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PHASE TRANSITIONS AND CRITICAL PHENOMENA

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PHASE TRANSITIONS IN LIQUID CRYSTALS

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Résumé. — Ce texte est la transcription d'un exposé d'introduction dans lequel on discute deux transitions de phase : la transition némantique-isotrope et la transition smectique A-némantique. On souligne l'importance d'éléments qualitatifs simples, parmi lesquels les théories de Landau, les longueurs de cohérence et les propriétés d'échelle.

Abstract. — The present text is the transcription of an introductory lecture discussing two phase transitions: nematic-isotropic and smectic A-nematic. The emphasis is on simple qualitative features, including Landau theories, coherence lengths and scaling properties.

1. Introduction. — I would like to talk about two phase transitions today. First of all, I want to review the properties of the nematic to isotropic phase transition with which you are all familiar. Then I want to bring you up to date on the current research on the smectic A to nematic phase transition.

2. Nematic-isotropic transition. — The isotropic liquid phase is liquid, which means that the molecules translate freely, and is optically isotropic, which means that the molecules tumble freely. There is no long range order. The nematic phase is liquid, but is locally optically uniaxial. One can describe the local order by specifying, for example, the dielectric tensor. It is more common to specify the magnitude of the anisotropy $S$ and the direction of the local optical axis $n$. This is a phenomenological description of the local order. One can alternatively use a microscopic picture in which the long axis of the molecules is preferentially parallel to the director and the strength of the order parameter is $S = \frac{1}{4} \cos^2 \theta - \frac{1}{2}$. In the absence of external forces, if the molecules in one part of the sample are pointed in a particular direction, the molecules a macroscopic distance away will point in the same direction. The nematic phase exhibits long range orientational order. The orientational order parameter $S$ is finite in the nematic phase, decreases as one approaches the phase transition and drops abruptly to zero in the isotropic phase. The phase transition is first order.

In the isotropic liquid phase near the phase transition there are still strong forces tending to orient the molecules parallel to each other. The forces are not strong enough to generate long range order but cause short range order; two molecules will be more or less parallel if they are close enough to each other. The distance over which the directions of the long axes are appreciably correlated is called the correlation length $\xi$. The correlation length increases as one approaches the phase transition. A very useful physical picture of this pretransition effect is that of flickering droplets. If one could take a snapshot of the molecules and examine it, one would find regions of the liquid in which the long axes are more or less parallel to each other and regions of the liquid in which the long axes are disordered. It is useful to think of the ordered regions as droplets of nematic in a sea of disordered liquid. The radius of a typical droplet is the correlation length. If one were to take snapshots at a later time to follow the time evolution of a droplet, one would find that the droplets grow and shrink in a characteristic time $\tau$, the relaxation time. Thus our droplets are not long lived, like raindrops, but flicker. It takes longer for the larger droplets to relax, so the relaxation time increases as one approaches the phase transition.

This physical picture is useful for qualitative arguments about pretransition phenomena. If one applies a magnetic field to the isotropic liquid, the droplets will tend to orient in the field producing a weak optical anisotropy. This magnetically induced birefringence will grow stronger as one approaches the transition because the droplets increase in size. The flickering droplets will also produce depolarized Rayleigh scattering. Both these effects have been observed by Stinson and Litster [1].

Let me describe briefly the theories of the nematic phase. There are two kinds of theories-microscopic and phenomenological. The Maier-Saupe theory [2] is microscopic. One writes down an intermolecular potential, uses the self-consistent field method, and calculates the order parameter $S$ and the specific heat versus temperature. Pretransition phenomena are left out of the theory. The other theories are phenomeno-
logical. In the Oseen-Frank elastic theory [3] one supposes that $S$ is constant and writes down an expression for the free energy in terms of the director. This theory describes static distortions of the nematic. The theory was extended to dynamic phenomena by Leslie and Ericksen [4] by including coupling of the director to the fluid motion and by including viscous dissipative processes. Near the phase transition or in the isotropic liquid phase variations in $S$ are important. De Gennes [5] has introduced a time-dependent Landau theory to include this effect which provides the mathematical description of the flickering droplets. The theory is in good agreement with experiments of the pretransition effects.

3. Smectic A-nematic transition. — You are all, I am sure, more or less familiar with the work on the nematic phase. I told you that story so that I could tell you this one. Entirely analogous things are happening now on the smectic A-nematic phase transition.

In the smectic A phase, the molecules sit on planes with the interplanar spacing about equal to the molecular length and with the long axis perpendicular the planes. We can describe the planes phenomenologically with a complex order parameter $\psi(x)$. The magnitude of the order parameter describes the strength of the planes; it vanishes in the nematic phase. The phase of the order parameter described the position and interplanar spacing of the planes. One smectic plane is the surface on which the phase is constant; the next smectic plane is the surface on which the phase is $2\pi$ greater. This sort of description is necessary to describe smectic planes which may be curved and whose interplanar spacing may not be constant. The phase transition may be either first or second order. In the first order case, the magnitude of $\psi$ decreases as one approaches the phase transition from below and drops abruptly to zero at the transition. In the second order (or continuous) case, the order parameter falls continuously to zero as one approaches the transition. The current interest is in the second order case.

There is, by now, a fairly large body of theoretical work on the second order transition which I want to describe for you. The microscopic theory by Kobayashi and by myself [6] was an extension of the Maier-Saupe theory to the smectic A phase. The theory produced a reasonable phase diagram and first indicated that the smectic A-nematic transition would be second order if the temperature range of the nematic phase were large enough.

Next de Gennes and I [7] proposed a phenomenological Landau theory to describe the static distortions of the smectic order parameter $\psi$ and the nematic director $\mathbf{n}$. This is an extension of the Oseen-Frank theory to the smectic A phase. The form of the free energy is similar to the Ginzburg-Landau theory of superconductivity with the vector potential of that theory replaced by the nematic director. The theory describes the static behavior of smectic droplets in the nematic phase just above the phase transition. There is one difference in the two versions of the theory. My version was a classical Landau theory which predicts a mean field behavior of the correlation length $\xi \sim (T - T_c)^{-1/2}$. De Gennes described the critical behavior of the smectic order parameter by noting the analogy to liquid helium (which also has a complex order parameter) and the fact that the critical behavior should be universal; he finds $\xi \sim (T - T_c)^{-2/3}$. The analogy to the superconductor does not help in predicting critical behavior because the superconductor does not exhibit critical fluctuations. De Gennes also predicted a pretransition increase in the bend and twist elastic constants. The expression for bend is

$$K_{33} = K_{33}^0 + \frac{ckT^2}{d^2}$$

where $c$ is a constant of order unity and $d$ is the smectic interplanar spacing. One can understand this behavior within the simple picture of smectic droplets in the nematic phase. Bending or twisting the smectic planes causes a change of the interplanar spacing which is energetically very costly. Thus the smectic droplets resist bending or twisting and this results in a larger elastic constant for the liquid as a whole. The free energy of the director is modified by coupling to the smectic order parameter. There is an inverse effect; the free energy of the smectic order parameter is modified by coupling to the director. The transition temperature is decreased by bend or twist distortions; thus the thermal fluctuations of the bend and twist modes decrease the transition temperature to the smectic phase. The smectic droplet is uniaxial and is characterized by two correlation lengths, $\xi_0$ parallel to the director and $\xi_1$ perpendicular to the director. In the presence of bend or twist distortions, it is energetically costly to have smectic droplets large in the transverse direction; this suppresses the transverse correlation length $\xi_1$.

This static Landau theory was extended to a dynamical Landau theory by Brochard and Janig [8] using the helium analog, and by myself [9], within the mean field method. When the liquid moves across the smectic planes, molecules must jump from one smectic plane to the next. This process is dissipative and results in a viscous drag of the smectic planes on the liquid and a new viscosity coefficient $\gamma_3$. When the director is rotated, the smectic droplets are forced to rotate also and the liquid flow across the smectic planes contribute a viscous torque proportional to $\gamma_3$ to the rotational viscosity term $\gamma_1$. The expression

$$\gamma_1 = \gamma_1^0 + \frac{c_1^e \gamma_3 kT^2}{c_1}$$

where $c_1$ is the coefficient of the longitudinal kinetic energy of the smectic order parameter. $\gamma_2$ and one of the fluid viscosities $\eta_{M}^{t}$ are renormalized in a similar
way. Within the mean field model $\eta_2$ is constant but from the helium analog $\eta_2 \sim \xi^{-1/2}$.

Both the static and dynamic Landau calculations treat the coupling of the smectic order parameter and the director as a perturbation. The dimensionless coupling constant is $kT\xi^2/K_{23} d^2$. If this parameter is small, it is far from the phase transition, the helium analog should provide the correct critical behavior. Halperin, Lubensky and Ma [10] have tried to calculate directly the critical behavior by applying Wilson's renormalization group methods to the Landau theory. They find, however, that the phase transition is not continuous, but is slightly first order. This comes about for the following reason. The transition temperature is suppressed by thermal fluctuations which also carry a good bit of entropy. On the other hand, in the smectic phase bend and twist are forbidden and the apparent transition temperature is higher. On heating, before the smectic can reach its continuous transition temperature the entropy of the director fluctuations forces a first order transition to the nematic phase. This argument is too crude, however, because the director fluctuations are reduced by the stiffening of the elastic constants. It is a delicate question then whether or not the stiffening of the elastic constants is strong enough to force a continuous suppression of the director fluctuations. The Wilson theory says not — that the transition should be first order and take place when the dimensionless coupling constant is of order one.

It is clear that one should discuss two regimes of temperature in this problem: 1) a precritical regime where the coupling constant is small and the helium analog should be approximately correct (this regime is $T - T_c > 1^\circ C$ in CBOOA) and 2) a critical regime where the coupling constant is large and the transition may be first order ($T - T_c < 1^\circ C$).

Most of these effects have been observed experimentally and we are at the stage of making careful quantitative measurements to compare with the theory. Most of the work is on cyanobenzylidene octyloxyaniline (CBOOA). The X-ray work [11] on CBOOA measured the correlation lengths of the smectic droplets and found a different temperature dependence for $\xi_1$ and $\xi_2$, in disagreement with the helium analog. By computing corrections to the helium analog, it may be possible to explain this data. The pretransition increase in $K_{22}$ and $K_{33}$ has been observed in Freedericks transition [12] and Rayleigh scattering [13] experiments. The theory here is certainly qualitatively correct although there is some disagreement on what the exponents are. Meiboom [14] first observed the pretransition increase in $\gamma_1$ in a Zvetkov experiment and this motivated me to do the dynamical theory. More experimental work will be reported in this session. On the question of whether or not the transition is slightly first order, the only published data is the observation of a small discontinuity in the density at the transition by Cladis and Torza [15].

In summary, I believe we are advancing at a brisk pace toward a quantitative understanding of this very interesting phase transition. I have told you everything I know; I shall be very interested in hearing the research papers in today’s session.

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