Phase stability under irradiation: Ballistic effects

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We propose a simple mean-field description of solid solutions in the presence of irradiation-induced atomic mixing. The equilibrium configuration of the system is described by a concentration profile which is a steady-state solution of the appropriate diffusion equation. For clustering solid solutions, we show that a Lyapunov functional may be built, the minimum of which yields the equilibrium configuration. In a simple case (regular solution in the Bragg-Williams approximation together with simplifying assumptions on the concentration dependence of the diffusion coefficients), a law of corresponding states is found: The equilibrium configuration of the solid under irradiation flux ϕ and temperature T is identical to the configuration at $\phi = 0$ and $T' = T(1+\Delta)$ where Δ has a simple expression in terms of the irradiation parameters and of material characteristics. As a prototype of ordering solid solutions, the Bragg-Williams approximation of the $B2$ structure is treated. A Lyapunov function is found; the above law of corresponding configurations is checked numerically and found to be obeyed fairly precisely. With the above law taken as a guide, interesting features are anticipated. In particular, we speculate on the possibility for obtaining equilibrium between an amorphous and a crystalline phase, the latter being a long-range-ordered or random solid solution.

I. INTRODUCTION

Phase stability under irradiation is a fascinating problem which has received long-standing attention,[1] motivated both by its intrinsic interest and its relevance in several technological problems such as the integrity of structural materials of the core components of nuclear reactors, the long-term integrity of nuclear-waste confinement materials, and alloy preparation by ion implantation or ion-beam mixing. It was recognized very early that, apart from ionization processes which may be neglected in metallic systems, irradiation may destroy precipitates,[2] disorder long-range-ordered compounds,[3] amorphize crystalline solids,[4] or accelerate sluggish phase transformations.[5] More recently, it was discovered that irradiation may additionally induce precipitation in undersaturated solid solutions.[6(a)] The latter effect has stimulated a large body of experimental and theoretical work during the last decade.[6(b)]

As far as theory is concerned, we are faced with many models which lack universality. Surprisingly enough, the theory of irradiation-induced precipitation (IIP) is the least *ad hoc* one; indeed, it has been recognized that IIP corresponds to a specific branch of solutions of the general equations of the chemical-rate theory of alloys under irradiation.[7] For specific cases, the above equations (of the diffusion-reaction type) may be written under various forms:[7,8] They all describe, with various levels of sophistication, the coupled diffusion of defects and solute atoms, and the elimination of defects either by mutual recombination or at point-defect sinks.

In contrast, the theories of irradiation-induced— precipitate dissolution,[9] or irradiation-induced disordering,[10,3(g)] or amorphization[11] lack universality. Indeed, they all rest on the idea that the steady-state configuration of the system under irradiation is such that the disordering effects of irradiation (hereafter called ballistic effects) are equilibrated by irradiation-enhanced diffusion back to the equilibrium state. This idea, however, is applied locally, e.g., on a precipitate (which shrinks due to solute ejection toward the matrix and grows because of rapid diffusion of the solute back to the precipitate) or on an amorphous zone (which is assumed to be produced at the core of a displacement spike and to anneal by amorphous-crystal—interface migration). More sophisticated models[12] consider the equilibrium between a precipitate, the degree of long-range order of which is altered by irradiation, and the matrix: irradiation-sustained disorder in the precipitate would induce precipitate resolution in the supersaturated solid solution.

The striking feature of this set of models is their lack of generality: their common basic idea has been applied so locally (precipitate, amorphous zone, etc.) that no general behavior of an alloy under irradiation may be anticipated.

The purpose of this paper is to reformulate the theory of ballistic effects on phase stability in a more universal way and therefore allow for some general predictions.

The leading idea of the paper is that the competition between irradiation-induced mixing and irradiation-enhanced diffusion back to low-energy configurations should be modeled for the configuration of the alloy as a whole and not locally as just mentioned. The technique we use is to describe the equilibrium configuration under irradiation as a solute concentration profile which is a steady-state solution of the appropriate solute diffusion equation. The search for such a solution rests on various techniques. In the case of unmixing systems we will be able to build a Liapunov functional for the problem and find the equilibrium solution in terms of the extremals of

this functional.[13] In the case of ordering systems, we instead directly solve a simple model. The remarkable fact is that, in both cases, under not too restrictive conditions, ballistic effects result in a law of corresponding states: The equilibrium configuration of a solid-solution model under irradiation at temperature T and flux ϕ is the configuration the system would have outside irradiation ($\phi=0$) at a temperature $T'=T(1+\Delta)$, the dilatation Δ being a function of the irradiation flux and temperature as well as of materials parameters. Other results are found, such as the possibility of stabilizing exotic phases by irradiation.

In the following, we first describe the phenomenological model we use to describe the contribution of ballistic effects to interdiffusion (Sec. II), then study mixing and unmixing in the presence of such effects (Sec. III), and later ordering and disordering (Sec. IV). Finally (Sec. V), we extend the results of Secs. III and IV in a more speculative way to other phase transformations, e.g., equilibrium between ordered and disordered phases, or between amorphous and crystalline phases.

II. PHENOMENOLOGICAL MODEL FOR BALLISTIC DIFFUSION

Since we are going to look for steady-state solutions of the diffusion equation in the presence of ballistic diffusion, let us first derive a balance equation for the number density $n_i(x)$ of the ith component ($i=1,2$) when ballistic jumps only occur. For the sake of simplicity we restrict ourselves to a one-dimensional problem. Following Collins,[14] we write

$$\frac{\partial n_i(x)}{\partial(\phi t)} = \int dz [n_i(x-z)F_i(x-z,z) - n_i(x)F_i(x,z)], \quad (1)$$

where $F_i(x,z)$ is the probability density that an atom i can be ejected from x to a site located between $x+z$ and $x+z+dz$ per incident particle, and ϕ is the irradiation flux. Performing a Taylor expansion of the right-hand side (rhs) of Eq. (1) yields

$$\frac{\partial n_i(x)}{\partial t} = \frac{\partial^2}{\partial x^2} \mathscr{D}_i^{(2)} n_i) + \cdots, \quad (2)$$

where $\mathscr{D}_i^{(2)}$ is the second moment of $\phi F_i(x,z)$, i.e.,

$$\mathscr{D}_i^{(2)} = \tfrac{1}{2}\phi \int z^2 F_i(x,z) dz. \quad (3)$$

In Eq. (2) we retained only even moments of F_i, which implies that irradiation is assumed to be isotropic, a reasonable assumption for cascade-producing irradiations. Stopping the expansion to second order implies short-range replacements.

In the particular case where the probability for an atom to be ejected a distance z away is independent of the local environment (composition and atomic structure), F_i is a function of z only, and Eq. (2) reduces to the simple form

$$\frac{\partial n_i(x)}{\partial t} = -\mathrm{div}J_i, \quad J_i = -\mathscr{D}_i \frac{\partial n_i(x)}{\partial x} \quad (4)$$

where $\mathscr{D}_i$ is the ballistic diffusion coefficient of species i defined by Eq. (3) with $F_i(x,z)=F_i(z)$.

Equation (4) describes the ballistic flux of species i with

respect to the lattice. If the ballistic diffusion coefficients of species 1 and 2 ($\mathscr{D}_1$ and $\mathscr{D}_2$) are not equal, matter will accumulate at certain points of the lattice; this will result, we assume, in dislocation climb, i.e., in a movement of the lattice with respect to the laboratory frame of reference. If we assume dislocation climb to be isotropic, no void to nucleate, and equal atomic volumes for species 1 and 2, the flux of say, species 2 in the laboratory, is

$$J^B = J_2 - n_2 N_v^{-1}(J_1 + J_2), \quad (5a)$$

$$J^B = [c\mathscr{D}_1 + (1-c)\mathscr{D}_2] \left[-N_v \frac{\partial c}{\partial x} \right], \quad (5b)$$

where c is the atomic fraction of species 2 and N_v is the number of atoms per unit volume. Equations (5) have the structure of a chemical-diffusion equation,[15] and we define, by analogy, the "ballistic chemical-diffusion coefficient" $\tilde{\mathscr{D}}_B$ by

$$J^B = -\tilde{\mathscr{D}}_B N_v \frac{\partial c}{\partial x}, \quad \tilde{\mathscr{D}}_B = c\mathscr{D}_1 + (1-c)\mathscr{D}_2. \quad (6)$$

The above phenomenology rests on a continuum description of the solid. It therefore does not correctly describe the evolution of concentration profiles which vary rapidly with distance, such as concentration modulations in an ordered structure. For such cases, we propose a discrete version of Eq. (1),

$$\frac{\partial c_i(p)}{\partial t} = \gamma_i \sum_{p'} [b_i(p-p',p)c_i(p-p') - b_i(p,p-p')c_i(p)], \quad (7)$$

where p labels the lattice sites, γ_i is the ballistic jump frequency of species i, $c_i(p)$ is the atomic fraction of species i on site p, and $b_i(p-p',p)$ is the a priori probability that a jump starting from site $p-p'$ will stop at site p. In writing Eq. (7), γ_i was assumed to be independent of local composition. Assuming, as before, that b_i is neither dependent on local composition nor on the direction of the jumps, Eq. (7) becomes

$$\frac{\partial c_i(p)}{\partial t} = \sum_{m=0}^{\infty} \gamma_i b_i(m)[-2c_i(p) + c_i(p+m) + c_i(p-m)]. \quad (8)$$

Equation (8) is written in the lattice frame of reference. We show, in Appendix A, that in the case of an almost uniform concentration $\bar{c}$ (e.g., initial stage of ordering), Eq. (8) may be written in the laboratory frame of reference as

$$\frac{\partial c(p)}{\partial t} \simeq \sum_{m=0}^{\infty} \tilde{\Gamma}_B(m)[-2c(p) + c(p+m) + c(p-m)], \quad (9a)$$

where $c(p)$ is the concentration of species 1 on site p, with

$$\tilde{\Gamma}_B(m) = (1-\bar{c})\gamma_2 b_2(m) + \bar{c}\gamma_1 b_1(m). \quad (9b)$$

$\tilde{\Gamma}_B(m)$ may be called a partial ballistic jump frequency for chemical mixing. The meaning of $\tilde{\Gamma}_B(m)$ appears if we Fourier-transform Eq. (9a). Setting

$$c(k) = \sum_{p=-\infty}^{+\infty} e^{ikp} c(p) \quad (10a)$$

yields

$$\frac{\partial c(k)}{\partial t} = -c(k) \sum_{m=0}^{\infty} \{2\tilde{\Gamma}_B(m)[1-\cos(mk)]\} \ . \quad (10b)$$

In the long-wavelength limits of the concentration waves $(k \rightarrow 0)$, the summation on the rhs of Eq. (10b) reduces to

$$k^2 \sum_{m=0}^{\infty} \tilde{\Gamma}_B(m)m^2 \ ,$$

i.e., $k^2 \tilde{\mathscr{D}}_B/a^2$, according to Eqs. (3) and (6), a being the lattice parameter. Equation (10b) is reminiscent of the diffusion equation used by Cook et al.[16] for describing the early stages of ordering outside irradiation, with the complication in Eq. (10b) resulting from the spectrum of ballistic jump distances. As an example, simple numerical evaluation of the rhs of Eqs. (10) shows that Fick's law [Eq. (4)] fails to describe the time evolution of harmonics with wavelengths shorter than 15 lattice parameters when ballistic jumps occur to third-nearest neighbors. As will be seen in Sec. IV, the structure of the rhs of Eq. (10b) has far-reaching consequences on the stability of ordered compounds under irradiation.

III. SOLUBILITY LIMIT IN THE PRESENCE OF BALLISTIC EFFECTS

In this section we first present the method to be used, then discuss the specific case of the regular solid-solution model, and finally discuss general features of the results.

A. General method

We want to build a diffusion equation which describes atomic interdiffusion under the influence of two driving forces: atomic collisions and thermodynamic forces. For the sake of simplicity we assume that the interdiffusion flux is simply the sum of the ballistic flux [Eq. (6)] and the diffusion flux driven by the gradient of chemical potential. Following Cahn,[17] we write the latter flux as

$$J_B^{\text{th}} = -MN_v \left[f'' \frac{\partial c}{\partial x} - 2\kappa \frac{\partial^3 c}{\partial x^3} \right] \ . \quad (11)$$

In Eq. (11), f'' is the second derivative, with respect to concentration, of the free energy per atom, in a system of uniform concentration c, κ is the gradient energy (positive for an unmixing system), and M is the atomic mobility[18] given by

$$M = \frac{c(1-c)}{k_B T}[cD_1^* + (1-c)D_2^*] = \frac{c(1-c)}{k_B T}\tilde{D} \ , \quad (12)$$

where D_1^*, D_2^*, and $\tilde{D}$ are, respectively, the tracer-diffusion coefficients of species 1 and 2 and the chemical-diffusion coefficient.[15] As in Sec. II, c is the atomic fraction of species 2.

The total diffusion flux can be written as

$$J = J^{\text{th}} + J^B \ , \quad (13a)$$

$$J = -MN_v \left[\left[f'' + \frac{\tilde{\mathscr{D}}_B}{M} \right] \frac{\partial c}{\partial x} - 2\kappa \frac{\partial^3 c}{\partial x^3} \right] \ , \quad (13b)$$

where Eq. (6) has been used for J^B. Indeed, Eq. (6) is the continuum description of ballistic effects and is consistent with the continuum description of thermal diffusion [Eq. (11)].

The equilibrium configuration of the solid solution under irradiation is the concentration profile c(x) which yields no flux of matter: J=0 in Eq. (13b). It will now be argued that such a concentration profile may be found from an extremum principle.

Indeed, let us define an effective free-energy density $\varphi(c)$ such that

$$\varphi''(c) = f'' + \frac{\tilde{\mathscr{D}}_B}{M} = f'' + \frac{k_B T}{c(1-c)} \frac{\tilde{\mathscr{D}}_B}{\tilde{D}} \ . \quad (14)$$

It is shown in Appendix B that the functional $\tilde{F}\{c(x)\}$, defined by

$$\tilde{F}\{c(x)\} = N_v \int \left[\varphi(c) + \kappa \left[\frac{dc}{dx} \right]^2 \right] dx \ , \quad (15)$$

is a Liapunov functional for the diffusion equation

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \ , \quad (16)$$

where J is given by Eq. (13b) together with the condition of matter conservation in the solid (closed system). The demonstration in Appendix B parallels that given by Cahn and Hilliard for the case of thermal diffusion.[19] Indeed, $\tilde{F}$ in Eq. (15) has the following properties.

(a) Under steady-state conditions in a closed system [$J=0$; Eq. (13)], the functional derivative of $\tilde{F}$, $\delta\tilde{F}/\delta c$, is uniform through the system,

$$\frac{\delta\tilde{F}}{\delta c} = N_v \left[\varphi' - 2\kappa \frac{\partial^2 c}{\partial x^2} \right] = \mu \ . \quad (17)$$

(b) The condition $\delta\tilde{F}/\delta c = \mu$ is the condition for $\tilde{F}$ [Eq. (15)] to be an extremum with the constraint of conserved matter in the system.

(c) $\tilde{F}$ in Eq. (15) is a decreasing function of time whenever the flux J [Eq. (13b)] is nonzero.

(d) Under steady-state conditions, the compositions of the coexisting phases are given by the rule of the common tangent applied to the function $\varphi(c)$.

The above four properties demonstrate that the function $\varphi(c)$ plays, under irradiation, exactly the same role as $f(c)$ plays outside irradiation in defining the equilibrium configuration. We shall take advantage of this property throughout this paper. We thus justify the denomination of φ as an effective free energy. Of course, $\varphi(c)$ is defined to within a linear term $(ac+b)$ to be determined by some physical conditions at specific concentrations (see below). It should be noticed that the abscissas of the contact points of the common tangents to $\varphi(c)$ are not affected by the above linear term.

As shown by Eq. (13), irradiation affects the solute fluxes in two ways: (i) via the ballistic effects on one hand [$\tilde{\mathscr{D}}_B$ in Eq. (13)], and (ii) via the irradiation-sustained point-defect supersaturation which increases the mobility M on the other. Indeed, M is proportional to the tracer-diffusion coefficients in the alloy [Eq. (12)]: It is expected

to be proportional to the vacancy supersaturation,

$$M(\phi,T) \propto M(0,T)c_v(\phi,T)/c_v(0,T) , \tag{18}$$

where $c_v(\phi,T)$ is the vacancy atomic fraction at irradiation flux and temperature, equal to ϕ and T, respectively. More precisely, Eq. (14) reveals the following consequences of ballistic effects.

(1) The critical temperature (as predicted by this mean-field theory) is depressed. Indeed, at the critical point outside irradiation, $f''(c)=0$, but $\varphi''(c)$ is positive according to Eq. (14), i.e., the solution is supercritical under irradiation. At the critical point under irradiation ($\varphi''=0$), f'' is negative according to Eq. (14), i.e., the temperature is lower than the critical temperature outside irradiation.

(2) The same argument applies to the spinodal curve, which is a well-defined curve in the simple theories we use here: The spinodal is shifted to lower temperatures by ballistic effects.

(3) The lower the temperature, the smaller M is in Eq. (14), since $\tilde{\mathscr{D}}$ in Eq. (12) decreases as $e^{-E/k_B T}$ and the defect concentration saturates in Eq. (18). The second term on the rhs of Eq. (14) may become so large at sufficiently low temperatures that ballistic effects will stabilize the single-phase solid solution (irradiation-induced—precipitate dissolution).

In order to reach more precise conclusions, we need specific expressions for $f(c)$ and $\tilde{D}(c)$. We examine a very simple model in more detail in the next subsection.

B. Regular solution with constant $\mathscr{D}_B/\tilde{D}$

The simplest model we can think of is a regular solution model for which

$$f(c)=\omega c(1-c)+k_B T[c \ln c +(1-c)\ln(1-c)] \tag{19a}$$

and

$$f''(c)=-2\omega+k_B T/c(1-c) , \tag{19b}$$

where ω is the ordering energy. Let us also assume that $\mathscr{D}_B/\tilde{D}$ [Eq. (14)] is independent of c in the range of interest ($0 \le c \le 1$).

The effective free energy per atom $\varphi(c)$ is obtained by integrating Eq. (14) twice with respect to c. As boundary conditions, we impose $\varphi=f$ for $c=0$ and 1 since no chemical mixing can occur in the pure matrices. We obtain

$$\varphi(c)=\omega c(1-c)+ k_B T \left[1+\frac{\mathscr{D}_B}{\tilde{D}}\right]$$

$$\times [c \ln c +(1-c)\ln(1-c)] . \tag{20}$$

The interpretation of Eq. (20) is straightforward: ballistic effects increase the configurational entropy; they are equivalent to a rise in temperature.

Equation (20) gives the following law of corresponding states: *The equilibrium configuration of the solid solution at temperature T under an irradiation flux which fixes the value of $\mathscr{D}_B/\tilde{D}$ to Δ is the configuration that the same solid solution would have outside irradiation at a temperature*

$$T'=T(1+\Delta) , \tag{21}$$

with

$$\Delta=\mathscr{D}_B/\tilde{D} . \tag{22}$$

It should be kept in mind that Δ is a function of the irradiation flux and temperature.

The relative temperature shift Δ may be estimated very simply. The balance equations for irradiation-induced vacancies and interstitials are, at low temperature,

$$\frac{\partial c_\alpha}{\partial t}=G-Rc_ic_v-k^2 D_\alpha c_\alpha , \tag{23}$$

where $\alpha=i$ or v, G is the Frenkel-pair production rate, R is the recombination factor

$$R=4\pi r_c(D_i+D_v)N_v , \tag{24}$$

k^2 is the sink strength, and D_α is the α defect diffusion coefficient. In Eq. (24), r_c is the recombination radius. Under steady-state conditions ($D_ic_i=D_vc_v$) and at sufficiently low temperatures, for mutual recombination to be the dominant defect-recovery mechanism, the vacancy concentration is such that

$$c_v \simeq \left[\frac{G}{N_v 4\pi r_c D_v}\right]^{1/2} . \tag{25}$$

The irradiation-enhanced chemical-diffusion coefficient may be approximated by

$$\tilde{D}_{\text{irr}} \simeq \tilde{D}(c_v/c_v^0) , \tag{26}$$

and Δ [Eq. (22)] may be approximated by

$$\Delta \simeq \frac{\phi \sigma_r b^2}{\tilde{D}(T,\phi=0)}c_v^0 \left[\frac{4\pi r_c D_v N_v}{\phi \sigma_d}\right]^{1/2} , \tag{27}$$

$$\Delta \simeq \frac{c_v^0(T)}{\tilde{D}(T,\phi=0)}(\phi D_v)^{1/2}g , \tag{28}$$

with the geometric factor g given by

$$g=\sigma_r b^2 \left[\frac{4\pi r_c N_v}{\sigma_d}\right]^{1/2} . \tag{29}$$

In Eqs. (27) and (29), σ_r is the replacement cross section, i.e., the number of atoms which change position per unit dose; σ_d is the displacement cross section, i.e., the number of vacancies generated per unit dose; b^2 is the average length of ballistic jumps; and ϕ is the irradiation flux. If we assume $\tilde{D}$ to be thermally activated (which holds in a limited temperature interval[20]), then Δ has the following temperature dependence:

$$\Delta=\Delta_0 e^{E_\Delta/k_B T} , \tag{30a}$$

$$E_\Delta=E_{\tilde{D}}-E_F-E_m/2 \simeq E_m/2 , \tag{30b}$$

where $E_{\tilde{D}}$, E_F, and E_m are, respectively, the activation energies for chemical diffusion, vacancy formation, and vacancy migration. Since $E_{\tilde{D}}$ is of the order of E_F+E_m, E_Δ is positive in Eq. (30b) and Δ is a decreasing function of temperature as expected: Indeed, the higher the temperature, the higher the configurational entropy and the

weaker the contribution of ballistic jumps to the disorder of the solid solution.

Figure 1 represents typical variations of T' as a function of T for reasonable parameter values: At high temperatures, $T' \simeq T$, while at low temperature, T' increases abruptly. The v shape of the curve $T'(T)$ has a very important practical consequence: thermal-equilibrium configurations at temperatures T lower than T'_m, the minimum value of T', cannot be reached under irradiation. The steady-state configurations to be reached under irradiation correspond to the equilibrium configurations at temperatures larger than T'_m (cf. Fig. 1). Moreover, at lower and lower temperatures, T' increases and may overcome the thermal-solvus temperature at the concentration of the solid solution. This simple model therefore accounts for irradiation-increased solubility. Figure 2 is a schematic representation of the solvus under irradiation as deduced from the thermal solvus using Eq. (21),

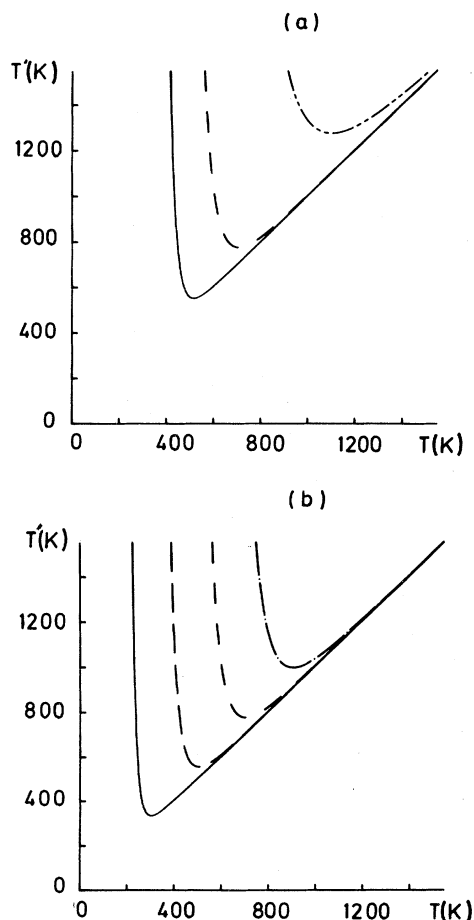$$T^{irrad}_{solvus} = T^{thermal}_{solvus} / [1 + \Delta(T^{irrad}_{solvus})] .$$ (31)

FIG. 1. Equivalent temperature T' as a function of irradiation temperature for (a) a fixed value of E_Δ (0.7 eV) and various values of Δ_0 (——, 10^{-8}; — — —, 10^{-6}; —··—··—··, 10^{-4}), and (b) for $\Delta_0 = 10^{-6}$ and various values of E_Δ (——, 0.3 eV; — — —, 0.5 eV; — — —, 0.7 eV; —·—·—·, 0.9 eV).
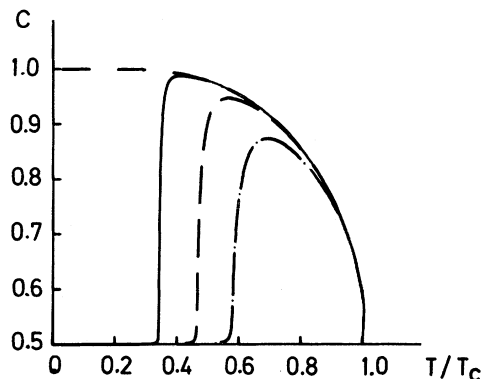

FIG. 2. Solubility limit C under irradiation in the Bragg-Williams approximation. C is the solution of the implicit equation

$$C = \{1 + \exp[(2 - 4C)T_c / T']\}^{-1} ,$$

where T' is given by Eq. (21) with $E_\Delta = 0.7$ eV and various values of Δ_0 (——, 10^{-8}; — — —, 10^{-6}; —·—·—·, 10^{-5}). $T_c = 1250$ K.

C. More general cases

The above procedure may be applied to less restrictive cases, i.e., nonregular $f(c)$- and c-dependent $\mathscr{D}_B / \tilde{D}$ in Eq. (14). Each case, however, must be dealt with separately, and such an exercise is beyond the scope of this paper.

One should, however, notice that, due to the similarity of the diffusion equation (13b) with the standard form (11), precipitates under irradiation should behave much in the same way as outside irradiation, namely, precipitates should grow in supersaturated solid solutions or shrink in undersaturated solid solutions: The solubility limit is simply shifted by irradiation. The ballistic effects, as described here, provide no mechanism by which a precipitate should reach a steady-state size under irradiation. This conclusion is at variance with existing models of ballistic effects on precipitate size.[9] We think that the latter models omitted the contribution of ballistic jumps to solute diffusion in the matrix. As far as we are aware, experimental evidence for the occurrence of such a stable size is rare.[21] A stable size might result from effects not taken into account here, such as a strong concentration dependence of ballistic diffusion coefficients, or inhomogeneity of the defect recombination process (e.g., at a precipitate-matrix interface), or strong solute-defect fluxes coupling. Such effects deserve further study.

IV. ORDER-DISORDER REACTION UNDER IRRADIATION

The results obtained in the preceding section may be extended to the order-disorder reaction under irradiation, and it is to be expected that, at least for model systems described in the Bragg-Williams approximation, the steady-state value of the long-range-order parameter under irradiation as a function of temperature has the same shape as the solubility limit depicted in Fig. 2. In

this section, however, we treat two different problems in some detail: the steady-state value of the long-range-order parameter under irradiation, for an initially-ordered solid solution, and the spinodal ordering kinetics under irradiation, for an initially fully disordered solid solution.

A. Steady-state value of the long-range-order parameter

Several kinetic treatments of the problem are available.[10,3g] Here we present a simple new treatment which parallels that for unmixing. For the sake of simplicity, we deal with the $B2$ crystal structure in the Bragg-Williams approximation.

Let us call Γ_α (Γ_β) the frequency at which B atoms leave the α sublattice towards the β one (the β sublattice towards α), Γ_B the frequency of ballistic jumps between sublattices α and β, and c_α and c_β the atomic fraction of B atoms on sublattices α and β. With the above notations, S being the long-range-order parameter, the following relations hold:

$$c_\alpha + c_\beta = 1 , \tag{32a}$$

$$S = 2c_\alpha - 1 = 1 - 2c_\beta . \tag{32b}$$

Outside irradiation, we may write the following balance equation for, say, c_α:

$$\frac{dc_\alpha}{dt} = -\mathfrak{z}\Gamma_\alpha c_\alpha + \mathfrak{z}\Gamma_\beta c_\beta , \tag{33}$$

while under irradiation, a ballistic term should be added,

$$\frac{dc_\alpha}{dt}\bigg|_B = \mathfrak{z}\Gamma_B(-c_\alpha + c_\beta) . \tag{34}$$

Indeed, Eq. (34) simply states that ballistic mixing tends to make the composition between the two sublattices uniform. $\mathfrak{z}$ in Eqs. (33) and (34) is the number of nearest neighbors.

In Eq. (33), Γ_α and Γ_β are obviously functions of the degree of long-range order. As shown in Appendix C,

$$\Gamma_\beta/\Gamma_\alpha = e^{\omega S/k_B T} , \tag{35}$$

where ω is the ordering energy: $\omega = 2k_B T_c$ where T_c is the critical temperature.

The equilibrium value of the long-range-order parameter is given by the solution of the implicit equation (Appendix C)

$$S = \tanh(ST_c/T) . \tag{36}$$

Under irradiation, the same procedure now gives S as the solution of the implicit equation (cf. Appendix C)

$$S = \sinh(ST_c/T)/[\cosh(ST_c/T) + \Gamma_B/\Gamma] , \tag{37}$$

where Γ is defined as an average thermal jump frequency,

$$\Gamma = (\Gamma_\alpha \Gamma_\beta)^{1/2} . \tag{38}$$

Since the S dependence of the jump frequencies is only specified by Eq. (35), i.e., as a constraint on the ratio $\Gamma_\beta/\Gamma_\alpha$, Γ in Eq. (38) may be chosen as S independent. As in the preceding section, for the chemical-diffusion coefficient $\tilde{D}$, we write the irradiation-enhanced average

jump frequency $\Gamma(T,\phi)$ as

$$\Gamma(T,\phi) = \Gamma(T,0)c_v/c_v^0 , \tag{39}$$

and Γ_B/Γ in Eq. (37) is written as Δ in Eqs. (27) and (28) with Γb^2 instead of $\tilde{D}$ in the denominator,

$$\Gamma_B/\Gamma = g'(c_v^0/\Gamma)(\phi D_v)^{1/2} , \tag{40}$$

with

$$g' = \sigma_r \left[\frac{4\pi r_c}{\Omega \sigma_d} \right]^{1/2} . \tag{41}$$

Unlike in the simplified unmixing problem dealt with in the preceding section, we cannot reduce ballistic effects to a temperature dilatation with a simple expression for the dilatation coefficient. However, Eqs. (36) and (37) have been solved numerically. The result is shown in Fig. 4 for various values of Γ_B/Γ including $\Gamma_B/\Gamma = 0$. From Fig. 3, a law of corresponding states similar to that established for the unmixing case (Sec. III) may be constructed numerically, i.e., the long-range-order—parameter value at temperature T and irradiation flux ϕ *equals that at a temperature T' under zero irradiation flux.* The relationship $T'(T)$ deduced from Fig. 3 is depicted in Fig. 4. As can be seen, Eq. (21) gives the correct form for this law. However, Δ in Eq. (21) is not equal to Γ_B/Γ. For $\Gamma_B/\Gamma = 10^{-6}e^{+0.7/k_B T}$, for instance, we find, from Figs. 3 and 4, $\Delta = 5.3 \times 10^{-6}e^{+0.61/k_B T}$. Conversely, setting $\Delta = \Gamma_B/\Gamma$ and computing S from Eq. (36) with $T' = (1+\Delta)T$ instead of T on the rhs of Eq. (36) gives an S-versus-T curve which is very close to the correct one (Fig. 3). Indeed, the two curves superimpose except in the narrow temperature range where the almost vertical part of $S(T)$ at low T connects to the thermal-equilibrium curve $S(T)$. Even in this region, the deviation is small, as depicted in Fig. 3. Therefore the law of corresponding configurations as stated for the unmixing case is approximately followed.

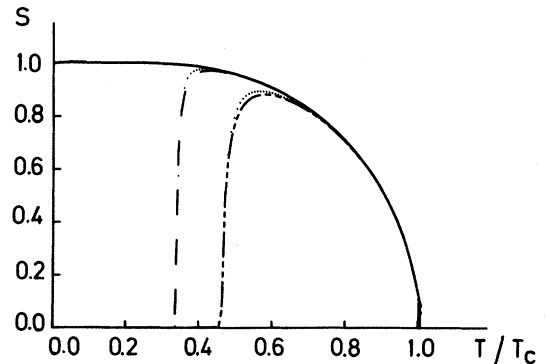There is still a difference in the degree of sophistication

FIG. 3. Steady-state long-range-order—parameter values for various γ_0 and E_γ in $\Gamma_B/\Gamma = \gamma_0 e^{E_\gamma/k_B T}$, and $T_c = 1250$ K, computed either from Eq. (37) or (36) with T' instead of T, where T' is given by Eq. (21) with $\Delta = \Gamma_B/\Gamma$. $\gamma_0 = 10^{-8}$ and $E = 0.7$ eV, — — — [Eq. (37)] and $\cdots$ [Eqs. (36) and (21)]. $\gamma_0 = 10^{-6}$ and $E = 0.7$ eV, — $\cdot\cdot$ — $\cdot\cdot$ — $\cdot\cdot$ [Eq. (37)] and $\cdots$ [Eqs. (36) and (21)].
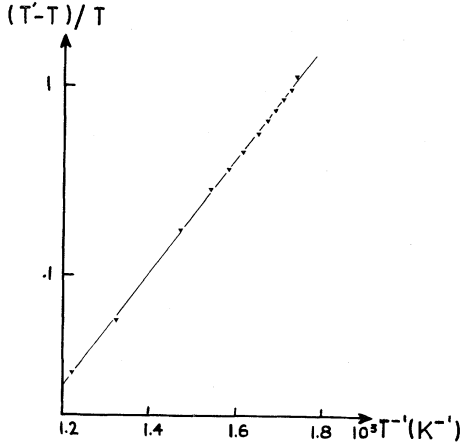
FIG. 4. Temperature dilatation $\Delta = (T' - T)/T$ vs $1/T$ as measured in Fig. 4 for $\Gamma_B/\Gamma = 10^{-6}e^{0.7/k_BT}$ and S computed from Eq. (37). Least-squares fit yields $\Delta = 5.3 \times 10^{-6}e^{0.61/k_BT}$.

for the descriptions we just gave of unmixing and ordering systems. In the general unmixing problem (Sec. III A), we have proposed a Lyapunov functional for the problem, $\tilde{F}$ [Eq. (15)], which plays the role that the free-energy functional plays outside irradiation. In Appendix D we propose a Lyapunov function $\varphi(S)$ for the ordering problem, i.e., we give the expression of $\varphi(S)$ such that φ decreases with time if S is not a steady-state solution of the balance equation under irradiation [Eqs. (D1) and (D2)] and φ is minimum for S values which are stable steady-state solutions of the latter (and respectively maximum for unstable steady states). Unlike in the unmixing case, however, the function $\varphi(S)$ does not reduce to the free energy when ballistic effects are suppressed. The function $\varphi(S)$ may, however, be useful in discussing the relative stability of various ordered structures under irradiation.

B. Spinodal ordering under irradiation

We now consider the kinetics of ordering of a fully disordered solid solution, under conditions where the ordered structure develops homogeneously rather than by domain growth.[16] We follow the phenomenology by Cook, de Fontaine, and Hilliard,[16] according to whom the rate of growth (or decay) of the amplitude of a concentration wave of wave vector $\vec{k}$ is given by

$$\alpha(k) = -M[K(k)]^2\{f_{\overline{c}}'' + 2\kappa[K(k)]^2\} . \tag{42}$$

In Eq. (42), $f_{\overline{c}}''$ is the second derivative of the free-energy density with respect to concentration, evaluated at the average alloy concentration, M is the atomic mobility as defined by Eq. (12), κ is the gradient energy (negative for an ordering system), and K is given by

$$K(k) = [2(1 - \cos k)]^{1/2}/a , \tag{43}$$

with a the lattice parameter and $k = 2\pi a/\lambda$ with λ the wavelength of the concentration wave. The presence of K^2 instead of k^2 in Eq. (42) comes from the fact that here we are dealing with the time evolution of concentration

waves with a wavelength not much larger than the lattice parameter.

Ballistic effects will add a negative contribution to the rhs of Eq. (42). In order to be consistent with Eqs. (42) and (43), ballistic diffusion must be described by Eq. (9a).

As shown in Eq. (10b), the decay rate of concentration waves due to ballistic effects is

$$\alpha_B(k) = -\sum_m \tilde{\Gamma}_{(m)}^B\{2[1 - \cos(km)]\} . \tag{44}$$

Combining Eqs. (42) and (44), the growth (or decay) rate of concentration waves under irradiation is

$$\alpha_{\text{tot}}(k) = -MK^2(\varphi_{\overline{c}}'' + 2\kappa K^2) , \tag{45}$$

with

$$\varphi_{\overline{c}}'' = f_{\overline{c}}'' + \frac{k_BT}{\overline{c}(1-\overline{c})} \frac{\sum_m \tilde{\Gamma}^B(m)[1 - \cos(km)]}{\tilde{\Gamma}(1 - \cos k)} , \tag{46}$$

where the notation $\tilde{\Gamma} = \tilde{D}/a^2$ has been used.

In Eqs. (45) and (46), M and $\tilde{\Gamma}$ are to be understood as the radiation-enhanced mobility and jump frequency, as in Sec. III.

Simple examination of Eqs. (45) and (46) reveals the following features.

(i) Ballistic effects oppose spinodal ordering: Indeed, in ordering systems, $f_{\overline{c}}'' > 0$, and as shown by Eqs. (45) and (46), $\varphi_{\overline{c}}''$ is larger than $f_{\overline{c}}''$. The driving force for the growth of concentration waves is decreased. For appropriate parameter values, it may be cancelled $(\varphi_{\overline{c}}'' + 2\kappa K^2 = 0)$.

(ii) The above effect is wave-vector dependent as soon as ballistic jumps are not restricted to nearest-neighbor sites. As shown in Fig. 5, second-nearest-neighbor ballistic jumps contribute weakly to the erosion of short-wavelength harmonics $(k \gtrsim 0.8)$; third-nearest-neighbor ballistic jumps have no effect at all on $k = \frac{2}{3}$ harmonics, etc. The above mechanism may contribute to the higher resistance to ballistic effects of the short-range-ordered
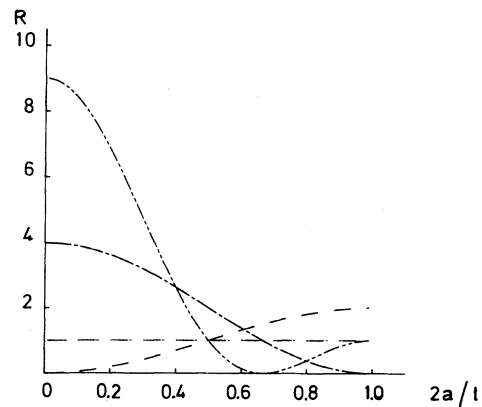

FIG. 5. Wave-number dependence of the relative ballistic contributions to the decay rate of concentration waves, for various ballistic jump distances: ———, first-nearest neighbor (NN); —·—·—·, second NN; —··—··—··, third NN. The short-dashed curve (— — —) corresponds to the amplification rate resulting from the gradient-energy term κ.
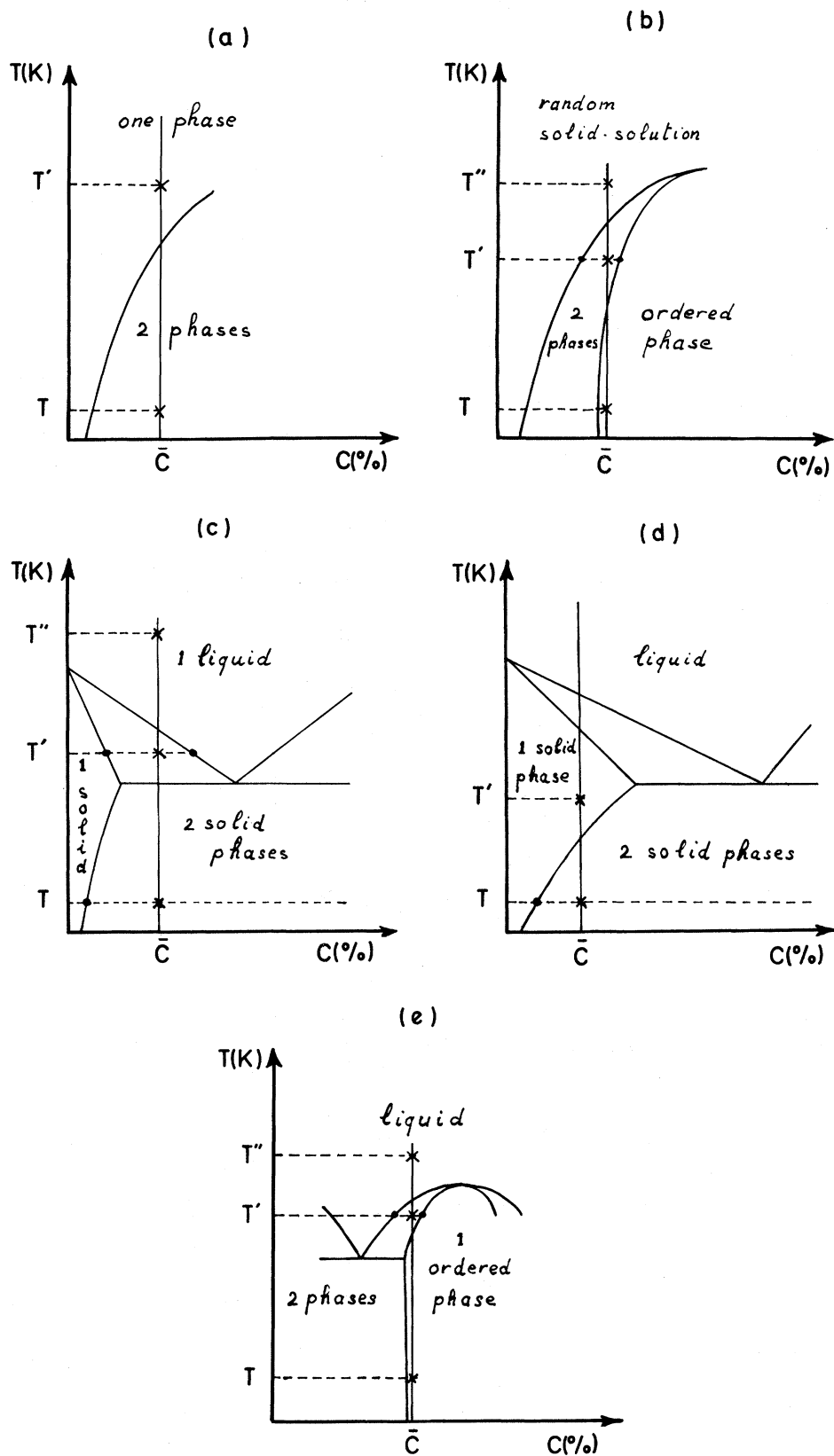
FIG. 6. Typical alloy behaviors to be anticipated under the action of ballistic effects. (a) Precipitate dissolution. (b) T', unmixing in the ordered compound; T'', complete disordering. (c) T', coexistence between an amorphous and a crystalline phase of different composition; T'', complete amorphization. (d) T', precipitate dissolution, higher T', as in (c). (e) T', coexistence of amorphous zones and an ordered compound; T'', complete amorphization.

structure with respect to the long-range one in Ni$_4$Mo as observed by Banerjee, Urban, and Wilkens.[22] Indeed, the short-range-ordered (SRO) structure has a shorter wavelength compared to the long-range-ordered (LRO) structure.[23]

(iii) The growth rate of those harmonics which are weakly affected by ballistic effects is indeed enhanced by irradiation. Indeed, atomic mobility [M in Eq. (45)] is enhanced by the point-defect supersaturation sustained by irradiation.

In conclusion, in ordering solid solutions with fixed concentration, ballistic effects decrease the LRO-parameter values according to a law of corresponding states (Fig. 4); they affect the relative growth rates of various harmonics of concentration: It is to be expected that certain harmonics which only appear as rapid transients outside irradiation may become a dominant feature of the decomposition path under irradiation. Since we have seen that the "strength" with which concentration harmonics are destroyed by ballistic effects depends on the wave vector, it may be speculated that ordered structures with appropriate wave vectors would be stable under irradiation and unstable outside irradiation. The occurrence of the SRO structure in Ni$_4$Mo under low-temperature irradiation where the long-range-ordered structure is unstable, may be an example of such a behavior.[22] A detailed application of the present technique to Ni$_4$Mo is in progress.

V. DISCUSSION AND CONCLUSIONS

In the preceding sections we have proposed a technique for computing steady-state configurations of solid solutions in the presence of ballistic effects.

For unmixing as well as ordering simple model systems, the following rule of corresponding configurations could be stated, as a first approximation. The configuration of a solid solution under irradiation at temperature T and flux ϕ is the equilibrium configuration that this solution would have outside irradiation at a temperature $T' = T[1 + \Delta(T, \phi)]$; in the limit of high irradiation flux ϕ and low defect mobility, the scaling factor Δ varies as $\phi^{1/2} e^{E/k_B T}$. The lower the point-defect mobility, the larger the scaling factor [Eq. (30)].

All of the models that we have dealt with are extremely simple in many respects. More realistic cases are now under study. Nevertheless, it is tempting to explore the possible consequences of the rule of corresponding configurations and check if it reveals any interesting behaviors of solid solutions under irradiation.

Figure 6 is a schematic representation of typical portions of phase diagrams. On each portion a vertical line is drawn showing the concentration of the solution. Along this line several points labeled T, T' and T'' represent, respectively, the irradiation temperature and the homologous temperature under moderate and high irradiation fluxes ($T' = T[1 + \Delta(T, \phi_1)]$ and $T'' = T[1 + \Delta(T, \phi_2)]$, $\phi_2 > \phi_1$).

Figure 6(a) shows an example of irradiation-induced—precipitate dissolution, as discussed in Sec. III. Figure 6(b) shows a case of an ordering reaction of the first kind. At higher flux (ϕ_2) the homologous tempera-

ture T'' is in the disordered one-phase field: one expects irradiation-induced disordering. At lower flux (ϕ_1) the homologous temperature T' is in the two-phase field: one expects a coexistence of ordered and disordered domains of different composition. This situation is reminiscent of the observations of Potter et al.[24] in Ni$_3$Al. There, the γ phase was observed to nucleate inside the ordered γ' phase under heavy-ion, high-dose irradiation.

Figure 6(c) is a case of a two-phase alloy which amorphizes under high flux irradiation: Indeed, under high flux irradiation, the corresponding state (T'') has the structure of a liquid. We notice an interesting feature which appears at moderate flux (T'), namely that the structure would be an equilibrium between an amorphous and a crystalline solid solution of different compositions.

Figure 6(d) shows a case where a two-phase alloy would first transform to a single-phase one (T'). This is the situation which has been studied in Ref. 25. At higher fluxes we would recover the situations depicted in Fig. 6(c).

Finally, Fig. 6(e) depicts the case of an ordered compound which experiences congruent melting. For sufficiently high fluxes one might expect amorphization of such a compound, without prior disordering (T''). We are aware of one such example, namely Ni-Ti under 1-Mev-electron irradiation.[26] It is noticeable that amorphization started along the dislocation lines; it is precisely a region of higher atomic displacement efficiency,[27] and where the point defects would have a short lifetime due to elimination at the dislocation core. As a consequence, Δ in Eq. (21) should be large.

We are quite aware of the speculative nature of the above arguments. We believe, however, that the possible typical behaviors just revealed are sufficiently interesting to deserve a systematic experimental study.

Finally, it is clear that in this paper we have concentrated on ballistic effects, and that the description of solute diffusion by defect jumps has been oversimplified. In particular, solute drag by defect fluxes has not been considered, so that the model just presented cannot account for irradiation-induced precipitation. We believe that the applicability of the present model is restricted to low temperature, while solute-defect-flux coupling is relevant at higher temperature. Elaborating a model for phase stability under irradiation valid for the entire range of temperature is still an open question.

ACKNOWLEDGMENTS

APPENDIX A: DISCRETE BALLISTIC DIFFUSION EQUATION

The ballistic flux of atoms of species i across the plane located between sites p and $p + 1$ is

$$J_i(p+\tfrac{1}{2})=\gamma_i\left[\sum_{s=-\infty}^{p}\sum_{s'=p+1}^{\infty}b_i(s,s')c_i(s)\right.$$

$$\left.-\sum_{s=p+1}^{\infty}\sum_{s'=-\infty}^{p}b_i(s,s')c_i(s)\right].\qquad(A1)$$

γ_i is the ballistic jump frequency of species i, $b_i(s,s')$ is the *a priori* probability that a ballistic jump that originated at site s will end at site s', and $c_i(s)$ is the atomic fraction of species i at site s. Assuming as before that $b_i(s,s')=b_i(s',s)$, we obtain

$$J_i(p+\tfrac{1}{2})=\gamma_i\sum_{s=-\infty}^{p}\sum_{s'=p+1}^{\infty}\{b_i(s,s')[n_i(s)-n_i(s')]\},\qquad(A2)$$

with the following change of notation:

$$s=p+u,\quad s'=p+v,\quad v-u=m,\qquad(A3)$$

and noting that

$$b(s,s')=b(s'-s),\qquad(A4)$$

Eq. (A2) can be written as

$$J_i(p+\tfrac{1}{2})=\gamma_i\sum_{v=1}^{\infty}\sum_{m=v}^{\infty}b(m)[n_i(p+v-m)-n_i(p+v)].\qquad(A5)$$

The flux J_i is evaluated in the lattice frame of reference. With the same restrictions as stated for establishing the continuum description [Eq. (5a)], the flux of species 2 in the laboratory frame of reference is

$$J=J_2-c_2(J_1+J_2),\qquad(A6)$$

i.e., according to Eq. (A5),

$$J=\sum_{v=1}^{\infty}\sum_{m=v}^{\infty}\widetilde{\Gamma}(m)[c_2(p+v-m)-c_2(p+v)],\qquad(A7)$$

where the following notation has been used:

$$\widetilde{\Gamma}(m)=[1-c_2(p)]\gamma_2 b_2(m)+c_2(p)\gamma_1 b_1(m).\qquad(A8)$$

As can be seen, $\widetilde{\Gamma}(m)$ is a function of the local concentration. The continuity equation

$$\frac{\partial c_2(p)}{\partial t}=J(p+\tfrac{1}{2})-J(p-\tfrac{1}{2}),\qquad(A9)$$

together with the assumption that $\widetilde{\Gamma}(m)$ is not concentration dependent (valid for the early stages of ordering where $c_2\simeq\bar{c}_2$, the average concentration), yields Eq. (9a) in the text,

$$\frac{\partial c_2}{\partial t}=\sum_m[(1-\bar{c}_2)\gamma_2 b_2(m)+\bar{c}_2\gamma_1 b_1(m)]$$

$$\times[c_2(p-m)-2c_2(p)+c_2(p+m)].\qquad(A10)$$

APPENDIX B: LYAPUNOV FUNCTIONAL FOR THE DIFFUSION PROBLEM (REF. 19)

The diffusion equation (13b) may be written as

$$J=-MN_v\frac{\partial}{\partial x}\left[\varphi'-2\kappa\frac{\partial^2 c}{\partial x^2}\right],\qquad(B1)$$

where φ' is obtained by integrating φ'' [Eq. (14)] once with respect to c, with the appropriate boundary condition. For a closed system, the steady-state concentration profile $c(x)$ ensures that $J=0$ or

$$N_v\left[\varphi'-2\kappa\frac{\partial^2 c}{\partial x^2}\right]=\mu.\qquad(B2)$$

Equation (B2) is simply the condition for the functional

$$\widetilde{F}\{c(x)\}=N_v\int\left[\varphi(c)+\kappa\left|\frac{dc}{dx}\right|^2\right]dx\qquad(B3)$$

to be the extremum with the constraint of matter conservation,

$$\int c(x)dx=\bar{c}\int dx.\qquad(B4)$$

Indeed, Eq. (B2) is the Euler equation for the latter problem,

$$\frac{\delta\widetilde{F}}{\delta c}=\mu,\qquad(B5)$$

where $\delta/\delta c$ means the functional derivative with respect to $c(x)$.

Property (c) in Sec. III A may be demonstrated as follows. Let us compute, for a closed system bounded by the surface S, enclosing a volume V, the following integral:

$$\int_S\frac{\delta\widetilde{F}}{\delta c}\vec{J}\cdot\vec{n}\,dS=\int_V\mathrm{div}\left[\frac{\delta\widetilde{F}}{\delta c}\vec{J}\right]dV,\qquad(B6)$$

where $\vec{n}$ is the unit vector normal to the surface pointing to the exterior. Since the system does not exchange solute with the exterior, the lhs of Eq. (B6) is zero and the divergence theorem together with the continuity equation

$$\frac{\partial c}{\partial t}=-\mathrm{div}\vec{J},\qquad(B7)$$

and with Eq. (B1), gives

$$\int_V\frac{\delta\widetilde{F}}{\delta c}\frac{\partial c}{\partial t}dV=-\int_V\frac{|\vec{J}|^2}{M}dV.\qquad(B8)$$

The lhs of Eq. (B8) is nothing but $d\widetilde{F}/dt$. Since M is a positive quantity, Eq. (B8) simply means

$$\frac{d\widetilde{F}}{dt}\le 0,\qquad(B9)$$

where the equality holds when $|\vec{J}|=0$ everywhere, i.e., under steady-state conditions. $\widetilde{F}$ is therefore a Liapunov functional for the diffusion problem.[13]

Property (d) in Sec. III A is based on the following argument:[28,29] Under steady-state condition $J=0$, i.e., according to Eqs. (B1) and (B2),

$$\frac{\partial\varphi}{\partial c}-\frac{\mu}{N_v}=2\kappa\frac{\partial^2 c}{\partial x^2}.\qquad(B10)$$

With the following interpretation of the variables, $c\leftrightarrow$ positions, $x\leftrightarrow$ time, Eq. (B10) describes the movement of a particle of mass 2κ in the potential $V=-\varphi+\mu c/N_v$. Two-phase equilibrium exists when the common tangent to V is horizontal (Fig. 7).
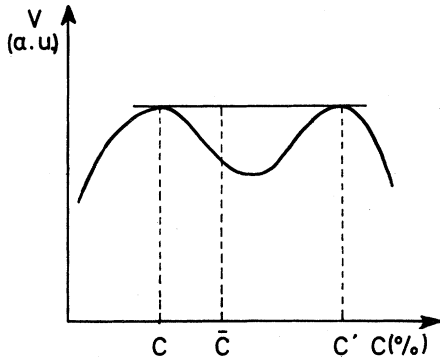
FIG. 7. Common tangent to V is horizontal.

The positions of the contact points (c,c') give the compositions of the coexisting phases. Indeed, the particle may stay at c an infinite time, i.e., the phase of composition c may have infinite extension. The same is true for c'. If the average position of the particle (composition of the system) is constrained to the value $\bar{c}$, the only solution compatible with the value V of the potential is the particle leaving c at zero velocity, and reaching c' at zero velocity, after a rapid excursion between c and c', or, in alloy language, the composition c extending to $x = -\infty$, and c' extending to $x = +\infty$ with a narrow region (interfacial region) with a composition intermediate between c and c'.

APPENDIX C: STATIONARY DEGREE OF LONG-RANGE ORDER

We briefly recall the Bragg-Williams treatment of the $B2$ structure.

The internal energy per atom is

$$u = c_\alpha c_\beta \omega , \tag{C1}$$

where c_α and c_β are the B-atom fraction on sites of the α and β sublattices, respectively; ω is the ordering energy defined as

$$\omega = \mathcal{z}(\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}) , \tag{C2}$$

where $\mathcal{z}$ is the coordination number and the ϵ_{ij} are the pair interaction energies.

The entropy per atom is taken as that of an ideal mixture on each sublattice,

$$s = -k_B(c_\alpha \ln c_\alpha + c_\beta \ln c_\beta) , \tag{C3}$$

where k_B is Boltzmann's constant.

With the above approximations, the ordering reaction is found to be of the second kind with the critical temperature given by

$$T_c = \omega/2k_B . \tag{C4}$$

Remembering Eqs. (32a) and (32b) of Sec. IV A, and minimizing the free energy $u - Ts$ with respect to c_α, yields the equilibrium value of c_α as the solution of

$$c_\alpha/(1-c_\alpha) = e^{-\omega(1-2c_\alpha)/k_B T} , \tag{C5}$$

which may be written as

$$(1+S)/(1-S) = e^{\omega S/k_B T} . \tag{C6}$$

The steady-state solution of the kinetic equation (33), Sec. IV A, may be written as

$$c_\alpha/c_\beta = (1+S)/(1-S) = (\Gamma_\beta/\Gamma_\alpha) . \tag{C7}$$

The dependence of $\Gamma_\beta/\Gamma_\alpha$ is obtained by equating Eqs. (C6) and (C7),

$$\Gamma_\beta/\Gamma_\alpha = e^{\omega S/k_B T} , \tag{C8}$$

which is Eq. (35).

The steady-state solution of the kinetic equation in the presence of ballistic effects results from

$$0 = -(\Gamma_\alpha + \Gamma_B)c_\alpha + (\Gamma_\beta + \Gamma_B)c_\beta , \tag{C9}$$

or

$$(1+S)/(1-S) = (\Gamma_\beta + \Gamma_B)/(\Gamma_\alpha + \Gamma_B) . \tag{C10}$$

Defining Γ by

$$\Gamma_\beta = \Gamma e^{\omega S/2k_B T}, \quad \Gamma_\alpha = \Gamma e^{-\omega S/2k_B T} , \tag{C11}$$

and defining δ by

$$\delta = \Gamma_B/\Gamma , \tag{C12}$$

simple manipulation of Eq. (C10) leads to

$$S = \sinh(\omega S/2k_B T)/[\cosh(\omega S/2k_B T) + \delta] , \tag{C13}$$

which is simply Eq. (37) in Sec. IV A.

Outside irradiation ($\Gamma_B = 0$), Eqs. (C13) and (C4) reduce to Eq. (36) in the text.

APPENDIX D: LYAPUNOV FUNCTION FOR THE TIME EVOLUTION OF THE LONG-RANGE-ORDER—PARAMETER VALUE

Equations (33) and (34) give, under irradiation,

$$\frac{dc_\alpha}{dt} = \mathcal{z}[(\Gamma_\beta + \Gamma_B)c_\beta - (\Gamma_\alpha + \Gamma_B)c_\alpha] , \tag{D1}$$

or, with Eq. (32b),

$$\frac{dS}{dt} = \mathcal{z}[(\Gamma_\beta + \Gamma_B)(1-S) - (\Gamma_\alpha + \Gamma_\beta)(1+S)] , \tag{D2}$$

$$\frac{dS}{\mathcal{z}dt} = -S(\Gamma_\alpha + \Gamma_\beta + 2\Gamma_B) + \Gamma_\beta - \Gamma_\alpha . \tag{D3}$$

Taking advantage of Eq. (C11), we obtain

$$\frac{dS}{d\tau} = -2S[\cosh(\omega S/2k_B T) + \delta] + 2\sinh(\omega S/2k_B T) , \tag{D4}$$

where τ is a reduced time given by $\tau = \mathcal{z}\Gamma t$; Γ is defined by Eq. (C11).

If Eq. (D4) can be written as

$$\frac{dS}{d\tau} = -\frac{\partial\varphi}{\partial S} , \tag{D5}$$

φ is a Lyapunov function for the problem. Indeed, if S^* is an extremum of φ, $dS/d\tau = 0$; S^* is a steady-state solution of (D5). Moreover, if S is not a steady-state solution,

$$\frac{d\varphi}{d\tau} = \frac{\partial\varphi}{\partial S}\frac{dS}{d\tau} = -\left[\frac{\partial\varphi}{\partial S}\right]^2 < 0 \ . \tag{D6}$$

Therefore, φ is a decreasing function of time whenever S is not a steady-state solution of Eq. (D5).

Finally, if $\varphi(S^*)$ is a minimum, S^* is a (locally) stable steady-state solution, while if $\varphi(S^*)$ is a maximum, S^* is an unstable steady-state solution. Indeed, we let s be the small departure from S^*; expanding Eq. (D5) to first order in s yields

$$\frac{ds}{dt} = -s\frac{\partial^2\varphi}{\partial S^2}\bigg|_{S^*} \ . \tag{D7}$$

From Eq. (D7), we see that if $\varphi(S^*)$ is a minimum $(\partial^2\varphi/\partial S^2 > 0)$, then ds/dt is negative if s is positive and vice versa; S^* is a stable steady-state solution. The reverse is true if $\varphi(S^*)$ is a maximum.

The function $\varphi(S)$ for Eq. (D4) is a primitive of the rhs. We write

$$\frac{d\varphi}{dS} = 2S[\cosh(ST_c/T) + \delta] - 2\sinh(ST_c/T) \ , \tag{D8}$$

where the notation $T_c = \omega/2k_B$ has been used. Integrating Eq. (D8) yields

$$\varphi(S) = \varphi(0) + S^2\delta$$

$$+ \frac{2T}{T_c}\left[S\sinh\left[\frac{ST_c}{T}\right]\right.$$

$$\left. - \left[1 + \frac{T}{T_c}\right]\cosh\left[\frac{ST_c}{T}\right]\right] \ . \tag{D9}$$

We see from Eq. (D8) that $S = 0$ is a steady-state solution that is stable $(d^2\varphi/dS^2 > 0)$ if $(1+\delta)T > T_c$ or $T' > T_c$, where T' is given by Eq. (21) with $\Delta = \delta$. The latter condition is fulfilled for two different values of T according to the shape of $T'(T)$ (cf. Fig. 1), one close to the critical point T_c and one at a lower temperature. The law of corresponding states given in the text is thus strictly valid for the shift of the critical point and for defining the low-temperature threshold for complete disordering.

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