# Images, Landau expansions, and symmetry changes

Serge Galam
*Département de Recherches Physiques, T22-E3, Université Pierre et Marie Curie (UA71), 75252 Paris Cedex 05, France*

Dorian M. Hatch
*Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602*
(Received 1 August 1986)

The phase diagrams obtained from the fourth-degree Landau expansions associated with the $C_4$ and $C_{4v}$ images are compared. While the first image yields a Landau expansion with a four-dimensional parameter space $(\alpha_1,\alpha_2,\beta_1,\beta_2)$, the second yields a potential which is contained in the three-dimensional subspace with $\beta_2=0$. Within this subspace the phase diagrams of both $C_4$ and $C_{4v}$ are identical. Two ordered phases (with the order parameter along either an axis or a diagonal, respectively) are separated by a first-order line. Analysis of symmetry changes involved lead, however, to different results. In the $C_{4v}$ case the two phases have distinct symmetries. On the other hand the $C_4$ image implies identical symmetry in the two ordered phases. Physical interpretation of the phase diagram is thus directly related to the actual image. Experimental consequences are discussed.

## I. INTRODUCTION

The study of phase transitions and the construction of phase diagrams are articulated around minima of the free energy. Precise determination of the actual free energy is therefore of central importance. The phenomenological approach of mean field[1] provides a potential which can be expanded in powers of the order parameters. Landau theory defines a quantitative framework upon which to build the free-energy expansion using group theory.[2] The degree before which such an expansion cannot be stopped if all possible lower symmetries are to be obtained is determined by the group structure of the higher-symmetry phase and the symmetry of the order parameter. Higher-degree terms are then irrelevant with respect to the list of possible lower symmetries.[3,4]

In this paper it is shown that minimization of the free energy without a symmetry analysis can be misleading. The case of $C_4$ and $C_{4v}$ images is explicitly presented. While the two corresponding phase diagrams are identical in some subspace of the parameter space, the symmetry analysis shows drastic differences.

The paper is organized as follows: Sec. II contains a group theoretical analysis of the $C_4$ and $C_{4v}$ images; the fourth-degree free energies are studied in Sec. III and the phase diagrams are obtained; implementation of the phase diagrams by a symmetry analysis is presented in Sec. IV; and a discussion is contained in Sec. V.

## II. GROUP THEORY ANALYSIS

Starting with a space group associated with a high-symmetry phase (disordered) an order parameter is an entity transforming under symmetry transformations as a space-group irreducible representation. The image of this representation is the complete set of distinct matrices arising from the representation. In this paper we concentrate on the $C_{4v}$ and $C_4$ images. Both images are sets of matrices in two dimensions, i.e., they correspond to the transformation properties of a two component order parameter ($n=2$).

The symmetry operators ($2\times2$ matrices) contained in the $C_{4v}$ images in an appropriate basis are[5]

$$E,\ C_2,\ C_4^{\pm},\ \sigma_x,\ \sigma_y,\ \sigma_{da},\ \sigma_{db}\ . \tag{2.1}$$

The various image subgroups allowed from the series (2.1) are the distinct largest sets of matrices leaving some order parameter direction invariant. There exist three such image subgroups for $C_{4v}$, namely

$$(E,\sigma_x)\ \text{or}\ (E,\sigma_y)\ , \tag{2.2a}$$

$$(E,\sigma_{da})\ \text{or}\ (E,\sigma_{db})\ , \tag{2.2b}$$

and

$$(E)\ . \tag{2.2c}$$

The first two correspond respectively to an order parameter ordering along an axis [for example, $(0,\pm a)$ or $(\pm a,0)$] or a diagonal $(\pm a,\pm a)$. The third one is associated to some general direction $(a,b)$.

In parallel the $C_4$ image is a subgroup of $C_{4v}$ which contains the operations

$$E,\ C_2,\ C_4^{\pm}\ . \tag{2.3}$$

From the series (2.3) only one image subgroup can be realized for any order parameter direction, namely

$$(E)\ . \tag{2.4}$$

The basic invariants used in building the free energy expansion associated to $C_{4v}$ are

$$I_1=r^2\ ,$$

and (2.5)

 

$$I_2 = r^4 \cos(4\theta) ,$$

where $r^2 = x^2 + y^2$, $\tan\theta = y/x$, and $(x,y)$ are the two components of the order parameter. In the $C_4$ case there exist three invariants[4,5] which are

$$I_1 = r^2 ,$$

$$I_2 = r^4 \cos(4\theta) , \tag{2.6}$$

and

$$I_3 = r^4 \sin(4\theta) .$$

## III. FREE ENERGY EXPANSION

Using expressions (2.5) the fourth degree Landau expansion associated to $C_{4v}$ is

$$F_1 = \alpha_1 r^2 + \alpha_2 r^4 + \beta_1 r_4 \cos(4\theta) , \tag{3.1}$$

where $\alpha_1$, $\alpha_2$, and $\beta_1$ are Landau coefficients. The free energy related to $C_4$ is

$$F_2 = F_1 + \beta_2 r^4 \sin(4\theta) , \tag{3.2}$$

with an additional coefficient $\beta_2$.

Minimization of $F_1$ with respect to $\theta$ gives two solutions which are

$$\sin(2\theta) = 0 ,$$

and (3.3)

$$\cos(2\theta) = 0 .$$

The first solution represents an order parameter ordering along an axis while the second one is associated with an ordering along a diagonal. The corresponding image subgroups are respectively (2.2a) and (2.2b). The subgroup (2.2c) can be obtained from minima only by including sixth and eighth degree terms in (3.1).[6,7]

In parallel, expression $F_2$ (3.2) has only one minimum defined by

$$\tan(4\theta) = \frac{\beta_2}{\beta_1} . \tag{3.4}$$

The only symmetry operation leaving some order parameter direction invariant is the identity operation in agreement with the result (2.4).

The case $\beta_2 = 0$ in Eq. (3.4) produces exactly the solutions (3.3). This means that in the plane ($\alpha_1$, $\alpha_2$, $\beta_1$) the phase diagram obtained using Eq. (3.2) is identical to the one given by Eq. (3.1). The projection of the phase diagrams onto ($\alpha_1$, $\beta_1$) is shown in Fig. 1. For $\alpha_1 > 0$ there is a disordered phase. Two ordered phases exist at $\alpha_1 < 0$. When $\beta_1 > 0$ the order parameter lies along an axis while it lies along a diagonal for $\beta_1 < 0$. At $\beta_1 = 0$ there is a first-order transition between the above two ordered phases.

## IV. PHASE DIAGRAMS AND SYMMETRY

Implementation of Fig. 1 by symmetry analysis gives the following results.

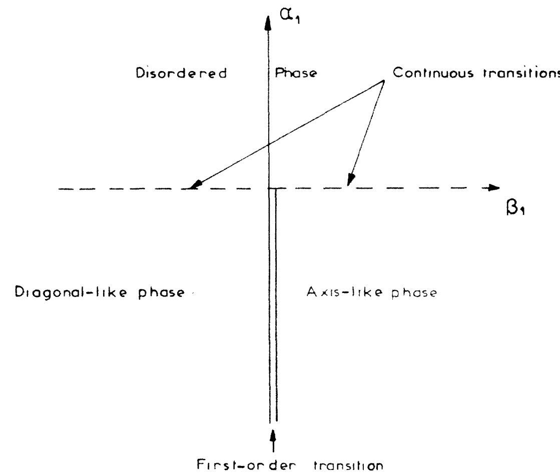


FIG. 1. Projection of the phase diagrams onto $(\alpha_1, \beta_1)$.

(i) In the $C_{4v}$ case, the phase diagram of Fig. 1 represents a first-order transition between two ordered phases which have inequivalent image subgroups. The image subgroups are those in (2.2a) and (2.2b). The *abstract* group associated to both image subgroups is unique however, namely $c_{1h}$. The two image subgroups also yield inequivalent space groups. These space groups are the set of space group elements which are associated by the representation to the two image subgroups, respectively.

(ii) In the $C_4$ case with $\beta_2 = 0$ the phase diagram of Fig. 1 represents a first-order transition between two ordered phases which have the identical image subgroup (2.4) and thus identical space groups.

While case (i) presents no difficulty case (ii) needs additional comment. A first-order transition between identical phases is well known, in particular for the liquid-gas transition. However, a first-order line between identical phases is expected to end at a critical point. A path should exist to pass from one phase into another *without a transition.* While it is indeed the case for the liquid-gas transition it is not the case here. From the free energy (3.1) such an event is impossible. Thus the first-order line $\beta_1 = 0$ in Fig. 1 is quite unusual (singular) when associated to $C_4$ while quite normal (regular) with $c_{4v}$. It is worth noticing that a similar situation occurs for $C_4$ at $\beta_2 = 0$ [from Eq. (3.2)] when $\beta_1 = 0$. The two identical phases have then one ordering along $\theta = \pi/8$ and $\theta = 3\pi/8$, respectively. In fact a similar situation occurs whenever the system passes through the origin ($\beta_1 = \beta_2 = 0$) along a line. Thus the phase diagram is similar for arbitrary $\beta_1$ and $\beta_2$.

It is usually believed that the free energy is entirely responsible for determining the phase diagram. However in the present study the very same formal free energy (taking $\beta_2 = 0$ for $C_4$) leads to different physical situations depending on the image involved. The nature of the singularity obtained in the phase diagram needs to be clarified.

## V. DISCUSSION

The physical interpretation of the result of the last section is not complete at this stage. Possible explanations of the singularity at $\beta_2=\beta_1=0$ in Fig. 1 for the $C_4$ image are the following.

(i) There is nothing contradictory at $\beta_1=0$ related to the $C_4$ image. We get the surprising result, however, of a first-order transition between two identical phases with no way to pass from one phase into the other without a transition. The two phases correspond to the same symmetry but a discontinuous jump in order parameter values.

(ii) The singularity at $\beta_1=0$ is so basic that this line becomes unphysical—meaning that $\beta_1$ can indeed never be null. Such a case would create a very peculiar situation. While allowed by minimization of the free energy some regions of the phase diagram would appear to be forbidden from symmetry constraints. In the case of terbium molybdate (TMO), which is associated to the $C_4$ image it was suggested that the condition $\beta_1=0$ will affect the transitions from the disordered phase and indeed induces a fluctuation driven first-order transition from the disordered phase.[8]

The only way to decide between the two explanations (i) and (ii) is by performing some experiment which will determine if it is possible or not to pass the $\beta_1=0$ line in the phase diagram of Fig. 1 for a system whose image is $C_4$. A possible candidate for such an experiment seems to be the rare earth TMO. Given some fixed orientation of the order parameter in an ordered phase the test would be to apply some non-symmetry-breaking field (perhaps pressure) which alters appropriately $\beta_1$. In order to select explanation (i) some sudden jump in the orientation would be sought. In explanation (ii) it would be expected that a mechanism for its exclusion would be found. In a following paper we will show that the results of this analysis are not unique to $C_4$ and $C_{4v}$. Similar results are present for other order parameters, for example, four component parameters ($n=4$).

[1] P. Weiss, J. Phys. Radium **6**, 667 (1907).

[2] G. Ya Lyubarski, *Theory of Groups* (Pergamon, New York, 1963), pp. 136–167.

[3] S. Galam, Phys. Rev. B **31**, 1554 (1985).

[4] Yu. M. Gufan and V. P, Sakhnenko, Zh. Eksp. Teor. Fiz. **63**, 1909 (1972) [Sov. Phys.—JETP **36**, 1009 (1973)].

[5] D. M. Hatch and H. T. Stokes, Phys. Rev. B **31**, 4350, 1985.

[6] S. Galam and J. L. Birman, Phys. Rev. Lett. **51**, 1066 (1983).

[7] D. M. Hatch and H. T. Stokes, Phys. Rev. B **33**, 7811, 1985.

[8] S. Galam (unpublished).