Physica A 487 (2017) 74–92

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Generalized parametric model for phase transitions in the presence of an intermediate metastable state and its application

Alexandr A. Barsuk [a], Florentin Paladi [a,b,*]

[a] Department of Theoretical Physics, Moldova State University, A. Mateevici str. 60, Chisinau MD-2009, Republic of Moldova
[b] University of Missouri, 1601 S. Providence Road, Columbia, MO 65211, USA

HIGHLIGHTS

- Generalized parametric model is developed to study first-order phase transitions.
- Bifurcation and stability analysis for the equilibrium states is performed.
- Thermodynamic systems are described by the Landau-type kinetic potential.
- Mean transition time for the lysozyme protein is analyzed.
- Detailed bifurcation analysis of the cubic equation solutions is presented.

ARTICLE INFO

Article history:
Received 2 March 2017
Received in revised form 7 May 2017
Available online 27 June 2017

Keywords:
Phase transitions
Landau-type potential
Metastable state
Bifurcation and stability analysis
Nucleation
Lysozyme

ABSTRACT

The previously proposed model for the kinetics of first-order phase transitions (Barsuk et al., 2013) is generalized for r order and m control parameters. Bifurcation and stability analyses of the equilibrium states in thermodynamic systems described by the Landau-type kinetic potential with two order parameters is performed both in the absence of an external field, and in the presence of constant and periodic external fields. Kinetics of thermodynamic systems described by such potential in a small neighborhood of the equilibrium states is also studied. Mean transition time for lysozyme protein in dependence of control parameters is obtained based on the developed model. A detailed bifurcation analysis of the cubic equation solutions is given in Appendix.

1. Introduction

Nowadays, the theory of supercooled liquids and glasses, proteins and molten polymers, and other complex nanomaterials is under intensive developing by means of computer simulations as well as by parametric macroscopic modeling based on the Landau-type kinetic potential [1–6]. The control parameters presented in the kinetic potential are associated to the diffusion and viscosity as intrinsic characteristics of the material, as well as to the system heterogeneity and the influence of constant or periodic external field. Anomalous generation and extinction phenomenon of crystal nuclei at very low temperatures in non-equilibrium supercooled liquids containing hydroxyl group, namely *o*-benzylphenol, salol, and 2,2′-dihydroxybenzophenone, observed during the progress of crystal nucleation and growth below the glass transition temperature reflect the impact of real structural fluctuation on the irreversible structural relaxation in supercooled liquids

* Corresponding author. Fax: +373 22244248.
E-mail address: fpaladi@usm.md (F. Paladi).

http://dx.doi.org/10.1016/j.physa.2017.05.067
0378-4371/

and glasses [7–9]. In this context it was noticed that crystallization would have a heterogeneous origin. Meanwhile, it is difficult to explain these results based only on the heterogeneity which contribute to the generation of crystal nuclei, so one could not explain why the nucleation occurs only at such low temperatures and why the formed crystal nuclei disappear, as well as the what is the impact of external field on phase transitions in the presence of an intermediate state. It is necessary, therefore, to take into account the metastable intermediate state in the supercooled liquids. Furthermore, a mathematical model for phase transitions was discussed in the framework of bifurcation theory [1]. Recently, techniques in the bifurcation analysis for continuous mechanical systems, concentrating on polynomial equations and implicitly given functions, were presented in [10]. Time evolution of the single order parameter x associated to the fluid phase was described by a nonlinear first-order ordinary differential equation (ODE), and a similar approach was presented for critical aspects of some bifurcations in the context of thermodynamic geometry [11].

In the present work, we examine the generalized parametric model based on Landau-type kinetic potential based on bifurcation and stability analysis for the first order phase transition in the presence of an intermediate metastable state. We analyzed the impact of an external field on the first order phase transition. The values of control parameters are estimated based on experimental data for the mean transition time between stable liquid and crystalline phases in the region of coexistence of two liquid states for lysozyme protein [12]. In general, the obtained results are related to the theory of structural relaxation in complex systems, and some aspects of kinetics of phase transitions in the presence of an intermediate metastable state, including generation of crystal nuclei as clusters of new phase [13,14].

2. Theoretical framework of the model with r order and m control parameters

The kinetic processes corresponds to the first-order phase transitions in systems which can be described r order parameters and m control parameters, namely $x_1, x_2, \ldots, x_r$ and $\alpha_1, \alpha_2, \ldots, \alpha_m$, respectively. The system of nonlinear first-order ODEs in the form

$$\begin{aligned} \frac{dx_1}{dt} &= f_1\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right), \\ \frac{dx_2}{dt} &= f_2\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right), \\ &\ldots \\ \frac{dx_r}{dt} &= f_r\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right) \end{aligned} \tag{1}$$

represents the mathematical model of phase transitions discussed in the article, where t is time. For the initial conditions, at $t = t_0$, given by

$$x_1\left(t_0\right) = x_{10}, x_2\left(t_0\right) = x_{20}, \ldots, x_r\left(t_0\right) = x_{r0}, \tag{2}$$

and assuming that the functions $f_i\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right)$, where $i = 1, 2, \ldots, r$, meet the conditions of the existence and uniqueness of solution for the system (1), i.e. the functions $f_i\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right)$ and their first order partial derivatives $\partial f_i/\partial x_k$ are continuous in the region of the variables under consideration $x_1, x_2, \ldots, x_r$ [15].

A trajectory defined in the r-dimensional space with the following parametric representation, as a solution for Cauchy problem (1) and (2), $x_1 = x_1\left(t\right), x_2 = x_2\left(t\right), \ldots, x_r = x_r\left(t\right)$, passes through values $x_{10}, x_{20}, \ldots, x_{r0}$. The steady states are determined by the equation $dx_i/dt = 0$, where $i = 1, 2, \ldots, r$, or

$$f_1\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right) = 0, \ldots, f_r\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right) = 0. \tag{3}$$

This system of nonlinear equations serves to find the equilibrium values of the order parameters. Thus, Eqs. (3) will be analyzed as an implicit dependence of these parameters on control parameters $\alpha_1, \alpha_2, \ldots, \alpha_m$, i.e.

$$x_1^s = x_1^s\left(\alpha_1, \alpha_2, \ldots, \alpha_m\right), \ldots, x_r^s = x_r^s\left(\alpha_1, \alpha_2, \ldots, \alpha_m\right), \tag{4}$$

so we can further apply the fundamental theorem of mathematical analysis for implicit functions [16,17]. There is a unique solution in a small neighborhood of the fixed values $\alpha_{10}, \alpha_{20}, \ldots, \alpha_{m0}$ and $x_{10}^s = x_1^s\left(\alpha_{10}, \alpha_{20}, \ldots, \alpha_{m0}\right), \ldots, x_{r0}^s = x_r^s\left(\alpha_{10}, \alpha_{20}, \ldots, \alpha_{m0}\right)$ for which $f_1\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right) = 0, \ldots, f_r\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right) = 0$, and the non-zero determinant of the Jacobi matrix (Jacobian)

$$J\left(x_{10}^s, x_{20}^s, \ldots, x_{r0}^s; \alpha_{10}, \alpha_{20}, \ldots, \alpha_{m0}\right) \neq 0, \tag{5}$$

where $J\left(x_1, x_2, \ldots, x_r; \alpha_1, \alpha_2, \ldots, \alpha_m\right) = \det \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_r} \\ \cdots & \cdots & \cdots \\ \frac{\partial f_r}{\partial x_1} & \cdots & \frac{\partial f_r}{\partial x_r} \end{bmatrix}$.