Phase transitions in liquid crystals - Brief introduction

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1. Introduction

In this chapter, after a brief introduction into the field of liquid crystals which includes classification, characterization of the main types, and the definition of the order parameters, we present the Landau-de Gennes theory of phase transition. We discuss the nematic-isotropic phase transition as an example of first order phase transition and nematic-smectic A phase transition as an example of the second order phase transition. In the last section the interface dynamics is discussed. First we present the two models of solidification of a pure substance from its melt: the sharp interface model and the phase field model. Finally we present some results concerning the phase field model for liquid crystals for front propagation in a temperature gradient.
1.1. Liquid crystals

Many organic materials exhibit more than a single transition in passing from solid to liquid. The molecular order in these intermediate phases, known as “mesophases”, lies between that of a solid and that of an isotropic liquid. Two different types of mesophases have been observed: (i) plastic crystalline mesophases that have a long-range positional order, but are characterized by substantial rotational disorder and (ii) liquid crystals which possess a long-range orientational order, but the positional order is reduced or completely disappeared.

Liquid crystals [1, 2, 3, 4] possess many of the mechanical properties of a liquid, e.g. high fluidity and the inability to support shear. On the other hand, they have some properties similar to crystals, e.g. they are birefringent and have anisotropic magnetic and electric susceptibilities.

Two types of liquid crystals must be differentiated: (i) thermotropic and (ii) lyotropic. The transitions involving thermotropic liquid crystals are effected by changing temperature. Lyotropic liquid crystals are found in solutions and concentration is the important controllable parameter.

Based upon their symmetry, Friedel in 1922 [5] distinguishes three major classes - the nematic, the cholesteric, and the smectic.

1.1.1. Nematic and cholesteric liquid crystal

The nematic molecular order is shown schematically in Fig. 1.1.

Figure 1.1. The arrangement of molecules in the nematic phase.
The main features are the following.

1. There is no long-range order between the centers of mass of molecules.
2. The molecules tend to be parallel to some common axis, labelled by a unit vector $\vec{n}$, called “director”.
3. The direction of $\vec{n}$ is arbitrary in space.
4. The states of director $\vec{n}$ and $-\vec{n}$ are indistinguishable.

Locally, a cholesteric is very similar to a nematic. Again, the centers of mass have no long-range order and the molecular orientation shows a preferred axis labelled by a director $\vec{n}$. However, $\vec{n}$ is not constant in space. The preferred conformation is helical (see Fig. 1.2).

**Figure 1.2.** The arrangement of molecules in the cholesteric phase; the plans have been drawn for convenience, but do not have any specific physical meaning.

1.1.2. **Smectic A liquid crystals**

There are three different main types of smectic, giving rise to different macroscopic textures. We shall briefly present here the major characteristics of the smectic A phase (see Fig. 1.3).

1. A layer structure. The layer thickness can vary from a value close to the length of the molecule in thermotropic liquid crystals to the periodicities as large as several $\mu$m in lyotropics.
2. Inside each layer, the centers of mass show no long-range order; each layer is a two-dimensional fluid.
3. The system is optically uniaxial, the optical axis being the normal to the plane of the layers.
4. The directions $\vec{n}$ and $-\vec{n}$ are equivalent.

As an example (very much experimentally studied) we cite octyl-4-cyanobiphenyl (8CB) with chemical formula shown in Fig. 1.4, which is smectic A between 24°C and 34°C, and nematic between 34°C and 42.6°C.

![Figure 1.3](image.png)

Figure 1.3. The arrangement of molecules in the smectic A phase.

![Figure 1.4](image.png)

Figure 1.4. The chemical formula of octyl-4-cyanobiphenyl (8CB).

### 1.1.3. Order parameter

The transition between phases of different symmetry can be described in terms of an order parameter $Q$ that must satisfy the following requirements:

(i) $Q = 0$ in the more symmetric (less ordered) phase and (ii) $Q \neq 0$ in the less symmetric (more ordered) phase.

The orientational nematic order parameter is a traceless, symmetric, second rank tensor with components given by [3, 4]

$$Q_{\alpha\beta} = S(3n_\alpha n_\beta - \delta_{\alpha\beta})/2,$$

where the unit vector $\vec{n}$ is the nematic director, and $S$ is the scalar order parameter defined as parameter defined as $S = \frac{1}{2}(3\cos^2 \theta - 1)$, where $\theta$ is the angle between long molecular axis and the director. $S = 0$ in the isotropic liquid and $S = 1$ in a fully oriented nematic phase.
The additional one-dimensional translational order of the smectic-A phase is described by the complex order parameter [3, 4]:

\[ \Psi(r) = \psi(r) \exp(-iq_0 u(r)), \]  

(1.2)

with \( \psi = |\Psi| \) characterizing the strength of the density modulation and \( u(r) \) the smectic layer displacement relative to that of perfect 1D crystalline order of layer periodicity \( d = 2\pi/q_0 \).

\[ 1.2. \text{Phase transitions. Landau-de Gennes theory} \]

In terms of the order parameter, two different types of phase transitions can be distinguished. A phase transition is said to be first order when the order parameter changes discontinuously at the transition. At a second order phase transition, the order parameter is continuous but is discontinuous in its first derivative. In what follows, we shall refer to nematic-isotropic phase transition as an example of first order phase transition and to nematic-smectic A phase transition as an example of a second order phase transition.

\[ 1.2.1. \text{Nematic-isotropic phase transition} \]

The Landau-de Gennes theory [3] apply the general rules of Landau theory [6] originally proposed by Landau for second order phase transitions to nematic-isotropic first order phase transition. In the framework of this model, the Landau-de Gennes free energy density is given by:

\[ f(T, Q) = a_N(T - T^*)Q_{\alpha\beta}Q_{\beta\alpha} - B_NQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + C_N(Q_{\alpha\beta}Q_{\beta\alpha})^2, \]  

(1.3)

where \( T^* \) is the undercooling limit temperature of the isotropic phase and the coefficients \( a_N, B_N, \) and \( C_N \) depend only on the substance (for 8CB they have the following values: \( a_N = 3.3 \cdot 10^5 \text{erg/Kcm}^3, B_N = 8.9 \cdot 10^6 \text{erg/cm}^3, \) and \( C_N = 5.6 \cdot 10^6 \text{erg/cm}^3 \)). We note two properties of the expansion (1.3) [8]:

(i) There is no term linear in \( Q \). This allows for the possibility of an isotropic phase. In the case of external fields, a linear term has to be included, making the isotropic phase impossible.

(ii) The term of order three causes the transition to be first order.

Using the representation (1.1) for the order parameter, the corresponding Landau-de Gennes free energy density is given by:

\[ f(T, S) = \frac{3}{2}a_N(T - T^*)S^2 - \frac{3}{4}B_NS^3 + \frac{9}{4}C_NS^4, \]  

(1.4)

which describes a first order nematic-isotropic phase transition. For \( T = T_{NI} = T^* + B_N^2 / 24a_NC_N, \) the two phases, nematic (\( S_{\text{nem}} = B_N/6C_N \)) and isotropic (\( S_{\text{iso}} = 0 \)) coexist in equilibrium.
We now non-dimensionalize the free energy. The orientational order parameter is normalized with respect to its value at the transition \( S = S/S_{\text{nem}} \), using the reduced temperature \( u = \frac{T - T_{NI}}{T_{NI} - T^*} \). The dimensionless free energy density is now \( \bar{f} = f/f_0 \), where \( f_0 = B_N^0 / 24^2 C_N^3 \). Omitting the bar notation, the non-dimensional free energy density becomes:

\[
f(u, S) = S^2(1 - S)^2 + uS^2.
\]  

(1.5)

Now the nematic-isotropic phase transition temperature is \( u_{NI} = 0 \) and the value of the order parameter at the transition is \( S_{NI} = 1 \).

Minimizing \( f \), we obtain the equilibrium values of the order parameter corresponding to the two phases:

\[
S_{\text{ISO}} = 0; \quad S_{\text{nem}} = \frac{3}{4} \left[ 1 + \left( 1 - \frac{8(1 + u)}{9} \right)^{1/2} \right].
\]  

(1.6)

Four temperature regions can be distinguished:

1. \( u > u^* = 1/8 \): the isotropic phase is stable; the minimum corresponding to the nematic does not exist;
2. \( 0 = u_{NI} < u < u^* \): the isotropic phase is stable; the nematic is metastable;
3. \( -1 = u^* < u < u_{NI} \): the nematic phase is stable; the isotropic phase is metastable;
4. \( u < u^* \): the nematic phase is stable; the minimum corresponding to the nematic phase does not exist. Both temperatures \( u^* \) and \( u^+ \) belong to the spinodal.

The nematic orientational scalar order parameter as a function of temperature is plotted in Fig. 1.5.

![Figure 1.5. The reduced nematic order parameter as a function of temperature.](image)
The order parameter changes discontinuously at the transition, feature which is characteristic to a first order phase transition. At $\tau = \tau_{NI} = 0$, the two phases, nematic and isotropic, coexist in equilibrium. This model predicts a sharp interface between them.

### 1.2.2. Nematic-smectic A phase transition

The Landau-de Gennes free energy density for the nematic-smectic A phase transition is given by [3]:

$$f(T, \psi) = \frac{1}{2} a_A (T - T_c) \psi^2 + \frac{1}{4} C_A \psi^4,$$

where $T_c$ is the nematic-smectic A phase transition temperature. For 8CB the coefficients have the following values: $a_A = 5 \cdot 10^5$ erg/Kcm$^3$ and $C_A = 4 \cdot 10^6$ erg/cm$^3$ [7]. We introduce the non-dimensional free energy $\overline{f} = f/C_A$ and the reduced temperature $u = a_A (T - T_c)/C_A$. Eliminating overbars, the non-dimensional form of the free energy density becomes:

$$f(\tau, \psi) = \frac{1}{2} u \psi^2 + \frac{1}{4} \psi^4.$$  

(1.8)

This form of the free energy describes a nematic-smectic A second-order phase transition that takes place at $u = u_c = 0$. Below this temperature, $f$ has the smectic minimum at $\psi_{Sm} = \sqrt{-u}$, which disappears for $u > u_c$. The nematic minimum $\psi_{nem} = 0$ exists for $u > u_c$ and becomes a maximum when $u < u_c$. Since the two phases cannot be simultaneously stable, a well-defined interface does not exist between them at $u_c$.

The smectic A order parameter as a function of temperature is plotted in Fig. 1.6. The order parameter changes continuously at the transition, but there is a jump in its first derivative with respect to temperature, feature which is characteristic to a second order phase transition.

![Figure 1.6](image.png)

**Figure 1.6.** The smectic A order parameter as a function of temperature.
To sum up, the main differences between the first order (nematic-isotropic) and the second order (nematic-smectic A) phase transition are the following:

1. In the first order phase transition the order parameter changes discontinuously while in the second order phase transition the order parameter is continuous but its first derivative with respect to temperature has a jump.
2. The possibility of existence of metastable states in the case of first order phase transition.
3. At phase transition temperature, it exists a (sharp) interface between the two coexisting phases in the case of first order phase transition. The interface does not exist in the case of second order phase transition.

1.2.3. Nematic-isotropic diffuse interface

We consider a nematic-isotropic system at temperature $u_{NI} = 0$. The two phases coexist in equilibrium. There are three distinct regions inside the system: (i) the nematic phase with $S = 1$, (ii) the isotropic phase with $S = 0$, and (iii) the diffuse interface, an intermediate region in which $S$ varies from 1 to 0. To consider this case, we have to add at the bulk Landau-de Gennes free energy density, an elastic free energy density which takes into account the spatial variation of the order parameter. In this way, the free energy can be written as:

$$F = \int [f(T, Q) + \frac{1}{2}L(\partial_{\alpha}Q_{\beta\gamma})^2]dV,$$

where $f$ is the bulk Landau-de Gennes free energy density defined in Eq. (1.3) and $L$ is a positive elastic constant. We suppose a planar nematic-isotropic interface perpendicular to $z$ axis, situated at $z = 0$, such that the nematic lies in the region $z < 0$ and the isotropic phase in the region $z > 0$. In this case, the non-dimensional form of the free energy per unit area can be written as:

$$F = \int_{-\infty}^{\infty} \left[ S^2(1 - S)^2 + \frac{\xi^2}{2} \left( \frac{dS}{dz} \right)^2 \right] dz,$$

where $\xi = (16LC/B^2)^{1/2} \approx 10^{-6}$ is the correlation length of the order parameter. Thus, the elastic constant $L$ defines a length scale. Measuring lengths in unit of $\xi$ and minimizing the free energy with respect to order parameter profile $S(z)$ we obtain the corresponding Euler-Lagrange equation:

$$\frac{d^2S}{dz^2} = \frac{df}{dS},$$

which must be solved subject to far field boundary conditions:
Integrating Eq. (1.11) once, and imposing the boundary conditions, gives \((dS/dz)^2 = 2f\). This result can be used in Eq. (1.10) to give the energy per unit area of the interface, that is the surface tension, as

\[
\sigma = \int_{-\infty}^{\infty} (dS/dz)^2 = \frac{\sqrt{2}}{6}.
\]

(1.13)

Note that, the two terms in Eq. (1.9) contribute equally to the interface energy.

Integrating Eq. (1.11) twice, we obtain the order parameter profile,

\[
S(z) = \frac{1}{2} \left(1 - \tanh \frac{z}{\sqrt{2}}\right),
\]

(1.14)

where we have fixed the “center” of the interface, defined by \(S = 1/2\) to be at \(z = 0\) by the extra condition \(S(0) = 1/2\). The order parameter profile is plotted in Fig. 1.7. The three regions are shown. The nematic and isotropic phases coexist in equilibrium with a diffuse interface between them.

**Figure 1.7.** The nematic order parameter profile for a planar nematic-isotropic diffuse interface.

### 1.3. Interface dynamics

We discuss comparatively the dynamics of nematic-isotropic and nematic-smectic A interfaces, respectively. To present the subject in a general form, the less symmetric phase will be called as the ordered phase and the more symmetric one as the disordered phase.

Thermodynamic fluctuations drive small regions of the system, droplets, into ordered phase. In general these droplets are small, and energy price of the ordered-disordered interface is sufficiently large that the ordered droplet is
unfavorable from the free energy point of view and disappears. The relative cost of the droplet surface decreases, however, and eventually a sufficiently large droplet is nucleated. The important, and rather difficult physics, concern the nucleation rate.

With the droplet nucleation the first stage of phase transformation is over. In the second stage of phase transformation the droplets grow, because larger droplets have lower free energy. The speed of growth depends on the difference in the free energy between the ordered and the disordered phases. This second stage of the phase transformation is analyzed here.

1.3.1. Sharp interface model

In the sharp interface or free boundary formulation [9, 10, 11], the interface separating two bulk phases is regarded as a singular surface on which associated physical mechanisms are localized and represented as boundary conditions to be applied at the surface. In the case of solidification of a pure substance from its melt, the process is governed entirely by heat flow. That is, the rate of solidification at any point along the liquid-solid interface is governed by how rapidly the latent heat generated at that point can be conducted into the bulk of the sample or removed at the boundaries. The standard free boundary problem is defined by the equations:

\[
\begin{align*}
\partial_t T &= D \nabla^2 T, \\
LV &= D c_p (\partial_n T |^- - \partial_n T |^+), \\
T_i &= T_M(1 - \sigma/LR) - \beta V, \\
\end{align*}
\]

where \( T_M \) is the melting temperature, \( L \) is the latent heat of melting per unit volume, \( c_p \) is the heat per unit volume at constant pressure, \( D \) is the thermal diffusivity, \( V \) is local normal velocity of the interface, \( \sigma \) is the solid-liquid surface tension, \( R \) is the principal radius of curvature of the interface, and \( \beta \) is the kinetic coefficient. The first equation is just the normal diffusion equation for the temperature. The second equation expresses the heat conservation of the interface, where \( LV \) is the heat generated at the surface per unit time, and the r. h. s. is the rate at which heat flows into the bulk phases on either side. The third relation is essentially the local kinetic equation which expresses the microscopic physics at the interface. \( T_M(1 - \sigma/LR) \) is the melting temperature of curved interface, a form of Gibbs-Thomson relation which predicts a reduction of the melting temperature for small particles. The key quantity is the ratio \( \sigma/L \) which sets the (microscopic) length scale. With this meaning of \( T_M(1 - \sigma/LR) \), the third relation expresses the linear growth law, where \( 1/\beta \) has the meaning of a mobility.
Eqs. (15), together with appropriate boundary conditions for the temperature far away from the interface, constitute the basic equations that describe the growth of a dendrite into a pure melt. The basic instability underlying the formation of these dendrites is the Mullins-Sekerka instability [12]. Eqs. (15) appear to be linear equations, but they are not. The reason is that they involve the unknown position and shape of the interface through the boundary conditions, and the dynamics of the interface depends in turn on the diffusion field: the location of the interface has to be found self-consistently in the course of solving these equations. This is why such a so-called free boundary problem is so highly nonlinear and complicated [13, 14, 15, 16, 17].

1.3.2. Phase-field model

To avoid the complication of the free boundary problem, several authors have introduced different models, often referred to as phase-field models [17, 18, 19, 20], in which the transition from one phase to another one is described by introducing a continuum equation for the appropriate order parameter. Instead of a sharp interface, one then has a smooth but thin transition zone of width $W$, where the order parameter changes from one (meta)stable state to another one.

For concreteness, let us consider the following phase-field model used to study solidification:

$$
\begin{align*}
\tau \partial_t \psi &= W^2 \nabla^2 \psi - \partial_\psi F(\psi, \lambda u), \\
\partial_t u &= D \nabla^2 u + \partial_t h(\psi)/2,
\end{align*}
$$

where $F(\psi, \lambda u)$ is a function that has the form of a double-well where the relative height of the two minima is temperature dependent, $h(\psi)$ describes the generation of the latent heat, $u = (T - T_m)/(L/c_p)$ denotes the dimensionless temperature field, $\tau$ is the characteristic time of attachment of atoms at the interface, and $\lambda$ is a dimensionless parameter that controls the strength of the coupling between the phase and diffusion fields. The first is the time dependent Ginzburg-Landau equation for the order parameter, and the second one is based on a modification of the heat equation to allow a source term that accounts for latent heat production at the moving interface. It is commonly accepted that Eqs. (16) represent a phenomenological description of the underlying microscopic physics of the solid-liquid interface. In the limit of $W \to 0$ they reduce to the standard free boundary problem Eqs. (15) [21, 22]. For a detailed asymptotic analysis and simulations in two and three dimensions we refer to [19].
1.3.3. Phase-field model for liquid crystals. Front propagation in a temperature gradient

The relevant phase field theory of liquid crystals [23, 24] turns out to be just the dynamical generalization of the familiar Landau-de Gennes theory of liquid crystals interface [25].

In this section we present the results obtained using a phase-field model in the directional solidification of a liquid crystal [26], in particular a moving interface as it is dragged along at a fixed, controllable velocity in a temperature gradient, also controllable. The experiment consists in a (nearly) two-dimensional sample (a thin sandwich of liquid crystal between two glass plates) that is placed into a temperature gradient that points in the plane of the sample. The temperature gradient is set by putting the sample across the gap between two ovens. The temperatures of the ovens are chosen so that there is a phase transition in between, giving rise to a straight interface. The sample is set into motion at a velocity $V$; after a transient, the interface freezes at $-V$ in order to stay at the same temperature. We ignore the release of latent heat at the interface and assume that the temperature field is imposed by the glass plates.

All the theoretical results presented apply to first and second order phase transitions described by a non conserved order parameter $\phi$. There are two typical lengths in the problem: the thermal length $l_u$ inversely proportional to the temperature gradient and proportional to a temperature shift characteristic of the phase transition, and the correlation length $l_\phi$ which gives the width of the front, i.e. of the $\phi$-order parameter profile. In the following we set $\varepsilon = l_\phi / l_u$. For usual phase transitions $\varepsilon \ll 1$, so that $\varepsilon$ can be considered as the small parameter of the theory ($\varepsilon \approx 10^{-5}$ for nematic-isotropic and nematic-smectic A phase transitions and $\varepsilon \approx 0.1$ for cholesteric-nematic front [27]).

The free energy is represented by the functional,

$$
\mathcal{F} = \int \left[ \frac{1}{2} L \left| \nabla \phi \right|^2 + f(\phi, T) \right] d\mathbf{r},
$$

(1.17)

where $L$ is an elastic constant, $\phi(\mathbf{r}, t)$ the non conserved order parameter, and $T$ the temperature. The form of the free energy density $f(\phi, T)$ depends on the order of the phase transition (e.g., for a first-order phase transition inside the region enclosed by the spinodal, $f(\phi, T)$ has a double-well structure with respect to $\phi$ in which the two local minima correspond to the ordered and disordered phases).

A planar front moving in the $+x$ direction is solution of the equations:

$$
\beta \phi_t = -\frac{\delta \mathcal{F}}{\delta \phi} = L\phi_{xx} - f_\phi,
$$

(1.18)
\[ T = T_0 + Gx, \]  

(1.19)

where \( \beta \) is a transport coefficient. The subscript means the differentiation with respect to that variable, \( G \) is the imposed temperature gradient, and \( T_0 \) is a reference temperature which gives the origin \( x = 0 \) of the \( x \)-axis perpendicular to the interface. \( D = L/\beta \) is the diffusion coefficient of the order parameter [3].

We rewrite Eqs. (18) and (19) in the dimensionless form by scaling the free energy density: \( \bar{f} = f/f_0 \), where \( f_0 \) is the “unit” of the free energy density, and by measuring length in units of \( l_\phi = (L/f_0)^{1/2} \) and time in units of \( T_\phi^2 / D \), where \( l_\phi \) is the width of the spatially diffuse interface region where \( \phi \) varies rapidly. Eq. (19) sets the scale of the thermal field: \( l_u = \Delta T / G \), where \( \Delta T \) is the characteristic temperature variation of the system. Eliminating overbars, Eq. (18) and (19) then become:

\[ \phi_t = \phi_{xx} - f_\phi, \]  

(1.20)

\[ u = u_0 + \varepsilon x, \]  

(1.21)

where \( u = (T - T_c)/\Delta T \), \( u_0 = (T_0 - T_c)/\Delta T \) (\( T_c \) is the phase transition temperature) and \( \varepsilon = l_\phi / l_u = Gl_\phi / \Delta T \) is the (small) parameter of the theory.

In the following, we discuss comparatively the phase transition kinetics in “free” and “directional” growth. In “free” growth, the temperature is constant and given by \( T_0 \) or \( u_0 \) in the dimensionless form: the system responds by fixing the interface velocity. In directional growth, the sample is placed in a fixed temperature gradient and is pushed with a constant velocity. In that way, the growth velocity is imposed and the system responds by fixing the position of the interface (and, so, its temperature) in the thermal gradient.

In the following, we will call \( v \) the front velocity and \( u_0(v) \) the reduced temperature of the isothermal system in which the interface moves with velocity \( v \). In directional solidification, we will take the origin of the \( x \)-axis, not at \( T_c \), but at the temperature \( T_0 = T_0(v) \) corresponding to the reduced temperature \( u_0(v) \). This choice is more convenient from a theoretical point of view to treat the influence of the thermal gradient as a perturbation to the isothermal system. Finally, we will neglect the latent heat release and the change in temperature of the interface due to heat diffusion. It is possible to show that this assumption can always be satisfied provided that the sample is thin enough: the front temperature is thus fixed by the glass plates limiting the sample.

**First-order phase transition**

We consider a planar ordered-disordered interface moving with a constant velocity \( V \) (in the directional solidification experiment \( -V \) is the pulling sample...
velocity). The dimensionless interface velocity is given by \( v = \frac{Vl_{\phi}}{D} \) where \( l_{\phi}/D \) is a velocity characteristic of the system (for instance, it is of the order of m/s at the solid-liquid transition in metals or plastic crystals, and of the order of mm/s at the nematic-isotropic phase transition [4, 28]). In the frame \( \xi \) of the front (\( \xi = x - vt \) in free growth and \( \xi = x \) in directional solidification), Eqs. (20) and (21) rewrite as,

\[
\phi_{\xi\xi} + v \phi_{\xi} = 2\phi(1 + u_0 + \varepsilon \xi - 3\phi + 2\phi^2).
\] (1.22)

with the far-field boundary conditions,

\[
\phi = \begin{cases} 
\phi_{\text{ord}} = \frac{3}{4} \{ 1 + [1 - \frac{8(1 + u_0 + \varepsilon \xi)}{9}]^{1/2} \} & \text{as } \xi \to -\infty \\
\phi_{\text{disord}} = 0 & \text{as } \xi \to \infty.
\end{cases}
\] (1.23)

We first give the solution of time-dependent Ginzburg-Landau equation equation (1.22) in the absence of a thermal gradient (\( \varepsilon = 0 \)). This solution describes the dynamics of formation of the ordered phase when the disordered phase is cooled quickly to a temperature at which it is less stable than the ordered phase. A crucial point is to know whether the system has been quenched into a region where the disordered phase is metastable (\( -1 < u_0 < 0 \)), or unstable (\( u_0 < -1 \)). In the temperature \( -1 < u_0 < 0 \) the stable ordered solution grows into the metastable disordered region with velocity \( v \). The solution of Eq. (1.22) subject to the boundary conditions

\[
\phi(-\infty) = \phi_{\text{ord}} = \frac{3}{4} \left\{ 1 + \left[ 1 - \frac{8(1 + u_0)}{9} \right]^{1/2} \right\}
\]

and

\[
\phi(\infty) = \phi_{\text{disord}} = 0
\]

is given by

\[
\phi(\xi) = \frac{\phi_{\text{ord}}}{2} \left( 1 - \tanh \frac{\xi - \xi_i}{w} \right),
\] (1.24)

where

\[
w = \frac{\sqrt{2}}{\phi_{\text{ord}}},
\] (1.25)

is the characteristic thickness of the moving interface and

\[
v = 3\sqrt{2}(\phi_{\text{ord}} - 1).
\] (1.26)
its velocity. The constant $\xi_i$ gives the location of the interface at time $t = 0$ in the frame of the laboratory: it is arbitrary because the position of the interface is arbitrary in an isothermal system. If $u_0 = 0$, $\phi_{\text{ord}} = 1$, and $v = 0$ (the two phases coexist in equilibrium, the well depths of the free energy are equal and the interface is stationary). As expected, Eq. (1.26) yields a positive velocity when $-1 < u_0 < 0$ (the ordered phase grows into the disordered one) and a negative one (the ordered phase melts) when $u_0 > 0$. In the neighborhood of $u_0 = 0$ we can linearize the interface velocity in the undercooling, yielding:

$$v \simeq -3\sqrt{2}u_0,$$  \hspace{1cm} (1.27)

This is a well-known result of the classical Stefan model for solidification. We mention that when $-1 < u_0 < 0$ the time-dependent Ginzburg-Landau Eq. (1.22) has a discrete set of moving front solutions corresponding to lower values of velocity. The stability analysis shows that only the solution (1.24) corresponding to the largest velocity (1.26) is stable and dynamically relevant [17].

For $u_0 < -1$ the disordered phase is thermodynamically unstable. Nucleation of the order takes place through a “phase-ordering” kinetics process, in which the ordering takes place quickly locally, although the system retains topological defects which it gradually expels [29]. When the disordered state is unstable, depending on the nonlinearities, one can distinguish two regimes:

(i) Fronts whose propagation is driven (“pushed”) by the nonlinearities, resemble very much to the fronts that propagate into a metastable state (“pushed” or “nonlinear marginal stability” regime).

(ii) If linearities mainly cause saturation, fronts propagate with a velocity determined by linearization about the unstable state, as if they were “pulled” by the linear stability (“pulled” or “linear marginal stability” regime) [30].

To calculate the linear marginal stability velocity, we linearize Eq. (1.22) around the state $\phi = \phi_{\text{disord}} = 0$ and write the particular solution in the form of normal modes,

$$\phi(\xi, t) = A \exp[i(k\xi - \omega t)].$$  \hspace{1cm} (1.28)

The corresponding dispersion relation reads:

$$\omega = i[-2(1 + u_0) - k^2],$$  \hspace{1cm} (1.29)

where $u_0 < -1$. When the wavenumber $k$ is given real, for $0 < k < \sqrt{-2(1 + u_0)}$, the temporal growth rate $\omega^f (=\text{Im}\omega)$ is positive, the perturbation will grow out,
and the basic front is unstable. The long-time appearance of the profile is dominated by the mode \( k' \) (\( \equiv \text{Re}k \)) corresponding to the maximum growth rate \( \omega_{\text{max}}^i \). The condition \( \partial \omega^i / \partial k' = 0 \) yields \( \omega_{\text{max}}^i = -2(1 + u_0) + (k')^2 \). The envelope velocity is given by \( v_{\text{en}} = \omega_{\text{max}}^i k' = \frac{-2(1 + u_0)}{k'} + k' \) and the group velocity is \( v_{\text{gr}} = \frac{\partial \omega_{\text{max}}^i}{\partial k'} = 2k' \). If the basic front is unstable and \( v_{\text{en}} > v_{\text{gr}} \) (\( k' < \sqrt{-2(1 + u_0)} \)), at any fixed station, perturbations grow initially and, as the tail of the wave packet passed by, they ultimately decrease exponentially: the instability is convective. If the basic state is unstable and \( v_{\text{en}} < v_{\text{gr}} \) (\( k' > \sqrt{-2(1 + u_0)} \)), perturbations exponentially increase in time at any fixed station in the laboratory frame: the instability is then said to be absolute. The absolute-convective transition is reached when \( v_{\text{en}} = v_{\text{gr}} \), condition which yields:

\[
k^i* = \sqrt{-2(1 + u_0)} \quad \text{and} \quad v^* = 2\sqrt{-2(1 + u_0)}.
\] (1.30)

The general properties of front propagation into unstable states drive the velocity of initially localized fronts to a selected value \( v^* \), the so-called “linear marginal stability velocity”. \( v^* \) is the minimum velocity of the continuum convective instability branch (this statement can be qualitatively explained by the fact that the growth of a crystal is dominated by the growth of the slowest facet).

To describe the linear-nonlinear marginal stability (“pulled”-“pushed”) transition we look at the asymptotic behavior of the solution (1.24): \( \phi|_{\xi \to \infty} \sim \exp(-\sqrt{2} \phi_{\text{ord}} \xi) \) which yields a wavevector \( k = \sqrt{2} \phi_{\text{ord}} \). If \( k < k^* \) (\( u_0 < u_{0c} \)) the front is moving with \( v^* \). If \( k > k^* \) (\( u_0 > u_{0c} \)) the front is moving with \( v^+ = 3 \sqrt{2}(\phi_{\text{ord}} - 1) \) (the nonlinear marginal stability velocity). The transition between these two regimes is reached when \( k = k^* \), condition which yields the “critical” value of the temperature:

\[
u_{0c} = -10.
\] (1.31)

For this temperature \( v^* = v^+ = 6 \sqrt{2} \).

In directional solidification, the front is stationary in the frame of the laboratory, so that one must take \( \xi = x \). The results of asymptotic analysis of Eq. (1.22) for \( \varepsilon \ll 1 \) are the following:

(i) The leading-order solution for \( \tilde{\phi}_0 \) in the outer region (\( \rho = \varepsilon x \)) is given by:

\[
\tilde{\phi}_0 = \begin{cases} \tilde{\phi}_{\text{ord}} = \frac{3}{4} \left[ 1 + \left[ 1 - \frac{8(1 + u_0 + \rho)}{9} \right]^{1/2} \right] & \text{as} \quad \rho < 0 \\ \tilde{\phi}_{\text{disord}} = 0 & \text{as} \quad \rho > 0. \end{cases}
\] (1.32)
(ii) The leading order solution for $\phi_0$ in the inner region is given by:

$$
\phi_0(x) = \frac{\phi_{\text{ord}}}{2} \left( 1 - \tanh \frac{x - x_i}{w} \right),
$$

(1.33)

where

$$
\phi_{\text{ord}} = \frac{3}{4} \left\{ 1 + \left[ 1 - \frac{8(1 + u_0)}{9} \right]^{1/2} \right\}
$$

In this expression, $u_0$ is the reduced temperature of the isothermal system in which the front propagates at velocity $v$. It is given by Eq. (1.26), or equivalently by:

$$
u_0 = -\frac{\sqrt{2}}{6} v - \frac{v^2}{9}.
$$

(1.34)

(iii) Solving the first order problem in the inner region we find the solvability condition:

$$
\int_{-\infty}^{\infty} x \exp(\nu x) \phi_0 \frac{d\phi_0}{dx} dx = 0,
$$

(1.35)

which yields $x_i(v)$ in the limit of $\varepsilon \to 0$. Note that $x_i(v)$ gives the position of the front with respect to the position $x = 0$ that corresponds to the reduced temperature $u_0(v)$ given by Eq. (1.34). As a consequence, $x_i(v)$ (or equivalently $u_i - u_0 = (T_i - T_0)/\Delta T = \varepsilon x_i$) shows directly the effect of the thermal gradient on the front position (or on the front temperature with respect to $T_0$, the temperature of the isothermal system at which the front propagates at velocity $v$) in a directional solidification experiment.

The results are presented in Figs. 1.8 and 1.9. The order parameter profiles (at $v = 1$) for the two limiting values of $\varepsilon$ are shown in Fig. 1.8 (in the graph the origin of the $x$-axis is taken at the temperature $T_0(v = 1) = T_c - 0.347\Delta T$, calculated from Eq.(1.34)).

For $\varepsilon = 10^{-5}$ the numerical profile is identical with the leading-order inner profile of the asymptotic analysis Eq. (1.33), whereas the influence of the thermal gradient becomes important at $\varepsilon = 10^{-1}$.

We have plotted in Fig. 1.9 the reduced temperature of the interface $u_i - u_0$ as a function of $\varepsilon$. The thermal gradient tends to decrease the temperature of the interface at this velocity, but this effect is always very small even at large value of $\varepsilon$. 
Figure 1.8. The numerical profile of the order parameter, at $v = 1$, for the moving interface (first order phase transition).

Figure 1.9. The relative temperature of the moving interface for the first order phase transition as a function of $\varepsilon$.

Second order phase transition

In directional solidification, the time-dependent Ginzburg-Landau equation describing the second order phase transition has the form:

$$\phi_{xx} + u\phi_x = (u_0 + \varepsilon x)\phi + \phi^3,$$

with the far-field boundary conditions,

$$\phi = \begin{cases} 
\phi_{\text{ord}} = (-u_0 - \varepsilon x)^{1/2} & \text{as } x \to -\infty \\
\phi_{\text{disord}} = 0 & \text{as } x \to \infty.
\end{cases}$$

In the absence of thermal gradient (isothermal system), for $u_0 < 0$ (i.e. $T \leq T_c$), Eq. (1.36) (in which $x$ must be replaced by $\xi = x - vt$) describes the dynamics of formation of an ordered phase when the disordered parent phase is
cooled quickly at a temperature at which the ordered phase is thermodynamically stable and the disordered phase is unstable. Due to instability of the disordered phase, the nucleation of the ordered phase takes place only through a “phase-ordering” kinetics process [29]. In this case, Eq. (1.36) has a solution for any positive value of $v$. From the continuous family of uniformly translating front solutions the system selects the “pulled” front which moves with a velocity $v^*$ determined by the linear behavior of the dynamical equation (1.36) [17, 30]. The origin lies in the fact that any perturbation about the unstable (disordered) phase grows out and spreads by itself. This leads to a natural spreading velocity of linear perturbations, and $v^*$ is nothing but this velocity itself (the linear marginal stability velocity). Eq.(1.36) gives:

$$v^* = 2\sqrt{-u_0}.$$  

(1.38)

In directional solidification, $v$ is the imposed velocity. By identifying $v$ with $v^*$ in the corresponding isothermal system, we get from Eq. (1.38) the reduced temperature in this case:

$$u_0 = -v^2/4.$$  

(1.39)

The numerical results are presented in Figs. 1.10 and 1.11.

The order parameter profiles for two different velocities are represented in Fig. 1.10 (with the same observation that the origin of the $x$ axis depends on $v$ for each profile). They show that the interface width decreases when the velocity increases.

The influence of the thermal gradient on the temperature of the interface (again defined at the inflexion point of the $\phi$-profile) is shown in Fig. 1.11.

![Figure 1.10](image-url)  

**Figure 1.10.** The order parameter profile (second order phase transition) for two values of velocity.
Figure 1.11. Plots of the temperatures of the moving interface (second order phase transition) in temperature gradient and in a isothermal system as a function of velocity.

Again the influence of the thermal gradient is completely negligible for $\varepsilon = 10^{-5}$ (the corresponding curve coincides with the $u_0$ one). For $\varepsilon = 0.1$, its influence becomes significant and much larger than in the case of the first order phase transition.

Some comments are in order to be done here. For an isothermal system, the dynamics of front propagation in the case of first order phase transition (propagation of a stable (order) state into a metastable (disorder) one) is fundamentally different from that in the second order phase transition (propagation of a stable (order) state into an unstable (disorder) one). In the first case, the propagation of the front is driven by the nonlinearities of Eq. (1.22) (considered for $\varepsilon = 0$), and as a consequence its velocity is “fixed” by the temperature. In the second case, the dynamics of the front is governed by the linearization of Eq. (1.36) (considered for $\varepsilon = 0$) about the unstable (disorder) state and as a consequence there is a continuous set (for any positive value of $\nu$) of solutions (the continuum convective instability branch in the previous section). To determine the front velocity, the experimental observation (that the growth of a crystal is dominated by the growth of the slowest facet) is used, and so $\nu^*$ (the minimum velocity of the continuum convective instability branch usually called the linear marginal stability velocity) is obtained.

In a thermal gradient, the velocity is imposed and the system responds by fixing the interface position $x_i$, and so its temperature $u_i = u_0 + \varepsilon x_i$. In our calculations we have conventionally considered $u_0$ the reduced temperature of the isothermal system in which the interface moves with the same velocity $\nu$ (see Eq. (1.34) for the first order phase transition and, respectively, Eq. (1.39) for the second order phase transition). We emphasize that the choice of $u_0$ is
arbitrary; on the other hand, the interface temperature $u_i$ in the thermal gradient only depends on velocity $v$ and thermal gradient $\varepsilon$, and is independent on the choice of $u_0$. The presence of the thermal gradient does not change the main feature of the first order phase transition concerning the propagation of the stable state into the metastable one. Thus, it may be considered as a perturbation to the isothermal system, its influence on the interface temperature being small even for large values of $\varepsilon$. On the contrary, the influence of the thermal gradient becomes important in the case of second order phase transition due to the fact that now the disorder state is no longer unstable. This leads to two main differences. First, for given values of velocity $v$ and thermal gradient $\varepsilon$, the system responds by selecting a well-defined front with an interface temperature $u_i$ significantly different from the corresponding temperature $u_0$ of the isothermal system given by the marginal linear stability principle (see Fig. 11). Second, in the case of the second order phase transition, for the isothermal system there is no (melting) front at temperatures larger than $T_c$. On the contrary, in the “directional melting” the front is experimentally observed and described by the model.

Bibliography

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