

# A Dynamical Test of Phase Transition Order: New Things in Old Places or Old Wine in New Bottles<sup>1</sup>

P. E. Cladis<sup>2</sup>

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We first discuss nonlinear aspects of phase transition theory applied to a particular liquid crystal phase transition. A simple derivation is given to show how two coupled Goldstone modes (one appearing as gauge fluctuations of the ordered phase) can force a phase transition, against all expectations, to take place discontinuously (theory of Halperin, Lubensky, and Ma)—but the discontinuity may be immeasurably small. Then, we describe a new dynamical test of phase transition order, developed by Cladis *et al.*, that turns out to be more sensitive than x-ray diffraction and adiabatic calorimetry. Quantitative data found by this new method are in excellent agreement with the measurements of adiabatic calorimetry and x-ray diffraction as well as expectations implicit in the predictions of HLM.

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**KEY WORDS:** Phase transitions; front propagation; dynamical systems; phase transition order, critical phenomena.

## 1. INTRODUCTION

The subtitle of this talk is taken from Maurice Goldhaber's definition of physics: *Physics is discovering new things in old places. Chemistry is discovering old things in new places.*<sup>(1)</sup> Perhaps (and this is my addendum to Goldhaber's definition), materials science is discovering new things in new places. I like his definition. It applies to what I am going to talk about this evening—*A dynamical test of phase transition order: new things in old places*, or, perhaps more *à propos* after the sumptuous banquet provided by our hosts, *Old wine in new bottles*.

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<sup>1</sup> This is the text of an after-banquet talk given at the CNLS Workshop on the Dynamics of Concentrated Systems.

<sup>2</sup> AT & T Bell Laboratories, Murray Hill, New Jersey 07974.

I will illustrate how this test may be useful, using an example drawn from liquid crystals. The liquid crystal state of matter is new in the old field of condensed matter physics. It is an example of a concentrated system that some have thought too complex to teach us new physics. However, after hearing the many interesting results found in even more complicated systems at this workshop, I feel like the victim of the Johnstown flood who died and went to heaven. For his induction into heavenly society, St. Peter asked him to give a talk about the most stupendous event he experienced on earth. After thinking a bit, he said, "I know what I'll talk about. I'll talk about the Johnstown flood. It was the most stupendous event I witnessed on earth. Tons of water came flooding over a dam killing and destroying everything in its path." St. Peter looked sceptical and asked him "Are you sure about that?" "Sure," replied the new saint, "the drama and the power of a great roaring tentacle of water crushing and destroying everything in its grasp will knock their socks off." "Well, I don't know," said St. Peter, "You know, Noah's going to be there." Evidently, the difference between me and the Johnstown saint is that there are many Noahs in this audience-- many *survivors* of even greater battles against complexity to knock socks off.

Tonight, I discuss phase transitions (this is an old place), illustrating some of its features, using a particular phase transition that occurs in liquid crystals, the nematic-smectic A phase transition<sup>(2)</sup> (this is a new thing to phase transitions). When this transition takes place continuously, without a latent heat to mark the transition temperature, it is called a continuous transition or, for historical reasons, a second-order transition. Transitions showing a latent heat at the transition temperature take place discontinuously and are called, again for historical reasons, first-order phase transitions.<sup>(3)</sup> This introduces some confusion, because the word "order" will be used in two contexts: to refer to the type of transition (does it take place continuously or discontinuously?) and to characterize what is different between the two states, or phases of a system (as in order versus disorder).

Sometimes, the magnitude of the discontinuity, as measured by the latent heat, at a phase transition can be changed by varying an external variable such as by adding impurities into the system. The question is, does there exist a critical value for the external field that changes the transition type from discontinuous (first order) to continuous (second order)? A theoretical answer given by Halperin, Lubensky, and Ma (HLM)<sup>(4)</sup> about 15 years ago was: No, if the ordered phase has broken continuous symmetry characterized by a gauge, a characteristic measure of length (for the nematic to smectic A transition) or momentum (for superconductors). This may not be too intelligible now, but what should be understood is that

under well-specified conditions, that apply (as far as we know) to the nematic–smectic A transition, the answer is no: this phase transition must necessarily be discontinuous—but the magnitude of the discontinuity may be very small.

The question is important because advances in our understanding of continuous transitions far outstrips our understanding of discontinuous ones. In fact, most of what I will talk about in the sections on phase transitions has to do with continuous phase transitions.

Experimental support for the theory of HLM has been inconclusive. Using the usual tools of x-ray diffraction<sup>3</sup> and adiabatic calorimetry,<sup>(7)</sup> many liquid crystal materials are observed to have discontinuous nematic–smectic A transitions, but a few compounds have continuous ones within the precision of experiments.<sup>(5–9)</sup> Adiabatic calorimetry turns out to be a more stringent test of discontinuous transitions than x-ray diffraction: transitions observed by diffraction to be continuous<sup>(8)</sup> have small but measurable latent heats.<sup>(7,9)</sup> By analyzing how the latent heat approaches zero, some indication of the existence of the HLM coupling<sup>(4)</sup> has most recently been found.<sup>(9)</sup> However, there are a few compounds that both x-ray diffraction and adiabatic calorimetry agree has a transition that is so close to being continuous that neither technique can observe discontinuities.

For the new part, I will discuss how the phase transition type—that is, does the phase transition take place continuously (second order) or discontinuously (first order)?—influences the existence and propagation of interfaces.<sup>(10)</sup> We believe this is the first time interfacial properties have been used to determine the order of a phase transition. I will be illustrating theoretical conclusions using the same liquid crystal example. A comparison of our data with data obtained using standard tools shows our new dynamic tool as more sensitive for distinguishing between the two types of transitions,<sup>(11)</sup> e.g., better than ten times more sensitive than the finest adiabatic calorimetry measurements currently available, which in turn are about ten times more sensitive than the finest available x-ray measurements. However, I want to stress that the real power of the dynamical technique rests on the fact that it gives a qualitative indication of the order of a phase transition. Finally, our experimental results can be shown to be consistent with the HLM picture of this phase transition being weakly discontinuous.

<sup>3</sup> See ref. 5 for a review of the experimental work; for a review of the theoretical work see ref. 6.

## 2. PHASE TRANSITIONS

The business of phase transitions belongs to the realm of statistical physics or statistical mechanics. To give you an idea of this field of physics, I want to quote the opening sentences from the book *States of Matter* by David L. Goodstein.<sup>(12),4</sup>

*Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.*

*Perhaps it will be wise to approach the subject cautiously.*

Now that you have been forewarned, let us think about phase transitions: the way that matter changes from one state to another. Phase transitions may be grouped into two classes: those that involve a latent heat and those that do not. The first kind, those that involve a latent heat, are called discontinuous or first-order phase transitions and those that do not, continuous or second-order phase transitions.

## 3. EHRENFEST'S FORMULATION OF PHASE TRANSITIONS

Ehrenfest's formulation<sup>(3)</sup> of phase transitions in terms of thermodynamic variables uses a free energy  $G(P, T)$ . In terms of  $G$ , at a *first-order* phase transition between phases 1 and 2, as a function of temperature, say, at the transition temperature  $T_c$ ,  $G_1 = G_2$ , but there is a discontinuity in the *first* derivative:  $\partial G_1/\partial T - \partial G_2/\partial T \sim L$ , where  $L$  is the latent heat. At a *second-order* phase transition, again,  $G_1 = G_2$ , and  $\partial G_1/\partial T = \partial G_2/\partial T$ , but there is a discontinuity in the *second* derivative  $\partial^2 G_1/\partial T^2 - \partial^2 G_2/\partial T^2 \sim \Delta C_p/T$ , the specific heat jump at the transition.

Soon after Ehrenfest published these ideas, it was noticed (Fig. 1) that if  $G_1 < G_2$  for  $T > T_c$ , then for a second-order phase transition it would still be less for  $T < T_c$ . That is, phase 2 would never appear, because it always has a larger free energy. From the many suggestions<sup>(3)</sup> made to preserve the Ehrenfest formalism and still obtain a phase transition, Gorter's idea has proven to be seminal and was eventually formalized by Landau. Gorter's suggestion was that the transformation takes place because above  $T_c$ , the phase  $G_1$  simply no longer exists: "something" has gone to zero at  $T_c$ . As we will see, that "something" is called the order parameter.

Another difficulty with Ehrenfest's formulation of second-order phase transitions was that many transitions that did not exhibit a latent heat (notably, phase transitions in liquid systems) did not show discontinuities

<sup>4</sup> This book has many interesting stories, but is probably too early to offer a simple overview of critical phenomena as in ref. 14.

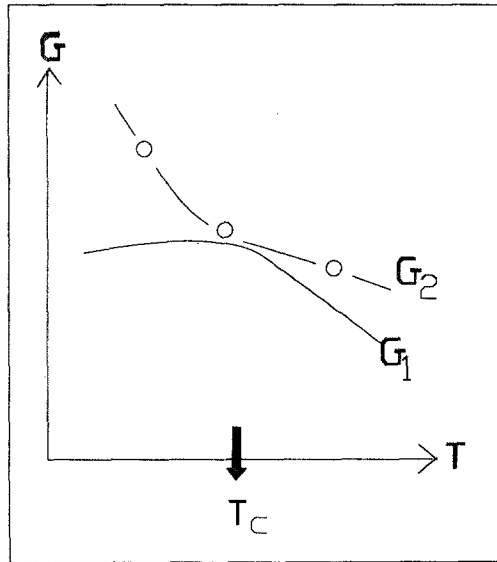


Fig. 1. If two functions of temperature,  $G_1$  and  $G_2$ , and their first derivatives with respect to temperature match at  $T_c$ , then, if  $G_1 < G_2$  for  $T > T_c$ ,  $G_1$  will still be less than  $G_2$  for  $T < T_c$ .

in the specific heat at  $T_c$  either. This last point has been cleared up with the modern theory of critical phenomena, a generalized theory of phase transitions.

#### 4. LANDAU ORDER PARAMETERS

Landau first introduced the concept of an order parameter, which I will designate generically as  $\psi$ , to characterize what changes at a phase transition.<sup>(3)</sup> In the following, order will be used in a different sense than "type" of phase transition. An order parameter is a quantity that characterizes the symmetry and dimensionality  $n$  of the ordered, usually lower-temperature phase.  $\psi$  is a new thermodynamic variable and it is not always easy to define. In particular, its dimension  $n$  is a subtle quantity. Very often, discovering the appropriate value for  $n$  is an important step in understanding the whole problem. A working definition of  $n$  is the number of variables that has to be defined to characterize a "ground state," i.e., the lowest energy configuration of the ordered state.<sup>(14),5</sup>

<sup>5</sup> In my opinion, ref. 14 is the best distillation of the essence of critical phenomena. I have used it extensively in this presentation.

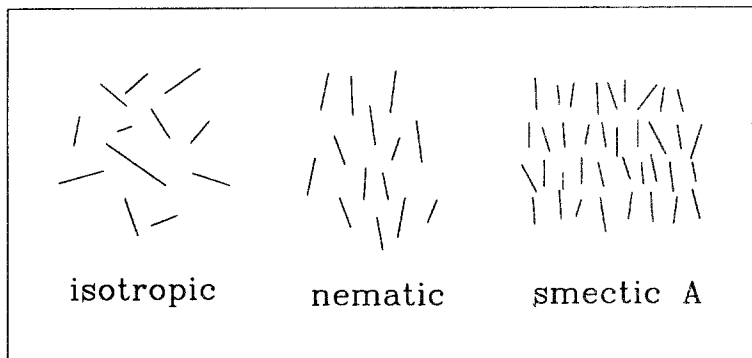


Fig. 2. Director configuration for the isotropic, nematic, and smectic A phases.

The power of the order parameter concept rests on a deep truth: symmetry cannot change continuously even if the magnitude of the order parameter does.<sup>(13-15)</sup> Second-order transitions are often called symmetry breaking because the disordered phase has more symmetry than the ordered phase. For example, the isotropic liquid state has continuous rotational symmetry in three dimensions (Fig. 2), whereas in the nematic phase the system selects one direction out of the infinitely many options available, thereby reducing its degree of rotational symmetry. The continuous symmetry of the isotropic phase has been broken. Because there is no reason for one direction to be “better” than any other, the total energy of the new phase is invariant under a continuous rotation of the selected direction. Another way of saying this is that an infinite number of ground states is available to the system. With so many ground states, low-energy excited states with energy  $\rightarrow 0$  with inverse wavelength can easily form.<sup>(16)</sup> This turns out to be an important concept. Such low-energy excited states are called Goldstone modes and are a property of systems that have broken continuous symmetry. They are particularly easy to excite in systems that are weakly interacting, such as liquid systems. At a phase transition, the existence of these low-energy excited states may even prevent the formation of the ordered state.

The smectic A phase is a layered structure (Fig. 2) with the director, the direction of orientational order, parallel to the layer normal. The smectic A phase breaks the continuous translational order of the nematic phase. The smectic A order parameter is a periodic density wave in one dimension. An amplitude  $\psi$  specifies how well the layers are defined and a phase<sup>6</sup>  $\phi$  gives the positions of the layers in space. The broken symmetry

<sup>6</sup> This quantity is commonly called the phase of the order parameter. This terminology is not to be confused with phase as in phase transition. Using the same word to refer to two different ideas is a difficulty to be aware of when discovering new things in old places. It is particularly a problem for those discovering new things in new places.

in the smectic A phase is the continuous translation symmetry of the nematic phase along the direction of orientational order, written as  $\mathbf{n}$  and not to be confused with the order parameter dimension  $n$ . The Goldstone mode for this broken symmetry is related to where layers begin. Translating all the layers an infinitesimal amount in the  $z$  direction (replacing  $\phi$  by  $\phi + \delta$ , where  $\delta$  can be infinitesimally small) does not change the energy. It is important to realize that the direction of orientational order is a macroscopic quantity that is not easily defined on the scale of the smectic layers  $\sim 30 \text{ \AA}$ . Thus, when layers start to form near the transition to the smectic A phase, the order parameter has to contend with Goldstone modes from two broken symmetries.

In 1970, MacMillan was the first to suggest where to look for a second-order nematic–smectic A transition.<sup>(17)</sup> He proposed investigating systems where the smectic A phase formed at a much lower temperature than the nematic phase. He reasoned that the deeper one was in the nematic phase, that is, far from the isotropic phase where orientational fluctuations are largest, the calmer the sea of low-energy excited states, allowing a second-order nematic–smectic A transition to take place. It was well known from magnetism (Rodbell–Bean coupling) that a coupling between fluctuations of a broken symmetry and another order parameter, like the smectic A order parameter, could drive a second-order transition first order. Perhaps if these fluctuations were small, the “true” second-order character of the transition would emerge.<sup>(2)</sup>

In 1973, Halperin, Lubensky, and Ma were at an Aspen summer workshop together, and they concluded that the coupling between the low-lying energy states of the broken translation order of the smectic A phase and local fluctuations in the direction of the orientational order guaranteed that this transition was fundamentally first order.<sup>(4)</sup> Their idea also applies to the normal metal–superconducting transition that is formally similar to the nematic–smectic A transition.<sup>(18)</sup> But, in fact, the coupling they were thinking about is most devastating when interactions are weak, as they are typically in phase transitions in liquid systems,<sup>(16)</sup> such as the N–A transition, where director fluctuations are much larger than fluctuations in layering.

## 5. LANDAU FORMULATION OF PHASE TRANSITIONS (MEAN FIELD)

Landau said that near a phase transition, the free energy of the system could be written as a polynomial  $f$  of a scalar function of the order parameter,  $\psi$ , say.<sup>(13)</sup> If  $\psi$  is a complex number, this could be its magnitude. His strategy was to replace the sum of all possible states of the order parameter by the one that minimized a free energy, a “mean field.”

The Landau description of phase transitions is known as the mean field limit. It is not clear why it works. The surprising fact is that it is exact for  $d$ , the dimension of space, greater than or equal to a critical dimension,  $d_c = 4$ .<sup>(14)</sup>

In terms of  $\psi$ , then,

$$F = \int_V dV (a\psi^2 + b'\psi^3 + b\psi^4 + \dots). \quad (1)$$

$V$  is the volume of the space being considered. If the coefficient of the cubic term is not zero, the transition is first order. If the coefficient of the quartic term is negative, the transition is still first order even without a cubic term.

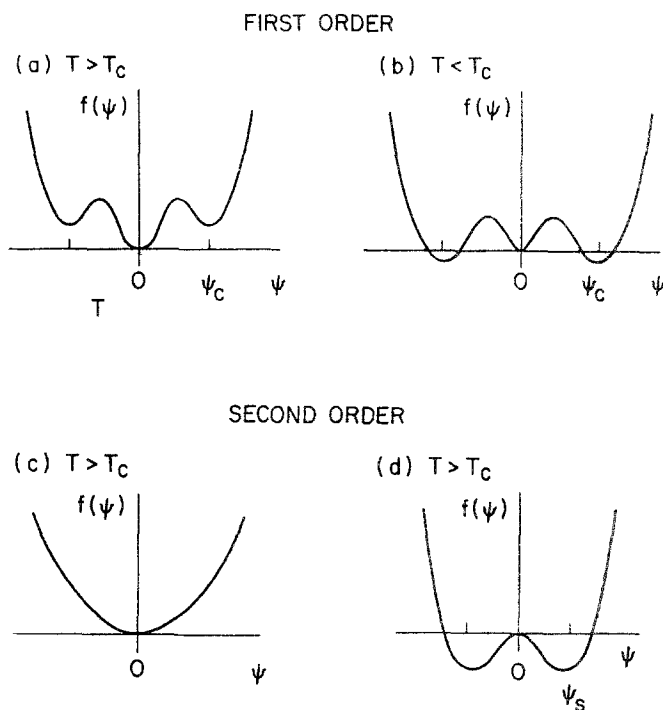


Fig. 3. Graphs of the free energy as a function of the order parameter  $\psi$  for a first- and second-order phase transition. To understand how an interface propagates, we think of it as a particle in a potential described by the free energy. At a first-order phase transition, the interface moves from the stable into the metastable state. Which state is metastable and which stable depends only on temperature, so the interface can propagate when the temperature is jumped above as well as below  $T_c$ . The potential is not similar for a second-order phase transition. Although difficult to realize experimentally, interfaces may propagate for a temperature quench. For a temperature jump above  $T_c$ , a single time constant can be defined allowing the ordered state to exponentially relax to the disordered one everywhere.



When  $b' = 0$  and  $b > 0$ , the transition is second order. The point on a phase diagram where  $b = 0$  is a special one called a Landau tricritical point (LTP), where the order of a transition crosses over from being first order to second order (and vice versa) where there is no cubic term in Eq. (1). It corresponds to the case where the three minima of a first-order phase transition coalesce to a single minimum at  $\psi = 0$ . Tricritical points are not understood on as deep a level as second-order transitions. Another field variable is usually invoked to study their stability, so that a tricritical point is the meeting point of three phase transition lines.

In the higher temperature phase, the so-called *disordered state*, the magnitude of the order parameter is zero. It is nonzero only in the ordered state. At a second-order phase transition, the order parameter grows continuously from zero at the transition temperature while at a first-order transition, it jumps discontinuously from zero to a finite value just below the transition temperature.

To show these results requires a little algebra<sup>(13)</sup> and just to fix ideas, let us look at a second-order phase transition where  $b' = 0$  and  $b > 0$ . Minimizing the free energy with respect to the order parameter, the solutions are

$$\psi^2 = \left( -\frac{a}{b}, 0 \right) \quad (2)$$

We want  $\psi$  to have a real, nonzero solution below  $T_c$  but not above  $T_c$ . The condition that  $-a/b$  be positive below the transition temperature  $T_c$ , zero at  $T_c$ , and negative above  $T_c$  gives, to lowest order,  $a = a_0\varepsilon$ , where  $\varepsilon = (T - T_c)/T_c$  and  $b$  is *independent of temperature*. Below  $T_c$ ,  $|\psi|^2 = -(a_0/b)\varepsilon \neq 0$  and above  $T_c$ ,  $\psi = 0$ .

With just the information in Eq. (1), the temperature dependence of all the thermodynamic parameters characterizing the transition can be found. For example, the specific heat  $C_p = -T \partial^2 F / \partial T^2 = C_0 + a_0^2/b$  has a finite discontinuity at  $T_c$ . In practice, fluid systems do not show a jump in heat capacities at  $T_c$ ; consequently, this result is considered a failure of classical theory to explain second-order phase transitions that was removed by incorporating fluctuations into the problem. What are fluctuations?

## 6. FLUCTUATIONS

The existence of a latent heat means that a fixed amount of energy is associated with the transformation from one state to another. At a first-order transition, a  $\psi \neq 0$  fluctuation into the disordered state costs a finite amount of energy determined by the latent heat and so one has a

nucleation problem (the two states are local minima). For a second-order transition, where  $f(\psi) = f(-\psi)$ , there is no latent heat, so fluctuations cost little energy and there is no nucleation problem. Above  $T_c$  one imagines a new equilibrium state where on average the magnitude of the order parameter is zero, but locally, the order parameter fluctuates, that is, varies in a random, time-dependent way, between positive and negative values maintaining  $\langle \psi \rangle = 0$  (Fig. 4). The fluctuations are not out of an equilibrium state; instead, the equilibrium state is an average over these fluctuations weighted by a probability distribution.<sup>(12)</sup>

In a fluctuation-dominated picture of the disordered state, it costs energy to vary the order parameter in space, so a term

$$F_G = \int_V dV \frac{1}{2M} \left( \nabla\psi - \frac{2\pi i}{D} \delta\mathbf{n} \psi \right)^2 \tag{3}$$

has to be added to Eq. (1).  $\delta\mathbf{n}$  is the gauge of the ordered state described by the phase  $\phi$  of the order parameter. When the normal to the smectic planes is in the  $z$  direction,  $\phi = (2\pi/D)z$ , where  $D$  is the layer spacing. In this case, the gauge represents the natural length of the ordered state, the distance between layers: a periodic variation of the order parameter with period given by this gauge does not increase the energy of the system. In the disordered *state*, *orientation* fluctuations of the gauge (not fluctuations in the magnitude of the layer spacing) must be considered, since they define the direction of the Goldstone modes of (i.e., couple to) the order

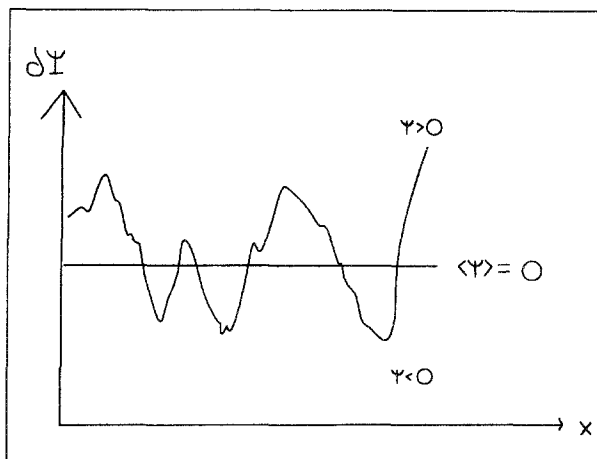


Fig. 4. Picture of a fluctuation. The fluctuations are not out of an equilibrium state; rather, the equilibrium state is an average over these fluctuations weighted by a probability distribution.

parameter fluctuations [i.e., where a layer starts: replacing  $\phi = (2\pi/D)z$  by  $\phi = (2\pi/D)z + \delta$ ]. HLM discovered that the coupling between gauge fluctuations and order parameter fluctuations in the disordered state forced transitions involving a gauge (such as the nematic–smectic A transition) to be necessarily discontinuous in three dimensions because it introduced a non-analytic cubic term into Eq. (1).

The gradient term [Eq. (3)] constrains the spatial extent of the order parameter variations. The length over which order parameter fluctuations are correlated is called the coherence length  $\xi$ . It is the mean distance the order parameter requires to change from a positive to a negative value (Fig. 4). Minimizing [Eq. (1) + Eq. (3)] leads to a differential equation that defines the coherence length, the length over which order parameter excursions are correlated:  $\xi = 1/(Ma)^{1/2}$ , or  $\xi = \xi_0 \varepsilon^{-1/2}$ . As  $T \rightarrow T_c$ ,  $\xi$  diverges to be infinite at the transition.

$\xi_0$  is an important quantity. It gives a measure of the range of the interactions characteristic of the system and can be compared to the correlation length of fluctuations in the order parameter.  $\xi_0$  is, in some sense, a measure of what fluctuation correlations have to beat to control the phase transition.<sup>(14)</sup> If  $\xi_0$  is large, the system's range of interactions is long, resulting in a "stiff" order parameter, so one has to be closer to  $T_c$  for fluctuations to be correlated on a comparable scale than for materials with a small  $\xi_0$ .

The mean field, or classical limit (Landau limit) refers to a range of temperatures not too far from the transition temperature and not too close so that the  $\psi^4$  term approaches zero more slowly as  $T \rightarrow T_c$  than the term quadratic in  $\psi$ . Whether or not this is the case depends on the temperature dependence of  $b$ , the coefficient of the fourth-order term. When this term is independent of temperature, as it is in Landau's formulation, fluctuations do not control the transition in three dimensions.

If  $b \rightarrow 0$  more slowly than  $a$  as  $T \rightarrow T_c$ , then the importance of the fourth-order term grows and can no longer be obviously neglected. Fluctuations become *critical*, i.e., are correlated over distances comparable to  $\xi_0$  and classical theory breaks down.

Halperin, Lubensky, and Ma (HLM) predicted that the coupling between transverse fluctuations  $\delta \mathbf{n}$  of the orientational order parameter and fluctuations in the smectic A order parameter that I will also write for simplicity as  $\psi$ , not  $\delta \psi$ , resulted in a cubic term so that the transition is inescapably first order in  $d=3$ .<sup>(4)</sup> To see this,<sup>(14)</sup> we first consider Eq. (1) + Eq. (3) specifically for the nematic–smectic A transition near  $T_{NA}$ :

$$f(\psi, \delta n) = f_0 + \frac{a}{2} \psi^2 + \frac{b}{4} \psi^4 + \xi_0^2 \left| \left( \nabla - \frac{2\pi i}{D} \delta \mathbf{n} \right) \psi \right|^2 + K(\nabla \times \delta \mathbf{n})^2 \quad (4)$$

The Goldstone modes of the nematic phase appear as gauge fluctuations and  $K(\nabla \times \delta \mathbf{n})^2$  is the elastic energy associated with it. When fluctuations in the gauge field are much stronger than fluctuations in  $\psi$  [ $b$  is small in Eq. (4)], the spectrum of  $\delta \mathbf{n}$  can be obtained by Fourier transforming Eq. (4) and assuming equipartition, to obtain

$$\langle \delta n_k \rangle^2 \sim \frac{1}{k^2 + \psi^2}$$

Order parameter fluctuations open a gap in the spectrum of orientational fluctuations at small  $k$ . Fourier transforming back, one finds

$$\langle \delta n^2 \rangle \sim \int \frac{k^{d-1} dk}{k^2 + \psi^2} \sim -\psi^{d-2} \quad (5)$$

Substituting Eq. (5) back into Eq. (4), then, for  $2 < d < 4$ ,

$$f(\psi, \mathbf{n}) = f_0 + \frac{a'}{2} \psi^2 + \frac{b}{4} \psi^4 - C |\psi|^d \quad (4')$$

Although the term quadratic in  $\psi$  is enhanced by a contribution  $\sim +2\pi$  when  $d=3$ , a *negative*, nonanalytic cubic term remains from the integration. Evidently, for this effect, the dimensionality of space is important. For sufficiently large  $b$ , fluctuations in  $\psi$  become important and the above procedure becomes questionable.<sup>(11)</sup> Thus, the best way to test the HLM result is close to an LTP where  $b \sim 0$ .<sup>(9)</sup>

The HLM coupling mechanism is the exclusion of twist and bend deformations in the layered smectic A phase and is formally similar to the Meissner effect in superconductors. Twist and bend deformations are incompatible with a layered structure, since they introduce dislocations in the layering.<sup>(14,18)</sup>

In more general terms, this is an example of a "Higgs mechanism." The transverse vectorial mode of  $\delta \mathbf{n}$  (i.e., the photon, a gauge field with zero mass) couples to a scalar mode, namely the phase  $\phi$  of the smectic A order parameter (Goldstone mode with zero mass), resulting in a composite mode of finite mass (each mode providing a mass for the other) because of the coupling.<sup>(14)</sup>

The simplicity of the HLM argument makes it particularly compelling near an LTP where mean field behavior prevails. But, as mentioned earlier, when discussing the order parameter for this transition, many materials have been found to exhibit a second-order nematic-smectic A phase transition: latent heats are immeasurably small and the coherence length as a function of temperature marches steadily on to infinity with often strange

exponents, but nevertheless with no sign of deviating to a finite value at  $T_c$ . It has been a puzzle to many theorists and experimentalists alike for these past 15 years.

## 7. CRITICAL REGIME AND SCALING RELATIONS<sup>(12,14)</sup>

In the general case of fluctuation-dominated phase transitions, a correlation function  $\Gamma \sim 1/r^{d-2+\eta}$  is defined.  $\Gamma$  defines the exponent  $\eta < 1$  that affects the rate fluctuation correlations decay and is assumed independent of the magnitude of the coupling constant, that is, the constant of proportionality. By introducing  $\eta$ , phase transitions in  $d \leq 2$  can be studied. The temperature dependence of  $\xi$  in the disordered state is defined as  $\xi \sim \xi_0 \varepsilon^{-\nu}$ , where  $\nu$  is a critical exponent to be determined and defined to be positive. The temperature dependence of all physical quantities in the disordered state can be related to the exponents  $\nu$  and  $\eta$ . These in turn depend only on  $n$  and  $d$ . For example, the exponent for the correlation length  $\nu$  does not depend on the magnitude of the coupling constant  $\xi_0$ .

One assumes phenomena characterized by a particular length scale to be independent of dimensional parameters whose scale is very different. The reason critical exponents can be interpreted in powers of length is because scaling transformations do not uniformly dilate all lengths, but only that length  $\xi$  that governs the physics.<sup>(14)</sup> Some parameters are *relevant* and some are *irrelevant* for determining the stability of the state of the system. Scaling relations are a way to define formally the relevant parameters controlling the transition and to show how they are all related to the fundamental length  $\xi$ . Because of the long-range nature of the correlations in fluctuations, the system is powered by collective rather than single-particle properties.

## 8. SCALING RELATIONS FROM NAIVE DIMENSIONAL ANALYSIS<sup>(12,14)</sup>

Naive dimensional analysis can be used to deduce the temperature dependence of all the relevant parameters. To do this, one notes that the energy density  $f$  divided by a temperature is an inverse volume,  $f/T \sim 1/\xi^d$ . Then, with the definition of  $\Gamma$

$$\Gamma(\xi) = \langle \psi(0) \psi(\xi) \rangle \sim \frac{1}{\xi^{d-2+\eta}} \quad (6)$$

the temperature dependence of the order parameter is

$$\psi \sim \xi^{(2-d-\eta)/2} \sim \Delta T^\beta$$

$$2\beta = \nu(d + \eta - 2).$$

An interesting feature of the scaling relations is that they depend only on the dimension of space  $d$  and none of them depend explicitly on the dimension of the exponents that have been observed at the nematic-smectic A transition.

The scaling relations are more universal than the precise magnitudes of the exponents. Two lengths can be measured in the nematic phase on approaching the smectic A transition,  $\xi_{\parallel}$  and  $\xi_{\perp}$ , and each diverges as  $T \rightarrow T_c$  with different exponents. Nevertheless, defining  $\xi = (\xi_{\parallel} \xi_{\perp}^2)^{1/3}$ , scaling relations hold<sup>(8)</sup>—in many cases.

## Surface Tension

A striking visual feature of the gas-liquid critical point is that the interface between the phases vanishes. This is called *critical opalescence*. The surface tension  $\sigma$  vanishes at the critical point  $(T_c, P_c)$ . Since we are particularly interested in the dynamics of interfaces, it is instructive at this point to be aware that surface tension  $\sigma$  goes to zero at a second-order phase transition with an exponent  $\mu$ .<sup>(12)</sup> Surface tension is an energy per area or an energy density times a length,  $f \times \xi$ , and  $f$  scaled by temperature is again  $\xi^{-d}$ , so

$$\sigma \sim \varepsilon^\mu \sim f\xi \sim \xi^{-d+1} \sim \varepsilon^{\nu(d-1)} \quad (7)$$

or  $\mu = \nu(d-1)$ . So, for  $d=1$ , the surface tension is independent of temperature. But when fluctuations dominate in 3d,  $\mu=4/3$ . If scaling applies in the classical regime,  $\nu=1/2$ ,  $\mu=1$ , i.e., the surface tension goes linearly to zero as  $T \rightarrow T_c$ .

## 9. G. I. TAYLOR AND RELEVANT PARAMETERS

As we have seen, dimensional analysis is a powerful technique to learn a great deal about a complicated phenomena. But, you need to be able to put your finger on the essential features of the problem. And that is where the talent lies: distinguishing between relevant and irrelevant dimensions. An amusing anecdote of the power of dimensional analysis that illustrates this is the story<sup>(12)</sup> of how G. I. Taylor deduced the yield of the first nuclear explosion from a series of photographs of the expanding fireball in *Life*

magazine (Fig. 5). He realized he was seeing a strong shock expanding into an undisturbed medium of density  $\rho$ . The photographs gave him the radius  $L$  of the fireball as a function of time  $t$ . Thus,  $L$  and  $t$  are relevant and  $M$  must be irrelevant. The radius, with dimensions of length, depended on  $E$  ( $ML^2/t^2$ ), the initial energy released by the bomb,  $\rho$  ( $M/L^3$ ), and  $t$ . He wrote these three quantities in a way so that their net dimensions came out to a length and the irrelevant parameter, mass, canceled:

$$r(t) \sim \left( \frac{ML^2}{t^2} \cdot \frac{L^3}{M} \cdot t^2 \right)^{1/5} \sim \left( \frac{E}{\rho} t^2 \right)^{1/5} \tag{8}$$

A log-log plot of  $r$  vs.  $t$  ( $2\frac{1}{2}$  decades in  $r$  and 4 in  $t$ ), measured from the pictures, gave a slope of  $2/5$  that checked the irrelevancy of  $M$ . The factor

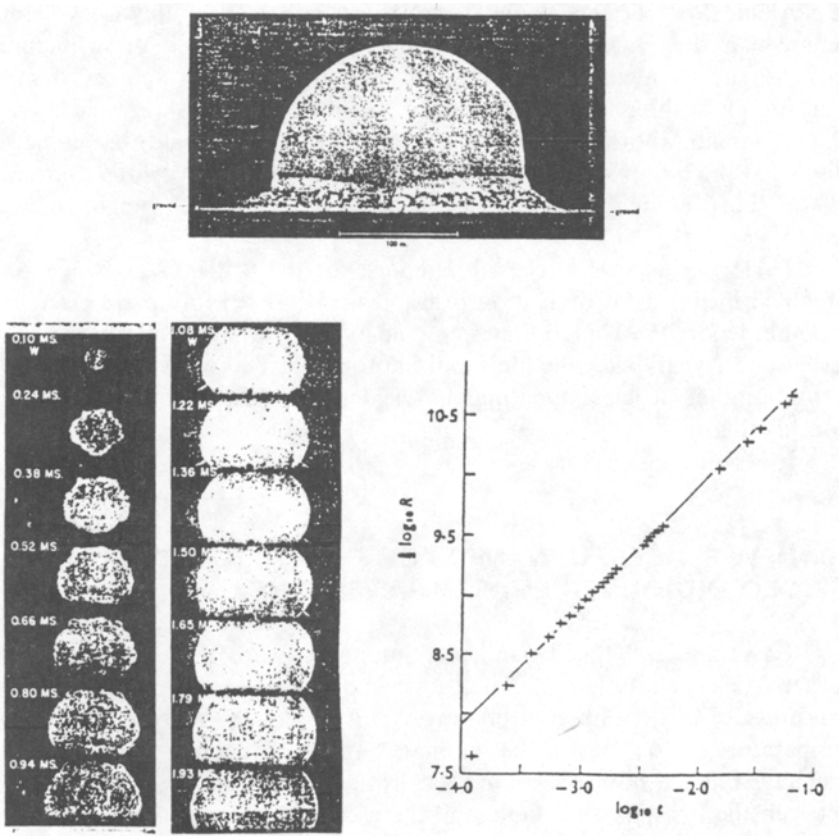


Fig. 5. Some of the photographs of an atomic bomb explosion used by G. I. Taylor to check his deduction of the yield of the bomb from dimensional analysis.

$E/\rho$  could be obtained from an extrapolation of  $r$  when  $t = 1$ . Since  $\rho$ , the density of undisturbed air, was known,  $E$ , the energy not radiated outside the ball of fire, was determined to within a factor of order 1. Actually, Taylor also calculated the constant of proportionality and made several estimates. The one he favored was  $E \sim 7 \times 10^{20}$  ergs  $\leftrightarrow$  16,800 tons TNT (using 1 g TNT liberates 1000 calories).<sup>(19)</sup>

So, as Goodstein says,<sup>(12)</sup> “For a person who can grasp the essential physics (what are relevant and what are irrelevant parameters) of a problem well enough to use dimensional analysis, our nation’s deepest secret was published in *Life* magazine!”

This is a good story, but exaggerated for the entertainment of students. The filmed sequence and photographs that G. I. Taylor measured to check his expression were made by several people, one a director here at Los Alamos, not *Life* magazine. I thought it best to check this story before telling it at Los Alamos and asked our librarians to find those pictures in *Life*. They hunted for a couple of days and called their sources at *Life*, but found nothing. So I telephoned Goodstein, who suggested I call P. G. Saffman, a former student of G. I. Taylor. Saffman said that he never discussed the bomb with Taylor, but suggested I look at Taylor’s *Collected Works* and they just happened to be on our library shelf: bingo, there it was!

Taylor wrote several classified reports for the British War Office, one of which included his derivation of Eq. (8) in 1941—before there even was a bomb, before the United States entered WW II. After the bomb had been tested and 2 years after the films and photographs had been *declassified*, he wrote another article estimating the yield of the bomb from the pictures and his theory.<sup>(19)</sup>

It is still a good story.

## 10. NEW PLACES: DYNAMICS OF FRONTS AT FIRST- AND SECOND-ORDER PHASE TRANSITIONS

To understand the dynamics of interfaces, we consider it analogous to a particle in a potential  $f(\psi)$ ,<sup>(10)</sup> as shown in Fig. 3. For a *first-order transition*, in a temperature range close enough to the transition temperature,  $f(\psi)$  has three minima. Above  $T_c$ , their stabilities are exchanged. Since both phases are locally stable, the energy of an interface between the two phases is finite and there is a nucleation barrier, resulting in hysteresis: the system can be undercooled or superheated. Temperature determines which side of the interface is stable and which side is metastable and the front moves from the stable into the metastable state: front



propagation for first-order transitions is reversible with temperature. Such behavior has been called an *inverted bifurcation*.

A second-order transition can be neither undercooled or superheated.<sup>(3,13)</sup> A sharp interface does not exist between the two phases, but the dynamics of an ordered state confined by a temperature step, say, may be studied. When the temperature step is released so that  $T$  is uniform and below  $T_c$ , the disordered state is unstable ( $df/d\psi|_0=0$ ), and the ordered state propagates into the unstable state. The propagation of a "confined" state when released from captivity has recently been observed by Fineberg and Steinberg<sup>(20)</sup> near the threshold for convection. Releasing the temperature step so  $T$  is uniform and above  $T_c$ , the disordered state is stable. A net force exists everywhere in the ordered state ( $df/d\psi \sim \psi$ ), proportional to the magnitude of  $\psi$ , defining a single time constant for relaxation to the  $\psi=0$  state. The irreversible behavior with temperature exhibited by an interface moving in a second-order potential has been called a *forward bifurcation*.

Thus, the direct observation, first of all, of an interface, and second, of the interface propagating in both directions is powerful evidence that the transition is first order or discontinuous.

### Propagation Speed

The temperature dependence of the interface speed depends on the order of the phase transition. In a potential characteristic of a first-order transition where the two states are metastable, its speed is linear in temperature, going through zero at  $T_c$ . For a second-order transition, the speed varies like  $\epsilon^{1/2}$  and can only be seen for  $T < T_c$ . The time-dependent Ginzburg-Landau equation can be used to formalize these results.

The time-dependent Ginzburg-Landau equation is found by equating the Euler-Lagrange condition applied to the free energy density to the time derivative of the order parameter:<sup>(10)</sup>

$$\gamma \frac{d\psi}{dt} = \frac{\partial}{\partial x} \frac{\partial f}{\partial \psi'} - \frac{\partial f}{\partial \psi} = \frac{1}{M} \frac{\partial^2 \psi}{\partial x^2} - a\psi - b\psi^3, \quad \psi' = \frac{\partial \psi}{\partial x} \quad (9)$$

where  $\psi$  is now a function of  $x$  and time  $t$ . Multiplying through by  $d\psi/dx$ , then integrating, a relation between the front speed  $v$ , the front profile  $d\psi/dx$ , and the energy density can be obtained as

$$v\gamma \int_{-\infty}^{+\infty} dx \left( \frac{d\psi}{dx} \right)^2 = - \int_{-\infty}^{+\infty} dx \frac{d\psi}{dx} \frac{df}{d\psi} = f_s - f_n \quad (10)$$

**First-Order Case (Well-Defined Profile).** In this case,

$$f_s - f_n = L\varepsilon$$

where  $L$  is the latent heat. Thus, from Eq. (10), the front speed is linear in temperature and the front propagates from the stable into the metastable state. To determine the front speed in terms of  $\xi_c$ , the magnitude of the coherence length at the first-order transition temperature  $T_{NA}$ , we consider two points.

*In the Vicinity of a Landau Tricritical Point.* In the vicinity of an LTP,  $b \approx 0$  in Eq. (9) and the three minima of a first-order transition are close to each other. In this limit,  $f$  can be represented<sup>(21)</sup> as

$$f = \psi_0^4 \psi^2 - \psi_0^2 \psi^4 + \psi^6$$

Thus,  $1/\xi_c^2 \sim \psi_0^4$  and the latent heat scales with the coefficient of the fourth-order term, or  $L \sim \psi_0^2 \sim 1/\xi_c$ , and is infinite at the LTP in the absence of a cubic term. Counting powers of  $\psi_c$  and  $\xi_c$  on the left-hand side of Eq. (10) and equating them to  $L\varepsilon \sim \psi_c^2 \varepsilon$ , we obtain

$$v\gamma\xi_c \frac{\psi_c^2}{\xi_c^2} \sim L\varepsilon \sim \psi_c^2 \varepsilon$$

Thus  $v/\varepsilon \sim \xi_c$ : the closer the system is to a second-order transition, the steeper the dependence of speed on temperature. At the LTP, in the absence of a cubic term,  $v/\varepsilon$  is infinite.

*HLM Effect (Cubic Corrections at the LTP).* When a cubic term is added to the free energy density, the latent heat at the LTP (or the jump in entropy at the LTP,  $\Delta S^*$ ) is not zero, and is used to scale the data. Anisimov *et al.* found they could fit all the known calorimetry data to a functional form derived under these assumptions:<sup>(9,11)</sup>

$$\left(\frac{\Delta S}{\Delta S^*}\right) - \left(\frac{\Delta S}{\Delta S^*}\right)^{1/2} = \frac{\alpha R}{\Delta S^*} (x - x^*) \equiv y - y^* \quad (11)$$

where  $y - y^*$  is a Landau parameter relating the distance to the LTP. However, two compounds could not be placed on the curve because their latent heat was too small to measure.

The susceptibility can also be related to the latent heat under the same conditions, resulting in the following expression:<sup>(11)</sup>

$$\frac{\chi_c^*}{\chi_c} = \frac{A_c}{A_c^*} = \left(\frac{\Delta S}{\Delta S^*}\right)^2 \left[ \frac{1}{3} + \frac{2}{3} \left(\frac{\Delta S}{\Delta S^*}\right)^{-3/2} \right] \quad (12)$$

where  $\chi_c$  is the susceptibility on the transition line. Assuming the anisotropic generalization of hyperscaling holds, we can then use this expression to deduce  $v \sim \xi_c \sim \chi_c^{1/2}$  from the latent heat data.

### Second-Order Case (No Well-Defined Profile or Confined Ordered State).

1.  $T > T_c$ : Fronts do not propagate. This can be seen using Eq. (9), for in this case,  $\gamma \partial\psi/\partial t = -|a|\psi$ . The time dependence is therefore given by a simple exponential decay:  $\psi = \psi_0 \exp(-|a|t/\gamma)$ . A single time constant can be defined for any initial value of  $\psi$  allowing the whole system to relax at the same rate to the  $\psi = 0$  state.

2.  $T < T_c$ : If a front, or an interface, can be confined at a second-order transition, it may propagate, but only one way with temperature. The bifurcation is *forward*. The temperature dependence of its speed can be found by scaling as  $f_s - f_n \sim 1/\xi^d$  and

$$\psi \sim \xi^{(2-d-\eta)/2} \rightarrow \frac{d\psi}{dx} \sim \xi^{-(d+\eta)/2} \rightarrow \left(\frac{d\psi}{dx}\right)^2 \sim \xi^{-(d+\eta)}. \quad (13)$$

Substituting Eqs. (13) into Eq. (10) and counting powers of  $\xi$ ,

$$v \sim \frac{dx}{dt} \sim \frac{1}{\xi^{d+1}} \left(\frac{d\xi}{d\psi}\right)^2 \sim \xi^{-d-1+d+\eta} \sim \xi^{-(1-\eta)}. \quad (14)$$

The predictions of marginal stability<sup>(22)</sup> (mean field) for fronts propagating from an unstable part of the potential into a stable part can be recovered by the mean field exponents,  $\eta = 0$  and  $v = 1/2$ .

## 12. APPLICATION TO THE 8CB AND 9CB-10CB MIXTURES

To test how the speed of a front propagating at a first-order phase transition under isothermal conditions depends on its distance from a second-order phase transition, we required a system where both the latent heat and the coherence length had been determined. A system that met these requirements was the 9CB-10CB and 8CB-10CB mixtures 9CB, nonylcyanobiphenyl; 10CB, decylcyanobiphenyl; 8CB, octylcyanobiphenyl.

According to the best available x-ray<sup>(8)</sup> measurements, the nematic-smectic A transition in 8CB is second order and the 9CB-10CB mixtures exhibit a tricritical point at 9.7% by weight of 10CB in 9CB. Mixtures with more 10CB in 9CB appear first order, and those with less, second order. On the other hand, calorimetry measurements<sup>(7)</sup> for these compounds suggest that the 9CB-10CB system is always first order, whereas 8CB is

second order. This then gives an idea of the relative precision with which the order of a transition can be made using the standard tools. Adiabatic calorimetry clearly measures a latent heat in several compounds that x-ray diffraction sees as being second order. However, even adiabatic calorimetry failed to see a latent heat for 8CB.

Based on the dynamics of the fronts exhibited by these materials, our results are: first, they all exhibit the dynamic characteristics of a first-order transition, and second, the behavior of the interface speed as a function of  $T - T_c$  and the coherence length at the first-order transition temperature  $T_c$ , i.e.,  $\xi(T_c) = \xi_c$ , is consistent with the behavior expected on the first-order side of a tricritical point. The order of magnitude of the microscopic time that emerges from these measurements,  $\tau \simeq 7.5 \times 10^{-9}$  sec, is reasonable.<sup>(10)</sup>

### 13. DISCUSSION OF EXPERIMENTAL SETUP

The experiment was to start from a uniform state just above (or below)  $T_c$ , then change the temperature at a rate of  $0.01^\circ\text{C}/\text{msec}$  to  $T$ , just below (or above)  $T_c$ , then record the front passage as it was observed through a microscope with a video monitor.

Although it is, in principle, easy to check experimentally whether, in a given sample, front propagation is *inverted*, that is, propagates both on cooling and heating, or *forward*, that is, propagates only on cooling, to obtain quantitative data: (1) samples must be small, to allow the temperature to change fast enough to ensure that the front is propagating under isothermal conditions, and (2) samples must be of uniform thickness with the director perfectly oriented perpendicular to the field of view. We resolved the first by preparing small sample cells: typically 1 cm by 1.5 cm by  $13 \mu\text{m}$ . A  $2 \times 2.5 \times 0.7 \text{ mm}^3$  platinum resistance thermometer was thermally sunk to the cell just outside the field of view to monitor sample temperature during the passage of the front. We resolved the second by using the powerful surface treatment of Patel *et al.*<sup>(23)</sup> that provides a defect-free alignment over the entire sample.

The alignment process developed to align smectic materials gave extremely well-oriented samples.<sup>(23)</sup> The direction of  $\mathbf{n}$  in the plane of the transparent substrates (both glass and sapphire substrates were used) was imposed by buffing the glass plates with a machine especially designed for this purpose. It precisely determines the orientation of  $\mathbf{n}$ . The director was oriented in the plane of the glass, so that the observation direction is exactly perpendicular to the direction of broken translational symmetry characterizing this transition. Technically, this is difficult to achieve over

such large areas of the cell: in these cells  $n$  was uniformly oriented over the *entire* cell. They were the best oriented cells I have ever seen. We have not observed fronts in similar cells when making these observations parallel to the direction of broken symmetry. Bechhoeffer<sup>(24)</sup> has told me that in a temperature gradient they are able to see an interface in 8CB in this direction. It is very subtle and they have so far not been able to film it.

The chemical purity of the samples was checked and found to be state of the art—99% pure. This was necessary because, as we have seen, impurities are used to change the order of a transition.

Sample cells were made by sealing together with Torr seal epoxy (a low-vapor epoxy designed for sealing leaks in high-vacuum systems) a pair of glass or sapphire plates separated by Mylar spacers to determine cell thickness. Both the thickness and uniformity of the cells were checked using a section microscope. After several cells had been made, the most uniform, with thicknesses ranging from 11 to 15  $\mu\text{m}$ , were selected for vacuum filling with the liquid crystal material.

To control the temperature of the samples, we used a Mettler microscope hot-stage. The design of this oven consists of two boxes, one inside the other. In the inside box, there are two heating plates positioned above and below the sample. The temperature of the two plates is electronically controlled by a servo provided by a platinum resistance thermometer in the bottom plate. There is a 2.5-mm hole in the top and bottom plates that allows light to pass through the oven. The inside box is completely enclosed in another box with two larger holes covered by glass slides to let the light pass through the sample into the microscope optics. The temperature gradients inside the inner box were checked and found to be immeasurably small in the optically accessible area that is 2.5 mm in diameter.

The temperature set point mechanism was interfaced to an AT & T PC 6300 and temperature changes of  $0.01^\circ\text{C}/\text{msec}$  could be made. Although the interior thermal mass of the oven is small, thermal relaxation times were on the order of 1 sec. As mentioned above, the temperature of the cell during the passage of the front was measured with a small platinum resistance thermometer thermally sunk to the sample cell. It can be read with a precision of  $0.01^\circ\text{C}$ .

### Temperature Gradients

Suppose there is a temperature gradient across the field of view; then the front speed will no longer be a linear function of temperature, since it will accelerate or decelerate, depending upon whether it travels “down” the gradient or “up.” Thus, whether gradients are large enough to be a

problem can be assessed by monitoring how uniformly a front propagates across the field of view by recording its trajectory on tape. This is, indeed, a sensitive way to measure temperature gradients.

Another way to check the effect of temperature gradients is to rotate the sample  $90^\circ$  relative to the heating plates and the field of view. If the front persists in traveling the same way, then temperature gradients are large enough to dominate these experiments. If the front now travels from "top" to "bottom" rather than left to right, say, then it can be concluded that although it is impossible to say how much of a temperature gradient there is, it is too small to influence the measurements. Indeed, to observe a front at a second-order transition in these materials, a large temperature gradient (about  $\sim 1^\circ\text{C}/10\ \mu\text{m}$ ) is required. We can absolutely exclude the existence of such a gradient in our setup.

Monochromatic light was used from a weak sodium lamp especially designed for light microscope observations. This was done mainly to avoid heating effects from the source of illumination. In some samples, such as 80CB, the front could be stabilized in the middle of the field of view and made to move slightly back and forth simply by raising or lowering the condensing stage of the microscope when the usual white light source was used. This is most probably a result of UV absorption by the glass plates, since there is no absorption band for CB compounds at the relevant wavelengths.

The sample was viewed with a light-sensitive video camera. With the camera, the front could be observed on a monitor even though it was difficult to see by direct visual observation, given the low intensity of the illumination. A polarizer and analyzer were used and adjusted to just slightly off the extinction position.

The time of flight of the front was recorded using a VCR interfaced to the camera. The VCR was also controlled by the AT & T PC 6300. Recorded passages of the front motion were then played back and from a measure of the number of frames taken to travel across a premeasured distance corresponding to an  $\sim 1\text{-mm}$  path of the front, a speed was determined for the temperature of the cell during the front motion. The time resolution of this measurement is 0.1 sec. These recordings also enabled us to check the uniformity of the front speed during its time of flight. Only those observations made under isothermal conditions, determined by monitoring the PT100 thermometers thermally sunk to the cell, were used.

The velocity as a function of temperature was plotted for both directions of the front propagation. It was found that the two sets of data fell on a straight line that was used to determine the transition temperature  $T_{\text{NA}}$  for that particular sample. Once the data had been replotted as a function of  $\varepsilon = (T - T_{\text{NA}})/T_{\text{NA}}$  using the computed value for  $T_{\text{NA}}$ , the slope  $v/\varepsilon$  was determined (Fig. 6).

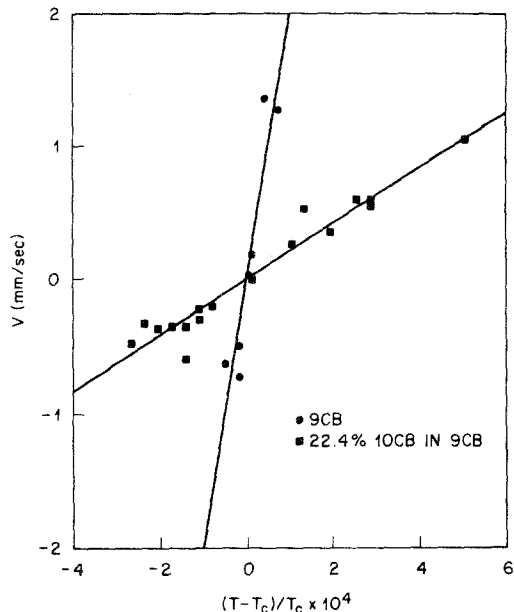


Fig. 6. Interface speed  $v$  as a function of distance to the transition temperature  $v$ . The closer the system is to a second-order phase transition, the steeper the slope  $v/\epsilon$ .

In all our experiments,<sup>7</sup> we observe interfaces between the nematic and smectic A phases near  $T_c$ . Furthermore, interfaces are found to propagate into the disordered state as well as into the ordered state. Qualitatively, therefore, the dynamic signature of the nematic to smectic A phase transition is consistent with first-order behavior, an *inverted* bifurcation.

No systematic dependence of the front speed on its orientation relative to the director was detected. This means that either it is too small for our experiments to resolve or the transition has indeed selected a  $\xi$  that is independent of the director orientation  $\mathbf{n}$ . Thus, the scale we adopt to describe our data is  $\xi = (\xi_{\parallel} \xi_{\perp}^2)^{1/3}$  consistent with the "anisotropic" scaling arguments of the MIT group deduced by considering the available heat capacity, light scattering, and x-ray scattering data.<sup>(8)</sup>

Using the available latent heat<sup>(7)</sup> and x-ray<sup>(8)</sup> data, we verified that the relationship  $L \sim \xi_c^{-1}$  holds over the range 14%–28% 10CB in 9CB,

<sup>7</sup> The following is a list of the compounds we studied where fronts were observed on heating and cooling through the N-A transition: 8OCB and the mixture 1.5% 60CB in 80CB; the 80CB-DB70CN mixtures 15%, 20%, and 32% 80CB in DB70CN; 40.8 and the mixture 1.5% 40.8 in 80CB; 8CB; 9CB; the 9CB-10CB mixtures 4.7%, 5%, 5.8%, 8.9%, 9%, 9.7%, 14.1%, 14.2%, 15.6%, 20.1%, 22.4%, and 28.1% 10CB in 9CB; and 10E6.

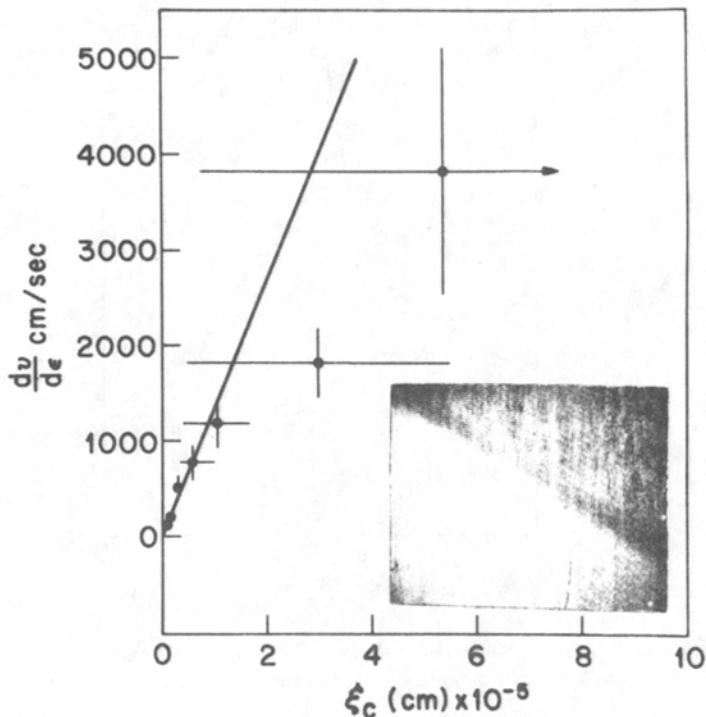


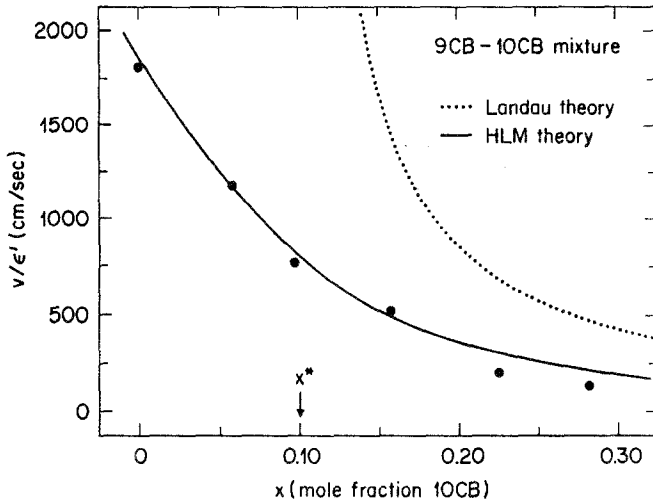
Fig. 7. Plot of  $v/\varepsilon$  vs.  $\xi_c$ , the magnitude of the coherence length at  $T_c$ .

corresponding to a factor of three in  $\xi_c$ . We therefore used it to estimate  $\xi_c$  for concentrations below 14%, for which measured values of  $\xi_c$  are unavailable. An upper limit for the latent heat is taken to estimate  $\xi_c$  for 8CB.<sup>(7)</sup> Figure 7 shows  $dv/d\varepsilon$  versus  $\xi_c$  so obtained.

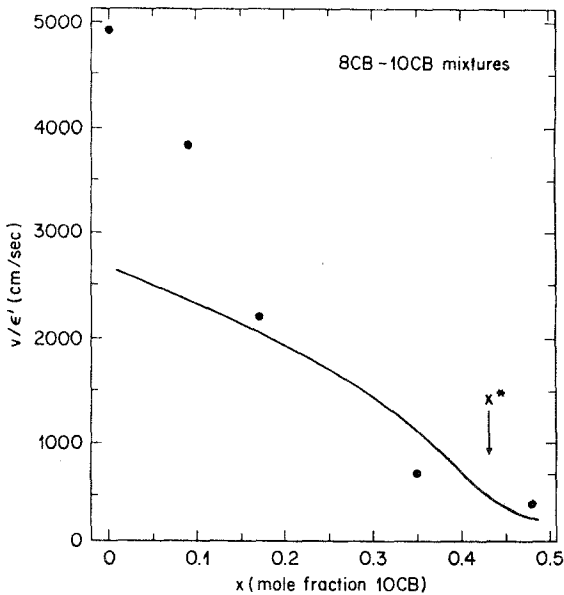
#### 14. EXPERIMENTAL RESULTS

A photomicrograph of the front in 9CB is shown as an inset in Fig. 7. The field of view is about  $1\text{ mm} \times 1\text{ mm}$ . In the figure, each data point represents a different mixture corresponding to the composition range 0–28.2% 10CB in 9CB. Using only points where the uncertainty in  $\xi_c$  is insignificant, the straight line describing the data is  $dv/d\varepsilon$  (cm/sec)  $\simeq 1.3 \times 10^8$  (sec<sup>-1</sup>)  $\xi_c$  (cm). The microscopic time characterizing the transition is  $\tau \simeq 7.5 \times 10^{-9}$  sec. Taking a typical diffusion constant for nematic and smectic A phases,  $D = 4 \times 10^{-7}$  cm<sup>2</sup>/sec, at similar temperatures,<sup>(25)</sup> in time  $\tau$  a molecule diffuses  $\sim 6$  Å, which is adequate to relax the smectic order parameter.





(a)



(b)

Fig. 8. Introducing a cubic term into the free energy (solid line) allows one to scale all the data by their value at the Landau tricritical point (LTP) where the coefficient of the fourth-order term is zero.  $v/\epsilon'$  vs. distance to the LTP ( $y^*$ ). (a) 9CB-10CB (most of the data are close to the LTP) and (b) 8CB-10CB (most of the data are far from the LTP).

We note that the magnitude of  $dv/dc$  is of order 10 m/sec in Fig. 7. This shows that these nematic-smectic A interfaces grow nearly as easily as the solid-liquid interfaces in simple atomic systems. Computer simulations<sup>(26)</sup> on Lennard-Jones systems suggest a slope of about 80 m/sec for argon, while experimental data<sup>(27)</sup> for Si are consistent with a slope of the same order. Clearly, the weakness of the first-order transition contributes to the fast growth of these liquid crystal interfaces.

Figure 8a shows the same data (9CB-10CB) as a function of  $y - y^*$  [Eq. (11)] assuming the HLM theory and the latent heat measurements of Thoen *et al.*<sup>(7)</sup> The only adjustable parameter here is the choice for the concentration corresponding to the LTP,  $y^*$ . The 9CB-10CB mixtures are all near the LTP. The agreement seems remarkable and shows that front velocity measurements give qualitatively the same results as the finest adiabatic calorimetry measurements<sup>(7)</sup> in this limit. On the other hand, the 8CB-10CB mixtures (Fig. 8b) strayed further from the LTP, although still qualitatively showing the dynamical signature of a first-order phase transition; quantitative deviations are seen from mean field expectations as expected.

## 15. CONCLUSIONS

Measurements of front velocities are a new tool for determining the order of a transition. We have used it to show that even transitions that fall below the resolution of x-ray and adiabatic calorimetry exhibit the dynamic signature of a first-order transition. By scaling all data from diffraction, calorimetry, and dynamic measurements with their value at the Landau tricritical point, a universal plot can be made that is consistent with the existence of a small cubic term in the Landau free energy. All the data are in excellent, if long overdue, agreement with the appreciation of subtleties of phase transitions by Halperin, Lubensky, and Ma.<sup>(4)</sup>

## ACKNOWLEDGMENTS

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