Physica **89A** (1977) 597–604 © *North-Holland Publishing Co.*

PHASE TRANSITIONS WITH SEVERAL ORDER PARAMETERS*

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Received 17 February 1977

The predictions of catastrophe theory for phase transitions involving more than one order parameter are given. These predictions are compared with those of other theories. For the simplest transition involving two order parameters it is found that there is a parameter which does not affect the topology of the phase diagram, which does affect certain angles in the diagram, and whose measured value will not depend on the scale of external physical variables. Comparison with renormalization theory predictions for this parameter leads to general observations on the relation of catastrophe theory and renormalization theory.

1. Introduction

There have been a number of recent papers[1,2]) which discuss continuous phase transitions involving two or more order parameters. In this paper we present some of the predictions of catastrophe theory[3–5]) for such transitions. A new feature which emerges is the presence of parameters which affect the geometry (angles) of a phase diagram but not the topology. Thus we shall show that for two coupled order parameters there is a quantity associated with the transition which does not depend on the way external physical parameters have been experimentally defined but which is nevertheless computable from various angles in the phase diagram. This quantity appears not to survive as a continuous variable under scaling and this fact will lead us to some later comments on the relation between renormalization theory and catastrophe theory.

The simplest phase transition involving more than one order parameter is that for which the free energy takes the form

$$F_0 = x^4 + y^4 \tag{1}$$

(x and y being one component order parameters) at the critical point. The potential F_0 has been studied[6–8]) under the designation "double cusp" catas-

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trophe. What is significant mathematically about this potential is that it is the simplest for which two different definitions of the "dimension of the catastrophe" are possible. The "dimension of the catastrophe" corresponds physically to the number of thermodynamic parameters needed to elicit all phenomena associated with a given phase transition. (The Gibbs phase rule is a statement about an analogous number).

The two sorts of dimensions are the "topological" and "algebraic" dimensions. We shall find that the topological dimension of F_0 [eq. (1)] agrees with that found by Griffiths for the same potential and that the motivation behind this definition is roughly the following. If by varying some n parameters in the neighborhood of a critical point one gets a particular phase diagram and if for a range of values of some other parameter g this phase diagram shows no qualitative (i.e. topological) change, then g is not needed in the local description of the phase transition. Hence if there is no parameter which can further qualitatively affect the phase diagram and if the n parameters already used are essential in the sense of the foregoing sentence, then the dimension of the phase transition is n.

The algebraic dimension of F_0 [eq. (1)] is one greater than the topological dimension and one of the purposes of this paper is to explore the physical significance of this additional parameter. A parameter of this sort has, to our knowledge, not made any appearance in physical problems: it is an invariant number associated with a phase transition (in that it cannot be eliminated or changed by a smooth change of coordinates) but it is not a critical exponent and does not affect the topology of the phase diagram. As remarked above, coupled order parameters represent the first opportunity to see such a parameter (the 180° rule[9]), which is also concerned with angular rather than topological information in a phase diagram, is an inequality and therefore does not involve an additional parameter).

We first give the values of the algebraic dimensions of a class of catastrophes and then return to discuss the topological dimension of the potential F_0.

2. The algebraic dimension

The potential for a catastrophe involving N order parameters has the form

$$A_0(x_1, \ldots, x_N) = \sum_{i=1}^{N} x_i^{2t_i}, \tag{2}$$

where $\{x_i\}$ are the order parameters and $\{t_i\}$ are integers greater than 2 [the "types"[4,5]) of the catastrophes in each of the order parameters separately]. The form A_0 obtains at the catastrophe point itself; at nearby points in thermodynamic phase space there will be lower order monomials also. The universal unfolding of A_0 has the form

$$A(x_1, \ldots, x_N; \{a\}) = A_0 + \sum_{i_1, \ldots, i_N} a_{i_1 \ldots i_N} x_1^{i_1} \ldots x_N^{i_N}. \tag{3}$$

The number of parameters $\{a\}$ needed for the universal unfolding is the algebraic dimension of the catastrophe. In the interpretation of phase transitions as catastrophes these parameters are functions of thermodynamic phase space. The monomials in $x_1, \ldots, x_N$ are free energy contributions that arise at the particular point in thermodynamic phase space for specific values of the x_i. The actual state (for thermodynamics) is the absolute minimum of A.

The number of parameters needed for the universal unfolding (3) is known in the mathematical literature[10]), and is obtained as follows. Let R be the ring of polynomials in N variables over the reals. Let I be the ideal whose basis consists of the first partial derivatives of A_0. Then the ring $R' \equiv R/I$ is also a vector space. The dimension of the vector space is one more than the algebraic dimension of the catastrophe. Furthermore, the monomials that appear in the unfolding (3) are just those basis vectors (i.e., the basis vectors can be so chosen). The reals, which form a subspace of R', are excluded by requiring that A take some specified value at a specified point. The algebraic dimension D is therefore

$$D = \left[\prod_{i=1}^{N} (2t_i - 1)\right] - 1.$$

The monomials that appear are

$$x^{i_1} \ldots x^{i_N}$$

with each i_j satisfying

$$0 \leq i_j \leq 2t_j - 2$$

except for $i_1 = i_2 = \cdots = i_N = 0$.

For the potential F_0 of eq. (1) the universal unfolding is

$$F = x^4 + y^4 + gx^2y^2 + a_{12}xy^2 + a_{21}x^2y + ax^2 + by^2 + a_{11}xy + a_{10}x + a_{01}y \qquad (4)$$

(where the special notation $g = a_{22}$, $a = a_{20}$, $b = a_{02}$ is used for later convenience). The algebraic dimension of F_0 is therefore eight.

3. The topological dimension

The catastrophe theory analogue of the phase diagram is the bifurcation set [defined and studied in ref. 6] which appears to differ from the physical phase diagram only in the way first order transitions are handled. Specifically the bifurcation set includes what in mean field theory would be called the "end of metastability" rather than the single line given by the Maxwell convention. (This is why the van der Waals gas phase transition is described as a "cusp" in the catastrophe literature).

Rather than attempt generality we discuss the reduction of the dimension of F_0 from 8 to 7. This reduction occurs because for all values of g in eq. (4), $|g| < 2$, the phase diagram (or bifurcation set and its stratification) has the same form. By "phase diagram" is included the specification of which subsets are 2nd or higher order transitions – this corresponds to the stratification.

The foregoing result is proved by Looijenga[8]) and is related to the fact that F_0 has modulus one[11,12]). For completeness we include some remarks on the modulus. One can consider the orbit of the fourth order polynomial

$$P(x, y) = Ax^4 + Bx^3y + Cx^2y^2 + Dxy^3 + Ey^4$$

under real linear transformations in x and y. The invariants of lower order polynomials under such transformations are discrete, e.g. the number of real roots. But for fourth order polynomials there is a continuous invariant (clear from counting generators of GL(2, R)) which is just the cross ratio of the roots of $P(1, z) = 0$.

The general definition of modulus[12]) relates to the number of such continuous parameters and that number is here unity, the number by which the algebraic dimension is reduced to reach the topological dimension.

The eighth parameter in F is g and it is this parameter which does not affect the phase diagram. On the other hand, the cross ratio R of the roots of the fourth order part of F_0 is

$$R = 2/(2 - g). \tag{5}$$

Consequently for non zero g no linear transformation can bring F to the form $x^4 + y^4$ and therefore no smooth transformation near the identity can either. It follows that R and hence g is an invariant number associated with the potential F.

4. Measurability of g

Although g does not affect the topology of the phase diagram it has a simple physical interpretation: it is a measure of the extent to which the order parameters x and y interfere or cooperate.

Suppose there is a phase transition for which by symmetry arguments the free energy near the critical point can be put in the form

$$F = x^4 + y^4 + gx^2y^2 + ax^2 + by^2. \tag{6}$$

Then the phase diagram in the a–b plane has four regions:

I. $a > 0$, $b > 0$; $x = y = 0$ neither ordering exists,
II. $a < 0$, $b > \frac{1}{2}ga$; $y = 0$; x is ordered and $x^2 = -\frac{1}{2}a$,
III. $b < 0$, $a > \frac{1}{2}gb$. $x = 0$; y is ordered and $y^2 = -\frac{1}{2}b$,
IV. $a < \frac{1}{2}gb$ and $b < \frac{1}{2}ga$. Both are ordered and $x^2 = \gamma(-a + \frac{1}{2}gb)$, $y^2 = \gamma(-b + \frac{1}{2}ga)$ with $\gamma^{-1} = 2 - \frac{1}{2}g^2$.

For all $g(|g| < 2)$ these diagrams are topologically equivalent, as expected. Measurability of g depends on the requirement that a and b be differentiable functions of the measured and controlled physical quantities. The region IV (both ordered) takes up more or less than a quadrant, depending on the sign of g. The boundary between regions III and IV makes an angle θ with the b-axis with

$$\tan\theta = \tfrac{1}{2}g. \tag{7}$$

In the a–b plane θ (and hence g) is measurable. But a and b are not the physically measured quantities; rather we assume that a and b are smooth functions of those quantities and it is in fact the experiments on the ordering or non ordering of x and y which fix the relation between (a, b) and physical quantities such as temperature, pressure, chemical potentials, external fields, etc., denoted collectively by P. Up to scale the positive a and b axes can be determined by the values of P where x and y (separately) become ordered.

If a and b are not just continuous functions of P but are differentiable functions also, then we can follow the axes to negative a and b and find that the line along which y becomes ordered takes a sharp bend once x is ordered too. The angle of this bend is just the angle θ given in eq. (7) above. Of course the angle will be θ only for correct *relative* scaling of a and b – but the relative scale of a and b can be fixed by requiring that the bending angle for x ordering in the presence of y and the angle for y ordering in the presence of x be the same. That is, the angle of the III–IV boundary with the b–axis is required to be the same as the angle of the II–IV boundary with the a–axis.

The significance of g can now be summarized as follows: There is at most one value of g for which a and b can be taken as differentiable functions of the external physical parameters P.

The actual calculation of g from experimental data is simple. Using whatever coordinates he pleases (so long as he preserves the symmetries $x \to -x$, $y \to -y$) the experimenter obtains 3 independent angles representing the opening angles of the various physical regions depicted in fig. 1. Let $m_0 = 0$, $m_1 = \tan\phi_1$, $m_2 = \tan(\phi_1 + \phi_2)$, $m_3 = \tan(\phi_1 + \phi_2 + \phi_4)$. Then by transforming to primed coordinates such that $m_0' = m_0 = 0$, $m_1' = \infty$, $m_2' = 1/m_3'$ (equal angles) we obtain

$$\tfrac{1}{2}g = m_2' = \frac{-m_2\,\mathrm{sign}(m_1)}{m_2 - m_1}\left|\left[\frac{m_2 m_3}{(m_2 - m_1)(m_3 - m_1)}\right]^{-1/2}\right|. \tag{8}$$

There is no ambiguity in this number, inasmuch as when the four parameters of a linear transformation are reduced by 2 (irrelevance of scale and rotation)

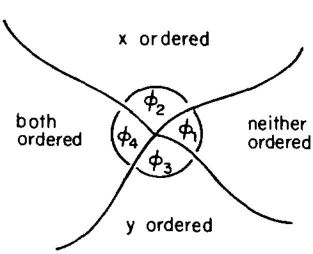

Fig. 1. Phase diagram with $x \to -x$ and $y \to -y$ symmetry.

there are just 2 left to satisfy $m_1' = \infty$ and $m_2' = 1/m_3'$. The singularity in (8) at $m_1 = 0$ is reasonable since vanishing m_1 implies that $|g| = 2$.

4. Effect of renormalization

Scaling of the function F of eq. (6) has been studied[13–15]) in the ϵ-expansion. It is found that $g = 0, 2$ and 6 are fixed points, which is to say that close enough to the critical point there is either an uncoupling of the order parameters ($g = 0, 6$) or tangency of two lines in the phase diagram ($g = 2$ and $\phi_1 = \phi_4 = 0$, $\phi_2 = \phi_3 = \pi$ in fig. 1). $g = -2$ does not seem to be a fixed point despite its special role in the graph of F. Hence there is also the possibility that the phase transition between x ordering and y ordering is first order. This is what Fisher has called "bicritical," while the $g = 2$ case is termed tetra-critical.

One therefore expects that far enough from the critical point for the mean field theory description to apply, some particular value of g could be measured, while closer in the values of this parameter would become limited.

5. Scaling and flow in catastrophe theory

The foregoing results on g shed light on an intimate relation between scaling theory and catastrophe theory. In both theories one considers a particular function (the hamiltonian H in scaling, and the potential A in catastrophe theory) and its orbit under a class of transformations. H flows under the scale transformations to other hamiltonians. A flows under some class of smooth functions to other potentials. In both cases one wishes to consider functions in the same orbit (or going to the same point) as equivalent to one another. It follows that the separatrices of orbits and the fixed points play special roles with respect to the equivalence classes. Furthermore, by identifying coefficients in the Hamiltonian or potential with external physical variables these equivalence classes are interpreted as phases.

Differences between the two theories arise because of differences in the class of allowable transformations. Catastrophe theory allows all C^∞ (bijective) coordinate changes. It is not so easy to characterize the scaling transformations, since they usually arise from a specific physical scale transformation and so there are probably many C^∞ maps which are not scale transformations. On the other hand, scale transformations are not required to be differentiable and for two hamiltonians to represent the same phase they need only flow to the same limit point. This is why the parameter g is lost in renormalization but not in catastrophe theory. If one takes a weakened form of catastrophe theory in which only topologically distinct phase diagrams (bifurcation sets and stratification) are distinguished then one has weakened the smoothness requirements of catastrophe theory and one gets substantially the same phase diagrams as in renormalization theory.

6. Conclusions

Phase transitions involving several order parameters may require for their full characterization more than just the topological form of the phase diagram. Put differently, there are properties of the transition whose full expression requires more thermodynamic parameters than are needed to generate the phase diagram. For the simplest such transition there is already one additional parameter and in this paper we have shown how its measurement depended on specific information about angles between various lines in a phase diagram.

There are therefore two sorts of external parameters in higher order phase transitions: those essential to the topology of the phase diagram and those which enter only for finer questions (i.e. questions involving smoother classes of transformation – differentiable in the example of this paper). The existence of the second class is related to the distinction between the algebraic and topological dimensions of a catastrophe. It is only parameters of the second class which can disappear (i.e. become irrelevent to the phase diagram) under scaling transformations.

Our observations on the role of g in renormalization and catastrophe theory help provide a formal mathematical answer to one of the puzzles of phase transitions: if mean field theory is so bad (on critical exponents), how come it is often so good (on the qualitative description of phase diagrams)? The answer is that catastrophe theory – without differentiability requirements[16]) on the mappings to which potentials are subject – breaks up the space of potentials in essentially the same way as does renormalization theory. (This is because in both theories a phase is essentially an equivalence class of potentials and potentials are equivalent if they flow into each other or into a common point.) On the other hand, while relaxing differentiability requirements in catastrophe theory will change some features of the phase diagram it will not change the topology (in the sense of *continuous* mappings); hence in catastrophe theory the topology of the phase diagram is the same as if one had maintained differentiability requirements – but this is the mean field topology.

These remarks help clarify what might have seemed an unjustifiably good agreement with the experiment in ref. 5 where continuous but non differentiable functions were used to get correct critical exponents. The most ambitious aim of catastrophe theory is to get *all* singular behavior from the polynomials alone, but it would seem that for phase transitions (or at least for our description of phase transitions as catastrophes) one must postulate in addition a continuous but non differentiable map from the coefficients and variables in the polynomial to the physically observed quantities. Such a map was proposed in ref. 4 and it is renormalization theory that justifies its introduction.

Acknowledgement

I am grateful to Martin Golubitsky for his careful and lucid explanation of a number of points in catastrophe theory. I also wish to thank A. Aharony, L. Benguigui, Y. Imry, C. Kuper, M. Revzen, B. Shapiro and R. Shtokhamer for useful discussions and D. Fowler, R. Griffiths and E. Looijenga for helpful correspondence.

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16) Strictly speaking, one continues to define equivalence in terms of C^{∞} functions but then considers the topological equivalence of phase diagrams (bifurcation sets, etc.) under merely continuous transformations.