CAHN-HILLIARD EQUATIONS AND PHASE TRANSITION DYNAMICS FOR BINARY SYSTEMS

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ABSTRACT. The process of phase separation of binary systems is described by the Cahn-Hilliard equation. The main objective of this article is to give a classification on the dynamic phase transitions for binary systems using either the classical Cahn-Hilliard equation or the Cahn-Hilliard equation coupled with entropy, leading to some interesting physical predictions. The analysis is based on dynamic transition theory for nonlinear systems and new classification scheme for dynamic transitions, developed recently by the authors.

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1. INTRODUCTION

Cahn-Hilliard equation describes the process of phase separation, by which the two components of a binary fluid spontaneously separate and form domains pure in each component. The main objective of this article is to provide a theoretical approach to dynamic phase transitions for binary systems.

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Classically, phase transitions are classified by the Ehrenfest classification scheme, based on the lowest derivative of the free energy that is discontinuous at the transition. In general, it is a difficult task to classify phase transitions of higher order, which appears in many equilibrium phase transition systems, such as the PVT system, the ferromagnetic system, superfluids as well as the binary systems studied in this article.

For this purpose, a new dynamic transition theory is developed recently by the authors. This new theory provides an efficient tool to analyze phase transitions of higher order. With this theory in our disposal, a new dynamic classification scheme is obtained, and classifies phase transitions into three categories: Type-I, Type-II and Type-III, corresponding mathematically to continuous, jump, and mixed transitions, respectively; see the Appendix as well as two recent books by the authors [3, 4] for details.

There have been extensive studies in the past on the dynamics of the Cahn-Hilliard equations. However, very little is known about the higher order transitions encountered for this problem, and this article gives a complete classification of the dynamics transitions for binary systems. The results obtained lead in particular to various physical predictions. First, the order of phase transitions is precisely determined by the sign of a nondimensional parameter $K$ such that if $K > 0$, the transition is first-order with latent heat and if $K < 0$, the transition is second-order. Second, a theoretical transition diagram is derived, leading in particular to a prediction that there is only second-order transition for molar fraction near $1/2$. This is different from the prediction made by the classical transition diagram. Third, a critical length scale is derived such that no phase separation occurs at any temperature if the length of the container is smaller than the critical length scale. These physical predictions will be addressed in another article.

This article is organized as follows. In Section 2, both the classical Cahn-Hilliard equation and the Cahn-Hilliard equation coupled with entropy are introduced in a unified fashion using a general principle for equilibrium phase transitions outlined in Appendix B. Sections 3-6 analyze dynamic transitions for the Cahn-Hilliard equation in general domain, rectangular domain, with periodic boundary conditions, and for the Cahn-Hilliard equation coupled with entropy. Physical conclusions are given in Section 7, and the dynamic transition theory is recalled in Appendix A.

2. Dynamic Phase Transition Models for Binary Systems

Materials compounded by two components $A$ and $B$, such as binary alloys, binary solutions and polymers, are called binary systems. Sufficient cooling of a binary system may lead to phase separations, i.e., at the critical temperature, the concentrations of both components $A$ and $B$ with homogeneous distribution undergo changes, leading to heterogeneous distributions in space. Phase separation of binary systems observed will be in one of two main ways. The first is by nucleation in which sufficiently large nuclei of the second phase appear randomly and grow, and this corresponds to Type-II phase transitions. The second is by spinodal decomposition in which the systems appear to nuclear at once, and periodic or semi-periodic structure is seen, and this corresponds to Type-I phase transitions.

Since binary systems are conserved, the equations describing the Helmholtz process and the Gibbs process are the same. Hence, without distinction we use the term "free energy" to discuss this problem.
Let \( u_A \) and \( u_B \) be the concentrations of components \( A \) and \( B \) respectively, then \( u_B = 1 - u_A \). In a homogeneous state, \( u_B = \bar{u}_B \) is a constant, and the entropy density \( S_0 = \bar{S}_0 \) is also a constant. We take \( u, S \) the concentration and entropy density deviations:

\[
u = u_B - \bar{u}_B, \quad S = S_0 - \bar{S}_0\]

By (B.1) and (B.2), the free energy is given by

\[
F(u, S) = F_0 + \int_{\Omega} \left[ \frac{\mu_1}{2} |\nabla u|^2 + \frac{\mu_2}{2} |\nabla S|^2 + \frac{\beta_1}{2} |S|^2 + \beta_0 Su + \beta_2 u^2 + \sum_{k=1}^{2p} \alpha_k u^k \right] dx.
\]

Since entropy is increasing as \( u \to 0 \), and by

\[
\frac{\delta}{\delta S} F(u, S) = -\mu_2 \Delta S + \beta_1 S + \beta_0 u + \beta_2 u^2 = 0,
\]

we have

\[
\beta_0 = 0, \quad \beta_1 > 0, \quad \beta_2 > 0,
\]

which implies that \( S \) is a decreasing function of \( |u| \).

According to (B.11) and (B.5), we derive from (2.1) and (2.2) the following equations governing a binary system:

\[
\begin{align*}
\frac{\partial S}{\partial t} &= k_1 \Delta S - a_1 S - a_2 u^2, \\
\frac{\partial u}{\partial t} &= -k_2 \Delta^2 u + b_0 \Delta (Su) + \Delta f(u),
\end{align*}
\]

where \( k_1, k_2, b_0, a_1, a_2 \) are positive constants, and

\[
f(u) = \sum_{k=1}^{2p-1} b_k u^k, \quad b_{2p-1} > 0 \quad (p \geq 2).
\]

Physically sound boundary condition for (2.3) is either the Neumann boundary condition:

\[
\frac{\partial u}{\partial n} = \frac{\partial \Delta u}{\partial n} = 0, \quad \frac{\partial S}{\partial n} = 0 \quad \text{on } \partial \Omega,
\]

with \( \Omega \subset \mathbb{R}^n \) (\( 1 \leq n \leq 3 \)) being a bounded domain, or the periodic boundary condition:

\[
u(x + KL) = u(x), \quad S(x + KL) = S(x)
\]

with \( \Omega = [0, L]^n, K = (k_1, \ldots, k_n), 1 \leq n \leq 3. \)

For simplicity, in this section we always assume that \( p = 2. \) Thus, function (2.4) is rewritten as

\[
f(u) = b_1 u + b_2 u^2 + b_3 u^3, \quad b_3 > 0.
\]

Based on Theorem A.1, we have to assume that there exists a temperature \( T_1 > 0 \) such that \( b_1 = b_1(T) \) satisfies

\[
b_1(T) \begin{cases} 
> 0 & \text{if } T > T_1, \\
\leq 0 & \text{if } T = T_1, \\
< 0 & \text{if } T < T_1.
\end{cases}
\]
If we ignore the coupled action of entropy in (2.1), then the free energy $F$ is in the following form

$$ F(u) = F_0 + \int_{\Omega} \left[ \frac{\mu_1}{2} |\nabla u|^2 + \frac{\alpha_1}{2} u^2 + \frac{\alpha_2}{3} u^3 + \frac{\alpha_3}{4} u^4 \right] dx, $$

and the equations (2.3) are the following classical Cahn-Hilliard equation:

\begin{align*}
\frac{\partial u}{\partial t} &= -k \Delta^2 u + \Delta f(u), \\
\int_{\Omega} u(x,t) dx &= 0,
\end{align*}

where $f(u)$ is as in (2.7).

3. Phase Transition in General Domains

In this section, we shall discuss the Cahn-Hilliard equation from the mathematical point of view. We start with the nondimensional form of equation. Let

$$ x = lx', \quad t = \frac{l^4}{k} t', \quad u = u_0 u', \quad \lambda = -\frac{l^2 b_1}{k}, \quad \gamma_2 = \frac{l^2 b_2 u_0}{k}, \quad \gamma_3 = \frac{l^2 b_3 u_0^2}{k}, $$

where $l$ is a given length, $u_0 = \bar{u}_B$ is the constant concentration of $B$, and $\gamma_3 > 0$. Then the equation (2.9) can be rewritten as follows (omitting the primes)

\begin{align*}
\frac{\partial u}{\partial t} &= -\Delta^2 u - \lambda \Delta u + \Delta (\gamma_2 u^2 + \gamma_3 u^3), \\
\int_{\Omega} u(x,t) dx &= 0, \\
u(x,0) &= \varphi.
\end{align*}

Let

$$ H = \left\{ u \in L^2(\Omega) \mid \int_{\Omega} u dx = 0 \right\}. $$

For the Neumann boundary condition (2.5) we define

$$ H_1 = \left\{ u \in H^4(\Omega) \cap H \mid \frac{\partial u}{\partial n} = \frac{\partial \Delta u}{\partial n} = 0 \text{ on } \partial \Omega \right\}, $$

and for the periodic boundary condition (2.6) we define

$$ H_1 = \left\{ u \in H^4(\Omega) \cap H \mid u(x + KL) = u(x) \ \forall K \in \mathbb{Z}^n \right\}. $$

Then we define the operators $L_\lambda = -A + B_\lambda$ and $G : H_1 \to H$ by

\begin{align*}
A u &= \Delta^2 u, \\
B_\lambda u &= -\lambda \Delta u, \\
G(u) &= \gamma_3 \Delta u^2 + \gamma_3 \Delta u^3.
\end{align*}

Thus, the Cahn-Hilliard equation (3.1) is equivalent to the following operator equation

\begin{align*}
\frac{du}{dt} &= L_\lambda u + G(u), \\
u(0) &= \varphi
\end{align*}
It is known that the operators defined by (3.2) satisfy the conditions (A.2) and (A.3).

We first consider the case where \( \Omega \subset \mathbb{R}^n (1 \leq n \leq 3) \) is a general bounded and smooth domain. Let \( \rho_k \) and \( e_k \) be the eigenvalues and eigenfunctions of the following eigenvalue problem:

\[
-\Delta e_k = \rho_k e_k, \\
\frac{\partial e_k}{\partial n} \big|_{\partial \Omega} = 0, \\
\int_{\Omega} e_k \, dx = 0.
\]

The eigenvalues of (3.4) satisfy \( 0 < \rho_1 \leq \rho_2 \leq \cdots \leq \rho_k \leq \cdots \), and \( \lim_{k \to \infty} \rho_k = \infty \).

Hence, \( \{ e_k \} \) is also an orthogonal basis of \( H \) under the following equivalent norm

\[
\| u \|_1 = \left[ \int_{\Omega} |\Delta^2 u|^2 \, dx \right]^{1/2}.
\]

We are now in position to give a phase transition theorem for the problem (3.1) with the following Neumann boundary condition:

\[
\frac{\partial u}{\partial n} = 0, \quad \frac{\partial \Delta u}{\partial n} = 0 \quad \text{on } \partial \Omega.
\]

**Theorem 3.1.** Assume that \( \gamma_2 = 0 \) and \( \gamma_3 > 0 \) in (3.1), then the following assertions hold true:

1. If the first eigenvalue \( \rho_1 \) of (3.4) has multiplicity \( m \geq 1 \), then the problem (3.1) with (3.5) bifurcates from \( (u, \lambda) = (0, \rho_1) \) on \( \lambda > \rho_1 \) to an attractor \( \Sigma_\lambda \), homeomorphic to an \( (m-1) \)-dimensional sphere \( S^{m-1} \), and \( \Sigma_\lambda \) attracts \( H \setminus \Gamma \), where \( \Gamma \) is the stable manifold of \( u = 0 \) with codimension \( m \).
2. \( \Sigma_\lambda \) contains at least \( 2m \) singular points. If \( m = 1, \Sigma_\lambda \) has exactly two steady states \( \pm u_\lambda \), and if \( m = 2, \Sigma_\lambda = S^1 \) has at most eight singular points.
3. Each singular point \( u_\lambda \) in \( \Sigma_\lambda \) can be expressed as

\[
u_\lambda = (\lambda - \rho_1)^{1/2} w + o(|\lambda - \rho_1|^{1/2}),
\]

where \( w \) is an eigenfunction corresponding to the first eigenvalue of (3.4).

**Proof.** We proceed in several steps as follows.

**Step 1.** It is clear that the eigenfunction \( \{ e_k \} \) of (3.4) are also eigenvectors of the linear operator \( L_\lambda = -A + B_\lambda \) defined by (3.2) and the eigenvalues of \( L_\lambda \) are given by

\[
\beta_k(\lambda) = \rho_k(\lambda - \rho_k), \quad k = 1, 2, \cdots.
\]

It is easy to verify the conditions (A.4) and (A.5) in our case at \( \lambda_0 = \rho_1 \). We shall prove this theorem using the attractor bifurcation theory introduced in [3].
We need to verify that $u = 0$ is a global asymptotically stable singular point of (3.3) at $\lambda = \rho_1$. By $\gamma_2 = 0$, from the energy integration of (3.1) we can obtain

\[
\frac{1}{2} \frac{d}{dt} \int_\Omega u^2 dx = \int_\Omega [-|\Delta u|^2 + \rho_1 |\nabla u|^2 - 3\gamma_3 u^2 |\nabla u|^2] dx
\]

\[
\leq -C \int_\Omega |\Delta v|^2 dx - 3\gamma_3 \int_\Omega u^2 |\nabla u|^2 dx,
\]

where $C > 0$ is a constant, $u = v + w$, and $\int_\Omega vwdx = 0$, and $w$ is a first eigenfunction. It follows from (3.7) that $u = 0$ is global asymptotically stable. Hence, for Assertion (1), we only have to prove that $\Sigma_\lambda$ is homeomorphic to $S^{m-1}$, as the rest of this assertion follows directly from the attractor bifurcation theory introduced in [3].

**Step 2.** Now we prove that the bifurcated attractor $\Sigma_\lambda$ from $(0, \rho_1)$ contains at least $2m$ singular points. Let $g(u) = -\Delta u - \lambda u + \gamma_3 u^3$. Then the stationary equation of (3.1) is given by

\[
\Delta g(u) = 0,
\]

\[
\int_\Omega u dx = 0,
\]

which is equivalent, by the maximum principle, to

\[
- \Delta u - \lambda u + \gamma_3 u^3 = \text{constant},
\]

\[
\int_\Omega u dx = 0,
\]

\[
\frac{\partial u}{\partial n}|_{\partial \Omega} = 0.
\]

By the Lagrange multiplier theorem, (3.8) is the Euler equation of the following functional with zero average constraint:

\[
F(u) = \int_\Omega \left[ \frac{1}{2} |\nabla u|^2 - \frac{\lambda}{2} u^2 + \frac{\gamma_3}{4} u^4 \right] dx,
\]

\[
u \in \left\{ u \in H^1(\Omega) \cap H \left| \frac{\partial u}{\partial n}|_{\partial \Omega} = 0, \int_\Omega u dx = 0 \right. \right\}.
\]

Since $F$ is an even functional, by the classical Krasnoselskii bifurcation theorem for even functionals, (3.9) bifurcates from $\lambda > \rho_1$ at least to $2m$ mini-maximum points, i.e., equation (3.8) has at least $2m$ bifurcated solutions on $\lambda > \rho_1$. Hence, the attractor $\Sigma_\lambda$ contains at least $2m$ singular points.

**Step 3.** To complete the proof, we reduce the equation (3.3) to the center manifold near $\lambda = \rho_1$. By the approximation formula given in [3], the reduced equation of (3.3) is given by:

\[
\frac{dx_i}{dt} = \beta_i(\lambda)x_i - \gamma_3 \rho_1 \int_\Omega v^3 e_1 dx + o(|x|^3)
\]

for $1 \leq i \leq m$, where $v = u + w$ and $w$ is a first eigenfunction.
where \( \beta_1(\lambda) = \rho_1(\lambda - \rho_1) \), \( v = \sum_{i=1}^{m} x_i e_i \), and \( \{e_1, \ldots, e_m\} \) are the first eigenfunctions of (3.4). Equations (3.10) can be rewritten as

\[
\frac{dx_i}{dt} = \beta_1(\lambda)x_i - \gamma_3\rho_1 \int_{\Omega} \left( \sum_{j=1}^{m} x_j e_{ij} \right)^3 e_{1j} dx + o(|x|^3).
\]

Let

\[
g(x) = \left( \int_{\Omega} v^3 e_{11} dx, \ldots, \int_{\Omega} v^3 e_{1m} dx \right), \quad v(x) = \sum_{j=1}^{m} x_j e_{1j}.
\]

Then for any \( x \in \mathbb{R}^m \),

\[
< g(x), x > = \sum_{i=1}^{m} x_i \int_{\Omega} v^3 e_{11} dx = \int_{\Omega} v^4 dx \geq C|x|^4,
\]

for some constant \( C > 0 \).

Thus by the attractor bifurcation theorem \( 3 \), it follows from (3.11) and (3.12) that the attractor \( \Sigma_1 \) is homeomorphic to \( S^{m-1} \). Hence, Assertion (1) is proved. The other conclusions in Assertions (2) and (3) can be derived from (3.11) and (3.12). The proof is complete. \( \square \)

Physically, the coefficients \( \gamma_2 \) and \( \gamma_3 \) depend on \( u_0 = \bar{u}_B \), the temperature \( T \), and the pressure \( p \):

\[
\gamma_k = \gamma_k(u_0, T, p), \quad k = 2, 3.
\]

The set of points satisfying \( \gamma_2(u_0, T, p) = 0 \) has measure zero in \( (u_0, T, p) \in \mathbb{R}^3 \). Hence, it is more interesting to consider the case where \( \gamma_2 \neq 0 \).

For this purpose, let the multiplicity of the first eigenvalue \( \rho_1 \) of (3.4) be \( m \geq 1 \), and \( \{e_1, \ldots, e_m\} \) be the first eigenfunctions. We introduce the following quadratic equations

\[
\sum_{i,j=1}^{m} a_{ij}^k x_i x_j = 0 \quad \text{for } 1 \leq k \leq m,
\]

\[
a_{ij}^k = \int_{\Omega} e_i e_j e_k dx.
\]

**Theorem 3.2.** Let \( \gamma_2 \neq 0 \), \( \gamma_3 > 0 \), and \( x = 0 \) be an isolated singular point of (3.13). Then the phase transition of (3.1) and (3.3) is either Type-II or Type-III. Furthermore, the problem (3.1) with (3.5) bifurcates to at least one singular point on each side of \( \lambda = \rho_1 \), and has a saddle-node bifurcation on \( \lambda < \rho_1 \). In particular, if \( m = 1 \), then the following assertions hold true:

1. The phase transition is Type-III, and a neighborhood \( U \subset H \) of \( u = 0 \) can be decomposed into two sectorial regions \( \hat{U} = \hat{D}_1(\pi) + \hat{D}_2(\pi) \) such that the phase transition in \( D_1(\pi) \) is the first order, and in \( D_2(\pi) \) is the \( n \)-th order with \( n \geq 3 \).

2. The bifurcated singular point \( u_{\lambda} \) on \( \lambda > \rho_1 \) attracts \( D_2(\pi) \), which can be expressed as

\[
u_{\lambda} = (\lambda - \rho_1) e_1 / \gamma_2 a + o(\lambda - \rho_1),
\]

where, by assumption, \( a = \int_{\Omega} e_1^2 dx \neq 0 \).

3. When \( |\gamma_2| = \varepsilon \) is small, the assertions in the transition perturbation theorems (Theorems A.8 and A.9) hold true.
Remark 3.1. We shall see later that when $\Omega$ is a rectangular domain, i.e.,
$$\Omega = \Pi_{k=1}^n (0, L_k) \subset \mathbb{R}^n \quad (1 \leq n \leq 3),$$
then $a = \int_{\Omega} e_1^3 dx = 0$. However, for almost all non-rectangular domains $\Omega$, the first eigenvalues are simple and $a \neq 0$. Hence, the Type-III phase transitions for general domains are generic.

Proof of Theorem 3.2. Assertions (1)-(3) can be directly proved using Theorems A.5, A.8, and A.9. By assumption, $u = 0$ is a second order non-degenerate singular point of (3.3) at $\lambda = \rho_1$, which implies that $u = 0$ is not locally asymptotically stable. Hence, it follows from Theorems A.3 and the steady state bifurcation theorem for even-order nondegenerate singular points [3] that the phase transition of (3.1) with (3.5) is either Type-II or Type-III, and there is at least one singular point bifurcated on each side of $\lambda = \rho_1$.

Finally, we shall apply Theorem A.6 to prove that there exists a saddle-node bifurcation on $\lambda < \rho_1$.

It is known that
$$\text{ind}(L + G, 0) = \begin{cases} \text{even} & \text{if } \lambda = \rho_1, \\ 1 & \text{if } \lambda < \rho_1. \end{cases}$$
Moreover, since $L + G$ defined by (3.2) is a gradient-type operator, we can derive that
$$\text{ind}(L_{\rho_1} + G, 0) \leq 0.$$ Hence there is a bifurcated branch $\Sigma_{\lambda}$ on $\lambda < \rho_1$ such that
$$\text{ind}(L + G, u_{\lambda}) = -1 \quad \forall u_{\lambda} \in \Sigma_{\lambda}, \quad \lambda < \rho_1.$$ It is clear that the eigenvalues (3.6) of $L_{\lambda}$ satisfy (A.4) and (A.5). For any $\lambda \in \mathbb{R}$ (3.3) possesses a global attractor. Therefore, for bounded $\lambda, b < \lambda \leq \rho_1$, the bifurcated branch $\Sigma_{\lambda}$ is bounded:
$$\|u_{\lambda}\|_H \leq C \quad \forall u_{\lambda} \in \Sigma_{\lambda}, \quad -\infty < b < \lambda \leq \rho_1.$$ We need to prove that there exists $\tilde{\lambda} < \rho_1$ such that for all $\lambda < \tilde{\lambda}$ equation (3.3) has no nonzero singular points.

By the energy estimates of (3.3), for any $\lambda < \tilde{\lambda} = -\gamma_2^2/2\gamma_3$ and $u \neq 0$ in $H$,
$$\int_\Omega |\Delta u|^2 - \lambda |\nabla u|^2 + 2\gamma_2 u|\nabla u|^2 + 3\gamma_3 u^2|\nabla u|^2 \, dx \\
\geq \int_\Omega |\Delta u|^2 dx + \int_\Omega |\nabla u|^2(-\lambda - 2\gamma_2 u + 3\gamma_3 u^2)dx \\
\geq \int_\Omega |\nabla u|^2 dx + \int_\Omega |\nabla u|^2(-\lambda + \gamma_3 u^2 + 2\gamma_3(u - \frac{\gamma_2}{\gamma_3})^2 - \frac{\gamma_2^2}{2\gamma_3})dx \\
\geq \int_\Omega |\nabla u|^2 dx + \int_\Omega |\nabla u|^2(-\lambda - \frac{\gamma_2^2}{2\gamma_3})dx > 0.$$ Therefore, when $\lambda < \tilde{\lambda}$, (3.3) has no nontrivial singular points in $H$. Thus we infer from Theorem A.6 that there exists a saddle-node bifurcation on $\lambda < \rho_1$. This proof is complete. □
4. Phase Transition in Rectangular Domains

The dynamical properties of phase separation of a binary system in a rectangular container is very different from that in a general container. We see in the previous section that the phase transitions in general domains are Type-III, and we shall show in the following that the phase transitions in rectangular domains are either Type-I or Type-II, which are distinguished by a critical size of the domains.

Let $\Omega = \Pi_{k=1}^n (0, L_k) \subset \mathbb{R}^n$ (1 $\leq n \leq 3$) be a rectangular domain. We first consider the case where

(4.1) $L = L_1 > L_j \quad \forall 2 \leq j \leq n.$

**Theorem 4.1.** Let $\Omega = \Pi_{k=1}^n (0, L_k)$ satisfy (4.1). The following assertions hold true:

1. **If**

   \[ \gamma_3 < \frac{2L^2}{9\pi^2} \gamma_2^2, \]

   then the phase transition of (3.1) and (3.5) at $\lambda = \lambda_0 = \frac{\pi^2}{L^2}$ is Type-II. In particular, the problem (3.1) with (3.5) bifurcates from $(u, \lambda) = (0, \frac{\pi^2}{L^2})$ on $\lambda > \frac{\pi^2}{L^2}$ to exactly two equilibrium points which are saddles, and there are two saddle-node bifurcations on $\lambda < \frac{\pi^2}{L^2}$ as shown in Figure 4.1.

2. **If**

   \[ \gamma_3 > \frac{2L^2}{9\pi^2} \gamma_2^2, \]

   then the transition is Type-I. In particular, the problem bifurcates on $\lambda > \frac{\pi^2}{L^2}$ to exactly two attractors $u_T^1$ and $u_T^2$ which can be expressed as

   (4.2) $u_{1,2}^T = \pm \sqrt{2(\lambda - \frac{\pi^2}{L^2})^{1/2}} \cos \frac{\pi x_1}{L} + o(\lambda - \frac{\pi^2}{L^2})^{1/2},$

   where $\sigma = \frac{3\gamma_2^2}{2} - \frac{L^2\gamma_2^2}{3\pi^2}.$

**Proof.** With the spatial domain as given, the first eigenvalue and eigenfunction of (3.4) are given by

\[ \rho_1 = \frac{\pi^2}{L^2}, \quad e_1 = \cos \frac{\pi x_1}{L}. \]

The eigenvalues and eigenfunctions of $L_\lambda = -A + B_\lambda$ defined by (3.2) are as follows:

(4.3) $\beta_K = |K|^2 (\lambda - |K|^2),$

(4.4) $e_K = \cos \frac{k_1 x_1}{L_1} \cdots \cos \frac{k_n x_n}{L_n},$
where
\[ K = \left( \frac{k_1 \pi}{L_1}, \cdots, \frac{k_n \pi}{L_n} \right) \quad \forall k_i \in \mathbb{Z}, \quad 1 \leq i \leq n, \]
\[ |K|^2 = \pi^2 \sum_{i=1}^{n} \frac{k_i^2}{L_i^2} \quad |K|^2 \neq 0. \]

By the approximation of the center manifold obtained in [3], the reduced equation of (3.3) to the center manifold is given by
\[ \frac{dy}{dt} = \beta_1(\lambda)y - \frac{2\pi^2}{(L_1 \cdots L_n)L_1^2} \int_{\Omega} \left[ \gamma_2 y^2 e_1^3 + \gamma_3 y^3 e_1^3 + \gamma_2 (ye_1 + \Phi(y))^2 e_1 \right] dx, \]
where \( y \in \mathbb{R}, \Phi(y) \) is the center manifold function, and
\[ \beta_1(\lambda) = \frac{\pi^2}{L_1^2} (\lambda - \frac{\pi^2}{L_2}). \]

Direct calculation implies that
\[ \int_{\Omega} e_1^3 dx = \int_0^{L_1} \cdots \int_0^{L_n} \cos^3 \frac{\pi x_1}{L} dx = 0. \quad (4.7) \]
\[ \int_{\Omega} e_1^4 dx = L_2 \cdots L_n \int_0^{L} \cos^4 \frac{\pi x_1}{L} dx_1 = \frac{3}{8} L_2 \cdots L_n. \quad (4.8) \]

By (4.7) and \( \Phi(y) = O(|y|^2) \) we obtain
\[ \int_{\Omega} (ye_1 + \Phi)^2 e_1 dx = 2y \int_{\Omega} \Phi(y)e_1^2 dx + o(|y|^3) \quad (4.9) \]

It follows that
\[ \Phi(y) = \sum_{|K|^2 > \pi^2/L^2} \phi_K(y)e_K + o(|y|^2) \]
\[ \phi_K(y) = \frac{\gamma_2 y^2}{-\beta_K \|e_K\|^2} \int_{\Omega} \Delta e_1^2 \cdot e_K dx = \frac{|K|^2 \gamma_2 y^2}{\beta_K \|e_K\|^2} \int_{\Omega} e_K e_1^2 dx. \]

Notice that
\[ \int_{\Omega} e_K e_1^2 dx = \begin{cases} 0 & \forall K \neq \left( \frac{2\pi}{L_1}, 0, \cdots, 0 \right), \\ L_1 \cdots L_n/4 & \forall K = \left( \frac{2\pi}{L_1}, 0, \cdots, 0 \right). \end{cases} \]

Then we have
\[ \Phi(y) = \frac{\gamma_2 y^2}{2(\lambda - 4\pi^2/L^2)} \cos \frac{2\pi x_1}{L} + o(|y|^2). \]

Inserting \( \Phi(y) \) into (4.9) we find
\[ \int_{\Omega} (ye_1 + \Phi)^2 e_1 dx = \frac{\gamma_2 y^3}{\lambda - \frac{4\pi^2}{L^2}} \int_{\Omega} \cos \frac{2\pi x_1}{L} e_1^2 dx + o(|y|^3) \]
\[ = \frac{L_2 \cdots L_n}{4} \frac{\gamma_2}{\lambda - \frac{4\pi^2}{L^2}} y^3 + o(|y|^3). \]
Finally, by (4.7), (4.8) and (4.10), we derive from (4.5) the following reduced equation of (3.3):

$$\frac{dy}{dt} = \beta_1(\lambda) y - \frac{\pi^2}{2L^2} \left( \frac{3\gamma_3}{2} + \frac{\gamma_2^2}{\lambda - \frac{4\pi^2}{L^2}} \right) y^3 + o(|y|^3).$$

Near the critical point $\lambda_0 = \frac{\pi^2}{L^2}$, the coefficient

$$\frac{3\gamma_3}{2} + \frac{\gamma_2^2}{\lambda - \frac{4\pi^2}{L^2}} = \frac{3\gamma_3}{2} - \frac{L^2\gamma_2^2}{3\pi^2}.$$

Thus, by Theorem A.2 we derive from (4.11) the assertions of the theorem except the claim for the saddle-node bifurcation in Assertion (1), which can be proved in the same fashion as used in Theorem 3.2. The proof is complete. □

We now consider the case where $\Omega = \Pi_{k=1}^n (0, L_k)$ satisfies that

$$L = L_1 = \cdots = L_m > L_j \quad \text{for} \quad 2 \leq m \leq 3, m < j \leq n.$$

**Theorem 4.2.** Let $\Omega = \Pi_{k=1}^n (0, L_k) \text{ satisfy } (4.12)$. Then the following assertions hold true:

1. If

$$\gamma_3 > \frac{26L^2}{27\pi^2 \gamma_2},$$

then the phase transition of the problem (3.1) with (3.5) at $\lambda_0 = \frac{\pi^2}{L^2}$ is Type-I, satisfying the following properties:

(a) The problem bifurcates on $\lambda > \frac{\pi^2}{L^2}$ to an attractor $\Sigma_\lambda$, containing exactly $3^m - 1$ non-degenerate singular points, and $\Sigma_\lambda$ is homeomorphic to an $(m-1)$-dimensional sphere $S^{m-1}$.

(b) For $m = 2$, the attractor $\Sigma_\lambda = S^1$ contains 4 minimal attractors, as shown in Figure 4.2.

(c) For $m = 3$, $\Sigma_\lambda = S^2$ contains 8 minimal attractors as shown in Figure 4.3(a), if

$$\gamma_3 < \frac{22L^2}{9\pi^2 \gamma_2},$$

and contains 6 minimal attractors as shown in Figure 4.3(b) if

$$\gamma_3 > \frac{22L^2}{9\pi^2 \gamma_2}.$$

2. If

$$\gamma_3 < \frac{26L^2}{27\pi^2 \gamma_2},$$

then the transition is Type-II. In particular, the problem has a saddle-node bifurcation on $\lambda < \lambda_0 = \frac{\pi^2}{L^2}$, and bifurcates on both side of $\lambda = \lambda_0$ to exactly $3^m - 1$ singular points which are non-degenerate.

**Proof.** We proceed in several steps as follows.

**Step 1.** Consider the center manifold reduction. It is known that the eigenvalues and eigenfunctions of $L_\lambda = -A + B_\lambda$ are given by (4.3) and (4.4) with $L_1 = \cdots = L_m$. As before, the reduced equations of (3.3) are given by

$$\frac{dy}{dt} = \beta_1(\lambda) y + g(y) + o(|y|^3),$$

$$\frac{dy}{dt} = \beta_1(\lambda) y - \frac{\pi^2}{2L^2} \left( \frac{3\gamma_3}{2} + \frac{\gamma_2^2}{\lambda - \frac{4\pi^2}{L^2}} \right) y^3 + o(|y|^3).$$
Figure 4.2. For $m = 2$, $\Sigma_\chi = S^1$ and $Z_{2k} \ (1 \leq k \leq 4)$ are attractors.

Figure 4.3. For $m = 3$, $\Sigma_\chi = S^2$, (a) $\pm Z_k \ (1 \leq k \leq 4)$ are attractors, (b) $\pm Y_k \ (1 \leq k \leq 3)$ are attractors.

where $y = (y_1, \cdots, y_m) \in \mathbb{R}^m$, $\beta_1(\lambda)$ is as in (4.6), and

$$g(y) = \frac{2\pi^2}{L_1 \cdots L_m L_1^2} (G_2(y) + G_3(y) + G_{23}(y)),$$

$$G_2(y) = -\gamma_2 \left( \int_\Omega v^2 e_1 dx, \cdots, \int_\Omega v^2 e_m dx \right),$$

$$G_3(y) = -\gamma_3 \left( \int_\Omega v^3 e_1 dx, \cdots, \int_\Omega v^3 e_m dx \right),$$

$$G_{23}(y) = -\gamma_2 \left( \int_\Omega u^2 e_1 dx, \cdots, \int_\Omega u^2 e_m dx \right).$$
Here \( e_i = \cos \pi x_i / L \) for \( 1 \leq i \leq m \), \( L \) is given by (4.12), \( v = \sum_{i=1}^{m} y_i e_i, u = v + \Phi(y) \) and \( \Phi \) is the center manifold function. Direct computation shows that

\[
\int_{\Omega} v^2 e_i dx = \int_{\Omega} \left( \sum_{j=1}^{m} y_j \cos \pi x_j / L \right)^2 \cos \pi x_i / L dx = 0,
\]

(4.14)

\[
\int_{\Omega} v^3 e_i dx = \int_{\Omega} \left( \sum_{j=1}^{n} y_k \cos \pi x_j / L \right)^3 \cos \pi x_i / L dx
\]

\[
= 3 \left( L_1 \ldots L_n \right) \left( \frac{1}{2} y_i^3 + y_i \sum_{j \neq i} y_j^2 \right),
\]

\[
\int_{\Omega} u^2 e_i dx = \left( \sum_{j=1}^{m} y_j e_j + \Phi(y) \right)^2 e_i dx
\]

(4.15)

\[
= 2 \sum_{j=1}^{m} y_j \int_{\Omega} \Phi(y) e_j e_i dx + \int_{\Omega} \Phi^2(y) e_i dx.
\]

We need to compute the center manifold function \( \Phi(y) \). As in [3], we have

(4.16)

\[
\Phi(y) = \sum_{|K| > \pi^2 / L^2} \phi_K(y) e_K + O(|y|^2) + O(|y| \beta),
\]

where

\[
\phi_K(y) = \frac{\gamma_2}{\beta_K(\lambda) - e_K, e_K} > \int_{\Omega} \Delta u^2 e_K dx
\]

\[
= \frac{|K|^2 \gamma_2}{\beta_K(\lambda) - e_K, e_K} > \int_{\Omega} u^2 e_K dx
\]

\[
= \frac{|K|^2 \gamma_2}{\beta_K < e_K, e_K} \sum_{i,j=1}^{m} y_i y_j \int_{\Omega} e_i e_j e_K dx.
\]

It is clear that

\[
\int_{\Omega} e_i e_j e_K dx = \int_{\Omega} \cos \frac{\pi x_i}{L} \cos \frac{\pi x_j}{L} e_K dx = 0,
\]

if

\[
K \neq K_i + K_j, \quad K_i = \left( \frac{\pi}{L_1} \delta_{1i}, \ldots, \frac{\pi}{L_n} \delta_{ni} \right).
\]

By (4.3) and (4.4) we have

\[
\phi_K(y) = \frac{\gamma_2 y_i y_j (2 - \delta_{ij})}{\lambda - |K|^2} < e_K, e_K > \int_{\Omega} e_i e_j e_K dx
\]

\[
= \begin{cases} 
\frac{\gamma_2 y_i^2}{2(\lambda - \frac{4\pi^2}{L^2})}, & \text{if } i = j, \\
\frac{2\gamma_2 y_i y_j}{(\lambda - \frac{2\pi^2}{L^2})}, & \text{if } i \neq j,
\end{cases}
\]
for $K = K_i + K_j$. Thus, by (4.16), we obtain

$$
\Phi(y) = \sum_{i=1}^{m} \frac{\gamma_2}{2(\lambda - \frac{4\pi^2}{L^2})} y_i^2 \cos \frac{2\pi x_i}{L} + \sum_{i>r}^{m} \frac{2\gamma_2}{(\lambda - \frac{2\pi^2}{L^2})} y_i y_r \cos \frac{\pi x_i}{L} \cos \frac{\pi x_r}{L}.
$$

Inserting $\Phi(y)$ into (4.15) we derive

$$
\int_{\Omega} u^2 e_i dx = \frac{\gamma_2}{\lambda - \frac{4\pi^2}{L^2}} \int_{\Omega} \left[ \frac{y_i^3}{\lambda - \frac{4\pi^2}{L^2}} + \frac{4y_i}{\lambda - \frac{2\pi^2}{L^2}} \sum_{j<i} y_j^2 \right] + o(|y|^3).
$$

Direct computation gives that

$$
\int_{\Omega} u^2 e_i dx = \frac{3\gamma_3}{2} + \frac{\gamma_2^2}{\lambda - \frac{4\pi^2}{L^2}}, \quad \sigma_2 = 3\gamma_3 + \frac{4\gamma_2^2}{\lambda - \frac{2\pi^2}{L^2}}.
$$

**Step 2.** It is known that the transition type of (3.3) at the critical point $\lambda_0 = \frac{\pi^2}{L^2}$ is completely determined by (4.18), i.e., by the following equations

$$
\frac{dy_i}{dt} = -\frac{\pi^2}{2L^2} \left[ \sigma_1 y_i^3 + \sigma_2 y_i \sum_{j<i} y_j^2 \right] + o(|y|^3) \quad \forall 1 \leq i \leq m,
$$

where

$$
\sigma_1 = \frac{3\gamma_3}{2} + \frac{\gamma_2^2}{\lambda - \frac{4\pi^2}{L^2}}, \quad \sigma_2 = 3\gamma_3 + \frac{4\gamma_2^2}{\lambda - \frac{2\pi^2}{L^2}}.
$$

**Step 3.** We consider the case where $m = 2$. Thus, the transition type of (4.20) is equivalent to that of the following equations

$$
\frac{dy_1}{dt} = -y_1 \left[ \sigma_0^0 y_1^2 + \sigma_0^0 y_2^2 \right],
$$

$$
\frac{dy_2}{dt} = -y_2 \left[ \sigma_0^0 y_1^2 + \sigma_0^0 y_2^2 \right].
$$

We can see that on the straight lines

$$
y_1^2 = y_2^2,
$$
equations (4.22) satisfy that
\[ \frac{dy_2}{dy_1} = \frac{y_2}{y_1} \quad \text{for} \quad \sigma_1^0 + \sigma_2^0 \neq 0, \quad (y_1, y_2) \neq 0. \]
Hence the straight lines (4.23) are orbits of (4.22) if \( \sigma_1^0 + \sigma_2^0 \neq 0 \). Obviously, the straight lines (4.24)
\[ y_1 = 0 \text{ and } y_2 = 0 \]
are also orbits of (4.22).

There are four straight lines determined by (4.23) and (4.24), and each of them contains two orbits. Hence, the system (4.22) has at least eight straight line orbits. Hence it is not hard to see that the number of straight line orbits of (4.22), if finite, is eight.

Since (3.3) is a gradient-type equation, there are no elliptic regions at \( y = 0 \); see [3]. Hence, when \( \sigma_1^0 + \sigma_2^0 > 0 \) all the straight line orbits on (4.23) and (4.24) tend to \( y = 0 \), as shown in Figure 4.4 (a), which implies that the regions are parabolic and stable, therefore \( y = 0 \) is asymptotically stable for (4.22). Accordingly, by the attractor bifurcation theorem in [3], the transition of (4.18) at \( \lambda_0 = \pi^2/L^2 \) is Type-I.

When \( \sigma_1^0 + \sigma_2^0 < 0 \) and \( \sigma_1^0 > 0 \), namely
\[ 2 \frac{L^2\gamma_2^2}{9} < \frac{26 L^2\gamma_2^2}{27} \pi^2 < \gamma_3 < \frac{26 L^2\gamma_2^2}{27} \pi^2, \]
the four straight line orbits on (4.23) are outward from \( y = 0 \), and other four on (4.24) are toward \( y = 0 \), as shown in Figure 4.4 (b), which implies that all regions at \( y = 0 \) are hyperbolic. Hence, by Theorem A.3 the transition of (4.18) at \( \lambda_0 = \pi^2/L^2 \) is Type-II.

When \( \sigma_1^0 \leq 0 \), then \( \sigma_2^0 < 0 \) too. In this case, no orbits of (4.22) are toward \( y = 0 \), as shown in Figure 4.4 (c), which implies by Theorem A.3 that the transition is Type-II.

Thus by (4.21), for \( m = 2 \) we prove that the transition is Type-I if \( \gamma_3 > \frac{26 L^2}{27\pi^2} \gamma_2^2 \), and Type-II if \( \gamma_3 < \frac{26 L^2}{27\pi^2} \gamma_2^2 \).

---

**Figure 4.4.** The topological structure of flows of (4.18) at \( \lambda_0 = \pi^2/L^2 \), (a) as \( \gamma_3 > \frac{26 L^2}{27\pi^2} \gamma_2^2 \); (b) as \( \frac{24 L^2}{9\pi^2} \gamma_2^2 < \gamma_3 < \frac{26 L^2}{27\pi^2} \gamma_2^2 \); and (c) \( \gamma_3 \leq \frac{24 L^2}{9\pi^2} \gamma_2^2 \).
STEP 4. Consider the case where \( m = 3 \). Thus, equation (4.20) are written as

\[
\begin{align*}
\frac{dy_1}{dt} &= -y_1[\sigma_1^0 y_1^2 + \sigma_2^0 (y_2^2 + y_3^2)], \\
\frac{dy_2}{dt} &= -y_2[\sigma_1^0 y_2^2 + \sigma_2^0 (y_1^2 + y_3^2)], \\
\frac{dy_3}{dt} &= -y_3[\sigma_1^0 y_3^2 + \sigma_2^0 (y_1^2 + y_2^2)].
\end{align*}
\]

(4.25)

It is clear that the straight lines

\[
y_i = 0, \quad y_j = 0 \quad \text{for } i \neq j, \ 1 \leq i, j \leq 3,
\]

(4.26)

\[
\begin{cases}
y_i^2 = y_j^2, \quad y_k = 0 & \text{for } i \neq j, i \neq k, j \neq k, 1 \leq i, j, k \leq 3, \\
y_i^2 = y_2^2 = y_3^2,
\end{cases}
\]

(4.27)

consist of orbits of (4.25). There are total 13 straight lines in (4.26) and (4.27), each of which consists of two orbits. Thus, (4.25) has at least 26 straight line orbits. We shall show that (4.25) has just the straight line orbits given by (4.26) and (4.27).

In fact, we assume that the line

\[
y_2 = z_1 y_1, \quad y_3 = z_2 y_1 \quad (z_1, z_2 \text{ are real numbers})
\]

is a straight line orbit of (4.25). Then \( z_1, z_2 \) satisfy

\[
\begin{align*}
\frac{dy_2}{dy_1} &= z_1 = \frac{\sigma_1^0 z_1^2 + \sigma_2^0 (1 + z_2^2)}{\sigma_1^0 + \sigma_2^0 (z_1^2 + z_2^2)}, \\
\frac{dy_3}{dy_1} &= z_2 = \frac{\sigma_1^0 z_2^2 + \sigma_2^0 (1 + z_1^2)}{\sigma_1^0 + \sigma_2^0 (z_1^2 + z_2^2)}.
\end{align*}
\]

(4.28)

It is easy to see that when \( \sigma_1^0 \neq \sigma_2^0 \) the solutions \( z_1 \) and \( z_2 \) of (4.28) take only the values

\[
z_1 = 0, \pm 1; \quad z_2 = 0, \pm 1.
\]

In the same fashion, we can prove that the straight line orbits of (4.25) given by

\[
y_1 = \alpha_1 y_3, \quad y_2 = \alpha_2 y_3, \quad \text{and} \quad y_1 = \beta_1 y_2, \quad y_3 = \beta_2 y_2
\]

have to satisfy that

\[
\alpha_1 = 0, \pm 1 \quad \text{and} \quad \beta_1 = 0, \pm 1 \quad (i = 1, 2).
\]

Thus, we prove that when \( \sigma_1^0 \neq \sigma_2^0 \), the number of straight line orbits of (4.25) is exactly 26.

When \( \sigma_1^0 = \sigma_2^0 \), we have that \( \gamma_3 = \frac{22 L^2}{9 \pi^2 \gamma_2^2} \) which implies that \( \sigma_1^0 = \sigma_2^0 > 0 \). In this case, it is clear that \( y = 0 \) is an asymptotically stable singular point of (4.25). Hence, the transition of (4.18) at \( \lambda_0 = \pi^2/L^2 \) is I-type.

When \( \sigma_1^0 + \sigma_2^0 > 0 \) and \( \sigma_1^0 \neq \sigma_2^0 \), all straight line orbits of (4.25) are toward \( y = 0 \), which implies that the regions at \( y = 0 \), are stable, and \( y = 0 \) is asymptotically stable; see 3. Thereby the transition of (4.18) is Type-I.

When \( \sigma_1^0 + \sigma_2^0 < 0 \) with \( \sigma_1^0 > 0 \), we can see, as in the case of \( m = 2 \), that the regions at \( y = 0 \) are hyperbolic, and when \( \sigma_1^0 + \sigma_2^0 < 0 \) with \( \sigma_1 \leq 0 \) the regions at \( y = 0 \) are unstable. Hence, the transition is Type-II.

STEP 5. We prove Assertion (1). By Steps 3 and 4, if \( \gamma_3 > \frac{26 L^2}{27 \pi^2 \gamma_2^2} \), the reduced equation (4.18) bifurcates on \( \lambda > \lambda_0 = \pi^2/L^2 \) to an attractor \( \Sigma_{\lambda} \). All bifurcated
equilibrium points of (3.3) are one to one correspondence to the bifurcated singular points of (4.18). Therefore, we only have to consider the stationary equations:

\[(4.29) \quad \beta_1(\lambda)y_i - \frac{\pi^2}{2L^2}[\sigma_1 y_i^3 + \sigma_2 y_i \sum_{j \neq i} y_j^2] + o(|y|^3) = 0, \quad 1 \leq i \leq m,\]

where \(\sigma_1\) and \(\sigma_2\) are as in (4.19).

Consider the following approximative equations of (4.29)

\[(4.30) \quad \beta_1(\lambda)y_i - y_i(a_1 y_i^2 + a_2 \sum_{j \neq i} y_j^2) = 0 \quad \text{for } 1 \leq i \leq m,\]

where \(a_1 = \pi^2\sigma_1/2L^2\), \(a_2 = \pi^2\sigma_2/2L^2\). It is clear that each regular bifurcated solution of (4.30) corresponds to a regular bifurcated solution of (4.29).

We first prove that (4.30) has \(3^m - 1\) bifurcated solutions on \(\lambda > \lambda_0\). For each \(k (0 \leq k \leq m - 1), (4.30) \) has \(C_m \times 2^{m-k}\) solutions as follows:

\[(4.31) \quad y_{j_1} = 0, \ldots, y_{j_k} = 0 \quad \text{for } 1 \leq j_i \leq m,\]

\[(4.31) \quad y_{r_1}^2 = \cdots = y_{r_{m-k}}^2 = \beta_1(a_1 + (m - k - 1)a_2)^{-1} \quad \text{for } r_i \neq j_i.\]

Hence, the number of all bifurcated solutions of (4.30) is

\[
\sum_{k=0}^{m-1} C_m \times 2^{m-k} = (2 + 1)^m - 1 = 3^m - 1.
\]

We need to prove that all bifurcated solutions of (4.30) are regular. The Jacobian matrix of (4.30) is given by

\[(4.32) \quad Dv = \begin{pmatrix}
\beta_1 - h_1(y) & 2a_2y_1y_2 & \cdots & 2a_2y_1y_m \\
2a_2y_2y_1 & \beta_1 - h_2(y) & \cdots & 2a_2y_2y_m \\
\vdots & \vdots & \ddots & \vdots \\
2a_2y_my_1 & 2a_2y_my_2 & \cdots & \beta_1 - h_m(y)
\end{pmatrix},
\]

where

\[h_i(y) = 3a_1y_i^2 + a_2 \sum_{j \neq i} y_j^2.\]

For the solutions in (4.31), without loss of generality, we take

\[y_0 = (y_1^0, \ldots, y_m^0),\]

\[y_i^0 = 0 \quad 1 \leq i \leq k,\]

\[y_{k+1}^0 = \cdots = y_m^0 = \beta_1^{1/2}(a_1 + (m - k - 1)a_2)^{-1/2}\]

Inserting them into (4.32) we find

\[(4.33) \quad Dv(y_0) = \begin{pmatrix}
\beta I_k & 0 \\
0 & A_{m-k}
\end{pmatrix},
\]

where

\[\beta = \beta_1 \left(1 - \frac{(m - k)a_2}{a_1 + (m - k - 1)a_2}\right) = \frac{\sigma_1 - \sigma_2}{\sigma_1 + (m - k - 1)\sigma_2},\]

\[A_{m-k} = \begin{pmatrix}
\beta_1 - (3a_1 + (m - k - 1)a_2)(y_{k+1}^0)^2 & \cdots & 2a_2(y_{k+1}^0)^2 \\
\vdots & \ddots & \vdots \\
2a_2(y_{k+1}^0)^2 & \cdots & \beta_1 - (3a_1 + (m - k - 1)a_2)(y_{k+1}^0)^2
\end{pmatrix}.
\]
Direct computation shows that
\[
\det A_{m-k} = \frac{\pi^{2m} \beta_m}{(a_1 + (m-k-1)a_2)^m L^{2m}} \det \begin{pmatrix}
-\sigma_1 & \sigma_2 & \cdots & \sigma_2 \\
\sigma_2 & -\sigma_1 & \cdots & \sigma_2 \\
\vdots & \vdots & \ddots & \vdots \\
\sigma_2 & \sigma_2 & \cdots & -\sigma_1
\end{pmatrix},
\]
where \(\sigma_1, \sigma_2\) are given by (4.19).

Obviously, there are only finite number of \(\lambda > \pi^2/L^2\) satisfying
\[
\beta(\lambda) = \frac{(\sigma_1(\lambda) - \sigma_2(\lambda))\beta_1(\lambda)}{\sigma_1(\lambda) + (m-k-1)\sigma_2(\lambda)} = 0,
\]
\[
\det A_{m-k}(\lambda) = 0.
\]
Hence, for any \(\lambda - \pi^2/L^2 > 0\) sufficiently small the Jacobian matrices (4.32) at the singular points (4.31) are non-degenerate. Thus, the bifurcated solutions of (4.30) are regular.

Since all bifurcated singular points of (3.1) with (3.5) are non-degenerate, and when \(\Sigma_\lambda\) is restricted on \(x_i x_j\)-plane (1 \(\leq i,j \leq m\)) the singular points are connected by their stable and unstable manifolds. Hence all singular points in \(\Sigma_\lambda\) are connected by their stable and unstable manifolds. Therefore, \(\Sigma_\lambda\) must be homeomorphic to a sphere \(S^{m-1}\).

Assertion (1) is proved.

**Step 6. Proof of Assertions (2) and (3).** When \(m = 2\), by Step 5, \(\Sigma_\lambda = S^1\) contains 8 non-degenerate singular points. By a theorem on minimal attractors in [3], 4 singular points must be attractors and the others are repellors, as shown in Figure 4.2.

When \(m = 3\), we take the six singular points
\[
\pm Y_1 = (\pm \beta_1 a_1^{-1}, 0, 0), \pm Y_2 = (0, \pm \beta_1 a_1^{-1}, 0), \pm Y_3 = (0, 0, \pm \beta_1 a_1^{-1})
\]
Then the Jacobian matrix (4.32) at \(Y_i\) (1 \(\leq i \leq 3\)) is
\[
Dv(\pm Y_i) = \begin{pmatrix}
\rho_1 & 0 \\
0 & \rho_2 \\
0 & \rho_3
\end{pmatrix},
\]
where \(\rho_j = \beta_1 \left(1 - \frac{\sigma_j}{\sigma_1}\right)\) as \(j \neq i\) and \(\rho_i = -2\beta_1\). Obviously, as \(\sigma_2 < \sigma_1\), 0 < \(\rho_j\) (\(j \neq i\)) and \(\rho_i < 0\), in this case, \(\pm Y_k\) (1 \(\leq k \leq 3\)) are repellors in \(\Sigma_\lambda = S^2\), which implies that \(\Sigma_\lambda\) contains 8 attractors \(\pm z_k\) (1 \(\leq k \leq 4\)) as shown in Figure 4.3 (a). As \(\sigma_2 > \sigma_1, \rho_j < 0\) (1 \(\leq j \leq 3\)), the six singular point \(\pm Y_k\) (1 \(\leq k \leq 3\)) are attractors, which implies that \(\Sigma_\lambda\) contains only six minimal attractors as shown in Figure 4.3 (b). Thus Assertion (2) is proved.

The claim for the saddle-node bifurcation in Assertion (3) can be proved by using the same method as in the proof of Theorem 3.2 and the claim for the singular point bifurcation can be proved by the same fashion as used in Step 5.

The proof of this theorem is complete.

**Remark 4.1.** For the domain \(\Omega = [0, L] \times D \subset \mathbb{R}^n (1 < m < n)\) where \(n \geq 2\) is arbitrary and \(D \subset \mathbb{R}^{n-m}\) a bounded open set, Theorems 4.1 and 4.2 are also valid.
provided $\pi^2/L^2 < \lambda_1$, where $\lambda_1$ is the first eigenvalue of the equation

$$ -\Delta e = \lambda e, \quad x \in D \subset \mathbb{R}^{n-m}, $$

$$ \frac{\partial e}{\partial n} |_{\partial D} = 0, $$

$$ \int_D edx = 0. $$

**Remark 4.2.** In Theorem 4.2, the minimal attractors in the bifurcated attractor $\Sigma_\lambda$ can be expressed as

$$ u_\lambda = (\lambda - \pi^2/L^2)^{1/2} e + o(|\lambda - \pi^2/L^2|^{1/2}), $$

where $e$ is a first eigenfunction of (3.4). The expression (4.34) can be derived from the reduced equations (4.18).

We address here that the exponent $\beta = 1/2$ in (4.34), called the critical exponent in physics, is an important index in the phase transition theory in statistical physics, which arises only in the Type-I or the continuous phase transitions. It is interesting to point out that the critical exponent $\beta = 1$ in (3.14) is different from these $\beta = 1/2$ appearing in (4.2) and (4.34). The first one occurs when the container $\Omega \subset \mathbb{R}^3$ is a non rectangular region, and the second one occurs when $\Omega$ is a rectangle or a cube. We shall continue to discuss this problem later from the physical viewpoint.

5. Phase Transitions Under Periodic Boundary Conditions

When the sample or container $\Omega$ is a loop, or a torus, or bulk in size, then the periodic boundary conditions are necessary. In this section, we shall discuss the problems in a loop domain and in the whole space $\Omega = \mathbb{R}^n$.

Let $\Omega = S^1 \times (r_1, r_2) \subset \mathbb{R}^2$ be a loop domain, $0 < r_1 < r_2$. Then the boundary condition is given by

$$ u(\theta + 2k\pi, r) = u(\theta, r) \quad \text{for} \quad 0 \leq \theta \leq 2\pi, \quad r_1 < r < r_2, \quad k \in \mathbb{Z}, $$

$$ \frac{\partial u}{\partial r} = 0, \quad \frac{\partial^3 u}{\partial r^3} = 0 \quad \text{at} \quad r = r_1, r_2. $$

Assume that the gap $r_2 - r_1$ is small in comparison with the mean radius $r_0 = (r_1 + r_2)/2$. With proper scaling, we take the gap $r_2 - r_1$ as $r_2 - r_1 = 1$. Then this assumption is

$$ r_0 = (r_1 + r_2)/2 \gg 1, \quad r_2 - r_1 = 1. $$

With this condition, the Laplacian operator can be approximately expressed as

$$ \Delta = \frac{\partial^2}{\partial r^2} + \frac{1}{r_0^2} \frac{\partial^2}{\partial \theta^2}. $$

With the boundary condition (5.1) and the operator (5.3), the eigenvalues and eigenfunctions of the linear operator $L_\lambda = -A + B_\lambda$ defined by (3.2) are given by

$$ \beta_K(\lambda) = K^2(\lambda - K^2), $$

$$ e^1_K = \cos k_1 \theta \cos k_2 \pi (r - r_1), $$

$$ e^2_K = \sin k_1 \theta \cos k_2 \pi (r - r_1), $$

$$ K^2 = \frac{k_1^2}{r_0^2} + \frac{k_2^2}{r_0^2}, \quad k_1, k_2 \in \mathbb{Z}. $$
Figure 5.1. All points in $\Sigma_\lambda$ are singular points.

Figure 5.2. The point $\lambda^*$ is a singularity separation point from where two invariant sets $\Sigma_\lambda$ and $\Gamma_\lambda$ are separated with $\Sigma_\lambda$ being an attractor, and $\Gamma_\lambda \rightarrow 0$ as $\lambda \rightarrow \lambda_0$.

By (5.2), the first eigenvalue of $L_\lambda$ is

$$\beta_1(\lambda) = \frac{1}{r_0^2}(\lambda - \frac{1}{r_0^2}),$$

which has multiplicity 2, and the first eigenfunctions are $e_1 = \cos \theta$ and $e_2 = \sin \theta$.

**Theorem 5.1.** Let $\Omega = S^1 \times (r_1, r_2)$ satisfy (5.2). Then the following assertions hold true:

1. If

$$\gamma_3 > \frac{2r_0^2}{9}\gamma_2^2,$$

then the phase transition of (3.1) with (5.1) at $\lambda_0 = 1/r_0^2$ is Type-I. Furthermore, the problem (3.1) with (5.1) bifurcates on $\lambda > \lambda_0 = r_0^{-2}$ to a cycle attractor $\Sigma_\lambda = S^1$ which consists of singular points, as shown in Figure 5.1, and the singular points in $\Sigma_\lambda$ can be expressed as

$$u_\lambda = \sigma^{-1/2} \left( \lambda - \frac{1}{r_0^2} \right)^{1/2} \cos(\theta + \theta_0) + o \left( |\lambda - \frac{1}{r_0^2}|^{1/2} \right),$$

$$\sigma = \frac{3}{4} \gamma_3 - \frac{1}{6} r_0^2 \gamma_2,$$

where $\theta_0$ is the angle of $u_\lambda$ in $\Sigma_\lambda$.

2. If

$$\gamma_3 < \frac{2r_0^2}{9}\gamma_2^2,$$

then the transition is Type-II. Moreover, the problem bifurcates on $\lambda < \lambda_0$ to a cycle invariant set $\Gamma_\lambda = S^1$ consisting of singular points, and there is a singularity separation at $\lambda^* < \lambda_0$, where $\Gamma_\lambda$ and an $S^1$ attractor $\Sigma_\lambda = S^1$ are generated such that the system undergoes a transition at $\lambda = \lambda_0$ from $u = 0$ to $u_\lambda \in \Sigma_\lambda$, as shown in Figure 5.2.
Proof. Let \( v = y \cos \theta + z \sin \theta, \) \( u = v + \Phi(y, z), \) and \( \Phi \) is the center manifold function. Then the reduced equations of (3.1) with (5.1) are given by
\[
\frac{dy}{dt} = \beta_1(y) + \frac{1}{\pi} \int_{r_0}^{r_1} \int_{0}^{2\pi} [\gamma_2 \Delta v^2 + \gamma_3 \Delta v^3 + \gamma_2 \Delta u^2] e_1 \, dr \, d\theta,
\]
(5.4)
\[
\frac{dz}{dt} = \beta_1(z) + \frac{1}{\pi} \int_{r_0}^{r_1} \int_{0}^{2\pi} [\gamma_2 \Delta v^2 + \gamma_3 \Delta v^3 + \gamma_2 \Delta u^2] e_2 \, dr \, d\theta.
\]
Direct computation shows that (5.4) can be rewritten as
\[
\frac{dy}{dt} = \beta_1(y) - \frac{1}{\pi r_0^2} \left[ \frac{3 \pi}{4} \gamma_3 y (y^2 + z^2) + \int_{0}^{2\pi} 2 \gamma_2 \Phi [y \cos \theta + z \sin \theta \cos \theta | \, d\theta \right],
\]
(5.5)
\[
\frac{dz}{dt} = \beta_1(z) - \frac{1}{\pi r_0^2} \left[ \frac{3 \pi}{4} \gamma_3 z (y^2 + z^2) + \int_{0}^{2\pi} 2 \gamma_2 \Phi [z \sin \theta + y \cos \theta \sin \theta \, d\theta \right],
\]
and the center manifold function \( \Phi = \Phi(y, z) \)
is
\[
\Phi = \frac{2 \gamma_2}{\beta_2(\lambda) r_0^2} (y^2 - z^2) \cos 2\theta + \frac{4 \gamma_2}{\beta_2(\lambda) r_0^2} y z \sin 2\theta,
\]
where
\[
\beta_2(\lambda) = \frac{4}{r_0^2} (\lambda - \frac{4}{r_0^2}).
\]
Putting \( \Phi \) into (5.5), we obtain the approximate equations of (5.4) as follows
\[
\frac{dy}{dt} = \beta_1 y - \frac{1}{r_0^2} \left[ \frac{3 \pi}{4} \gamma_3 y (y^2 + z^2) + \frac{\gamma_2^2}{2(\lambda - 4 r_0^2)} \right] y (y^2 + z^2),
\]
(5.6)
\[
\frac{dz}{dt} = \beta_1 z - \frac{1}{r_0^2} \left[ \frac{3 \pi}{4} \gamma_3 z (y^2 + z^2) + \frac{\gamma_2^2}{2(\lambda - 4 r_0^2)} \right] z (y^2 + z^2).
\]
At \( \lambda = \lambda_0 = r_0^{-2} \), we have
\[
\frac{3 \gamma_3}{4} + \frac{\gamma_2^2}{2(\lambda - 4 r_0^2)} = \frac{3 \gamma_3}{4} - \frac{1}{6} r_0^2 \gamma_2.
\]
In the same fashion as used in Theorem 4.2 we derive from (5.6) the assertions of this theorem. Here the statement that the bifurcated cycle \( \Sigma = S^1 \) consists of singular points can proved by that the equation (3.1) with (5.1) is invariant under the translation
\[
u(\theta, r) \rightarrow u(\theta + \theta_0, r) \quad \forall \theta_0 \in \mathbb{R}^1,
\]
which ensures that the singular points of (3.1) with (5.1) arise as a cycle \( S^1 \). Thus, the theorem is proved.

Now, we consider the problem that the equation (3.1) is defined in the whole space \( \Omega = \mathbb{R}^n \) \( (n \geq 2) \), with the periodic boundary condition
\[
u(x + 2K \pi) = u(x) \quad \forall K = (k_1, \ldots, k_n) \in \mathbb{Z}^n.
\]
In this case, the eigenvalues and eigenfunctions of \( L_{\lambda} \) are given by
\[
\beta_k(\lambda) = |K|^2 (\lambda - |K|^2), \quad K = (k_1, \ldots, k_n), \quad |K|^2 = k_1^2 + \cdots + k_n^2,
\]
\[
e_1^K = \cos(k_1 x_1 + \cdots + k_n x_n), \quad e_2^K = \sin(k_1 x_1 + \cdots + k_n x_n).
\]
It is clear that the first eigenvalue \( \beta_1(\lambda) = \lambda - 1 \) of \( L_\lambda \) has multiplicity \( 2n \), and the first eigenfunctions are
\[
e^1_j = \cos x_j, \quad e^2_j = \sin x_j \quad \forall 1 \leq j \leq n.
\]

**Theorem 5.2.**

(1) If
\[
\gamma_3 > \frac{14}{27} \gamma_2^2,
\]
then the phase transition of (3.1) with (5.7) at \( \lambda_0 = 1 \) is Type-I. Moreover,
(a) the problem bifurcates from \((u, \lambda) = (0, 1)\) to an attractor \( \Sigma_\lambda \text{homeomorphic to a} \ (2n-1)\text{-dimensional sphere} S^{2n-1} \), and
(b) for each \( k \ (0 \leq k \leq n-1) \), the attractor \( \Sigma_\lambda \) contains \( C^n_k \)-dimensional tori \( T^{n-k} \) consisting of singular points.

(2) If
\[
\gamma_3 < \frac{14}{27} \gamma_2^2,
\]
then the transition is Type-II.

**Proof.** We only have to prove Assertion (2), as the remaining part of the theorem is essentially the same as the proof for Theorem 4.2.

Since the space of all even functions is an invariant space of \( L_\lambda + G \) defined by (3.2), the problem (3.1) with (5.7) has solutions given in (4.31) with \( m = n \) in the space of even functions.

By the translation invariance of (3.1) and (5.7), for each \( k \ (0 \leq k \leq n-1) \) and a fixed index \((j_1, \cdots, j_k)\), the steady state solution associated with (4.31) generates an \((n-k)\)-dimensional torus \( T^{n-k} \) which consists of steady state solutions of (3.1) and (5.7). For example if \((j_1, \cdots, j_k) = (1, \cdots, k)\), the \((n-k)\)-dimensional singularity torus \( T^{n-k} \) is
\[
T^k = \left\{ u(x + \theta) = \sum_{j=k+1}^n y_j \cos(x_j + \theta_j) + o(|y|), \quad \forall (\theta_{n+1}, \cdots, \theta_n) \in \mathbb{R}^{n-k} \right\},
\]
where \( u(x) \) is the steady state solution of (3.1) with (5.7) associated with (4.31) with \( y_1 = \cdots = y_k = 0, y_{k+1} = \cdots = y_n \).

Obviously, for a fixed \((j_1, \cdots, j_k)\), the \(2^{n-k}\) steady state solutions of (3.1) and (5.7) associated with (4.31) are in the same singular torus \( T^{n-k} \). Furthermore, for two different index \( k \)-tuples \((j_1, \cdots, j_k)\) and \((i_1, \cdots, i_k)\), the two associated singularity tori are different. Hence, for each \( 0 \leq k \leq n-1 \), there are exactly \( C^n_k \) \((n-k)\)-dimensional singularity tori in \( \Sigma_\lambda \). Thus the proof is complete. \( \square \)

6. **Cahn-Hilliard Equations Coupled with Entropy**

When a phase separation takes place in a binary system, the entropy varies, and if the phase transition is Type-II, it will yield latent heat. Hence, it is necessary to discuss the equations (2.3), which are called the Cahn-Hilliard equations coupled with entropy.
To make the equations (2.3) non-dimensional, let
\[ x = l x', \quad t = \frac{1}{k_2} t'^4, \quad u = u_0 u', \quad S = S_0 S', \]
\[ \mu = \frac{k_1^2}{k_2}, \quad \alpha_1 = \frac{1}{k_2} t'^4 a_1, \quad \alpha_2 = \frac{l^2}{k_2 S_0} u_0^2 a_2, \quad \lambda = -\frac{l^2}{k_2} b_1, \]
\[ \gamma_1 = \frac{l^2}{k_2} S_0 b_0, \quad \gamma_2 = \frac{l^2}{k_2} u_0^{2} b_2, \quad \gamma_3 = \frac{l^2}{k_2} u_0^{2} b_3. \]
Omitting the primes, equations (2.3) are in the following form
\[ \frac{\partial S}{\partial t} = \mu \Delta S - \alpha_1 S - \alpha_2 u^2, \]
\[ \frac{\partial u}{\partial t} = -\Delta^2 u - \lambda \Delta u + \Delta (\gamma_1 S u + \gamma_2 u^2 + \gamma_3 u^3), \]
\[ \int_{\Omega} u(x, t) dx = 0, \]
\[ \frac{\partial}{\partial n} (u, \Delta u, S) = 0 \quad \text{on} \partial \Omega, \]
\[ u(x, 0) = \varphi(x). \]

By assumptions (2.2) and (2.4), the coefficients satisfy
\[ \mu > 0, \quad \alpha_1 > 0, \quad \alpha_2 > 0, \quad \gamma_1 > 0, \quad \gamma_3 > 0. \]

Theorem 6.1. Let \( \Omega = \prod_{n=1}^{n}(0, L_k) \subset \mathbb{R}^n \) satisfy that \( L = L_1 = \cdots = L_m > L_j (1 \leq m \leq n) \) for any \( j > m \).

1. For the case where \( m = 1 \), let
\[ \sigma = \frac{3}{2} \gamma_3 - \frac{\alpha_2 \gamma_1}{\alpha_1} - \frac{\alpha_2 \gamma_1 L^2}{2(\alpha_1 L^2 + 4 \pi^2 \mu)} - \frac{L^2 \gamma_2^2}{3 \pi^2}. \]
(a) If \( \sigma < 0 \), then the phase transition of (6.1) at \( \lambda = \pi^2/L^2 \) is Type-II and Assertion (1) in Theorem 4.1 holds true.
(b) If \( \sigma > 0 \) the phase transition is Type-I and Assertion (2) in Theorem 4.1 holds true.

2. For the case where \( m \geq 2 \), let
\[ \sigma = \frac{9}{2} \gamma_3 - \alpha_2 \gamma_1 \left( \frac{L^2}{\alpha_1} + \frac{2 L^2}{(\alpha_1 L^2 + 4 \pi^2 \mu)} + \frac{2 L^2}{\alpha_1 L^2 + 2 \pi^2 \mu} \right) - \frac{13 L^2 \gamma_2^2}{3 \pi^2}. \]
(a) If \( \sigma > 0 \), the phase transition of (6.1) at \( \lambda = \pi^2/L^2 \) is Type-I and Assertions (1) and (2) in Theorem 4.2 hold true.
(b) If \( \sigma < 0 \), then the phase transition is Type-II and Assertion (3) in Theorem 4.2 holds true.

Proof. It suffices to compute the reduced equations of (6.1) on the center manifold. Similar to (4.18), the second order approximation of the reduced equation can be expressed as
\[ \frac{dy_i}{dt} = \beta_1 y_i - \frac{\pi^2}{2 L^2} [\sigma_1 y_i^3 + \sigma_2 y_i \sum_{j \neq i} y_j^2] \]
\[ - \frac{2 \pi^2}{L_1 \cdots L_n L^2} \sum_{j=1}^{m} y_j \int_{\Omega} \Phi_1(y) \cos \frac{\pi x_i}{L} \cos \frac{\pi x_j}{L} dx, \]
where \( \beta_1, \sigma_1 \) and \( \sigma_2 \) are as in (4.18), and the center manifold function \( \Phi_1(y) \) derived from the first equation in (6.1) can be expressed as

\[
\Phi_1(y) = \sum_{|K| \geq 0} \Phi_K(y) \varphi_K
\]

(6.3)

\[
\Phi_K(y) = \frac{-\alpha_2}{\lambda_K \| \varphi_K \|^2} \int_\Omega \left( \sum_{i=1}^m y_i \cos \frac{\pi x_i}{L} \right)^2 \varphi_K dx
\]

where \( \lambda_K \) and \( \varphi_K \) are the eigenvalues and eigenfunctions of the following equation

\[
-\mu \Delta \varphi_K + \alpha_1 \varphi_K = \lambda_K \varphi_K,
\]

\[
\frac{\partial \varphi_K}{\partial n} |_{\partial \Omega} = 0,
\]

which are given by

\[
\lambda_K = \alpha_1 + \mu K^2 \pi^2,
\]

\[
\varphi_0 = 1, \quad \varphi_K = \cos \frac{k_1 \pi x_1}{L_1^2} \cdots \cos \frac{k_n \pi x_n}{L_n^2},
\]

\[
K = (k_1/L_1, \cdots, k_n/L_n), \quad |K|^2 = \sum_{i=1}^n k_i^2/L_i^2 \quad \text{for } k_i \in \mathbb{Z}, \quad 1 \leq i \leq n.
\]

Let

\[
K = (\delta_1/L_1, \cdots, \delta_m/L_m).
\]

Then we find

\[
\Phi_0 = \frac{-\alpha_2}{\alpha_1 L_1 \cdots L_m} \int_\Omega \left( \sum_{i=1}^m y_i \cos \frac{\pi x_i}{L} \right)^2 dx = \frac{-\alpha_2}{2\alpha_1} \sum_{j=1}^m y_j^2,
\]

\[
\Phi_K = \frac{-\alpha_2}{\lambda_K \| \varphi_K \|^2} \int_\Omega \left( \sum_{i=1}^m y_i \cos \frac{\pi x_i}{L} \right)^2 dx
\]

\[
= \begin{cases} 
0 & \text{if } K \neq K_l + K_r, \\
\frac{-\alpha_2}{\lambda_K \| \varphi_K \|^2} \sum_{i,j=1}^m y_i y_j \int_\Omega \cos \frac{\pi x_i}{L} \cos \frac{\pi x_j}{L} \varphi_K dx & \text{if } K = K_l + K_r,
\end{cases}
\]

for some \( 1 \leq r, l \leq m \). Thus we derive that

\[
\Phi_K = \begin{cases} 
\frac{-\alpha_2}{\lambda_K \| \varphi_K \|^2} \int_\Omega \cos^2 \frac{\pi x_i}{L} e_k & \text{if } K = K_j + K_j, \quad 1 \leq j \leq m \\
\frac{-2\alpha_2}{\lambda_K \| \varphi_K \|^2} y_i y_j \int_\Omega \cos \frac{\pi x_i}{L} \cos \frac{\pi x_j}{L} e_K & \text{if } K = K_i + K_j, \quad i \neq j \\
\frac{-\alpha_2}{2(\alpha_1 + 4\pi^2 \mu/L^2)} y_j^2 & \text{if } K = 2K_j, \quad 1 \leq j \leq m \\
\frac{-2\alpha_2}{\alpha_1 + 4\pi^2 \mu/L^2} y_i y_j & \text{if } K = K_i + K_j, \quad i \neq j, \quad 1 \leq i, j \leq m.
\end{cases}
\]
Putting \( \Phi_0 \) and \( \Phi_K \) in (6.3) we obtain
\[
\Phi_1 = \frac{-\alpha_2}{2\alpha_1} \sum_{j=1}^{n} y_j^2 - \frac{\alpha_2}{2(\alpha_1 + 4\pi^2\mu/L^2)} \sum_{j=1}^{n} y_j^2 \cos \frac{2\pi x_j}{L} - \frac{2\alpha_2}{\alpha_1 + 2\pi^2\mu/L^2} \sum_{i<j} y_i y_j \cos \frac{\pi x_i}{L} \cos \frac{\pi x_j}{L}.
\]

Then, inserting \( \Phi_1 \) into (6.2), we derive the following reduced equations:
\[
\frac{dy_i}{dt} = \beta_1(\lambda)y_i - \frac{\pi^2}{2L^2} \left[ \left( \sigma_1 - \frac{\alpha_2\gamma_1}{\alpha_1} - \frac{\alpha_2\gamma_1}{2(\alpha_1 + 4\pi^2\mu/L^2)} \right) y_i^3 + \left( \sigma_2 - \frac{\alpha_2\gamma_1}{\alpha_1} - \frac{2\alpha_2\gamma_1}{\alpha_1 + 2\pi^2\mu/L^2} \right) \sum_{j \neq i} y_j^2 \right], \quad 1 \leq i \leq m.
\]

Then the remaining part of the proof can be achieved in the same fashion as the proofs for Theorems 4.1 and 4.2. The proof is complete. \( \square \)

**Remark 6.1.** From the phenomenological viewpoint, the coefficient \( \mu > 0 \) in (6.1) is small. If let \( \mu = 0 \), then in the equilibrium state we have that \( \lambda = -\frac{a_2}{a_1}u^2 \).

In this case, (6.1) are referred to the original Cahn-Hilliard equation (3.1) with \( \gamma_3' = \gamma_3 - \alpha_2\gamma_1/\alpha_1 \) as the coefficient of the cubic term, and the criterion \( \sigma = 0 \) in Assertions (1) and (2) of Theorem 6.1 are respectively equivalent to
\[
\gamma_3' = \frac{2L^2\gamma_2}{9\pi^2}, \quad \text{and} \quad \gamma_3' = \frac{26L^2\gamma_2}{27\pi^2},
\]
which coincide with these in Theorems 4.1 and 4.2. Hence, if we consider the coefficient \( \mu > 0 \) small, then the criterion \( \sigma = 0 \) are respectively equivalent to
\[
\gamma_3' = \frac{2L^2\gamma_2}{9\pi^2} - \frac{4\pi^2\mu_3\gamma_1}{3\alpha_1^2L^2}, \quad \text{and} \quad \gamma_3' = \frac{26L^2\gamma_2}{27\pi^2} - \frac{4\pi^2\mu_3\gamma_1}{3\alpha_1^2L^2}.
\]

Hence the item \( -(4\pi^2\mu_3\gamma_1)/3\alpha_1^2L^2 \) is the effect yielded by \( \mu \Delta S \). \( \square \)

### 7. Physical remarks

We now address the physical significance for the phase transition theorems obtained in the previous sections.

**7.1. Equation of critical parameters.** For a binary system, the equation describing the control parameters \( T, p, \Omega \) at the critical states is simple.

We first consider the critical temperature \( T_c \). There are two different critical temperatures \( T_1 \) and \( T_0 \) in the Cahn-Hilliard equation. \( T_1 \) is the one given by (2.8), at which the coefficient \( b_1(T, p) \) or \( \lambda = -l^2b_1(T, p)/k \) will change its sign, and \( T_0 \) satisfies that \( \lambda_0 < \lambda_1 \), and for fixed \( p \),
\[
\lambda(T) \begin{cases} < \rho_1 & \text{if } T > T_0, \\ = \rho_1 & \text{if } T = T_0, \\ > \rho_1 & \text{if } T < T_0, \end{cases}
\]
where \( \rho_1 \) is the first eigenvalue of (3.4), which depends on the geometrical properties of the material such as the size of the container of the sample \( \Omega \). When \( \Omega = (0, L)^n \times D \subset \mathbb{R}^n \) is a rectangular domain with \( L > \) diameter of \( D, \rho_1 = \pi^2/L^2 \).
Hence, in general at the critical temperature $T_1$ a binary system does not undergo any phase transitions, but the phase transition does occur at $T = T_0$.

At $T_1$ and $T_0$ we know that

$$\lambda(T_1) = 0, \quad \lambda(T_0) = \rho_1.$$  

For a rectangular domain, $\rho_1 = \pi^2 / L^2$, therefore from (7.2) we see that $T_1$ is a limit of the critical temperature $T_0$ of phase transition as the size of $\Omega$ tends to infinite.

In fact, for a general domain, it is easy to see that the first eigenvalue $\rho_1$ of the Laplace operator is inversely proportional to the square of the maximum diameter of $\Omega$:

$$\rho_1 \sim \frac{1}{L^2},$$

where $L$ represents the diameter scaling of $\Omega$.

Thus the equation of critical parameters in the Cahn-Hilliard equation, by (7.2) and (7.3), is given by

$$\lambda(T, p) = \frac{C}{L^2},$$

where $C > 0$ is a constant depending on the geometry of $\Omega$. According to the Hildebrand theory (see Reichl [7]), the function $\lambda(T, p)$ can be expressed in an explicit formula. If regardless of the term $|\nabla u|^2$, the molar Gibbs free energy takes the following form

$$g = \mu_A(1 - u) + \mu_B u + RT(1 - u) \ln(1 - u) + RT u \ln u + au(1 - u),$$

where $\mu_A, \mu_B$ are the chemical potential of $A$ and $B$ respectively, $R$ the molar gas constant, $a > 0$ the measure of repel action between $A$ and $B$. Therefore, the coefficient $b_1$ in (2.7) with constant $p$ is

$$b_1 = \frac{\partial^2 g}{\partial u^2}|_{u=u_0} = \frac{1}{u_0(1-u_0)}RT - a \quad (a = a(p)),$$

where $u_0 = \bar{u}_B$ is the constant concentration of $B$. Hence

$$\lambda(T, p) = -\frac{I^2}{k}b_1 = \frac{2aI^2}{K} - \frac{I^2 R}{ku_0(1-u_0)}T.$$

Thus, equation (7.4) is expressed as

$$\frac{I^2 R}{ku_0(1-u_0)} T = \frac{2aI^2}{K} - \frac{C}{L^2}.$$  

Equation (7.6) gives the critical parameter curve of a binary system with constant pressure for temperature $T$ and diameter scaling $L$ of container $\Omega$. Because $T \geq 0$, from (7.5) we can deduce the following physical conclusion.

**Physical Conclusion 7.1.** Under constant pressure, for any binary system with given geometrical shape of the container $\Omega$, there is a value $L_0 > 0$ such that as the diameter scaling $L < L_0$, no phase separation takes place at all temperature $T \geq 0$, and as $L > L_0$ phase separation will occur at some critical temperature $T_0 > 0$ satisfying (7.6).  

We shall see later that it is a universal property that the dynamical properties of phase transitions depend on the geometrical shape and size of the container or sample $\Omega$.  


7.2. **Physical explanations of phase transition theorems.** We first briefly recall the classical thermodynamic theory for a binary system. Physically, phase separation processes taking place in an unstable state are called spinodal decompositions; see Cahn and Hilliard [1] and Onuki [6]. When consider the concentration \( u \) as homogeneous in \( \Omega \), then by (7.5) the dynamic equation of a binary system is an ordinary differential equation:

\[
\frac{du}{dt} = -\frac{dg}{du} = 2au - RT \ln \frac{u}{1-u} + \mu_A - \mu_B - a.
\]

Let \( u_0 (0 < u_0 < 1) \) be the steady state solution of (7.7). Then, by the Taylor expansion at \( u = u_0 \), omitting the \( n \)th order terms with \( n \geq 4 \), (7.7) can be rewritten as

\[
\frac{dv}{dt} = \lambda v + b_2 v^2 + b_3 v^3,
\]

where

\[
v = u - u_0, \quad \lambda = 2a - \frac{1}{u_0(1-u_0)}RT, \quad b_2 = \frac{1-2u_0}{2u_0^2(1-u_0)^2}RT, \quad b_3 = -\frac{1}{3} \frac{1-2u_0-2u_0^2+3u_0^3}{u_0(1-u_0)^4}RT.
\]

It is easy to see that

\[
b_2 \begin{cases} 
0 & \text{if } u_0 = \frac{1}{2}, \\
\neq 0 & \text{if } u_0 \neq \frac{1}{2}, \end{cases}
\]

\[
b_3 < 0 \quad \forall 0 < u_0 < 1.
\]

It is clear that the critical parameter curve \( \lambda = 0 \) in the \( T-u_0 \) plane is given by

\[
T_0 = 2au_0(1-u_0)/R,
\]

which is schematically illustrated in the classical phase diagram; see the dotted line in Figure 7.1. We obtain from (7.8) the following transition steady states:

\[
v^\pm = \frac{-1}{2b_3} \left( b_2 \pm \sqrt{b_2^2 - 4b_3\lambda} \right) \quad \text{for } b_2^2 - 4b_3\lambda > 0.
\]

By Theorem 3.2 we see that there is \( T^* = T^*(u_0) \) satisfying that \( b_2^2 - 4b_3\lambda = 0 \); namely,

\[
T^* = \frac{2au_0(1-u_0)}{R(1-\beta(u_0))}, \quad \beta(u_0) = \frac{3(1-2u_0)^2(1-u_0)}{16(1-u_0-2u_0^2+3u_0^3)},
\]

such that if \( T_0 < T < T^* \),

\[
v^+ \quad \text{is} \begin{cases} 
\text{locally stable (metastable)} & \text{for } 0 < u_0 < \frac{1}{2}, \\
\text{unstable} & \text{for } \frac{1}{2} < u_0 < 1,
\end{cases}
\]

\[
v^- \quad \text{is} \begin{cases} 
\text{locally stable (metastable)} & \text{for } \frac{1}{2} < u_0 < 1, \\
\text{unstable} & \text{for } 0 < u_0 < \frac{1}{2}.
\end{cases}
\]
Figure 7.1. Typical phase diagram from classical thermodynamic theory.

Figure 7.2. The state \( u_0 = \bar{u}_B \) is stable if \( T_c = T_0 < T \), and the state \( u_0 \) is unstable if \( T < T_0 \), where \( T_0 \) is as in (7.1).

Here

\[
T^*(u_0) = \frac{T_0(u_0)}{1 - \beta_0(u_0)} \geq T_0(u_0)
\]

is illustrated by the solid line in Figure 7.1. This shows that the region \( T_0(u_0) < T < T^*(u_0) \) is metastable, which is marked by the shadowed region in Figure 7.1. See, among others, Reichl [7], Novick-Cohen and Segal [5], and Langer [2] for the phase transition diagram from the classical thermodynamic theory.

In the following we shall discuss the spinodal decomposition in a unified fashion by applying the phase transition theorems presented in the previous sections.

As mentioned in the Introduction, phase separation processes of binary systems occur in two ways, one of which proceeds continuously depending on \( T \), and the other one does not. Obviously, the classical theory does not explain these phenomena. In fact, the first one can be described by the Type-I phase transition, and the second one can be explained by the Type-II and Type-III phase transitions.

We first consider the case where the container \( \Omega = \Pi_{i=1}^{n} (0, L_i) \) with \( L = L_1 = \cdots = L_m > L_j (j > m) \) is a rectangular domain. Thus, by Theorems 4.1 and 4.2 (or Theorem 6.1) there are only two phase transition types: Type-I and Type-II, with the type of transition depending on \( L \). We see that if

\[
L^2 < \begin{cases} 
\frac{9 \pi^2 \gamma_3}{2} & \text{for } m = 1, \\
\frac{27 \pi^2 \gamma_3}{26} & \text{for } m \geq 2,
\end{cases}
\]

then the transition is Type-I, i.e., the phase pattern formation gradually varies as the temperature decreases. In this case, no meta-stable states and no latent heat appear. The phase diagram is given by Figure 7.2 where the solid lines \( u_i^T \) (i = 1, 2) represent the transition solutions.
If $L$ satisfies that

$$L^2 > \begin{cases} 9 \frac{\pi^2 \gamma_3}{2} \\ \frac{27 \pi^2 \gamma_3}{26} \frac{\gamma_2^2}{2} \end{cases} \text{ for } m = 1, \quad \text{for } m \geq 2,$$

then the phase transition is Type-II. Namely, there is a leaping change in phase pattern formation at the critical temperature $T_c$. The phase diagram for Type-II transition is given by Figure 7.3.

In Figure 7.3, $T_0$ is the critical temperature as in (7.1), $T^*$ is defined by (7.9) and $u_0$ is the saddle-node bifurcation point of (7.8). The constant concentration $u = u_0$ is stable in $T < T_c$, is meta-stable in $T_0 < T < T^*$, and is unstable in $T < T_0$. The two bifurcated states $U_1^T$ and $U_2^T$ from $T^*$ are meta-stable in $T_0 < T < T^*$, and are stable in $T < T_0$. Here for $i = 1, 2$, $U_i^T = u_i^T + u_0$, and $u_i$ are the separated solutions of (3.1) with (3.5) from $T^*$.

There is a remarkable difference between Type-I and Type-II transitions. The Type-I phase transition occurs at $T = T_0$ and Type-II does in $T_0 < T < T^*$. Furthermore, latent heat is accompanied the Type-II phase transition. Actually, when a binary system undergoes a transition from $u_0$ to $U_i^T$ ($i = 1, 2$), there is a gap $|U_i^T - u_0|^2 = |u_i^T|^2 > \varepsilon > 0$ for any $T_0 < T < T^*$. By the first equation in (6.1) it yields a jump of entropy between $u_0$ and $U_i^T$:

$$\delta S_i = \int_{\Omega} S dx = -\frac{\alpha_2}{\alpha_1} \int_{\Omega} |u_i^T|^2 dx < 0,$$

where $S = S_i - \bar{S}_0$ represents the entropy density deviation. Hence the latent heat is given by

$$\delta H = T \delta S_i = -\frac{\alpha_2 T}{\alpha_1} \int_{\Omega} |u_i^T|^2 dx < 0,$$

which implies that the process from $u_0$ to $U_i^T$ is exothermic, and the process from $U_i^T$ to $u_0$ is endothermic.

Now, we consider the case where the container $\Omega$ is non rectangular. Thus, by Theorem 3.2 the transition is Type-III, and its phase diagram is given by Figure 7.4.

In Figure 7.4, $T_0$ and $T^*$ are the same as those in Figure 7.3. The state $u_0$ is stable in $T^* < T$, is metastable in $T_0 < T < T^*$, and unstable in $T < T_0$. The equilibrium state $U_1^T$ separated from $T^*$ is metastable in $T_0 < T < T^*$, and is stable in $T < T_0$. However, the equilibrium state $U_2^T$ separated from $T^*$ is unstable in $T_0 < T < T^*$, and is metastable in $T < T_0$. 

Figure 7.3. A Type-II phase transition.
Similar to the Type-II, the Type-III phase transition has also latent heat, which occurs in \( T_0 < T < T^* \). But the difference between Type-II and Type-III is that Type-II has \( 2m \) (\( m \geq 1 \)) stable equilibrium states separated from \( T = T^* \), but Type-III has just one. The \( 2m \) stable states of a Type-II transition are of some symmetry caused by \( \Omega \), and we shall investigate it later. A particular aspect of Type-III is that there is a state \( U_T^* \) bifurcated from \( (u, T) = (u_0, T_0) \), which is rarely observed in experiments.

### 7.3. Symmetry and periodic structure.

Physical experiments have shown that in pattern formation via phase separation, periodic or semi-periodic structure appears. From Theorems 5.1 and 5.2 we see that for the loop domains and bulk domains which can be considered as \( \mathbb{R}^n \) or \( \mathbb{R}^m \times D \) (\( D \subset \mathbb{R}^{n-m} \)) the steady state solutions of the Cahn-Hilliard equation are periodic, and for rectangular domains they are semi-periodic, and the periodicity is associated with the mirror image symmetry.

Let \( \Omega = (0, L)^m \times D \) (\( m \geq 1 \)). By Remark 4.1 Theorem 4.1 is valid for \( \Omega \). Actually, in this case the following space

\[
\tilde{H} = \left\{ u \in L^2(\Omega) \mid u = \sum_{|K|=1}^{\infty} y_k \cos \frac{k_1 \pi}{L} x_1 \cdots \cos \frac{k_m \pi}{L} x_m \right\} \subset H
\]

is invariant for the Cahn-Hilliard equation (3.1) and (3.5). All separated equilibrium states in Theorem 4.1 are in \( \tilde{H} \). From the physical viewpoint, all equilibrium states \( u(x) \) and their mirror image states \( u(L-x', x'') \) are the same to describe the pattern formation. Mathematically, under the mirror image transformation

\[
x \rightarrow (L-x', x''), \quad x' = (x_1, \ldots, x_m), \quad x'' = (x_{m+1}, \ldots, x_n),
\]

the Cahn-Hilliard equation (3.1) with (3.5) is invariant. Hence, the steady state solutions will appear in pairs. In particular, for Type-I phase transition, there is a remarkable mirror image symmetric. We address this problem as follows.

Let \( m = 1 \) in \( \Omega = (0, L)^m \times D \). By (4.2) there are two bifurcated stable equilibrium states, and their projections on the first eigenspace are

\[
u_1 = y \cos \frac{\pi x_1}{L}, \quad u_2 = -y \cos \frac{\pi x_1}{L}, \quad y = \sqrt{2(\lambda - \pi^2/L^2)}/\left(\frac{3}{2} \gamma_3 - \frac{L^2}{3\pi^2 \gamma_2^2}\right).
\]

It is clear that \( u_2(x_1) = u_1(L-x_1) \).
Let $m = 2$. By Theorem 4.2 the bifurcated attractor $\Sigma_3$ contains 8 equilibrium states, whose projections are given by

$$
\begin{align*}
  u_1^\pm &= \pm y_0 e_1, \\
  u_2^\pm &= \pm y_1 (e_1 + e_2), \\
  u_3^\pm &= \pm y_0 e_2, \\
  u_4^\pm &= \pm y_1 (-e_1 + e_2),
\end{align*}
$$

where $e_1 = (\cos \frac{\pi x}{L}, 0)$ and $e_2 = (0, \cos \frac{\pi x}{L})$ form an orthogonal basis in $\mathbb{R}^2$, and

$$
\begin{align*}
  y_0 &= \sqrt{2(\lambda - \pi^2/L^2)/\sigma_1}, \\
  y_1 &= \sqrt{2(\lambda - \pi^2/L^2)/\sqrt{\sigma_1 + \sigma_2}}
\end{align*}
$$

with $\sigma_1, \sigma_2$ as in (4.19).

These eight equilibrium states constitute an octagon in $\mathbb{R}^2$, as shown in Figure 7.5, and they are divided into two classes: $A_1 = \{u_1^\pm, u_3^\pm\}$ and $A_2 = \{u_2^\pm, u_4^\pm\}$ by the $\pi/2$-rotation group $G(\frac{\pi}{2})$. Namely, with the action of $G(\frac{\pi}{2})$, $A_i$ ($i = 1, 2$) are invariant:

$$
Bu \in A_i, \quad \forall u \in A_i \text{ and } B \in G(\frac{\pi}{2}),
$$

where $G(\frac{\pi}{2})$ consists of the orthogonal matrices

$$
\begin{align*}
  B_1^\pm &= \pm \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \\
  B_2^\pm &= \pm \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \\
  B_3^\pm &= \pm \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\
  B_4^\pm &= \pm \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.
\end{align*}
$$

The stability of the equilibrium states $u_k$ is associated with both classes $A_1$ and $A_2$, i.e., either the elements in $A_1$ are stable, or those in $A_2$ are stable; see Figure 4.2. By (4.33) we can derive the criterion as follows

- $u_{2k+1}^\pm \in A_1$ are stable $\iff \frac{22 L^2 \gamma_2^2}{9 \pi^2} > \gamma_3 > \frac{26 L^2 \gamma_2^2}{27 \pi^2}$ for $k = 0, 1$,
- $u_{2k}^\pm \in A_2$ are stable $\iff \gamma_3 > \frac{22 L^2 \gamma_2^2}{9 \pi^2}$ for $k = 1, 2$.

In Figure 7.5 we see that elements in $A_1$ and $A_2$ have a $\pi/4$ difference in their phase angle. However, in their pattern structure, $u_{2k+1}^\pm \in A_1$ and $u_{2k}^\pm \in A_2$ also have a $\pi/4$ deferece at the angle between the lines of $u_{2k+1}^\pm = 0$ and $u_{2k}^\pm = 0$. In fact, the lines that

$$
\begin{align*}
  u_1^+ &= -u_1^- = y_0 \cos \frac{\pi x_1}{L} = 0, \\
  u_3^+ &= -u_3^- = y_0 \cos \frac{\pi x_2}{L} = 0
\end{align*}
$$

**Figure 7.5.** The eight equilibrium states in the case where $m = 2$ given by Theorem 4.2.
are given by \( x_1 = L/2 \) and \( x_2 = L/2 \) respectively, as shown in Figure 7.6(a), and the lines

\[
\begin{align*}
\pm u_2 &= -\pm u_2 = y_1 \left( \cos \frac{\pi x_1}{L} + \cos \frac{\pi x_2}{L} \right) = 0, \quad \text{and} \\
\pm u_4 &= -\pm u_4 = y_1 \left( -\cos \frac{\pi x_1}{L} + \cos \frac{\pi x_2}{L} \right) = 0
\end{align*}
\]

are given by \( x_2 = L - x_1 \) and \( x_2 = x_1 \) respectively as shown in Figure 7.6(b).

**Figure 7.6.**

Let \( m = 3 \). Then the bifurcated attractor \( \Sigma_\lambda \) contains 26 equilibrium states which can be divided into three classes by the 3-dimensional \((\pi/2, \pi/2, \pi/2)\)-rotation group \( G(\pi/2, \pi/2, \pi/2) \) as follows

\[
\begin{align*}
A_1 &= \{ u_1^\pm = \pm y_0 e_1, u_2^\pm = \pm y_0 e_2, u_3^\pm = \pm y_0 e_3 \}, \\
A_2 &= \{ u_4^\pm = \pm y_1 (e_1 + e_2), u_5^\pm = \pm y_1 (e_1 + e_3), u_6^\pm = \pm y_1 (e_2 + e_3), \\
&\quad u_7^\pm = \pm y_1 (-e_1 + e_2), u_8^\pm = \pm y_1 (-e_1 + e_3), u_9^\pm = \pm y_1 (-e_2 + e_3) \}, \\
A_3 &= \{ u_{10}^\pm = \pm y_1 (e_1 + e_2 + e_3), u_{11}^\pm = \pm y_1 (-e_1 + e_2 + 3_3), \\
&\quad u_{12}^\pm = \pm y_1 (e_1 - e_2 + e_3), u_{13}^\pm = \pm y_1 (e_1 + e_2 - e_3) \}.
\end{align*}
\]

Only these elements in \( A_1 \) or in \( A_3 \) are stable, and they are determined by the following criterion

- Elements in \( A_1 \) is stable if \( \begin{align*}
\frac{22 L^2 \gamma_2^2}{9 \pi^2} > \gamma_3 > \frac{26 L^2 \gamma_2^2}{27 \pi^2},
\end{align*} \]

- Elements in \( A_3 \) is stable if \( \gamma_3 > \frac{22 L^2 \gamma_2^2}{9 \pi^2} \).

### 7.4. Critical exponents

From (4.2) and (4.34) we see that for Type-I phase transition of a binary system the critical exponent \( \beta = 1/2 \). In this case, it is a second order phase transition with the Ehrenfest classification scheme, and there is a gap in heat capacity at critical temperature \( T_0 \). To see this, by (4.2) and (4.34) we have

\[
\begin{align*}
u_T = \begin{cases} 0 & \text{if } T_0 < T, \\
(\alpha(\lambda(T) - \pi^2/L^2)^{1/2} e_1 + \alpha(\lambda - \pi^2/L^2)^{1/2}) & \text{if } T < T_0,
\end{cases}
\end{align*}
\]
and the free energy for (3.1) at \( u^T \) is
\[
F(u^T) = \int_{\Omega} \left[ \frac{1}{2} |\nabla u^T|^2 - \frac{\lambda}{2} |u^T|^2 + o(|u^T|^2) \right] \, dx
\]
\[
= \int_{\Omega} \frac{1}{2} [-\Delta u^T - \lambda u^T] u^T + \frac{1}{3} \gamma_2 (u^T)^3 + \frac{1}{4} \gamma_3 (u^T)^4 \, dx
\]
\[
= \begin{cases} 
0 & \text{if } T_0 < T, \\
-\frac{\alpha^2}{2} (\lambda - \pi^2/L^2)^2 \cdot \int_{\Omega} [e_1^2 + \frac{\alpha^2}{4} \gamma_3 e_1^4] \, dx + o(|\lambda - \pi^2/L^2|^2) & \text{if } T > T_0.
\end{cases}
\]
Thus, the heat capacity \( C \) at \( T = T_0 \) satisfies
\[
C^+ - C^- = -T_0 \frac{\partial^2 F(u^T)}{\partial T^2} \bigg|_{T_0^+} + T_0 \frac{\partial^2 F(u^T)}{\partial T^2} \bigg|_{T_0^-} = \alpha_1 T_0 \left( \frac{d\lambda}{dT} \right)^2 \bigg|_{T=T_0}.
\]
It is known that \( d\lambda/dT \neq 0 \); hence the heat capacity at \( T = T_0 \) has a finite jump.

From (3.14) we know that for the Type-III case, the critical exponent \( \beta = 1 \).
Thus, it is not hard to deduce that the continuous phase transition in Type-III is
of the 3rd order.

**Appendix A. Dynamic Transition Theory for Nonlinear Systems**

In this appendix we recall some basic elements of the dynamic transition theory
developed by the authors [3, 4], which are used to carry out the dynamic transition
analysis for the binary systems in this article.

**A.1. New classification scheme.** Let \( X \) and \( X_1 \) be two Banach spaces, and \( X_1 \subset X \) a compact and dense inclusion. In this chapter, we always consider the
following nonlinear evolution equations
\[
(A.1) \quad \frac{du}{dt} = L_\lambda u + G(u, \lambda),
\]
\( u(0) = \varphi, \)
where \( u : [0, \infty) \to X \) is unknown function, and \( \lambda \in \mathbb{R}^1 \) is the system parameter.

Assume that \( L_\lambda : X_1 \to X \) is a parameterized linear completely continuous field
depending continuously on \( \lambda \in \mathbb{R}^1 \), which satisfies
\[
(A.2) \quad L_\lambda = -A + B_\lambda \quad \text{a sectorial operator,}
\]
\[
(A.3) \quad G(u, \lambda) = o(\|u\|_{X_\alpha}), \quad \forall \lambda \in \mathbb{R}^1.
\]
Hereafter we always assume the conditions (A.2) and (A.3), which represent that
the system (A.1) has a dissipative structure.

**Definition A.1.** We say that the system (A.1) has a transition of equilibrium from
\( (u, \lambda) = (0, \lambda_0) \) on \( \lambda > \lambda_0 \) (or \( \lambda < \lambda_0 \)) if the following two conditions are satisfied:

(1) when \( \lambda < \lambda_0 \) (or \( \lambda > \lambda_0 \)), \( u = 0 \) is locally asymptotically stable for (A.1);
(2) when $\lambda > \lambda_0$ (or $\lambda < \lambda_0$), there exists a neighborhood $U \subset X$ of $u = 0$ independent of $\lambda$, such that for any $\varphi \in U \setminus \Gamma_\lambda$ the solution $u_\lambda(t, \varphi)$ of (A.1) satisfies
\[
\limsup_{t \to \infty} \|u_\lambda(t, \varphi)\|_X \geq \delta(\lambda) > 0,
\]
\[
\lim_{\lambda \to \lambda_0} \delta(\lambda) \geq 0,
\]
where $\Gamma_\lambda$ is the stable manifold of $u = 0$, with codim $\Gamma_\lambda \geq 1$ in $X$ for $\lambda > \lambda_0$ (or $\lambda < \lambda_0$).

Obviously, the attractor bifurcation of (A.1) is a type of transition. However, bifurcation and transition are two different, but related concepts. Definition A.1 defines the transition of (A.1) from a stable equilibrium point to other states (not necessary equilibrium state). In general, we can define transitions from one attractor to another as follows.

Let the eigenvalues (counting multiplicity) of $L_\lambda$ be given by
\[
\{\beta_j(\lambda) \in \mathbb{C} \mid j = 1, 2, \ldots\}
\]
Assume that
\[
\begin{align*}
\text{Re} \beta_i(\lambda) &< 0 & \text{if } \lambda < \lambda_0, \\
\text{Re} \beta_i(\lambda) &= 0 & \text{if } \lambda = \lambda_0, \\
\text{Re} \beta_i(\lambda) &> 0 & \text{if } \lambda > \lambda_0, \quad \forall 1 \leq i \leq m, \\
\text{Re} \beta_j(\lambda_0) &< 0 & \forall j \geq m + 1.
\end{align*}
\]
(A.4) (A.5)

The following theorem is a basic principle of transitions from equilibrium states, which provides sufficient conditions and a basic classification for transitions of nonlinear dissipative systems. This theorem is a direct consequence of the center manifold theorems and the stable manifold theorems; we omit the proof.

**Theorem A.1.** Let the conditions (A.4) and (A.5) hold true. Then, the system (A.1) must have a transition from $(u, \lambda) = (0, \lambda_0)$, and there is a neighborhood $U \subset X$ of $u = 0$ such that the transition is one of the following three types:

1. **Continuous Transition:** there exists an open and dense set $\tilde{U}_\lambda \subset U$ such that for any $\varphi \in \tilde{U}_\lambda$, the solution $u_\lambda(t, \varphi)$ of (A.1) satisfies
\[
\lim_{\lambda \to \lambda_0} \limsup_{t \to \infty} \|u_\lambda(t, \varphi)\|_X = 0.
\]
In particular, the attractor bifurcation of (A.1) at $(0, \lambda_0)$ is a continuous transition.

2. **Jump Transition:** for any $\lambda_0 < \lambda < \lambda_0 + \varepsilon$ with some $\varepsilon > 0$, there is an open and dense set $U_\lambda \subset U$ such that for any $\varphi \in U_\lambda$, \[
\limsup_{t \to \infty} \|u_\lambda(t, \varphi)\|_X \geq \delta > 0,
\]
where $\delta > 0$ is independent of $\lambda$. This type of transition is also called the discontinuous transition.

3. **Mixed Transition:** for any $\lambda_0 < \lambda < \lambda_0 + \varepsilon$ with some $\varepsilon > 0$, $U$ can be decomposed into two open sets $U_1^\lambda$ and $U_2^\lambda$ ($U_1^\lambda$ not necessarily connected):
\[
U = U_1^\lambda + U_2^\lambda, \quad U_1^\lambda \cap U_2^\lambda = \emptyset,
\]
such that
\[
\lim_{\lambda \to \lambda_0} \limsup_{t \to \infty} \|u(t, \varphi)\|_X = 0 \quad \forall \varphi \in U_1^\lambda,
\]
\[
\limsup_{t \to \infty} \|u(t, \varphi)\|_X \geq \delta > 0 \quad \forall \varphi \in U_2^\lambda.
\]

With this theorem in our disposal, we are in position to give a new dynamic classification scheme for dynamic phase transitions.

**Definition A.1** (Dynamic Classification of Phase Transition). The phase transitions for (A.1) at \(\lambda = \lambda_0\) is classified using their dynamic properties: continuous, jump, and mixed as given in Theorem A.1, which are called Type-I, Type-II and Type-III respectively.

An important aspect of the transition theory is to determine which of the three types of transitions given by Theorem A.1 occurs in a specific problem. By reduction to the center manifold of (A.1), we know that the type of transitions for (A.1) at \((0, \lambda_0)\) is completely dictated by its reduction equation near \(\lambda = \lambda_0\), which can be expressed as:
\[
(A.6) \quad \frac{dx}{dt} = J_\lambda x + PG(x + \Phi(x, \lambda), \lambda) \quad \text{for } x \in \mathbb{R}^m,
\]
where \(J_\lambda\) is the \(m \times m\) order Jordan matrix corresponding to the eigenvalues given by (A.4), \(\Phi(x, \lambda)\) is the center manifold function of (A.1) near \(\lambda_0\), \(P : X \to E_\lambda\) is the canonical projection, and
\[
E_\lambda = \cup_{1 \leq i \leq m} \cup_{k \in \mathbb{N}} \{u \in X_1\mid (L_\lambda - \beta_i(\lambda))^k u = 0\}
\]
is the eigenspace of \(L_\lambda\).

By the spectral theorem, (A.6) can be expressed into the following explicit form
\[
(A.7) \quad \frac{dx}{dt} = J_\lambda x + g(x, \lambda),
\]
where
\[
g(x, \lambda) = (g_1(x, \lambda), \cdots, g_m(x, \lambda)),
\]
\[
g_j(x, \lambda) = \langle G\left(\sum_{i=1}^m x_i e_i + \Phi(x, \lambda), \lambda\right), e_j^*\rangle \quad \forall 1 \leq j \leq m.
\]
Here \(e_j\) and \(e_j^*\) (\(1 \leq j \leq m\)) are the eigenvectors of \(L_\lambda\) and \(L_\lambda^*\) respectively corresponding to the eigenvalues \(\beta_j(\lambda)\) as in (A.4).

In particular, if \(G(u, \lambda)\) has the Taylor expansion
\[
(A.9) \quad G(u, \lambda) = G_k(u, \lambda) + o(\|u\|_{X_\lambda}^k),
\]
for some \(k \geq 2\), where \(G_k(u, \lambda)\) is a \(k\)-multilinear operator, then (A.7) can be rewritten as
\[
(A.10) \quad \frac{dx}{dt} = J_\lambda x + g_k(x, \lambda) + o(|x|^k),
\]
where
\[
g_k(x, \lambda) = (g_{k1}(x, \lambda), \cdots, g_{km}(x, \lambda)),
\]
\[
g_{kj}(x, \lambda) = \langle G_k(\sum_{i=1}^n x_i e_i, \lambda), e_j^*\rangle \quad \forall 1 \leq j \leq m.
\]
When $x = 0$ is an isolated singular point of $g_k(x, \lambda)$, in general the transition of (A.1) is determined by the first-order approximate bifurcation equation of (A.10) as follows:

(A.11) \[ \frac{dx}{dt} = J_{\lambda}x + g_k(x, \lambda). \]

The following theorem is useful to distinguish the transition types of (A.1) at $(u, \lambda) = (0, \lambda_0)$.

**Theorem A.2.** Let the conditions (A.4) and (A.5) hold true, and $U \subset \mathbb{R}^m$ be a neighborhood of $x = 0$. Then we have the following assertions:

1. If the transition of (A.1) at $(0, \lambda_0)$ is continuous, then there is an open and dense set $\tilde{U} \subset U$ such that for any $x_0 \in \tilde{U}$ the solution $x(t, x_0)$ of (A.7) at $\lambda = \lambda_0$ with $x(0, x_0) = x_0$ satisfies

   \[ \lim_{t \to \infty} x(t, x_0) = 0. \]

2. If there exists an open and dense set $\tilde{U} \subset U$ such that for any $x_0 \in \tilde{U}$ the solution $x(t, x_0)$ of (A.7) at $\lambda = \lambda_0$ satisfies

   \[ \limsup_{t \to \infty} |x(t, x_0)| \neq 0, \]

   then the transition is a jump transition.

3. If the transition is mixed, then there exists an open set $\tilde{U} \subset U$ such that for any $x_0 \in \tilde{U}$ the solution $x(t, x_0)$ of (A.7) at $\lambda = \lambda_0$ with $x(0, x_0) = x_0$ satisfies

   \[ \lim_{t \to \infty} x(t, x_0) = 0. \]

4. If the vector field in (A.7) at $\lambda = \lambda_0$ satisfies

   \[ < J_{\lambda_0}x + g(x, \lambda_0), x > \quad \forall x \in U, \ x \neq 0, \]

   then the transition of (A.1) at $(0, \lambda_0)$ is an $S^{m-1}$-attractor bifurcation, and the transition is continuous.

5. If the vector field $g(x, \lambda_0)$ given by (A.8) satisfies

   \[ < g(x, \lambda_0), x > \quad \forall x \in U, \ x \neq 0, \]

   then the transition is jump.

In general, the conditions in Assertions (1)-(3) of Theorem A.2 are not sufficient. They, however, do give sufficient conditions when (A.1) has a variational structure. To see this, let (A.1) be a gradient-type equation. Under the conditions (A.4) and (A.5), in a neighborhood $U \subset X$ of $u = 0$, the center manifold $M^c$ in $U$ at $\lambda = \lambda_0$ consists three subsets

\[ M^c = W^s + W^u + D, \]

where $W^s$ is the stable set, $W^u$ is the unstable set, and $D$ is the hyperbolic set of (A.7). Then we have the following theorem.

**Theorem A.3.** Let (A.1) be a gradient-type equation, and the conditions (A.4) and (A.5) hold true. If $u = 0$ is an isolated singular point of (A.1) at $\lambda = \lambda_0$, then we have the following assertions:
(1) The transition of (A.1) at \((u, \lambda) = (0, \lambda_0)\) is continuous if and only if \(u = 0\) is locally asymptotically stable at \(\lambda = \lambda_0\), i.e., the center manifold is stable: \(M^c = W^s\). Moreover, (A.1) bifurcates from \((0, \lambda_0)\) to minimal attractors consisting of singular points of (A.1).

(2) If the stable set \(W^s\) of (A.1) has no interior points in \(M^c\), i.e., \(M^c = \bar{W}^u + \bar{D}\), then the transition is jump.

A.2. Transitions from simple eigenvalues. We consider the transition of (A.1) from a simple critical eigenvalue. Let the eigenvalues \(\beta_j(\lambda)\) of \(L_\lambda\) satisfy (A.4) and (A.5) with \(m = 1\). Then the first eigenvalue \(\beta_1(\lambda)\) must be a real eigenvalue. Let \(e_1(\lambda)\) and \(e^*_1(\lambda)\) be the eigenvectors of \(L_\lambda\) and \(L^*_\lambda\) respectively corresponding to \(\beta_1(\lambda)\) with

\[
L_{\lambda_0} e_1 = 0, \quad L^*_{\lambda_0} e^*_1 = 0, \quad <e_1, e^*_1> = 1.
\]

Let \(\Phi(x, \lambda)\) be the center manifold function of (A.1) near \(\lambda = \lambda_0\). We assume that

\[
(A.12) \quad <G(xe_1 + \Phi(x, \lambda_0), \lambda_0), e^*_1> = \alpha x^k + o(|x|^k),
\]

where \(k \geq 2\) an integer and \(\alpha \neq 0\) a real number.

---

**Figure A.1.** Topological structure of the jump transition of (A.1) when \(k=\text{odd}\) and \(\alpha > 0\): (a) \(\lambda < \lambda_0\); (b) \(\lambda \geq \lambda_0\). Here the horizontal line represents the center manifold.

**Figure A.2.** Topological structure of the continuous transition of (A.1) when \(k=\text{odd}\) and \(\alpha < 0\): (a) \(\lambda \leq \lambda_0\); (b) \(\lambda > \lambda_0\).
Figure A.3. Topological structure of the mixing transition of (A.1) when \( k = \text{even} \) and \( \alpha \neq 0 \): (a) \( \lambda < \lambda_0 \); (b) \( \lambda = \lambda_0 \); (c) \( \lambda > \lambda_0 \). Here \( U_1^\lambda \) is the unstable domain, and \( U_2^\lambda \) the stable domain.

Theorem A.4. Assume (A.4) and (A.5) with \( m = 1 \), and (A.12). If \( k = \text{odd} \) and \( \alpha \neq 0 \) in (A.12) then the following assertions hold true:

1. If \( \alpha > 0 \), then (A.1) has a jump transition from \((0, \lambda_0)\), and bifurcates on \( \lambda < \lambda_0 \) to exactly two saddle points \( v_1^\lambda \) and \( v_2^\lambda \) with the Morse index one, as shown in Figure A.1.
2. If \( \alpha < 0 \), then (A.1) has a continuous transition from \((0, \lambda_0)\), which is an attractor bifurcation as shown in Figure A.2.
3. The bifurcated singular points \( v_1^\lambda \) and \( v_2^\lambda \) in the above cases can be expressed in the following form
   \[
   v_{1,2}^\lambda = \pm |\beta_1(\lambda)/\alpha|^{1/(k-1)} e_1(\lambda) + o(|\beta_1|^{1/(k-1)}).
   \]

Theorem A.5. Assume (A.4) and (A.5) with \( m = 1 \), and (A.12). If \( k = \text{even} \) and \( \alpha \neq 0 \), then we have the following assertions:

1. (A.1) has a mixed transition from \((0, \lambda_0)\). More precisely, there exists a neighborhood \( U \subset X \) of \( u = 0 \) such that \( U \) is separated into two disjoint open sets \( U_1^\lambda \) and \( U_2^\lambda \) by the stable manifold \( \Gamma_\lambda \) of \( u = 0 \) satisfying the following properties:
   (a) \( U = U_1^\lambda + U_2^\lambda + \Gamma_\lambda \).
   (b) the transition in \( U_1^\lambda \) is jump, and
   (c) the transition in \( U_2^\lambda \) is continuous. The local transition structure is as shown in Figure A.3.
2. (A.1) bifurcates in \( U_2^\lambda \) to a unique singular point \( v^\lambda \) on \( \lambda > \lambda_0 \), which is an attractor such that for any \( \varphi \in U_2^\lambda \),
   \[
   \lim_{t \to \infty} \|u(t, \varphi) - v^\lambda\|_X = 0,
   \]
   where \( u(t, \varphi) \) is the solution of (A.1).
3. (A.1) bifurcates on \( \lambda < \lambda_0 \) to a unique saddle point \( v^\lambda \) with the Morse index one.
4. The bifurcated singular point \( v^\lambda \) can be expressed as
   \[
   v^\lambda = -(\beta_1(\lambda)/\alpha)^{1/(k-1)} e_1 + o(|\beta_1|^{1/(k-1)}).
   \]

A.3. Singular Separation. In this section, we study an important problem associated with the discontinuous transition of (A.1), which we call the singular separation.
Definition A.2. (1) An invariant set \( \Sigma \) of (A.1) is called a singular element if \( \Sigma \) is either a singular point or a periodic orbit.

(2) Let \( \Sigma_1 \subset X \) be a singular element of (A.1) and \( U \subset X \) a neighborhood of \( \Sigma_1 \). We say that (A.1) has a singular separation of \( \Sigma \) at \( \lambda = \lambda_1 \) if

(a) (A.1) has no singular elements in \( U \) as \( \lambda < \lambda_1 \) (or \( \lambda > \lambda_1 \)), and

(b) there are branches of singular elements \( \Sigma_\lambda \), which are separated from \( \Sigma_1 \) for \( \lambda > \lambda_1 \) (or \( \lambda < \lambda_1 \)), i.e.,

\[
\lim_{\lambda \to \lambda_1} \max_{x \in \Sigma_\lambda} \text{dist}(x, \Sigma_1) = 0.
\]

A special case of singular separation is the saddle-node bifurcation defined as follows.

Definition A.3. Let \( u_1 \in X \) be a singular point of (A.1) at \( \lambda = \lambda_1 \) with \( u_1 \neq 0 \). We say that (A.1) has a saddle-node bifurcation at \( (u_1, \lambda_1) \) if

(1) the index of \( L_{\lambda_1} + G \) at \( (u_1, \lambda_1) \) is zero, i.e., \( \text{ind}(-(L_{\lambda_1} + G), u_1) = 0 \),

(2) there are two branches \( \Gamma_1(\lambda) \) and \( \Gamma_2(\lambda) \) of singular points of (A.1), which are separated from \( u_1 \) for \( \lambda > \lambda_1 \) (or \( \lambda < \lambda_1 \)), i.e., for any \( u_\lambda \in \Gamma_i(\lambda) \) \( (i = 1, 2) \) we have

\[
u_\lambda \to u_1 \text{ in } X \text{ as } \lambda \to \lambda_1,
\]

and

(3) the indices of \( u_\lambda \in \Gamma_i(\lambda) \) are as follows

\[
\text{ind}(-(L_{\lambda} + G), u_\lambda) = \begin{cases} 1 & \text{if } u_\lambda \in \Gamma_2(\lambda), \\ -1 & \text{if } u_\lambda \in \Gamma_1(\lambda). \end{cases}
\]

Intuitively, the saddle-node bifurcation is schematically shown as in Figure A.4, where the singular points in \( \Gamma_1(\lambda) \) are saddle points and in \( \Gamma_2(\lambda) \) are nodes, and the singular separation of periodic orbits is as shown Figure A.5.

Figure A.4. Saddle-node bifurcation.

For the singular separation we can give a general principle as follows, which provides a basis for singular separation theory.

Theorem A.6. Let the conditions (A.4) and (A.5) hold true. Then we have the following assertions.

(1) If (A.1) bifurcates from \( (u, \lambda) = (0, \lambda_0) \) to a branch \( \Sigma_\lambda \) of singular elements on \( \lambda < \lambda_0 \) which is bounded in \( X \times (\infty, \lambda_0) \) then (A.1) has a singular separation of singular elements at some \( (\Sigma_0, \lambda_1) \subset X \times (\infty, \lambda_0) \).
If the bifurcated branch $\Sigma_\lambda$ consists of singular points which has index $-1$, i.e.,

$$\text{ind}(-(L_\lambda + G), u_\lambda) = -1 \quad \forall u_\lambda \in E_\lambda, \quad \lambda < \lambda_0,$$

then the singular separation is a saddle-node bifurcation from some $(u_1, \lambda_1) \in X \times (-\infty, \lambda_0)$.

We consider the equation (A.1) defined on the Hilbert spaces $X = H, X_1 = H_1$. Let $L_\lambda = -A + \lambda B$. For $L_\lambda$ and $G(\cdot, \lambda) : H_1 \to H$, we assume that $A : H_1 \to H$ is symmetric, and

\begin{align*}
(A.13) & \quad < Au, u >_H \geq c\|u\|_{H_1}^2, \\
(A.14) & \quad < Bu, u >_H \geq c\|u\|_H^2, \\
(A.15) & \quad < Gu, u >_H \leq -c_1\|u\|_{H_1}^p + c_2\|u\|_H^2,
\end{align*}

where $p > 2, c, c_1, c_2 > 0$ are constants.

**Theorem A.7.** Assume the conditions (A.3), (A.4) and (A.13)-(A.15), then (A.1) has a transition at $(u, \lambda) = (0, \lambda_0)$, and the following assertions hold true:

1. If $u = 0$ is an even-order nondegenerate singular point of $L_\lambda + G$ at $\lambda = \lambda_0$, then (A.1) has a singular separation of singular points at some $(u_1, \lambda_1) \in H \times (-\infty, \lambda_0)$.

2. If $m = 1$ and $G$ satisfies (A.12) with $\alpha > 0$ if $k$=odd and $\alpha \neq 0$ if $k$=even, then (A.1) has a saddle-node bifurcation at some singular point $(u_1, \lambda_1)$ with $\lambda_1 < \lambda_0$.

**A.4. Transition and Singular Separation of Perturbed Systems.** We consider the following perturbed equation of (A.1):

$$\frac{du}{dt} = (L_\lambda + S^\varepsilon_\lambda)u + G(u, \lambda) + T^\varepsilon(u, \lambda),$$

where $L_\lambda$ and $G_\lambda$ are as in (A.1), $S^\varepsilon_\lambda : X_\sigma \to X$ is a linear perturbed operator, $T^\varepsilon_\lambda : X_\sigma \to X$ a $C^1$ nonlinear perturbed operator, and $X_\sigma$ the fractional order space, $0 \leq \sigma < 1$. Also assume that $G_\lambda, T^\varepsilon_\lambda$ are $C^3$ on $u$, and

\begin{align*}
\|S^\varepsilon_\lambda\| & < \varepsilon, \\
\|T^\varepsilon_\lambda\| & < \varepsilon, \\
T^\varepsilon(u, \lambda) & = o(\|u\|_{X_\sigma}).
\end{align*}

Let (A.4) and (A.5) with $m = 1$ hold true, $G(u, \lambda) = G_2(u, \lambda) + o(\|u\|_{X_1}^2)$, where $G_2(\cdot, \lambda)$ is a bilinear operator, and

$$b = < G_2(e, \lambda_0), e^* > \neq 0,$$
where \( e \in X \) and \( e^* \in X^* \) are the eigenvectors of \( L_\lambda \) and \( L^*_\lambda \) corresponding to \( \beta_1(\lambda) \) at \( \lambda = \lambda_0 \) respectively.

We now consider the transition associated with the saddle-node bifurcation of the perturbed system \((A.16)\). Let \( h(x, \lambda) \) be the center manifold function of \((A.1)\) near \( \lambda = \lambda_0 \). Assume that

\[
(A.19) \quad < G(xe + h(x, \lambda_0), \lambda_0), e^* > = b_1 x^3 + o(|x|^3),
\]

where \( b_1 \neq 0 \), and \( e \) and \( e^* \) are as in \((A.18)\).

Then we have the following theorems.

**Theorem A.8.** Let the conditions \((A.4)\) and \((A.5)\) with \( m = 1 \), and \((A.19)\) hold true, and \( b_1 < 0 \). Then there is an \( \varepsilon > 0 \) such that if \( S^*_\lambda \) and \( T^*_\lambda \) satisfy \((A.17)\), then the transition of \((A.16)\) is either continuous or mixed. If the transition is continuous, then Assertions (2) and (3) of Theorem A.4 are valid for \((A.16)\). If the transition is mixed, then the following assertions hold true:

1. \((A.16)\) has a saddle-node bifurcation at some point \((u_1, \lambda_1) \in X \times (-\infty, \lambda_0^*)\), and there are exactly two branches

\[
\Gamma^i_\lambda = \{(u^i, \lambda) \mid \lambda_1 < \lambda < \lambda^*_0 + \delta\} \quad i = 1, 2,
\]

separated from \((u_1, \lambda_1)\) as shown in Figure A.4, which satisfy that

\[
\|u^i_2\|_X \neq 0 \quad \forall (u^i_1, \lambda) \in \Gamma^i_\lambda, \quad \lambda_1 < \lambda < \lambda^*_0 + \delta,
\]

\[
\lim_{\lambda \to \lambda^*_0} \|u^i_1\|_X = 0 \quad \forall (u^i_1, \lambda) \in \Gamma^i_\lambda.
\]

2. There is a neighborhood \( U \subset X \) of \( u = 0 \), such that for each \( \lambda \) with \( \lambda_1 < \lambda < \lambda^*_0 + \delta \) and \( \lambda \neq \lambda^*_0 \), \( U \) contains only two nontrivial singular points \( u^1_\lambda \) and \( u^2_\lambda \) of \((A.16)\).

3. For each \( \lambda_1 < \lambda < \lambda^*_0 + \delta \), \( U \) can be decomposed into two open sets \( U = U^1_\lambda + U^2_\lambda \) with \( U^1_\lambda \cap U^2_\lambda = \emptyset \), such that

- if \( \lambda_1 < \lambda < \lambda^*_0 \),

  \[0 \in U^1_\lambda, \quad u^1_\lambda \in U^1_\lambda, \quad u^2_\lambda \in \partial U^1_\lambda \cap \partial U^2_\lambda, \]

  with \( u = 0 \) and \( u^2_\lambda \) being attractors which attract \( U^1_\lambda \) and \( U^2_\lambda \) respectively, and

- if \( \lambda^*_0 < \lambda < \lambda^*_0 + \delta \),

  \[u^1_\lambda \in U^1_\lambda, \quad u^2_\lambda \in U^2_\lambda, \quad 0 \in \partial U^1_\lambda \cap \partial U^2_\lambda, \]

  with \( u^1_\lambda \) and \( u^2_\lambda \) being attractors which attract \( U^1_\lambda \) and \( U^2_\lambda \) respectively.

4. Near \((u, \lambda) = (0, \lambda^*_0)\), \( u^1_\lambda \) and \( u^2_\lambda \) can be expressed as

\[
\begin{align*}
\lambda \to \lambda^*_0 \quad & u^1_\lambda = \alpha_1(\lambda, \varepsilon) e + o(\alpha_1), \\
\lambda \to \lambda^*_0 \quad & u^2_\lambda = \alpha_2(\lambda, \varepsilon) e + o(\alpha_2), \\
\lim_{\lambda \to \lambda^*_0} \alpha_1(\lambda, \varepsilon) &= 0, \\
\alpha_2(\lambda^*_0, \varepsilon) &\neq 0,
\end{align*}
\]

where \( e \) is as in \((A.19)\).

**Theorem A.9.** Assume the conditions \((A.4)\) and \((A.5)\) with \( m = 1 \), and \((A.19)\) with \( b_1 > 0 \). Then, there is an \( \varepsilon > 0 \) such that when \( S^*_\lambda \) and \( T^*_\lambda \) satisfy \((A.17)\), the transition of \((A.16)\) is either jump or mixed. If it is jump transition, then
Assertions (1) and (3) of Theorem A.4 are valid for (A.16). If it is mixed, then the following assertions hold true:

1. (A.16) has a saddle-node bifurcation at some point $(u_1, \lambda_1) \in X \times (\lambda_0, +\infty)$, and there are exactly two branches
   \[ \Gamma^\lambda_i = \{(u^\lambda_i, \lambda) | \lambda^0_\varepsilon - \delta < \lambda < \lambda_1 \} \quad (i = 1, 2), \]
   separated from $(u_1, \lambda_1)$, which satisfy
   \[ \lim_{\lambda \to \lambda^0_\varepsilon} \|u^\lambda_2\|_X = 0 \quad \forall (u^\lambda_2, \lambda) \in \Gamma_2^\ast, \quad \lambda^0_\varepsilon - \varepsilon < \lambda < \lambda_1, \]
   \[ \lim_{\lambda \to \lambda^0_\varepsilon} \|u^\lambda_1\|_X = 0 \quad \forall (u^\lambda_1, \lambda) \in \Gamma_1^\lambda. \]

2. There is a neighborhood $U \subset X$ of $u = 0$, such that for each $\lambda$ with $\lambda^0_\varepsilon - \delta < \lambda < \lambda_1$, $U$ contains only two nontrivial singular points $u^\lambda_1$ and $u^\lambda_2$ of (A.16).

3. For every $\lambda^0_\varepsilon - \delta < \lambda < \lambda_1$, $U$ can be decomposed into three open sets
   \[ U = U^\lambda_0 + U^\lambda_1 + U^\lambda_2 \text{ with } U_i \cap U_j = \emptyset \; (i \neq j) \]
   such that
   \begin{enumerate}
   \item if $\lambda^0_\varepsilon - \delta < \lambda < \lambda^0_\varepsilon$, then
     \[ u = 0 \in U^\lambda_0, \quad u^\lambda_1 \in \partial U^\lambda_0 \cap \partial U^\lambda_1 \quad (i = 1, 2), \]
     with $u = 0$ being an attractor which attracts $U^\lambda_0$ and $U^\lambda_1 (i = 1, 2)$ two saddle points with the Morse index one, and
   \item if $\lambda^0_\varepsilon < \lambda < \lambda_1$, then
     \[ u^\lambda_1 \in U^\lambda_1, \quad u^\lambda_2 \in \partial U^\lambda_2 \cap \partial U^\lambda_1, \quad 0 \in \partial U^\lambda_1 \cap \partial U^\lambda_0, \]
     with $u^\lambda_1$ being an attractor which attracts $U^\lambda_1$ and $u^\lambda_2$ and $u = 0$ being saddle points with the Morse index one.
   \end{enumerate}

4. Near $(0, \lambda^0_\varepsilon)$, $u^\lambda_1$ and $u^\lambda_2$ can be expressed by (A.20).

**Appendix B. Ginzburg-Landau Models**

In this subsection, we introduce the time-dependent Ginzburg-Landau model for equilibrium phase transitions.

We start with thermodynamic potentials and the Ginzburg-Landau free energy. As we know, four thermodynamic potentials—internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy—are useful in the chemical thermodynamics of reactions and non-cyclic processes.

Consider a thermal system, its order parameter $u$ changes in $\Omega \subset \mathbb{R}^n \; (1 \leq n \leq 3)$. In this situation, the free energy of this system is of the form

\[ \mathcal{H}(u, \lambda) = \mathcal{H}_0 + \int_{\Omega} \left[ \frac{1}{2} \sum_{i=1}^m \mu_i |\nabla u_i|^2 + g(u, \nabla u, \lambda) \right] dx \]

where $N \geq 3$ is an integer, $u = (u_1, \ldots, u_m)$, $\mu_i = \mu_i(\lambda) > 0$, and $g(u, \nabla u, \lambda)$ is a $C^r \; (r \geq 2)$ function of $(u, \nabla u)$ with the Taylor expansion

\[ g(u, \nabla u, \lambda) = \sum \alpha_{ijk} u_i D_j u_k + \sum_{|I|=1}^N \alpha_I u^I + o(|u|^N) - f X, \]

where $I = (i_1, \ldots, i_m)$, $i_k \geq 0$ are integer, $|I| = \sum_{k=1}^m i_k$, the coefficients $\alpha_{ijk}$ and $\alpha_I$ continuously depend on $\lambda$, which are determined by the concrete physical problem, $u^I = u_1^{i_1} \cdots u_m^{i_m}$ and $f X$ the generalized work.
A thermal system is controlled by some parameter $\lambda$. When $\lambda$ is far from the critical point $\lambda_0$ the system lies on a stable equilibrium state $\Sigma_1$, and when $\lambda$ reaches or exceeds $\lambda_0$ the state $\Sigma_1$ becomes unstable, and meanwhile the system will undergo a transition from $\Sigma_1$ to another stable state $\Sigma_2$. The basic principle is that there often exists fluctuations in the system leading to a deviation from the equilibrium states, and the phase transition process is a dynamical behavior, which should be described by a time-dependent equation.

To derive a general time-dependent model, first we recall that the classical Le Châtelier principle amounts to saying that for a stable equilibrium state of a system $\Sigma$, when the system deviates from $\Sigma$ by a small perturbation or fluctuation, there will be a resuming force to restore this system to return to the stable state $\Sigma$.

Second, we know that a stable equilibrium state of a thermal system must be the minimal value point of the thermodynamic potential.

By the mathematical characterization of gradient systems and the Le Châtelier principle, for a system with thermodynamic potential $H(u, \lambda)$, the governing equations are essentially determined by the functional $H(u, \lambda)$. When the order parameters $(u_1, \cdots, u_m)$ are nonconserved variables, i.e., the integers

$$\int_{\Omega} u_i(x,t)dx = a_i(t) \neq \text{constant},$$

then the time-dependent equations are given by

$$\frac{\partial u_i}{\partial t} = -\beta_i \frac{\delta}{\delta u_i} H(u, \lambda) + \Phi_i(u, \nabla u, \lambda),$$

(B.3)

$$\frac{\partial u}{\partial n}|_{\partial \Omega} = 0 \quad \text{(or } u|_{\partial \Omega} = 0),$$

$$u(x,0) = \varphi(x),$$

for any $1 \leq i \leq m$, where $\delta/\delta u_i$ are the variational derivative, $\beta_i > 0$ and $\Phi_i$ satisfy

$$\int_{\Omega} \sum_i \Phi_i \frac{\delta}{\delta u_i} H(u, \lambda)dx = 0.$$  

(B.4)

The condition [B.4] is required by the Le Châtelier principle. In the concrete problem, the terms $\Phi_i$ can be determined by physical laws and [B.4].

When the order parameters are the number density and the system has no material exchange with the external, then $u_j$ ($1 \leq j \leq m$) are conserved, i.e.,

$$\int_{\Omega} u_j(x,t)dx = \text{constant}. $$

(B.5)

This conservation law requires a continuous equation

$$\frac{\partial u_j}{\partial t} = -\nabla \cdot J_j(u, \lambda),$$

(B.6)

where $J_j(u, \lambda)$ is the flux of component $u_j$. In addition, $J_j$ satisfy

$$J_j = -k_j \nabla (\mu_j - \sum_{i \neq j} \mu_i),$$

(B.7)

where $\mu_i$ is the chemical potential of component $u_i$,

$$\mu_j - \sum_{i \neq j} \mu_i = \frac{\delta}{\delta u_j} H(u, \lambda) - \phi_j(u, \nabla u, \lambda),$$

(B.8)
and φ_j(u, λ) is a function depending on the other components u_i (i ≠ j). When m = 1, i.e., the system consists of two components A and B, this term φ_j = 0. Thus, from (B.6)-(B.8) we obtain the dynamical equations as follows

\[ \frac{\partial u_j}{\partial t} = \beta_j \Delta \left[ \frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) - \phi_j(u, \nabla u, \lambda) \right], \]

(B.9)

\[ \frac{\partial u}{\partial n}|_{\partial \Omega} = 0, \quad \frac{\partial \Delta u}{\partial n}|_{\partial \Omega} = 0, \]

\[ u(x, 0) = \varphi(x), \]

for 1 ≤ j ≤ m, where β_j > 0 are constants, φ_j satisfy

\[ \int_\Omega \sum_j \Delta \phi_j \cdot \frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) dx = 0. \]

(B.10)

If the order parameters (u_1, ..., u_k) are coupled to the conserved variables (u_{k+1}, ..., u_m), then the dynamical equations are

\[ \frac{\partial u_i}{\partial t} = -\beta_i \frac{\delta}{\delta u_i} \mathcal{H}(u, \lambda) + \Phi_i(u, \nabla u, \lambda), \]

\[ \frac{\partial u_j}{\partial t} = \beta_j \Delta \left[ \frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) - \phi_j(u, \nabla u, \lambda) \right], \]

(B.11)

\[ \frac{\partial u_i}{\partial n}|_{\partial \Omega} = 0 \quad (\text{or } u_i|_{\partial \Omega} = 0), \quad \frac{\partial u_j}{\partial n}|_{\partial \Omega} = 0, \quad \frac{\partial \Delta u_j}{\partial n}|_{\partial \Omega} = 0, \]

\[ u(x, 0) = \varphi(x). \]

for 1 ≤ i ≤ k and k + 1 ≤ j ≤ m.

The model (B.11) gives a general form of the governing equations to thermodynamic phase transitions. Hence, the dynamics of equilibrium phase transition in statistic physics is based on the new Ginzburg-Landau formulation (B.11).

Physically, the initial value condition u(0) = \varphi in (B.11) stands for the fluctuation of system or perturbation from the external. Hence, \varphi is generally small. However, we can not exclude the possibility of a bigger noise \varphi.

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