DYNAMICAL THEORY OF THERMODYNAMICAL PHASE TRANSITIONS

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ABSTRACT. The objective of this paper is establish the basic dynamical theory for thermodynamic phase transitions. The main components of the theory include 1) dynamical equations of thermodynamical systems, 2) general principle of dynamical transitions, and 3) three basic theorems of thermodynamic phase transitions.

CONTENTS

1. INTRODUCTION

Phase transition is a universal phenomena in most, if not all, natural systems, and refers to the transformation of the system from one state to another, as the control parameter crosses certain critical threshold. In physics, a state often refers to a "stable" solution of the mathematical model.

Most problems in the natural sciences are described by either dissipative or conservative systems. A systematic dynamic transition theory for dissipative systems has been developed by the authors through a sequence of paper starting around 2004, and the theory and its wide range of applications are synthesized in the authors' book [4]. The theory demonstrates a general principles that phase transitions of all dissipative systems can be classified into three categories: continuous, catastrophic, and random.

The goals of phase transition theories are

(1) to determine the definition and types of phase transitions,
(2) to derive the critical parameters,
(3) to obtain the critical exponents, and
(4) to understand the mechanism and properties of phase transitions, such as supercooled and superheated states and the Andrews critical points, etc.

There are two routes for studying phase transitions: one is Landau's approach using thermodynamic potentials, and the other is a microscopic approach using statistical theory. These routes are complementing to each other. Our dynamical transition theory follows the Landau's route, but is not a mean field theory approach. It is based, however, on the thermodynamical potential.

The objective of this paper is to provide a fundamental theory of thermodynamic phase transitions based on the dynamic transition theory and its various applications. The main ingredients of the paper are as follows.

FIRST, for a thermodynamic system, there are three different levels of physical quantities: control parameters λ, the order parameters (state functions) $u = (u_1, \cdots, u_N)$, and the thermodynamic potential F. These are well-defined physical quantities, fully describing the system. The potential is a functional of the order parameters, and is used to represent the thermodynamic state of the system.

In a recent paper [5], we postulated a potential-descending principle (PDP) for statistical physics, which gives rise to a dynamic equation for thermodynamical systems; see (4) and (5) in Section 2 below. Then for a given basic equilibrium state $\bar{u}$, the deviation from the basic state $\bar{u}$ satisfies a dissipative dynamical system given by (6), which dictates the phase transition dynamical behavior of the system.

SECOND, with the potential functional F, the basic state $\bar{u}$, and the dynamical equation (6) at our disposal, the dynamical transition theory can then be applied, and we obtain in this paper three theorems,

providing a full theoretical characterization of thermodynamic phase transitions.

THIRD, the first theorem, Theorem 1, states that as soon as the linear instability occurs, the system always undergoes a dynamical transition, to one of the three types: continuous, catastrophic and random. This theorem offers the detailed information for the *phase diagram* and the *critical threshold* λ_c in the control parameter $\lambda = (\lambda_1, \cdots, \lambda_N) \in \mathbb{R}^N$. They are precisely determined by the following equation:

$$(1) \qquad \beta_1(\lambda_1, \cdots, \lambda_N) = 0.$$

Here β_1 is the first eigenvalue of the linear operator L_λ given by

$$(2) \qquad L_\lambda w \equiv -\left(\frac{\partial^2 F(\bar{u}; \lambda)}{\partial u_i, \partial u_j}\right) w = \beta_1(\lambda)w,$$

where F is the potential functional.

FOURTH, the second theorem, Theorem 2, provides the corresponding relationship between the Ehrenfest classification and the dynamical classification. The Ehrenfest classification identifies experimental quantities to determine the transition types, while the dynamical classification provides a full theoretical characterization of the transition.

This theorem establishes a natural bridge between theory and experiments. With the corresponding relationship given in this theorem, we obtain a precise and easy theoretical approach to determine the transition order, the critical exponents, and the transition diagram, which are encoded in the following transition equation:

$$(3) \qquad \frac{du_\lambda}{dt} = \beta_1(\lambda)u_\lambda + a(\lambda)u_\lambda^2 + b(\lambda)u_\lambda^3 + \text{h.o.t.}$$

We remark here that the detailed information on critical exponents is entirely encoded in the potential functionals, and again, our approach is not a mean-field theory.

Also, the theorem shows that there are only first, second and third-order thermodynamic transitions. The third-order transition can hardly be determined by thermodynamic parameters experimentally. The dynamical transition theory, however, offers an easy and clear approach to identify the third-order transition.

FIFTH, the last theorem, Theorem 3, states that both catastrophic and random transitions lead to saddle-node bifurcations, and both latent heat, superheated and supercooled states always accompany the saddle-node bifurcation associated with the first order transitions.

Theorem 2 with the transition equation 3 provides the needed information on the dynamic phase diagrams; this is important for understanding the dynamical behavior of transition states.

We further emphasize that the three theorems lead to three important diagrams: the phase diagram, the transition diagram and the dynamical diagram. These diagrams appear only to be derivable by the dynamical transition theory presented in this paper. In addition, our theory achieves the fourth goal of phase transition theories as stated in the beginning of this Introduction, which is hardly achievable by other existing theories.

The paper is organized as follows. Section 2 establishes the dynamical equation for thermodynamic equations, and Section 3 recalls the general principle for dynamical transitions. Section 4 describes the Ehrenfest classification. Section 5 states and proves the the three basic theorems for thermodynamic phase transitions.

2. Dynamic Equations of Statistical Physics

For a given thermodynamic system, the order parameters (state functions) $u = (u_1, \cdots, u_N)$, the control parameters λ, and the thermodynamic potential F are well-defined quantities, fully describing the system. The potential is a functional of the order parameters, and is used to represent the thermodynamic state of the system. There are four commonly used thermodynamic potentials: the internal energy, the Helmholtz free energy, the Gibbs free energy, and the enthalpy.

In a recent paper [5], we postulated the following potential-descending principle (PDP) for statistical physics:

Principle 1 (Potential-Descending Principle [5]). *For each thermodynamic system, there are order parameters $u = (u_1, \cdots, u_N)$, control parameters λ, and the thermodynamic potential functional $F(u; \lambda)$. For a non-equilibrium state $u(t; u_0)$ of the system with initial state $u(0, u_0) = u_0$, we have the following properties:*

1) *the potential $F(u(t; u_0); \lambda)$ is decreasing:*

$$\frac{d}{dt} F(u(t; u_0); \lambda) < 0 \qquad \forall t > 0;$$

2) *the order parameters $u(t; u_0)$ have a limit*

$$\lim_{t \to \infty} u(t; u_0) = \bar{u};$$

3) *there is an open and dense set $\mathcal{O}$ of initial data in the space of state functions, such that for any $u_0 \in \mathcal{O}$, the corresponding $\bar{u}$ is a minimum of F, which is called an equilibrium of the thermodynamic system:*

$$\delta F(\bar{u}; \lambda) = 0.$$

We have shown that PDP is a more fundamental principle than the first and second laws, and provides the first principle for describing irreversibility, leads all three distributions: the Maxwell-Boltzmann distribution, the Fermi-Dirac distribution and the Bose-Einstein distribution in statistical physics. Consequently, the potential-descending principle is the first principle of statistical physics.

Also importantly, based on PDP, the dynamic equation of a thermodynamic system in a non-equilibrium state takes the form

$$(4) \quad \frac{\mathrm{d}u}{\mathrm{d}t} = -A\delta F(u, \lambda) \qquad \text{for isolated systems,}$$

$$(5) \quad \begin{cases} \dfrac{\mathrm{d}u}{\mathrm{d}t} = -A\delta F(u, \lambda) + B(u, \lambda), \\ \displaystyle\int A\delta F(u, \lambda) \cdot B(u, \lambda) = 0 \end{cases} \qquad \text{for coupled systems,}$$

where δ is the derivative operator, B represents coupling operators, and A is a symmetric and positive definite matrix of coefficients. We refer interested readers to [5] for details.

Phase transition is a universal phenomena in most, if not all, natural systems. In fact, the central problem in statistical physics is on phase transitions. A phase transition refers to the transition of the system from one state to another, as the control parameter crosses certain critical threshold. In physics, a state often refers to a "stable" solution of the mathematical model, and in statistical physics, a state refers to an equilibrium state. Consequently, in thermodynamic phase transitions, we can consider a basic equilibrium state $\bar{u}$, and study the dynamic transitions of this state $\bar{u}$. If we write

$$u = \bar{u} + u',$$

then the dynamic law (4) or (5) leads to an equation for the deviation order parameter u'. After suppressing the primes, we arrive at the following dynamic equation for the deviation order parameter u:

$$(6) \qquad \frac{du}{dt} = L_\lambda u + G(u, \lambda).$$

Again u is the order parameter, λ is the control parameter of the system, L_λ is a linear operator, and $G(u, \lambda)$ is the nonlinear operator.

For all thermodynamic phase transitions, (6) is a dissipative dynamical system, and $u = 0$ represents the basic equilibrium state $\bar{u}$.

3. Principle of Phase Transition Dynamics

A comprehensive and unified dynamic transition theory for dissipative systems have been developed recently by the authors with applications to a wide range of problems in nonlinear sciences; see refer [4] and the references therein. In connection to applications, the dynamic transition theory provides a systematic approach for classifying and determining the detailed information of the transition.

A thorough examination of the dynamic transition theory and its applications enable us to postulate the following general principle of phase transition dynamics.

Principle 2 (Principle of Phase Transition Dynamics [4]). *Phase transitions of all dissipative systems can be classified into three categories:*
   (1) *continuous transition if* $\lim_{\lambda \to \lambda_0} u_\lambda = \bar{u}$*;*
   (2) *catastrophic transition if* $\lim_{\lambda \to \lambda_0} u_\lambda \neq \bar{u}$*; and*
   (3) *random transition if both* $\lim_{\lambda \to \lambda_0} u_\lambda = \bar{u}$ *and* $\lim_{\lambda \to \lambda_0} u_\lambda \neq \bar{u}$
       occur.
Here $\bar{u}$ is the basic state, and u_λ are the transition states (physically, transition states correspond to local attractors).

A few remarks are now in order.

First, the validity of the above principle is ensured by the dynamic transition theorem [4, Theorem 2.1.3]. In addition, all applications of the dynamic transition theory so far are in agreement with this principle. In fact, such principle is also valid for transition associated with pattern formations.

Second, this is a universal principle, applicable to phase transitions of all dissipative systems in Nature. It cannot be derived from classical bifurcation theory.

Third, it offers a guiding principle for studying phase transitions of natural systems.

4. Ehrenfest Classification

Paul Ehrenfest was the first who gave a definition and a classification of thermodynamic phase transitions in terms of singularities, at the critical threshold, of such thermodynamic observable parameters as heat capacity, magnetic susceptibility, etc., which are observable; see [1]. Phase transitions are then classified based on the behavior of the thermodynamic potentials, and were labeled by the n-th order derivative of the potential that is discontinuous at the transition.

More precisely, consider a thermodynamic system with potential functional $F(u, \lambda)$.

Definition 1 (Ehrenfest Classification Scheme). *Let λ_0 be a critical point, and u_λ are equilibrium states near $\lambda = \lambda_0$. A phase transition of the system at $\lambda = \lambda_0$ is of the n-th order if*

$$\frac{\partial^k F(u_\lambda, \lambda)}{\partial \lambda^k}$$

are continuous with respect to λ at $\lambda = \lambda_0$ for any $0 \leq k \leq n-1$, and

$$\frac{\partial^n F(u_\lambda, \lambda)}{\partial \lambda^n}$$

is discontinuous at $\lambda = \lambda_0$.

Under this scheme, phase transitions are labeled by the lowest-order derivative of the potential that is discontinuous at the transition. First-order phase transitions exhibit a discontinuity in the first derivative of the potential with a thermodynamic variable. In principle, there could be third, fourth, and higher-order phase transitions. In fact, we shall prove that there are only first, second and third order transitions.

Now we recall the physical meaning of the derivatives of $F(u, \lambda)$ on λ in statistical physics. For a thermodynamic system, the first order derivatives include

- the entropy: $S = -\partial F / \partial T$, and
- the (observable) phase volume: $V = \partial F / \partial p$ or density.

The second order derivatives are

- the heat capacity in the constant pressure: $C_p = -T\frac{\partial^2 F}{\partial T^2}$,
- the compression coefficient $\kappa = -\frac{1}{V}\frac{\partial^2 F}{\partial p^2}$,
- the thermal expansion coefficient $\alpha = \frac{1}{V}\frac{\partial^2 F}{\partial T \partial p}$, and
- magnetic susceptibility: $\partial^2 F / \partial M \partial H$, where M is the magnetization of the material and H is magnetic field strength.

Thus, for the first-order phase transition, the discontinuity of $\partial F / \partial p$ at critical point $\lambda_0 = (T_0, p_0)$ implies the discontinuity of phase volume:

$$(7) \qquad \Delta V = V^2 - V^1 = \frac{\partial F^+}{\partial p} - \frac{\partial F^-}{\partial p},$$

and the discontinuity of $\partial F / \partial T$ implies that there is a gap between both phase entropies:

$$(8) \qquad \Delta S = S^2 - S^1 = -\frac{\partial F^+}{\partial T} + \frac{\partial F^-}{\partial T}.$$

Physically, ΔS is a non-measurable quantity, hence, we always use latent heat $\Delta Q = T\Delta S$ to determine the first order phase transition, and ΔQ stand for the absorbing heat for transition from phase $\bar{u}$ to

phase u_λ. In the two phase coexistence situation, ΔQ and ΔV are related by the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta Q}{T\Delta V}.$$

For second-order phase transitions, the variance of heat capacity (or specific heat), compression coefficient, the thermal expansion coefficient and magnetic susceptibility at the critical value, are important measurable physical quantities.

5. Three Basic Theorems of Thermodynamic Phase Transitions

5.1. **First Theorem.** We have proved a dynamical transition theorem [4, Theorem 2.1.3]. It shows that for (6), as soon as the linear instability occurs, the system always undergoes a dynamical transition. As a direct application of this general transition theorem, we arrive immediately at the following first theorem of thermodynamic phase transitions.

Theorem 1. *Consider a thermodynamic system* (6). *Let* $\beta_1(\lambda), \beta_2(\lambda), \cdots \in \mathbb{R}$ *be eigenvalues* [1] *of the linear operator* L_λ. *If*

(9)
$$\beta_i(\lambda) \begin{cases} < 0 & \text{if } \lambda < \lambda_0, \\ = 0 & \text{if } \lambda = \lambda_0, \quad 1 \le i \le m, \\ > 0 & \text{if } \lambda > \lambda_0 \end{cases}$$
$$\beta_j(\lambda_0) < 0 \qquad\qquad\qquad m+1 \le j,$$

then the system (6) *always undergoes a dynamic transition to one of the three types of dynamic transitions: continuous, catastrophic and random, as* λ *crosses the critical threshold* λ_0.

In the physics literature, (9) is called the principle of exchange of stabilities. It is important to note that this theorem provides the detailed information for the phase diagram in the control parameter space:

(10) $$\beta_1(\lambda) = 0.$$

For example, in the Cahn-Hilliard equation describing the binary system [3, 4], the control parameters are $\lambda = (T, u_0, L)$, where T is the temperature, u_0 is molar density, and L is the length scale of the system. The phase diagram is then obtained by solving (10). For fixed L, the phase diagram is given by Figure 1:

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[1]The linear operator $L_\lambda = -\left(\frac{\partial^2 F(\bar{u};\lambda)}{\partial u_i, \partial u_j}\right)$ is always self-adjoint, and all eigenvalues of L_λ are real.
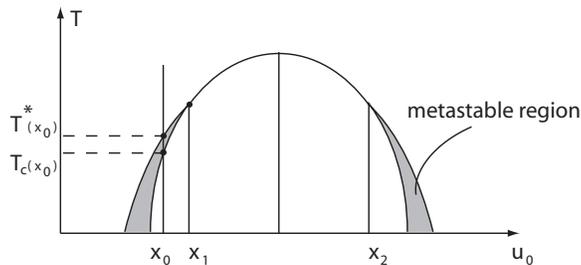
FIGURE 1. Tu_0-phase diagram for a fixed length scale L; see [3, Fig. 4] and [4, Fig. 3.23].

For a fixed molar density u_0, the TL phase diagram was derived and given by Figure 2:
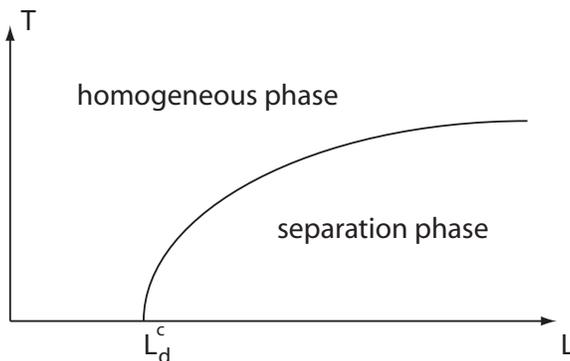

FIGURE 2. TL phase diagram for fixed u_0; see [3, Fig. 6] and [4, Fig. 3.25].

5.2. **Second Theorem.** We have at our disposal the Ehrenfest classification and our dynamic classification based on Principle 1; the latter is applicable for both equilibrium and non-equilibrium phase transitions.

The second theorem of thermodynamic phase transitions shows that there are only first, second and third order transitions, and provides the relationship between the Ehrenfest and dynamic classifications.

Theorem 2. *For the phase transition of a thermodynamic system, there exist only first-order, second-order and third-order phase transitions. Moreover the following relations between the Ehrenfest classification and the dynamical classification hold true:*

second-order $\Longleftrightarrow$ *continuous*

first-order $\longleftarrow$ *catastrophic*

either first or third-order $\longleftarrow$ *random*

first-order $\longrightarrow$ *either catastrophic or random*

third-order $\longrightarrow$ *random with asymmetric fluctuations.*

Proof. By Theorem 1, we only have to examine the three types of dynamical transitions. Before we proceed, we observe that the first eigenvalue $\beta_1(\lambda)$ satisfies

$$(11) \qquad \beta_1(\lambda) = \alpha(\lambda)(\lambda - \lambda_c), \qquad \alpha(\lambda_c) \neq 0.$$

First, it is clear from the dynamical transition theory [4] that a catastrophic dynamic transition must be of first-order.

Second, consider the case where the dynamical transition at λ_c be continuous. By the dynamical transition theory [4], we have shown that the transition states near λ_c are given by

$$(12) \qquad u_\lambda = \begin{cases} A(\lambda - \lambda_c)^{1/m} + o((\lambda - \lambda_c)^{1/m}) & \text{for } \lambda > \lambda_c, \\ 0 & \text{for } \lambda < \lambda_c, \end{cases}$$

where $m \geq 2$ and $A \neq 0$. In fact, physically, $2 \leq m \leq 3$; see among others [6].

Also, in view of the derivation of the equation (6) from (4) and (5), since u is the deviation order function, we let

$$(13) \qquad \widetilde{F}(u, \lambda) = F(u + \bar{u}, \lambda) - F(\bar{u}, \lambda),$$

where F is the potential functional of the thermodynamic system. Then near λ_c, $\widetilde{F}$ takes the following form:

$$(14) \qquad \widetilde{F}(u_\lambda, \lambda) = \frac{1}{2}\beta_1(\lambda)u_\lambda^2 + \text{h.o.t.}$$

Therefore, in view of (12), we have

$$(15) \qquad \widetilde{F}(u_\lambda, \lambda) = \begin{cases} A(\lambda - \lambda_c)^{1+\frac{2}{m}} + \text{h.o.t} & \text{for } \lambda > \lambda_c, \\ 0 & \text{for } \lambda < \lambda_c. \end{cases}$$

Hence a continuous dynamical transition leads to a second-order transition in the Ehrenfest sense.

Third, we consider the case where the dynamical transition at λ_c is random. If the fluctuation is symmetric, then the transition must be of first-order. Otherwise, it can either be a first-order transition or the transition with the following transition states [4]:

$$(16) \qquad u_\lambda = \begin{cases} A(\lambda - \lambda_c) + \text{h.o.t} & \text{for } \lambda > \lambda_c, \\ 0 & \text{for } \lambda < \lambda_c, \end{cases}$$

The potential functional is then written as

$$
(17) \qquad \widetilde{F}(u_\lambda, \lambda) = \begin{cases} A(\lambda - \lambda_c)^3 + \text{h.o.t} & \text{for } \lambda > \lambda_c, \\ 0 & \text{for } \lambda < \lambda_c. \end{cases}
$$

This gives rise to a third-order transition.

Theorem 1 shows that there are only three types of dynamical transitions, which lead to only first, second and third-order transitions. Therefore, there are no higher than third-order transitions in thermodynamics and the relations between the Ehrenfest classification and the dynamical classification given in the theorem hold true as demonstrated above. The proof is complete. $\qquad\square$

A few remarks are now in order.

First, the Ehrenfest transition types are determined by experiments. The dynamical transition theory provides a systematic theory to easily determine the types and transition states. The above theorem establishes a natural bridge between theory and experiments.

Second, the third-order transition can hardly be determined by thermodynamic parameters experimentally. The dynamical transition theory, however, offers a simple approach to identify the third-order transition.

Third, the above theorem leads to transition diagrams, providing an important characteristic of phase transitions. In fact, the dynamical transition theory includes a systematic technical approach in determining the transition types and states, based on the central manifold reduction idea; see [4] for details. In particular, for a thermodynamic phase transition, the approach gives rise to the following transition equation, which encodes the all the needed information on transition types and states:

$$
(18) \qquad \frac{du_\lambda}{dt} = \beta_1(\lambda)u_\lambda + a(\lambda)u_\lambda^2 + b(\lambda)u_\lambda^3 + \text{h.o.t.}
$$

Then the transition types are determined by the coefficients $a(\lambda)$ and $b(\lambda)$ as follows:

(1) If $a(\lambda_c) \neq 0$, then the transition is random;
(2) If $a(\lambda_c) = 0$, then

$$
\begin{aligned}
b(\lambda_c) > 0 \qquad &\Longrightarrow \qquad \text{catastrophic transition} \\
b(\lambda_c) < 0 \qquad &\Longrightarrow \qquad \text{continuous transition.}
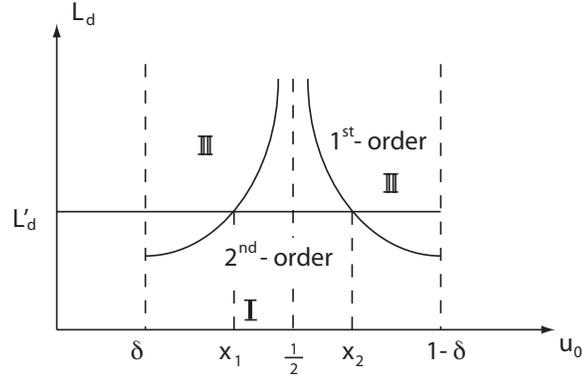\end{aligned}
$$

FIGURE 3. Lu_0-transition diagram: region II is the first order transition region with latent heat, and region I is the second order transition region.

If $a(\lambda) \equiv 0$, the equation

$$b(\lambda) = 0$$

gives the transition diagram. For example, in the Cahn-Hilliard equation describing the binary system, the following is a typical such transition diagram [4, Fig. 3.24].

5.3. **Third Theorem.** For a thermodynamic system, there is no bifurcation point for given pressure control parameter with the temperature higher than the critical threshold. Also, given pressure, at very high temperature, the only stable state is the basic equilibrium state $\bar{u}$. Consequently, based on the topological degree theory [2], both catastrophic and random transitions will give rise to saddle-node bifurcations at a temperature T_c^0 higher than the critical threshold T_c^1. We refer readers to Figure 4 for a better understanding of superheated and supercooled states.
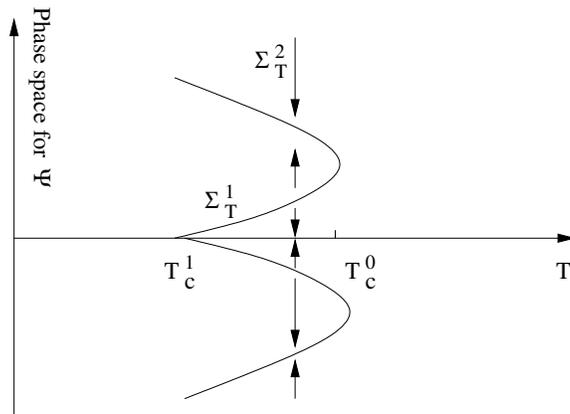
FIGURE 4. Catastrophic transition: the basic state $\psi = 0$ in $T_c^1 < T < T_c^0$ is supercooled, the transition states Σ_T^2 are superheated; see [4, Fig. 3.31 on page 202].

Also, if the transition is of the first-order, the jump of the thermodynamic potential ΔF at $T_c^1 \leq T \leq T_1^0$ corresponds to the latent heat, and the two metastable states are the superheated and supercooled states of the system.

Namely, we obtain the following third theorem for thermodynamic phase transitions.

Theorem 3. *For a thermodynamic system* (6), *the following statements hold true:*

(1) *both catastrophic and random transitions lead to saddle-node bifurcations; and*

(2) *both latent heat, superheated and supercooled states always accompany the saddle-node bifurcations associated with the first order transitions.*

This theorem, together with (18), offers precise information on the dynamic phase diagrams. For example,Figure 4, Figure 5 and Figure 6 are such dynamical phase diagrams, derived from the dynamical transition theory.

REFERENCES

[1] P. EHRENFEST, *Phasenumwandlungen im ueblichen und erweiterten Sinn, classifiziert nach den entsprechenden Singularitaeten des thermodynamischen Potentiales*, NV Noord-Hollandsche Uitgevers Maatschappij, 1933.

[2] T. MA AND S. WANG, *Bifurcation theory and applications*, vol. 53 of World Scientific Series on Nonlinear Science. Series A: Monographs and Treatises, World Scientific Publishing Co. Pte. Ltd., Hackensack, NJ, 2005.
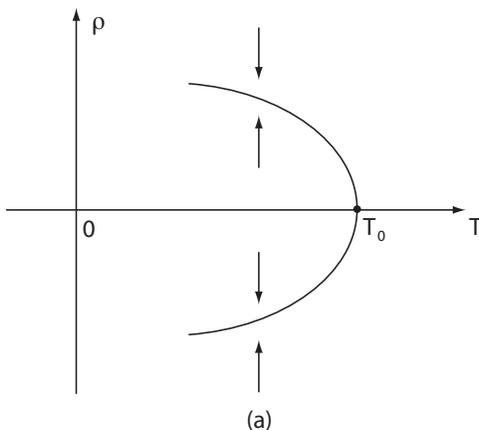
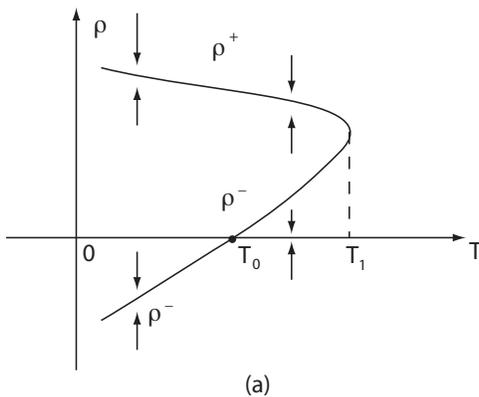FIGURE 5. Dynamic phase diagram for continuous transition; see [4, Fig. 3.3 on p.138].

FIGURE 6. Dynamical phase diagram of random transition for $a_2 > 0$; see [4, Fig. 3.4 on p. 139].

[3] ——, *Phase separation of binary systems*, Physica A: Statistical Physics and its Applications, 388:23 (2009), pp. 4811–4817.

[4] ——, *Phase Transition Dynamics*, Springer-Verlag, 2013.

[5] ——, *Dynamic law of physical motion and potential-descending principle*, Indiana University Institute of Scientific Computing and Applied Mathematics Preprint #1701, (2017).

[6] H. E. STANLEY, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press, New York and Oxford, 1971.

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