N O T E S O N T H E T H E O R Y
O F P H A S E T R A N S I T I O N S

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- 1 - THE STATISTICAL THEORY OF PHASE TRANSITIONS.

The statistical derivation of phase transitions always involves the evaluation of the partition function (or sum-over-states) Z

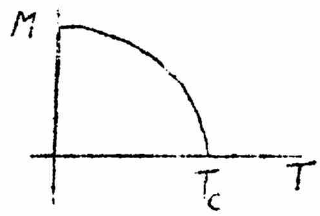
$$Z = \underset{(i)}{S}\, G_i\, e^{-E_i/kT}$$

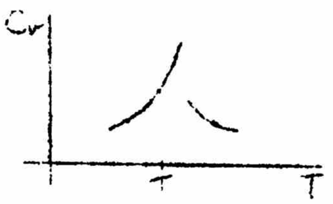
of the system over its possible levels i with energy E_i and multiplicity G_i , from which the thermodynamical functions can be derived, since Z is connected with the free energy Ψ by

$$Z = e^{-\Psi/kT}$$

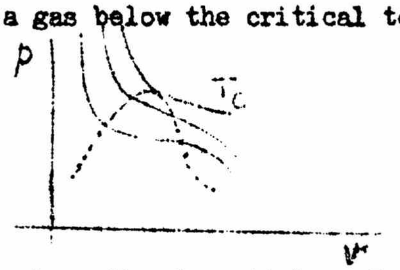
For systems of interacting particles the summation $\underset{(i)}{S}$ can only be performed in very few cases .

As examples of phase transitions we mention the behaviour of ferromagnetic substances (occurrence of a Curie transition temperature) :





and the condensation of a gas below the critical temperature T_c :



For a finite number N of particles G_i is finite and Z is an analytic function of T . Transitions can only occur in the limiting case $N \longrightarrow \infty$. In the case of the gas for instance one has to consider

N , $v \to \infty$ with finite number density N/v and for the free energy this yields

$$\lim_{N,\, v \to \infty} \Psi = N\, \psi\, (T, v),$$

when ψ (the free energy per particle) should only depend on the intensive variables T and v .

The exact solution of this limiting problem has only been carried out for the 2-dimensional Ising-model of a ferromagnetic substance and the condensation of a Bose-Einstein gas .

The Ising-model consists of a given lattice on each of the sites of which a spin is situated . The spin parameter S_i can take the values ± 1 . Each spin is assumed to interact only with its nearest neighbors (4 in the 2-dim. case) . The energy of a certain configuration is then

$$E = -\tfrac{1}{2} J \sum_n S_i S_j - \mu H \sum_i S_i ,$$

where $\sum_n$ is taken over all interacting pairs . Note that this is different from the actual ferromagnetic case , where the interaction involves the scalar product ($S_i \cdot S_j$) and where the S_i are q-numbers . The interaction energy J is the increase in energy if two neighbouring spins change from parallel to anti-parallel (in an anti- ferromagnetic lattice $J < 0$). H is the magnetic field and μ the magnetic moment of each atom . With

$$L = J / 2kT \quad \text{and} \quad C = \mu H / kT$$

the partition function is

$$\mathop{S}_{(s_i)} e^{L \sum_n s_i s_j + C \sum_i s_i}$$

In the case of a <u>gas</u> , we suppose the intermolecular forces to be additive and central so that the potential energy can be written as

$$\mathcal{U} = \sum_{i<j} \phi(r_{ij})$$

and the (classical) partition function then is

$$Z = e^{-\Psi/kT} = \frac{1}{N!\,h^{3N}} \int_{-\infty}^{\infty}\cdots\int d\vec{p}_1 \ldots d\vec{p}_N \int_V \cdots \int d\vec{r}_1 \ldots d\vec{r}_N \, e^{-\left[\sum_i \vec{p}_i^{\,2}/2m + \mathcal{U}\right]/kT}$$

$$= \frac{(2\pi m k T/h^2)^{3N/2}}{N!} \int_V \cdots \int e^{-\mathcal{U}/kT} \, d\vec{r}_1 \ldots d\vec{r}_N \qquad (1)$$

(the factor h^{-3N} makes Z dimensionless) .The remaining configurational integral in general cannot be evaluated exactly .

Of course, approximate theories exist for the magnetic problem (Weiss) and the condensation problem (e.g, Van der Waals) . But , apart from their approximate character , such theories presuppose thermodynamics (for instance in the use of the so-called Maxwell rule) which from the point of view of statistics is rather unsatisfactory , since statistical mechanics should provide the basis for thermodynamics .

In the following we will outline the main features of the 2-dimensional Ising-problem and the Bose-Einstein problem . It will turn out that the mathematical mechanism in the existing theories is completely different in these two cases. The question of a unified mathematical method then arises .

- 2. THE ISING-PROBLEM.

We first consider the one domensional case of N lattice points (linear chain) taking the lattice points on a circle, we can identify the points N + 1 and 1 . If we do not take into account the magnetic field, the partitism function is

. . . .
1 2 i N

$$Z = e^{-\Psi/kT} = \sum_{s_1=-1}^{+1} \cdots \sum_{s_N=-1}^{+1} e^{L s_1 s_2} e^{L s_2 s_3} \cdots e^{L s_{N-1} s_N} e^{s_N s_1}$$

Considering the s_i as matrix indices and introducing the matrices $V_{s_i s_j} = e^{L s_i s_j}$ one has $Z = \sum V_{s_1 s_2} V_{s_2 s_3} \cdots V_{s_N s_1} = Trace\,(V^N)$,

where $$V = \begin{pmatrix} e^{L} & e^{-L} \\ e^{-L} & e^{L} \end{pmatrix}$$

Let λ_1 and λ_2 be the eigenvalues of V . On diagonalizing V , one can write

$$Z = \lambda_1^N + \lambda_2^N$$

The secular equation is

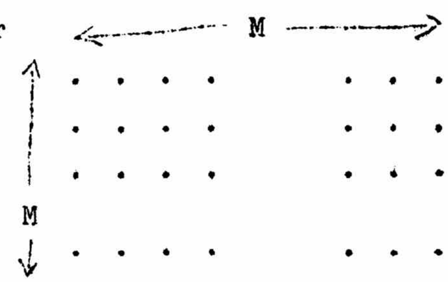
$$\begin{vmatrix} e^{L} - \lambda & e^{-L} \\ e^{-L} & e^{L} - \lambda \end{vmatrix} = 0 \longrightarrow \begin{cases} \lambda_1 = 2 \cosh L \\ \lambda_2 = 2 \sinh L \end{cases}$$

Since N is very large , only the largest eigenvalue λ_1 is important and therefore

$$\Psi = -kTN \log \lambda_1(T) \qquad (\sim N)$$

from which the entropy , the energy etc .. follow . λ and therefore Ψ are analytic functions of T , so here the Ising-model does not lead to a phase transition (in the 1-dimensional case a Curie point never occurs) .

<u>The two-dimensional</u> Ising-model has been treated along the same lines by Onsager . With $N = M^2$, we consider each column of M atoms as a unit, interacting with neighbouring colums . To get rid of boundary conditions we now identify the (M +1) - th column with the first one



and the (M + 1) -th row with the first row by winding the lattice on a torus . Each column interacts with neighbouring ones ,each unit has 2^M states , which can be denoted by a matrix index $(s_{1i}, s_{2i}, \cdots s_{Mi})$. Again one can use the matrix method and

$$Z = \text{Trace}\ (V^M) = \sum_{k}^{2^M} \lambda_k^M$$

where now V is a $2^M \times 2^M$ - matrix , but the determination of the eigenvalues now is a major problem . Onsager developed a method (simplified by Onsager and Kaufman) to determine the largest eigenvalue . For $N \to \infty$ the result is again $\Psi(T) = N\psi(T)$ with

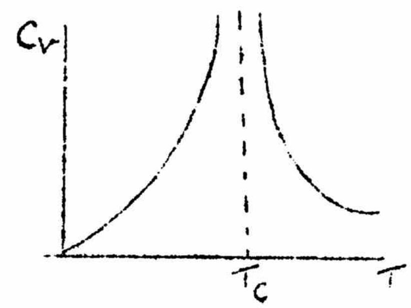
$$-\psi/kT = \frac{1}{N}\log Z = \log(2\cosh 2L) + \frac{1}{\pi}\int_0^{\pi/2} \log\frac{1}{2}\left\{1+\sqrt{1-K^2\sin^2\varphi}\right\} d\varphi ,$$

where

$$K = 2\sinh 2L / \cosh^2 2L .$$

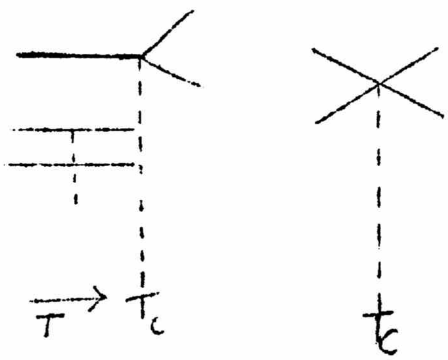
Now a transition point occurs since $\psi(T)$ has a singular point . The critical temperature T_c is determined by

$$\sinh 2 L_c = 1 \qquad\qquad (L_c = 0.4407 ..)$$



At the transition point T_c the specific heat C_v becomes infinite .

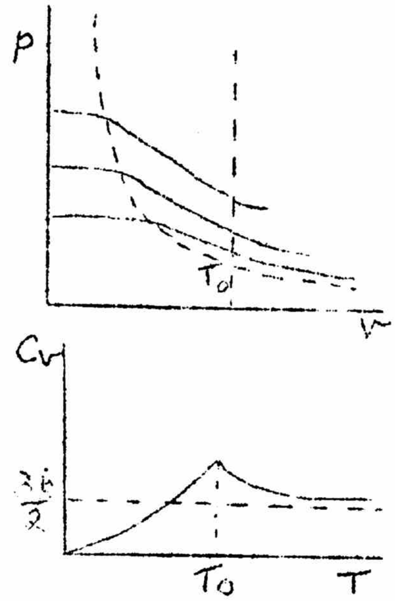
In Onsager's treatment the largest eigenvalue turned out to be 2-fold degenerate up to the temperature T_c. One might expect that in other cases, the discontinuity arises from a crossing of eigenvalues at T_c in such a way that , in taking the largest eigenvalues one has to jump over from one to the other at T_c .



The 3-dimensional Ising-problem is still unsolved , it is even unknown if C_v remains finite in the transition region .

- 3 - THE BOSE -EINSTEIN CONDENSATION .

For a system of N identical non-interacting particles, obeying Bose-Einstein statistics and enclosed in a volume V , the statistical treatment leads for $N \longrightarrow \infty$ with constant density to a condensation



phenomenon ; with decreasing specific volume v at constant temperature the pressure turns out to be constant below a critical volume v_c . The (p , v)- curve has a discontinuity in the second derivative at v_c . The condensation accurs for every isotherm , the locus of the transition points being $p \sim v^{-5/3}$. With decreasing temperature at constant v a transition occurs at T_0 (v) , where the specific heat C_v shows a discontinuity in the first derivative .

The treatment is slightly different from the discussion of the ordinary gas .(For the treatment, starting from an integral like 1 see Kahn and Uhlenbeck , Physica 5 (1938) 399) If ε_i are the translatory energy levels of a particle in a volume V and n_i the occupation numbers of the levels , the energy E is $\sum_i n_i \varepsilon_i$ and the partition function is

$$Z = S' e^{-(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \cdots)/kT}$$

where the prime in S' means summation over all occupations ,satisfying $\sum_i n_i = N$. Then Z is the coefficient of z^N in the generating function (S without restriction and $\beta = 1/kT$) :

$$F(z) = S e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \cdots)} z^{n_1 + n_2 + \cdots}$$

$$= \prod_i \sum_{n_i=0}^{\infty} (z e^{-\beta \varepsilon_i})^{n_i} = \prod_i (1 - z e^{-\beta \varepsilon_i})^{-1} = e^{-\sum_i \log(1 - z e^{-\beta \varepsilon_i})}$$

With $N, V \to \infty$ at constant $v = V/N$, the energy spectum becomes continuous [illegible] one can therefore replace the sum by an integral :

$$\sum_i \to \frac{V}{h^3}\int d\vec{p}\, \log(1-ze^{-\beta p^2/2m}) = -\frac{V}{h^3}\sum_{k=0}^{\infty}\frac{z^k}{k}\int d\vec{p}\, e^{-k\beta p^2/2m}$$

$$= -\frac{4\pi V}{h^3}\sum_k \frac{z^k}{k}\int_0^{\infty} dp\, p^2 e^{-k\beta p^2/2m} = V\left(\frac{2\pi m k T}{h^2}\right)^{3/2}\chi(z)$$

where $\chi(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^{5/2}}$

Since Z is the coefficient of z^N in $F(z)$, we have , introducing the de Broglie-wavelength

$$\lambda = h/\sqrt{2\pi m k T}$$

and taking z to be a complex variable ,

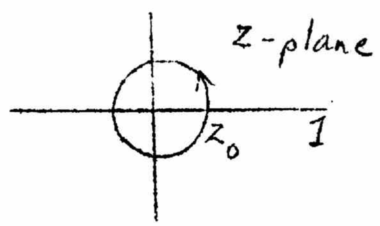
$$Z = \frac{1}{2\pi i}\oint \frac{dz}{z^{N+1}}\, e^{V\chi(z)/\lambda^3} \simeq \frac{1}{2\pi i}\oint dz\, e^{N\{v\chi(z)/\lambda^3 - \log z\}}$$

according to Cauchy's theorem . The closed contour of integration should enclose $z = 0$.

The integral is known as Kramer's integral (Kramers, Leiden comm ., suppl. № 83 , 1936) and can be evaluated by the method of steepest descent. We rewrite ($a = v/\lambda^3$)

$$Z = \frac{1}{2\pi i}\oint e^{Ng(z,a)} \quad \text{with} \quad g(z,a) = a\chi(z) - \log z$$

and consider first the case :



<u>I. a >> 1</u> . $\chi(z)$ is increasing and g has a maximum at z_0 given by

so the saddlepoint $z_0 << 1$. Taking the contour through z_0 , we can replace the integral by an integral over $z = z_0 + i\eta$ with η from $-\infty$ to $+\infty$. Here

$$g(z_0, a) = g(z_0, a) - \tfrac{1}{2}\eta^2 g''(z_0, a) + \cdots$$

with $g''(z_0, a) > 0$ and

$$Z \simeq \frac{e^{Ng(z_0,a)}}{2\pi i}\, i\int_{-\infty}^{\infty} e^{-\frac{1}{2}Ng''\eta^2}\, d\eta = \frac{1}{2\pi}\sqrt{\frac{2\pi}{Ng''}}\; e^{Ng(z_0,a)}$$

$$-\Psi/kT = Ng(z_0, a) = N\psi(T, v)$$

so for $N \to \infty$

$$\Psi = -kTNg(z_0, a) = N\psi(T, v)$$

where $\psi(T, v)$ is continuous . With $p = -\partial\psi/\partial v$ this leads to the decreasing portion of the (p, v) - curve for large v .

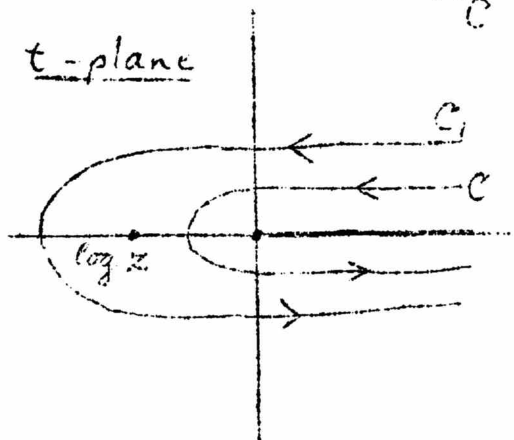
<u>II. Small v</u> . With decreasing v z_0 will go to 1 , which leads to a critical value of v (or a) since $\chi(z)$ singular at $z = 1$. The critical value $a_c = v_c/\lambda^3$ is given by

$$a_c^{-1} = \chi(1) = \sum_{k=1}^{\infty} \frac{1}{k^{3/2}} = \zeta\left(\tfrac{3}{2}\right) = 2 \cdot 61 \ldots = \gamma .$$

We now have to consider the contour integral through z_0 for $z_0 \to 1$.

Since $\chi(z)$ converges within the unit circle it has an integral representation which is (cf. W. Opechowski, Physica (I937) 7I5) .

$$\chi(z) = \frac{1}{2}\frac{z}{\Gamma(\frac{5}{2})}\int_C \frac{t^{3/2}}{e^t - z}\,dt$$



The integrand is double-valued and has a pole at $t = \log z$, so one has to make a cut along the positive real t-axis and C should not include the point $\log z$ For small z the integrand can be developed

$$\int_C \frac{t^{3/2}}{e^t - z}\,dt = \int_C \frac{t^{3/2}e^{-t}\,dt}{1 - ze^{-t}} = \sum_{k=1}^{\infty} z^{k-1}\int_C t^{3/2}e^{-kt}\,dt$$

and since the last integral is the Hankel integral for 2 $\Gamma(\frac{5}{2})/k^{5/2}$;

we again find the original series

$$\chi(z) = \sum_{k=1}^{\infty} z^k/k^{5/2}$$

If $z \to 1$, $\log z \to 0$ and C would enclose the pole . But as long as $z < 1$ we have , replacing the path C by C_1

$$\int_{C_1} = \int_C + (\text{ residu in } t = \log z\ ) = \int_C + 2\pi i(\log z)^{3/2}$$

or $$\chi(z) = \frac{z}{2\Gamma(\frac{5}{2})}\int_{C_1}\frac{t^{3/2}\,dt}{e^t - z} + \frac{4\sqrt{\pi}}{3}\,z\,(-\log z)^{3/2}$$

The integral is regular around $Z = 1$, and can be developed in powers of $(1 - Z)$. Thus one gets

$$\chi(z) = \delta - \gamma(1-z) + \cdots + \frac{4\sqrt{\pi}}{3}(1-z)^{3/2} + \cdots$$

where $\delta = \zeta(\tfrac{1}{2})$ and $\gamma = \chi'(1) = \zeta(\tfrac{3}{2})$. In the Z - plane $Z = 1$ is a branchpoint .

With $y = \sqrt{1-z}$ we then find

$$g(z,a) = a\delta + (1 - a\gamma)y^2 + \frac{4a\sqrt{\pi}}{3}y^3 + \cdots$$

Since $a_c\gamma = 1$, we have $1 - a\gamma > 0$ for $a < a_c$, so the integrand e^{Ng} has a maximum along the positive real axis and $y = 0$ is a saddlepoint in the y - plane . We thus can put $y = i\eta$ and have

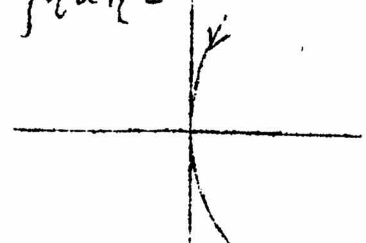
$$Z \cong \frac{2}{2\pi i}\int_{-i\infty}^{+i\infty} y\,dy\; e^{Ng(a,y)}$$

$$= -\frac{e^{N\delta a}}{\pi i}\int_{-\infty}^{+\infty}\eta\,d\eta\; e^{N\{(1-a\gamma)y^2 + 4a\sqrt{\pi}y^3/3 + \cdots\}} =$$

$$= -\frac{e^{N\delta a}}{\pi i}\int_{-\infty}^{+\infty} e^{-N(1-a\gamma)\eta^2}\{1 + \frac{4a\sqrt{\pi}N}{3}i^3\eta^3 + \cdots\}\eta\,d\eta =$$

$$= -\frac{e^{N\delta a}}{\pi i}\int_{-\infty}^{+\infty} -i\eta^4 d\eta\,\frac{4a\sqrt{\pi}}{3}\,e^{-N(1-a\gamma)\eta^2}N =$$

$$= \frac{e^{N\delta a}}{\pi}\,\frac{4aN\sqrt{\pi}}{3}\cdot\frac{3}{4}\,\frac{\sqrt{\pi}}{\{N(1-a\gamma)\}^{5/2}}$$



y - plane

z - plane

The saddle point $z_0 = 1$ is a turning point for the path of steepest descent . It is reached for $v = v_c$. For $v < v_c$ the saddle point sticks to $z_0 = 1$. From the obtained expression for Z in the case $v < v_c$ we find

$$\log Z = N \delta a + \text{terms of order } \log N$$

so for $N \to \infty$

$$\Psi = N \psi \quad \text{where} \quad \psi = -a\delta k T = -v\delta k T/\lambda^3$$

and $$p = -\partial \psi / \partial v = \delta k T/\lambda^3 ,$$

so for $v < v_c$ the <u>pressure is independent of v</u>. At $v = v_c$ the pressure and $\partial p/\partial v$ are continuous , but $\partial^2 p/\partial v^2$ is discontinuous . Since $v_c = \lambda^3/\gamma \sim T^{-3/2}$ the locus of transition points is $\sim T^{-3/2}$. There exists no critical temperature since at any T condensation occurs for sufficiently small v .

From the foregoing it is clear that the mathematical mechanisms of the Ising-problem and the Bose-Einstein condensation are completely different . A unitary mathematical formalism for both cases of phase transitions (the only cases which have been solved in an exact way) might be found in the theory of linear graphs , which we will discuss now .

<u>- 4 - THE THEORY OF LINEAR GRAPHS</u> .

I. <u>Introduction</u> . A linear graph is a collection of points and of lines , joining these points . A graph can be connected or disconnected .

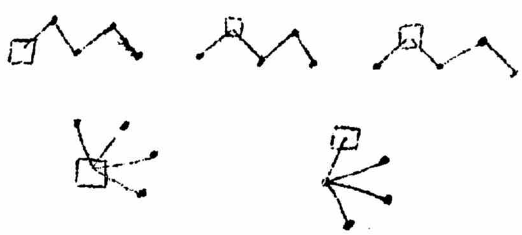
Examples are :

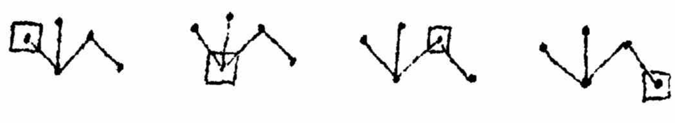
a . Cayley trees : linear graphs without cycles .

With 5 points there are only 3 topologically different Cayley trees .

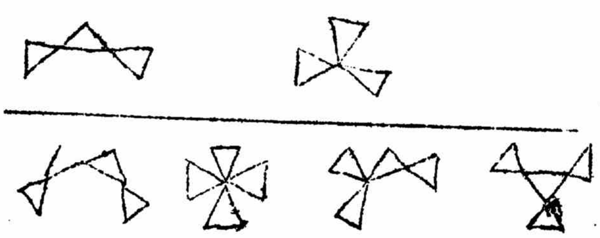
For all kinds of graphs, the general problem is to determine the number of topologically different graphs . The answer will be different for distinguishable points and for indistingouishable points .

Cayley investigated the number of isomers $C_n H_{2n+2}$. The carbon chains of these isomers form Cayley trees with the restriction that the maximum number of lines arriving at each point (the " branching number ") is 4 . In the case of isomers of $C_n H_{2n+1} OH$ and similar compounds there is one preferred C-atom , the carbon chain forms a to-called <u>rooted Cayley-tree</u> . For $n = 5$, there are evidently 9 rooted by trees .





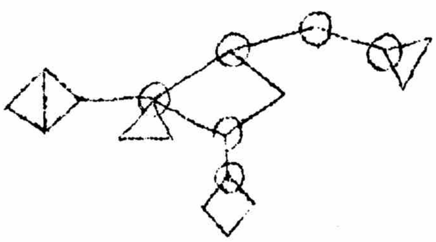
b . Cacti : Cayley trees with triangles as units instead of lines . With 3 or 4 triangles there are resp. 2 and 4 cacti .



c. Husimi trees : Cayley trees arbitrary polygo s as units or also : linear graphs in which each line belongs to at most one cycle . In pure Husimi

trees the units are equal, in mixed trees they are different .

In a general linear graph one can distinguish articulation points . An articulation point is such that by omitting it , the graph is divided in two or more parts . A connected graph without articulation points we will call a star . Clearly a general connected graph is divided by its articulation points in stars . If one omits in the stars all the internal lines and draws



only the " outline ", which is a polygon, one gets a mixed Husimi tree . In this sense, the general connected graph is a generalization of a Husimi tree, just as a star is a generalization of a polygon.

One of the general problems of graph theory is a combinatorial problem . It arises in various fields of physics and is characteristic for successive approximation methods , e.g. in the virial deve pment . An analogous case is the quantum mechanical perturbation problem , where the so-called Feynman graphs appear .

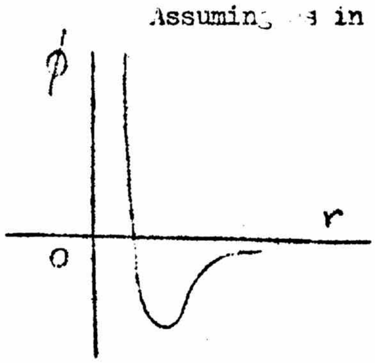
- 5 - APPLICATION TO PHASE TRANSITIONS.

I. The condensation problem . As we saw in parag.1 , the central problem is the evaluation of the partition function and in particular the

the configuration integral

$$Q_N = \int_V \cdots \int e^{-U/kT} \, d\vec{r}_1 \cdots d\vec{r}_N \qquad (1)$$

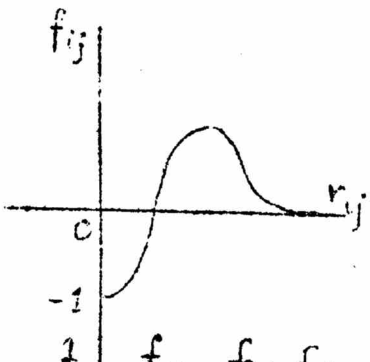
Assuming as in § 1 $U = \sum_{i<j} \phi(r_{ij})$ we can write (Mayer)



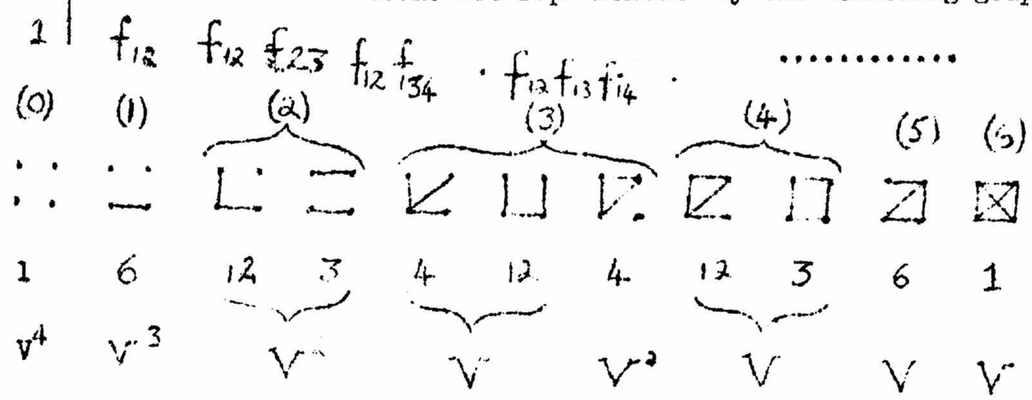
$$e^{-U/kT} = \prod_{i<j} e^{-\phi(r_{ij})/kT} = \prod_{i<j} (1+f_{ij}) \qquad (2)$$

where

$$f_{ij} = e^{-\phi(r_{ij})/kT} - 1$$



The problem of developing $\prod$ is clearly connected with the theory of graphs , since one can represent all terms of a certain type by a linear graph and then determine the number of these terms. For N = 4 (2^b terms) the different types of terms are represented by the following graphs :



We have indicated the number of lines in each graph (= number of factors f in the terms) and the numbers of terms of each type .

Q_N can now be expanded in powers of V . We consider a certain " partitio " of the N (numbered) molecules in m , single molecules , m_2 pairs, m_3 triples ..., m_ℓ sets of molecules where

$$\sum_{\ell=1}^{N} \ell \, m_\ell = N \qquad (3)$$

Two special types for $N = 4$ are for instance (1,2) (3,4) ($m_2 = 2$, $m_\ell = 0$ for $m \neq \ell$) and (1,2,3) (4) ($m_1 = 1$, $m_3 = 1$) . In (2) we take together all terms belonging to the considered partitio , that is in which the given pairs, triples , ... each form a connected graph in the graph representation . The <u>cluster function</u> $U_\ell \, (\vec{r}_1 , \ldots , \vec{r}_\ell)$ is defined as the sum of all terms represented by connected graphs of ℓ points . For instance:

$$U_2 \; (1,2) = f_{12}$$

$$U_3 \, (1,2,3) = f_{12} f_{23} + f_{13} f_{32} + f_{21} f_{13} + f_{12} f_{23} f_{31} =$$

(3) + (1)

$$U_4 \, (1,2,3,4) =$$

(4) + (12) + (12) + (3) + (6) + (1)

It is clearly a symmetric function of $\vec{r}_1 , \ldots , \vec{r}_\ell$. The <u>cluster integral</u> is defined by

$$b_\ell = \frac{1}{\ell ! \, V} \int \cdots \int d\vec{r}_1 \ldots d\vec{r}_\ell \; U_\ell \; .$$

In the ℓ - fold integral over the connected graph we first can perform the integration over ℓ -1 molecules and the result is practically independent of the position of the ℓ -th molecule since each f is only different from zero for small distances of the molecules . The integration over the ℓ -th molecule then leads to a factor V . Therefore for large V (and fixed ℓ) the b_ℓ will become asymptotically independent of V and are then only functions of the temperature . Define b_ℓ 1 . For a definite partitio we have the general contribution

$$\prod_\ell (V \; b_\ell \; \ell !)^{m_\ell} \qquad (4)$$

Since the partitio with given numbers m can be realized in

$$N \; ! \Big/ \left\{ (1!)^{m_1} (2!)^{m_2} \; \ldots\ldots \; m_1 \; ! \; m_2! \; \ldots\ldots \right\} \qquad (5)$$

different ways, we find

$$Q_N = \mathcal{S}' \frac{N \; !}{(1!)^{m_1} (2!)^{m_2} \ldots m_1 ! \; m_2 ! \; ..} \prod_\ell (V \; \ell ! b_\ell)^{m_\ell} = \mathcal{S}' \frac{N \; !}{m_1 ! \; m_2 \ldots} \prod_\ell \; (Vb_\ell)^{m_\ell} \qquad (6)$$

where $\mathcal{S}'$ means summation over all values m_ℓ , obeying (3).

For instance , for N = 4 the partitio 4= 2+2, represented by the single graph  , gives a contribution (V_2 ! b_2 $)^2$ and it occurs 3 times . This follows also from (4) and (5) for m_2 = 2, m_ℓ = 0 for $\ell \neq 2$. The partitio 4 = 3 + 1 is represented by the graphs  and  . It gives a contribution (V_3 ! b_3) (V_1 ! b_1) and it occurs four times (since all the permutations of the three connected points are included in U_3) . This follows again from (4) and (5) with N=4, m_1 = 1, m_3 =3 , all other m_ℓ = 0 .

Q_N has now been expanded in powers of V and we are interested in its behaviour for large N . With the assumed intermolecular potential ϕ the function f_{ij} will have a large positive part if the temperature is not too high, and this will lead to $b_\ell > 0$. We suppose this to be the case, so all terms in (6) are positive . The terms in (6) are then of the same form as the volume in the Γ - space of a gas of N molecules, corresponding to a certain occupation of cells in the μ-space and, like there, for one special distribution (for one set of the m) the term is extremely large . We therefore can replace Q_N by this maximum term , which is the " Maxwell - Boltzmann distribution " for the m_ℓ . To find this term we calculate the maximum of

$$\log. F = \log. \frac{N!}{m_1!m_2!\ldots} (Vb_1)^{m_1}(Vb_2)^{m_2}\ldots =$$

$$= N \log. N - N - \sum_\ell (m_\ell \log m_\ell - m_\ell) + \sum_\ell m_\ell \log Vb_\ell ,$$

(here we have applied the Stirling formula to N ! and the m_ℓ ! which is allowed since the small values of m_ℓ do not play a part) with the auxiliary condition (3) ,

$$\delta \log. F = - \sum_\ell \log m_\ell \delta m_\ell + \sum_\ell \log Vb_\ell \delta m_\ell = 0$$

with

$$\sum_\ell \ell \delta m_\ell = 0 .$$

Applying the Lagrange method of undetermined multipliers, we find

$$- \log \bar{m}_\ell + \log Vb_\ell + \beta \ell = 0$$

or

$$\bar{m}_\ell = Vb_\ell e^{\beta \ell} \equiv Vb_\ell z^\ell ,$$

where the parameter z (which depends on the volume) is determined by the condition (3) for the $\bar{m}_\ell$:

$$\boxed{\frac{N}{V} = \frac{1}{v} = \sum_{\ell=1}^{N} \ell b_\ell z^\ell} \qquad (7)$$

This is the first Mayer equation . By taking the second variation it can be verified that $F(\bar{m}_\ell)$ is indeed a very sharp maximum . Replacing Q_N by $F(\bar{m}_\ell)$, we find with the use of (7) from the partition function

$$\Psi = -kT \log Z = -\frac{3}{2} RT \log T + \text{const.}\, NT + NkT \log z - kTV \sum_\ell b_\ell$$

hence

$$p = -\left(\frac{\partial \Psi}{\partial V}\right)_T = -\frac{NkT}{z}\frac{\partial z}{\partial V} + kT\sum_\ell b_\ell z^\ell + kTV\sum_\ell \ell b_\ell z^{\ell-1}\frac{\partial z}{\partial V}$$

which in view of (7) yields the second Mayer equation

$$\frac{p}{kT} = \sum_{\ell=1}^{N} b_\ell z^\ell . \qquad (8)$$

The equation of state is now obtained by eliminating z from (7) and (8) . Since (7) cannot explicitly be solved for z , this has to be done by successive approximation and one finds p/kT as a series in $1/v$, that is the virial expansion for the equation of state .

For large v , z is small . If we only take the first terms in (7) and (8) , we find the first approximation

$$\frac{p}{kT} = z = \frac{1}{v}$$

i.e., the ideal gas law . The first correction is obtained by inserting this first approximation for z in the quadratic terms of (7) and (8) :

$$(7) \longrightarrow \frac{1}{v} = z + 2b_2\left(\frac{1}{v}\right)^2 \quad \text{or} \quad z = \frac{1}{v} - 2b_2\left(\frac{1}{v}\right)^2$$

then $(8) \rightarrow \frac{p}{RT} = \frac{1}{v} - 2\, b_2 \left(\frac{1}{v}\right)^2 + b_2 \left(\frac{1}{v}\right)^2 = \frac{1}{v}\left(1 - \frac{b_2}{v}\right)$

so that in the virial expansion

$$p = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots\right)$$

the second virial coefficient is $B = -N\, b_2$. From our previous definition of b_2 , we can express B in terms of the intermolecular potential

$$B(T) = -N\, b_2 = -\frac{N}{2V} \iint \left(e^{-\phi(r_{12})/kT} - 1\right) d\vec{r}_1\, d\vec{r}_2 =$$

$$= -\frac{N}{2V} \int d\vec{r}_2 \int \left(e^{-\phi(\rho)/kT} - 1 \right) d\left(\vec{r}_1 - \vec{r}_2\right) .$$

where $\rho = |\vec{r}_1 - \vec{r}_2|$, or

$$B(T) = 2\pi N \int_0^\infty \left(1 - e^{\phi(\rho)/kT}\right) \rho^2\, d\rho .$$

From measurements of B at various temperatures one can infer the parameters , determining the intermolecular potential .

The question now arises if the above treatment leads to a condensation . The answer is determined by the behaviour of the series $\chi(z) = \sum_l b_l z^l$ occuring in the second Mayer equation , the discussion goes along the same lines as that of the Kramers integral and is given in the paper of Kahn and Uhlenbeck and in Kahn's thesis (On the theory of the equation of state , Utrecht, 1938) . The series plays the same part as the series $\sum z^l / l^{5/2}$ in the case of the Bose-Einstein condensation . Kahn was able to prove that condensation only occurs if $\chi(z)$ fulfilled the following conditions (analogous to the properties of the series in the case of Bose- Einstein condensation) :

1) $\chi(z)$ has a singular point z_0 on the positive real axis (according to Hadamard's theorem this will be the case if $b_\ell > 0$ and if a singular point exists) ,

2) $\chi(z_0)$ and $\chi'(z_0)$ finite ,

3) some additional conditions which are satisfied if in a region around z_0

$$\chi(z) = f(z) + (z - z_0)^{\alpha} g(z)$$

where α is not integer and > 1 ($\alpha = \frac{3}{2}$ in the Bose-Einstein case) and $f(z)$ and $g(z)$ are analytic in this region .

For this case Kahn proved that the isotherm shows a horizontal portion . But the investigation of $\chi(z)$ involves the study of the cluster integrals b_ℓ and this problem is in general still far from solved .

From the foregoing, it is clear that the theory of condensation leads to two different problems :

a . The combinatorial (or topological) proble : how many terms contribute to the cluster integral ?

b . The integral problem : the evaluation of the different " irreducible " integrals .

For the condensation problem it will be of special interest to investigate the situation for large ℓ , since this will determine the convergence properties of the series $\chi(z)$.

The first problem is now completely solved . It is a problem of the number of topologically different graphs of a certain type . Cayley was the first to deal with such problems in a systematic way , but he did not succeed in finding the complete answer , even for the case of the Cayley trees . Much progress was achieved by a paper of Polya (Acta Math . 68 (1938) 145) and the case of Cayley trees was solved by Otter (Ann. Math. 49 (1948) 583)

Further literature :

R.J. Riddell, Dissertation , Univ. of Michigan (1951) .

R.J. Riddell and G.E. Uhlenbeck , J. Chem. Phys. 21 (1953) 2056 .

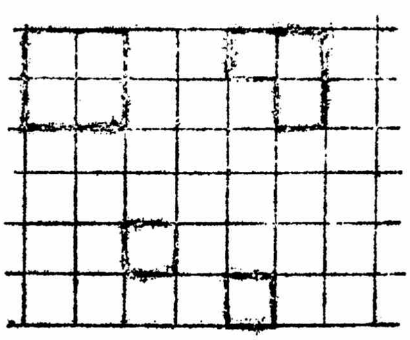
G.W. Ford , Dissertation , Univ. of Michigan (1954.)

- § 6 . OTHER APPLICATIONS OF THE THEORY OF GRAPHS .

As was already mentioned before , the determination of the n-th term in successive approximation methods generally leads to a combinatorial problem (how many contributions ?) and an integral problem . Examples are :

a. The Ising problem . The connection with graph theory was given by van der Waerden (Zs. f. Physik 118 (1941) 473) ; see also the review article by Newell and Montroll (Rev. Mod.Phys. 25 (1953) 353) .

The combinatorial problem is : how many different graphs with given length are possible in a certain lattice ? Consider a square lattice .



The integral problem is very easy : the integral is 1 for every closed graph and zero for every non-closed graph . The combinatorial problem is to find the number of closed graphs (1 of length 4 , 3 of length 8 , etc) .

b . The connection with the Bose-Einstein condensation , especially for systems of interacting particles . The application of graph theory is presumably possible , though this has not yet been verified (Butler and Friedman , Phys. Rev. 98 (1955) 287,294 ; also Luttinger and Yang).

c . Perturbation problems in field theory . Here the problem is to determine the number of irreducible Feyman diagrams . It has been solved by Hurst (Ploc.Roy.Soc. 214 (1952) 44) and Riddell (Phys. Rev. 91 (1953) 1241) .

§ 7 . THE PRINCIPAL THEOREM .

Passing on to the general method of graph theory, we now give the principal theorem, due to Polya (reference above) .

Think of a collection of " figures", each with a certain " content" which is described by a set of integers. The content may for instance be a number k of red balls and a number ℓ of red of white balls . Let us assume that there are $a_{k\ell}$ different figures of content (k,ℓ) and let the numbers $a_{k\ell}$ be given in the form of a generating function :

$$f(x,y) = \sum_{k,\ell} a_{k\ell}\, x^k y^\ell \tag{1}$$

(in general a function of n variables if the content is described by n integers). We now consider s points in space, to each of which we will associate 1 figure so that we obtain a certain configuration . Let H_s be some permutation group of s points , of degree s and order h .

Two configurations then will be considered as equivalent if they can be transformed into each other by a permutation belonging to H_s. The content of a configuration is the sum of the contents of the figures.

Problem : Given the function $f(x,y)$, find the number $A_{k\ell}$ of non-equivalent configurations with total content (k, ℓ), expressed by the generating function

$$F(x, y) = \sum_{k,\ell} A_k \; x^k y^\ell \qquad (2)$$

Solution : Each permutation of H_s can be written uniquely in its cyclic representation (such that each object occurs in one and only one cycle) and then consists of j_1 cycles of 1, j_2 cycles of 2,.. j_s cycles of s, where

$$\sum_{k=1}^{s} k_{j_k} = s, \qquad (3)$$

With the variables $f_1, \ldots, f_s$, we introduce the polynomial

$$\mathfrak{Z}(H_s) \equiv \frac{1}{h} \underset{(j_i)}{S'} \; g(j_1, j_2 \ldots j_s) \, f_1^{j_1} f_2^{j_2} \ldots f_s^{j_s} \qquad (4)$$

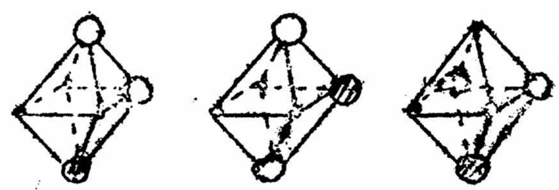
the cycle index of H_s, where $g(j_1, \ldots j_s)$ is the number of permutations in H_s with j_1 cycles of one, ... j_s cycles of s ar where S' should be consistent with (3). Also $S' g(j_1, j_2, \ldots j_s) = h$.

The solution of the problem is then

$$F(x,y) = \frac{1}{h} \; S' \; g(j_1 \ldots j_s) \, f^{j_1}(x,y) \, f^{j_2}(x^2, y^2) \ldots f^{j_s}(x^s, y^s) \equiv \mathfrak{Z}\{H_s, f(x,y)\} \qquad (5)$$

We will not give the proof (cf. Polya) , but give some examples .

1) Let the s points be the vertices of an octahedron and the content of a configuration be 3 red , 2 blue and 1 white ball. In how many different ways can the 6 balls be distributed over the 6 vertices if two arrangements which are transformed into each other by a rotation are considered the same ? The answer is 3 . The figures are the 3 types of balls, the content is 1 red ball (1,0,0) 1 blue ball (0,1,0) or 1 white ball (0,0,1).



$$f (x,y,z) = x + y + z$$

s = 6 and H_s is the octahedron group of rotations , with h = 24 , for which

$$\mathfrak{Z}(H_s) = \frac{1}{24} (f_1^6 +6 f_1^2 f_4 + 3 f_1^2 f_2^2 + 6 f_2^3 + 8 f_3^2)$$

so

$$F (x , y,z) = \frac{1}{24}\left\{ f^6 (x,y,z) + 6 f^2(x,y,z) f (x^4, y^4, z^4) + \dots\right\}$$

The answer is then the coefficient of $x^3 y^2 z$, that is 3 .

2) The same problem if no rotation is allowed . This is the elementary problem to distribute the balls over 6 points and the answer is $\frac{6!}{1!2!3!} = 60$. Again $f (x, y, z)= x+ y + z$ and $s = 6$. H_s is now the unit element , h = 1 . $\mathfrak{Z}(H_s) = f_1^6$ and $F(x,y,z) =(x + y + z)^6$. The coefficient of $x^3 y^2 z$ is $\frac{6!}{1!\,2!\,3!}$

3) . <u>Number of saturated alcohols</u> $C_n H_{2n+1}$ OH (not including the stereo-isomers) . The counting series id $F(x) = \sum_{n=0} A_n x^n$ with $A_0 \equiv 1$. Starting with the C-atom that carries the - OH , we see that A_n is the number of <u>rooted</u> Cayley trees with n points each of branching number 4.

The figures to be placed on the 3 remaining valencies ($s = 3$) are again rooted carbon chains, including zero chains, so clearly $f(x) = F(x)$. Since we do not pay attention to stereo-isomers , H_s is the complete symmetric permutation group G_3 of 3 objects , which is of the order $h = 3\,! = 6$ and for which

$$\mathcal{Z}(G_3) = \frac{1}{6}\left(f_1^3 + 3 f_1 f_2 + 2 f_3 \right) .$$

Applying Polya's theorem we have to bear in mind that in $\mathcal{Z}\{G_3, f(x)\} = \mathcal{Z}\{G_3, F(x)\}$ only the n-1 remaining C-atoms (to be placed at the 3 valencies of $\rangle C - OH$) are counted . To count also the root we have to shift all the coefficients in this series to the next pow of x . This is done by multiplying the series with x (then adding 1 to account for the first term $A_0 \equiv 1$) . So Polya's theorem yields

$$F(x) = 1 + x\,\mathcal{Z}\{G_3, F(x)\} = 1 + \frac{x}{6}\left\{F^3(x) + 3\,F(x)F(x^2) + 2\,F(x^3)\right\} ,$$

from which F (x) can be found by inserting the counting series $\sum_n A_n x^n$ and successively equating the coefficients of equal powers on both sides :

$$F(x) = 1 + x + x^2 + 2x^3 + 4x^4 + 8x^5 + 17x^6 + \ldots$$

4) <u>Number of alcohols $C_n H_{2n+1}$ O H, including stereo isomers.</u>

The derivation is the same as in 3) apart from the fact the valencies are now placed according to a tetrahedron and that now only rotations over 120° around one valency axis are allowed . H_s is now the cyclic group S_3 of 3 objects , of order 3 . This leads to

$$\mathcal{Z}(S_3) = \frac{1}{3}\left(f_1^3 + 2 f_3\right) ,$$

$$F(x) = 1 + \frac{x}{3}\left\{F^3(x) + 2F(x^3)\right\} ,$$

which yields

$$F(x) = 1 + x + x^2 + 2x^3 + 5x^4 + 11x^5 + \dots\dots$$

5) The Cayley formula . We now ask for the counting series $T(x)$ for the number T_n of rooted Cayley trees (where the " branching number " of each point is no longer restricted to 4 as was the case for the saturated alcohols) . T_n is the number of these trees with n lines ($n + 1$ points) and

$$T(x) = \sum_{n=0}^{\infty} T_n x^n$$

with $T_0 = 1$, $T_1 = 1$, $T_2 = 2, \dots$ The lines starting from the root we call main branches ; let s be the number of main branches . The figures to be placed at the s main branches are again rooted Cayley trees and the figure series is again the counting series for these rooted trees . H_s is the full symmetric group G_s of s objects, of order s ! For this group the number $g(j_1, \dots j_s)$ of eq. (4) is

$$g(j_1, \dots j_s) = \frac{s!}{1^{j_1} 2^{j_2} 3^{j_3} \dots j_1! \, j_2! \, j_3! \dots}$$

The factors $j_1!, j_2!$ ... account for the permutations of the j_1, cycles among each other, of the j_2 cycles among each other etc . and the factors k^{j_k} account for the fact that (12 ...k) = (23 ...k 1) = ... (k...321).

The cycle index therefore is

$$\mathcal{Z}(G_s) = \frac{1}{s!} \sum{}' \frac{s!}{1^{j_1} 2^{j_2} \ldots j_1! \, j_2! \ldots} f_1^{j_1} f_2^{j_2} \ldots \qquad (6)$$

($\sum{}'$ according to eq. (3) . Applying Polya's theorem we find :

$$T(x) = 1 + \sum_{s=1}^{\infty} x^s \mathcal{Z}\{G_s, T(x)\} \qquad (7)$$

The factor x^s ensures that we also count the s lines of the root (cf. example 3) , the summation is over all possible numbers of main branches . Inserting (6) into (7) we find

$$T(x) = 1 + \sum_{s=1}^{\infty} \sum{}' \frac{x^{j_1 + 2j_2 + \ldots + s j_s}}{1^{j_1} j_1! \, 2^{j_2} j_2! \ldots} T^{j_1}(x) \, T^{j_2}(x^2) \ldots$$

and since $s \longrightarrow \infty$ the prime can be omitted :

$$T(x) = \prod_{r=1}^{\infty} \sum_{j_r=0}^{\infty} \frac{1}{j_r!} \left\{ \frac{x^r \, T(x^r)}{r} \right\}^{j_r} = \prod_{r=1}^{\infty} e^{x^r \, T(x^r)/r}$$

or

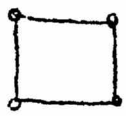
$$T(x) = e^{\sum_{r=1}^{\infty} x^r \, T(x^r)/r} \qquad (8)$$

the <u>Cayley equation</u> , which yields after development

$$T(x) = 1 + x + 2x^2 + 4x^3 + 9x^4 + 20x^5 + 48x^6 + \ldots$$

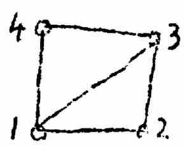
One can raise the question whether such a series has only a formal meaning or it has really a region of convergence . We shall later see that the series has a region of convergence and that the singular point which is nearest to the origin in the complex plane lies on the positive real axis (as it should for a series with positive coefficients according to Hadamard's theorem) . We then also return to the connection of the series with the mathematical formation of the condensation phenomenon .

§ 8 . GENERALIZATIONS . We will now use Polya's theorem to count more complicated graphs . We first introduce the notion of the group of a graph , denoted by Γ: this is the group of covering operations (all operations which transform the graph into itself) . The order of Γ is the symmetry number of the graph . We consider some examples .



If the graph is a rectangle , Γ is the dieder group D_4 of rotations and reflections of a rectangle (order 8) . For a rectangle with 2 diagonals (a complete graph of 4 points) any permutation of the 4 points is allowed and is the symmetric group

G_4 of permutations of four objects (order 4 ! = 24) . For a rectangle with one diagonal , Γ consists of the unit element, the 2 " flips " around the lines 1-3 and 2-4 , and their



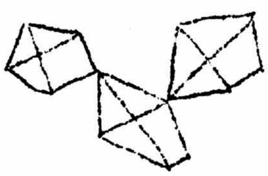
product, so is the four group $E, (13), (24), (13)(24)$.

If we want to keep a given point fixed , the number of covering operations will be restricted . They form a subgroup of Γ , which we will call the derived group Γ_q where q denotes the fixed point . In the first two examples Γ_q is the same whate‥r the choice of the point q . In the third example Γ_q is different ‥r $q = 1$ (or 3) and $q = 2$ (or 4) . Without proof we mention the theorem

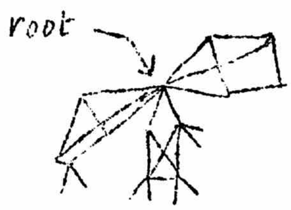
$$\mathfrak{Z}'(\Gamma) \equiv \frac{\partial}{\partial f_1} \mathfrak{Z}(\Gamma) = \sum_q \mathfrak{Z}(\Gamma_q) \qquad (1)$$

where the sum is taken over different derived groups (N.B. In evaluating $\mathfrak{Z}(\Gamma_q)$ the fixed point q should of course not be included in the cyclic representation of Γ_q . One can easily verify the theorem for the above examples .

In considering now more complicated graphs we first suppose all the " building blocks " to be the same (as the lines in Cayley trees or the triangles in cacti and so consider in general pure star trees (generalisation of Husimi trees) .



a) Pure rooted star trees . Let T_n be the number of different pure rooted star trees of n (equal) stars and let us again introduce the counting series $t(x) = \sum_{n=0} T_n x^n$ with $T_0 \equiv 1$ We will derive an implicit equation for $T(x)$ in two steps, using in each step Polya's theorem .



I . As in ex. 5) of §7 , we call stars starting from the root (e.g. the pentagons with 2 diagonals in the figure) the main branches . If T_{nm} is the number of trees with n stars and

m main branches, we can introduce the generating function

$$T_m(x) = \sum_{n=0}^{\infty} T_{n\,m}\, x^n \qquad (2)$$

and clearly have

$$T(x) = \sum_{m=0}^{\infty} T_m(x) \qquad (T_o(x) \equiv 1) \qquad (3)$$

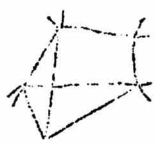
We now can reduce $T_m(x)$ to $T_1(x)$ by considering the root as an m-fold point on each of which 1 rooted tree of 1 main branch is hung . For the configuration the figure series is $T_1(x)$, the number of points $s = m$, the group H_s is the full symmetric group G_m (any permutation of the m rooted subtrees is allowed) and Polya's theorem gives us the configuration series

$$T_m(x) = \mathcal{Z}\left\{ G_m, T_1(x) \right\} \qquad (4)$$

If we now insert (4) in (3), we find (in the same way as in § 7 eq. (8) was derived from eq. (7)

$$T(x) = e^{\sum_{r=1}^{\infty} T_1(x^r)/r} \qquad (5)$$

II. To find $T_1(x)$, we again apply Polya's theorem . The s points for the figures are the vertices of the 1 main branch , except the root (in the example $s = 4$) the figures series is $T(x)$, the group H_s is formed by all the permutations of the points of the main branch which conserve its structure and keep the root fixed , that is, Γ_q of the star. Polya's theorem gives then the configurational series



root

$$T_1(x) = \sum x \, Z\{\Gamma_q,\ T(x)\}, \qquad (6)$$

where the factor **x** compensates the fact that the main branch is not counted by Z and where the sum should be taken over the topologically different possible choices of a point of the main branch as the root .

Applying theorem (1) we can rewrite (6) as

$$T_1(x) = x \, Z'\{\Gamma,\ T(x)\} \qquad (7)$$

which combines with (5) to yield

$$T(x) = e^{\sum_{r=1}^{\infty} x^r Z'\{\Gamma,\ T(x^r)\}/r} \qquad (8)$$

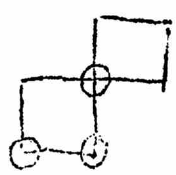
As an example, consider the case where the stars are rectangles .
$\Gamma = D_4$ and $Z(\Gamma) = \frac{1}{8}\{f_1^4 + 2f_1^2 \cdot f_2 + 3f_2^2 + 2f_4\}$ so $Z'(\Gamma) = \frac{1}{2}\{f_1^3 + f_1 f_2\}$

The trees are pure Husimi trees and the counting series $Q(x)$ satisfies

$$Q(x) = e^{\sum_{r=1}^{\infty} x^r \{Q^3(x^r) + Q(x^r)\,Q(x^{2r})\}/2r}$$

from which one finds

$$Q(x) = 1 + x + 3x^2 + 11x^3 + 46x^4 + 208x^5 + \dots$$



For $n=2$ there are 3 trees , arising from the 3 different possible positions of the root .

b) <u>Mixed rooted star trees</u> . The stars can now be chosen out of a given finite collection (think of polygons with given numbers of diagonals) As an example we consider rooted Husimi trees of n_2 lines and n_3 triangles and introduce a counting series of 2 variables

$$H(x,y) = \sum_{n_2,n_3} H(n_2, n_3)\, x^{n_2} y^{n_3}, \qquad (H(0,0) = 1)$$

The reasoning is the same as for pure trees : one considers the counting series $H_{k\ell}(x,y)$ for this type of trees with k lines and ℓ triangles together forming $k+\ell$ main branches . At these $k+\ell$ main branches, we hang the figures . Consider first $\ell = 0$ (only k main lines) The figures series is $H(x,y)$ and thus are k points , $_3 = G_k$ and we would get $H_{k0}(x,y) = x^k\, \mathcal{Z}\left\{G_k ; H(x,y)\right\}$. Then consider $k=0$ (only main triangles) . For each main triangle , the figure series would then be the configurational series of the mixed rooted trees hung on the 2 remaining corners of that main triangle, that is

$$\mathcal{Z}\left\{G_2\,,\, H(x,y)\right\} = \frac{1}{2}\left\{H^2(x,y) + H(x^2, y^2)\right\} .$$

Using this as the figure series for the figures to be hung on the ℓ main triangles, we find

$$H_{0\ell}(x,y) = y^{\ell}\, \mathcal{Z}\left[G_\ell\,,\, \mathcal{Z}\left\{G_2\,,\, H(x,y)\right\}\right] .$$

For arbitrary values of K and ℓ , we have :

$$H_{k\ell}(x,y) = H_{k0}(x,y)\; H_{0\ell}(x,y)$$

and with

$$H(x,y) = \sum_{k,\ell} H_{k\ell}(x,y)$$

we find (along the same lines as was done in § 7, ex.5)

$$H(x,y) = \exp\left[\sum_{r=1}^{\infty} \frac{x^r}{r} H(x^r, y^r) + \sum_{s=1}^{\infty} \frac{y^s}{2s}\left\{H^2(x^s, y^s) + H(x^{2s}, y^{2s})\right\}\right] \qquad (9)$$

which leads to

$$H(x,y) = 1 + x + y + 2x^2 + 3xy + 2y^2 + 4x^3 + 10x^2y + 10xy^2 + 5y^3 + \ldots$$

c) Pure free star trees . We denote the counting series as $t(x) = \sum_n t_n x^n$.

1) Cayley trees (star is line) . For this case Otter (Ann. of Math. 49 (1948) 583) derived

$$t(x) = T(x) - \frac{1}{2} x \left\{ T^2(x) - T(x^2) \right\}$$

$T(x)$ is the corresponding counting series for rooted trees . Note that in this section both $t(x)$ and $T(x)$ are counted according to the number of stars .

2) Cacti (star is triangle) . Harary and Uhlenbeck (Proc. Nat. Ac. U.S. 39 (1953) 315) showed for this case .

$$t(x) = T(x) - \frac{1}{3} \quad T^3(x) - T(x^3)$$

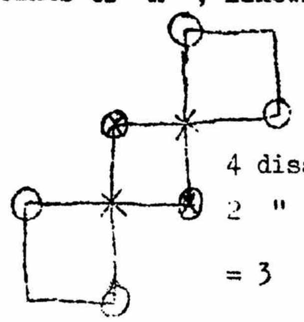
3) Husimi trees with rectangles . Harary and Uhlenbeck derived

$$t(x) = T(x) - x\left\{\frac{3}{8} T^4(x) + \frac{1}{4} T^2(x) T(x^2) - \frac{3}{8} T^2(x^2) - \frac{1}{4} T(x^4)\right\}$$

Of course, in each case $t(x) < T(x)$. The general answer for arbitrary stars has been given by Norman (Michigan Univ. diss. 1954) :

$$t(x) = T(x) - x\, T(x)\, \mathcal{Z}'\left\{\Gamma, T(x)\right\} + x\, \mathcal{Z}\left\{\Gamma, T(x)\right\} \qquad (10)$$

<u>Proof</u> : Consider a definite star tree H of n equal stars . We call two points similar if there exists a covering operation of H which transforms these points into each other . Let $\rho(H)$ be the number of dissimilar points of H , likewise s(H) the total number of dissimilar stars in H and ρ_i the number of dissimilar points in the i-th class of dissimilar stars . We have the



<u>Lemma</u> :
$$\rho(H) - 1 = \sum_{i=1}^{s(H)} (\rho_i - 1) \quad (11)$$

<u>Proof</u> : Consider the endpoint stars of H . They are of various classes . Remove all similar endpoint stars of a definite class, say class 1. Each of them contains ρ_1 dissimilar points . In this way one removes ρ_1 -1 dissimilar points because an endpoint star by definition has only one articulation point, and this articulation point must be one of the dissimilar points and it is not removed by removing the endpoint star . In the remaining tree, one removes the next class of similar endpoint stars, by which one takes away ρ_2-1 dissimilar points , etc . One finally is left with a tree of only one class of stars in which there are now $\rho_{s(H)}$ dissimilar points left . This proves the Lemma .

Consider next the collection of all free pure trees of n stars . For each of them (11) applies . To make them rooted trees, each of the dissimilar points can be choosen as the root . Summing eq. (11) over all the free trees we therefore obtain

$$T_n - t_n = \sum_{H_n} \sum_{i=1}^{s(H_n)} p_i \quad - \sum_{H_n} s(H_n) \equiv A_n - B_n \qquad (12)$$

or for the corresponding counting series ($A(x) = \sum_n A_n x^n$, etc)

$$t(x) = T(x) - A(x) + B(x) \qquad (13)$$

A_n is the total number of dissimilar points in all the free pure trees of n stars , each counted k -fold if it occurs in k dissimilar stars . B_n is the total number of dissimilar stars in this collection of n-starred trees . It is equal to the number of ways of hanging rooted star trees (altogether n-1 stars) at the corners of one bas star, where two configurations are counted as one if they are transformed into each other by a covering operation of the group Γ of the star . We therefore can apply Polya's theorem to find $B(x)$. The figure series is $T(x)$ (rooted star trees !), s= number of points of the star and the group H_s is precisely Γ . The configuration series is therefore $Z\{\Gamma, T(x)\}$ and

$$B(x) = x\, Z\{\Gamma, T(x)\}$$

(the factor x ensures that the basic star is also counted ; one could also add unity to include $B_0 = 1$, but it would be cancelled by a term -1 in (13) resulting from $- A(x)$. We thus see that $B(x)$ of (13) gives rise to the last term on the right-hand side of (10) .

In a similar way ,Norman should that $- A(x)$ leads to the second term on the right-hand side of (10) .

§ 9. CONVERGENCE AND ASYMPTOTIC BEHAVIOUR OF COUNTING SERIES .

We will examplify the underlying problems for the case of Cayley trees for the counting series of which we derived (§ 7, eq.(8) in the case of rooted trees .

$$T(x) = \sum_{n=0}^{\infty} T_n x^n = e^{\sum_{r=1}^{\infty} x^r T(x^r)/r} \qquad (T_0 \equiv 1) \qquad (1)$$

The convergence and the analytic behaviour of T (x) were first investigated by Otter .

a) T(x) converges . Since the coefficients T_n are positive , $T(x^r) < T^r(x)$ for $x > 0$. From this it follows that for $x > 0$, $T(x)$ has as a majorant the function $Y(x)$ which satisfies

$$Y(x) = e^{\sum_{r=1}^{\infty} x^r Y^r(x)/r}$$

Now

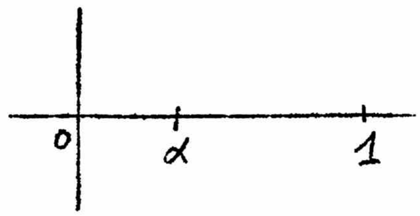
$$Y(x) = e^{-\ln(1-xY)} = \frac{1}{1-xY}$$

or

$$Y(x) = (1 - \sqrt{1-4x})/2x .$$

Hence the convergence radius of $y(x)$ is $\frac{1}{4}$. The convergence radius of T(x) is therefore at least $\frac{1}{4}$. Furthermore , clearly $\alpha < 1$, so $\frac{1}{4} \leq \alpha < 1$.

b) $T(\alpha) = a$ is finite . According to Hadamard's theorem for a series with positive coefficients , the first singular point lies on the positive real axis, it is the point α . In order to prove that $\lim_{x \to \alpha} T(x)$



exists and has a finite value a , we remark that $\overline{t}(x) > \exp\ (x\ T(x))$ (countains only the first term of $\sum$ in (1) for $x > 0$, so

$$\frac{T(x)}{\ln T(x)} < \frac{1}{x}$$

Since t (x) is monotonically increasing , it follows that T(x) bounded for $x \leq \alpha$

c) $\underline{T(\alpha) = \alpha^{-1}}$ Consider the function

$$F(x,y) \equiv e^{xy + \frac{1}{2}x^2 T(x^2) + \dots} - y \qquad (2)$$

For $x < \alpha$ the equation $F(x,y) = 0$ has the unique solution $y = T(x)$ and $F(\alpha, a) = 0$. Around $x = \alpha$, $y = a$ the function $F(x,y)$ is analytic in x and in y (in x since around $x = \alpha < 1$, we have $x^2 < \alpha$, so $T(x^2)$ is analytic , etc) . From this it follows that

$$\left(\frac{\partial F}{\partial y}\right)_{\substack{x=\alpha \\ y=a}} = 0 \qquad (3)$$

Suppose that $(\partial F/\partial y)$ were $\neq 0$. We could then develop $F(x, y)$ around $x = \alpha$, $y = a$ (where F is analytic) and from the theory of implicit functions it then would follow that y exists as an analytic function of x in this region . But this is contradictory to the fact that $x = \alpha$ is a singular point for $y = T(x)$.

From (2) and (3) we find

$$\left(\frac{\partial F}{\partial y}\right)_{\substack{x=\alpha \\ y=a}} = \left\{ x\, e^{xy + \frac{1}{2}x^2 T(x^2) + \dots} - 1 \right\}_{\substack{x=\alpha \\ y=a}} = 0$$

d) Value of α. Inserting $x = \alpha$ in (1), we obtain

$$t(\alpha) = \frac{1}{\alpha} = e^{1 + \frac{1}{2}\alpha^2 T(\alpha^2) + \dots}$$

which can be solved for α by successive approximation. The first approximation would be $\alpha = e^{-1} = 0,368 \dots$ Otter computed α to 7 decimals and found $\alpha = 0,3383219 \dots$

e) α is a branch point of finite order. From (2) it follows that

$$\left(\frac{\partial F}{\partial x}\right)_{\substack{x=\alpha \\ y=a}} = T(\alpha)\left\{ a + \alpha T(\alpha^2) + \alpha^3 T'(\alpha^2) + \dots \right\} \neq 0 \qquad (4)$$

Since $F(x,y)$ is analytic in x and in y around $x = \alpha$, $y = a$, this implies that in this region x is an analytic function of y, and α is a branchpoint of finite order.

$$\left(\frac{dx}{dy}\right)_{\substack{x=\alpha \\ y=a}} = -\left(\frac{\partial F / \partial y}{\partial F / \partial x}\right)_{\substack{x=\alpha \\ y=a}} = 0$$

in view of (3) and (4).

f) α is a branchpoint of order 2. One easily computes $\partial^2 F(\alpha, a) / \partial y^2 = \alpha$. Therefore

$$\left(\frac{d^2x}{dy^2}\right)_{\substack{x=\alpha \\ y=a}} = -\left(\frac{\partial^2 F / \partial y^2}{\partial F / \partial x}\right)_{\substack{x=\alpha \\ y=a}} \neq 0$$

and so $T(x)$ must branch as $\sqrt{\alpha - x}$ at $x = \alpha$ and around this point

$$T(x) = \frac{1}{\alpha} + b\sqrt{\alpha - x} + R(x)(\alpha - x) + \ldots \quad , \qquad (5)$$

where $R(x)$ is regular . To calculate b we take the logarithmic derivative of (1)

$$T'(x) / T(x) = x\,T'(x) + x^3\,T'(x^2) + \ldots \quad + T(x) + x\,T(x^2) + \ldots$$

so that

$$x\,T'(x)\left\{1 - x\,T(x)\right\} = T(x) \sum_{\nu=2}^{\infty} \left\{ x^{\nu}\,T(x^{\nu}) + x^{2\nu+2}\,T'(x^{\nu+1}) \right\}$$

With (5) this gives

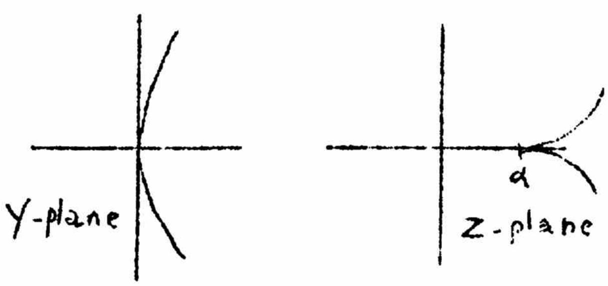
$$\frac{1}{2}\alpha^2 \cdot b^2 = \frac{1}{\alpha}\left[1 + \sum_{\nu=2}^{\infty} \left\{ \alpha^{\nu}\,T(\alpha^{\nu}) + \alpha^{2\nu}\,T'(\alpha^{\nu}) \right\}\right]$$

From this Otter computed $b = 7{,}924780$.

g) Asymptotic behaviour . In order to find the asymptotic behaviour of the T_n we consider the Cauchy integral (around the origin)

$$T_{n-1} = \frac{1}{2\pi i} \oint \frac{T(z)}{z^n}\, dz$$

and apply the method of steepest descent . The discussion is the same as that of the Kramers integral : putting $y = \sqrt{\alpha - z}$ around $z = \alpha$, one sees that in the y-plane $y=0$ is a steep maximum along the real axis ,so the path of steepest descent is the imaginary axis . α is again a turning point for the path of steepest descent in the z - plane . Putting $y = i\eta$ one finds



$$T_{n-1} \simeq \frac{b}{2\sqrt{\pi}} \cdot \frac{\alpha^{-n+\frac{3}{2}}}{n^{3/2}}$$

so that the numbers increase exponentially . Already for n = I0 this formula is quite good : it gives $T_9 \simeq 708$, whereas the exact result is $T_9 = 719$

h) Free Cayley trees . As a special case of the Norman formula , we have for the counting series (see § 8, c 1)

$$t(x) = T(x) - \frac{1}{2}\, x \left\{ T^2(x) - T(x^2) \right\} \qquad (6)$$

So t (x) has the same radins of convergence α as T(x) . The behaviour around $x = \alpha$ is sligtly different . Inserting (5) into (6) one sees that the coefficient of $\sqrt{\alpha - x}$ cancels and

$$t(x) = t(\alpha) - D(\alpha - x)^{3/2} + \dots \qquad (7)$$

Again , α is a branchpoint of the order 2 , but the behaviour of t (x) is different . For D one finds $\frac{1}{3}\ \alpha^2\ b^3$ and for the asymptotic behaviour

$$t_{n-1} \simeq \frac{3D}{4\sqrt{\pi}} \cdot \frac{\alpha^{-n+\frac{5}{2}}}{n^{5/2}}$$

i) Generalization . The above treatment can be generalized to include such cases as cacti and pure Husimi trees . The counting numbers then rise faster and α is smaller . Ford (diss. I954; Michigan) showed, that the general behaviour remains the same for arbitrary mixed Husimi trees (counted acoording to the number of points) . Even for this case the behaviour of the counting series is as $\sqrt{\alpha - x}$ for rooted trees and as $(\alpha - x)^{3/2}$ for free trees . And even for all mixed star trees(counted again according to the number of points) this result is found with the restriction that the constituting stars consists of a finite and fixed number of linearly independent cycles .

§ 10 . THE POSSIBLE CONNECTION WITH THE CONDENSATION PROBLEM .

In answering the question of the connection between graph theory and the condensation problem, we recall first the Mayer equations (§5) , in which the cluster integrals

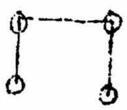
$$b_\ell (T) \; \frac{1}{\ell ! V} \int \cdots \int U_\ell (\vec{r}_1 \ldots \vec{r}_\ell) \; d\vec{r}_1 \ldots d\vec{r}_\ell \qquad (1)$$

occured . The cluster function U_ℓ was defined as the sum of all products of functions f_{ij} represented by connected graphs of ℓ points and therefore U_ℓ is symmetric in the $\vec{r}_1 \ldots , \vec{r}_\ell$. This is the first point where graph theory comes in .

Furthermore , in Kahn's treatment of the condensation problem the necessary conditions for the behaviour of the series $\chi (z) = \sum_1^N b_\ell z^\ell$ (occuring in the second Mayer equation) were given in order that condensation should occur . As a matter of fact, we saw that the generating functions (the counting series) investigated in the preceding section , precisely satisfy these conditions . This suggests a connection with the theory of graphs .

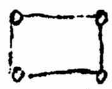
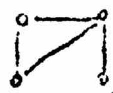
Let us first investigate the cluster integrals . We then have to consider all connected graphs of ℓ points and we order them first according to their number of lines . Let this number be k . With given ℓ then :
$\ell - 1 \leq k \leq \frac{1}{2} \ell (\ell - 1)$. With $k = \ell - 1$, the graph contains no cycles

and is a Cayley tree . For $k = \ell$, there is one cycle in the graph , which now is a mixed Husimi tree with 1 cycle (polygon) . Going on in this way , we see that if the graphs are ordered according to increasing k , they are



$k = \ell - 1$

at the same time arranged ccording to the number of cycles , which runs from

 ,  $k = \ell$

0 (for k = -1) up to $\frac{1}{2}(\ell -1)(\ell -2)$ (for $k = \frac{1}{2}\ell(\ell -1) - 1$)

With given ℓ and k , we can further distinguish the different types of such graphs . Let $\gamma(\ell, k)$ be the number of topologically different connected graphs of ℓ points and k lines . For $\gamma(\ell, k)$ a functional relation is known .

Consider finally a definite graph i out of the $\gamma(\ell, k)$ different ones . The corresponding contribution to b_ℓ contains $\ell! / s_i(\ell, k)$ equal terms , where $s_i(\ell, k)$ is the symmetry number of the connected graph i with ℓ points and k lines ($\equiv$ the order of the group of that graph) , since there are ℓ ! permutations of the points and $s_i(\ell, k)$ covering operations of that graph . So, we can rewrite (1) as

$$b_\ell(T) = \frac{1}{\ell! V} \sum_{k=-1}^{\frac{1}{2}\ell(\ell-1)} \sum_{i=1}^{\gamma(\ell,k)} \frac{\ell!}{s_i(\ell, k)} J_i(\ell, k) \qquad (2)$$

An extensive discussion of this cluster integrals and the virial coefficients , to which they give rise , is given by Riddell and Uhlenbeck , J.Chem.Phys. 21 (1953) 2056 .

Consider first the coefficient $c_i(\ell,k) = \ell!/s_i(\ell,k)$, that is the number of connected graphs with ℓ <u>individualized</u> points and k lines of topological class i . Then

$$c(\ell,k) = \sum_{i=1}^{\gamma(\ell,k)} c_i(\ell,k) \qquad (3)$$

is the <u>total</u> number of connected graphs with ℓ individualized points and k lines . This number can be found . We introduce the series

$$N(x,y) = \sum_{\ell=1}^{\infty} \sum_{k=0}^{\frac{1}{2}\ell(\ell-1)} \frac{x^{\ell} y^k}{\ell!} \binom{\frac{1}{2}\ell(\ell-1)}{k} \qquad (4)$$

which is the counting series for all graphs (connected and disconnected) with ℓ individualized points and k lines , since the binomial coefficient clearly gives the number of possible ways to take k lines out of $\frac{1}{2}\ell(\ell-1)$, which is the maximum number of lines for ℓ points . Analogously , we introduce

$$C(x,y) = \sum_{\ell=1}^{\infty} \sum_{k=\ell-1}^{\frac{1}{2}\ell(\ell-1)} c(\ell,k) \frac{x^{\ell} y^k}{\ell!} \qquad (5)$$

For these two series the relation

$$C(x,y) = \log\left\{1 + N(x,y)\right\} \qquad (6)$$

can be proved (cf. the above mentioned paper ; a simpler proof has been given by Ford in his dissertation) . The numbers $c(\ell,k)$ are therefore determined by (4) ,(5) and (6) and one finds

$$c(\ell,k) = \binom{\frac{1}{2}\ell(\ell-1)}{k} - \ell\binom{\frac{1}{2}(\ell-1)(\ell-2)}{k} + \text{correction terms} .$$

For large ℓ , and k not near to its limits $\ell - 1$ and $\frac{1}{2}\ell(\ell-1)$ the second term is very small with respect to the first one , which means that in that case the majority of the graphs are connected , a plausible result .

In order to find an asymptotic expression for $\gamma(\ell,k)$ we consider the number $\pi(\ell,k)$ of topological different graphs of ℓ points and K lines, connected or disconnected . It has been determined by Polya in the form of the counting polynomial

$$F(y) = \sum_{k=0}^{\frac{1}{2}\ell(\ell-1)} \pi(\ell,k)\, y^k \qquad (7)$$

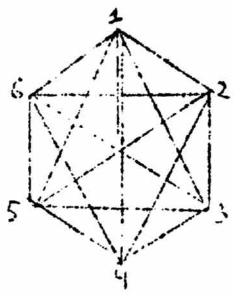
by means of the Polya theorem . The derivation is as follows .

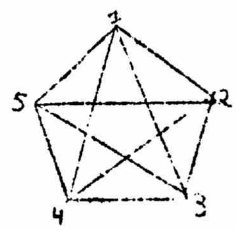
Since we consider free graphs , the ℓ points are equivalent so their group is the full symmetric group G_ℓ . We can say that our figure collection consists of two objects : a line and no line . The figure counting series is therefore 1 + y . However , we do not hang these figures on the ℓ points. Now every permutation of the ℓ points induces a permutation of the $\frac{1}{2}\ell(\ell-1)$ pairs of points . These permutations therefore form a permutation group of degree (number of objects) $\frac{1}{2}\ell(\ell-1)$. We will call it the <u>pair group</u> $\mathcal{H}_\ell$. According to Polya's theorem then

$$F_\ell(y) = \mathfrak{Z}\{\mathcal{H}_\ell, 1+y\} \qquad (8)$$

To find the cycle index, one has to determine what permutation of type $\{i_1, i_2, \ldots, i_{\frac{1}{2}\ell(\ell-1)}\}$ (i_1 one-cycles , i_2 two-cycles , etc) corresponds to a permutation of type $\{j_1, j_2, \ldots, j_\ell\}$ in G_ℓ . One has to distinguish :

<u>a</u> . Points , occuring in one cycle , say of length ν . Arrange



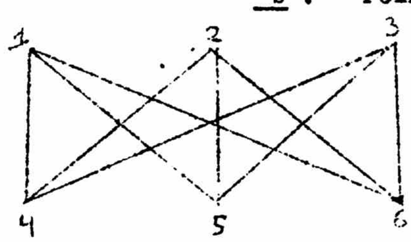


the ν points on a polygon and number them . Now under a cyclic permutation $(1,2,\ldots,\nu)$ the point pair 1-2 goes into the pair 2 - 3 , etc, which percisely gives rise to a point pair cycle of length ν . Further, pair 1-3 goes into 2-4 , etc, which gives rise to another point-pair cycle of length ν . So one can go on .Clearly one gets :

- for ν odd : $\frac{1}{2}(\nu-1)$ cycles of length ν in the pair group ,
- " ν even: $\frac{1}{2}(\nu-1)$ " " " " " "

and one cycle (consisting of the main diagonals) of length $\frac{1}{2}\nu$.

<u>b</u> . Points occuring in different cycles .



If the cycles are all of equal length (say ν) then they clearly induce ν cycles of length ν in the pair group . If the cycles are of unequal length (say ν_1,ν_2) then their permutations will induce cycles of length $m(\nu_1,\nu_2)$ = least common multiplier of ν_1, ν_2 and the number of such cycles will be $d(\nu_1,\nu_2)$ = largest common divisor of ν_1, ν_2. Remember $m(\nu_1,\nu_2)\, d(\nu_1,\nu_2) = \nu_1\nu_2$

Since there are $\ell\,!\,/\prod k^{j_k} j_k\,!$ permutations of type $(j_1,j_2\ldots j_\ell)$ in G_ℓ one gets for the cycle index of $\mathcal{H}_\ell$:

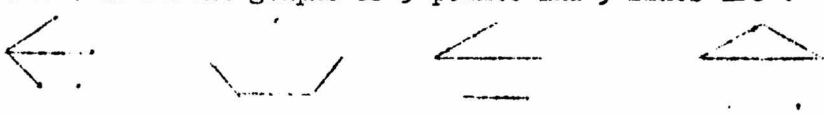
$$\zeta(\mathcal{H}_\ell) = \frac{1}{\ell!} \sum_{(j_k)} \frac{\ell!}{\prod_{k=1}^{\ell} j_k!\, k^{j_k}} \prod_{k\ \mathrm{odd}} \beta_k^{\frac{1}{2} j_k (k-1)} \prod_{k\ \mathrm{even}} \beta_k^{\frac{1}{2} j_k (k-2)} \beta_{\frac{1}{2}k}^{j_k} \times$$

$$\times \prod_k \beta_k^{\frac{1}{2} j_k (j_k - 1) k} \prod_{k<\ell} \beta_{m(k,\ell)}^{j_k j_\ell d(k,\ell)} \qquad (9)$$

$F_\ell(y)$ follows from (8) and (9) . For $\ell = 5$, one finds , e.g.,

$F_5(y) = 1 + y + 2y^2 + 4y^3 + 6y^4 + 6y^5 + 6y^6 + 4y^7 + 2y^8 + y^9 + y^{10}$

The 4 different graphs of 5 points and 3 lines are :



From the explicit expression for $F_\ell(y)$ one can also derive the asymptotic behavior of $\pi(\ell,k)$. For large ℓ , and k not near to the end points of its domain $(0 \leftrightarrow \frac{1}{2}\ (\ \ -1))$ one finds :

$$\pi(\ell,k) \cong \frac{1}{\ell!} \binom{\frac{1}{2}\ell(\ell-1)}{k} \qquad (10)$$

which means that the majority of the graphs have no symmetry (the binomial coefficient gives the number of connected + disconnected graphs with ℓ individualized points and k lines , the factor $1/\ell\,!$ removes the distinguishability of the points) .

We see therefore , that for large ℓ and " average " values of k the majority of the graphs are connected and have no symmetry , so that

$$\gamma(\ell,k) \cong \frac{1}{\ell!}\, c(\ell,k) \cong \pi(\ell,k) \qquad (11)$$

Returning to eq.(2), let us suppose that $J_i(\ell, k)/N$ is approximately constant (independent of k and ℓ) . The behaviour of b_ℓ would then be

$$b_\ell \sim \frac{J}{\ell!} \sum_{k=\ell-1} C(\ell, k) \cong J \sum_{k=0}^{\frac{1}{2}\ell(\ell-1)} \frac{1}{\ell!} \binom{\frac{1}{2}\ell(\ell-1)}{k} = \frac{J}{\ell!} \, 2^{\frac{1}{2}\ell(\ell-1)}$$

and

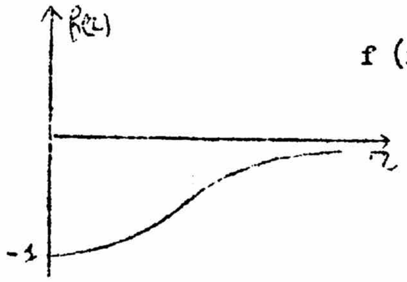
$$\chi(z) \sim \sum_\ell \frac{1}{\ell!} \, 2^{\frac{1}{2}\ell(\ell-1)} \, z^\ell$$

therefore $\chi(z)$ would always be divergent for $z > 0$. So we have to know something about the dependence of $J_i(\ell, k)$ on k . The integral should decrease for larger values of k in order that $\chi(z)$ be convergent . This will actually be the case since adding a line between two points means that we introduce a factor in the integrand which requires the two points to be less than a certain distance apart . Thus with increasing k the integrand will differ from zero over a smaller region of the 3ℓ- dimensional phase space .

§ II . THE INTEGRAL PROBLEM . The integrals $J_i(\ell, k)$ should cause the convergence of $\chi(z)$ by suppressing a large number of configurations . To study the behaviour of the integral ,we have to introduce a special type of intermolecular potential, or rather a special choice for the function f (r). For this purpose, it is useful to consider :

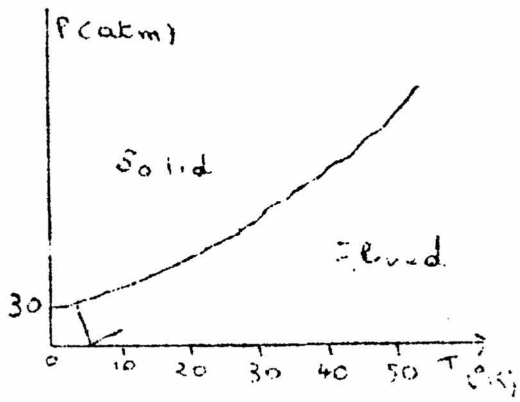
A. The Gaussian model . In § 5 , we gave the general behaviour of f (r) for short-range repulsion + long-range attraction (e.g. the Lennard-Jones potential) . If we would take $f(r) = A\,e^{-\alpha r^2}$ with $A > 0$

(corresponding to attractive forces only) we would suppress the negative part of $f(r)$ and clearly we could not expect $\chi(z)$ to be convergent . To include the repulsive part of the intermolecular force , we could add a term $-(1+A)\, e^{-\beta r^2}$ (remember that $f(o) = -1$) . However, it is of interest to consider only one Gaussian

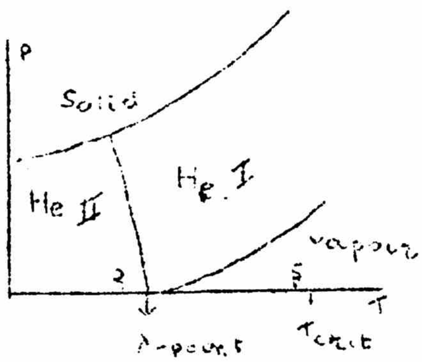


$$f(r) = -e^{-\alpha r^2}$$

corresponding to repulsive forces only . The motivation of this choice is the striking and paradoxical result of Kirkwood and co-workers, who showed from the behaviour of the phase integral and on the basis of the so-called " superposition approximation " that a gas of molecules with only repulsive forces (e.g. elastic spheres) shows a phase transition : at high pressure the system is split up into two phases with different density and entropy , a solid phase (arrangements of ordered molecules) surrounded by a liquid phase (series of articles from Kirkwood and Monroe, J. Chem. Phys. 9 (1941) 514 up to Kirkwood , Maun and Alder , J.Chem. Phys. 18 (1950) 1040) Although perhaps hard to believe , one must admit that there is no rigorous argument which disproves the existence of such a " condensation " . In addition there is the suggestion that perhaps the Kirkwood transition has something to do with the solidification of helium , which is known to occur at tempera-tures many times the critical temperature (5 º k) if the pressure is high enough .

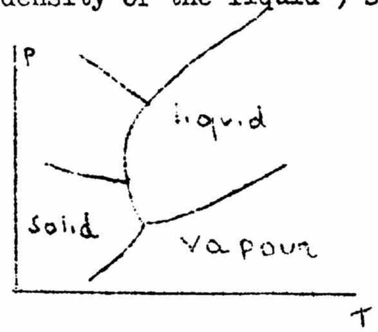


This can hardly be ascribed to the weak attractive forces between the helium atoms which are of the order of $k\,T_{crit.}$ The solidification of a gas is perhaps a general consequence of the sharp repulsive forces. (For helium the intermolecular force is very well knaown ; as for all chemically non-active molecules it consists of a Van der Waals attraction on which a sharp repulsive core is superimposed) .



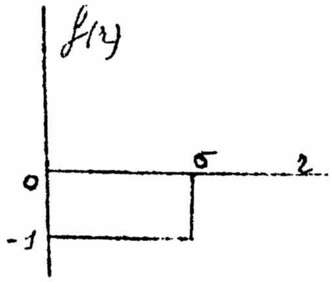
PHASE DIAGRAM OF HELIUM

It might well be a general fact of nature that any assembly of molecules can at any temperature be brought into the solid state if one raisesthe pressure high enough . Even the phase diagram of water (where the density of the solid state is less than the density of the liquid) shows this behaviour .



PHASE DIAGRAM OF WATER.

If this is indeed a general fact of nature the explanation in terms of the intermolecular forces should be found in some general feature of these forces . Such a feature is the presence of a sharp repulsive core .



With only repulsive forces one would think of elastic spheres of diameter σ . However, the cluster integrals are hard to calculate for this case and the virial coefficients have only been calculated up to the 4 th one . Since the kirkwood transition will according to the above discussion be independent of the special form of the repulsive potential, we will consider the Gaussian model (1) for the function f( ) . We then have to consider for a connected graph of type i

$$\frac{1}{V} \gamma_i(\ell, k) = \frac{A^k}{V} \int_V \cdots \int e^{-\sum_{n,m}^{\ell} |\vec{r}_n - \vec{r}_m|^2} d\vec{r}_1 \ldots d\vec{r}_\ell \qquad (2)$$

with $A = -1$, where the sum is over those lines n, m which occur in the graph . This sum can be written as a quadratic form

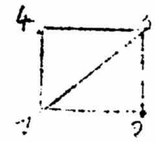
$$\sum_{n,m} |\vec{r}_n - \vec{r}_m|^2 = \sum_{n=1}^{\ell} \sum_{m=1}^{\ell} \Delta_{nm} \; r_n \, r_m \qquad (3)$$

where Δ_{nm} is given by

$$\Delta_{nm} \begin{cases} = -1 & \text{if the line } (n,m) \text{ occurs} \\ = 0 & \text{" " does not occur} \\ = \text{number of lines attached to the point} & (= \text{branching number if } n = m \end{cases}$$

We then introduce the matrix with elements Δ_{nm} , the graph matrix for this connected graph . Δ_{nm} clearly is symmetric . The diagonal elements are the branching numbers of the ℓ points , the off-diagonal elements are either 0 or -1 . As an example , we give the graph matrix for one special graph of 4 points :

$$\begin{pmatrix} 3 & -1 & -1 & -1 \\ -1 & 2 & -1 & 0 \\ -1 & -1 & 3 & -1 \\ -1 & 0 & -1 & 2 \end{pmatrix}$$



B . Properties of the graph matrix .

a. The determinant $\|\Delta\|$ is zero . This is immediately clear from the definition of Δ_{nm} since by adding all columns to the first one the elements of the first column become (branching number - branching number) = 0 .

b. The minors of rank $\ell - 1$ are all equal (in absolute value). (For disconnected graphs the complexity is zero) . Their value is called the graph complexity $d_i(\ell, k)$ We will show this for the ℓ principal minors (obtained by striking out the n-th row and column) . If we take the position of the first point as the origin , $r_1 = 0$ and the first row and column of Δ do not occur in (3) , the quadratic form thus being determined by the (1,1) - minor . The integration over r_1 then leads to a factor V and one gets

$$\frac{1}{V} \mathcal{J}_i(\ell,k) = A^k \int_V \dots \int e^{-\alpha \sum_{n=2}^{\ell} \sum_{m=2}^{\ell} \Delta_{nm} r_n r_m} d\vec{r}_2 \dots d\vec{r}_\ell =$$

$$= A^k \left(\frac{\pi}{\alpha}\right)^{3/2(\ell-1)} \left\{ d_i(\ell,k) \right\}^{-3/2}$$

where $d_i(\ell, k)$ is the minor obtained by striking out the first row and column in Δ. Clearly, the same value is obtained by striking out the n-th row and column, since the result cannot depend on the choice of the origin. The ℓ principal minors have therefore the same absolute value.

With $(r/\alpha)^{3/2} = 2b$ (the first virial coefficient, following from the Gaussian model, then becomes equal to b) the expression for the cluster integral becomes

$$b_\ell = (2b)^{\ell-1} \sum_{k=\ell-1}^{\frac{1}{2}\ell(\ell-1)} A^k \sum_{i=1}^{\gamma(\ell,k)} \frac{1}{s_i(\ell,k)} \frac{1}{\left\{d_i(\ell,k)\right\}^{3/2}} \tag{4}$$

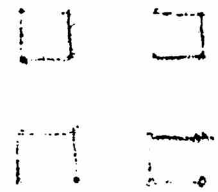
c. For connected graphs with articulation points (star trees) the complexity is the product of the complexities of the constituing stars :

$$d_i(\ell, k) = \prod_{\text{all stars}} d^{\text{star}}$$

This is again obvious from the integral representation.

d. The complexity of a star is equal to the number of different Cayley trees of ℓ individualized points that can be formed from the ℓ points and k lines, occuring in the star. This theorem was already known to Kirchhoff (collected Works), who derived it in connection with the theory of electric circuits. The general proof is given by Ford (diss.1954, Univ. of Michigan). The idea of the proof is to write out the complexity, then each term corresponds to one Cayley tree. We give an example :

$$\Delta = \begin{pmatrix} 2 & -1 & 0 & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ -1 & 0 & -1 & 2 \end{pmatrix} \quad d = 4$$



e. The maximum value of $d_i(\ell,k)$ for a given value of ℓ is $\ell^{\ell-2}$ and is obtained for a complete graph (all pairs connected, $k = \frac{1}{2}\ell(\ell-1)$) . For a complete graph $\Delta_{nm} = \ell-1$ if $n = m$ and $= -1$ for $n \neq m$. The matrix Δ has ℓ rows and columns and $\|\Delta\| = 0$ whereas forming the principal minor ,we get a cyclic determinant, the value of which is $\ell^{\ell-2} = d$. Using

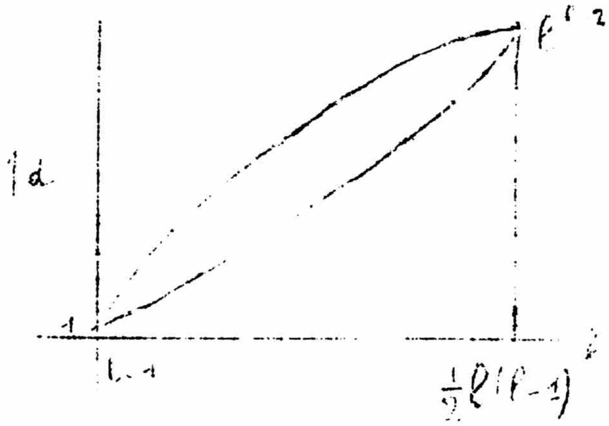
$$\begin{pmatrix} \ell-1 & -1 & -1 & \dots & -1 \\ -1 & \ell-1 & -1 & \dots & -1 \\ -1 & -1 & \ell-1 & \dots & -1 \\ \dots & \dots & \dots & \dots & \dots \\ -1 & -1 & -1 & \dots & \ell-1 \end{pmatrix}$$

the Kirchhoff theorem one can therefore conclude that there are $\ell^{\ell-2}$ Cayley trees with ℓ individualized points , which is a classical result .

f.
$$\sum_{i=1}^{\gamma(\ell,k)} c_i(\ell,k)\, d_i(\ell,k) = \ell^{\ell-2} \binom{\frac{1}{2}(\ell-1)(\ell-2)}{k-\ell+1} \qquad (5)$$

The proof of this theorem (due to Ford) is simple . The left-hand side is the total number of all possible Cayley trees of ℓ individualized points and k lines (including disconnected trees since then $d_i = 0$) This number can also be found by starting with a complete graph of ℓ points, $\frac{1}{2}\ell(\ell-1)$ lines . From this graph, we can form $\ell^{\ell-2}$ different Cayley trees of ℓ points, $\ell-1$ lines . Consider one of them . From the remaining $\frac{1}{2}(\ell-1)(\ell-2)$ lines, discard $k-\ell+1$ lines . This will lead to a connected graph which contains the chosen Cayley tree and any way of discarding leads to a different graph . Therefore the chosen Cayley tree will be contained in $\binom{\frac{1}{2}(\ell-1)(\ell-2)}{k-\ell+1}$ different graphs . This leads to the number on the right- hand side of (5) .

C. The integral problem . At the end of § 10 , we saw that the integral $\mathcal{J}_i(\ell,k)$ is decreasing if k approaches the maximum of its domain. From (4) we see that for the Gaussian model one needs to know something about the distribution of the values of (Cayley tree) and that $d = \ell^{\ell-2}$ for $k = \frac{1}{2}\ell(\ell-1)$ (complete graph) . For values of k between these limits there will be a certain range of d_i- values . Suppose we can introduce a distribution function $n(\ell, k, d)$ for the values of d .



We know :

$$\sum_d n(\ell, k, d) = C(\ell, k)$$ = total number of connected graphs of ℓ individualized points and k lines , asymptotically $\cong \binom{\frac{1}{2}\ell(\ell-1)}{k}$,

$$\sum_d d\, n(\ell, k, d) = \ell^{\ell-2}\binom{\frac{1}{2}(\ell-1)(\ell-2)}{k-\ell+1}$$ according to (5)

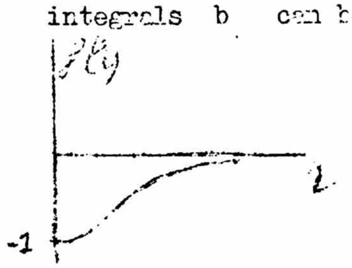
So, we know the zeroth and first moments of this distribution function and if the distribution were a Gaussian one , the knowledge of the second moment (or the spread) would be sufficient to determine the complete distribution function .

The Gaussian character has been investigated by tests (diss.Ford) . For $\ell = 7$ there are about 40 values of d for k near the middle of its domain (remember that for increasing ℓ the overwhelming majority of all graphs have k in the middle) and the histogram of these values showed indeed a Gaussian behaviour .

But a rigorous proof of the Gaussian character is probably a very fundamental problem .

§ 12 . RESULTS . The final answers are meagre .

I - For the Gaussian model of repulsive forces the first 7 cluster integrals b can be calculated . For the virial expansion of the equation of state .

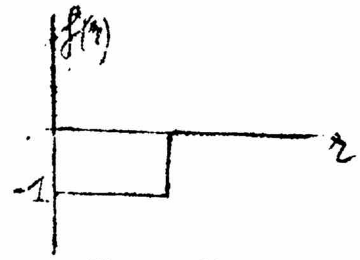


$$\frac{p\,v}{k\,T} = 1 + \frac{B_2}{v} + \frac{B_3}{v} + \ldots\ldots$$

one finds

$$\frac{p\,v}{k\,T} = 1 + \frac{b}{v} + 0.257\,\frac{b^2}{v^2} - 0.125\,\frac{b^3}{v^3} + 0.013\,\frac{b^4}{v^4} + 0.038\,\frac{b^5}{v^5} - 0.030\,\frac{b^6}{v^6} + \ldots$$

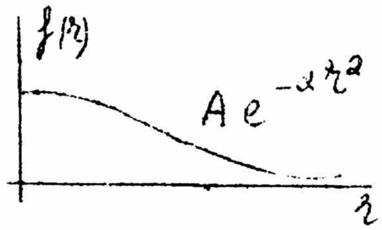
As far as calculated, the series of cluster integrals b_ℓ is alternating (both for the Gaussian model and for elastic spheres) .



$$\frac{pv}{kT} = 1 + \frac{b}{v} + 0.625\,\frac{b^2}{v^2} + 0.287\,\frac{b^3}{v^3} + 0.116\,\frac{b^4}{v^4} + \ \ldots$$

The coefficient B_3 was already given by Boltzmann, B_4 by van Laar and checked by Nÿboer and Van Hove (Phys.Rev. 85 (1952) 777) . B_5 was given by Rosenbluth (J.Chem. Phys. 22 (1954) 884) .

II - One can also consider the Gaussian model for purely attractive forces . With $A > 0$, the integral $\mathcal{J}_i\,(\ell, k)$ and also b_ℓ are always positive.

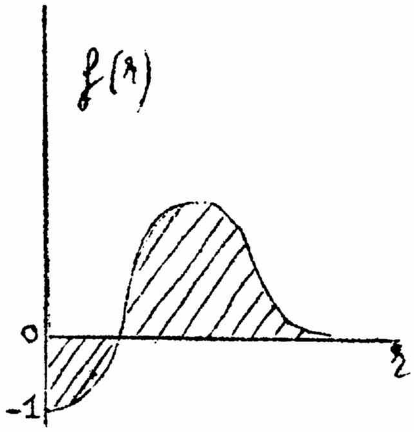


With increasing k (increasing complexity of the graph) $\mathcal{J}_i\,(\ell, k)$ decreases . Taking the maximum value $\ell^{\ell-2}$ for d in (4) one then can find lower limits for the b_ℓ and it turns out that the series $\chi\,(z) = \sum_\ell b_\ell z^\ell$ is always divergent . So the integrals $\mathcal{J}_i\,(\ell, k)$ do not decrease fast enough to overcome the increase in the total number of connected graphs with ℓ points .

With purely attractive forces the free energy Ψ would always be proportional to the number of pairs of molecules (so $\sim N^2$) instead of proportional to N .

Van Hove (Physica 15 (1949) 951) has shown that the sharp repulsive core is necessary for the proportionality of all thermodynamic quantities with N and therefore for the existence of an equation of state . The divergence of $\chi\,(z)$ for the attractive Gaussian model is in agreement with Van Hove's result .

III - For an attractive intermolecular force with a repulsive core



$f(r)$ is of the form given in the figure . At low temperature the area under the positive part is large with respect to the area under the negative part . The integrals for k in the beginning of its domain will then certainly be positive (graphs which are Cayley trees, Husimi trees with one cycle , with 2 cycles etc) . For larger values of k the contributions of smaller values of r become more and more important (the graph is " clustered up " , new factors f_{nm} require that the molecules are less than a certain distance apart) . This will allow changes in sign of the $\mathcal{J}_i(\ell, k)$, and for higher values of k they will be alternating in sign . With many cycles , it seems therefore likely that the contributions of all the graphs for the largest values of k will roughly cancel each other . This would lead to a certain " cut off" . In his thesis , Ford showed that for a reasonable cut off the series $\chi(\zeta)$ has exactly the Kahn properties for condensation as a consequence of the theorem mentioned in § 9 , i on the counting series of mixed star trees . But, of course, this should not be considered as a rigorous proof for the occurrence of condensation.

IV - With <u>purely repulsive forces</u> there remains the Kirkwood conjecture . In the Gaussian model $A = -1$, so the integrals $\mathcal{J}_i(\ell, k)$ are alternating in sign with increasing k . Because of the strong cancellation it is hard to make asymptotic estimates for the b_ℓ . Ford derived a number of inequalities and estimates . The obtained estimated values of b_ℓ gave rise to series $\chi(z)$ which had the first singular point on the negative real axis , which would contradict the possibility of a Kirkwood condensation . But a definite conclusion would only be possible with estimates of b_ℓ, more exact than those given by Ford .

NOTES ON THE THEORY OF PHASE TRANSITIONS

by

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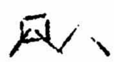
University of Michigan .

E R R A T A

Page	Line	Read :
2	1	$N,V \to \infty$ ... N / V
	3	$\lim\limits_{N,V \to \infty} \Psi$
5	1	λ_1 and therefore ...
	2 from below	$\int_0^{\pi/2}$
7	13	... like (1) see ...
8	5	add : $(\lvert z \rvert < 1)$
	1 from below	... given by
		$g'(z_0,a) = a\chi'(z_0)-z_0 = 0$ or $z_0\chi'(z_0) = \frac{1}{a}$
9	7	$-\Psi / kT = N\, g\,(z_0,a) - \frac{1}{2} \log N + \ldots$
	3 from below	$a_c^{-1} = \chi'(1) = \ldots$
10	2	Physica 4
13	5 from below	9 rooted Cayley trees .
		figure :  instead of 

Page	Line	Read
14	1	Cayley trees with arbitrary polygons .
15	1o	$N = 4$ (2^6 terms)
	3 from below	$\sim V^4 \quad V^3 \ldots$
16	2	... in m_1 single ...
	3	m_ℓ sets of ℓ molecules .
17	3	$b_1 \equiv 1$
	10 from below	$(V\, 2\,!\, b_2)^2$
	7 from below	$(V\, 3\,!\, b_3)\,(V\, 1\,!\, b_1)$
18	5	for one set of the m_ℓ
19	5	$- k\, T\, V \sum_\ell b_\ell z^\ell$
24	7	$A_{\ldots}$
	1 from below	$\equiv \mathcal{J} \left\{ H_s, f(x,y) \right\}$
26	2	$\sum_{n=0}^{\infty} A_n x^n$
28	3	k^{j_k}
30	6 from below	$T(x) = \sum_{n=0}^{\infty} T_n x^n$
33	7	and there are k points , $H_s = G_k$
	9	(only ℓ main triangles)
34	1	$\frac{y^s}{2\, s}$

Page	Line	Read
34	6 from below	$t(x) = T(x) - \frac{1}{3} x \left\{ T^3(x) - T(x^3) \right\}$
35	7,8	$p_1 = 3$, $p_2 = 2$
36	1 from below	Norman showed
37	6 " "	The convergence radius α of
38	1 " "	add :
		so $\alpha T(\alpha) = 1$ or $a = T(\alpha) = \frac{1}{\alpha}$
39	2	$T(\alpha) = \frac{1}{\alpha} =$
43	6 from below	of the ℓ points
	4 " "	$\sum_{k=\ell-1}^{\frac{1}{2}\ell(\ell-1)}$
44	7 from below	$x^\ell y^k$
45	8	$F_\ell(y)$
	9/8 from below	.. on the ℓ points, but on the $\frac{1}{2}\ell(\ell-1)$ pairs of points . Now ...
	5 " "	pair group $\mathcal{H}_\ell$
46	4	(1,2, ... , u)
	10	for u even : $\frac{1}{2}(u-2)$ cycles
47	1	$S^\ell \frac{\ell!}{(j_k) \prod_{k=1}^{\ell} j_k! k^{j_k}}$

Page	Line	Read
47	9 from below	$\left(0 < \cdots \leq \frac{1}{2}\ell\,(\ell - 1)\right)$
48	4	$\sum_{k=\ell-1}^{\frac{1}{2}\ell(\ell-1)}$
52	1 from below	$A^{k}\left(\frac{\pi}{\alpha}\right)^{3(\ell-1)/2}$
53	5	With $(\pi/\alpha)^{3/2} = 2b$
55	7	about the distribution of the values of $d_i(\ell,k)$ for given ℓ and k. We know that $d = 1$ for $k = \ell-1$ (Cayley tree) ...
57	1	For comparison we give the virial expansion for elastic spheres :