta_2$ larger than $r_0$, that is particle 1 is frozen to the wall, 2 is free, $\epsilon_1 = \epsilon$; $\epsilon_2 = 0$, the integrand is $a$. In $C$, $\zeta_1 > r_0$, $\zeta_2 < r_0$, the particles 1 and 2 stick together (form a molecule)

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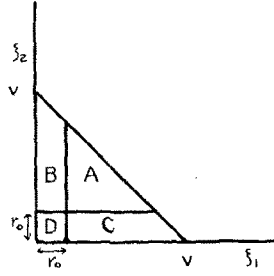[8] See, e.g., K. F. Herzfeld, *Kinetische Theorie der Wärme*, Braunschweig (1925).

FIG. 2. Configuration plane for two molecules.

but are free from the wall, $\epsilon_1 = 0$, $\epsilon_2 = \epsilon$, the integrand is again $a$. In $D$ finally both $\zeta_1$ and $\zeta_2$ are smaller than $r_0$, particle 1 sticks to the wall, particle 2 sticks to particle 1, $\epsilon_1 = \epsilon_2 = \epsilon$, the integrand is $a^2$.

In general, it is evident that the integrand of (1) can only have the values $a^l$, with $l = 0 \cdots N$. Assume at first $V > Nr_0$. Then all values actually occur. The problem is equivalent to finding the volume of the phase space for which the integrand has the value $a^l$, subject to the condition $\sum_m \zeta_m < V$.

It is readily seen that this part of the phase space consists of $\binom{N}{l}$ unconnected, equally large regions, namely the $\binom{N}{l}$ possible combinations in which $l$ coordinates are smaller, the others larger than $r_0$. It is therefore sufficient to find for each $l$ the volume of the special region, $A_l$, for which only the *first* $l$ coordinates $\zeta$ are smaller than $r_0$. Then

$$\Phi = \sum_l \binom{N}{l} a^l A_l. \tag{21}$$

The volume $A_l$ is given by the integral

$$A_l = \int_0^{r_0} d\zeta_1 \int_0^{r_0} d\zeta_2 \cdots \int_0^{r_0} d\zeta_l \int_{r_0}^{V-(N-l+1)r_0-\sum_{m=1}^{l}\zeta_m} d\zeta_{l+1} \cdots \int_{r_0}^{V-r_0-\sum_{m=1}^{N-2}\zeta_m} d\zeta_{N-1} \int_{r_0}^{V-\sum_{m=1}^{N-1}\zeta_m} d\zeta_N. \tag{31}$$

Integration leads to

$$A_l = \int_0^{r_0} d\zeta_1 \cdots \int_0^{r_0} d\zeta_l [1/(N-l)!] \left\{ V - (N-l)r_0 - \sum_{m=1}^{l} \zeta_m \right\}^{N-l} \tag{3'1}$$

and finally to

$$A_l = (1/N!) \sum_{m=0}^{l} (-1)^m \binom{l}{m} \{ V - (N-l+m)r_0 \}^N. \tag{41}$$

In the case that $V < Nr_0$ we can define $N'$ such that

$$N'r_0 < V < (N'+1)r_0. \tag{51}$$

It is evident then that because of the limitation $\sum_m \zeta_m \leqq V$ no more than $N - N'$ coordinates $\zeta_m$ can be $> r_0$ at the same time, the integrand can only take values $a^l$ with $l \geqq N - N'$ or

$$A_l = 0 \qquad \text{for} \qquad l < N - N'. \tag{4a1}$$

For $l > N - N'$ (31 and 3'1) are modified by the fact that the upper limit of the first $l$ integrals is no more simply $r_0$, but has to be replaced (for the $k$th integral) by the smaller of the two numbers $r_0$

or $V-(N-k)r_0-\sum_{m=0}^{k-1}\zeta_m$. Then integration leads to

$$A_l = \frac{1}{N!}\sum_{m=0}^{l-(N-N')}(-1)^m\binom{l}{m}\{V-(N-l+m)r_0\}^N. \tag{4bI}$$

If for $V=Nr_0$ we define $N'$ as $N=N,'$ (4I) is contained in (4bI).
Introducing the label $\lambda$ for $N-l+m$, (4bI) reads

$$A_l = \frac{1}{N!}\sum_{\lambda=0}^{N'}(-1)^{N+l+\lambda}\binom{l}{N-\lambda}(V-\lambda r_0)^N. \tag{6I}$$

Formally the sum runs only from $N-l$ to $N'$, but the factorial coefficient renders the lower terms 0. $\Phi$ is obtained by putting (6I) and (4aI) into (2I). Exchanging the order of the summation we obtain

$$\Phi = \frac{1}{N!}\sum_{\lambda=0}^{N'}(-1)^\lambda\frac{N!}{(N-\lambda)!\lambda!}(V-\lambda r_0)^N\sum_{l=N-N'}^{N}(-1)^{N-l}\frac{\lambda!}{(N-l)!(\lambda-N+l)!}a^\lambda.$$

Since $N-N'<\lambda$ the second sum is simply the expression $a^N(1-1/a)^N$ and the final result is:

$$\Phi = \frac{1}{N!}\sum_{\lambda=0}^{N'}\binom{N}{\lambda}(1-a)^\lambda a^{N-\lambda}(V-\lambda r_0)^N. \tag{7I}$$

## Appendix II

For $-\epsilon/kT>1$, $a\gg1$, one can write in (3)

$$(1-a)^\lambda a^{N-\lambda} = a^N(1/a-1)^\lambda = (-1)^\lambda a^N e^{-(\lambda/a)}.$$

Furthermore develop

$$(V-\lambda r_0)^N = V^N(1-\lambda r_0/V)^N = V^N\sum_{0}^{N}(-1)^i\lambda^i(r_0/V)^i\binom{N}{j}$$

and interchange the order of summation in respect to $\lambda$ and $j$. Then (3) takes the form

$$\Phi = (a^N/N!)V^N\sum_{j=0}^{N}\binom{N}{j}(-1)^i(r_0/V)^i\sum_{j=0}^{N}\binom{N}{\lambda}(-1)^\lambda\lambda^i e^{-(\lambda/a)}$$

$$= (a^N/N!)V^N\sum_{j=0}^{N}\binom{N}{j}(r_0/V)^i[d^i/d(1/a)^i]\sum_{\lambda=0}^{N}(-1)^\lambda\binom{N}{\lambda}e^{-(\lambda/a)}$$

$$= (a^N/N!)V^N\sum_{i}\binom{N}{j}(r_0/V)^i[d^i/d(1/a)^i](1-e^{-(1/a)})^N$$

$$= (a^N/N!)V^N\sum_{i}\binom{N}{j}(r_0/V)^i[d^i/d(1/a)^i](1/a)^N$$

$$= \frac{V^N}{N!}\sum_{i=0}^{N}\binom{N}{j}\frac{N!}{(N-j)!}\left(\frac{r_0a}{V}\right)^i = \frac{V^N}{N!}\sum_{j=0}^{N}\binom{N}{j}\frac{N!}{(N-j)!N^i}\left(\frac{r_0Na}{V}\right)^i. \tag{1II}$$

Introduce the abbreviation $x$ according to (4). The limits of $x$ are $x=0$ for $V=\infty$ ; $x=a\gg1$ for $V=r_0N$. Consider first $(A+B)!$ for $A\gg B\gg1$. We have according to Stirling's formula

$$\ln (A+B)! = (A+B)[\ln (A+B)-1]-\ln [2\pi(A+B)]^{\frac{1}{2}}$$
$$= (A+B)[\ln A-1+\ln (1+B/A)]-\ln [2\pi(A+B)]^{\frac{1}{2}}.$$

Up to and including terms in $(B/A)^2$, we have $\ln (1+B/A)=B/A-B^2/2A^2$. Therefore

$$\ln (A+B)! = (A+B)[\ln A-1]+B\left(1+\frac{1}{2}\frac{B}{A}\right)-\ln [2\pi(A+B)]^{\frac{1}{2}}. \tag{2II}$$

Let us call $j_0$ the value of $j$ that gives the largest term in (1II), and $\xi=(j-j_0)/j_0$, $j=j_0(1+\xi)$. One can write then

$$\ln \left\{\binom{N}{j} \frac{1}{(N-j)!N^j}x^j\right\} = \ln N!-\ln (j_0+j_0\xi)!-2 \ln [N-j_0-j_0\xi]!+j_0(1+\xi) \ln \frac{x}{N}$$

$$= \ln N!-j_0(1+\xi)[\ln j_0-1]-j_0\xi(1+\xi/2)-2(N-j_0-j_0\xi)[\ln (N-j_0)-1]!$$

$$+2j_0\xi(1+\tfrac{1}{2}j_0\xi/(N-j_0))+j_0(1+\xi) \ln (x/N)+\tfrac{1}{2} \ln [8\pi^3(N-j_0)^2j_0]$$

$$= \ln N!+j_0\left[\ln \frac{x(N-j_0)^2}{Nj_0}-1\right]-2N[\ln (N-j_0)-1]+j_0\xi \ln \frac{x(N-j_0)^2}{Nj_0}$$

$$-(j_0/2)\xi^2[1+2j_0/(N-j_0)]+\tfrac{1}{2} \ln [8\pi^3(N-j_0)^2j_0]$$

$$= -\ln N!-2N \ln \left(1-\frac{j_0}{N}\right)+j_0 \ln \frac{x(N-j_0)^2}{Nj_0}-j_0+j_0\xi \ln \frac{x(N-j_0)^2}{Nj_0}$$

$$-(j_0/2)\xi^2(N+j_0)/(N-j_0)+\tfrac{1}{2} \ln [8\pi^3(N-j_0)^2j_0]. \tag{3II}$$

The maximum occurs for $x(N-j_0)^2/Nj_0=1$, or if we call $j_0/N=y$,

$$(x/y)(1-y)^2 = 1. \tag{4II}$$

We have then

$$\Phi = [8\pi^3(N-j_0)^2j_0]^{\frac{1}{2}} \frac{V^N}{N!} \frac{e^{-Ny}}{(1-y)^{2N}} \sum \exp \left(-\frac{Ny}{2}\frac{1+y}{1-y}\xi^2\right). \tag{5II}$$

Instead of taking the sum, one can write an integral, introducing $u^2=(Ny/2)[(1+y)/(1-y)]\xi^2$. The limits, being given by $j=0$ and $j=N$ or $u=-[(Ny/2)(1+y)/(1-y)]^{\frac{1}{2}}$ and $u=[N(1-y^2)/2y]^{\frac{1}{2}}$, can be replaced by $-\infty$ and $\infty$. Therefore

$$\Phi = 4\pi^2N(1-y)\left(\frac{1-y}{1+y}\right)^{\frac{1}{2}} \frac{V^N}{N!} \frac{e^{-Ny}}{(1-y)^{2N}}$$

and if we take the $N$th root formula (6) is found.