

## **“Statistical” Symmetry with Applications to Phase Transitions<sup>1</sup>**

**Joseph L. Birman<sup>2</sup> and H.-R. Trebin<sup>3</sup>**

*Received July 16, 1984*

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Hermann proposed that mesomorphic media should be classified by assigning certain “statistical symmetry groups” to each possible partially ordered array. Two translational groups introduced were called superordinate and subordinate. We find that the average density in such a partially ordered medium has the superordinate symmetry  $\mathcal{E}_1$ , while the pair correlation function has the subordinate symmetry  $\mathcal{E}_2$ . A complete listing is made of all compatible combinations of  $\mathcal{E}_1$  and  $\mathcal{E}_2$  in two and three dimensions. This leads to more possible symmetries than Hermann obtained, e.g., also to nonstoichiometric crystals. The order parameter space for the systems is found to be the quotient space  $\mathcal{E}_1/\mathcal{E}_2$ . In most cases it is identical to the order parameter space of low-dimensional *XY* spin systems. The Landau free energy is expanded as functional of the two-particle correlation function  $K$ ; the translation group is found to be  $\mathcal{E}_1 \times \mathcal{E}_2$ . A Landau mean-field theory can then be carried out by expanding the system free energy into a series of invariants of the active irreducible representations of  $K$  and mapping the free energy onto that for an *XY* planar spin system. We predict novel critical behavior for transitions between mesomorphic phases and “go no-go” selection rules for continuous transitions. We give the structure factors for X-ray scattering so changes in all such phase transitions are observable. The statistical symmetry groups, which describe point and translational symmetries of the mesophases, are classified. Proposals are made to include quasi-long-range or topological order in the classification scheme.

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**KEY WORDS:** Mesomorphic media; symmetry; phase transitions; statistical symmetry; long-range order; Landau theory.

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<sup>1</sup> This work supported in part by National Science Foundation (Division of International Programs), the PSC-BHE—Faculty Research Award CUNY and Deutsche Forschungsgemeinschaft.

<sup>2</sup> Physics Department, City College—City University of New York, New York, New York 10031.

<sup>3</sup> Institut für Theoretische Physik der Universität, D-8400 Regensburg, Federal Republic of Germany.

## 1. INTRODUCTION

“Statistical symmetry” seems to be a contradiction in terms. In condensed matter physics symmetry is the set of isometries of a completely ordered system such as a crystal. These isometries map corresponding points onto one another. A statistical array is disordered. A probability distribution of site occupancy is required to specify the array. No symmetry, apart from trivial (identity operation) seems present in the disordered system.

Several attempts have been made to ascribe symmetry to liquid crystal and other disordered systems. One of the more innovative and imaginative attempts is due to the mathematical crystallographer Carl Hermann. In the work reported here we have combined Hermann’s ideas with simple physical models, such as point particle and two-component  $XY$  spin. As a result, considerable progress was achieved in deepening and extending his ideas for concrete physical systems. Among the new features emerging is the possibility of describing phase transitions between disordered systems in a novel manner.

Professor Ilya Mikhaelovich Lifshitz had a continuing interest in the physics of phase transitions and disordered systems. We dedicate this paper to the memory of this esteemed scientist: it was a privilege to have known him.

The history of our subject goes back at least to 1922, when George Friedel<sup>(1)</sup> coined the term “mesomorphous states” (*Les états mesomorphes*) to describe media, which have an intermediate order between that of an amorphous solid (or isotropic fluid) and that of an ideal crystal. With regard to symmetry, the amorphous solid is a continuum, invariant under all operations of the Euclidean group  $E(3)$  (rigid arbitrary translations and rotations, and reflections), whereas the crystal is specified by a discrete space group. The 230 space groups were enumerated by Schoenflies<sup>(2)</sup> in 1891. A classification of the mesomorphous states by symmetry groups was first attempted in the 1920s and 1930s with the advent of systematic research on liquid crystals. It appeared natural to associate a mesomorphous phase with each subgroup of  $E(3)$ . Schubnikov,<sup>(3)</sup> and later Beckers *et al.*<sup>(4)</sup> determined the continuous subgroups of  $E(3)$  (the “continua”). The mixed continuous and discrete subgroups (the “semicontinua”) were listed by Schubnikov<sup>(5)</sup> and Goshen *et al.*,<sup>(6)</sup> Kastler *et al.*,<sup>(7)</sup> Kléman and Michel,<sup>(8)</sup> and Michel.<sup>(9)</sup> The possible symmetries of anisotropic fluids and their phase transitions were investigated by Boccara<sup>(10)</sup> within the Landau formalism. Janner and Janssen<sup>(11)</sup> proposed a high-dimensional crystallography of incommensurate solids. Another, nonsymmetry approach to the classification of mesophases was made by Hosemann<sup>(12)</sup> with the concept of paracrystals. Starting from a regular lattice, Hosemann introduced spatial deviations of the lattice points

from equilibrium. Defining sets of *a priori* fixed anisotropic mean square deviations, he arrived at a variety of perturbed lattices, which were identified with mesophases.

A different classification scheme was established in 1931 by Carl Hermann.<sup>(13)</sup> He arranged the mesophases, using two groups of "statistical translations," namely, a superordinate group ("Übergeordnete Gruppe"), and a subordinate group ("Untergeordnete Gruppe"). Despite considerable interest in Hermann's ideas through the years, there has been almost no development of the theory along lines suggested by his proposal.

We have analyzed Hermann's work and identified the physical observables addressed by his groups. These are the average density and the pair correlation function. The symmetry properties of both are combined in the two-particle (or density-density) correlation function. It then develops that in a point particle model of the system the superordinate group characterizes the translational type of the average density, i.e., discriminating between fluids, layer systems, rod lattices, and crystals. The subordinate group denotes the symmetry of substructures (chains or nets), distributed regularly or randomly in space. As has already been mentioned by Landau<sup>(14)</sup> and reiterated by Goshen *et al.*,<sup>(6)</sup> the many-particle correlation functions alone determine the symmetry of anisotropic fluids, for which the average density is isotropic and homogeneous. Hence we conclude: in the Hermann classification, the two-particle correlation function is central. In this paper we only consider the translational symmetry aspects of this correlation function.

In Section 2, we briefly outline Hermann's procedure. In Section 3, the translation symmetry of the two-particle correlation function  $K(\mathbf{r}_1, \mathbf{r}_2)$  is investigated. Two translation groups,  $\mathcal{E}_1$  and  $\mathcal{E}_2$ , are defined and identified with Hermann's super- and subordinate group. The direct product  $\mathcal{E}_1 \times \mathcal{E}_2$  yields the total translation group of  $K(\mathbf{r}_1, \mathbf{r}_2)$ . By listing the compatible combinations of both groups, all of Hermann's mesophases are retrieved and additional ones are discovered. We then look for possible phase transitions between the mesophases. In Section 4, most of them are mapped to low-dimensional systems of plane rotators, the order parameter spaces being given by the factor groups  $\mathcal{E}_1/\mathcal{E}_2$ . This allows qualitative formulation of phase sequences. Having recognized the two-particle correlation function as a central quantity in the description of mesomorphous phases, we use it as an order parameter in a phenomenological Landau theory of phase transitions (Section 5). In Section 6, remarks are made about the overall ("statistical") symmetry of mesophases, including point symmetry operations.

Mesomorphous phases, even of identical symmetry, can exist as ergodic or nonergodic states (compare fluids and amorphous solids). We do not

discuss the question posed by Zocher<sup>(15)</sup> or by Kastler *et al.*<sup>(7)</sup> of whether certain symmetry classes can be realized only by nonergodic (completely or partially disordered) systems not reaching thermal equilibrium. We will comment on the classification of strongly fluctuating systems, which *a priori* do not possess long-range order, and we will touch on the notion of "topological order" in Section 7.

## 2. HERMANN'S CLASSIFICATION SCHEME

In his analysis of homogeneous mesomorphous media, Hermann<sup>(13)</sup> identified certain structural units: volume elements of identical molecular arrangement (within certain statistical limits). The centers of any two structural units are connected by a vector. The resulting set of vectors is termed "statistical translations of the first kind." This set is processed in two steps. It is completed by addition and subtraction of the vectors to obtain a group, the so-called *superordinate* group. A subset of that set is extracted, which itself forms a group, whose translations leave the individual system invariant. This second group is the *subordinate* group. Both superordinate and subordinate group are needed to uniquely label a mesomorphous system. Whereas the subordinate group is discrete and defined in less than or equal to three directions, the superordinate group is continuous (more exactly: dense) along certain spatial directions, discrete along the complementary directions. Those directions, along which the subordinate group has translations, are labeled *D* ("direct translations"), those along which the superordinate group is discrete, are labeled *R* ("reciprocal translations"), and the remaining directions are labeled *S* ("statistical translations"). From the combinations of the three symbols, Hermann derived 20 translational types, nine of which he excluded as physically unrealistic or geometrically forbidden. In Fig. 1, the characteristic sets and groups are depicted for the following model systems: an amorphous solid (*SS*), a crystal [*(RD)*, *(RD)*], an ensemble of parallel chains displaced vertically and laterally at random (*SD*), and a crystal whose vertical planes have shifted randomly (*RD*). If, for example, several structures *SSD* with different chain directions are superposed, the symbol *D* is replaced by *P<sub>d</sub>* ("pseudotranslations"), where *d* denotes the degree of freedom of the chain directions: if *d* = 0, the set of directions is discrete, if *d* = 1, it is a one-dimensional manifold, if *d* = 2, a solid angle or the entire sphere. By including the pseudotranslations, Hermann obtained 11 additional translational types of mesophases.

Bernal and Fankuchen<sup>(16)</sup> classified plant viruses, Mabis<sup>(17)</sup> several organic compounds, by Hermann's method. In the articles of Mabis<sup>(17)</sup> or Hosemann and Müller<sup>(18)</sup> illustrated examples of the translational types are presented. However from Hermann's description of the translational groups,

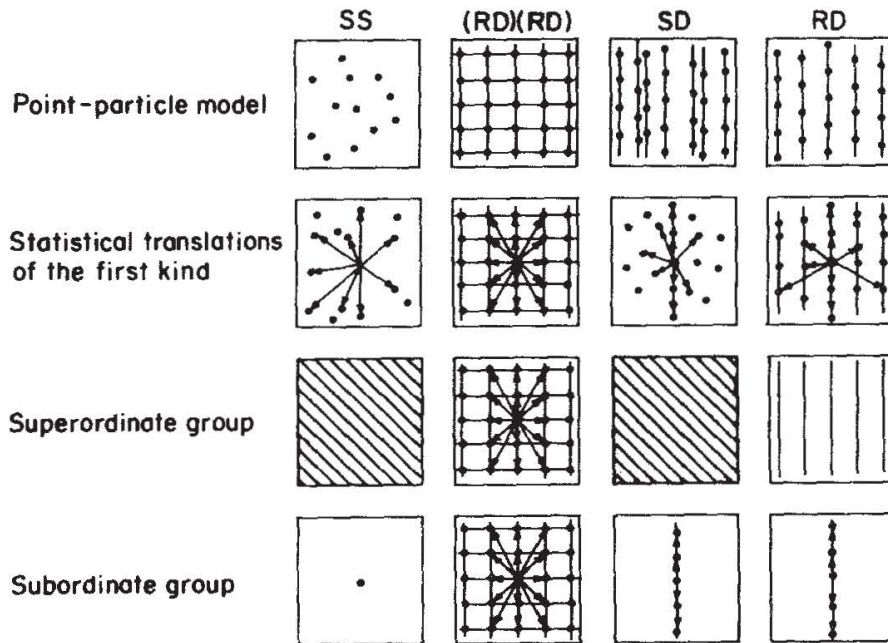


Fig. 1. Four models of two-dimensional Hermann systems; *SS*: amorphous solid; *(RD)(RD)*: crystal; *SD*: parallel chains of atoms, displaced vertically and horizontally at random; *RD*: crystal, whose vertical planes are displaced at random. In the first row, the point-particle model for each system is shown, in the following rows the statistical translations of the first kind, the superordinate and the subordinate groups as defined by Hermann.<sup>(13)</sup>

it is not evident what physical quantity is described by these groups. We shall show the connection between the two-particle correlation function, for point particle systems, and the translational symmetry of super- and subordinate groups.

### 3. TRANSLATION SYMMETRY OF THE TWO-PARTICLE CORRELATION FUNCTION

#### 3.1. Group Theoretical Considerations

In this section we analyze the translation symmetry of various correlation functions in a point-particle model.

For a system of  $N$  point particles of mass 1, which are placed at points  $\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_N$ , the density is

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{s}_i) \quad (1)$$

The mean density,

$$\bar{\rho}(\mathbf{r}) = \langle \rho(\mathbf{r}) \rangle = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{s}_i) \right\rangle \quad (2)$$

is obtained by configurational or temporal average. The two-particle correlation function is defined as

$$K(\mathbf{r}_1, \mathbf{r}_2) = \langle \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \rangle = \left\langle \sum_{i,j}^N \delta(\mathbf{r}_1 - \mathbf{s}_i) \delta(\mathbf{r}_2 - \mathbf{s}_j) \right\rangle \quad (3)$$

It yields the probability for two particles to be found: one at  $\mathbf{r}_1$  and one at  $\mathbf{r}_2$ , respectively. Now operators  $T(\mathbf{t}_1, \mathbf{t}_2)$  are introduced, which translate  $K$  separately in the two arguments:

$$T(\mathbf{t}_1, \mathbf{t}_2) K(\mathbf{r}_1, \mathbf{r}_2) = K(\mathbf{r}_1 - \mathbf{t}_1, \mathbf{r}_2 - \mathbf{t}_2) \quad (4)$$

The composition law is

$$T(\mathbf{t}_1, \mathbf{t}_2) T(\mathbf{t}'_1, \mathbf{t}'_2) = T(\mathbf{t}_1 + \mathbf{t}'_1, \mathbf{t}_2 + \mathbf{t}'_2) \quad (5)$$

We investigate the structure of the translational invariance group  $\mathcal{E}$  of  $K$ . First note the permutation symmetry

$$K(\mathbf{r}_1, \mathbf{r}_2) = K(\mathbf{r}_2, \mathbf{r}_1)$$

From this follows:

1. If  $T(\mathbf{t}_1, \mathbf{t}_2) \in \mathcal{E}$ , then also  $T(\mathbf{t}_2, \mathbf{t}_1) \in \mathcal{E}$ .
2. If  $T(\mathbf{0}, \mathbf{t}) \in \mathcal{E}$ , then also  $T(\mathbf{t}, \mathbf{0})$  and  $T(\mathbf{t}, \mathbf{t}) \in \mathcal{E}$ .

Two subgroups of  $\mathcal{E}$  are defined: the "diagonal,"

$$\mathcal{E}_1 \equiv \{T(\mathbf{t}, \mathbf{t})\}$$

which translates both arguments of  $K$  identically and represents the usual symmetry under rigid motions, and the "row,"

$$\mathcal{E}_2 \equiv \{T(\mathbf{0}, \mathbf{t})\}$$

Because of property 2,  $\mathcal{E}_2$  can be regarded as subgroup of  $\mathcal{E}_1$ . By the homomorphism

$$\pi: \mathcal{E} \rightarrow \mathcal{E}_2$$

$$T(\mathbf{t}_1, \mathbf{t}_2) \rightarrow T(\mathbf{0}, \mathbf{t}_2 - \mathbf{t}_1)$$

each element of  $\mathcal{E}$  is projected on one of  $\mathcal{E}_2$ . It is easily proved that  $\pi$  is a surjective (onto) homomorphism. Since  $\pi$  eliminates the parallel motion of both arguments, it has the property

3.  $\text{Ker } \pi = \mathcal{E}_1$ . (This leads to the following isomorphism):
4.  $\mathcal{E}_2 = \mathcal{E} / \mathcal{E}_1$ .

A change to the variables  $\tilde{\mathbf{r}} = \mathbf{r}_2 - \mathbf{r}_1$ ,  $\mathbf{r} = \mathbf{r}_1$  is now useful. For brevity we use the symbol  $K$  also for the correlation function in the new coordinates:  $K(\mathbf{r}, \tilde{\mathbf{r}}) = K(\mathbf{r}_1, \mathbf{r}_2)$ . A translation  $T(\mathbf{t}_2, \mathbf{t}_1)$  acts on the new coordinates like

$$\begin{aligned} T(\mathbf{t}_1, \mathbf{t}_2) K(\mathbf{r}, \tilde{\mathbf{r}}) &= K(\mathbf{r} - \mathbf{t}_1, \tilde{\mathbf{r}} - (\mathbf{t}_2 - \mathbf{t}_1)) \\ &\equiv S(\mathbf{t}_1, \mathbf{t}_2 - \mathbf{t}_1) K(\mathbf{r}, \tilde{\mathbf{r}}) \end{aligned}$$

In the notation

$$\begin{aligned} T(\mathbf{t}_1, \mathbf{t}_2) &= S(\mathbf{t}_1, \mathbf{t}_2 - \mathbf{t}_1) \\ S(\mathbf{u}, \mathbf{v}) &= T(\mathbf{u}, \mathbf{u} + \mathbf{v}) \end{aligned}$$

the above-defined groups assume the form

$$\begin{aligned} \mathcal{E}_1 &= \{S(\mathbf{u}, \mathbf{0})\} \\ \mathcal{E}_2 &= \{S(\mathbf{0}, \mathbf{v})\} \end{aligned} \tag{6}$$

From this one recognizes immediately that the total translation group of  $K$  is the direct product

$$\mathcal{E} = \mathcal{E}_1 \times \mathcal{E}_2$$

In the following chapter we will study the four basic translational types  $S$ ,  $D$ ,  $R$ ,  $(RD)$ , using simple prototype models in one dimension. From these we will conclude, that Hermann's superordinate group is to be interpreted as  $\mathcal{E}_1$ , the subordinate group as  $\mathcal{E}_2$ .

### 3.1. Basic Translational Types in One Dimension

In Table I we present the probability density  $p$ , average mass density  $\bar{\rho}$ , two-particle correlation function  $K(x_1, x_2) = K(x, \tilde{x})$ ,  $x = x_1$ ,  $\tilde{x} = x_2 - x_1$ , and the pair correlation function

$$G(\tilde{x}) = \frac{1}{N} \int dx K(x, \tilde{x}) \tag{7}$$

for four simple one-dimensional model systems, each consisting of  $N$  point particles. These represent an amorphous solid ( $S$ ), a fluid of interpenetrating chains ( $D$ ), a nonstoichiometric crystal ( $R$ ), and a regular crystal  $[(RD)]$ .

Also the groups  $\mathcal{E}_1$  and  $\mathcal{E}_2$  are listed; these were determined from the form of  $K$ . From these examples the following conclusions can be verified:

1. The group  $\mathcal{E}_2$  always is discrete. Whenever the correlations are random along one direction (as for systems  $S$  and  $R$ ), the two-particle

Table I. The Basic Translational Types of One-Dimensional Mesophases<sup>a</sup>

	$S$	$D$	$R$	$(RD)$
$\mathcal{E}_1$	$R$	$R$	$Z$	$Z$
$\mathcal{E}_2$	$1$	$Z$	$1$	$Z$
$\rho(x)$	$\sum_l \delta(x - s_l)$	$\sum_{j=1}^J \sum_l \delta(x - al - f_j)$	$\sum_l c_l \delta(x - al)$	$\sum_l \delta(x - al)$
$p$	$p(s_l) = L^{-1}$	$p(f_j) = a^{-1}$	$p(c_l)$	$-$
$\bar{\rho}$	$N/L$	$Ja^{-1}$	$\langle c \rangle \sum_l \delta(x - al)$	$\sum_l \delta(x - al)$
$K(x, \bar{x})$	$\frac{N}{L} \{ \delta(\bar{x}) + N - 1 \}$	$Ja^{-1} \sum_l \delta(\bar{x} - al) + J(J-1)a^{-2}$	$\Delta c^2 \delta(\bar{x}) \sum_l \delta(x - al) + \langle c \rangle^2 \sum_{l,l'} \delta(x - al)$ $\times \delta(\bar{x} - al')$	$\sum_{l,l'} \delta(x - al) \delta(\bar{x} - al')$
$G(\bar{x})$	$\delta(\bar{x}) + N - 1$	$\sum_l \delta(\bar{x} - al) + (J-1)a^{-1}$	$\Delta c^2 \delta(\bar{x}) + \langle c \rangle^2 \sum_l \delta(\bar{x} - al)$	$\sum_l \delta(\bar{x} - al)$
$S(q)$	$N(N-1) \delta(q) + \frac{N}{2\pi}$	$NJa^{-1} \sum_m \delta\left(q - m \frac{2\pi}{a}\right) + NJ(J-1)a^{-1} \delta(q)$	$\Delta c^2 \frac{N}{2\pi} + \frac{N}{a} \langle c \rangle^2 \sum_m \delta\left(q - m \frac{2\pi}{a}\right)$	$\frac{N}{a} \sum_m \delta\left(q - m \frac{2\pi}{a}\right)$

<sup>a</sup> For the systems  $S$ ,  $D$ ,  $R$ , and  $(RD)$  the table lists: the superordinate group  $\mathcal{E}_1$ , the subordinate group  $\mathcal{E}_2$ , the density of the individual system, the probability density  $p$  for the system parameters, the average density  $\bar{\rho}$ , the two-particle correlation function in coordinates  $x = x_1$ , and  $\bar{x} = x_2 - x_1$ , the pair correlation function  $G(\bar{x})$ , and the structure factor  $S(q)$ ;  $N$ : number of particles;  $L$ : chain length.



correlation function contains the peaked self-correlation term  $\delta(\tilde{x})$ , and hence is of point symmetry only.

2. Systems can be constructed [like  $D$ ,  $(RD)$ ], whose two-particle correlation function has discrete translational symmetry. This fact disproves Landau’s statement,<sup>(14)</sup> that  $K$  can only have point symmetry.

3. In homogeneous systems like  $S$  and  $D$ ,  $\bar{\rho}$  is constant,  $K(x, \tilde{x})$  does not depend on  $x$ , and  $G(\tilde{x}) = K(x, \tilde{x})/\bar{\rho}$ . Apparently  $\mathcal{E}_1$  is then also the translation symmetry group of  $\bar{\rho}$ , and  $\mathcal{E}_2$  that of  $G$ . But this fact proves true also for inhomogeneous systems like  $R$  or  $(RD)$ .<sup>4</sup> Therefore the two-particle correlation function combines the symmetry properties of both  $\bar{\rho}$  and  $G$ .

Note that for an amorphous solid the combination  $\mathcal{E}_1 = R$  (continuous translational symmetry) and  $\mathcal{E}_2 = 1$  (no symmetry) expresses the two contradictory properties of complete homogeneity of the ensemble average, but absence of translational symmetry for the individual system.

The preceding characteristic features of the one-dimensional systems can also be found in the four two-dimensional systems of Fig. 1. From all the model systems it became evident that  $\mathcal{E}_1$  is the superordinate, and  $\mathcal{E}_2$  the subordinate translation group in the sense of Hermann, where  $\mathcal{E}_1$  refers to  $\bar{\rho}$ , and  $\mathcal{E}_2$  to  $G$ .

### 3.3. The Translational Types of Mesomorphous Phases

In Tables II and III all translational types of mesomorphous media are listed for two and three dimensions. The enumeration is based on the following three conditions:

1. Since in our classification only those systems are included whose ensemble average has a translational symmetry in all spatial directions,  $\mathcal{E}_1$  is nontrivial along all directions. Hence incommensurate systems cannot be classified by this method.<sup>5</sup>

2.  $\mathcal{E}_2$  is discrete.

3.  $\mathcal{E}_2$  is a subgroup of  $\mathcal{E}_1$ .

<sup>4</sup> Since  $\bar{\rho}$  and  $G$  are derived from  $K$  by the relations

$$\bar{\rho}(\mathbf{r}) = \frac{1}{N} \int d^3\tilde{\mathbf{r}} K(\mathbf{r}, \tilde{\mathbf{r}}); \quad G(\tilde{\mathbf{r}}) = (1/N) \int d^3\mathbf{r} K(\mathbf{r}, \tilde{\mathbf{r}})$$

the statement is more exactly:  $\mathcal{E}_1$  and  $\mathcal{E}_2$  are subgroups of the translation groups  $\mathcal{E}'_1$  and  $\mathcal{E}'_2$  of  $\bar{\rho}$  and  $G$ , respectively. But the translational type (trivial, discrete, continuous) of  $\mathcal{E}_1$  and  $\mathcal{E}_2$  is always the same as that of the primed groups, and inequalities  $\mathcal{E}_1 \neq \mathcal{E}'_1$ ,  $\mathcal{E}_2 \neq \mathcal{E}'_2$  hold only in pathological cases.

<sup>5</sup> In Hermann’s original procedure (Section II), a crystal is of type  $S$  along each incommensurably modulated direction, since the completion of two incommensurate vectors to a group is dense in the real numbers.

The second condition follows by observing the self-correlation peak along directions of random particle distribution, the third condition from the permutation symmetry  $K(\mathbf{r}_1, \mathbf{r}_2) = K(\mathbf{r}_2, \mathbf{r}_1)$ .

In Tables II and III we also present the translational symmetry of the structure factor

$$S(\mathbf{q}) = \frac{N}{(2\pi)^d} \int d^d \tilde{\mathbf{r}} e^{i\mathbf{q} \cdot \tilde{\mathbf{r}}} G(\tilde{\mathbf{r}}) \quad (8)$$

in reciprocal space. Whenever  $\mathcal{E}_1$  is isomorphic to the group of integers  $Z$  (discrete and periodic), then the structure factor is also periodic along the same (respectively, dual) direction. Whenever  $\mathcal{E}_1$  is isomorphic to the group  $R$  of real numbers, then  $S(\mathbf{q})$  only has point symmetry. We denote system  $A$  as reciprocal to system  $B$ , if the structure factor of  $A$  has the translational symmetry of the pair correlation function of  $B$ .

From the 20 systems in three dimensions, Hermann allowed nine as mesophases (marked by an asterisk). He stated, that due to geometrical restriction the phases  $DDD$ ,  $DD(RD)$ ,  $D(RD)(RD)$ ,  $RRR$ ,  $RR(RD)$ ,  $R(RD)(RD)$ , are equivalent to  $(RD)(RD)(RD)$ . The first three of these systems, indeed, are without physical significance, since they represent fluids of interpenetrating crystals.  $RRR$ , however, is the classification for nonstoichiometric crystals,<sup>6</sup>  $RR(RD)$  for crystals of missing chains,  $(RD)(RD)R$  for crystals of missing planes or commensurably intercalated solids. The phases  $RRS$ ,  $DDS$ ,  $SR(RD)$ ,  $SD(RD)$ , and  $S(RD)(RD)$  were excluded as too inhomogeneous. But some of these have been found in nature, for examples  $RRS$ , which is the translational type for discotic liquid crystals.<sup>(19)</sup>

The notation of Tables II and III is simplified in the following respects: first, the coordinate systems used must not necessarily be orthonormal. Secondly, for systems like  $SS(RD)$ , the primitive translation vector  $\mathbf{a}$  of  $\mathcal{E}_2$  may not necessarily stand perpendicular to the planes of the mass density wave  $\bar{\rho}$ , but is only required to have a nonzero component along the normal. Given  $\bar{\rho}$ , many compatible pair correlation functions can be constructed, for example, by rotating  $\mathbf{a}$  about the normal of the plane. The Hermann systems containing pseudotranslations are superpositions of systems, which are degenerate in this respect, and their X-ray patterns (structure factors) are superpositions like a powder spectrum. To limit the abundant variety of possible combinations, restrictions must be imposed, like the homogeneity

<sup>6</sup> It is interesting to note, that in a comment to Hermann's paper [*Z. Kristallogr.* 79:338 (1931)] P. P. Ewald asked the question of how to classify nonstoichiometric crystals ("durchlöcherter Gitter").

Table II. Translational Types of Two-Dimensional Mesomorphous Phases<sup>a</sup>

No.	$\mathcal{E}_1$	$\mathcal{E}_2$	Hermann symbol	Transl. type struct. fact	Reciprocity	$\mathcal{E}_1/\mathcal{E}_2$	Analogous system; characterization
1*	$R_x \times R_y$	1	SS	1	Self-rec.	$R^2$	Amorphous solid
2*	$R_x \times R_y$	$Z_y$	SD	1	4	$R \times U(1)$	1D spin fluid
3	$R_x \times R_y$	$Z_x \times Z_y$	DD	1	8	$U(1)^2$	—
4*	$R_x \times Z_y$	1	SR	$Z_y$	2	$R \times Z$	2D smectic liquid crystal
5*	$R_x \times Z_y$	$Z_y$	S(RD)	$Z_y$	Self-rec.	R	1D chain fluid
6*	$R_x \times Z_y$	$Z_x$	DR	$Z_y$	self-rec.	$U(1) \times Z_y$	1D spin lattice
7	$R_x \times Z_y$	$Z_x \times Z_y$	D(RD)	$Z_y$	9	$U(1)$	—
8	$Z_x \times Z_y$	1	RR	$Z_x \times Z_y$	3	$Z^2$	Nonstoich. crystal
9	$Z_x \times Z_y$	$Z_y$	R(RD)	$Z_x \times Z_y$	7	Z	Missing chains
10*	$Z_x \times Z_y$	$Z_x \times Z_y$	(RD)(RD)	$Z_x \times Z_y$	Self-rec.	1	Regular crystal

<sup>a</sup> The characteristic data for the two-dimensional Hermann systems are listed. For  $\mathcal{E}_2$  and  $\mathcal{E}_1/\mathcal{E}_2$  partly shorthand symbols are used, for example  $\mathcal{E}_2 = Z_y$  instead of  $\mathcal{E}_2 = 1_x \times Z_y$  for system 2, or  $\mathcal{E}_1/\mathcal{E}_2 = R^2$  instead of  $\mathcal{E}_1/\mathcal{E}_2 = R_x \times R_y$  for system 1. In the last column the corresponding plane-rotator model or a short characterization is given.

Table III. Translational Types of Three-Dimensional Mesomorphous Phases<sup>a</sup>

No.	$\mathcal{E}_1$	$\mathcal{E}_2$	Hermann symbol	Transl. type struct. fact.	Reciprocity	$\mathcal{E}_1/\mathcal{E}_2$	Analogous system; description
1*	$R_x \times R_y \times R_z$	1	SSS	1	Self-rec.	$R^3$	Amorph. system
2*	$R_x \times R_y \times R_z$	$Z_z$	SSD	1	5	$R^2 \times U(1)$	2D spin fluid
3	$R_x \times R_y \times R_z$	$Z_x \times Z_y$	SDD	1	11	$R \times U(1)^2$	1D fluid double spins
4	$R_x \times R_y \times R_z$	$Z_x \times Z_y \times Z_z$	DDD	1	17	$U(1)^3$	—
5*	$R_x \times R_y \times Z_z$	1	SSR	$Z_z$	2	$R^2 \times Z$	Smectic liq. crystal
6*	$R_x \times R_y \times Z_z$	$Z_z$	SS(RD)	$Z_z$	Self-rec.	$R^2$	2D fluid of chains
7*	$R_x \times R_y \times Z_z$	$Z_y$	SDR	$Z_z$	Self-rec.	$R \times U(1) \times Z$	2D smectic of spins
8*	$R_x \times R_y \times Z_z$	$Z_x \times Z_y$	DDR	$Z_z$	12	$U(1)^2 \times Z$	1D lattice double spins
9	$R_x \times R_y \times Z_z$	$Z_y \times Z_z$	SD(RD)	$Z_z$	13	$R \times U(1)$	1D spin fluid
10	$R_x \times R_y \times Z_z$	$Z_x \times Z_y \times Z_z$	DD(RD)	$Z_z$	18	$U(1)^2$	—
11	$Z_x \times Z_y \times R_z$	1	RRS	$Z_x \times Z_y$	3	$Z^2 \times R$	Rod lattice
12*	$Z_x \times Z_y \times R_z$	$Z_z$	RRD	$Z_x \times Z_y$	8	$Z^2 \times U(1)$	2D spin lattice
13	$Z_x \times Z_y \times R_z$	$Z_y$	R(RD)S	$Z_x \times Z_y$	9	$Z \times R$	2D smectic liq. crystal
14	$Z_x \times Z_y \times R_z$	$Z_x \times Z_y$	(RD)(RD)S	$Z_x \times Z_y$	Self-rec.	$R$	1D fluid of nets
15*	$Z_x \times Z_y \times R_z$	$Z_y \times Z_z$	R(RD)D	$Z_x \times Z_y$	Self-rec.	$Z \times U(1)$	1D spin lattice
16	$Z_x \times Z_y \times R_z$	$Z_x \times Z_y \times Z_z$	(RD)(RD)D	$Z_x \times Z_y$	19	$U(1)$	—
17	$Z_x \times Z_y \times Z_z$	1	RRR	$Z_x \times Z_y \times Z_z$	4	$Z^3$	Nonstoich. crystal
18	$Z_x \times Z_y \times Z_z$	$Z_z$	RR(RD)	$Z_x \times Z_y \times Z_z$	10	$Z^2$	Missing chains
19	$Z_x \times Z_y \times Z_z$	$Z_x \times Z_y$	(RD)(RD)R	$Z_x \times Z_y \times Z_z$	16	$Z$	Missing planes
20*	$Z_x \times Z_y \times Z_z$	$Z_x \times Z_y \times Z_z$	(RD)(RD)(RD)	$Z_x \times Z_y \times Z_z$	Self-rec.	1	Regular crystal

<sup>a</sup> Same data as in Table II, but for three spatial dimensions.

conditions in Hermann's original paper. These conditions, and not symmetry principles, determine the classification by pseudotranslations, and therefore we do not pursue it further.

#### 4. MAPPING OF HERMANN SYSTEMS TO PLANE ROTATOR MODELS

Most Hermann systems are equivalent to low-dimensional fluids or crystals consisting of two-dimensional unit spins. Let us take, for example, as representative for system *SD* the ensemble of chains of Fig. 1. If a straight line is drawn transverse to the chains, each chain is characterized by two coordinates: the position  $x \in R_x$  where it cuts the line, and the distance  $d$  of the first atom above the line. But  $d$  is defined only modulo the periodicity length of the chain, and therefore must be replaced by a phase factor  $\exp i\phi \in U(1)$ , where  $\phi = 2\pi d/a$ . The order parameter space is equal to  $R_x \times U(1)_y$  (the index  $y$  expresses the fact that it is the translational degree of freedom along the  $y$  direction, which has been replaced by the phase factor). The system *SD* thus has been mapped to a one-dimensional fluid of unit spins (*XY* spins, plane rotators).

Formally, an order parameter space is established as a coset space  $G/H$ , where  $G$  is an unbroken symmetry group, acting on the order parameter, and  $H$  the isotropy or fix-point group of the order parameter. This identification is well known from the topological theory of defects.<sup>(9,20,21)</sup> For the Hermann systems,  $H$  is equal to  $\mathcal{E}_2$ , which is the fix-point group of a subsystem, and  $G$  is equal to  $\mathcal{E}_1$ . In the above example the order parameter space  $R_x \times U(1)_y$  results from the factorization  $\mathcal{E}_1/\mathcal{E}_2 = R_x \times R_y/1_x \times Z_y = R_x \times (R_y/Z_y)$ , since the real numbers modulo the integers are isomorphic to  $U(1)$ , the unit circle in the complex plane. All the factor spaces  $\mathcal{E}_1/\mathcal{E}_2$  are listed in Tables II and III together with a short characterization. System *DDR*, for example, corresponds to a one-dimensional crystal of double spins ( $U(1)_x \times U(1)_y$ ), or tori.

If pseudotranslations are present, the order parameter space is enlarged by a degree of freedom. For system *SP*<sub>1</sub> it is  $\{R_x \times U(1)_y\} \times S^1$ , where  $\theta \in S^1$  is the angle of the chain direction, measured from a reference line.

In the language of spins, a transition *SD* → *RD* corresponds to an ordering of the paramagnetic spin fluid to a paramagnetic crystal (ordering of *positions*). A transition *SD* → *S(RD)* corresponds to an ordering of the spin *angles*, i.e., to a transition from a paramagnetic to a ferromagnetic fluid. Possible sequences of phase transitions are drawn in Fig. 2. The analogy should go beyond an isomorphism of order parameter spaces. The interaction potential for two chains can be assumed to consist of a distance-dependent hard core interaction  $V(x_2 - x_1)$ , and an angle-dependent

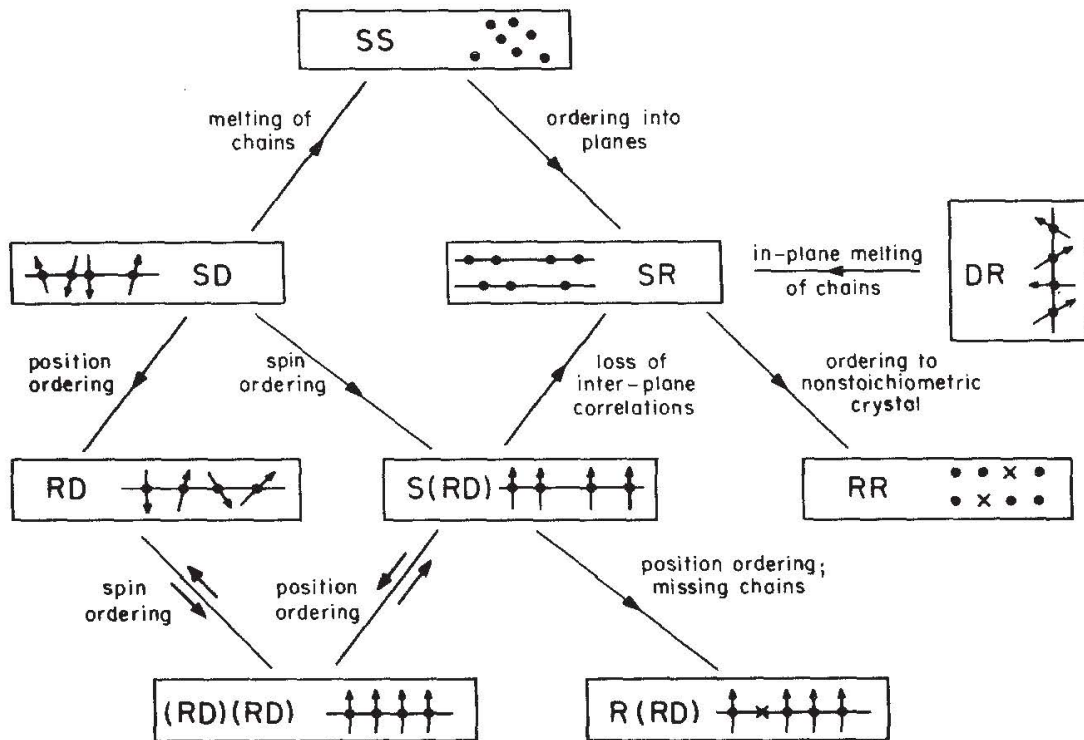


Fig. 2. Possible sequence of phase transitions for two-dimensional Hermann systems. For part of the systems the corresponding plane-rotator model is drawn. The arrows indicate the direction of symmetry breaking. Whenever two arrows are shown, one of the translational groups is broken, the other one is raised.

Heisenberg exchange term, proportional to  $\cos(\phi_2 - \phi_1)$ . If such strongly anisotropic mesophases could be prepared in thermodynamic equilibrium, they would be representatives for low-dimensional  $XY$  models. The transitions between these systems and the thermodynamic variables (correlation lengths, critical exponents) could easily be monitored, since each phase carries a specific X-ray pattern. Systems not reaching thermodynamic equilibrium represent spin glasses. However, the spin degree of freedom might be quenched here directly, possibly owing to an inertness of the chains, whereas in real spin glasses it is positional disorder that induces spin disorder.

The arrows in Fig. 2 point along the direction of symmetry breaking. Note that in the transition  $SS \rightarrow SD$  (chain crystallization) the symmetry is raised.  $\mathcal{E}_1$  does not change, but  $\mathcal{E}_2$  is increased from the trivial group to  $Z$ . In the transition  $RD \rightarrow (RD)(RD)$ , the superordinate group  $\mathcal{E}_1 = Z_x \times R_y$  is broken to  $Z_x \times Z_y$ , but the subordinate group  $\mathcal{E}_2 = 1_x \times Z_y$  is increased to  $Z_x \times Z_y$ . The Hermann systems provide many unusual possibilities for phase transitions. We now will investigate these by Landau theory.

## 5. A LANDAU THEORY FOR PHASE TRANSITIONS BETWEEN MESOPHASES

Since the two-particle correlation function  $K$  proved central in the description of mesophases, we will use it in place of the density function in a phenomenological Landau theory of phase transitions. But for this purpose we first have to study the irreducible representations of the symmetry group of  $K(\mathbf{r}_1, \mathbf{r}_2)$ .

### 5.1. Irreducible Representations of the Symmetry Group of $K$

We still leave aside the rotational symmetry of the two-particle correlation function. But we cannot ignore the invariance under the permutation operation  $PK(\mathbf{r}_1, \mathbf{r}_2) = K(\mathbf{r}_2, \mathbf{r}_1)$ , which leads to the subgroup relation  $\mathcal{E}_2 \subset \mathcal{E}_1$ . The group that has to be considered, is generated by the elements of  $\mathcal{E} = \mathcal{E}_1 \times \mathcal{E}_2$  and  $\mathcal{P} = \{1, P\}$ , and is denoted  $(\mathcal{P}, \mathcal{E})$ .

$P$  commutes with the elements of  $\mathcal{E}_1$ , but not with the elements of  $\mathcal{E}_2$ . Hence  $(\mathcal{P}, \mathcal{E})$  is nonabelian, but  $\mathcal{E}$  is an Abelian subgroup of  $(\mathcal{P}, \mathcal{E})$ . Irreducible representations of  $(\mathcal{P}, \mathcal{E})$  can therefore be constructed as is done for space groups.<sup>(22)</sup> One first looks for the irreducible representations of  $\mathcal{E}$ . Since in coordinates  $(\mathbf{r}, \tilde{\mathbf{r}})$  the subgroups  $\mathcal{E}_1$  and  $\mathcal{E}_2$  act separately on the two arguments, the irreducible representations of  $\mathcal{E}$  are direct products of those of  $\mathcal{E}_1$  and  $\mathcal{E}_2$ :

$$f_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r}, \tilde{\mathbf{r}}) = e^{i(\mathbf{k} \cdot \mathbf{r} + \tilde{\mathbf{k}} \cdot \tilde{\mathbf{r}})} f_{\mathbf{k}}^{(1)}(\mathbf{r}) f_{\tilde{\mathbf{k}}}^{(2)}(\tilde{\mathbf{r}}) \quad (9)$$

Here the "periodic" function

$$u_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r}, \tilde{\mathbf{r}}) = f_{\mathbf{k}}^{(1)}(\mathbf{r}) f_{\tilde{\mathbf{k}}}^{(2)}(\tilde{\mathbf{r}}) \quad (10)$$

is invariant under the operations of  $\mathcal{E}$ . Application of  $P$  turns the pair  $(\mathbf{r}, \tilde{\mathbf{r}})$  of spatial vectors into  $(\mathbf{r} + \tilde{\mathbf{r}}, -\tilde{\mathbf{r}})$ , and the pair  $(\mathbf{k}, \tilde{\mathbf{k}})$  of wave vectors into  $(\mathbf{k}, \mathbf{k} - \tilde{\mathbf{k}})$ :

$$Pf_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r}, \tilde{\mathbf{r}}) = e^{i(\mathbf{k} \cdot \mathbf{r} + (\mathbf{k} - \tilde{\mathbf{k}}) \cdot \tilde{\mathbf{r}})} f_{\mathbf{k}}^{(1)}(\mathbf{r} + \tilde{\mathbf{r}}) f_{\tilde{\mathbf{k}}}^{(2)}(-\tilde{\mathbf{r}}) \quad (11)$$

Owing to the subgroup relation  $\mathcal{E}_2 \subset \mathcal{E}_1$ ,  $u_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r} + \tilde{\mathbf{r}}, -\tilde{\mathbf{r}})$  remains invariant under the operations of  $\mathcal{E}$ . The next steps are (i) determine the group  $\mathcal{P}_{\mathbf{k}\tilde{\mathbf{k}}} \subset \mathcal{P}$  of the wavevector; (ii) determine an irreducible representation of  $\mathcal{P}_{\mathbf{k}\tilde{\mathbf{k}}}$ , say,  $\phi_1(\mathbf{r}, \tilde{\mathbf{r}})$ ; and (iii) attach  $\phi_2(\mathbf{r}, \tilde{\mathbf{r}}) = P\phi_1(\mathbf{r}, \tilde{\mathbf{r}})$ .

There are two possibilities:

1.  $\mathcal{P}_{\mathbf{k}\tilde{\mathbf{k}}} = 1$ . Then  $(\mathbf{k}, \tilde{\mathbf{k}})$  is not equivalent to (equal up to a reciprocal lattice vector) to  $(\mathbf{k}, \mathbf{k} - \tilde{\mathbf{k}})$ . The basis functions  $\phi_1$  and  $\phi_2$  transform differently under the operations of  $\mathcal{E}_2$ , and the representations are always two dimensional.

2.  $\mathcal{P}_{\mathbf{k}\tilde{\mathbf{k}}} = \mathcal{P}$ . Then  $k = 2\tilde{k} + \mathbf{H}$ , where  $\mathbf{H}$  is a vector reciprocal to the translations of  $\mathcal{E}_2$ . The representations are two and one dimensional. For one-dimensional representations the invariant function  $u_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r}, \tilde{\mathbf{r}})$  must be composed of plane waves of the form

$$\exp\{i(\mathbf{Q} \cdot \mathbf{r} + \tilde{\mathbf{Q}} \cdot \tilde{\mathbf{r}})\}, \quad \text{with } \mathbf{Q} = 2\tilde{\mathbf{Q}} + \mathbf{H}$$

Here  $\mathbf{Q}$  is a vector reciprocal to the translations of  $\mathcal{E}_1$ ;  $\tilde{\mathbf{Q}}$  and  $\mathbf{H}$  are reciprocal to the translations of  $\mathcal{E}_2$ .

## 5.2. Landau Expansion of the Thermodynamic Potential

We modify Landau's theory<sup>(14)</sup> by expanding the thermodynamic potential  $\Phi$  in functionals of the two-particle correlation function.  $K$  is separated into components  $K_0 + \delta K$ , where  $K_0$  is the correlation function of the high-symmetry phase. The term  $\delta K$  is expanded into basis functions of the irreducible representations of the higher symmetry group. In investigating lines of phase transitions, only one irreducible representation is needed. If we are dealing with translational symmetry only, the expansion is simple: denote by  $\phi$  the first basis function of an irreducible representation. Then  $\delta K$  must be symmetric with respect to  $P$ , and it must be real. Therefore  $\delta K$  is of the form

$$\delta K = \frac{1}{2}c\{\phi + P\phi + \phi^* + (P\phi)^*\} \quad (12)$$

which contains only a single real order parameter  $c$ . If we assume  $\phi$  to have the form of Eq. (9) and  $u_{\mathbf{k}\tilde{\mathbf{k}}}$  Eq. (10) to be real, then we obtain

$$\begin{aligned} \delta K = c\{ & \cos(\mathbf{k} \cdot \mathbf{r} + \tilde{\mathbf{k}} \cdot \tilde{\mathbf{r}}) u_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r}, \tilde{\mathbf{r}}) \\ & + \cos[\mathbf{k} \cdot \mathbf{r} + (\mathbf{k} - \tilde{\mathbf{k}}) \cdot \tilde{\mathbf{r}}] u_{\mathbf{k}\tilde{\mathbf{k}}}(\mathbf{r} + \tilde{\mathbf{r}}, -\tilde{\mathbf{r}})\} \end{aligned} \quad (13)$$

Novel features of phase transitions become apparent already when looking at transitions between the basic one-dimensional translational types  $S$ ,  $D$ ,  $R$ , and  $(RD)$ . The transitions  $S \rightarrow R$ ,  $S \rightarrow (RD)$  can be treated as in conventional Landau theory, so we concentrate on  $S \rightarrow D$  and  $D \rightarrow (RD)$ .<sup>7</sup> The transition  $R \rightarrow (RD)$  is similar to  $S \rightarrow D$ .  $D \rightarrow R$  can be studied as two-step transition  $D \rightarrow S \rightarrow R$ .

<sup>7</sup> The one-dimensional system  $D$  of interpenetrating chains is as unphysical as system  $DDD$  of interpenetrating crystals. But when going to higher dimensions, for example to system  $SD$ , the chains are pulled apart along the additional dimension.



For the transition  $D \rightarrow (RD)$ , the symmetric function  $u$  is independent of  $x = x_1$ , since  $D$  is homogeneous. If we take  $u$  as real and even in  $\tilde{x}$ , the expansion of  $\delta K$  assumes the form

$$\delta K = c\{\cos(kx + \tilde{k}\tilde{x}) + \cos[kx + (k - \tilde{k})\tilde{x}]\} u(\tilde{x}) \tag{14}$$

If the pair correlation is to retain its periodicity in the transition, the group of the wave vector must be  $\mathcal{P}$  (case 2 of Section 5.1). Hence  $\mathbf{k} = 2\tilde{\mathbf{k}} + \tilde{\mathbf{K}}$ , and  $\tilde{\mathbf{k}}$  must be commensurate with the reciprocal lattice vectors belonging to  $\mathcal{E}_2$ . If in addition the pair correlation does not change its symmetry (rigid chains),  $\tilde{\mathbf{k}}$  must be a reciprocal lattice vector. Let us assume  $\tilde{\mathbf{k}} = \mathbf{0}$ , so that

$$\delta K = c\{\cos kx + \cos k(x + \tilde{x})\} u(\tilde{x}) \tag{15}$$

Now  $k$  can only take the discrete values of a reciprocal lattice vector to  $\mathcal{E}_2$ . All the allowed irreducible representations are labeled by discrete indices. There are no Lifshitz terms and no third-order invariants. The Landau expansion is of the same form as for a ferromagnetic transition:

$$\Phi = \Phi_0 + A(\tilde{\mathbf{K}})c^2 + B(\tilde{\mathbf{K}})c^4 \tag{16}$$

allowing a second-order phase transition. For  $\tilde{K} = 2\pi/a$  one obtains a situation as in Fig. a (along the  $y$  direction a translational type  $S$  is assumed), for  $\tilde{K} = 3 \cdot 2\pi/a$  one obtains a situation as in Fig. 3b.

The transition  $S \rightarrow D$  is remarkable, because  $D$  is the high-symmetry phase (Section 4). Instead of dealing with symmetry restoration,<sup>(23)</sup> we consider the reverse process  $D \rightarrow S$ . Both phases are homogeneous. Therefore  $k = 0$ , and  $u(x, \tilde{x})$  does not depend on  $x$ . With  $u(\tilde{x})$  real and even we obtain

$$\delta K = 2c \cos \tilde{k}\tilde{x} u(\tilde{x})$$

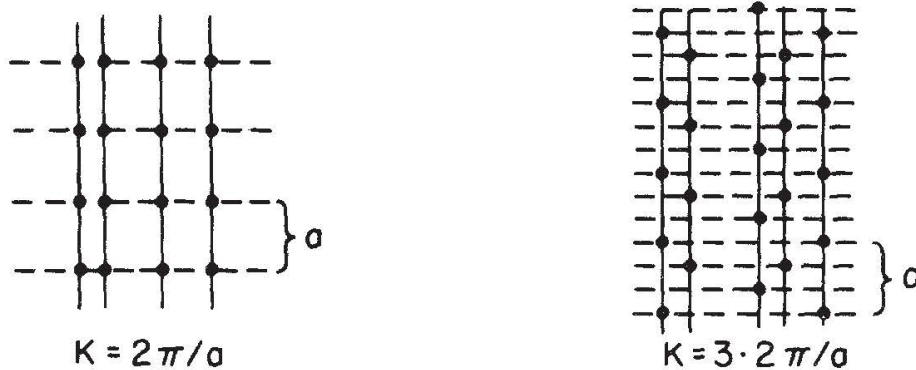


Fig. 3. Result of the phase transition  $SD \rightarrow S(RD)$  according to Landau theory for irreducible representations with wave vector  $k = K = 2\pi/a$  and  $3 \cdot 2\pi/a$ .

For the chains to lose periodicity,  $\tilde{k}$  must be incommensurate with the reciprocal lattice vectors of the subordinate group. Melting of chains can occur only via a transition to incommensurability.

Transitions of two- and three-dimensional systems can be found by combining the transitions of the elementary one-dimensional types. Here symmetry breaking and symmetry restoration can take place simultaneously, as for example in the transition  $RD \rightarrow (RD)(RD)$ . In this case, if the chains are rigid, the system is mapped to a plane rotator model, and the process corresponds to a ferromagnetic phase transition of a one-dimensional crystal. In other cases, the transition can be performed in two steps.

## 6. THE STATISTICAL SYMMETRIES

The statistical symmetries of a mesomorphous point particle system—as defined by Hermann—are the symmetries in the usual sense: translations, rotation, reflections, etc., which leave the configurational or temporal average invariant. With regard to this average, we have to be more specific. The translational symmetry is certainly that of the average density  $\bar{\rho}$ . However, the point symmetry of  $\bar{\rho}$  can be broken by the shape of the pair correlation function  $G$ , as demonstrated by the homogeneous system  $SSD$ . It is imaginable that the point symmetry of  $G(\mathbf{r})$  is again broken by higher correlations, for example by the triplet correlation function

$$G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{N} \int d^3r' \langle \rho(\mathbf{r}') \rho(\mathbf{r}' + \mathbf{r}_1) \rho(\mathbf{r}' + \mathbf{r}_2) \rangle \quad (17)$$

The point where this sequence of symmetry breaking ends determines the rotational part of the statistical symmetry.

Taking into account only  $\bar{\rho}$  and  $G$ , we can classify the statistical symmetry groups along the lines of Goshen *et al.*<sup>(6)</sup> by enumerating the subgroups of the Euclidean group  $E(3)$ . A coarse classification of these groups is given by the translational type of  $\bar{\rho}$ , i.e., by  $\mathcal{E}_1$ . The subgroups of  $E(3)$  compatible with  $\mathcal{E}_1$  are then restricted by the type of  $\mathcal{E}_2$ . The different three-dimensional Hermann systems, with the exception of  $DDD$ ,  $DD(RD)$ , and  $D(RD)(RD)$ , can be associated with the following statistical symmetry groups  $\mathcal{S}$ :

(i) If  $\mathcal{E}_1 = R_x \times R_y \times R_z$ , then  $\mathcal{S} = \mathcal{E} \wedge \mathcal{G}$ , where  $\wedge$  denotes the semidirect product, and  $\mathcal{G}$  is a subgroup of  $O(3)$ .

(ii) If  $\mathcal{E}_1 = R_x \times R_y \times Z_z$ , then  $\mathcal{S}$  is any one-dimensional space group (listed in Ref. 6).

(iii) If  $\mathcal{E}_1 = Z_x \times Z_y \times R_z$ , then  $\mathcal{S}$  is any of the 80 two-dimensional space groups (also Ref. 6).

(iv) If  $\mathcal{E}_1 = Z \times Z_y \times Z_z$ , then  $\mathcal{S}$  is any of the 230 three-dimensional space groups.

Given  $\mathcal{S}$ , the following restrictions are imposed by the subordinate groups:

- (a) If  $\mathcal{E}_2 = 1$ , there is no restriction.
- (b) If  $\mathcal{E}_2 = Z_x$ , then only subgroups of  $\mathcal{S} \cap [(R_x \times R_y \times R_z) \wedge D_{\infty h}^z]$  are allowed. The superscript in  $D_{\infty h}^z$  denotes the main rotation axis.
- (c) If  $\mathcal{E}_2 = Z_x \times Z_y$ , then only crystallographic point groups are allowed, i.e., subgroups of  $\mathcal{S} \cap [(R_x \times R_y \times R_z) \wedge D_{nh}^z]$   $n = 1, 2, 3, 4, 6$ .

Hermann also introduced the notion of a "semiexact symmetry group." This is a subgroup of  $\mathcal{S}$ , whose elements leave the individual substructures (the local order) invariant. A uniaxial nematic liquid crystal of symmetry  $D_{\infty h}$ , for example, could be composed of biaxial molecules, whose main axes are aligned, but whose biaxial directors are distributed at random. The semiexact symmetry group is  $D_{2h}$ . Correlation functions for the local order and their symmetries require methods taken from the statistical geometry of liquids and are beyond the scope of this paper.

## 8. FLUCTUATIONS

In low-dimensional systems, like two-dimensional crystals, or in media of strongly anisotropic correlations, like the smectic liquid crystals, true long-range order is absent.<sup>(24)</sup> The isomorphism between Hermann systems and low-dimensional  $XY$  models, and the anisotropic form of the two-particle correlation functions implies, that in most of the mesophases the order is destroyed by fluctuations. So does it make sense to classify the mesomorphous media by symmetry groups?

Order parameter fluctuations require the existence of an order parameter itself, i.e., an underlying long-range order which is disturbed. This order is classified by the statistical symmetries. But the statistical symmetry group  $H$ , together with an unbroken symmetry group  $G$ , also determines the type of fluctuations occurring. If  $G$  is the invariance group of the bulk free energy, that part of the order parameter space, which is affected by the low-energy fluctuations, corresponds to the coset space  $G/H$  (the same principle was applied in mapping the Hermann systems to plane rotator models in Section 4). We illustrate this statement by several examples.

In a two-dimensional ferromagnet, the bulk energy  $F = a\mathbf{M}^2 + b\mathbf{M}^4$  is invariant under rotations of the magnetization vector  $\mathbf{M}$ :  $G = SO(2)$ . The fix-point group of the ordered phase is trivial:  $H = 1$ . The coset space  $G/H = SO(2)$  is equal to the set of directions  $\{\phi \mid 0 \leq \phi < 2\pi\} = U(1)$  of  $\mathbf{M}$ . The

strongest fluctuations are those in  $\phi$ , and not those in the length  $|\mathbf{M}|$ . The correlation function characterizing the low-energy fluctuations is  $\langle \exp i\{\phi(\mathbf{r}) - \phi(\mathbf{0})\} \rangle$ , since the phase factor  $\exp i\phi$  serves as coordinate in  $U(1)$ . The same correlation function is applicable to system  $SS(RD)$ , where  $\phi = 2\pi d/a$  (Section 4).

In the crystallization of a two-dimensional liquid to the hexatic phase<sup>(25)</sup> the rotational symmetry of the pair correlation function is broken from  $G = SO(2)$  to  $H \cong C_6$ . The coset space  $G/H = SO(2)/C_6$  is one-sixth of the circle and is parametrized by  $\exp i6\theta$ , where  $\theta$  is the next neighbor bond angle. The correlation function investigated is  $\langle \exp i6\{\theta(\mathbf{r}) - \theta(\mathbf{0})\} \rangle$ . For the two-dimensional crystal one obtains:  $G = R_x \times R_y$ ,  $H = Z_x \times Z_y$ ,  $G/H \cong U(1)_x \times U(1)_y$ . The order parameter fluctuates in a torus, parametrized by  $\exp i\mathbf{Q} \cdot \mathbf{u}$ , where  $\mathbf{Q}$  is reciprocal lattice vector, and  $\mathbf{u}$  is a displacement. The fluctuations are characterized by the Debye–Waller correlation function  $\langle \exp i\mathbf{Q} \cdot \{\mathbf{u}(\mathbf{r}) - \mathbf{u}(\mathbf{0})\} \rangle$ .

In these examples, the correlation functions decrease algebraically as  $r^{-\eta}$  due to low-energy excitations (spin waves, phonons) and—since the first homotopy group is nontrivial—due to the presence of bound defect–antidefect pairs. The defects are vortices in the  $XY$  model, and screw dislocations with Burgers vector parallel to the chain in the system  $SS(RD)$ .

This type of order is denoted topological<sup>(26)</sup> or quasi-long-range. Order and fluctuations are labeled by a single Hermann symbol. When the defect pairs unbind, the correlation functions decay exponentially, giving rise to a new phase. One has to change the Hermann symbol with the onset of short-range order. Otherwise one would retreat to Hosemann's concept, where one basic structure is fixed, and the mesomorphous phases are simulated by different types and degrees of fluctuations.

## ACKNOWLEDGMENTS

We thank Professor Serge Galam and Professor Zhao Bin Su for valuable discussions.

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