# Long-Range Periodic Decomposition of Irradiated Solid Solutions

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On the basis of a previously proposed mean-field model of solid solutions under irradiation, asymptotic expressions are derived for the dispersion curves of the eigen-concentration modes in such solutions. Specific features of small-angle scattering from such solutions are anticipated, as well as the possiblity for time-periodic concentration oscillations.

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Crystalline solid solutions under heavy particle irradiations may be viewed as reaction-diffusion systems maintained in steady states far from equilibrium.[1] Indeed Frenkel pairs produced by irradiation migrate, enter association-dissociation reactions with solute atoms, and are eliminated at lattice discontinuities or by mutual recombination. The rate of Frenkel pair production is adjusted by the irradiation flux, an extra control parameter of the state of the system.

As shown in previous papers,[1,2] such states may exhibit a symmetry-breaking bifurcation for appropriate values of the control parameters (temperature, irradiation flux, concentration): In a particular case studied in detail,[2] it was found that *solute clustering* may occur beyond the bifurcation point, despite the fact that the solid solution is undersaturated outside the irradiation zone. The occurrence of homogeneous solute clustering in undersaturated solid solutions is now a well-documented fact and has been observed in AlZn, AlAg, AlSi, CuBe, NiBe, and WRe.[3]

As developed up to now,[1,2] the bifurcation analysis has omitted a study of the spectrum of the eigen-concentration modes of solid solutions under irradiation. Such spectra are of interest for analyzing small-angle-scattering data from solid solutions under irradiation[4] as well as for rationalizing the broad variety of microstructural evolutions which are observed under irradiation. Here I derive asymptotic expressions for the dispersion curves of the eigen-concentration modes in solid solutions under irradiation and discuss qualitative differences to be anticipated between the kinetics of concentration fluctuations in solid solutions under irradiation and outside irradiation.

The state of a binary solid solution under irradiation may be described by the space- and time-dependent interstitial, vacancy, and solute concentrations (respectively, $C_i$, $C_v$, and $C_s$) which obey the three following balance equations[1,2]:

$$\dot{C}_i = G - RC_iC_v - \operatorname{div}\vec{J}_i, \tag{1a}$$

$$\dot{C}_v = G - RC_iC_v - \operatorname{div}\vec{J}_v, \tag{1b}$$

$$\dot{C}_s = -\operatorname{div}\vec{J}_s. \tag{1c}$$

$G$, $R$, and $\vec{J}_\alpha$ ($\alpha = i,v,s$) are, respectively, the point-defect production rate, recombination rate, and the flux of species $\alpha$. $\dot{C}_\alpha$ stands for the time derivative of $C_\alpha$. The diffusion fluxes are coupled: each flux is a linear combination of the space derivatives of all the concentrations. Using the notation of Morral and Cahn[5] I write the following:

$$J_\alpha = \sum_\beta (-D_{\alpha\beta}{}^0 \partial C_\alpha/\partial x + D_{\alpha\beta}{}^1 \partial^3 C_\alpha/\partial x^3). \tag{2}$$

System (1) exhibits a *uniform steady-state* solution $(\overline{C}_i, \overline{C}_v, \overline{C}_s)$ the stability of which with respect to spatial concentration fluctuations is governed by the sign of the eigenvalues $\omega$ of the matrix

$$\underline{M} = -R\begin{pmatrix} \overline{C}_v & \overline{C}_i & 0 \\ \overline{C}_v & \overline{C}_i & 0 \\ 0 & 0 & 0 \end{pmatrix} - k^2\underline{D}, \tag{3}$$

where the elements of the diffusion matrix $\underline{D}$ are of the type

$$D_{\alpha\beta} = D_{\alpha\beta}{}^0 + k^2 D_{\alpha\beta}{}^1 \tag{4}$$

with $\alpha,\beta = i,v,s$. The $\omega$'s are solutions of the characteristic equation of $\underline{M}$ which may be written as

$$\omega^3 - \Sigma\omega^2 + P\omega - \pi = 0. \tag{5}$$

$\Sigma$, $P$, and $\pi$ are, respectively, the sum of the eigenvalues $\omega_p$ ($p = 1,2,3$), the sum of the double products $\omega_p\omega_q$, and the product $\omega_1\omega_2\omega_3$, which depend on $k^2$ [Eqs. (3) and (4)]. Solving Eq. (5) yields the dispersion curve $\omega(k)$ of the concentration modes in the system. As a result of the complexity of the solution, I focus on the long-wavelength (small-$k$) behavior of the concentration fluctuations by writing $\omega_p$ as a power expansion to fourth order in $k$. For centro-symmetric crystal structures one gets only even powers of $k$

$$\omega_p = \omega_{0p} + \omega_{1p}k^2 + \omega_{2p}k^4 + O(k^6). \tag{6}$$

On the other hand, the coefficients $\Sigma$, $P$, and $\pi$ in Eq. (5) may be rearranged as polynomials in $k^2$; one obtains

$$\Sigma = \Sigma_0 + \Sigma_1 k^2 + \Sigma_2 k^4, \tag{7a}$$

$$P = P_0 + P_1 k^2 + P_2 k^4 + P_3 k^6 + P_4 k^8, \tag{7b}$$

$$\pi = \pi_2 k^4 + \pi_3 k^6 + \pi_4 k^8 + \pi_5 k^{10} + \pi_6 k^{12}, \tag{7c}$$

where $\Sigma_j$ ($j = 0$ to 2), $P_j$ ($j = 0$ to 4), and $\pi_j$ ($j = 2$ to 6) are given by lengthy but straightforward expressions of $R$, $\overline{C}_i$, $\overline{C}_v$, $D_{\alpha\beta}{}^0$, and $D_{\alpha\beta}{}^1$. Taking advantage of Eqs. (6)–(7), and identifying the coefficients up to fourth order in $k$, gives the expressions of $\omega_{jp}$ ($j = 0$ to 2, $p = 1$ to 3) as functions of $R$, $\overline{C}_i$, $\overline{C}_v$, $D_{\alpha\beta}{}^0$, and $D_{\alpha\beta}{}^1$ ($\alpha, \beta = i, v, s$). The detailed expressions of $\omega_{jp}$ are too lengthy to be given here.[6] Such expressions might be used for numerical evaluation for specific diffusion models (i.e., once $D_{\alpha\beta}{}^0$ and $D_{\alpha\beta}{}^1$ are known as a function of $C_i$, $C_v$, and $C_s$). In this Letter, I rather discuss qualitative differences which are anticipated between the decomposition of solid solutions under irradiation and outside irradiation.

Outside the irradiation, for the sake of comparison, I still describe the state of the solid solution by Eqs. (1)–(2). At equilibrium, the fluxes vanish: The defect production rate outside irradiation, $G^0$, is therefore given by

$$G^0 = RC_i{}^0 C_v{}^0, \tag{8}$$

where $C_i{}^0$ and $C_v{}^0$ are the equilibrium vacancy and interstitial concentrations. The stability of the solid solution is still governed by the matrix $\underline{M}$ [Eq. (3)] where the defect concentrations are given by their equilibrium values $C_i{}^0$ and $C_v{}^0$. In metals outside irradiation, however, the self-interstitial concentration is vanishingly small. The matrix $\underline{M}$ therefore reduces to

$$\underline{M} = \underline{M}^0 = -k^2 \begin{pmatrix} D_{ii} + C_v{}^0 R/k^2 & 0 & 0 \\ D_{vi} + C_v{}^0 R/k^2 & D_{vv} & D_{vs} \\ D_{si} & D_{sv} & D_{ss} \end{pmatrix} \tag{9}$$

with $D_{\alpha\beta} = D_{\alpha\beta}{}^0 + k^2 D_{\alpha\beta}{}^1$. Indeed $D_{iv}$ and $D_{is}$ are proportional to $C_i$ and therefore vanish.

The structure of $\underline{M}^0$ shows that one of the three eigenmodes, say $\omega_3{}'$, has the decay rate

$$\omega_3{}' = -k^2 D_{ii} - C_v{}^0 R, \tag{10}$$

the associated eigenvector having $i$, $v$, and $s$ components. This mode is always stable ($D_{ii} > 0$, $C_v{}^0 R > 0$: $\omega_3{}' < 0$). The two next modes ($\omega_1{}'$ and $\omega_2{}'$) on the contrary are orthogonal to the "interstitial axis"; i.e., they describe fluctuations built of solute atoms and vacancies. These latter modes are indeed the eigenmodes of the submatrix $\underline{M}_v{}^0$,

$$\underline{M}_v{}^0 = -k^2 \begin{pmatrix} D_{vv} & D_{vs} \\ D_{sv} & D_{ss} \end{pmatrix} \tag{11}$$

which only implies the vacancy diffusion mechanism. Indeed in the limit $C_i{}^0 = 0$, $D_{ss}$ is a function of the vacancy properties only. The stability of the solid solution outside irradiation is therefore controlled by $\underline{M}_v{}^0$, as expected.

The same procedure as above yields the asymptotic expressions of $\omega_{0p}{}'$, $\omega_{1p}{}'$, and $\omega_{2p}{}'$ ($p = 1, 2$) as a function of $D_{vv}$, $D_{vs}$, $D_{sv}$, and $D_{ss}$.[6]

As can be seen by comparing Eqs. (3) and (11), the kinetics of concentration fluctuations under irradiation and outside irradiation are not controlled by the same set of parameters. Under irradiation, the amplification (or decay) rates $\omega_p$ are functions not only of the irradiation-enhanced thermal diffusion coefficients, but of parameters which are irrelevant outside irradiation: interstitial-implying diffusion coefficients, rate factor of the recombination reaction. This is a new illustration of the now well-recognized fact that irradiation does not simply enhance thermal processes.[3] Irradiation affects the kinetics of concentration fluctuations by increasing defect concentrations ($\overline{C}_i \gg C_i{}^0$, $\overline{C}_v \gg C_v{}^0$) and by increasing the ratio of interstitial to vacancy concentration: $C_i{}^0/C_v{}^0 \simeq \exp(-\Delta E_f/kT)$ while $\overline{C}_i/\overline{C}_v \simeq \exp(-\Delta E_m/kT)$,[7] where $\Delta E_f$ is the difference in formation energies of interstitials and vacancies ($\Delta E_f$ is several electronvolts in metals) and $\Delta E_m$ is the difference in migration energies ($\Delta E_m$ is less than one electronvolt in metals). As a consequence, apart from defect fluxes towards defect sinks, irradiation sustains a strongly biased recombination reaction ($R\overline{C}_i\overline{C}_v \gg RC_i{}^0C_v{}^0$), which affects solute concentration fluctuations via the nondiagonal terms of the diffusion matrix.

The detailed expressions of $\omega_{jp}$ and $\omega_{jp}{}'$ (Ref. 6) show the following:

(1) One concentration mode (which is irrelevant outside irradiation) has a negative amplification factor at the center of the Brillouin zone. Such a behavior was already noticed in crystals under irradiation[8] and more generally in Ginzburg-Landau-type reaction-diffusion systems.[9]

(2) The approximate shape of small-angle x-ray or neutron scattering (SANS) curves of irradiated solid solutions can be inferred from Eq. (6), since $\omega_p(k)$ are the inverse relaxation times (or amplification factors) of the amplitude of the concentration harmonics with wave vector $k$. In particular, provided that the power expansion in Eq. (6) holds for $k^2 \gg -\omega_{1p}/2\omega_{2p}$, the shape and location of the SANS peak of an irradiated solid solution may be predicted. The scattered intensity will peak at $k = k_M$, where

$$k_M{}^2 \simeq -\omega_{1p}/2\omega_{2p}, \qquad (12)$$

and peak will be narrower the higher the curvature of $\omega(k)$ at $k = k_M$. From Eqs. (6) and (12) we get that at $k = k_M$

$$\partial^2\omega_p/\partial k^2 = -4\omega_{1p}. \qquad (13)$$

In Eqs. (12) and (13) the index $p$ refers to the mode(s) with positive real amplification factors. Expressions similar to Eqs. (12) and (13) hold for the solid solution outside irradiation, with $\omega_{jp}'$ instead of $\omega_{jp}$.

As a consequence, the SANS curves obtained by Wagner, Poerschke, and Wollenberger[4] from irradiated NiCu alloys suggest that the following relationships are appropriate to their experimental conditions:

$$0 < -\omega_{1p}/2\omega_{2p} < -\omega_{1p}/2\omega_{2p}', \qquad (14a)$$

$$0 < \omega_{1p}' < \omega_{1p}. \qquad (14b)$$

(3) The smaller-wavelength behavior can be inferred from the term in $k^4$ in $\omega(k)$. Outside irradiation it is found that $\omega_{2p}'$ is nonzero only if $D_{\alpha\beta}'$ is finite. The short-wavelength behavior is therefore dictated by the contribution of the gradient energy to the chemical potential.[5] Under irradiation, this is no more the case: $\omega_{2p}$ does not vanish with $D_{\alpha\beta}'$. One therefore expects an alteration of the short-wavelength part of the SANS under irradiation as well.

(4) The possibility of time-periodic concentration fluctuations cannot be excluded. Indeed, the structure of $\omega_{12}$ and $\omega_{13}$ (Ref. 6) points to the possibility for $\omega_p$ [Eq. (6)] to be imaginary. This is reminiscent of recent experimental observations.[10] Interstitial loops were found to be continuously emitted from irradiation-produced fixed centers in NiCu alloys under electron irradiation: This implies a time-periodic variation of the interstitial and vacancy concentrations in the vicinity of these centers. The latter have been suggested to be Ni rich clusters.[10]

(5) A detailed analysis of the unstable eigenvectors of the $\underline{M}$ matrix would make it possible to predict whether the decomposition of the solid solution points to solute or to point-defect clustering.[2]

A numerical analysis of the implications of the above equations would be very interesting but is beyond the scope of this Letter.

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