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# Dynamical phase changes induced by point defect fluxes under irradiation

C. Abromeit <sup>a,\*</sup>, G. Martin <sup>b,1</sup>

<sup>a</sup> *Hahn-Meitner-Institut, Glienicke Str. 100, D-14109 Berlin, Germany*

<sup>b</sup> *SRMP, CEA Saclay, F-91191 Gif-sur-Yvette Cedex, France*

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## Abstract

A comprehensive mean field treatment of the unmixing of driven solid solutions is given. The stability fields of the stationary, non-equilibrium states which define a dynamical phase diagram are investigated by a linear stability analysis with respect to small concentration fluctuations. Their time evolution is determined by the atomic fluxes which are caused by thermodynamical, ballistic and Kirkendall forces which result from the coupling between solute and sustained point defect fluxes. In the case of a spinodally decomposing alloy, the influence of the irradiation is reflected in a modified amplification factor, from which the decomposition behavior and thus the dynamical phase diagram under irradiation is obtained. For a regular solution, a simple expression of an effective free energy of the system is obtained which proves to be very helpful for the discussion of alloy stability under external forcing. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The stability of an alloy under external influences such as ball milling or energetic particle irradiation cannot be treated by equilibrium thermodynamics. An appropriate description uses the concept of dynamical phase diagrams, which takes into account the changes of the thermodynamic equilibrium phase diagram due to irradiation-induced spatial redistributions of the alloy atoms. Martin and coworkers [1,2] have developed such a dynamical phase diagram for the case where the local composition of the alloy is changed by atomic fluxes due to ballistic jumps. However, phase changes are also triggered by the coupling of point defect fluxes to solute fluxes. They are intensively discussed in terms of the inverse Kirkendall effect (see for a review Refs. [3,4]). In this short contribution, the basis of a comprehensive discussion of the stability of alloys under external forcing

is outlined. The formulation includes phase changes by the ballistic mixing and by the point defect fluxes.

## 2. General expressions for the atomic fluxes

Besides the enhanced atomic mobility of solutes due to the point defect supersaturation under irradiation, point defect fluxes induce changes of the alloy composition. A well-known example is the irradiation induced solute segregation at extended sinks e.g. as grain boundaries, external surfaces etc. [3]. Point defect fluxes are also induced by chemical inhomogeneities for many reasons. Point defects may be homogeneously produced but they may recombine more frequently in solute-rich regions if the mobility is enhanced in these regions or if they are attracted in the latter regions by solute-defect binding. Conversely, an inhomogeneous defect production due to a chemical inhomogeneity will induce a point defect flux. Because of the existence of point defect sinks and the vacancy–interstitial recombination, such defect fluxes reach a steady state under irradiation.

The preceding effect will be described in terms of an effective free energy. A binary solid solution under irradiation is considered. Its configuration is described by

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\* Corresponding author. Tel.: +49-30 8062 2825; fax: +49-30 8062 3059; e-mail: abromeit@hmi.de

<sup>1</sup> Tel.: +33-1-6908 2810; fax: +33-1-6908 6867; e-mail: martin@srmp12.saclay.cea.fr

the three concentrations for interstitials ( $C_i$ ), vacancies ( $C_v$ ), and solute atoms ( $C_s$ ). In the homogeneous solid solution the concentrations are uniform ( $\bar{C}_x$ ). In a linear approximation the diffusion fluxes of the three components ( $\alpha, \beta = i, v, s$ ) are

$$J_\alpha = -\sum_{\beta} D_{\alpha\beta} \nabla C_\beta, \quad (1)$$

where for the sake of simplicity we omit the gradient energy contribution in the expression of the solute flux. The diffusion coefficients  $D_{\alpha\beta}$  can be written as

$$D_{\alpha\beta} = D_{\alpha\beta}^{\text{th}} + D_{\alpha\beta}^{\text{bal}}, \quad (2)$$

$$D_{\alpha\beta}^{\text{th}} = \sum_{\gamma} L_{\alpha\gamma} f_{\beta\gamma}. \quad (3)$$

The  $D_{\alpha\beta}^{\text{th}}$  in Eq. (2) are the thermally activated diffusion coefficients while the  $D_{\alpha\beta}^{\text{bal}}$  are the ballistic ones.  $D_{\alpha\beta}^{\text{th}}$  can be expressed in terms of the Onsager phenomenological coefficients  $L_{\alpha\gamma}$  and of the second derivatives of the free energy of the solid solution  $f$  with respect to the concentrations

$$f_{\beta\gamma} = \frac{\partial^2 f}{\partial C_\beta \partial C_\gamma}. \quad (4)$$

### 3. Point defect fluxes in adiabatic approximation

In order to assess the stability of the homogeneous solid solution under irradiation, the amplification factor for the evolution of a small compositional amplitude has to be known. However, the system contains the coupled fluctuations of the concentrations of solutes, interstitial atoms and vacancies. As the point defect concentrations adjust to a compositional fluctuation very rapidly, an adiabatic approximation for the elimination of the point defects kinetics is applicable. It can be shown, that the terms  $\nabla C_i$  and  $\nabla C_v$  of Eq. (1) can be expressed by  $\nabla C_s$  for a small solute concentration fluctuation. If only linear terms are taken into account, a scalar equation for the solute flux  $J_s$  is obtained.

Eq. (1) is re-written in order to separate the point defect and solute terms. We split the diffusion problem by introducing tensor quantities which are defined in the point defect (PD) subspace (i, v) of the concentration space (i, v, s): PD fluxes  $\mathbf{j}_d$ , PD concentrations  $\mathbf{c}_d$ , PD diffusion matrix:  $\mathbf{D}_d$  and PD–solute coupling  $\mathbf{d}_{ds}$  and  $\hat{\mathbf{d}}_{sd}$ :

$$\mathbf{j}_d = \begin{pmatrix} J_i \\ J_v \end{pmatrix}, \quad \mathbf{c}_d = \begin{pmatrix} C_i \\ C_v \end{pmatrix}, \quad (5)$$

$$\mathbf{D}_d = \begin{pmatrix} D_{ii} & D_{iv} \\ D_{vi} & D_{vv} \end{pmatrix}, \quad \mathbf{d}_{ds} = \begin{pmatrix} D_{is} \\ D_{vs} \end{pmatrix}, \quad \hat{\mathbf{d}}_{sd} = (D_{si} \quad D_{sv}).$$

With these definitions, the diffusion fluxes for the point defects are

$$\mathbf{j}_d = -\mathbf{D}_d \frac{\partial}{\partial x} \mathbf{c}_d - \hat{\mathbf{d}}_{ds} \frac{\partial}{\partial x} C_s, \quad (6)$$

and solute atom interdiffusion flux is

$$J_s = -\hat{\mathbf{d}}_{sd} \frac{\partial}{\partial x} \mathbf{c}_d - D_{ss} \frac{\partial}{\partial x} C_s, \quad (7)$$

where it is assumed, that the solute concentration fluctuation is one dimensional i.e.  $[(\partial C_s / \partial x) = -q c_s^0 \sin(qx)]$  and that the solute concentration amplitude is small ( $c_s^0 \ll \bar{C}_s$ ). The response of the point defects to such a compositional fluctuation is calculated from the diffusion controlled defect reaction scheme [5]

$$\frac{\partial}{\partial t} C_i = K_i - K_{iv} C_v C_i - K_{if} C_i - \frac{\partial}{\partial x} J_i = 0 \quad (8)$$

$$\frac{\partial}{\partial t} C_v = K_v - K_{iv} C_v C_i - K_{vf} C_i - \frac{\partial}{\partial x} J_v = 0.$$

In Eq. (8),  $K_x = K_x^{\text{irr}} + K_x^{\text{th}}$  is the sum of the irradiation-induced and thermal Frenkel pair production rate,  $K_{xf} = k_x^2 D_{xx}$  is the rate constant for the loss of point defects of type  $x$  at fixed point defect sinks with sink strength  $k_x^2$  such as dislocations, loops etc., and  $K_{iv}$  is the vacancy–interstitial recombination rate constant given by  $K_{iv} = 4\pi r(D_{ii} + D_{vv})/\Omega_a$ , where  $r$  stands for the i–v recombination radius and  $\Omega_a$  is the atomic volume. In principle,  $K_x$ ,  $K_{iv}$  and  $K_{xf}$  are functions of alloy composition ( $C_s$ ). The right-hand side of Eq. (8) is set to zero, according to the adiabatic relaxation of the fast variables ( $C_v, C_i$ ) compared to the slow one ( $C_s$ ).

Differentiating the Eq. (8) with respect to space gives in linear approximation in the amplitudes of the point defect fluctuations  $c_x = C_x(x) - \bar{C}_x$  the second order differential equation for the irradiation-induced point defect fluxes as

$$\mathbf{j}_d'' = -\mathbf{K}^2 \mathbf{c}_d' + \delta(-c_s^0 q \sin(qx)), \quad (9)$$

where

$$\mathbf{K}^2 = \begin{pmatrix} K_{iv} \bar{C}_v + K_{if} & K_{iv} \bar{C}_i \\ K_{iv} \bar{C}_v & K_{iv} \bar{C}_i + K_{vf} \end{pmatrix} \quad (10)$$

$$\delta = \begin{pmatrix} \frac{\partial K_i}{\partial C_s} - \frac{\partial K_{iv}}{\partial C_s} \bar{C}_v \bar{C}_i - \frac{\partial K_{if}}{\partial C_s} \bar{C}_i \\ \frac{\partial K_v}{\partial C_s} - \frac{\partial K_{iv}}{\partial C_s} \bar{C}_v \bar{C}_i - \frac{\partial K_{vf}}{\partial C_s} \bar{C}_v \end{pmatrix}.$$

For  $D_{ii} D_{vv} - D_{iv} D_{vi} \neq 0$ , the inverse matrix  $\mathbf{D}_d^{-1}$  exists and we obtain from Eqs. (6) and (9) the solution

$$\mathbf{j}_d = \mathbf{j}_d^0 * (-c_s^0 q \sin(qx)), \quad (11)$$

with flux amplitudes  $\mathbf{j}_d^0$ . They depend on the fluctuation length  $1/q$  as

$$\mathbf{j}_d^0(q^2) = -\frac{1}{q^2 + \mathbf{K}^2 \mathbf{D}_d^{-1}} (\mathbf{K}^2 \mathbf{D}_d^{-1} \mathbf{d}_{ds} + \delta). \quad (12)$$

The point defect concentration gradients  $\mathbf{c}_d'$  which are induced by the compositional fluctuation  $c_s^0(q)$  are

$$\mathbf{c}_d' = -\mathbf{D}_d^{-1} (\mathbf{j}_d^0 + \mathbf{d}_{ds}) (-c_s^0 q \sin(qx)), \quad (13)$$

which will be used in Eq. (7). The solute flux which is induced by the point defect–solute diffusional coupling is then given by

$$J_s^{\text{defect fluxes}} = \hat{\mathbf{d}}_{\text{sd}} \mathbf{D}_d^{-1} (\mathbf{j}_d^0 + \mathbf{d}_{\text{ds}}) (-c_s^0 q \sin(qx)). \quad (14)$$

It contains the point defect reaction parameters  $\mathbf{K}^2$  and  $\delta$  and depends on the compositional fluctuation wavelength  $1/q$ . The point defect–solute coupling enters by the coupling vectors  $\hat{\mathbf{d}}_{\text{sd}}$  and  $\mathbf{d}_{\text{ds}}$ .

The expression for the flux amplitudes (12) has been used to calculate the amount of redistribution induced by a chemical inhomogeneity in the FeCrNi alloy under irradiation [6]. The parameters chosen for this system were taken from experimental results [7] and from theoretical estimations derived by Wolfer [8]. The non-diagonal elements of the diffusion matrix  $\mathbf{D}_d$  were neglected. A strong chemical bias in the local point defect annihilation was found (13%) independent of the irradiation intensity. The interstitials are preferentially driven to Ni rich regions, so that void nucleation and growth should be more pronounced in Ni depleted regions.

From Eqs. (12) and (13) approximate analytical expressions of the amplitudes of the defect concentration fluctuations can be obtained [9]. A detailed numerical study of Eq. (8) for a broad set of parameters has shown that the sign of the solutions depends on the defect reaction regime (sink or recombination case) [10]. Two examples are given in Fig. 1(a) and (b) where the parameters were taken from the data of the FeNiCr alloy under irradiation [6]. In the recombination regime (low temperature, large defect production rate, low sink densities), the concentration fluctuation amplitudes of the interstitials and the vacancies have the opposite sign, but in the sink dominant regime, (elevated temperature, small defect production rate, high sink densities) they have the same sign.

#### 4. Effective free energy

The evolution of a compositional fluctuation  $c_s(x, t) = c_s^0(q, t) \cos(qx)$  is generally described by

$$\frac{\partial}{\partial t} c_s(x, t) = -\frac{\partial}{\partial x} J_s(x, t), \quad (15)$$

where all contributions to the solute flux  $J_s(x, t)$  have to be added, i.e.

$$J_s(x, t) = J_s^{\text{thermal}}(x, t) + J_s^{\text{bal}}(x, t) + J_s^{\text{Defect fluxes}}(x, t). \quad (16)$$

The result is given to first order in the fluctuation amplitudes as

$$\frac{\partial}{\partial t} c_s^0(q, t) = \omega(q^2) c_s^0(q, t). \quad (17)$$

The amplification factor  $\omega(q^2)$  can be written

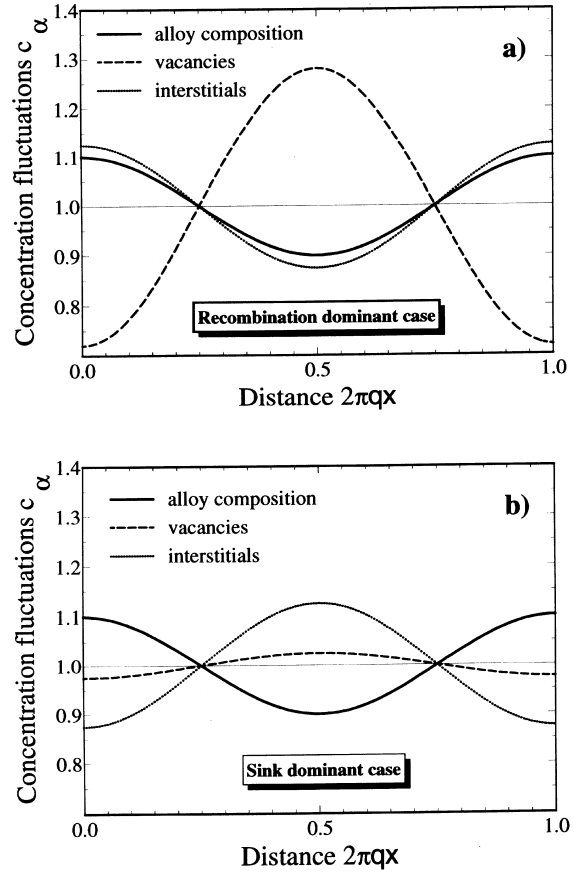


Fig. 1. Steady state fluctuations of point defect concentrations  $c_i$  and  $c_v$  induced by a fluctuation of alloy composition  $c_s$ . (a) Defect annihilation dominantly by recombination reaction. (b) Defect annihilation dominantly by sink reaction.

$$\omega(q^2) = -q^2 L^{\text{irr}} \left[ \frac{\partial^2 f}{\partial C_s^2} + 2\kappa q^2 + \frac{D^{\text{bal}}}{L^{\text{irr}}} - \frac{\hat{\mathbf{d}}_{\text{sd}} \mathbf{D}_d^{-1} (\mathbf{j}_d^0(q^2) + \mathbf{d}_{\text{ds}})}{L^{\text{irr}}} \right], \quad (18)$$

with  $L^{\text{irr}}$  is the irradiation enhanced mobility and  $\kappa$  is the gradient energy coefficient. From Eq. (18) an effective free energy  $f_{\text{eff}}$  of an alloy is determined which describes the spinodal boundaries under irradiation

$$\frac{\partial^2 f_{\text{eff}}}{\partial C_s^2} = -\frac{1}{L^{\text{irr}}} \lim_{q^2 \rightarrow 0} \left( \frac{\omega(q^2)}{q^2} \right) = \frac{\partial^2 f}{\partial C_s^2} + \frac{D^{\text{bal}}}{L^{\text{irr}}} + \frac{\hat{\mathbf{d}}_{\text{sd}} (\mathbf{K}^2)^{-1} \delta}{L^{\text{irr}}}. \quad (19)$$

Generally, the instability limit of the solid solution is given by the change of the sign of  $\partial^2 f / \partial C_s^2$  in the homogeneous state, i.e. ( $q^2 = 0$ ). However, for special cases under irradiation as we will show below, the amplification factor  $\omega(q^2)$  can be positive in a certain interval of  $q^2 > 0$  despite the fact  $(\partial^2 f_{\text{eff}} / \partial C_s^2) > 0$ . This

irradiation-induced instability starts from an inhomogeneous state ( $q^2 > 0$ ) and is produced by the coupling of the point defect fluxes and the solute atom fluxes.

### 5. Effective temperature of a regular solution model

For the sink dominant defect reaction regime  $K_{iv}\bar{C}_z \ll K_{zf}$  the non-diagonal terms in the matrix  $\mathbf{K}^2$  can be neglected. The expression for the effective free energy assumes the simple form

$$\frac{\partial^2 f_{\text{eff}}}{\partial C_s^2} = \frac{\partial^2 f}{\partial C_s^2} + \frac{D^{\text{bal}}}{L^{\text{irr}}} + \frac{D_{si}K_{if}^{-1}\delta_i + D_{sv}K_{vf}^{-1}\delta_v}{L^{\text{irr}}}. \quad (20)$$

The application of Eq. (20) for a regular solution model gives a modified effective temperature  $T_{\text{eff}}$ , where both effects, the ballistic and the defect flux coupling effect, are incorporated. Using

$$\frac{\partial^2 f}{\partial C_s^2} = -2\Omega + \frac{k_B T}{C_s(1 - C_s)}, \quad (21)$$

with  $\Omega$  the ordering energy and the irradiation-enhanced mobility for binary alloys

$$L^{\text{irr}} = D_{\text{ch}}^{\text{irr}} \frac{C_s(1 - C_s)}{k_B T}, \quad (22)$$

where  $D_{\text{ch}}^{\text{irr}}$  is the irradiation enhanced chemical diffusion coefficient, we obtain

$$T_{\text{eff}} = T \left( 1 + \frac{D^{\text{bal}}}{D_{\text{ch}}^{\text{irr}}} + \frac{D_{si}K_{if}^{-1}\delta_i + D_{sv}K_{vf}^{-1}\delta_v}{D_{\text{ch}}^{\text{irr}}} \right). \quad (23)$$

Depending on the sign of the third term in the RHS, positive or negative changes of the effective temperature  $T_{\text{eff}}$  compared to the actual irradiation temperature  $T$  are possible: unlike ballistic effects, which always stabilize the homogeneous solid solution, defect fluxes can either have a stabilizing or a destabilizing effect.

### 6. Examples for the evolution of a compositional fluctuation

For a demonstration of the general behavior, we discuss the function  $\omega(q^2)$  (see Eq. (18)) only for the case  $K_{iv}\bar{C}_z \ll K_{zf}$ , i.e. the point defects annihilate dominantly at non-biased sinks ( $K_{zf} = D_{zz}k^2$ ). We assume that the point defect diffusion matrix is diagonal. With these approximations we obtain the amplification factor

$$\omega(q^2) = -q^2 L^{\text{irr}} \left( \frac{\partial^2 f}{\partial C_s^2} + 2\kappa q^2 + \frac{D^{\text{bal}}}{L^{\text{irr}}} \right) - \frac{q^2}{q^2 + k^2} \hat{\mathbf{d}}_{\text{sd}} \mathbf{D}_{\text{d}}^{-1} (\delta - q^2 \mathbf{d}_{\text{ds}}). \quad (24)$$

The second term contains the coupling of the defect fluxes to the solute concentration fluctuation and to the

solute fluxes. Because of the non-classical  $q^2$  dependence of this second term, unexpected behaviors can appear for particular wavelengths as demonstrated in Fig. 2(a), (b) and (c). There, the amplification factor is displayed in the simple form

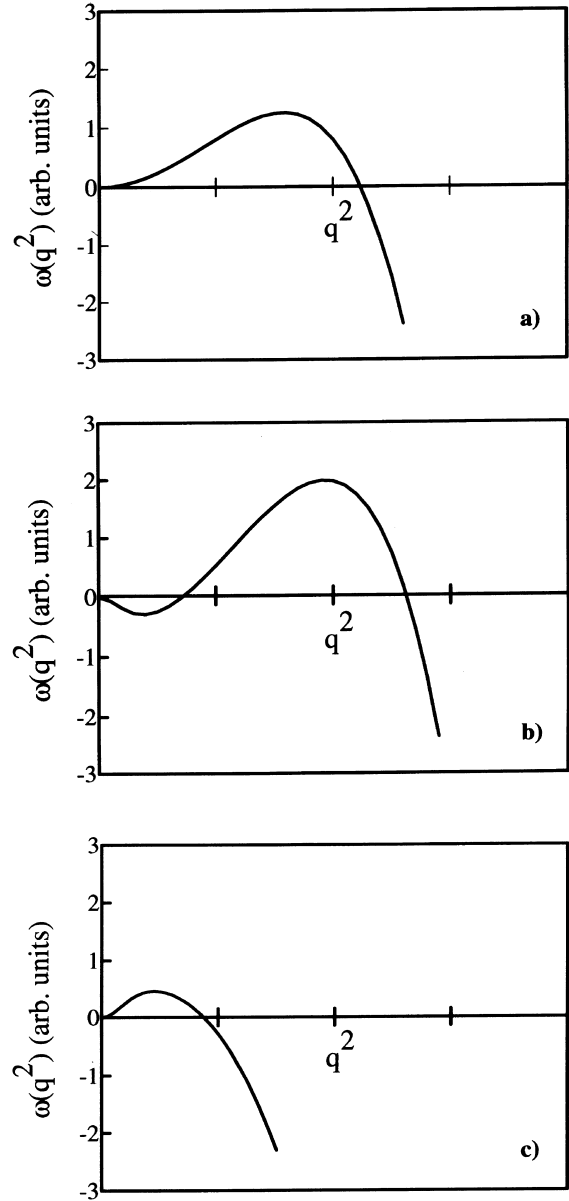


Fig. 2. Amplification factor  $\omega(q^2)$  under irradiation according to Eq. (18) for an unstable solid solution. (a) Without point defect-solute flux coupling. (b) Enhancement by point defect-solute flux coupling. Notice the damping of long wavelengths. (c) Attenuation by point defect-solute flux coupling.

$$\omega(q^2) = \omega^{\text{th+bal}}(q^2) - \frac{q^2}{q^2 + k^2} \left( \frac{D_{\text{si}}\delta_{\text{i}}}{D_{\text{ii}}} + \frac{D_{\text{sv}}\delta_{\text{v}}}{D_{\text{vv}}} \right) + \frac{q^4}{q^2 + k^2} \left( \frac{D_{\text{si}}D_{\text{is}}}{D_{\text{ii}}} + \frac{D_{\text{sv}}D_{\text{vs}}}{D_{\text{vv}}} \right), \quad (25)$$

with

$$\omega^{\text{th+bal}}(q^2) = -q^2 L^{\text{irr}} \left( \frac{\partial^2 f}{\partial C_s^2} + 2\kappa q^2 + \frac{D^{\text{bal}}}{L^{\text{irr}}} \right).$$

Inside the spinodal regime,  $\omega^{\text{th+bal}}(q^2) > 0$  in a certain  $q^2$  interval, interstitial fluxes and/or vacancy fluxes can cause growth or decay of the compositional fluctuation amplitude. Whether an amplification is possible, depends on the sign and on the magnitude of the coupling matrix elements of the various point defects. Competition between interstitial fluxes and vacancy fluxes as well as the flux of one species alone can cause destabilization of the alloy. Outside the spinodal regime  $\omega^{\text{th+bal}}(q^2) < 0$  a thermally stable solute solution can spinodally decompose under irradiation as the amplification factor may have a positive maximum.

It is interesting to note, that the amplification factor under irradiation contains additional length scales, i.e. the mean free diffusion lengths of a point defect for annihilation at sinks  $\lambda_{\text{f}} = 1/\sqrt{k^2}$  and by recombination  $\lambda_{\text{iv}} = 1/\sqrt{K_{\text{iv}}\bar{C}_{\beta}/D_{\text{zx}}}$ . In addition to the spinodal wavelength  $\lambda_{\text{sp}}$ , such lengths produce a complicated microstructure of a decomposition under irradiation. This is seen from the amplification factor displayed in Fig. 2(b), where long-wave and short-wave fluctuations decay, but in an intermediate interval a fluctuation amplitude can grow. Such behavior suggests a reasonably well defined length scale to establish, different from that under thermal conditions. Besides of a shift of the wavelength

of decomposition, we therefore predict a more distinct spatial periodicity under irradiation. If the non-diagonal elements of  $\mathbf{D}_d^{-1}$  are taken into account, also higher order terms appear in the amplification factor, which can produce new instabilities in the system.

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