ON ONE-DIMENSIONAL REGULAR ASSEMBLIES

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1. *Introduction.* The grand partition function of any statistical assembly may be defined by the equation

$$G = \sum_{(E, N_i)} e^{-E/\mathbf{k}T} \prod_i \lambda_i^{N_i}, \tag{1}$$

where E denotes any value of the energy of the assembly, $\mathbf{k}$ is Boltzmann's constant, T the thermodynamic absolute temperature and λ_i a parameter which is later to be connected with the chemical potential, μ_i, of the ith species in the assembly by the simple formula

$$\lambda_i = e^{\mu_i/\mathbf{k}T}.$$

N_i denotes the number of systems of the ith species within the assembly and, like E, varies from example to example in the grand ensemble, of all distinguishable complexions, over which the summation in (1) has to be performed. When G is known explicitly, the average (thermodynamic) values of the extensive parameters N_i are to be determined, in terms of the chemical potentials and the temperature, from the formulae

$$N_i = \lambda_i \frac{\partial}{\partial \lambda_i} \ln G. \tag{2}$$

By a one-dimensional regular assembly we imply three things:

(i) that the systems of the assembly constitute a linear chain,

(ii) that interactions between the systems are additive for all pairs of systems in the assembly (i.e. we rule out saturation forces and non-additive interaction energies such as occur in valence bonding), and

(iii) that for any two systems this interaction energy is specified solely by the nature of the systems (i.e. the species concerned) and their distance apart (measured in terms of the number of other systems separating the systems concerned).

Thus we are supposing that, as well as contributing to the sum of the interaction energies, $E_{\text{int.}}$, any system of type i produces a factor $f_i(T)$ in G, due to its vibrational and rotational motions. Equation (1) may therefore be written

$$G = \sum_{(E_{\text{int.}}, N_i)} e^{-E_{\text{int.}}/\mathbf{k}T} \prod_i \lambda_i^{N_i}, \tag{1'}$$

where λ_i stands for $\lambda_i f_i(T)$. Moreover, by (i) and (ii), we are assuming that

$$E_{\text{int.}} = \sum_{\text{(pairs of nearest neighbours)}} \epsilon_{ij} + \sum_{\text{(pairs of second-nearest neighbours)}} \epsilon_{i..j} + \sum_{\text{(pairs of third-nearest neighbours)}} \epsilon_{i...j} + \dots,$$

so that, putting $e^{-\epsilon_{ij}/\mathbf{k}T} = x_{ij}$, etc., we may write (1') in the form

$$G = \sum_{\substack{N_i, N_{ij}, N_{i..j}, N_{i...j}, \dots \\ \text{(subject to a linear chain)}}} \prod_{i,j} x_{ij}^{N_{ij}} \prod_{i,j} x_{i..j}^{N_{i..j}} \prod_{i,j} x_{i...j}^{N_{i...j}} \dots \prod_i \lambda_i^{N_i}, \tag{1''}$$

where N_{ij} denotes, in any example, the number of pairs of nearest neighbours of (i, j)

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type, $N_{i,j}$ denotes the number of pairs of second-nearest neighbours of $(i, ., j)$ type, and so on.

With G expressed in this form, it is at once apparent that the equilibrium values of such parameters as N_{ij} are given by

$$N_{ij} = x_{ij} \frac{\partial}{\partial x_{ij}} \ln G, \tag{3}$$

and similar formulae.

In this note we shall

(a) find an explicit expression for G valid for any finite number, m, of different species and any finite range (up to lth-nearest neighbours) of interactions,

(b) deduce from this certain formulae governing the equilibrium values of N_i, N_{ij}, etc.; including, as a special case, Guggenheim's equations of quasi-chemical equilibrium (1),

(c) prove that critical conditions cannot occur in any such one-dimensional assembly with interactions of finite range.

The simplest non-trivial assembly covered by our formulae, one with $m = 2$ and $l = 1$, is homologous with the Ising model for a one-dimensional ferromagnet (2); with $m = 2$ and $l = 2$ our formulae reproduce those recently derived by Temperley for the more elaborate model of Ising type with second-nearest neighbour interactions (3). The conclusion (c), above, was also enunciated by Temperley (see also Montroll (4)) but we feel that the present, more explicit, treatment provides a rather more convincing proof than that suggested in Temperley's paper. We are not aware that the surprisingly simple form of G has previously been demonstrated, nor that it has been shown that when $l = 2$ Guggenheim's equations of quasi-chemical equilibrium follow directly therefrom. The analogous equations, when $l > 2$, though perhaps less useful, are also new to us.

The paper ends with a discussion of the effects of gaps, or 'holes' in the assembly. We have assumed, for the sake of simplicity, that such gaps do not occur in the assemblies first dealt with in §§ 2–5.

For the sake of brevity, it has been necessary altogether to suppress the more mathematical parts of the discussion, particularly in connexion with (c) above, and simply to assert that the necessary proofs can be supplied (though not without some little difficulty). The authors will gladly supply copies of these proofs to anyone particularly interested in these mathematical details.

2. *Determination of G when there are nearest-neighbour interactions only.* With only nearest-neighbour interactions between the systems, G can be determined by a process of induction, starting with the comparatively simple formulae appropriate to just one or two species. Indeed this was the way in which we first obtained the general formula for G valid for any number of species. But a simpler procedure, and one which better reveals the structure of G, is by means of a set of recurrence relationships; we shall here describe this latter method, restricting the discussion, merely for the sake of brevity, to the case of just two species.

Let $F_n^{(1)}$ and $F_n^{(2)}$ ($n \geqslant 1$) be the contributions to G from states in which n systems are

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present, the last system (in some agreed direction) being of species 1 or of species 2, respectively. We do not define $F_0^{(1)}$, $F_0^{(2)}$. We then obtain the recurrence relations

$$\left.\begin{aligned} F_{n+1}^{(1)} &= \lambda_1 x_{11} F_n^{(1)} + \lambda_1 x_{12} F_n^{(2)}, \\ F_{n+1}^{(2)} &= \lambda_2 x_{21} F_n^{(1)} + \lambda_2 x_{22} F_n^{(2)}, \end{aligned}\right\} \tag{4}$$

while $$F_1^{(1)} = \lambda_1, \quad F_1^{(2)} = \lambda_2.$$

Now let $$G^{(1)} = \sum_{(n)} F_n^{(1)}, \quad G^{(2)} = \sum_{(n)} F_n^{(2)}$$

so that $$G = 1 + G^{(1)} + G^{(2)}. \tag{5}$$

Then, from (4), we obtain

$$G^{(1)} = \lambda_1 + \sum_{(n)} F_{n+1}^{(1)} = \lambda_1 + \lambda_1 x_{11} G^{(1)} + \lambda_1 x_{12} G^{(2)},$$

i.e. $$(1 - \lambda_1 x_{11}) G^{(1)} - \lambda_1 x_{12} G^{(2)} = \lambda_1,$$

and similarly* $$-\lambda_2 x_{21} G^{(1)} + (1 - \lambda_2 x_{22}) G^{(2)} = \lambda_2.$$ (6)

Solving (6) for $G^{(1)}$ and $G^{(2)}$, and substituting in (5), we find

$$G = \frac{P}{\Delta}, \tag{7}$$

where $$\Delta = \begin{vmatrix} 1 - \lambda_1 x_{11} & -\lambda_1 x_{12} \\ -\lambda_2 x_{21} & 1 - \lambda_2 x_{22} \end{vmatrix} = \| \delta_{ij} - \lambda_i x_{ij} \|, \tag{8}$$

and P is a polynomial in λ_1, λ_2 and the x_{ij} whose precise value does not concern us (see below).

Before proceeding further we may at once observe that G is of the form given by (7) and (8) however many different species may be present, i.e. whatever the range of values, $1, 2, \ldots, m$, open to the suffixes i and j. The only restriction on complete generality so far imposed rests in the provisional limitation of the argument to include only interactions between adjacent systems.

3. *Conditions of chemical equilibrium, when there are nearest-neighbour interactions only.* For a thermodynamic assembly G is *large*. But P, the numerator in (7), is simply a finite polynomial and therefore the condition of thermodynamic equilibrium, or the chemical equation of state, for the assembly is necessarily

$$\Delta \sim 0 \tag{9}$$

and effectively, therefore,

$$G \sim 1/\Delta, \quad \text{where} \quad \Delta \equiv \| \delta_{ij} - \lambda_i x_{ij} \| \sim 0. \tag{10}$$

This, of course, is why we were able to say above that the precise value of P was of no concern to us.

Equations (2) and (3) now serve to determine the equilibrium values of any other quantities in which we may be interested. They now read

$$N_i \Delta = -\lambda_i \frac{\partial \Delta}{\partial \lambda_i}, \tag{2'}$$

and $$N_{ij} \Delta = -x_{ij} \frac{\partial \Delta}{\partial x_{ij}} \tag{3'}$$

* The species of the last system added is designated by the suffix of the corresponding λ on the right-hand side of (4), i.e. by the first suffix of an x_{ij}. Therefore, if we assume the systems arranged from left to right in the order of these suffixes, then we are building up the chain by adding systems to its left-hand end.

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(where we must remember that Δ is vanishingly small). Equation (3′) calls for a further comment, namely that N_{ij} is, so far, distinguished from N_{ji}; i.e. N_{ij} denotes the number of pairs of neighbours of (i, j) type while N_{ji} denotes the number of pairs of neighbours of (j, i) type. We shall investigate the conditions under which these two quantities are equal.

On using formula (10) for Δ, equation (2′) now gives

$$N_i\Delta = \sum_j \lambda_i x_{ij} X_{ij} \tag{11}$$

$$= -\sum_j (\delta_{ij} - \lambda_i x_{ij}) X_{ij} + \sum_j \delta_{ij} X_{ij} = -\Delta + X_{ii}$$

$$= X_{ii} \tag{12}$$

by equation (9), where X_{ij} is the cofactor of the 'i, j' element in Δ. Thus $N_i\Delta$ is given by the first minor of the corresponding diagonal element in Δ.

Similarly, differentiating Δ with respect to x_{ij}, we obtain

$$N_{ij}\Delta = \lambda_i x_{ij} X_{ij}. \tag{13}$$

From equations (11) and (13) we verify immediately that $N_i = \sum_j N_{ij}$. This physically trivial result provides a check on our formulae and, in particular, on the legitimacy of dropping the polynomial, P, from the numerator in equation (7). The analogous equality, $N_i = \sum_j N_{ji}$, is most easily verified if we first observe that Δ may, by straightforward algebraic manipulation, be expressed in the alternative forms

$$\Delta \equiv \| \delta_{ij} - \lambda_i x_{ij} \| = \| \delta_{ij} - \lambda_i^{\frac{1}{2}} \lambda_j^{\frac{1}{2}} x_{ij} \| = \| \delta_{ij} - \lambda_j x_{ij} \|. \tag{14}$$

Of more interest, perhaps, is the observation that $N_{ij} \neq N_{ji}$ unless $x_{pq} = x_{qp}$ for all pairs p, q *except in the case of only two species*, when $N_{ij} = N_{ji}$ even if $x_{ij} \neq x_{ji}$ (as we see at once on examining the two-rowed determinant appropriate to this simple problem). Of course $x_{pq} \neq x_{qp}$ implies $\epsilon_{pq} \neq \epsilon_{qp}$, but such directional energy effects, although unusual, do not seem to be, of necessity, physically excluded.

From equations (12) and (13) we find

$$N_{ii} = \lambda_i x_{ii} N_i \tag{15}$$

—which provides a physical meaning for the chemical quantity λ_i; $\lambda_i x_{ii}$ is the probability that a system of type i will be followed by another system of type i (however many different species there are present).

Finally, since $\Delta \sim 0$ we have (by the algebraic theorem on the minors of the adjoint determinant)

$$\begin{vmatrix} X_{ij} & X_{iq} \\ X_{pj} & X_{pq} \end{vmatrix} = 0, \quad \text{i.e.} \quad \frac{N_{ij} N_{pq}}{N_{iq} N_{pj}} = \frac{x_{ij} x_{pq}}{x_{iq} x_{pj}}. \tag{16}$$

On taking $j = i$ and $q = p$ we find, as a particular case of equation (16), the formulae

$$\frac{N_{ii} N_{pp}}{N_{ip} N_{pi}} = \frac{x_{ii} x_{pp}}{x_{ip} x_{pi}}. \tag{17}$$

If $x_{lm} = x_{ml}$ for all l, m, i.e. if there is no directional effect, equation (17) becomes

$$\frac{N_{ii} N_{pp}}{N_{ip}^2} = \frac{x_{ii} x_{pp}}{x_{ip}^2}, \tag{18}$$

which, if we remember that in our notation N_{ip} accounts for only half the total number

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of pairs of neighbours including systems of both i- and p-species ($= N_{ip} + N_{pi}$), is precisely what Guggenheim has called an equation of 'quasi-chemical equilibrium'. Thus we find that Guggenheim's equations of quasi-chemical equilibrium, which are particular cases of equations (16), are true, exactly, for any one-dimensional regular assembly, however many species are involved, provided that interactions are between nearest neighbours only and there are no directional energy effects. In this case equations (16) can be derived from equations (18).

Before discussing the non-occurrence of critical conditions it will be well to extend our formulae to take account of interactions between systems up to lth-nearest neighbours.

4. *Expression for G including interactions between systems up to lth-nearest neighbours.* We now consider the effect on G of interactions between more distant neighbours, and in fact, we consider the interaction of each system with the l nearest neighbours on either side. We denote by

$$F_n^{(i_1, i_2, \ldots, i_l)}$$

the contribution to G from states in which n systems in all are present, the last l being of types $i_1, i_2, \ldots, i_l$ in that order, the last of all being of type i_1. The symbol is only defined for $n \geqslant l$.

We write down recurrence relations for the $F_n^{(i_1, i_2, \ldots, i_l)}$ and deduce simultaneous equations for the m^l expressions $G^{(i_1, i_2, \ldots, i_l)}$. In the simultaneous equations the 'constant' terms are less simple than in the nearest neighbour case, $l = 1$, but they affect only the numerator in G and so do not concern us. In this way we are led to the equation

$$G \sim 1/\Delta, \quad \text{where} \quad \Delta \equiv \| \delta_{i_1 i_2 \ldots i_l, j_1 j_2 \ldots j_l} - \lambda_{i_1} x_{i_1 i_2 \ldots i_l j_l} \delta_{i_2 \ldots i_l j_1 \ldots j_{l-1}} \|, \tag{19}$$

and

$$\Delta \sim 0.$$

(The symbol $\delta_{i_1 i_2 \ldots i_l, j_1 j_2 \ldots j_l}$ is a generalized Kronecker δ-function and is 1 if $i_1 = j_1$, $i_2 = j_2, \ldots, i_l = j_l$ and 0 otherwise.)

For instance, when $l = 2$ and $m = 2$ we obtain

$$\Delta = \begin{vmatrix} 1 - \lambda_1 x_{111} & -\lambda_1 x_{112} & 0 & 0 \\ 0 & 1 & -\lambda_1 x_{121} & -\lambda_1 x_{122} \\ -\lambda_2 x_{211} & -\lambda_2 x_{212} & 1 & 0 \\ 0 & 0 & -\lambda_2 x_{221} & 1 - \lambda_2 x_{222} \end{vmatrix}. \tag{20}$$

The $(l+1)$-fold suffixed quantities x are derived from the new factors which appear in $e^{-E/kT}$ when a new system, of species indicated by the first suffix, is added to a sequence whose beginning is defined by the remaining, successive suffixes. If energies are additive in the sense described in the introduction then when $l = 2$, for instance, we have

$$x_{ijk} = e^{-(\epsilon_{ij} + \epsilon_{i,k})/kT} = x_{ij}^{(1)} x_{ik}^{(2)} \tag{21}$$

say, but actually the method outlined may be applicable even when energies are not additive in this sense; it is sufficient that a factor x with $l+1$ suffixes, as above, completely describes the corresponding energy change.

From the determinantal expression for Δ we obtain the chemical equation of state

$$\Delta \sim 0,$$

the equations

$$N_i \Delta = -\lambda_i \frac{\partial \Delta}{\partial \lambda_i}, \tag{22}$$

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and equations for the numbers of $(l+1)$-ads (triads (ijk) when $l = 2$), i.e.

$$N_{i_1 i_2 \dots i_l i_{l+1}} = -\frac{x_{i_1 i_2 \dots i_l i_{l+1}}}{\Delta} \frac{\partial \Delta}{\partial x_{i_1 i_2 \dots i_l i_{l+1}}}. \tag{23}$$

We can obtain formulae for the equilibrium numbers of other (shorter) ordered sequences by writing, in the case $l = 2$ for instance,

$$x_{ijk} = x_{ij} y_{ijk}$$

(this being an entirely formal substitution). Then, in this particular instance,

$$N_{ij} = -\frac{x_{ij}}{\Delta} \frac{\partial \Delta}{\partial x_{ij}}$$

and so on. All such differentiations are, of course, to be performed formally, i.e. without reference to the equilibrium condition $\Delta \sim 0$.

The corresponding generalizations of equations (15) and (16) now read (on taking $l = 2$ for definiteness)

$$N_{iii} = \lambda_i x_{iii} N_{ii}, \tag{15'}$$

and

$$\frac{N_{ikj} N_{pkq}}{N_{ikq} N_{pkj}} = \frac{x_{ikj} x_{pkq}}{x_{ikq} x_{pkj}}. \tag{16'}$$

For $l > 2$, k in (16′) stands for a set of $l-1$ suffixes. With additive energies as described above, (16′) becomes

$$\frac{N_{ikj} N_{pkq}}{N_{ikq} N_{pkj}} = e^{-(\epsilon_{i.j} + \epsilon_{p.q} - \epsilon_{i.q} - \epsilon_{p.j})/kT}, \tag{16''}$$

when it is seen to be an immediate generalization of Guggenheim's equations of quasi-chemical equilibrium. In particular, if all the $\epsilon_{i.j} = 0$, i.e. if the lth-neighbour interactions do not exist, then the right-hand side of (16″) is unity. Interpreted verbally for the case $l = 2$ this means that when there are only nearest-neighbour interactions then the chance of a system of species j following a system of species k is independent of the nature of the system which precedes the system of species k.

These generalizations of our earlier equations are perhaps of more formal than practical interest, and we shall not pursue them further here. It is sufficient to add that from equation (20), and with the assumption of additive energies, it is possible easily to derive, and verify, the results found by Temperley for Ising chains having second-nearest neighbour interactions (3).

5. *The non-occurrence of critical conditions.* Since we have obtained a single analytic formula for G, the grand partition function, it may, perhaps, be argued that further investigation of the occurrence or non-occurrence of critical conditions is quite unnecessary. For, thermodynamically, critical conditions are always marked by analytic discontinuities in isothermals giving vapour pressures (or other such curves) and, statistically, these curves are derived by simple processes of differentiating G, processes which cannot, in themselves, give rise to analytic discontinuity. The formula for G above is (sensibly) exact, and therefore must reproduce the true thermodynamic behaviour—and not an approximation to it involving hypothetical metastable states; consequently, in any assembly of the type considered, critical conditions are, *ipso facto*, impossible.

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This argument seems to us to be perfectly sound provided only that the assembly itself (which, after all, is defined by a hypothetical model) is actually a truly thermodynamic assembly. But we see no grounds for assuming, without further investigation, that this is indeed the case.

Critical conditions, however (or totally abnormal thermodynamic behaviour), are certainly excluded provided that the equations derived from G above ensure

(i) that any λ_i is a single-valued function of the N_i (or their ratios), and

(ii) that the N_i (more correctly, their ratios) are single-valued functions of the λ_i.

A complete proof of both (i) and (ii) has proved possible. The present paragraph simply describes the nature of the arguments used.

It follows from equation (22), together with the requirement $\Delta \sim 0$ for thermodynamic equilibrium, that for any small changes in the composition of the assembly, the temperature (all x's) remaining constant, we have

$$\left.\begin{aligned} \sum_i N_i \frac{d\lambda_i}{\lambda_i} &= 0, \\ \text{i.e. that the Gibbs-Duhem equation} \quad \sum_i N_i d\mu_i &= 0 \end{aligned}\right\} \tag{24}$$

is automatically satisfied.

Moreover it can, without difficulty, be shown that λ_i is a single-valued function of the ratios of the N_i provided that the quadratic differential form

$$\sum_i dN_i \frac{d\lambda_i}{\lambda_i} \quad \text{or} \quad \sum_i dN_i d\mu_i \tag{25}$$

is positive definite in the region defined by equation (24). (For the *thermodynamic* meaning of this requirement, see Gibbs (5).) The expression (25) can also be written as

$$\frac{1}{\Delta} \sum_{i \neq j} (X_{ii} - X_{ii,jj})\, d\mu_i d\mu_j, \tag{26}$$

where X_{ii} denotes (as above) a diagonal first minor, and $X_{ii,jj}$ a diagonal second minor of the determinant. (This notation is appropriate only for the case $l = 1$; for the more general case a more elaborate notation is required.) That (26) is positive definite, in the region defined by (24), can be verified without any great difficulty in the cases of assemblies with two and three different species and with interactions between nearest neighbours only. It has, however, been found possible to provide a complete proof of the condition (25), valid for any number of species and any finite range of interactions.

Proof of the second requirement, (ii), i.e. that the composition of the assembly is uniquely determined by the λ's, presents less difficulty. For simplicity we consider here the argument for the case of interactions between nearest neighbours only; extension of the formulae to cover any value of l is solely a matter of notation. Then, from (12), we have

$$\frac{N_i}{N_j} = \frac{X_{ii}}{X_{jj}}, \tag{27}$$

and N_i/N_j is determined as an algebraic function of the λ's. Consequently the

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composition is uniquely determined by the λ's unless two of the principal minors, X_{ii} and X_{jj}, of Δ should vanish simultaneously. That this is impossible, except in entirely trivial cases, can be shown without too much difficulty.

It can also be shown that every term in an expansion of $1/\Delta$ (in ascending powers of the λ's) is positive. This would not require proof if G were identically $1/\Delta$, since, by (1), G is made up of entirely positive terms. But we have shown only that G is effectively $1/\Delta$ for large assemblies; it is therefore of interest that every term in an expansion of $1/\Delta$ should be positive.

6. *Gaps in the assembly.* Before we can be entirely convinced that any one-dimensional regular assembly with interactions extending over only a finite range is incapable of manifesting critical conditions, we need to consider the modifications introduced into the above formulism when, in place of any system, we can have a gap or 'hole' in the assembly. Extended so to include 'holes', the theory will then be relevant to such a hypothetical problem as one-dimensional adsorption.

At first sight we take account of 'holes' by merely adding a new species (a 'hole'), specified by the suffix 0 say, whose chemical potential μ_0, vanishes, i.e. for which $\lambda_0 = 1$. But further consideration shows that the grand partition function for an assembly including gaps must be defined rather more carefully. If there are altogether N sites, occupied or unoccupied, and if G_N is the corresponding restricted grand partition function, then we have

$$\sum_{N=0}^{\infty} G_N \xi^N \sim \frac{1}{\Delta}, \tag{28}$$

where $$\Delta = \| \delta_{ij} - \lambda_i \xi x_{ij} \| \quad (i, j = 0, 1, 2, \ldots, m).$$

G_N can now be determined by the saddle-point method (which can be shown to be applicable). Alternatively, since we can show that $\lim_{N\to\infty} (G_N)^{1/N}$ exists, we may use the Cauchy-Hadamard theorem—every term in an expansion of $1/\Delta$ in powers of ξ being positive (see end of § 5). Thus $$\lim_{N\to\infty} (G_N)^{1/N} = \xi_0^{-1},$$

where ξ_0 is the smallest ξ for which $\| \delta_{ij} - \lambda_i \xi x_{ij} \| = 0$.

Therefore $$\ln G_N \sim -N \ln \xi_0$$

and the equation $$N_i = \lambda_i \partial \ln G_N / \partial \lambda_i$$

gives $$\frac{N_i}{N} = -\frac{\lambda_i}{\xi_0}\frac{\partial \xi_0}{\partial \lambda_i} \quad (i = 0, 1, 2, \ldots, m). \tag{29}$$

But $$\Delta \equiv \| \delta_{ij} - \lambda_i \xi_0 x_{ij} \| = 0,$$

and therefore $$\frac{\partial \Delta}{\partial \lambda_i} + \frac{\partial \Delta}{\partial \xi_0}\frac{\partial \xi_0}{\partial \lambda_i} = 0, \tag{30}$$

the differentiations of Δ in (30) being entirely formal. Consequently (29) may be written

$$\frac{N_i}{N} = \lambda_i \frac{\partial \Delta}{\partial \lambda_i} \Big/ \xi_0 \frac{\partial \Delta}{\partial \xi_0},$$

so that $$\frac{N_i}{N_j} = \lambda_i \frac{\partial \Delta}{\partial \lambda_i} \Big/ \lambda_j \frac{\partial \Delta}{\partial \lambda_j}, \tag{31}$$

an equation entirely analogous to equation (27).

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Moreover, since Δ is a homogeneous function of degree zero in the λ's and ξ_0^{-1}, we have

$$\sum_i \lambda_i \frac{\partial \Delta}{\partial \lambda_i} = \xi_0 \frac{\partial \Delta}{\partial \xi_0}, \quad \text{i.e.} \quad \sum_{i=0}^{m} N_i = N$$

as we require. Indeed we see that the introduction of ξ_0, implicit in (31), merely ensures this necessary condition together with $\lambda_0 = 1$.

Proof of the non-occurrence of critical conditions now follows precisely that outlined in the last paragraph.

Finally, we observe that it is possible to pass smoothly from the case in which 'holes' are allowed to that in which they are specifically excluded from the start, by making

$$x_{0i} \to 0 \quad \text{for} \quad i = 0, 1, 2, \ldots, m.$$

Physically this means that the energy of formation of a hole becomes too great for holes to occur in significant numbers. Formally it implies that the determinant

$$\| \delta_{ij} - \lambda_i \xi_0 x_{ij} \| \quad (i, j = 0, 1, 2, \ldots, m)$$

reduces to the determinant

$$\| \delta_{ij} - \lambda_i \xi_0 x_{ij} \| \quad (i, j = 1, 2, \ldots, m). \tag{32}$$

The presence of ξ_0 in (32), although there is no such factor in equation (10), is easily explained; for the equation which corresponds to the Gibbs-Duhem equation, (24), now reads (by (29) and (30))

$$\sum_{i=1}^{m} N_i \frac{d\lambda_i}{\lambda_i} + N d \ln \xi_0 = 0.$$

Comparison with the thermodynamic equation (at constant temperature)

$$\sum_{i=1}^{m} N_i d\mu_i - V dP = 0$$

enables us to identify ξ_0 with $e^{-vP/kT}$, where P is the external pressure and v is the change in the 'volume' of the assembly per system added (supposing that this is the same for all systems). Thus the more sophisticated treatment of the present paragraph shows us that we ought, strictly, to replace each λ_i in the formulae of §§ 1–5 by $\lambda_i e^{-vP/kT}$. This, of course, is perfectly intelligible, since we previously ignored the work done against the external pressure in building up the assembly.

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