THE KINETICS OF PHASE TRANSITIONS: I. THE ROLE OF HETEROGENEITY

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A kinetic model involving one order parameter was developed to study the impact of heterogeneity on the nucleation. The role of asymmetry on phase transitions in the presence of an intermediate metastable state is described in comparison with the generic model. In particular, the discovery of anomalous generation and extinction of crystal nuclei in nonequilibrium supercooled liquids reflects experimentally the effect of the real heterogeneous structure and its irreversible relaxation on the stability of nuclei. It was found that the cubic term in the order parameter of the Landau-type potential associated with the asymmetry of the system serves to increase the stability of crystalline state for the suitably varied control parameter. The cases which allow analytical solution of the problem and the realization of different transition scenarios are also discussed.

1. Introduction

Nucleation is the process the formation of new phases begins with; thus, it is a widely spread phenomenon in both nature and technology. Condensation and evaporation, crystal growth, deposition of thin films, and overall crystallization are only some of the processes in which nucleation plays a prominent role. *Fundamentally*, it is a topic in the physics of the phase transitions of first order. *Applicationally*, nucleation is a topic in the modern production of traditional and new materials and coatings for the needs of various technologies; therefore, nucleation theory, experiment, and practice are an interdisciplinary topic. *Academically*, it is an ingredient in the more general university courses on thermodynamics, solid state physics, physical chemistry, colloid and surface science, biophysics, etc. [1].

Discovery of the generation and extinction of crystal nuclei at very low temperatures [2-4] explores quite a different way to crystallize any liquid which is hard to crystallize, since it has been commonly recognized that the only way to crystallization is to wait for a long time at some temperatures. Considering that the crystal nucleation is just one extreme event in the fluctuation of a clustered structure, another metastable liquid phase with a structure different from the ordinary one would be also potentially nucleated in a similar procedure. Thus, stochastic generation of crystal nuclei can be considered a result of fluctuation of the cluster structure of a supercooled liquid. Another liquid phase with a structure different from the ordinary one could be generated in a similar procedure, and a liquid-liquid phase transition found experimentally in real systems is closely related to this phenomenon [5, 6]. The role of an intermediate metastable state in the fluctuation-induced transitions between two stable states was analyzed using kinetic models involving one or two order parameters [7, 8], the main aim being to highlight the conditions for which the transition rates can be amplified by the presence of an intermediate metastable state. The intermolecular attractive interactions are taken to be weak and short ranged, so the crystallization proceeding with crystal nucleation and growth processes is a very slow process in such substances. Meanwhile, the intrinsic transition dynamics can be really enhanced for particular combinations of control parameters. This situation might correspond to crystallization in a temperature range much below $T_{g\alpha}$ produced by molecular rearrangements at the interface between clusters due to the β relaxation process [9]: the α process is related to the rearrangement motion of molecules within the clusters, while the β process is due to the rearrangement of molecules in the gap between the clusters; so the α process, being just the β process modified through the formation of clusters as a result of intermolecular interactions, becomes equal to the β process at high temperature [10].

In the present work, the generic kinetic model involving one order parameter [8] is developed to study the impact of heterogeneity on phase transitions in the presence of intermediate metastable state. The Landau-type potential possessing a single order parameter associated to the fluid phase and three control parameters is considered, and we aim mainly to assess the above mentioned effect in the presence of an intermediate metastable state rather than to study the nucleation process quantitatively. In general, the universal features of transition scenario can be described by a six-degree potential with four control parameters which are associated with coupling the system to an external field, diffusion, asymmetry, and viscosity. Depending on the values of its control parameters, the potential has one, two, or three possible minima, and we study the problem by construction of the equilibrium phase diagrams. Pointing out the range of parameter values for which the enhancement or decline in nucleation rate is observed, it is possible to analyze the impact of heterogeneity on nucleation. In fact, the occurrence of structural fluctuations in a temperature range much below $T_{g\alpha}$ indicates that a supercooled liquid would really have a heterogeneous structure composed of regions of molecules giving rise to both the α and β relaxation processes.

2. Intrinsic mechanism of phase transitions in the presence of an intermediate metastable state

In the following, the process of crystal nuclei formation is associated to the dynamics of a set of order parameters in a force field in the presence of thermal fluctuations. In the approximation of a local equilibrium, it is assumed that the force field has the structure of the derivative of a Landau-type free energy function, up to proportionality factors related to diffusion, viscosity, etc. [8]. Firstly, one can limit the model to the case of a single order parameter x, and two control parameters, and let $U(x)$ be the corresponding effective potential. Evolution of x is described by Langevin equation

$$\frac{dx}{dt} = -\frac{\partial U}{\partial x} + F(t), \tag{1}$$

where $U(x) = -\lambda x^2/2 + \mu x^4/4 + x^6/6$, and $F(t)$ is the force associated with thermodynamic fluctuations (so-called "white noise" or stochastic thermal fluctuations). Assuming that white noise process accounting for the thermodynamic fluctuations has the mean value $\langle F(t) \rangle = 0$, the intrinsic transition dynamics as a function of the above-mentioned two control parameters, namely λ and μ, is described by steady-state solutions of the equation

$$x_s^5 + \mu x_s^3 - \lambda x_s = 0 \tag{2}$$

up to a proportionality factor related to the diffusion or the viscosity coefficient, which is absorbed in this equation in a redefinition of the time scale. Eq. (2) has the trivial solution $x_0 = 0$ for any possible value of λ. Meanwhile, the non-trivial solutions are $x_{1,2,3,4} = \pm\sqrt{(-\mu \pm \sqrt{\mu^2 + 4\lambda})/2}$. These solutions are physically unacceptable for $\lambda < 0$ and $\mu > 0$, because the problem gets a negative value for x_s^2. At $\lambda > 0$ there are two solutions

$$x_s^2 = \frac{-\mu + \sqrt{\mu^2 + 4\lambda}}{2}, (\lambda > 0). \tag{3}$$

For $\lambda < 0$ and $\mu < 0$ four non-trivial solutions are physically acceptable while condition $\mu^2 + 4\lambda > 0$ holds

$$x_+^2 = \frac{-\mu + \sqrt{\mu^2 + 4\lambda}}{2}, \tag{4}$$

$$x_-^2 = \frac{-\mu - \sqrt{\mu^2 + 4\lambda}}{2} \; (\lambda < 0, \mu < 0, \; \mu^2 + 4\lambda > 0). \tag{5}$$

Figure 1 depicts the bifurcation diagram for these steady-state solutions versus *λ*, i.e., the dependence of the order parameter *x* on the control parameter *λ* for *μ* = –2. As can be seen, the negative and positive branches resulting from x_+^2 are associated with the liquid, *L*1 and the crystalline, *C* phases, respectively. The branch $x_0 = 0$ is stable for *λ* < 0 and unstable for *λ* > 0; so, in the previous case it corresponds to the second fluid state *L*2. Notice that there are two limit point bifurcations at $\lambda = -\mu^2/4$, while two branches x_-^2 start from $x_s = 0$ through a bifurcation. Branches *L*1, *C,* and *L*2 (for *λ* < 0) correspond to minima of *U*(*x*), whereas the remaining ones corespond to maxima and are unstable. So, the transition from *L*1 to *C* for negative *λ* values involves the intermediate state *L*2. The overall dynamics involves three transitions *L*1→ *L*2, *L*2→*L*1, and *L*2→*C*: the first two transitions imply the crossing of an unstable state given by the negative root of x_-^2, whereas the third one refers to the crossing of the branch obtained from its positive root. It was shown [8] that the mean transition time between state *L*1 and state *C* decreases when the system enters the region of existence of *L*2. The particular value of *λ* for which the transition dynamics is the fastest one, i.e., the mean transition time goes through a minimum, corresponds to the "coexistence" of states *L*1 and *L*2: the potential barriers for the *L*1→ *L*2 and the *L*2→*L*1 transitions become identical. Therefore, the presence of such intermediate metastable state, namely, the fluid phase *L*2, enhances the nucleation process.

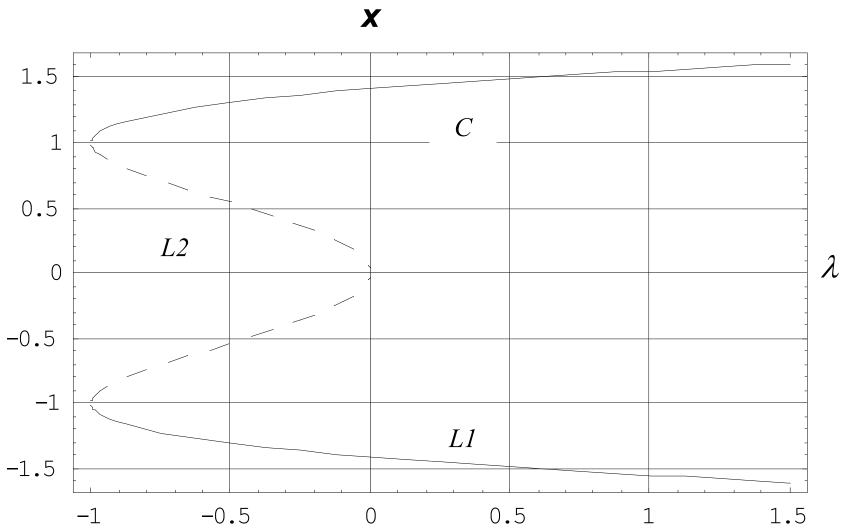

Fig. 1. Bifurcation diagram for the intrinsic transition dynamics of a homogeneous system. Parameter value *μ* = –2. The solid and broken lines stand for the stable and metastabile states; *C*, *L*1, and *L*2 represent crystalline and two liquid phases, respectively.

3. The role of heterogeneity in the first-order phase transitions

It was experimentally found that the nucleation starts at temperatures much below those calculated for the homogeneous nucleation [1]; so, we shall consider the heterogeneous nucleation which takes place when the old phase contacts and/or contains other phases and/or molecular species. While the supercooled liquid is microscopically heterogeneous in structure due to the presence of clusters, there should be an effect of asymmetry on the transition between phases in the real systems. The kinetic potential involving a single order parameter x and the coefficient of asymmetry ξ has the form

$$U(x) = -\lambda\frac{x^2}{2} + \xi\frac{x^3}{3} + \mu\frac{x^4}{4} + \frac{x^6}{6}, \tag{6}$$

where λ and μ are the control parameters related to the intrinsic transition dynamics [8]. Assuming that white noise process accounting for the thermodynamic fluctuations has the mean value $\langle F(t)\rangle = 0$, the possible states of the system x_s described by Eq. (6) are solutions of the equation $dx/dt = -\partial U/\partial x = 0$, so

$$x_s^5 + \mu x_s^3 + \xi x_s^2 - \lambda x_s = 0. \tag{7}$$

A trivial solution is $x_0 = 0$, which satisfies equation (7) for any values of parameters μ, ξ, and λ; the other four non-trivial solutions will be expressed in terms of control parameters as calculated as roots of the equation

$$x_s^4 + \mu x_s^2 + \xi x_s - \lambda = 0. \tag{8}$$

Note that (8) is already an incomplete four-degree equation, and this simplifies its analytical solution according to the Descartes-Euler method for solving polynomial equations. The four steady states solutions of Eq. (8) will thus take the form

$$x_{1,2,3,4} = \pm\sqrt{y_1} \pm \sqrt{y_2} \pm \sqrt{y_3}, \tag{9}$$

where the combination of signs is taken so as the following expression takes place

$$\sqrt{y_1}\sqrt{y_2}\sqrt{y_3} = -\frac{\xi}{8}, \tag{10}$$

and y_1, y_2 and y_3 are the solutions of the cubic equation

$$y^3 + \frac{\mu}{2}y^2 + \frac{\mu^2 + 4\lambda}{16}y - \frac{\xi^2}{64} = 0. \tag{11}$$

Next, we note $p = \mu/2$, $q = (\mu^2 + 4\lambda)/16$, and $r = -\xi^2/64$. Then Eq. (11) takes the form

$$y^3 + py^2 + qy + r = 0, \tag{12}$$

and, upon substitution $y = z - p/3$, this equation takes its final incomplete form

$$z^3 + az + b = 0, \tag{13}$$

where $a = -p^2/3 + q$ and $b = 2(p/3)^3 - pq/3 + r$. Solutions z_1, z_2, and z_3 of the incomplete cubic equation are

$$z_1 = A + B, \quad z_{2,3} = -\frac{A+B}{2} \pm i\sqrt{3}\frac{A-B}{2}, \tag{14}$$

where $A = \sqrt[3]{-\frac{b}{2} + \sqrt{Q}}$, $B = \sqrt[3]{-\frac{b}{2} - \sqrt{Q}}$, and $Q = \left(\frac{a}{3}\right)^3 + \left(\frac{b}{2}\right)^2$. Here A and B are, in general, complex quantities which satisfy the equation $AB = -a/3$ [11]. Next, we examine all possible cases for the model parameters; if $Q > 0$, then Eq. (13) has a physically acceptable solution and two complex conjugate roots; if $Q = 0$, then there are three physically acceptable solutions, at least two of which are equal. The solutions of these two cases are subject to the sign of the parameter a. Thus for $Q \geq 0$ and $a > 0$ one obtains the following results

$$z_1 = -2\sqrt{a/3}\,\mathrm{ctg}2\alpha, \tag{15}$$

$$z_{2,3} = \sqrt{a/3}(\mathrm{ctg}2\alpha \pm i\sqrt{3}\,\mathrm{cosec}2\alpha)\,, \tag{16}$$

where

$$\mathrm{tg}\alpha = \sqrt[3]{\mathrm{tg}\frac{\beta}{2}}\left(|\alpha| \le \frac{\pi}{4}\right), \quad \mathrm{tg}\beta = \frac{2}{b}\sqrt{\left(\frac{a}{3}\right)^3}\left(|\beta| \le \frac{\pi}{2}\right). \tag{17}$$

For $Q \ge 0$ and $a < 0$ we can write

$$z_1 = -2\sqrt{-a/3}\,\mathrm{cosec}2\alpha\,, \tag{18}$$

$$z_{2,3} = \sqrt{-a/3}(\mathrm{cosec}2\alpha \pm i\sqrt{3}\,\mathrm{ctg}2\alpha)\,, \tag{19}$$

where

$$\mathrm{tg}\alpha = \sqrt[3]{\mathrm{tg}\frac{\beta}{2}}\left(|\alpha| \le \frac{\pi}{4}\right), \quad \sin\beta = \frac{2}{b}\sqrt{\left(-\frac{a}{3}\right)^3}\left(|\beta| \le \frac{\pi}{2}\right). \tag{20}$$

If $Q < 0$, then $a < 0$ and there are three distinct real solutions

$$z_1 = 2\sqrt{-a/3}\,\cos\frac{\alpha}{3}\,, \tag{21}$$

$$z_{2,3} = -2\sqrt{-a/3}\,\cos\left(\frac{\alpha}{3} \pm \frac{2\pi}{3}\right), \tag{22}$$

where

$$\cos\alpha = -\frac{b}{2\sqrt{-(a/3)^3}}\,. \tag{23}$$

In all cases, one should consider the physically acceptable solutions. Note that the solution of initial equation (8) is voluminous, wherein additionally Eq. (10) is satisfied. Thus, depending on the values of the parameter Q, the solutions $x_{1,2,3,4}$ can be both physically acceptable and unacceptable; so, we shall examine further the dependence of Q on the initial control parameters μ, ξ, and λ by replacing the interim notations a, b, p, q, and r. Then the final equation for Q is given by

$$Q = \frac{1}{1728}\left(\lambda - \frac{\mu^2}{12}\right)^3 - \frac{1}{1728^2}\left(\frac{27\xi^2}{2} + 36\lambda\mu + \mu^3\right)^2. \tag{24}$$

Since $Q(\mu, \xi, \lambda)$ depends on three control parameters, we determine the sign of Q for different values of parameters λ and ξ, where $\mu = -2$. This will allow us to compare these results with the previously reported case for the intrinsic mechanism of phase transitions [8]; so, it will be possible to analyze the influence of asymmetry on the transition dynamics in the presence of an intermediate metastable state. The dependence of model parameter Q on control parameters λ and ξ is shown in Fig. 2. In this figure, one can easily follow the evolution of Q depending on the set of control parameters (λ, ξ): the output in the curve corresponds to $Q = 0$ (there are two distinct physically acceptable solutions), the region on the left contains values for

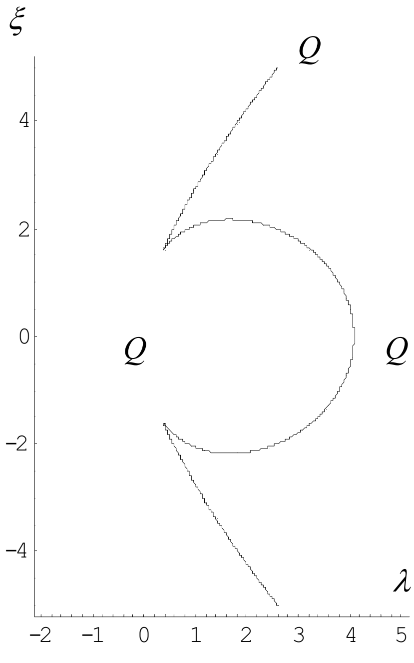

Fig. 2. Dependence of the model parameter Q on control parameters λ and ξ. There are two distinct regions where $Q < 0$ and $Q > 0$. Values in the curve correspond to $Q = 0$. Parameter value $\mu = -2$.

$Q < 0$ (there are three distinct physically acceptable solutions), and that on the right – for $Q > 0$ (there is only one such solution). The function $Q(\lambda, \xi)$ is symmetrical at $\xi = 0$ for any λ, because the dependence on ξ in Eq. (24) is squared. However, a particular interest in the construction of bifurcation diagram for the steady-state solutions of Eq. (8) versus λ is focused on the dependence of order parameter x in a special range of values, for example, $|\lambda| \in [0,4]$, $|\xi| \in [0,2]$, and, obviously, $\mu = -2$ as well as two limit point bifurcations at (0.33 ± 1.54). In this range of values for λ, as shown in Fig. 2 for $\xi = \pm 2$, there is a transition from $Q < 0$ to $Q = 0$, and then to $Q > 0$, and, again, $Q = 0$ and $Q < 0$, and, finally, $Q = 0$ and $Q > 0$, respectively, from left to right. The results analyzed in this section are summarized below in Table 1.

Table 1. Steady-state solutions of Eq. (8) obtained for the kinetic potential involving a single order parameter and the coefficient of asymmetry.

<table>
<tr><th colspan="2">Solution</th><th>Condition</th><th>Parameters</th></tr>
<tr><td colspan="2">$x_{1,2,3,4} = \pm\sqrt{y_1} \pm \sqrt{y_2} \pm \sqrt{y_3}$</td><td rowspan="3">$\sqrt{y_1}\sqrt{y_2}\sqrt{y_3} = -\dfrac{\xi}{8}$</td><td rowspan="2">$p = \mu/2$, $q = (\mu^2 + 4\lambda)/16$,
$r = -\xi^2/64$</td></tr>
<tr><td colspan="2">$y = z - \dfrac{p}{3}$</td></tr>
<tr><td colspan="2">$z_1 = A + B$,
$z_{2,3} = -\dfrac{A+B}{2} \pm i\sqrt{3}\dfrac{A-B}{2}$</td><td>$a = -\dfrac{p^2}{3} + q$, $b = 2\left(\dfrac{p}{3}\right)^3 - \dfrac{pq}{3} + r$,
$A = \sqrt[3]{-\dfrac{b}{2} + \sqrt{Q}}$, $B = \sqrt[3]{-\dfrac{b}{2} - \sqrt{Q}}$,
$Q = \dfrac{1}{1728}\left(\lambda - \dfrac{\mu^2}{12}\right)^3 - \dfrac{1}{1728^2}\left(\dfrac{27\xi^2}{2} + 36\lambda\mu + \mu^3\right)^2$</td></tr>
<tr><td colspan="4">Possible cases for $\mu = -2$</td></tr>
<tr><td colspan="2">$x_{1,2,3,4} = \pm\sqrt{y_1} \pm \sqrt{y_2} \pm \sqrt{y_3}$</td><td rowspan="3">$\sqrt{y_1}\sqrt{y_2}\sqrt{y_3} = -\dfrac{\xi}{8}$</td><td rowspan="3">$p = -1$, $q = (1+\lambda)/4$, $r = -\xi^2/64$
$b = \dfrac{\lambda}{12} - \dfrac{\xi^2}{64} + \dfrac{1}{108}$,
$A = \sqrt[3]{-\dfrac{b}{2} + \sqrt{Q}}$, $B = \sqrt[3]{-\dfrac{b}{2} - \sqrt{Q}}$,
$Q = \dfrac{1}{1728}\left(\lambda - \dfrac{1}{3}\right)^3 - \dfrac{1}{1728^2}\left(8 - \dfrac{27\xi^2}{2} + 72\lambda\right)^2$</td></tr>
<tr><td colspan="2">$y = z + \dfrac{1}{3}$</td></tr>
<tr><td colspan="2">$z_1 = A + B$,
$z_{2,3} = -\dfrac{A+B}{2} \pm i\sqrt{3}\dfrac{A-B}{2}$</td></tr>
<tr><td>1.</td><td>$Q < 0$</td><td colspan="2">values (λ, ξ) on the left side of the curve in Fig. 2; physically acceptable distinct solution $z_1 \neq z_2 \neq z_3$</td></tr>
<tr><td>2.</td><td>$Q = 0$</td><td colspan="2">values (λ, ξ) on the curve in Fig. 2; physically acceptable solutions z_1 and $z_2 = z_3$</td></tr>
<tr><td>3.</td><td>$Q > 0$</td><td colspan="2">values (λ, ξ) on the right side of the curve in Fig. 2; only one physically acceptable solution z_1</td></tr>
</table>

Figure 3 depicts the bifurcation diagram of the steady-state solutions of Eq. (8) versus λ, i.e., the dependence of the order parameter x on the control parameter λ in the range of values $\lambda \in [-4,4]$, and for $\mu = -2$ and $\xi = 0$, 1, and 2. As can be seen, the lowest negative and the highest positive branches are associated with the liquid, $L1$ and the crystalline, C phases, re-

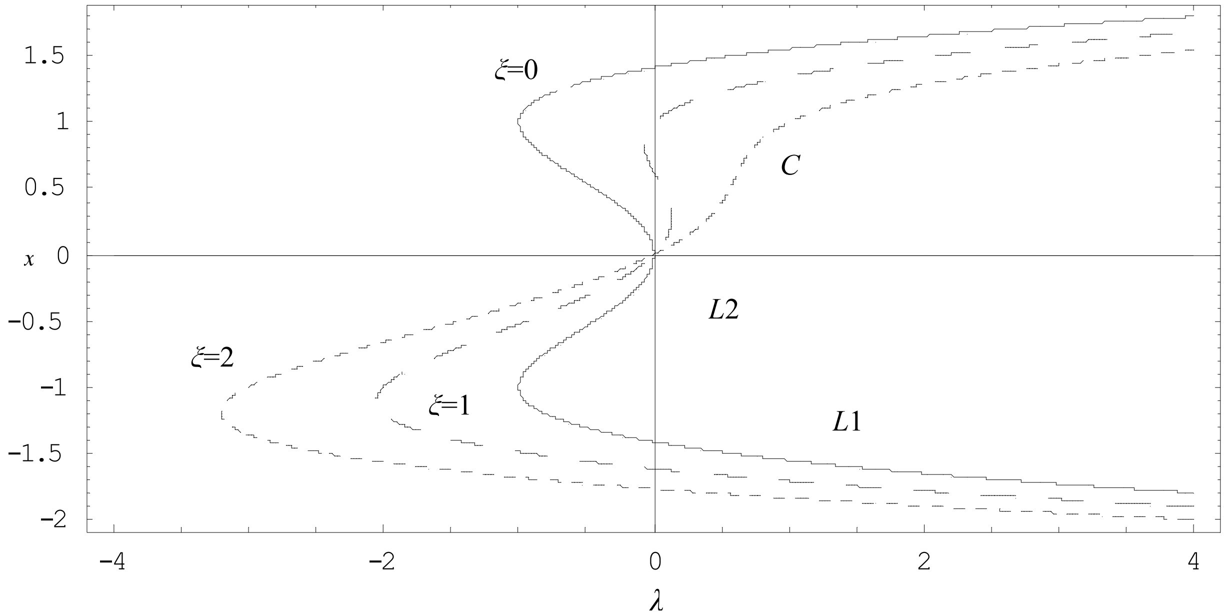

Fig. 3. Bifurcation diagram for a heterogeneous system. Solid line stands for the intrinsic transition dynamics ($\xi = 0$), and the broken and dotted curves correspond to the kinetic potential involving an additional asymmetry effect with $\xi = 1$ and 2. C, $L1$, and $L2$ represent crystalline and two liquid phases, respectively. Parameter value $\mu = -2$.

spectively. The branch $x_0 = 0$ for $\lambda < 0$ corresponds to the second fluid phase $L2$. The solid line corresponds to the referred case of the intrinsic transition dynamics as a function of the remaining two control parameters denoted by λ and μ, when $\xi = 0$. Branches $L1$, C, and $L2$ (for $\lambda < 0$) correspond to minima of the Landau-type potential $U(x)$, whereas the remaining ones are unstable and correspond to maxima. We see that, with an increase in the asymmetry of the system, i.e., as the absolute value of parameter ξ gets bigger, there is an increase in the stability of the fluid phase $L1$ for $\xi > 0$, whereas the stability of the crystalline C phase decreases, and vice versa for $\xi < 0$, when the stability of the liquid phase $L1$ decreases, there is an increase in the stability of the corresponding solid phase. Two limit point bifurcations change accordingly. These facts are represented in the figure by the broken and dotted curves drawn for $\xi = 1$ and 2, respectively. First-order phase transitions occur by the nucleation mechanism; based on the 'cluster structure model' [9, 10], this kinetic aspect of structure relaxation is understood as follows: the supercooled liquids and glasses are pictured to have a statically heterogeneous structure composed somehow of ordered clusters and the interfacial parts (of the clusters) with somewhat disordered arrangement. Furthermore, this study supports the idea that the role of heterogeneity in nucleation is to help the formation of the clusters of the new phase.

4. Conclusions

In this paper, a Landau-type potential based kinetic model involving one order parameter has been developed to study the effect of asymmetry on phase transitions in the presence of an intermediate metastable state. The analytical solutions of the problem were investigated, and the model provides a set of three control parameters necessary to realize different transition scenarios, which therefore assign a high degree of universality to this model as long as the respective control parameters are suitably varied.

The intrinsic transition dynamics shows that there is a particular value of λ for which the transition dynamics is the fastest one, and it corresponds to the "coexistence" of fluid phases

$L1$ and $L2$. The presence of such intermediate metastable state, namely, the fluid phase $L2$, enhances therefore the nucleation process. While the asymmetry of the system increases, there is an increase in the stability of the fluid phase for $\xi > 0$, whereas the stability of the crystalline phase decreases; and vice versa for $\xi < 0$, when the stability of the liquid phase decreases, there is an increase in the stability of the solid one. First-order phase transitions occur by the nucleation mechanism; so, these results are primarily related to the nucleation phenomena. In particular, our results support the 'cluster structure model' of supercooled liquids and glasses, according to which the role of heterogeneity in nucleation is to enhance the formation of crystal nuclei as clusters of the new phase. Finally, we can conclude that the model refers also to the problem of crystallization in substances where fluctuating metastable states have been already observed experimentally [2-4, 12-14]; also, it offers possible solutions for controlling the phase transitions in the presence of an intermediate metastable state.

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