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Submitted on 1 Jan 1983

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Mean-field theory of statistical assemblies of sterically interacting lines

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(Reçu le 30 novembre 1981, révisé le 31 août 1982, accepté le 16 septembre 1982)

Résumé. — On examine des ensembles statistiques de lignes sur des réseaux cubiques simples. Commençant par un gaz à boucles de diffusion on ajoute l’interaction stérique et des chaînes. L’interaction est traitée comme un champ moyen, ce qui n’est strictement valable que pour \( d > 4 \). Des transitions de phase sont caractérisées par l’apparition de lignes infinies. Ce formalisme peut être appliqué aux polymères thermiquement équilibrés, aux modèles de défauts de transitions de phase, et aux développements à haute température du modèle de spin. On retrouve les théories classiques de transitions de phase avec approximations Gaussiennes, en particulier leurs exposants critiques.

Abstract. — Statistical assemblies of lines on simple cubic lattices are considered. Beginning with a gas of diffusion loops we add steric interaction and chains. The interaction is treated by a mean-field ansatz strictly valid only for \( d > 4 \). Phase transitions are characterized by the appearance of infinite lines. The formalism can be applied to thermally equilibrated polymers, defect models of phase transitions, and to the high-temperature expansions of the \( n \)-vector model. The classical theories of phase transitions including the Gaussian approximations are recovered, in particular their critical exponents.

1. Introduction. — There are several kinds of statistical assemblies of physical lines. Dissolved polymers and polymer melts represent one class of them. The whole range from the single polymer via semidilute solutions to polymer melts has been studied comprehensively, as documented by the books of Flory [1] and de Gennes [2]. Typically, polymer chains or loops are regarded as random walks perturbing themselves and each other through some local repulsive interaction. Nearly all this research, experimental and theoretical, has been concerned with polymers of fixed length. However, the very useful formal analogy between polymer chains and high-temperature expansions (HTE’s) of the ferromagnetic \( n \)-vector model for \( n = 0 \) inevitably implies a distribution of chain lengths starting from zero length [2, 3].

The statistical mechanics of thermally equilibrated polymers which break and recombine from time to time has been very little explored. They are characterized by fluctuations in length and should form (open) chains and (closed) loops side by side. An analogy between solutions of thermally equilibrated polymers and the HTE graphs of the isotropic \( n \)-vector model was pointed out by Helfrich and Müller [4]. The spin dimensionality \( n > 0 \) becomes the loop multiplicity, i.e. the number of times each loop has to be counted (e.g. two times in the case of a polar polymer). The repulsive interaction of these lines on a lattice is steric in the sense that it is athermal and local. It may be called « soft » as it does not rule out intersections and multiple occupancy of bonds, in contrast to the « hard » excluded-volume effect obtained for \( n = 0 \). A large breaking energy of the polymers corresponds, in the ferromagnetic analogue, to a weak magnetic field.

More recently, Wheeler and Pfeuty [5] also used the \( n \)-vector model, i.e., HTE graphs on a lattice, in order to explain the equilibrium polymerization of liquid sulfur. They first modelled their system on the case \( n = 0 \), which necessarily eliminates loops. Subsequently Rys and Helfrich [6] as well as Pfeuty and Wheeler [7] discovered independently that the HTE graphs of an \( m \)-anisotropic \( n \)-vector model on a lattice in the limit \( n = 0 \) admit loops of multiplicity \( m \) while preserving the rigorous excluded-volume effect of the isotropic \( n \)-vector model in this limit [8]. There is speculation, but as yet no proof, that the critical exponents of these line assemblies are those of the isotropic \( n \)-vector model with spin dimensionality \( m \) rather than \( n \).

Other physical lines whose conformations are likely to resemble random walks are thermally excited defect-lines in an ordered medium. Theoretical treatments of ferromagnetic phase transitions are largely...
based on the Ginzburg-Landau Hamiltonian which is a continuum description. However, walls and lines in thermal equilibrium have been frequently considered in connection with the Ising model in 3d and 2d space, respectively [9, 10]. Thermalized dislocations have been employed in qualitative theories of ordinary melting in attempts to explain why it is a strongly first-order phase transition [11, 12]. Many years ago Feynman [13] suggested that the superfluid-fluid transition of $^4$He may be caused by the unlimited growth of vortex lines. Lately the same idea was applied to the $xy$ model in 3d space by Villain [14] and Holz [15] and very recently to type-II superconductors by Dasgupta and Halperin [16]. In the last three cases one is dealing with second-order phase transitions.

Their order parameters are two-dimensional ($n = 2$) so that the topologically stable defects are lines of multiplicity two [17]. Similar transitions were discovered in the last dozen years in the field of liquid crystals. If due to defects, they have to be brought about by dislocations or disclinations, depending on whether the ordering in question is translational or rotational. Examples of the first kind are the smectic-A to nematic transition [18] and, in principle, two more phase changes which may destroy at lower temperatures the two other periodicities of the original 3d crystal [19]. Rotational order is lost in the smectic-C to smectic-A transition [18] and in the transition from newly found smectic-hexatic to smectic-A [20].

Contrary to thermally equilibrated polymers, defect lines must always be closed for topological reasons (unless they start and end at the boundaries of a finite system). Statistical assemblies of loops only are related to the HTE graphs of the various types of the $n$-vector model at zero magnetic field. However, the analogy is impaired by the elastic interaction of dislocations and disclinations whose energy per unit length in general diverges logarithmically with line separation. Self-screening [21] and mutual screening [22] have been considered as possible mechanisms resolving this problem at least in principle. Vortex lines in type-II superconductors seem to be the only known defect lines in a 3d system whose interaction is local, i.e. drops exponentially with separation.

The unique anisotropic interaction of smectic-A dislocations whose energy also remains finite at all distances [23], was invoked to explain some strange observations at the smectic-A to nematic transition: anisotropic scaling of the correlation length of smectic ordering above [24] and a difference between the critical exponents of two moduli of smectic elasticity below the critical temperature [22]. The phase transition has also been found [25] in hydrous amphiphilic systems, a case in which the defect model is particularly appealing. The constituent bilayers can hardly vanish at the transition, but it is conceivable that dislocations of « infinite » length destroy the numerability of the layers, thus rendering the multilayer system nematic.

In the present paper we wish to develop simplified descriptions of statistical line assemblies consisting predominantly of finite-sized loops. They are related to the classical theories of ferromagnetic phase transitions. The main simplification is to regard the lines as diffusion paths and to express steric interaction essentially by a mean-field. Like other classical theories, the approach is correct only for space dimensionalities $d > 4$. However, it may be useful as an approximation and as a starting point for refinements for $d < 4$, similarly to customary mean-field theory.

Section 2 deals with assemblies of loops of finite size. The lines are closed diffusion paths on a lattice without any interaction. Each line element or link spans a nearest-neighbour bond and requires the same energy of formation. If viewed as a simplified HTE of the $n$-vector model, these loop gases correspond to the Gaussian approximation of the paramagnetic phase at zero magnetic field. In section 3, steric interaction is added in the form of a mean-field. The loop assemblies can then display phase transitions for $d > 2$, which are characterized by the first appearance of infinite lines. The density of infinite lines increases gradually from zero as the temperature is raised above the transition point, thus indicating a second-order phase change. Extending the rigorous mean-field picture by Edwards screening [2], one obtains the exact theory for $d > 4$ and an analogue to the Gaussian approximation of the ferromagnetic phase at zero magnetic field for $d < 4$. Open lines, i.e., chains, are added to the loops in section 4. The complete theory should be applicable to thermally equilibrated polymers if they are densely packed and if chains are much rarer than loops. Regarded as a ferromagnetic HTE in the presence of a magnetic field, the complete model yields, for $d > 4$, the critical exponents of magnetization and susceptibility, in addition to those of correlation length and specific heat which can be obtained without using open lines. It follows from the magnetic analogy that thermally equilibrated polymers will not undergo a true phase transition. However, they can exhibit strong cooperativity [4]. Section 5 deals in some detail with correlations in line assemblies to justify certain assumptions made in the preceding sections. A final discussion of the results is given in section 6. It is shown there that by omitting finite loops one arrives at a description of phase transitions resembling mean-field theory as closely as possible in the defect-line model.

2. Assemblies of pure diffusion loops. — Let us first study thermally generated diffusion loops without any steric interaction. In order to include all possible configurations of a loop consisting of $l$ links or bonds, we let a particle hop at random between nearest-neighbour lattice points, stop it after $l$ steps, and keep only those random walks that terminate at the starting point. For the sake of simplicity we consider square, simple cubic, or simple hypercubic lattices. With $a$
being the lattice parameter, the root-mean-square length $\sigma$ of an open-ended diffusion path is given by

$$\sigma^2 = a^2 l.$$  \hspace{1cm} (1)

The length $\sigma_k$ along each coordinate axis obeys

$$\sigma_k^2 = \frac{a^2 l}{d}.$$  \hspace{1cm} (2)

The probability of diffusion path closure is

$$\frac{d^d}{(2 \pi \sigma^2)^{d/2}} = \left(\frac{d}{2 \pi a^2}\right)^{d/2}.$$ \hspace{1cm} (3)

This formula averages over even $l$ (allowed) and odd $l$ (disallowed). Equations (1) to (3) are exact only for large enough $l$.

It is natural to define a spatial density $h(l) \, dl$ of loops in the interval $dl$ around $l$ in the following way:

$$h(l) \, dl = \frac{1}{d^d} \left(\frac{d}{2 \pi a^2}\right)^{d/2} \frac{d}{2} \left(2 \, dl \, \exp(-\varepsilon/kT)\right).$$ \hspace{1cm} (4)

The first factor represents the density of possible starting points which is identical to the density of lattice points. The divisor $d$ takes account of the fact that a closed path can start at any of its points and run through them in either direction. The number of starting points within a loop is taken to be $l$, regardless of how often it intersects itself. Closed lines with intersections can be represented by more than one diffusion path and one or more combinations of diffusion paths. The number of possible representations grows rapidly with the number of intersections. It is essential to count diffusion paths rather than line configurations. Otherwise the statistical weight of intersecting loops would be lowered, which amounts to a steric interaction of the lines. The factor $2$ is the coordination number of the simple cubic lattice. Finally, $\varepsilon$ is the energy required to form one link and the exponential $\exp(-\varepsilon/kT)$ is the associated Boltzmann factor.

It is instructive to cast (4) in the form

$$h(l) = \exp(-\varepsilon l + Ts) \, kT$$

and to split the entropy $s$ into

$$s = s_{pl} + s_{path} + s_{cl} + s_{int}$$

where we have the entropies of placing

$$s_{pl} = k d \ln a,$$

of choosing a path,

$$s_{path} = k l \ln (2d),$$

of closure,

$$s_{cl} = - k \frac{d}{2} \ln \left(\frac{2 \pi l}{d}\right)$$

and of interchangeability of starting points and direction

$$s_{int} = - k \ln (2l).$$

The thermal loop assemblies thus defined exhibit fixed points, even for $d = 1$ which is without further interest, at the temperatures $T_c$ where the probability of line continuation is unity, i.e. for

$$2d \exp(-\varepsilon/kT_c) = 1.$$ \hspace{1cm} (5)

This may be seen by considering an interval between $l_1$ and, say, $2l_1$ and regarding

$$\int_{l_1}^{2l_1} h(l) \, dl \sim l_1^{1-d/2},$$ \hspace{1cm} (6)

valid at fixed points, as the density of a « generation » of loops. Since the mean volume of a diffusion loop grows with $l^{d/2}$, the product of mean volume and density is the same for each generation. Evidently, loop packing is scale invariant in the Kadanoff sense, as is of course the shape distribution of diffusion loops.

At temperatures below the fixed point the loop density $h(l)$ contains a factor dropping exponentially with loop size. We may define a characteristic number of links $\lambda_d(T)$ as a function of temperature by the relation

$$2d \exp(-\varepsilon/kT) = \exp(-1/\lambda_d(T)).$$ \hspace{1cm} (7)

Expanding $\varepsilon/kT$ in $T - T_c$ and using (5) leads to

$$\frac{1}{\lambda_d} = \frac{T_c - T}{T_c} \ln (2d),$$ \hspace{1cm} (8)

valid near $T_c$ for $T < T_c$. Equation (4) can now be written in the generalized and condensed form

$$h(l) \, dl = K_d \, \frac{1}{1-d/2} \frac{d}{l} \, \exp(-l/\lambda_d)$$ \hspace{1cm} (9)

where for simple cubic lattices

$$K_d = \frac{1}{2 \pi d} \left(\frac{d}{2 \pi a^2}\right)^{d/2}.$$ \hspace{1cm} (10)

Regarding the extension of loops with $l = \lambda_d(T)$ as a measure of correlation in the loop assembly, we may define a correlation length $\xi$ by the simple relationship

$$\xi = a \lambda_d^{1/2}. $$ \hspace{1cm} (11)

This is a convenient, but formal definition; it will be shown to be proportional to the magnetic correlation length (see Section 5).

In order to derive the specific heat of diffusion loops assemblies we need the total energy density

$$U = \varepsilon L$$ \hspace{1cm} (12)

where

$$L = K_d \int_{l_c}^{\infty} \frac{dl}{l^{d/2}} \, \exp(-l/\lambda_d)$$ \hspace{1cm} (13)
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\( \xi \sim (T_c - T)^{-v} \) with \( v = \frac{1}{2} \) \n
\( C_\alpha \sim (T_c - T)^{-\alpha} \) with \( \alpha = \begin{cases} 2 - d/2 & \text{for } d = 2, 3, 4 \\ 0 & \text{for } d > 4 \end{cases} \) \n
The exponents are those of the Gaussian model for the paramagnetic phase [26, 27], the Hamiltonian of which contains only the \((T - T_{c\text{M}}) M_x^2\) and \((V M_x)^3\) terms, \( M_x \) being the components of magnetization. The pure diffusion loop model fails for \( T > T_c \) because of uninhibited loop growth, while the Gaussian model breaks down for \( T < T_{c\text{M}} \) due to unlimited growth of magnetization. The space dimensionality \( d = 4 \) is a borderline in both cases.

3. Mean-field description of steric interaction. —

We now proceed to a theory of statistical loop assemblies which includes steric interaction, thus replacing the catastrophe of the Gaussian model by a phase transition. For this purpose we introduce in some detail a mean-field description of steric interaction. In more than one way the space dimensionality \( d = 4 \) will again be a borderline.

Let us begin with calculating the number \( n_s \) of self-encounters of a diffusion path as a function of \( l \) and \( d \). Considering first an open-ended random walk, i.e. a chain, we find by simple reasoning for (hyper-) cubic lattices

\[
n_s = \left( \frac{d}{2\pi} \right)^{d/2} \int_{l_0}^{l_1} \frac{dl}{l^{(d-2)/2}} \int_{m_1}^{m_2} \frac{dm}{(m_2 - m_1)^{d/2}} \tag{18}
\]

where \( l_0 > 1 \) is a small number that remains to be specified and \( l \gg l_1 \). Carrying out the double integration leads to

\[
n_s = \left( \frac{d}{2\pi} \right)^{d/2} \times \left[ -\frac{d-4}{2} l_1^{d-2} + \frac{l}{2} l_1^{d/2-1} \right. \left. + \frac{l}{2} l_1^{d/2-1} \times \frac{d-4}{2} d-2 l_1^{d/2-2} \right] \tag{19a}
\]

except for \( d = 4 \) where

\[
n_s = \left( \frac{2}{\pi} \right)^2 \int_{l_1}^{l} \frac{dl}{l} - \ln l - \ln l \tag{19b}
\]

and for \( d = 2 \) where

\[
n_s = \frac{1}{\pi} [l_1 + l \ln l - l(1 + l_1)] \tag{19c}
\]

Evidently, for large \( l \) the terms linear in \( l \) dominate whenever \( d > 2 \). It is important to note that the third term in (19a) also diverges (and is negative) whenever \( 2 < d < 4 \), albeit with a less than linear power law, e.g. \( l^{1/2} \) for \( d = 3 \). In the uninteresting case \( d < 2 \) the corresponding term is positive and diverges faster than linearly, while it tends to zero with growing \( l \) for \( d > 4 \).

Next we write down and evaluate a formula for the number of self-encounters in a closed diffusion path, i.e. a loop. Under the same conditions as in the case of the chain we have for the loop

\[
n_s = \frac{1}{2} \int_{l_1}^{l_1} \frac{dl}{\pi m} \left( \frac{d}{2\pi m} \right)^{d/2} \left( \frac{d}{2\pi l} \right)^{d/2} \int_{m_1}^{m_2} \frac{dm}{(m_2 - m_1)^{d/2}} \times l. \tag{20}
\]
The integral in the numerator comes from considering one of the joints of the loop, say the one between link 1 and link 1, and breaking the loop at another joint, say between links m and m + 1. Then the integrand represents the probability of double closure of the diffusion paths of both parts of the chain at the joint between links l and 1. We have to integrate over all possible values of m and, as we refer to loops only, to divide by the closure probability of a diffusion path of length l. The factor l takes account of the necessity of adding up the contributions of all joints and the factor 1/2 corrects for double counting of intersections. Note that the loops are again taken to be ordered sequences of nearest-neighbour lattice points.

Equation (20) may be rewritten as

\[ n_s = \left( \frac{d}{2} \right)^{d/2} \int_1^{l/2} \frac{dm}{m^{d/2} (l - m)^{d/2}} l^{1 + d/2}. \]  

(21)

Inserting the Taylor expansion

\[ \frac{1}{(l - m)^{d/2}} = \frac{1}{p^{d/2}} + \sum_{p=1}^{\infty} \prod_{r=1}^{p} \left( \frac{d}{2} + r - 1 \right) \times \frac{1}{p^!} \frac{1}{p + 1 - d / 2}^{p + 1 - \delta} \times \frac{m^d}{p^!} \]  

(22)

and integrating, one obtains for \( l \) large enough to make its falling powers negligible

\[ n_s = \left( \frac{d}{2} \right)^{d/2} \left\{ \left[ \frac{1}{(1 - d/2)^{2d - d/2}} + \right. \right. \right. \]

\[ \left. \times \left. \frac{1}{p^!} \frac{1}{p - 1 - 2^{p - 1}} \right] + \right. \right. \]

\[ \times \left. \frac{l_l^{d - 1/2}}{d - 1} + \frac{l_l^{d - 1/2}}{2 - 1} l - \frac{d}{4 - d} l_l^{1 - d/2} \right\}. \]

(23a)

This formula is valid for all \( d \geq 2 \) except the special cases \( d = 4 \) and \( d = 2 \) which require logarithms.

One obtains for \( d = 4 \)

\[ n_s = \left( \frac{2}{\pi} \right)^2 \left\{ -2 + \sum_{p=1}^{\infty} \prod_{r=1}^{p} (1 + r) \times \right. \]

\[ \times \left. \frac{1}{p^!} \frac{1}{p - 1 - 2^{p - 1}} \right] + \right. \right. \]

\[ + \left. \frac{l_l^{d - 1/2}}{d - 1} + 2 \ln l - 2 \ln 2 l_l \right\}. \]

(23b)

and for \( d = 2 \)

\[ n_s = \frac{1}{\pi} \left\{ \sum_{p=1}^{\infty} \prod_{r=1}^{p} \frac{r}{p} \frac{1}{p^!} \frac{1}{p^2} \right\} l + \]

\[ + (\ln l - \ln 2 l_l) l - \frac{d}{4 - d} l_l^{1 - d/2} \}. \]

(23c)

Equation (23a) contains a constant, a term linear in \( l \), and one proportional to \( l^{2 - d/2} \). This is in agreement with what was found for chains.

The calculations indicate that only for \( d > 4 \) diffusion paths do, as a rule, not return upon themselves except for the unavoidable short-range self-encounters, i.e., those between consecutive line elements. Even in the presence of steric self-interaction they will, therefore, be random walks apart from short-range perturbations which change only the effective diffusion constant. While this result is certainly not new and can be obtained from simple dimensional analysis rather than integrations, a quantitative formula such as (23) may eventually be useful in further studies. Curiously, the \( l^{2 - d/2} \) term goes through zero around \( d = 3 \), being negative for larger and positive for smaller \( d \).

If a single loop does not return upon itself, apart from its closure, two different loops making contact at some point will also not meet each other somewhere else.

Consequently, steric interaction in loop assemblies can be approximately expressed by a mean-field for \( d > 4 \). Assuming now a strictly homogeneous field, which corresponds to the unphysical case of an infinite range of steric interaction, we may replace the probability of line continuation in the absence of interaction,

\[ e^{-1/4d} = 2 d \exp(-\phi/kT), \]

(24)

by the ansatz

\[ e^{-1/4d} = z_{eff} (1 - f_d(L)) \exp(-\phi/kT). \]

(25)

The effective coordination number \( z_{eff} < 2 \) \( d \) takes account of short-range steric self-interaction. The function \( f_d(L) \), where \( 0 \leq f_d(L) < 1 \), represents the mean steric interaction of one line with all others. \( L \) is equal to the total density of line elements. Obviously, the continuation probability (25) applies only to large enough loops (\( l \gg 1 \)). If the lines would occupy just a small fraction of the available lattice points we could approximate the function \( f_d(L) \) which depends on lattice type by

\[ f_d(L) = (c_d/N) L \]

(26)

where \( N \) is the density of lattice points. The factor \( c_d \) measures the strength of steric interaction and corrects for short-range repetitive encounters between different lines. In any event, \( f_d(L) \) must be a monotonically rising function.

Central to our treatment of critical behaviour are self-consistency relations for \( L = L(T) \). At temperatures below a phase transition we have finite loops only. The associated density of line elements is
Here $K_d(L)$ could be expressed by (10) for simple hypercubic lattices. We allow for the possibility that it is a (weak) function of $L$. The loop multiplicity $n$, omitted in section 2, has to be taken into account for the first time in (27).

Two possibilities may now be distinguished: firstly, there exists a critical temperature $T_c$ at which the continuation probability (25) reaches unity. Since it must not exceed this limit, which would mean uninhibited line growth, a further increase of temperature should lead to the formation of infinite lines. Distinguishing henceforth the total link densities of finite and infinite lines, we may write

$$L = L_{\text{fin}} + L_{\text{inf}}.$$  \hspace{1cm} (28)

The self-consistency relation (27) separates for $T > T_c$ into the two equations

$$z_{\text{eff}} \left[1 - f_d(L)\right] e^{-\frac{1}{kT}} = 1$$  \hspace{1cm} (29)

and

$$L_{\text{fin}} = nK_d(L) \int_0^{\infty} \frac{dl}{l^d/2}.$$  \hspace{1cm} (30)

The last three equations can be solved for $L$, $L_{\text{fin}}$, and $L_{\text{inf}}$.

Secondly, it is possible that there is no critical temperature. The estimate following (14) suggests rather high link densities at a transition, especially for small $d$ and large $n$. The prefactor of the Boltzmann factor in (25) may then drop to unity,

$$z_{\text{eff}} (1 - f_d(L)) = 1,$$  \hspace{1cm} (31)

while the loops are still of finite size. This would rule out the occurrence of a phase transition at any temperature. (However, the factor replacing the Boltzmann factor in HTE's and in the case of polymers can be larger than unity, which invalidates the present argument.)

In those cases where a transition exists the assembly of loops and lines may be conveniently described in its vicinity by means of the expansions

$$\frac{\varepsilon}{kT} = \frac{\varepsilon}{kT_c} - \frac{\varepsilon}{kT_c^2} (T - T_c)$$

and

$$f_d(L) = f_d(L_c) + f_d'(L_c) (L - L_c)$$

$$K_d(L) = K_d(L_c) + K_d'(L_c) (L - L_c).$$  \hspace{1cm} (32)

Insertion in (27) yields after some manipulations

$$L_c - L = \left[\frac{1}{K_d'(L_c)} + \frac{d - 2}{d - 4} \frac{L_c}{1 - f_d(L_c)}\right]^{-1} \times$$

$$\times \frac{d - 2}{d - 4} l_0 L_c \frac{\varepsilon}{kT_c^2} (T_c - T)$$  \hspace{1cm} (33)

valid for $T < T_c$. The assumption $d > 4$ is used again in evaluating the integral (27): according to (15) the derivatives of $L - L_c$ with respect to temperature remain finite at $T = T_c$ only for $d > 4$. From (28), (29), and (30) we derive

$$L - L_c = \frac{1 - f_d(L_c)}{f_d'(L_c)} \frac{\varepsilon}{kT_c^2} (T - T_c)$$  \hspace{1cm} (34)

$$L_{\text{fin}} - L_c = \frac{K_d(L_c) L_c}{K_d'(L_c)} (L - L_c)$$  \hspace{1cm} (35)

$$L_{\text{inf}} = \left[1 - \frac{K_d(L_c) L_c}{K_d'(L_c)} \frac{1 - f_d(L_c)}{f_d'(L_c)} \frac{\varepsilon}{kT_c^2} (T - T_c)\right]^{-1}$$  \hspace{1cm} (36)

valid for $T > T_c$. The line densities $L$ and $L_{\text{inf}}$ and possibly also $L_{\text{fin}}$ rise with temperature. For a calculation of critical behaviour one has to know $f_d(L)$ and $K_d(L)$ and to calculate $T_c$ and $L_c$ from the condition that (27) and (29) be simultaneously satisfied. In the above formulas, steric interaction was tacitly assumed to be the same for all $n$ types of lines. The predominance of small loops for which some of the above formulas are not exact requires special attention in a complete theory. At any rate, the whole concept of mean steric interaction must be expected to be seriously incorrect for the physical dimensionalities $d = 2$ and $3$.

A correlation length $\xi$ may be defined for $T < T_c$ similarly as in the pure diffusion model. According to (25) the characteristic number of links per line, $\lambda_d$, is given by

$$z_{\text{eff}} (1 - f_d(L)) \exp (-\frac{\varepsilon}{\varepsilon/kT}) = e^{-1/\lambda_d}.$$  \hspace{1cm} (37)

Near the critical point, $1/\lambda_d$ is proportional to $T_c - T$ for $d > 4$ and can be calculated by means of the above linearizations. Insertion in (11) gives the correlation length. A new definition of the correlation length is required on the high-temperature side of the transition. Here it is convenient, though again formal, to put $\xi$ equal to the mean distance of subsequent encounters of an infinite line with other infinite lines. A physical justification based on generalized Edwards screening of polymers will be given in section 5. If $N_{\text{inf}}$ is the density of such encounters, one has for the root-mean-square diffusion length

$$\xi = a \left(\frac{L_{\text{inf}}}{N_{\text{inf}}}\right)^{1/2}.$$  \hspace{1cm} (38)

Assuming

$$N_{\text{inf}} = a^d L_{\text{inf}}^2,$$  \hspace{1cm} (39)

one obtains the simple relationship

$$\xi = \frac{a}{(a^d L_{\text{inf}})^{1/2}}.$$  \hspace{1cm} (40)

where $L_{\text{inf}}$ is given for $d > 4$ and near $T_c$ by (36). It should be noted that our definition of $\xi$ neglects the fact that repetitive encounters occur with enhanced probability even for $d > 4$. 

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Steric interaction being athermal, the specific heat is given by

$$C_v = \frac{dU}{dT} = \frac{dL}{dT} \epsilon$$

(41)

as in the pure diffusion model. In the case $d > 4$, the derivative $dL/dT$ may be read from (33) for $T < T_c$ and from (34) for $T > T_c$. Clearly, the specific heat is well-defined on both sides of the transition, but makes a jump at $T = T_c$.

It follows from the last two paragraphs that for $d > 4$ in the presence of steric interaction

$$\xi \sim |T_c - T|^{-\nu} \quad \text{with} \quad \nu = \frac{1}{2} \quad (42a)$$

$$C_v \sim |T_c - T|^{-\alpha} \quad \text{with} \quad \alpha = 0 \quad (42b)$$

on both sides of a phase transition. These exponents apply also to $d = 4$ if the logarithms occurring in the above formulas are viewed as zero powers. Therefore, loop assemblies subject to steric interaction exhibit the critical exponents, $\nu$ and $\alpha$ of mean-field theory, provided the space dimensionality is $d \geq 4$.

It is easy to see why the diffusion model fails for $d < 4$ in the presence of steric interaction. Considering finite loops only ($T < T_c$) we read from (23) that the number $n_i$ of self-encounters of a diffusion loop has two terms dependent on $l$, one varying as $l$ and the other as $l^{2-d/2}$. On the assumption that each self-encounter reduces the entropy of choosing the path by the same amount the linear contribution to $n_i$ could be overcome by slightly raising the temperature. It would then be the $l^{2-d/2}$ term which destroys the fixed point of the diffusion model. The actual situation is, of course, more complicated. Our assumption about the entropy is too simple and we have neglected the steric interaction between different loops which also can meet at many places for $d < 4$. However, far enough below the critical point the diffusion model could be an acceptable approximation in suitable cases. This would tie in with the observation that in some 3d systems the Gaussian model gives a satisfactory description of the disordered phase for temperatures not too near $T_c$. Its critical exponents (17) would then be meaningful in a certain temperature range.

On the other side of the phase transition ($T > T_c$) we are faced with the additional problem of the widely spaced repetitive encounters between infinite lines. It might be argued that they become relatively less important as $L_{inf}$ increases, so that in a temperature range beginning somewhere above $T_c$, at least the proportionality of $\xi$ and $L^{-1/2}$ expressed by (40) is a good approximation. Where this is true, we have for $2 < d \leq 4$

$$\xi \sim (T - T_c)^{-\nu} \quad \text{with} \quad \nu = \frac{1}{2} \quad (43a)$$

$$C_v \sim \frac{\partial^2}{\partial T^2} \frac{1}{\xi^d} \sim (T - T_c)^{-\alpha} \quad \text{with} \quad \alpha = 2 - \frac{d}{2}.$$  

(43b)

The formula for the temperature dependence of the specific heat is based on the plausible assumptions that there are local fluctuations of $L_{inf}$ and that their mode number per unit volume is proportional to $1/\xi^3$. What we have obtained here as a possible behaviour is the equivalent of the Gaussian model of the ferromagnetic phase [27]. (See also section 5.)

4. Chains added to a loop assembly. — As was mentioned before, thermally excited defect-lines in (infinite) ordered systems must be closed for reasons of topology. However, open chains are possible besides loops in the case of thermally equilibrated polymers. They also occur in the HTEs of the $n$-vector model when there is a magnetic field. Let us start with the polymers: each line element covering one nearest-neighbour bond represents one monomer, $\epsilon$ now being its negative chemical potential. We also introduce an energy $\epsilon_b$ of line breaking which is twice the energy of one line end. The critical (or cooperative) behaviour of equilibrated polymers may be controlled by varying $\epsilon$ or $T$, or simply the concentration $L$.

If the lines do not interact at all or only through a mean-field, the chains can be superimposed on the loop assemblies. Without interaction the chain density for $T < T_c$ may be written as

$$\frac{1}{d^2} (2 \, d \, e^{-\epsilon_b/kT}) \frac{dL}{dT} e^{-\epsilon_b/kT}$$

(44)

in analogy to the loop density (4). Using a continuous function rather than a sum over integer values of $l$ makes sense only if the chains are long. This condition, also underlying (4), requires a line continuation probability near unity, i.e. the vicinity of a critical point. The factor $1/2$ corrects for double counting due to the two line ends. No correction is made for the probability of closure which is small in the case of long lines and for the coincidence of ends of different chains which is unlikely if the density of chains is low. The average number of monomers or elements per chain equals $\lambda_d$ as given by (8). If there is steric interaction through a mean-field, the line continuation probability (24) has to be replaced by (25).

The chain density is controlled by the energy of line breaking. For a low density of chains as compared to that of lattice points, one needs $\exp(-\epsilon_b/kT) \gg 1$. A low density of chain elements relative to that of other line elements is also desirable; it requires the more stringent condition $\lambda_d \exp(-\epsilon_b/kT) \ll 1$. Line multiplicities $n > 1$ pose no particular problem: all $n$ types of lines are superimposable on each other as they are on the loops. The breaking energy $\epsilon_b$ may vary from one type to another. However, we mostly assume the energy per line element, $\epsilon_b^*$, to be uniform.

The other side of the phase transition ($T > T_c$) is more interesting. We limit ourselves to $d > 4$. This is necessary to ensure that the density of line elements due to the finite loops larger than the correlation
length (40) is less than \( L_{\text{inf}} \) in a vicinity of \( T_c \), as may be seen from (9) with \( \lambda_d = \infty \). It is then sufficient to consider the effect of line breaking on the infinite lines only, provided the breaks are rare enough. With \( L_{\text{inf}} \) being the length of the infinite lines when unbroken, we obtain the density \( N_s \) of segments into which they separate from detailed balancing.

In the simplest possible case, that of line multiplicity \( n = 1 \), one has

\[
L_{\text{inf}} e^{-\epsilon_b/kT} = d^2(2 N_s)^2
\]

(45)

which is easily solved for \( N_s \). The average length \( \lambda_s \) of the segments follows from the relation

\[
L_{\text{inf}} = N_s \lambda_s.
\]

(46)

Breaking the infinite lines entails corrections of which we treat only first orders, denoting them by \( \Delta L_{\text{inf}} \) etc. Detailed balancing of the first-order corrections gives

\[
\Delta L_{\text{inf}} e^{-\epsilon_b/kT} = d^4 8 N_s \Delta N_s.
\]

(47)

As the finite segments exist in thermal equilibrium there is a further relationship. It expresses the fact that with breaks the continuation probability must be slightly less than unity. Linearizing (25), we obtain

\[
\frac{f_d(L) \Delta L}{1 - f_d(L)} + \frac{\Delta \epsilon}{kT} = \frac{1}{\lambda_s}.
\]

(48)

If \( L \) is constant, as may apply to thermally equilibrated polymers, we can calculate \( \Delta L_{\text{fin}} \) from \( \Delta \epsilon \) as given by (48). On the basis of the linearizations introduced in dealing with the phase transition of the loop assembly for \( T > T_c \), we find (\( -\Delta L_{\text{fin}} \)) \( \sim 1/\lambda_s \). Therefore \( \Delta L_{\text{inf}} \sim 1/\lambda_s \). The latter proportionality is obtained directly from (48) if \( \epsilon \) is constant, the case applying to HTE's of the \( n \)-vector model (see below). Inserting it in (47) leads to

\[
\Delta N_s \sim \frac{e^{-\epsilon_b/kT}}{(d^2)^2 L_{\text{inf}}}
\]

(49)

where one factor \( d^2 \) enters for reasons of dimensionality. The formula will be needed in the following.

Let us now consider integer line multiplicities \( n > 1 \). If the total number of line elements, i.e. constituent monomers, is the same for all types of lines, the breaking of the infinite lines can be treated separately for each type \( \kappa \). Of course, \( L_{\text{inf}} \) has to be replaced by \( L_{\text{inf}}/n \) in equations (45) to (47) and (49). With different \( \epsilon_b^n \) one obtains different \( N_s^\kappa \) and \( \epsilon^\kappa \) depends on \( \epsilon_b^n \), but only very weakly as long as the fraction of constituent monomers residing in chains is low. If \( \epsilon \) is strictly equal for all types of lines, as in the case of HTE line assemblies of the isotropic \( n \)-vector model, the density of segments belonging to infinite lines is proportional to \( \exp(-\epsilon_b^n/kT) \), \( \lambda_s^n \) being equal for all types. Incidentally, if there were only one infinite line and, as with defect-lines, no breaks whatsoever, the line could be of any type as long as \( \epsilon \) is uniform. Again, all these arguments are valid only on the assumption that steric interaction does not depend on line type.

It is not possible to have a true phase transition if line rupture prevents the formation of infinite loops or chains. However, there can be a cooperative effect which is the stronger the larger the polymer breaking energy. In practice, \( \epsilon_b \) must not be too large to avoid excessive equilibration times [4]. Obviously, the lack of a phase transition in thermally equilibrated polymers closely corresponds to its absence in ferromagnets subject to a magnetic field.

The remainder of the section is devoted to the HTEs of the \( n \)-vector model. The purpose is to derive the critical exponents of spontaneous magnetization and susceptibility from HTE line assemblies. All this will be done for \( d > 4 \) where mean-field theories are appropriate.

We use here the HTE of the classical isotropic \( n \)-vector model [4], but the single-bond HTE of the Ising model [28], the anisotropic \( n \to 0 \) vector model [6, 7], or quantum-mechanical formulations [29] could be employed as well. The Hamiltonian may be written as

\[
\mathcal{H} = - \sum_{\langle ij \rangle} n I s_i s_j - \sum_i n^{1/2} \mu s_i H.
\]

(50)

The spins \( s_i \) are \( n \)-dimensional unit vectors, \( I \) is the coupling constant, \( \mu \) the magnetic moment parallel to \( s_i \) and \( H \) the magnetic field. The summations extend over nearest-neighbour bonds \( ij \) and spin sites, \( i \). The associated partition function is

\[
Z = \prod_i \int d\Omega \frac{\prod_{\langle ij \rangle} \prod_k \exp(n \beta_M I s_i s_j) \times}{\prod_{\langle ij \rangle} \prod_k \exp(n \beta_M I s_i s_j) \times \prod_{\langle ij \rangle} \prod_k \exp(n \beta_M I s_i s_j)}.
\]

(51)

where \( \kappa \) denotes the components and \( \beta_M = 1/kT_M \), \( T_M \) being the temperature of the magnetic spin system. The HTE's of the exponentials are

\[
\exp(n^{1/2} \beta_M I s_i s_j) = 1 + \sum_{\kappa=1}^\infty \frac{1}{\kappa!} (n \beta_M I s_i s_j)^\kappa
\]

(52)

\[
\exp(n^{1/2} \beta_M I s_i s_j) = 1 + \sum_{\kappa=1}^\infty \frac{1}{\kappa!} (n^{1/2} \beta_M I s_i s_j)^\kappa
\]

(53)

It is well-known that with these HTEs the partition function can be represented as a statistical assembly of lines on a lattice. We have already studied the case of loops only, i.e. \( H = 0 \). A magnetic field adds chains (cooperative magnetization) and points (noncooperative magnetization).

Customarily, all \( n \) components are lumped together in numerical calculations of ferromagnetic critical behaviour. The analogy to assemblies of sterically
interacting lines of multiplicity $n$ is seen best if another approach is taken: one starts with nonintersecting loops and chains representing single components $\kappa$ to lowest order in $I$. With the help of

$$\int \frac{d\Omega}{\Omega} (s_\kappa)^2 = \frac{1}{n}$$

(54)

the correspondences between an ordinary line assembly and the HTE are then easily found to be

$$\beta_m I \leftrightarrow e^{-v/kT}$$

(55)

$$\beta_m \mu H_\kappa x \leftrightarrow e^{-v/kT}.$$  \hspace{0.5cm} (56)

The multiple passage of lattice points and nearest-neighbour bonds by lines of equal or different components produces steric interactions whose strengths were calculated earlier [30], but are not needed here. Evidently, the temperature axis is reversed in going from physical lines to the mathematical lines of the HTE and vice versa. This does not affect critical exponents near a critical point.

In order to deal with magnetic properties we have to know the magnetic moment associated with a chain. It may be deduced by contemplating a particular diffusion path of length $l$ connecting two points designated by $0$ and $l$. If there are no intersections the partition function for such a single path is given by

$$Z = \sum_{x=1} \prod_{i=0}^l \frac{d\Omega}{\Omega} (1 + \beta_m L_\kappa s_\kappa^x)(1 + \beta_m \mu H_\kappa s_\kappa^x) \times$$

$$\times \left(1 + \beta_m \mu H_\kappa s_\kappa^x\right)$$

(57)

The first term on the right-hand side represents the vacant path, each member of the sum the occupation by a chain of a component $\kappa$. The average magnetic moment associated with the single path has the components

$$m_\kappa = \sum_{x=1} \prod_{i=0}^l \frac{d\Omega}{\Omega} \mu(s_\kappa^0 + s_\kappa^x)(1 + \beta_m L_\kappa s_\kappa^x) \times$$

$$\times \left(1 + \beta_m \mu H_\kappa s_\kappa^x\right)(1 + \beta_m \mu H_\kappa s_\kappa^x)/Z$$

$$= 2 \mu \beta_m l_f \beta_m \mu H_\kappa.$$  \hspace{0.5cm} (58)

In deriving (57) and (58) use has been made of the fact that the integral of odd powers of $s_\kappa^x$ vanishes. We are interested in very small magnetic fields. The second term in (57) will then be much smaller than unity, thus being practically equal to the probability of finding a chain in place. Dividing the component $\kappa$ of mean magnetization $m$ by the probability of having a chain of component $\kappa$, one obtains the moment per line of component $\kappa$,

$$m_{\text{line},\kappa} = \frac{2}{L_\kappa \beta_m H_\kappa}.$$  \hspace{0.5cm} (59)

We are now in a position to derive the critical exponents of susceptibility and magnetization from the HTE for $d > 4$. It is advantageous to apply the magnetic field parallel to one of the coordinate axes so that all chains are of this component. For $T_M > T_{M_c}$, i.e. in the temperature range of finite loops, we compute from (59), (56), (44), and (7) the cooperative part of induced magnetization

$$M_{\text{ind}} = \frac{1}{d^d} \lambda_\kappa \mu^2 \beta_m H_1$$

(60)

if the field $H$ is along the $\kappa = 1$ axis. The noncooperative part of magnetization is readily seen to be negligible for $\lambda_\kappa \gg 1$. Inserting (8) results in

$$M_{\text{ind}} \sim (T - T_{M_c})^{-\gamma} \text{ with } \gamma = 1,$$

(61)

$\gamma$ being the critical exponent of susceptibility. The same critical exponent applies in the presence of steric interaction, $\lambda_\kappa$ then being given by (37). On the low-temperature side of the magnetic phase transition one has to express both spontaneous magnetization and susceptibility in terms of lines. At first sight there seems to be no ferromagnetism because no chains exist at $H = 0$. The curious finding appears related to the fact that the spontaneous magnetization can assume at least two opposite directions. A choice is made as soon as an infinitesimal field is applied to the (infinite) system. To compute the zero-order magnetization we employ the correspondence (56) in (45) and solve for $N_{s}$,

$$N_s = \frac{1}{2} \left(\frac{L_{\text{inf}}}{d^d}\right)^{1/2} \beta_m \mu H_1,$$

(62)

which with (59) gives

$$M_{\text{sp}} = N_s m_{\text{line}} = \mu \left(\frac{L_{\text{inf}}}{d^d}\right)^{1/2}.$$  \hspace{0.5cm} (63)

The critical behaviour following from (36) is

$$M_{\text{sp}} \sim (T_{M_c} - T)^{\beta} \text{ with } \beta = 1/2,$$

(64)

$\beta$ being the critical exponent of spontaneous magnetization. The induced magnetization $M_{\text{ind}}$ is governed by the first-order correction $\Delta N_s$ of $N_s$. Combination of (49), (56), and (59) yields

$$M_{\text{ind}} = \Delta N_s m_{\text{line}} \sim \frac{1}{(d^d)} \frac{L_{\text{inf}}}{\mu^2} \beta_m H$$

(65)

and with (36)

$$M_{\text{ind}} \sim (T_{M_c} - T)^{-\gamma} \text{ with } \gamma = 1,$$

(66)

$\gamma$ being the critical exponent of susceptibility, here below the ferromagnetic phase transition.
5. Remarks on correlation. — The correlation lengths (8) or (37) for \( T < T_c \) and (40) for \( T > T_c \) were adopted to express correlation in terms of loops and infinite lines, respectively. The definitions apply only to diffusion lines and were chosen because of their convenience. In ferromagnetism, i.e., in the HTE’s of the \( n \)-vector model, correlation is defined in terms of chain ends. As the latter are disallowed in defect-line assemblies, there is a need for other definitions.

It is shown in the following that for \( d > 4 \) our definitions in terms of loops or infinite lines differ from their counterparts in terms of chain ends only by numerical factors. For \( T < T_c \), \( (T_m > T_m) \) the correlation in the sense of HTE’s of the paramagnetic phase at \( H = 0 \) is that between the ends of a single finite chain, which may be written as

\[
\langle s_a(0) s_a(r) \rangle \sim \int_0^\infty \frac{1}{l^{d-2}} \exp \left(-\frac{r^2}{2a^2 l/d} - \frac{l}{\lambda} \right) dl.
\]

The formula is based on (44) and reflects the diffusive character of the chain. The integral involving a Bessel function is found in tables:

\[
\langle s_a(0) s_a(r) \rangle \sim \frac{1}{\rho^{d-2}} K_{1-d/2} \left( \frac{r}{\xi} \right) \frac{1}{r^{d-1/2}} \exp \left(-r/\xi \right)
\]

where

\[
\xi' = a\lambda^{1/2} j \sqrt{2d}.
\]

Evidently, the « physical » correlation length \( \xi' \) differs only by the factor \( \sqrt{2d} \) from \( \xi \) as given by (8). At the critical point, i.e., for \( \lambda = \infty \), the integral (67) is easily seen to be

\[
\langle s_a(0) s_a(r) \rangle \sim \frac{1}{\rho^{d-2}}.
\]

This is the power law of monomer-monomer correlation inside an infinite diffusive line. Taking mean steric interaction into account does not change the correlation length (69) or the power law (70); it only affects the temperature dependence of \( \lambda \) and the position of the critical point according to (37). There are changes, even for \( d > 4 \), if the local character of steric interaction is taken into consideration. However, they produce only another numerical factor in the proportionality between \( \xi' \) and \( \lambda^{1/2} \).

In the presence of infinite lines, i.e., for \( T > T_c \) \((T_m < T_m)\), there are two types of correlation, longitudinal and transverse, which both have a meaning in ferromagnetism whenever \( n \geq 2 \). An infinitesimal magnetic field along an (easy) direction is required to permit a clear distinction. In the language of lines, the field breaks the infinite lines into quasi infinite segments, which all belong to the spin component parallel to \( H \). The correlation function of other (easy) spin components perpendicular to the field is obtained by introducing a single line of such a component. Assuming as before [30] that steric interaction is independent of line type, we have the algebraic correlation of equation (70). The factor in front of the power law which now describes transverse correlation depends of course on temperature. Obviously, transverse correlation can also be defined for \( n = 1 \), and even for \( n = 0 \), if it is understood to be the correlation within one of the quasi infinite lines.

Longitudinal correlation in ferromagnets corresponds to Edwards correlation in solutions of strongly overlapping polymers [2]. Edwards screening takes the local character of steric interaction into account. It refers to the correlation between a monomer in a given line and the monomers in the same and the other lines, all lines being considered infinite.

Edwards [31] developed his theory for \( d = 3 \), assuming diffusive behaviour of the lines. The theory can be generalized to other dimensionalities. Here we assume \( d > 4 \), not only to ensure that sterically interacting lines behave like diffusion paths, but also to be able to neglect in a vicinity of \( T_c \) any contribution of the very large finite loops. The same necessity arose in connection with equation (45).

The Edwards theory of polymer screening is analogous to the Debye-Hückel theory of electrostatic screening. The potential of steric interaction caused by a monomer varies as the statistical density of the chain to which it belongs, thus being proportional to the diffusive correlation function (70). Its power law is identical to that of the generalized Coulomb potential for all space dimensionalities. The screened density satisfies the differential equation underlying Debye-Hückel theory, \( \Delta \rho \sim \rho \) \((\rho = \text{charge density})\). The solution for \( r/\xi' > 1 \) depends on \( r \) as

\[
\frac{1}{r^{d-1/2}} e^{-r/\xi'}
\]

which is equal to (68). The Debye-Hückel correlation length \( \xi'' \) is inversely proportional to the square root of the mean density. The equivalent in line assemblies is the line density, \( L_{\text{inf}} \) in our case. The relationship

\[
\xi'' \sim a(d^e L_{\text{inf}})^{-1/2},
\]

written such that the dimension is the same on either side, is consistent with our formal definition (40). We refer to the literature [2, 31] for the factor of proportionality which is not too far from unity for self-avoiding walks on a lattice.

Longitudinal correlation in the ferromagnetic phase of the \( n \)-vector model comprises an exponentially decaying short-range and a uniform long-range part. It may be represented, for \( H = 0 \), by a single line, mostly infinite, if this line and all other infinite lines are taken to be of the component parallel to the direction of spontaneous magnetization. The magnetic correla-
tion length refers to the short-range part, which is not affected if the infinite lines are broken into segments by a weak magnetic field. Although the chain end represents only half a charge as compared to a monomer inside an infinite chain, the correlation length should be identical to the Edwards screening length. Roughly speaking, \( \xi_0 \) now denotes the range in which the probability of finding the other end of the chain deviates from its uniform value at larger distances. Many details remain to be studied, e.g., the question of how often, as a function of chain end separation \( r \), two neighboring ends are connected by a finite line.

The temperature dependence of the correlation lengths \( \xi' \) and \( \xi'' \) (here derived in terms of diffusion lines) was shown above to be governed by the critical exponent \( \nu \) having its classical value \( 1/2 \). The same value is of course obtained by a direct analysis of ferromagnetic correlation without invoking HTE's and statistical lines. For \( r/a > 1 \) it is sufficient to use the continuum description provided by the Ginzburg-Landau Hamiltonian. Regardless of the method, classical critical behavior is to be expected only for \( d \geq 4 \). However, the analogy between ferromagnets and line assemblies has been extensively and successfully utilized in the case \( d = 3 \) for linear polymers (\( n = 0 \)) [2, 3]. Similar analogies may be expected to hold between ferromagnetism and line assemblies for natural \( n \) [4]. In fact, what is deduced from real spin systems about line assemblies does not require any assumptions. The magnetic analogue in the case \( n = 0 \) is, in contrast, an artifact the properties of which are obtained by extrapolating from natural \( n \).

As the present article is concerned with classical critical behaviour, we glance only at what appears to follow from the isotropic \( n \)-vector model in 3d space. For \( T < T_c \) (\( T_m > T_{Me} \)), the magnetic correlation function has the form (68). We cannot conclude from it that a long single-chain behaviour is essentially like a diffusion path. The same form is assumed in the case \( n = 0 \), where one deals with a single self-avoiding random walk [32]. At the critical point, the end-to-end correlation of a single chain becomes algebraic, varying as \( r^{d-2} \). The critical exponent \( \eta \), generally positive and much smaller than unity, is known to decrease with increasing \( n \). This suggests size-dependent screening of the steric self-interaction of a single chain. It might be caused by the finite loops, in particular by the fact that they occur in all sizes. For \( T > T_c \) \((T_m < T_{Me})\) the longitudinal magnetic correlation again takes the form (71). Here it suggests Edwards screening to work in 3d space, as it does in the case \( n = 0 \), but now in the presence of a loop gas besides the infinite lines. The resulting diffusive behaviour of long enough lines can be inferred more convincingly for \( n \geq 2 \), from transverse correlation which varies as \( r^{d-2} \) for large enough \( r \).

Finally, the question may be raised if the infinite lines in a loop gas form the blobs introduced by de Gennes in dealing with semi-dilute polymer solutions. Blobs are regions occupied by a section of a single quasi infinite line. They form at \( d < 4 \), reducing the number of encounters between different lines or line sections. Inside a blob, the line is a self-avoiding random walk. If the blob size is taken as unit length, the walk is diffusion-like. The nonclassical critical exponents of the loop gas at low dimensionalities suggest the existence of something similar to blobs. However, the situation is vastly complicated by the presence of the finite loops.

6. Discussion. — Using a lattice model, we have developed a mean-field theory of line assemblies, including fluctuations and correlation on both sides of the critical temperature. The lines were regarded essentially as diffusion paths. Steric interaction was the only one considered and treated mostly in terms of a mean-field. On the side of infinite lines, the strict mean-field picture had to be enlarged by Edwards screening in order to obtain finite correlation lengths. Definitions of the latter in terms of loop parameters were introduced and shown to be proportional to the correlation lengths in ferromagnetic HTEs, which refer to chain ends. At many different points it became apparent that the critical exponents here derived can be generally correct only for \( d \geq 4 \). The theory may be applied to three types of lines: thermally equilibrated polymers, thermalized defect-lines, and, if the temperature axis is reversed, to the mathematical lines of high-temperature expansions of the \( n \)-vector model.

The common theme was cooperative and critical behaviour. Phase transitions were characterized by the first appearance of infinite lines in addition to finite loops. The infinite lines were postulated \textit{ad hoc}. Actual systems are limited, which rules out truly infinite lines. It can be shown, e.g., by detailed balancing of infinite lines, which are artificially and randomly broken at two different joints and then permitted to randomly recombine, that the length of line belonging to \( L_{inf} \) may form a few loops, even for \( n = 1 \), rather than a single one. However, each of those should extend throughout the system so that the additional closure probability due to the confinement takes effect. In phase transitions mediated by defect-lines, the loss of topological order, translational or rotational, requires at least one defect-line traversing the system.

Mean-field theory in its strict sense disregards fluctuations and short-range correlation altogether, which makes it applicable to all space dimensionalities. A similar simplification is possible in the case of line assemblies. It consists in omitting all finite loops and assuming a perfectly homogeneous mean-field of steric interaction. In the absence of chains the system is then described by equation (29) in the form

\[
\kappa_0 (1 - f_d (L_{inf})) \exp (- \varepsilon/kT) = 1
\]

where \( f_d (L) \) is a regular function. This leads to \( L_{inf} \sim \)
(T - T_c) near the critical temperature which itself is also obtained from (29). There are no lines below T_c. With breakable lines, e.g., H 0 0, one has chains on both sides of the transition. Thus one obtains very straightforwardly α = 0, γ = 1, and β = 1/2 and a jump of the specific heat at the transitions. A single-line approximation lends itself to other theoretical representations, e.g., a free energy density containing terms linear and quadratic in L_{inf}. However, the model still contains fluctuations and correlations within the infinite line while both can be entirely suppressed in the usual continuum mean-field theory.

It is attractive to define an order parameter for line assemblies which agrees with the magnetic one of the n-vector model. As long as there are no open lines, the parameter could be expressed by M/(d/μ) = (L_{inf} d^d) 1/2. This is equation (63) rewritten in dimensionless quantities. The order parameter (L_{inf} d^d) 1/2 seems also satisfactory in the case of defect lines where, however, it signifies disorder rather than order. With a nonzero magnetic field the magnetic order parameter is represented by the total magnetization, i.e., the sum of a spontaneous and an induced part. In terms of HTE lines the total magnetization is given by the product of line density, N, and magnetic moment per line, m_{line} = 2/β_{inf} H. Upon dividing by μ/α we have the dimensionless order parameter, valid for λ ≫ 1,

\[ N, d^d \frac{1}{\beta_{inf} \mu H}. \]

Because of (56), the analogue for thermally equilibrated polymers is

\[ N, d^d \exp(\epsilon_0/2 kT). \]

With the help of section 4 it is readily seen that these order parameters tend to the value for pure loop assemblies,

\[ (L_{inf} d^d) 1/2 \]

for H → 0 or ε_b → ∞, respectively. Considering chain polymers only, Edwards and de Gennes [2] have defined the order parameter to be the density of chain ends, i.e. 2 N_c.

In the present article, statistical line assemblies have been treated in the simplest possible manner. This applies to the physical models: essentially only random walks without any interaction or with an averaged steric interaction were considered. As a consequence we did not leave the domain of the classical theory of critical phenomena. It also holds for the methods: Hamiltonians, partition functions, and the notion of entropy were used only sparingly. The theory that emerges is easy to visualize and produces some novel results such as the distribution function of diffusion loops and its fixed point, reformulations of the classical theory of phase transitions including the Gaussian approximations in terms of HTE line assemblies, and a precise definition of the order or disorder parameter. Line densities in diffusion loop assemblies were estimated for d = 3 and found to be reasonable with regard to phase transitions mediated by defect lines. The calculation of the number of self-encounters in diffusion chains and loops as a function of d may be useful in the future. Finally, the ferromagnetic analogy was used in the case d = 3 to predict, in a preliminary fashion, some properties of line assemblies containing finite loops (n ≫ 1).

It is hoped that the present work eventually helps in the study of actual, nonclassical critical behaviour. An obvious challenge in this respect is the renormalization of line assemblies for 2 ≤ d ≤ 4 in the presence of non-averaged steric interaction. It could be argued that the problem has already been solved, both by the aforementioned HTE of the isotropic n-vector model on a lattice and, without lattice and implicitly, by the perturbation expansion of the partition function of the Ginzburg-Landau Hamiltonian, which can be done in terms of line graphs [27]. However, it remains to be checked if the critical exponents are universal, i.e., do not depend on the strength of steric interaction. The Ginzburg-Landau Hamiltonian is a continuum description averaging over lattice cells. The line interaction of its HTE is treated as energetic and represented by a δ-function. It differs greatly from an excluded-volume effect which does not permit a perturbation calculation. If universality is confirmed one is still faced with the question of whether or not a phase transition occurs in a given lattice. Simple reasoning suggests that increasing the line multiplicity and decreasing the coordination number of the lattice will finally prevent the line assembly from reaching the transition, even if exp(− ε/kT) surpasses unity and tends toward infinity, as is possible in the case of polymers. Defect line assemblies pose the additional problems of elastic interaction.

**Acknowledgments.** — I am indebted to K. H. Biedermann, W. Müller, and F. Rys for fruitful discussions. Also, I am grateful for the hospitality of S. Doniach at Stanford University where this article was brought into its final form.
References

[30] It was shown in reference [4] for the isotropic n-vector model that the entropy reduction caused by an intersection of lines in a lattice point does not depend on whether the lines are of equal or different components. The same independence holds for multiple occupancy of a nearest-neighbour bond. This can be seen by (artificially) splitting the p lines on the same bond into p separate lines connecting the same two lattice points. No matter whether the components are equal or different, the reduction factor due to multiple occupancy is \(1/p\) instead of \((1/p_1) \cdots (1/p_n)\) as implicitly suggested by reference [4].