

Association Theory. The Discontinuous Case and the Structure of Liquids and Solids

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The assumption of the continuous case of association which is that all species of particles are always present is discussed. It is shown that a more appropriate model of the liquid or solid is given by the discontinuous case which postulates that certain smaller species are completely absent. A discussion of the nature and cause of the gas-liquid transition is given. This transition coincides with the change from a treatment by the continuous case to the discontinuous case. Various modifications of the mathematical treatment are derived and discussed.

In previous work^{1,2} a theory of association of matter was presented which led to an equation of state³ and finally to a derivation of Tait's equation.⁴ This theory was applied both to liquids⁵ and solids⁶ and showed success in enabling us to calculate the atomic radii⁷ of the five alkali metals from a knowledge of their compressibility data and their crystal form. However, a further detailed examination of the equations in this theory showed that there were some difficulties both conceptually and mathematically. Among other things, the number of 1-mers in liquids and solids under high pressure calculated by this theory were found to be too great. Careful analysis of the equations traced the difficulties to one assumption in the original derivation; this is the assumption that all species from 1-mer to m -mers were always present. If in these derived equations the concentration of any species became zero, then the mathematical equations broke down giving a singular case. This paper then is devoted to an examination of this assumption and to the consequences of removing its restrictions.

The Assumption of Continuous Distribution. The origin of this assumption probably lies in the kinetic derivation of the distribution equations, which assumes that we start with a hypothetical matrix of single atoms and from this build an associated substance. This is equivalent to assuming that we start a mass of matter at

infinite volume where there are no collisions and suddenly compress it to some arbitrary volume where the molecules start colliding and associating. This is an unnecessary concept, although a convenient one, since the same equations can be obtained by considering the equilibrium situation.⁸ The concept of this assumption was reinforced by the thought experiment¹ in which the individual frames of a hypothetical motion picture of a gas were examined one by one. In such examination, 1-mers, 2-mers, 3-mers, etc., were seen. From a dynamic point of view the 2-mers were static representations of binary collisions, the 3-mers, ternary collisions, etc. This picture is the one presented by the kinetic-molecular theory and is undoubtedly true of a gas. The extrapolation to liquids and solids came with

(1) For a review article see: R. Ginell, p 41-48, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," S. Gratch, Ed., American Society of Mechanical Engineers, New York, N. Y., 1965.

(2) R. Ginell, *Ann. N. Y. Acad. Sci.*, **60**, 521 (1955).

(3) R. Ginell, *J. Chem. Phys.*, **23**, 2395 (1955).

(4) R. Ginell, *ibid.*, **34**, 1249 (1961); **34**, 2174 (1961); **35**, 1135 (1961).

(5) R. Ginell, *ibid.*, **35**, 473 (1961).

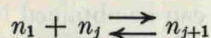
(6) R. Ginell and T. J. Quigley, *J. Phys. Chem. Solids*, **26**, 1157 (1965).

(7) R. Ginell and T. J. Quigley, *ibid.*, **27**, 1173 (1966).

(8) R. Ginell and J. Shurgan, *J. Chem. Phys.*, **23**, 964 (1955).

the derivation of Tait's law, and the successes and troubles started at this point.

The Liquid and Solid State. The correct approach is to extrapolate our thought experiment from the gas case described above to the liquid and solid cases. One must therefore look for an acceptable picture of a liquid and a solid. The subject of the nature of the liquid and solid state has been the subject of many papers and reviews, and an introduction to the current views can be found in a general text like Moelwyn-Hughes or Hirschfelder, *et al.*,⁹ and need not be detailed here. However, the association approach to liquids and solids is not widely known. Part of this problem has been considered^{10,11a} in connection with a discussion of close-packing in j -mers of large size, and the suggestion has been made that the essential difference between liquids and solids is one of symmetry. From this work it appears that higher j -mers that are packed in 4- or 6-symmetry give rise to particles of regular form which are recognizable as prototypes of crystals, while on the other hand higher j -mers that are packed in approximate 5-symmetry form particles of irregular shape, full of voids that seem to correspond to our current views of the structure of liquids. This work showed, moreover, that particles in 5-symmetry had more bonds and hence are more stable, at least in the smaller sizes, than particles in 6-symmetry. This symmetry difference leads to an explanation of the mechanism of nucleation. From our present work it seems that we must consider a liquid to consist of an array of such 5-symmetry particles separated by defects, all in equilibrium. The equilibrium is due to 1-mers breaking off one particle (j -mer), crossing the defect volume and joining another j -mer. The equation would be



The number of such 1-mers in the liquid is very small, the main bulk consisting of 5-symmetry j -mers. The equilibrium mechanism postulated here is very similar to the mechanism for the growth of crystals after heterogeneous nucleation.^{11b}

If one lowers the pressure on the liquid, one ultimately reaches the vapor pressure of the liquid. This is the pressure which these 1-mers exert in the liquid at this temperature. In solids, the process is the same except that the particles are now in 4- or 6-symmetry. Thus the liquid and solid both consist of large particles in 5- or 6- (or 4-) symmetry, respectively, in equilibrium with 1-mers. The question of whether 2-mers exist in the liquid depends in part on the abundance of 1-mers. The quantity of 3-mers is still smaller and there undoubtedly is a gap between these small particles and the large j -mers which form the bulk of the liquid or solid. In many ways this concept resembles Eyring's significant structures theory.¹² This theory postulates that liquids are composed of a mixture of gas-like particles and solid-like particles. This is equiv-

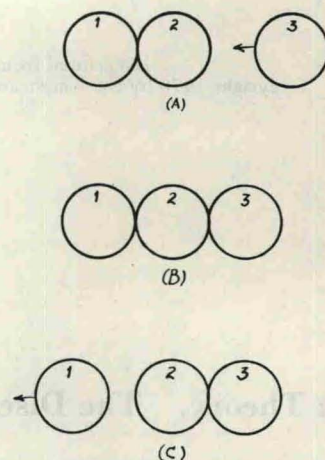


Figure 1. Straight line collision. The transfer of kinetic momentum is complete: (A) approach (origin of coordinates is on the 2-mer); (B) collision (the shapes of the molecules are distorted from spherical symmetry during the collision although this is not shown. During the lifetime of the 3-mer, the energy of the collision is stored as potential energy of distortion); (C) departure (molecule at opposite end departs taking all the kinetic energy. This is only true for a strictly straight line molecule).

alent to our 1-mers and j -mers. The difference in the theories is that we specify that the j -mers are 5-symmetric in liquids and 6- (or 4-) symmetric in solids, while Eyring's theory considers the solid-like particles to have the properties of solids and contains some arbitrary parameters. Our theory enables one to explain nucleation and the conversion of liquids to solids. This is impossible in Eyring's theory.

Liquid-Gas Transition. The concept of a discontinuous distribution raises several questions. The first: how and why does this distribution arise, and why is it more applicable to liquids and solids. Qualitatively this can be approached by a picture of this sort which turns out to give us a clearer understanding of the nature of the gas-liquid transition.¹³ Let us imagine that we have a gas at some elevated temperature. The particles present will probably be linear forms of the 1-mer, 2-mer, 3-mer, 4-mer, and perhaps 5-mer. (Occasionally a linear form of a higher j -mer may form.) The lifetime of such particles is very short. Let us reduce the temperature of the gas. The effect would be to decrease the energy and hence the velocity and momen-

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(10) R. Ginell, *J. Chem. Phys.*, **34**, 992 (1961).

(11) (a) J. D. Bernal, *Nature*, **185**, 68 (1960); *Sci. Amer.*, **203**, 124 (1960); (b) S. E. Brown and R. Ginell, pp 109-118, "Symp. Nucleation and Crystallization in Glasses and Melts," M. K. Reser, C. Smith, and C. H. Insley, Ed., American Ceramic Society 1962.

(12) H. Eyring, T. Ree, and N. Hirai, *Proc. Natl. Acad. Sci. U. S.*, **44**, 683 (1958), and subsequent papers.

(13) R. Ginell, Proceeding of the 1st International Conference on Thermodynamics and Calorimetry, Sept 1-5, 1969, Warsaw, Poland, in press.

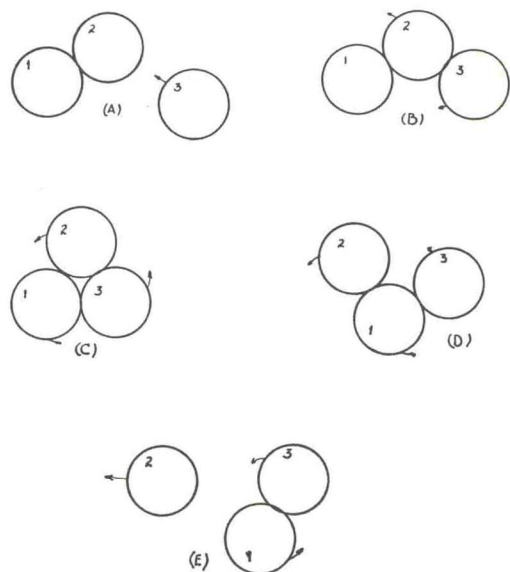


Figure 2. Collision of a 2-mer and a 1-mer. Partial transfer of kinetic momentum to rotational momentum. If the energy of impact is slight, collision may stop at step C. For a collision a little higher in energy, termination step may be step D. Step D is in equilibrium with step C and molecule will alternately have structure D and C. (A) approach; (B) collision: formation of first bond; (C) formation of second bond due to rotation (may stop at this stage); (D) degradation: breaking first bond. (Energy of collision too great to stop at C but may stop at this stage and oscillate between C and D); (E) complete degradation: breaking of second bond: (likelihood good that some rotational momentum remains, in part, in the molecule).

tum of the particles. Since every collision, except a direct line collision (Figure 1) results in the transfer of some of the kinetic momentum into rotational momentum, there is time for additional bonds to form. From geometric concepts, direct line collisions are rare, hence extra bonds are usually formed (see Figure 2). This means that as higher j -mers form, they tend to be more complex in terms of the number of bonds that an individual atom shares. The situation in the case of the formation of the 4-mer from the 3-mer and the 1-mer is shown in Figure 3. Here the 3-mer is triangular, and the rotation momentum of the 4-mer forces the formation of first, 1 additional bond and then 2 additional bonds. We would refer to such a bonding type as three-hole bonding (3-hole) since the triangular array of the 3-mer forms a hole bounded by 3 atoms. The breakup of such a bonded arrangement is simple. The bond was formed one bond at a time and breaks up one bond at a time. If we consider the energy of formation of a single bond to be the same, no matter where it occurs, and this is a plausible assumption at least as a first approximation, then the formation of a 3-hole bond consists of a series of three equally energetic steps while the reverse reaction of breakup of a 3-hole bond consists of the same three steps.

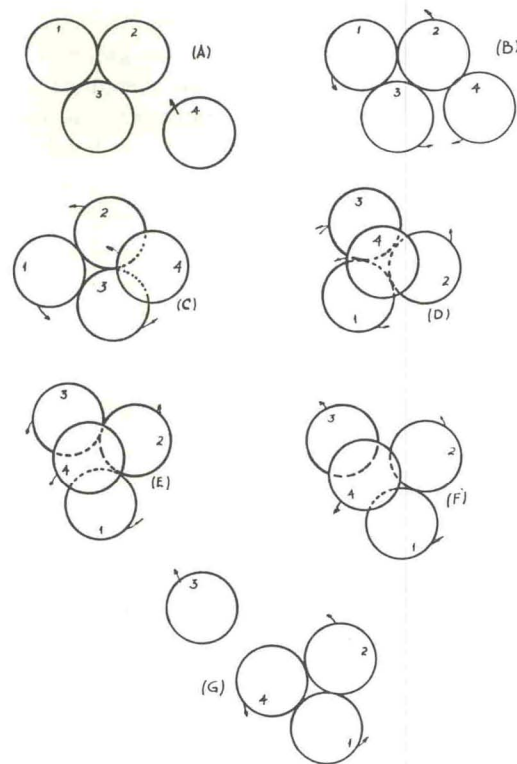


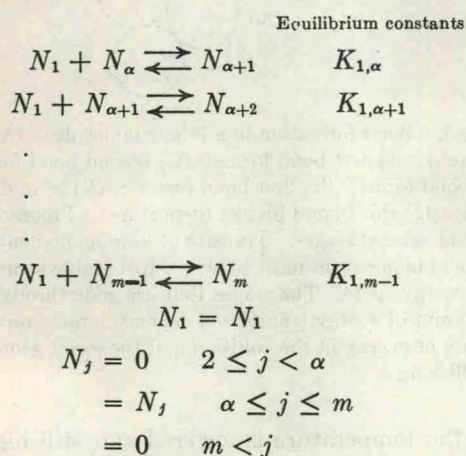
Figure 3. Bond formation in a 3-hole molecule: (A) approach; (B) first bond forms; (C) second bond forms; (D) third bond forms; (E) first bond breaks; (F) second bond breaks; (G) third bond breaks (departure). Process may stop at any of several stages. Transfer of kinetic momentum to rotational momentum most likely. Most stable structure (least energy) is D. The stages that are gone through and the amount of energy transferred depends largely on the quantity of energy in the collision and the exact geometry of the collision.

As the temperature is lowered and still higher compact forms have time to form, j -mers with 4 and 5 holes appear. The behavior of such bonds is in one way similar and in another way quite different from the formation of 3-hole bonds. In the formation of 4-hole bonds, the energy of the first step and the second step (Figure 4) is the same as in the 3-hole bond. However, the third step is different. In the 4-hole bond two bonds are formed simultaneously in the third step, while in the 3-hole bond only one bond is formed. The important difference is when we consider the process of breakup. In the 4-hole bond the first step demands that 2 bonds be broken simultaneously. This is energetically more difficult than breaking one bond. Hence energetics favor the 4-hole bond. It is more stable than the three-hole bond. In the 5-hole bond the stability of the bond increases still more, since 3 bonds are formed in the last step. Similar reasoning holds for the 6- and higher hole bonds. We call such highly stable particles multiply bonded structures. As the temperature of the gas is lowered, the point is reached where such multiply bonded structures start forming. Since they are more stable, they rapidly drain the gas of simply bonded

structures. Shortly this process results in the depletion of the simply bonded j -mers in the gas, and first the 2-mer and then the 3-mer and 4-mer disappear from the gas. The concentration of 1-mers is also decreased at this time. At this point where multiply bonded structures form there is an extra release of energy due to their formation. This compensates for the uniform dropping of the temperature, and a halt in the temperature drop ensues while the multiply bonded j -mers for either the liquid or the solid are forming. The fact that the species, 2-mer, 3-mer, etc. go to zero concentration results in a breakdown of the mathematics of the continuous case and results in a gap, giving rise to the discontinuous case.

Mathematical Derivation

The problem is now to put these ideas into mathematical form. For simplicity we shall consider the case where a gap exists between the 1-mers and the α -mer where α is some larger number. The general reactions existing are



where N_j = number of moles of particles of size j in a mass of substance of w grams.

The kinetic equations² or equilibrium equations⁸ are the same as for the continuous case (where all species are present) as is the solution, if certain definitions are modified. In Table I are to be found the equations and definitions for both the continuous case and the discontinuous case (gap exists). As can be seen from the table, the discontinuous case can be considered a singular case of the continuous case; a case where K_x becomes zero as soon as any one of the species disappears, or better, the continuous case can be considered a special case of the discontinuous case where $\alpha = 1$. As can be seen, the discontinuous case reduces to the continuous case when $\alpha = 1$.

Equation of State. The derivation for the equation of state does not change, and the equation of state for both cases is

$$P(1 - B/v) = CRT \quad (1)$$

where C is $\sum_1^m C_x$ and $B/v = \sum_1^m B_x C_x$ where B_x is the

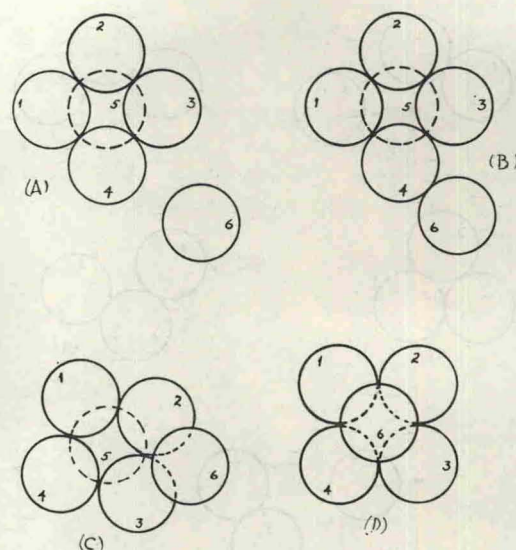


Figure 4. Bond formation in a 4-hole molecule: (A) approach; (B) first bond forms; (C) second bond forms; (D) third and fourth bonds form simultaneously. Degradation in reverse order. 2 bonds breaking simultaneously is the first step. Atom 5 as shown is necessary since without atom 5 the square planar structure of 1, 2, 3, 4 is not stable to kinetic forces and will rearrange to a tetrahedral structure. In a collision of this sort kinetic momentum is transferred to rotational momentum. Loss of this energy may be by the same mechanism or by colliding with a more complex j -mer.

covolume of a mole of x -mers. Hence this equation of state is valid for gases, liquids, and solids.

The Compressibility Equation. The point where the serious changes occur is in the equations derived from the compressibility equation. If one takes the derivative of the equation of state (eq 1) at constant temperature and rearranges it, one has

$$-\frac{dv}{dP} = \frac{u \frac{du}{dv}}{\left(-RT \frac{dC}{dv} \frac{du}{dv}\right) + P} \quad T = \text{constant} \quad (2)$$

where $u = (1 - B/v)$, letting

$$u \frac{du}{dv} = J \quad (3)$$

and

$$\frac{-RTdC}{dv} \frac{du}{dv} = L \quad (4)$$

one has

$$-\frac{dv}{dP} = \frac{J}{L + P} \quad T = \text{constant} \quad (5)$$

If J and L are constant with pressure changes then the equation is identical with the so-called Tait equation. We say so-called Tait equation because as explained by

Table I: Association Equations for Continuous and Discontinuous Cases

Continuous case Condition—all species present	Discontinuous case Gap exists—some species absent
$C_1 = C_1$ $C_x = C_x; 2 \leq x \leq m$ $= 0; m < x$ m is the size of the largest species $C_x = N_x/v$ $N_x =$ no. of moles of particles of size x in mass w $v =$ volume	$C_1 = C_1$ $C_x = 0; 2 \leq x < \alpha$ $= C_x; \alpha \leq x \leq m$ $= 0; m < x$ m is the size of the largest species Note: The gap need not start at 2 but could start at 3 or 4. This entails only slight modification.
Equilibrium constants (double index)	Equilibrium constants (double index)
$C_1 + C_x \rightleftharpoons C_{x+1}$ $K_{1,x} = \frac{C_{x+1}}{C_1 C_x} \quad 1 \leq x$	$C_1 + C_x \rightleftharpoons C_{x+1}$ $K_{x,1} = \frac{C_{x+1}}{C_1 C_x} \quad \alpha \leq x$
Equilibrium constants (single index)	Equilibrium constants (single index)
$K_1 = 1$ $K_x = 1/2 \prod_{y=1}^{x-1} K_{1,y} = \frac{C_x}{C_1^x} \quad 2 \leq x \leq m$ $K_x = 0; m < x$	$K_1 = 1$ $K_x = 0 \quad 2 \leq x < \alpha$ $K_\alpha = \frac{C_\alpha}{C_1^\alpha} \quad \alpha > 2$ $K_2 = \frac{C_2}{2C_1^2} = 1/2 K_{1,1} \quad \alpha = 1$ $K_x = K_\alpha \prod_{y=\alpha}^{x-1} K_{1,y} \quad \alpha < x \leq m$ $K_x = 0; m < x$ $\sum_{x=1}^m C_x = C_1 + \sum_{y=\alpha}^m K_y C_1^y$
$\sum_{x=1}^m C_x = \sum_{x=1}^m K_x C_1^x$	Actually this definition is redundant, since considering the conditions on K_x and C_x the continuous definition can be used.

Hayward^{14a} this is not the equation originally proposed by Tait but rather that called the Tait equation by Tamann. An interesting discussion of the various empirical two-constant compressibility equations is to be found in Hayward while a comparison of these equations is given by MacDonald.^{14b} As discussed by Hayward, the fit of the various equations depends on the quality of the data. Up to rather high pressures most of the proposed equations fit about equally as well; therefore one has to employ other criteria in choosing which equation to use. For practicality in interpolation one would as a matter of course use the simplest equation compatible with the precision desired. For use in drawing theoretical deductions the equation to be used is the one with the soundest theoretical basis. On this ground we have chosen to use eq 5 which we shall name the general compressibility equation (GCE) or the Tamann-Tait equation. In this equation which from its derivation is applicable to gases, liquids, and solids, it is not predetermined whether J and L are constant with pressure, temperature or not. This depends entirely on the state and conditions. For gases, J and L are apparently variables. For liquids there are various

cases; for liquid Helium I and II both J and L are constant with pressure,⁵ for Helium I, stable above the λ point, J is constant with temperature, L varies; for Helium II, stable below the λ point, L/J is constant with temperature with both J and L varying; according to other authors for a single class of substances J/v_0 is constant (v_0 is specific volume at a reference temperature) with temperature, both J and L being constant with pressure.^{15,16} In the case of the solid alkali metals⁶ both J and L are constant with pressure (Tamann-Tait law holds). Evidently a discussion of the compressibility equation of state will revolve around the constancy of J and L .

(14) (a) A. T. J. Hayward, N. E. L. Report 295, Natl. Eng. Lab., E. Kilbride, Glasgow, Scotland, 1967; *Brit. J. Appl. Phys.*, **18**, 965 (1967). (b) J. R. MacDonald, *Rev. Mod. Phys.*, **41**, 316 (1969).

(15) See for instance: A. Wohl, *Z. Phys. Chem.*, **99**, 234 (1921); A. Carl *ibid.*, **101**, 238 (1922); R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207-217 (1939).

(16) R. Ginell and A. M. Ginell, "Humidity and Moisture," Vol. III, A. Wexler and W. A. Wildhack, Ed., Reinhold Publishing Co., New York, N. Y., 1965, pp 363-386.

Some general relationships can be derived. One can rewrite eq 3 as

$$\frac{d \ln u}{dv} = \frac{1}{J} \quad (6)$$

from whence on integrating

$$u = Ee^{Jv} \quad (7)$$

E = constant of integration. From eq 7 and eq 1 we get that

$$C = \frac{PEe^{Jv}}{RT} \quad (8)$$

J and L Constant with Pressure. An important case of the compressibility equation is that when J and L are constant with pressure. Here eq 7 becomes

$$\left(1 - \frac{B}{v}\right) = Ee^{v/J} \quad (9)$$

$$C = \frac{PE}{RT} e^{v/J} \quad (10)$$

and

$$Z_n = \frac{\sum iC_i}{\sum C_i} = \frac{wRT}{M^0 v P E e^{v/J}} \quad (11)$$

where Z_n is the number average degree of association. Z_n exhibits a minimum with an increase in pressure. Differentiating eq 11 with respect to volume, and using eq 5 with J and L constant, we have

$$\frac{dZ_n}{dv} = Z_n \left[\frac{1}{v} - \frac{L}{PJ} \right]$$

Since at the minimum $dZ_n/dv = 0$, hence at this point

$$\frac{v}{P} = \frac{J}{L} \quad (12)$$

All these equations are the same for both the continuous and the discontinuous cases, and the quantities $(1 - B/v)$, C and Z_n are all calculatable in terms of constant of integration, E . In previous publications⁷ on the continuous case, the equations are slightly different from those given above, being given in terms of another integration constant, A . They can be reconciled by setting

$$E = ARTw/M^0 \quad (13)$$

where A is the constant of integration evaluated in ref 7. In that work A was evaluated by making the assumption that $Z_n = Zw = 1$ when $P/v = L/J$. This is true at the point where Z_n is a minimum.^{1,7} Since Zw and Z_n , the weight and number average degrees of association, are comparable quantities their behavior is similar and Zw should show a minimum around the same point where Z_n does. However, since from ref 4b

$$\varphi = -d \ln C_1/dv = A(L/J)v e^{v/J} \quad (14)$$

and from ref 1, $Zw = 1/v\varphi$, then

$$Zw = \frac{1}{A(L/J)v^2 e^{v/J}} \quad (15)$$

But the right-hand side of eq 15 exhibits no minimum, hence at pressures less than the pressure at the minimum, Zw becomes less than Z_n . This is manifestly impossible, since from the definitions of Zw and Z_n , their behavior must be parallel. Zw must always be greater than, or equal to Z_n .

Examining the derivation of Zw in ref 1, we see that eq 16 is derived under the assumption that $dK_x/dv = 0$. If all the j -mers are present, as they are in the continuous case, this is probably justified, but if the j -mers between $j = 2$ and $j = \alpha$ are absent, α being a new variable, the size of the smallest of the multiply packed j -mers, then it is not justified. Since $K_x = 0$ for $x < \alpha$ and $K_x \neq 0$ for $x \geq \alpha$, then as the pressure changes and species appear and disappear, α changes in value. Under these conditions the assumption that $dK_x/dv = 0$ is invalid.

If we redefine φ to be

$$\varphi = -(\partial \ln C_1/\partial v)_\alpha \quad (16)$$

then $(\partial K_x/\partial v)_\alpha = 0$ and $Zw = 1/v\varphi$ in terms of the new definition of φ . This can readily be seen by re-deriving the relationship of φ and Zw in the same way as in ref 4b.

Now from eq 1 we have

$$-\left(\frac{\partial v}{\partial P}\right)_\alpha = \frac{u/(\partial u/\partial v)_\alpha}{\frac{-RT(\partial C/\partial v)_\alpha}{(\partial u/\partial v)_\alpha} + P} \quad (17)$$

$$= \frac{J_v}{L_v + P}$$

where

$$J_v = u/(\partial u/\partial v)_\alpha \quad (18)$$

and

$$L_v = \frac{-RT(\partial C/\partial v)_\alpha}{(\partial u/\partial v)_\alpha} \quad (19)$$

These definitions of J_v and L_v are analogous to the definitions of J and L which one defined in terms of the total derivatives; but while J and L are constant with pressure changes, J_v and L_v are not constants.

Now since $C = \sum K_x C_1^x$

$$\begin{aligned} (\partial C/\partial v)_\alpha &= \sum x K_x C_1^x (\partial \ln C_1/\partial v)_\alpha \\ &= -\varphi \sum x C_x \end{aligned} \quad (20)$$

Whence using eq 19

$$\lambda = \frac{L_v}{J_v} = RT \varphi \sum x C_x / u \quad (21)$$

From eq 1, $Pu = CRT$; hence

$$\lambda = \frac{P\varphi \sum x C_x}{C} = P\varphi Z_n \quad (22a)$$

or

$$Z_n = \frac{\lambda}{P\varphi} \quad (22b)$$

for the discontinuous case. This result is analogous to that in the continuous case where

$$Z_n = L/JP\varphi \quad (22c)$$

From eq 15 and 22b one can see that when (and if) $Z_n = Z_w$, then $\lambda = P/v$; but there is no necessity for this to occur at the pressure corresponding to the minimum in Z_n . In Table II we have summarized the relevant equations for the continuous and discontinuous cases.

It can be seen by examining Table II that the definition of Z_n has not changed in going from the continuous case to the discontinuous case, but that the definition of Z_w has changed due to the appearance of the new variable λ . The problem now has become the evaluation of the constants of integration. As yet this is not possible in all cases.

Table II: Summary of Equations for the Degree of Aggregation, Z_n and Z_w for the Continuous and Discontinuous Cases^a

Continuous case	Discontinuous case
$Z_n = \frac{L}{Jp\varphi}$	$Z_n = \frac{\lambda}{P\varphi} = \frac{L_v}{J_v P\varphi}$
$= \frac{1}{APve^{v/J}}$	$= \frac{1}{A'Pve^{v/J}}$
$= \frac{RTw/M^0}{EPve^{v/J}}$	$= \frac{RTw/M^0}{E'Pve^{v/J}}$
$Z_w = 1/v\varphi$	$Z_w = 1/v\varphi$
$= \frac{J}{ALv^2e^{v/J}}$	$= \frac{1}{A'\lambda Pv^2e^{v/J}}$
$= \frac{JRTw/M^0}{ELv^2e^{v/J}}$	$= \frac{RTw/M^0}{E'\lambda v^2e^{v/J}}$
$\varphi = -\left(\frac{d \ln C_1}{dv}\right)$	$\varphi = -\left(\frac{\partial \ln C_1}{\partial v}\right)_\alpha$
$= (AvLe^{v/J})/J$	$= A'\lambda ve^{v/J}$

^a The constant A is different for the continuous and discontinuous cases. J and L are experimental and independent of which case is chosen for analysis. ^c $\lambda = L_v/J_v$ and it is a variable with pressure.

Further work is in progress on the mathematical and conceptual development of this theory.