Ordering phenomena in open systems: A model of an irradiated alloy in the self-consistent-field approximation

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We study the features of thermodynamics of open systems using the example of a model alloy under radiation. Ordering phase transitions are explored using a form of the self-consistent-field approximation. We show that the "mixing" of the positions of atoms done by radiation inhibits ordering and suppresses it at low temperatures. We also find that at small values of the order parameter, radiation either gives rise to stratification or increases free energy for homogeneous ordering, which apparently indicates that the system is unstable with respect to formation of inhomogeneous states.

1. INTRODUCTION

Statistical systems that are constantly under the influence of external forces ("open" systems[1]) can have unusual properties that are absent in equilibrium systems. A well-known example is alloys under radiation. Experimental data suggest that in certain conditions unusual structural states emerge in such alloys, states whose properties differ dramatically from those of equilibrium states (see, e.g., Refs. 2–4). Martin *et al.*[5–7] proposed a physical model that provides a meaningful description of the main qualitative properties of the configurational kinetics in irradiated alloys. Vaks and Kamyshenko[8] suggested general methods for finding the stationary states in the models described in Refs. 5–7 and examined the effect of radiation on the formation of layers in disordered alloys.

In the present paper (an extended version of Ref. 9) we employ methods developed in Ref. 8 for studying the special features of ordering in irradiated alloys. We show that the presence of disordering external forces, "ballistic" mixing of atoms by radiation, leads to suppression of homogeneous ordering and to unusual structural behavior, especially at small values of the order parameter, when the thermodynamic "driving force" for ordering is weak.

2. THE MODEL AND THERMODYNAMIC RELATIONS

We now describe the microscopic model used in our study. We examine alloys whose configurational Hamiltonian has the standard form, namely

$$H=E_0+\sum_{i\alpha}(V_1^\alpha+\psi_i^a)n_{i\alpha}+\sum_{i<j,\alpha\beta}V_{ij}^{\alpha\beta}n_{i\alpha}n_{j\beta}+\cdots . \tag{1}$$

Here the operator $n_{i\alpha}$ is equal to unity when the ith site is occupied by an atom of the α species and $n_{i\alpha}=0$ otherwise, ψ_i^α stands for the external-field potential (if it exists) for an atom α at the ith site, and the ellipses stand for many-particle interactions. In a binary A–B alloy the Hamiltonian (1) can be expressed only in terms of operators $n_{i\mathrm{A}}=n_i$ (or $n_{i\mathrm{B}}=1-n_i\equiv n_i'$), while for a one-component interstitial alloy Eq. (1) does not contain indices α and β. For simplicity we will examine only these two cases and also assume that only pair interactions are present, that is, the Hamiltonian incorporates only the terms explicitly written in (1).

As in Ref. 8, we assume that the time evolution of the distribution equation $P\{n_i\}$ is determined by the master equation

$$\frac{dP(\alpha)}{dt}=\sum_\beta[W(\alpha,\beta)P(\beta)-W(\beta,\alpha)P(\alpha)]\equiv\hat{S}P, \tag{2}$$

where α and β stand for different sets of n_i values, $\{n_i\}$, and $W(\beta,\alpha)$ is the probability of an $\alpha\to\beta$ transition per unit time. Following Refs. 5–8, we assume $W(\beta,\alpha)$ equal to the sum of probabilities of individual atomic "hops" between the ith and jth sites, probabilities that incorporate "thermal" and "ballistic" terms: $w_{ji}=\gamma_{ij}^{th}+\Gamma_{ji}^b$. The thermal terms γ^{th} exist even in the absence of radiation and describe ordinary migration of atoms in an alloy. The ballistic terms Γ^b describe the effects of mixing of atoms over the sites when the atoms are knocked out by high-energy radiation particles (neutrons, ions, or fast electrons). For the thermal hopping probability γ^{th} we assume the thermally activated form

$$\gamma_{ij}^{th}=\omega_{ij}\exp[-\beta(E_{ij}^s-E_{ij}^{in})]\equiv\gamma_{ij}^t\exp(\beta E_{ij}^{in}),$$

where ω_{ij} and E_{ij}^s are the "trial rate" and "saddle-point energy" for hopping (assumed to be independent of alloy configuration, i.e., the species of neighboring atoms), $\beta=1/T$ is the inverse temperature, and E_{ij}^{in} the "initial" (prior to hopping) energy of atoms related to cells i and j (averaged over fast phonon motion). The values of $\gamma_{ij}^t=\omega_{ij}\exp(-\beta E_{ij}^s)$ and the ballistic terms Γ_{ij}^b are assumed configuration-independent, in contrast to the E_{ij}^{in} entering into γ_{ij}^{th}. In Ref. 8 the expression for E_{ij}^{in} was taken, for the sake of simplicity, in the form corresponding to an interstitial alloy: $E_{ij}^{in}=E_j=n_j(\delta H/\delta n_j)$. For an A–B substitution alloy the E_{ij}^{in} also incorporate the configurational energy of the B atom in the i cell:

$$E_{ij}^{in}=n_i'\frac{\delta H}{\delta n_i'}+n_j\frac{\delta H}{\delta n_j}-n_i'n_j\frac{\delta^2H}{\delta n_i'\delta n_j}.$$

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Using a more realistic model of "hopping through vacancies" for γ_{ij}^{th} instead of the "direct hopping" model just discussed leads to more cumbersome expressions for the effective γ_{ij}^{in} but has no marked effect on the result below.

Actually, for a homogeneous alloy with equivalent sites Eq. (1) contains no fields ψ_i^α. However, considering the effect of a field that induces ordering clarifies some aspects of the theory. For this reason we consider below the general case of nonzero ψ_i^α assuming also (for the sake of simplicity) that the ballistic terms are field-dependent too: $\Gamma_{ij}^b = \Gamma_{ij} \exp(\beta\psi_i^{\mathrm{B}} + \beta\psi_j^{\mathrm{A}})$.

Allowing also for the fact that the hopping of an atom between the ith and jth sites is possible and alters the probability P only if the ith site was occupied and the jth site "vacant," that is, $W_{ji} = n_j' n_i w_{ji}$, where $n_j' = 1 - n_j$, we can write the transfer matrix $\hat{S}$ in (2) as

$$\hat{S} = \sum_{kl} (|n_k n_l'\rangle\langle n_l n_k'| w_{kl} - n_k n_l' w_{lk}), \tag{3}$$

where $w_{kl} \equiv \gamma_{kl}^t \exp(\beta E_{kl}^{in}) + \Gamma_{kl}^b$. In Eq. (3) we also used the Dirac notation for the state vectors, $|\cdots\rangle$ and $\langle\cdots|$, and the fact that n_i and n_i' are projection operators: $n_i^2 = n_i$, $(n_i')^2 = n_i'$, and $n_i n_i' = 0$.

Below we consider only stationary distributions $P\{n_i\}$, that is, solutions of the equation

$$\frac{dP}{dt} = \hat{S}P = 0. \tag{4}$$

The most general expression for $P\{n_i\}$ satisfying the physical requirement that the probability distribution for quasi-independent subsystems A and B be multiplicative, that is, $P_{\mathrm{A+B}} = P_{\mathrm{A}} P_{\mathrm{B}}$, can be written as

$$P\{n_i\} = \exp(A + \lambda\hat{N} - \hat{Q}), \tag{5a}$$

$$\hat{Q} = N_s a_0 + \sum_o (a_1 + h_i) n_i + \sum_{i<j} a_{ij} n_i n_j + \sum_{i<j<k} a_{ijk} n_i n_j n_k + \cdots, \tag{5b}$$

$$A = -\ln \mathrm{Tr} \exp(\lambda\hat{N} - \hat{Q}). \tag{5c}$$

Here N_s is the total number of sites, $\hat{N} = \Sigma_i n_i$ the total number of atoms, λ the generalized chemical potential, Tr(trace) stands for summation over all the sets $\{n_i\}$, and h_i is the effective external field at the ith site. The quasi-Hamiltonian $\hat{Q}$ is an analog of the Hamiltonian (1), but the "quasi-interactions" $a_{i\ldots j}$ must be found from the time-independent equation (4). If we assume that for a given N and given external parameters ζ (including not only the external fields and the radiation parameters but also the temperature, i.e., we consider, for the sake of simplicity, only the configurational degrees of freedom) the function $P\{n_i\}$ is single-valued (this assumption can be considered an analog of the ergodic hypothesis), we can assume that the $a_{i\ldots j}$ depend solely on ζ but not on the mean occupation numbers $c_i = \langle n_i\rangle$ (see Ref. 8).

As discussed in Ref. 8, Eqs. (5) can be used, by analogy with ordinary thermodynamics,[10] to define the thermodynamic potentials of stationary states: the potential A, the generalized chemical potential λ, and the generalized free energy $F = A + \lambda N$, where $n = \langle\hat{N}\rangle$; and here and in what follows the symbol $\langle\ldots\rangle = \mathrm{Tr}(\ldots)P$ stands for averaging over the distribution (5). Here $N_s a_0$ and a_1 in Eq. (5b) are the analogs of E_0 and V_1 in Eq. (1), and for single-phase states (discussed in Ref. 8), these quantities enter into the thermodynamic potentials F and λ as insignificant concentration-independent constants (discarded in Ref. 8). But, generally speaking, the values of a_0 and a_1 in different phases may differ. Hence, when considering equilibria between different phases, we will allow for the possibility of nonzero differences Δa_0 and Δa_1.

The entropy S is defined in the ordinary manner, $S = \ln \Delta\Gamma$, where $\Delta\Gamma$ is the number of different configurational states occupied by the alloy in steady-state conditions. Since A, F, and S and the quasienergy $Q = \langle\hat{Q}\rangle$ are extensive quantities (additive in the quasi-independent systems comprising the alloy), Eq. (5c) yields, to within statistical accuracy, the following expression for the free energy F:

$$F = A + \lambda N = Q - S. \tag{6}$$

Differentiating Eq. (5c) "along the steady-state line" yields the generalized first law of thermodynamics

$$dS = dQ - \lambda dN - \sum_\zeta q_\zeta d\zeta, \tag{7}$$

where[1)] $q_\zeta = \langle \partial\hat{Q}/\partial\zeta\rangle$.

The principle that the free energy for stationary states be a minimum (for given external parameters ζ and total number of particles N) can be derived from the generalized ergodic hypothesis mentioned previously, similar to the way the principle that the entropy be a maximum in closed systems was derived in Ref. 10, where the energies E_a of the subsystems must be replaced by the numbers of atoms in the subsystems, N_a. By analogy with macroscopic states of incomplete equilibrium in Ref. 10, we define "macrononstationary" states as representable by a set of quasi-independent locally-stationary small subsystems that become stationary (for fixed ζ and N_a) faster than the total system. Then the entropy S, the quasienergy Q, and the free energy F of such a macrononstationary state are defined as the sums of the contributions $S_a(N_a)$, $Q_a(N_a)$, and $F_a(N_a)$ from the locally-stationary subsystems a. Also, allowing for Eqs. (5) and reasoning along the same line as in Ref. 10, for a completely stationary state the probability of N_a particles being distributed over the subsystems can be written in a form similar to Eq. (7.17) in Ref. 10:

$$dw = \mathrm{const}\,\delta\left(\sum_a N_a - N\right)\exp(-F)\prod_a dN_a, \tag{8}$$

where $F = \Sigma_a F_a(N_a)$ is the free energy of the entire system interpreted as a function of the exact numbers of particles, N_a, of the subsystems. Since the most probable values of N_a are the mean values $\bar{N}_a$, at $N_a = \bar{N}_a$ the function $F(N_1, N_2, \ldots)$ must have the minimum possible value ($N = \Sigma_a N_a$). But the $\bar{N}_a$ are the values that correspond to complete time independence so that in the completely time-independent state the free energy has the minimum value in relation to all possible distributions of N_a over the subsystems, that is, the concentration distributions in the alloy. Generally speaking, for macrononstationary states the distribution of $\{N_a\}$ does not correspond to a minimum of F. Hence, approaching a completely stationary state must correspond to a decreasing free energy.

In the presence of two or a greater number of phases the requirements that the total F be minimized with respect to exchange of particles between phases lead to phase-equilibrium equations of the ordinary type:[10]

$$\lambda_1=\lambda_2,\quad F_1-\lambda_1 N_1=F_2-\lambda_2 N_2. \tag{9}$$

Note that the above derivation of the principle of decreasing free energy (as the similar derivation of the principle of increasing free entropy in Ref. 10) is based on the above-noted generalized ergodic hypothesis, that is, on the fact that for given N and ζ the stationary state in a given open system is assumed (as in a closed system) totally specified, or deterministic. This obviously excludes considering any nondeterministic behavior, e.g., chaotic behavior (in space or time). The difficulties discussed below with maintaining the principle of decreasing F for certain intervals of ζ suggest that at these values of the external parameters the noted assumptions about the deterministic behavior may become invalid.

3. GENERAL EQUATIONS FOR THE EFFECTIVE INTERACTIONS IN THE MEAN-FIELD APPROXIMATION

The equations for determining the quasi-interactions $a_{i\cdot\cdot j}$ can be obtained by multiplying Eq. (4) by the operators n_i, $n_i n_j$, $n_i n_j n_k$, etc. and averaging the products over all the configurations in (1). This yields the conditions for the mean occupation numbers $c_i=\langle n_i\rangle$ and the functions $g_{i\dots j}=\langle n_i \dots n_j\rangle$ to be time-independent:

$$\frac{dc_i}{dt}=\langle n_i\hat{S}\rangle=0, \tag{10a}$$

$$\frac{dg_{i\dots j}}{dt}=\langle n_i\dots n_j\hat{S}\rangle=0. \tag{10b}$$

The $g_{i\dots j}$ are linear functions of the correlators $K_{i\dots j}=\langle\xi_i\dots\xi_j\rangle$ of the fluctuations $\xi_i=n_i-c_i$, so that Eqs. (10) constitute the conditions that the density distribution and its fluctuations be stationary.

Using Eq. (3) for $\hat{S}$ and the transformations described in Ref. 8, we can write Eqs. (10) in a form that generalizes Eq. (7b) in Ref. 8 to the case of the substitution-alloy model described here:

$$\sum_{s;i\neq j\dots\neq k}\left\langle\left\{[\gamma_{is}^{t}\exp(\beta E_{is}^{in})+\Gamma_{is}^{b}]\exp\left(\lambda-\frac{\delta\hat{Q}}{\delta n_s}\right)\right.\right.$$
$$\left.\left.-\{i\to s\}\right\}n_i' n_s' n_j\dots n_k\right\rangle+\{i\to j,\dots,k\}=0, \tag{11}$$

where $i\to j,\dots,k$ stands for the sum of expressions obtained from the first term in Eqs. (11) via permutation of indices: $j\to j,\dots,i\to k$.

The mean values in Eqs. (11) are correlators for an alloy with the quasi-interactions $a_{i\dots j}$. Hence, to express them in terms of $a_{i\dots j}$ and c_i, we can resort to the approximate methods used in statistical physics such as the self-consistent-field method[11] and cluster methods.[12,13] In the absence of radiation, that is, when $\Gamma_{ij}^{b}=0$, Eqs. (11) obviously have solutions corresponding to thermal equilibrium, $a_{i\dots j}=\beta V_{i\dots j}$, as expected.

In studying Eqs. (11) it is convenient to shift from operators n_i to their mean values $c_i=\langle n_i\rangle$ and fluctuations $\xi_i=n_i-c_i$. Then the quasi-Hamiltonian $\hat{Q}=\hat{Q}(\xi)$ (5b) assumes the form

$$\hat{Q}=N_s(\sigma_0+a_0)+\sum_i(\sigma_1^i+a_1+h_i)\xi_i$$
$$+\sum_{n=2}^{\infty}\frac{1}{n!}\sum_{i_1\dots i_n}\sigma_n^{i_1\dots i_n}\zeta_{i_1}\dots\xi_{i_n}, \tag{12}$$

where the effective interaction $\sigma_n^{i_1\dots i_n}$ is expressed in terms of the quasi-interactions $a_{i\dots j}$ and the mean occupation numbers c_i by the following series:

$$\sigma_n^{i_1\dots i_n}=\sum_{m\geqslant 0,m+n\geqslant 2}^{\infty}\frac{1}{m!}\sum_{j_1\dots j_m}a_{i_1\dots i_n j_1\dots j_m}c_{j_1}\dots c_{j_m}. \tag{13}$$

Equations (10) for finding the $\sigma_n^{i\dots j}$ in the substitution alloys considered here (instead of (14) in Ref. 8 for interstitial alloys) assumes the form

$$\left\langle\sum_{s;\subset\neq j\dots\neq k}[c_i'c_s'-(c_i'\xi_s+c_s'\xi_i)+\xi_i\xi_s]\left\{\left(\bar{\gamma}_{si}g_i\left[-1\right.\right.\right.\right.$$
$$\left.\left.+\sum_l(\sigma_{il}-\beta v_{il}^{a}+\beta v_{sl}^{b})\xi_l+\cdots\right]-\{i\to s\}\right)$$
$$\left.\left.+\left(\Gamma_{si}^{b}g_i\left[-1+\sum_l\sigma_{il}\xi_l+\cdots\right]-\{i\to s\}\right)\right\}\xi_j\dots\xi_k\right\rangle$$
$$+\{i\to j,\dots,k\}=0. \tag{14}$$

Here $c_i'=1-c_i$, $g_i=\exp(\lambda_i-\sigma_1^i)$, where $\lambda_i=\lambda-a_1-h_1$, and the ellipses inside the square brackets stand for the terms with many-particle interactions $\sigma_{il\dots m}$ and products of interactions $\sigma_{il}\dots\sigma_{lm}$, terms similar to those in Eq. (14) in Ref. 8. The potentials v_{ij}^{a} and v_{ij}^{b} are related to the ordinary configuration potential $v=V^{\mathrm{AA}}+V^{\mathrm{BB}}-2V^{\mathrm{AB}}$ and the "asymmetric" potential $u=V^{\mathrm{AA}}-V^{\mathrm{BB}}$ through the following expressions:

$$v^a=\tfrac{1}{2}(v+u),\quad v^b=\tfrac{1}{2}(v-u).$$

The expression for the effective thermal hopping probability $\bar{\gamma}_{ij}=e_i^b\gamma_{ij}e_i^a$ consists of the factors

$$e_i^b=\exp(\beta\Phi_{\mathrm{B}i}),\quad e_j^a=\exp(\beta\Phi_{\mathrm{A}j}),$$

$$\gamma_{ij}=w_{ij}\exp(-\beta\epsilon_{ij}^{\mathrm{s}}),$$

where

$$\Phi_{\mathrm{B}i}=\psi_i^{\mathrm{B}}-\sum_k v_{ik}^{b}c_k$$

is the mean field acting on atom B at the ith site,

$$\Phi_{Aj}=\psi_j^A+\sum_k v_{jk}^a c_k$$

that acting on atom A at the jth site, and

$$\epsilon_{ij}^s=E_{ij}^s+V_{ij}^{BA}-\sum_k (V_{ik}^{BB}+V_{jk}^{AB})$$

is the renormalized value of the "barrier height" E_{ij}^s. Comparison of Eq. (14) in this paper with Eq. (14) in Ref. 8 shows that the interstitial-alloy model examined in Ref. 8 corresponds to the particular case of the substitution-alloy model (14) with $u_{ij}=v_{ji}$ and $\psi_i^B=0$. Hence in what follows we discuss only the general equations (14). Note that these equations and hence the thermodynamic properties in the open systems considered here depend not only on the configuration potentials v (as in ordinary equilibrium, alloys) but also on the asymmetric potentials u.

To obtain the explicit solutions of Eqs. (14), we use the self-consistent (or mean-) field approximation (MFA), described in Refs. 8 and 11, assuming that the potentials $v_{ij}=v(\mathbf{r}_{ij})$, where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ is the distance between the ith and jth sites, satisfy the conditions for applicability of this approximation. This means that the potentials $v(\mathbf{r})$ are long-range and that their Fourier components $v(\mathbf{k})=\Sigma_{\mathbf{k}}v(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})$ for values of $\mathbf{k}$ essential for the phase transitions considered here (i.e., close to $\mathbf{k}=0$ in the case of layer formation or to the superstructure vector $\mathbf{k}_s$ in the case of ordering) considerably exceed certain values of $v(\mathbf{r})$, that is, $|v(\mathbf{r})|\ll|v(k)|$ (see Ref. 11). Then in Eqs. (14) we can use for $g_i=\exp(\lambda_i-\sigma_1^i)$ the MFA expression $g_i=c_i/c_i'$ (obtained from the single-phase normalization condition), while in the Fourier components of Eqs. (14) in the variables $\mathbf{r}_{ij}$, $\mathbf{r}_{jk}$, etc. we can ignore all terms containing integrals over the quasimomenta (loop diagrams[11]) since they are of order $v(\mathbf{r})/v(\mathbf{k})$ with respect to terms without such integrals. Then Eqs. (14) for the correlators $K_n=\langle\xi_{i_1}\ldots\xi_{i_n}\rangle$ of the lowest rank n effectively "separate" from the equations with higher ranks n and can be solved explicitly. Here the equation with the lowest rank $n=1$ constitutes the single-site stationary (SSS) condition (10a); it amounts to discarding all the factors $\xi_j,\ldots,\xi_k$ in (14).

For a disordered phase in the absence of the fields ψ_i all the $c_i=c$ are equal to each other, and the SSS equation is satisfied identically owing to conservation of the total number of atoms. The Fourier component $\sigma_2(\mathbf{k})$ of the effective pair interaction σ_{ij} is expressed in terms of the Fourier components $\Gamma_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$ of the functions $\Gamma_{ij}=\Gamma(\mathbf{r}_{ij})=\Gamma(\mathbf{r})$ and $\gamma_{ij}=\gamma(\mathbf{r})$ by a formula of the same type as Eq. (14) in Ref. 8 for an interstitial alloy:

$$\sigma_2(\mathbf{r})=\frac{\beta v_{\mathbf{k}}}{1+\delta_{\mathbf{k}}},\quad \delta_{\mathbf{k}}=\frac{\Gamma_0-\Gamma_{\mathbf{k}}}{\bar{\gamma}_0-\bar{\gamma}_{\mathbf{k}}}. \tag{15}$$

However, $\bar{\gamma}_{\mathbf{k}}$ in substitution alloys is $\gamma_{\mathbf{k}}\exp(\beta u_0 c)$ rather than $\gamma_{\mathbf{k}}\exp(\beta v_0 c)$ (as in Eq. (14) of Ref. 8), where u_0 and v_0 are the values of $u(\mathbf{k})$ and $v(\mathbf{k})$ at $\mathbf{k}=0$, in accordance with the above-noted relation between substitution-alloy and interstitial-alloy models. The Fourier component $K(\mathbf{k})$ of the correlator $K_{ij}=K(\mathbf{r})$ is related to $\sigma_2(\mathbf{k})$ through the Krivoglaz formula[14]

$$K(\mathbf{k})=cc'\frac{1}{1+\sigma_2(\mathbf{k})cc'}. \tag{16}$$

Equations (15) and (16) show that the ballistic mixing of atoms by radiation leads to the suppression of the effective interactions by the factor $(1+\delta_{\mathbf{k}})^{-1}$, which strongly depends on the wave vector $\mathbf{k}$, temperature T, and (for $u_0\neq0$) concentration c. As T is reduced, the quantities γ_0 and $\gamma_{\mathbf{k}}$ in (15) exponentially decrease, which causes the effective interactions to disappear and disorder to arise in the system.

The quasi-energy $Q=\langle\hat{Q}\rangle$ in MFA is given by the terms in (12) independent of ξ_i. In the absence of the fields h_i in the disordered phase, the constants a_0 and a_1 in (12) can be dropped, so that $Q=N_s\sigma_0$, and the entropy S (per site) in MFA is $S_{\mathrm{MFA}}=-(c\ln c+c'\ln c')$. If we express the quantities $a_{i\ldots j}$ entering into σ_0 in terms of σ_n, the free energy if given by Eq. (17) of Ref. 8. That equation incorporated not only effective pair interactions σ_2 but also many-particle interactions σ_n with $n>2$, which for the systems considered here, as discussed in Ref. 8 and below, are generally not small and are essential even if the initial interactions v in (1) are purely pairwise and concentration-independent. To express this many-particle contribution to Q in terms of σ_2, we can use the Krivoglaz formulas (24) given below (or the similar formula (18) in Ref. 8), which are valid for systems in which the interactions $a_{i\ldots j}$ in (5b) are c_i-independent. Using Eq. (15) for σ_2, we arrive at the following expression for the chemical potential $\lambda(c)=dF/dc$ of the disordered phase:

$$\lambda(c)=\beta v_0 c+\ln\frac{c}{c'}+\frac{v_0}{u_0}\ln\frac{1+\Delta(c)}{1+\Delta(0)}. \tag{17}$$

Here the function $\Delta(c)=(\delta_{\mathbf{k}})_{\mathbf{k}\to0}$ in lattices with cubic symmetry can be written as a ratio of lattice sums:

$$\Delta(c)=\exp(c\varphi_c^u)\sum_{\mathbf{r}}\Gamma(\mathbf{r})r^2\bigg/\sum_{\mathbf{r}}\gamma(\mathbf{r})r^2, \tag{18}$$

where $\varphi_c^u=\beta u_0$. The free energy can be found from (17) by integrating the relation $dF/dc=\lambda(c)$. Note that when the asymmetric potential u_0 is nonzero (which generally is the case) the thermodynamic functions and the alloy's phase diagram are not symmetric with respect to substitution of the alloy components, $c\to c'$, in contrast to equilibrium alloys with pair interaction.

In describing ordered phases with several sublattices α, the quantities $c=c_\alpha\delta_{\alpha\beta}$, $v(\mathbf{k})=v_{\mathbf{k}}^{\alpha\beta}$, $\bar{\gamma}_{\mathbf{k}}=\bar{\gamma}_{\mathbf{k}}^{\alpha\beta}$, $\sigma_2(\mathbf{k})=\sigma_2^{\alpha\beta}(\mathbf{k})$, etc. becomes matrices in the sublattice indices α and β. Hence, the Fourier components of Eqs. (14) assume a matrix form. For centrosymmetrical crystals (considered below for the sake of simplicity) the matrices $M_{\mathbf{k}}$ entering into these equations are real, so that Hermitian conjugation for them means simply transposition: $M_{\mathbf{k}}^\dagger=M_{\mathbf{k}}$. The SSS equation becomes nontrivial and assumes the form

$$(cs_0^\dagger)c' - (c's_0)c = 0, \tag{19}$$

where $s_0 = \gamma_0 + \Gamma_0^{\mathrm{b}}$, and the product (aA) incorporating a vector a and a matrix A stands for $\delta_{\alpha\beta} \Sigma_\lambda a_\lambda A_{\lambda\alpha}$ and, similarly, $(Aa)_{\alpha\beta} = \delta_{\alpha\beta} \Sigma_\lambda A_{\alpha\lambda} a_\lambda$ in Eqs. (21) below. The trace of Eq. (19) vanishes owing to conservation of particle number, so that in an alloy with m different sublattices Eq. (19) determines $m-1$ order parameters.

For the Fourier components $K_{\mathbf{k}}$ of the pair correlator $K_{ij} = \langle \xi_i \xi_j \rangle$, Eq. (14) yields the following MFA equation:

$$[A_{\mathbf{k}}\sigma_2(\mathbf{k}) - \Phi_{\mathbf{k}} + R_{\mathbf{k}}]K_{\mathbf{k}} + K_{\mathbf{k}}[\sigma_2(\mathbf{k})A_{\mathbf{k}}^\dagger - \Phi_{\mathbf{k}}^\dagger + R_{\mathbf{k}}^\dagger] = 0. \tag{20}$$

Here $\Phi_{\mathbf{k}} = B_+^{\mathbf{k}} \beta v_{\mathbf{k}} + B_-^{\mathbf{k}} \beta u_{\mathbf{k}}$, and the matrices $A_{\mathbf{k}}$, $R_{\mathbf{k}}$, and $B_\pm^{\mathbf{k}}$ assume the form

$$A_{\mathbf{k}} = (c's_0)c - c's_{\mathbf{k}}c, \quad R_{\mathbf{k}} = (c's_{\mathbf{k}}c - cs_{\mathbf{k}}^\dagger)(c')^{-1}, \tag{21a}$$

$$B_\pm^{\mathbf{k}} = \tfrac{1}{2}\{(c'\bar{\gamma}_0)c - c'\bar{\gamma}_{\mathbf{k}}c \pm [c'(\bar{\gamma}_0 c) - c\bar{\gamma}_{\mathbf{k}}^\dagger c']\}, \tag{21b}$$

where $s_{\mathbf{k}} = \bar{\gamma}_{\mathbf{k}} + \Gamma_{\mathbf{k}}^{\mathrm{b}}$. Since the correlator $K_{\mathbf{k}}$ is related to $\sigma_2(\mathbf{k})$ through the (matrix) Krivoglaz equation (16), Eqs. (20) constitute a closed system of equations for finding the $\sigma_2(\mathbf{k})$.

The free energy $F = Q - S$ of the ordered phase in MFA is given by an expression that generalizes Eq. (17) in Ref. 8 for a disordered phase:

$$F = N_s a_0 + a_1 N + N_c\left(\sigma_0 - S_{\mathrm{MFA}} + \sum_\alpha h_\alpha c_\alpha\right). \tag{22}$$

Here N_c is the number of crystal cells,

$$S_{\mathrm{MFA}} = -\sum_\alpha (c_\alpha \ln c_\alpha + c'_\alpha \ln c'_\alpha),$$

and $N_c\sigma_0$ is given by Eq. (13) at $n=0$, with

$$\sigma_0 = \frac{1}{2!}\sum_{\alpha\beta} a_2^{\alpha\beta} c_\alpha c_\beta + \frac{1}{3!}\sum_{\alpha\beta\gamma} a_3^{\alpha\beta\gamma} c_\alpha c_\beta c_\gamma + \cdots, \tag{23}$$

where $a_x^{\alpha_1 \ldots \alpha_n}$ is the value of $a_n^{\alpha_1 \ldots \alpha_n}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1})$ with all $\mathbf{k}_i = 0$.

To express σ_0 in terms of the pair interactions $\sigma_2^{\alpha\beta}(\mathbf{k})$ determined by Eq. (20), one can use the recurrence differential formulas (RDF) of the type discussed by Krivoglaz,[14] which follow from Eqs. (13) for σ_n because, as noted, the quasi-interactions $a_{i\ldots j}$ are independent of c_α:

$$\frac{\partial}{\partial c_\gamma}\sigma_n^{\alpha\ldots\beta}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}) = \sigma_{n+1}^{\alpha\ldots\beta\gamma}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}, 0), \tag{24}$$

This relation is illustrated by the expression (15) and (16) in Ref. 8 for σ_3 and σ_2 for a disordered phase.

Thus, to find σ_0, we must solve Eqs. (20) for $\sigma_2^{\alpha\beta}(0)$ and use the RDF (24). However, the configuration-independent constants a_0 and a_1 cannot be determined by considering only a single homogeneous phase. To determine the difference of the values of these constants for different phases we must consider the time-independence condition at the boundary between the two phases, which constitutes a distinct inhomogeneous, problem. Hence, below we determine these differences, Δa_0 and Δa_1, between the ordered and disordered phases by employing the physical assumption that as the order parameter η tends to zero, the calculated expression for $F(\eta)$ must go over in a continuous manner to the free energy of the disordered phase.

4. THE A2↔B2 PHASE TRANSITION UNDER RADIATION

4.1. The order parameter and the effective interactions in the ordered phase

To illustrate the physical consequences of Eqs. (19)–(24), we take the simple case of A2↔B2 ordering (which is realized, for example in the CuZn alloy[10]) with a superstructure vector $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in a bcc lattice. Suppose that an external field ψ_i^α is responsible for the predominance of atoms of the A species in sublattice 1, that is $\psi_1^{\mathrm{A}} = -\psi_1^{\mathrm{B}} = -\psi_2^{\mathrm{A}} = \psi_2^{\mathrm{B}} = -\mathrm{h}/2\beta$. In describing the ordered phase B2 it is convenient to shift from sublattice occupation number c_α to their linear combinations, the mean concentration c and the order parameter η, namely, $c_1 = c + \eta$ and $c_2 = c - \eta$. Then the matrix elements $\bar{\gamma}_{\mathbf{k}}^{\alpha\beta}$, which enter into $s_{\mathbf{k}}$ in Eqs. (19) and (21), assume the form

$$\{\bar{\gamma}_{\mathbf{k}}^{11}; \bar{\gamma}_{\mathbf{k}}^{12}; \bar{\gamma}_{\mathbf{k}}^{21}; \bar{\gamma}_{\mathbf{k}}^{22}\} = \exp(c\varphi_c^u)\{\gamma_{\mathbf{k}}^{11}\exp(\eta\varphi^u);$$

$$\gamma_{\mathbf{k}}^{12}\exp(h - \eta\varphi);$$

$$\gamma_{\mathbf{k}}^{21}\exp(\eta\varphi - h); \gamma_{\mathbf{k}}^{22}\exp(-\eta\varphi^u)\}. \tag{25}$$

Here $\varphi = \beta v_\eta$ and $\varphi^u = \beta u_\eta$, where $v_\eta - v^{\eta\eta} = v_0^{11} - v_0^{12}$ in the two-sublattice description (corresponding to the ordered phase) or $v_\eta = v(\mathbf{k}_s)$ in the initial bcc lattice. Similarly, $u_\eta - u^{\eta\eta} = u_0^{11} - u_0^{12}$ in the two-sublattice description or $u_\eta = u(\mathbf{k}_s)$ in the initial bcc lattice. The matrix elements $(\Gamma_{\mathbf{k}}^{\mathrm{b}})^{\alpha\beta}$ are obtained from the right-hand side of (25) by replacing $\gamma_{\mathbf{k}}^{\alpha\beta}$ by $\Gamma_{\mathbf{k}}^{\alpha\beta}$ and φ_c^u, φ^u, and φ by zero.

In the matrix equations (19)–(21) it is also convenient to go from the sublattice representation $\alpha, \beta = 1, 2$ to the respective components μ, $\nu = c, \eta$. Then in the SSS equation (19) the c-component vanishes identically, while the η-component yields an equation for determining the order parameter $\eta = \eta(c,h)$. For what follows it is convenient to write this equation in symmetric form:

$$f(\eta, c, h) = \frac{1}{2}\ln\frac{\delta + e^{\eta\varphi}}{\delta + e^{-\eta\varphi}} + \frac{1}{2}\frac{c_1 c_2'}{c_2 c_1'} - h = 0, \tag{26}$$

where δ is $\exp(c\varphi_c^u)\varphi_0^{12}/\gamma_0^{12}$ in the two-sublattice description or $\delta_{\mathbf{k}} = (\Gamma_0 - \Gamma_{\mathbf{k}})/(\bar{\gamma}_0 - \bar{\gamma}_{\mathbf{k}})$ from Eqs. (15) at $\mathbf{k} = \mathbf{k}_s$ in a bcc lattice. For the particular case of $\varphi_c^u = \beta u_0 = 0$ and $h = 0$ Eq. (26) was first proposed and investigated by Bellon and Martin.[6]

Assuming that both h and η vanish in Eq. (26), we can find the generalized susceptibility $\kappa = (d\eta/dh)_{h=0}$ for the disordered phase:

$$\kappa^{-1} = (cc')^{-1} + \psi(1+\delta)^{-1}. \tag{27}$$

Comparison of (27) and (15) shows that κ^{-1} is the value of the inverse correlator $K^{-1}(\mathbf{k})$ in the disordered phase when $\mathbf{k}$ equals the superstructure vector $\mathbf{k}_s$. The equation $\kappa^{-1} = K^{-1}(\mathbf{k}_s) = 0$ determines the ordering spinodal curve in the (c,T) plane, that is, the equilibrium boundary of the

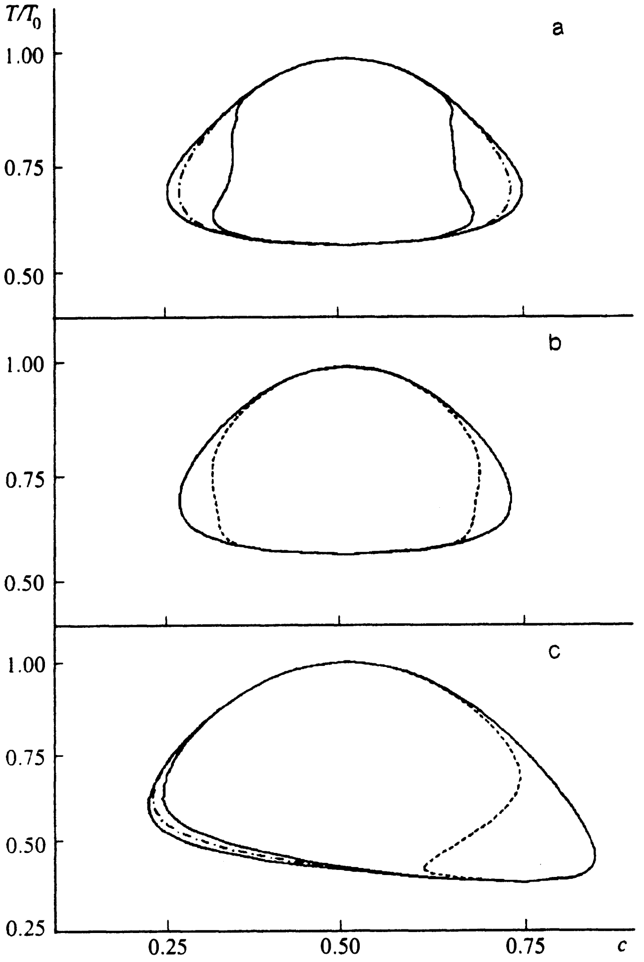

FIG. 1. Boundaries of ordered and disordered phases (solid curves), boundaries of "frustrated" ordered phases with $F(\eta)>F(0)$ (dashed curves), and ordering spinodal curves (dot-dash curves) calculated according to Eqs. (9), (42), and (27) with the use of the following expressions and values of parameters in Eq. (33): $\delta=\delta_0\exp(\beta\epsilon_s-c\beta u_0)$, $\gamma(\mathbf{r})=\gamma\exp(-r^2/r_t^2)$, $\Gamma(\mathbf{r})=\Gamma\exp(-r^2/r_b^2)$, and $\delta_0=10^{-4}$, where $\epsilon_s=5T_0$, with $T_0=\frac{1}{4}v_\eta$ the critical temperature in the absence of radiation, and $r_t=\frac{1}{2}a$, with a the bcc lattice constant. For the phase diagrams A, B, and C the parameters $(u_0/T_0, u_\eta/T_0, v_0/T_0, r_b/r_t)$ are equal to $(0,0,-2,2)$ (diagram A), $(0,0,2,5)$ (diagram B), and $(2,-2,2,2)$ (diagram C), respectively.

disordered phase with respect to spontaneous generation of concentration waves with $\mathbf{k}=\mathbf{k}_s$. Equation (27) shows that the ballistic mixing of atoms suppresses the tendency toward ordering, especially at low T, when the quantity $\delta\propto\exp(\beta\epsilon_s)$ exponentially increases. The shape of the emerging ordering spinodal curves in the (c,T) plane at fixed Γ and ϵ_s is shown in Fig. 1. As the ballistic-mixing parameter Γ grows, the ordered-phase region, which is limited by the spinodal curve, narrows (just as it did for lamination phase transitions, illustrated by Figs. 1(a) and 1(b) in Ref. 8), and for $\Gamma\gtrsim[\frac{1}{4}(-\beta v_0)-1]\gamma\exp(-\beta\epsilon_s)$ there is no ordering for any concentration.

The transition in Eqs. (20) to the (c,η)-representation shows that their coefficients $M_{\mathbf{k}}^{c\mu}$(where M is A, Φ, or R, and μ can be either c or η) tend to zero as $\mathbf{k}\to 0$, while the $M_0^{\eta\mu}$ remain finite. This leads to an essentially different structure of the c- and η-components of these equations when $\mathbf{k}\to 0$, and the same is true for their solutions $\sigma_{\eta\mu\ldots\nu}$ and $\sigma_{cc\ldots c}$.

We start with the $\eta\mu$-components of Eqs. (20). At $\mathbf{k}=0$ the matrix elements $A_0^{\eta\mu}\equiv A_{\eta\mu}$, $\Phi_0^{\eta\mu}$, and $R_0^{\eta\mu}$ assume the form

$$A_{\eta c}=c_2's_0^{21}c_1-c_1's_0^{12}c_2,\quad \Phi_0^{\eta c}=A_{\eta c}^t\varphi_c^u,\quad R_0^{\eta c}=0, \tag{28a}$$

$$A_{\eta\eta}=c_2's_0^{21}c_1+c_1's_0^{12}c_2,\quad \Phi_0^{\eta\eta}=A_{\eta\eta}^t\varphi,\quad R_0^{\eta\eta}=0, \tag{28b}$$

Here s_0 is the same as in (19), φ_c^u and φ are the same as in (18) and (25), and $A_{\mu\nu}^t$ stands for the "thermal" part of $A_{\mu\nu}$, obtained by dropping the ballistic terms in the matrix elements $s_0^{\alpha\beta}$ entering into $A_{\mu\nu}$ that is, by replacing $s_0^{\alpha\beta}$ with $\bar{\gamma}_0^{\alpha\beta}$.

In Eq. (28a) $A_{\nu c}$ vanishes owing to the SSS equations (19) or (26), with the result that Eqs. (20) for $\sigma_2^{\eta c}$ and$\sigma_2^{\eta\eta}$ at $\mathbf{k}=0$ separate from the equation for σ_2^{cc} and assume the form

$$\begin{aligned}&(A_{\eta\eta}\sigma_{\eta c}-A_{\eta c}^t\varphi_c^u)K_0^{cc}+(A_{\eta\eta}\sigma_{\eta\eta}-A_{\eta\eta}^t\varphi\varphi)K_0^{\eta c}=0,\\&(A_{\eta\eta}\sigma_{\eta c}-A_{\eta c}^t\varphi_c^u)K_0^{c\eta}+(A_{\eta\eta}\sigma_{\eta\eta}-A_{\eta\eta}^t\varphi\varphi)K_0^{\eta\eta}=0,\end{aligned} \tag{29}$$

where $\sigma_{\eta\mu}=\sigma_2^{\eta\mu}(0)$. If we consider (29) a system of homogeneous linear equations with respect to the quantities in parentheses, we see that when $\det K_0^{\mu\nu}\neq 0$ holds (which is practically always the case) it has only zero solutions. This makes it possible to find $\sigma_{\eta\mu}$ without calculating the correlators $K_0^{\mu\nu}$ explicitly:

$$\sigma_{\eta c}=\frac{A_{\eta c}^t}{A_{\eta\eta}}\varphi_c^u=\varphi_c^u\frac{\delta\sinh\eta\varphi}{1+2\delta\cosh\eta\varphi+\delta^2}, \tag{30a}$$

$$\sigma_{\eta\eta}=\frac{A_{\eta\eta}^t}{A_{\eta\eta}}\varphi=\varphi\frac{1+\delta\cosh\eta\varphi}{1+2\delta\cosh\eta\varphi+\delta^2}. \tag{30b}$$

The quantity $\sigma_2^{cc}(\mathbf{k})\equiv\sigma_{2\mathbf{k}}^{cc}$ is determined by the cc-component of Eqs. (20):

$$\begin{aligned}&(A_{\mathbf{k}}^{cc}\sigma_{2\mathbf{k}}^{cc}+A_{\mathbf{k}}^{c\eta}\sigma_{2\mathbf{k}}^{\eta c}-\Phi_{\mathbf{k}}^{cc}+R_{\mathbf{k}}^{cc})K_{\mathbf{k}}^{cc}+(A_{\mathbf{k}}^{cc}\sigma_{2\mathbf{k}}^{c\eta}+A_{\mathbf{k}}^{c\eta}\sigma_{2\mathbf{k}}^{\eta\eta}\\&\quad-\Phi_{\mathbf{k}}^{c\eta}+R_{\mathbf{k}}^{c\eta})K_{\mathbf{k}}^{\eta c}=0,\end{aligned} \tag{31}$$

where $\sigma_{2\mathbf{k}}^{\eta\mu}=\sigma_2^{\eta\mu}(\mathbf{k})$, and the coefficients $A_{\mathbf{k}}^{cc}=A_+(\mathbf{k})$, $A_{\mathbf{k}}^{c\eta}=A_-(\mathbf{k})$, $R_{\mathbf{k}}^{cc}=R_+(\mathbf{k})$, $R_{k4}^{c\eta}=R_-(\mathbf{k})$, and $\Phi_{\mathbf{k}}^{c\mu}$ are expressed in terms of the matrix elements $s_{0\mathbf{k}}^{\alpha\beta}=s_0^{\alpha\beta}-s_{\mathbf{k}}^{\alpha\beta}$ as follows:

$$\begin{aligned}&A_\pm(\mathbf{k})=\tfrac{1}{2}[c_1's_{0\mathbf{k}}^{11}+c_2's_{0\mathbf{k}}^{21})c_1\pm(c_1's_{0\mathbf{k}}^{12}+c_1's_{0\mathbf{k}}^{22})c_2],\\&R_\pm(\mathbf{k})=\tfrac{1}{2}(c_2's_{0\mathbf{k}}^{21}c_1-c_1's_{0\mathbf{k}}^{12}c_2)\zeta_\mp,\end{aligned} \tag{31a}$$

$$\begin{aligned}\Phi_{\mathbf{k}}^{cc}=A_+^t\beta v_{\mathbf{k}}^{cc},\quad \Phi_{\mathbf{k}}^{c\eta}=&(A_{t-}^{11}+A_{t-}^{22})\beta v_{\mathbf{k}}^{\eta\eta}\\&+(A_{t-}^{12}+A_{t-}^{21})\beta u_{\mathbf{k}}^{\eta\eta}.\end{aligned} \tag{32b}$$

Here $\zeta_\pm=1/c_1'\pm 1/c_c'$, $a_+^t=A_+^t(\mathbf{k})$ stands for the "thermal" part of $A_+(\mathbf{k})$, which corresponds to substituting $\bar{\gamma}_{0\mathbf{k}}^{\alpha\beta}=\bar{\gamma}_0^{\alpha\beta}-\bar{\gamma}_{\mathbf{k}}^{\alpha\beta}$ for all $s_{0\mathbf{k}}^{\alpha\beta}$ in $A_+(\mathbf{k})$ [in a way similar to Eqs. (28)], and $A_{t-}^{\alpha\beta}=A_{t-}^{\alpha\beta}(\mathbf{k})$ means the same substitution in the term of the expression (32a) for $A_-(\mathbf{k})$ that is proportional to the matrix element $s_{0\mathbf{k}}^{\alpha\beta}$.Since both $s_{0\mathbf{k}}^{\alpha\beta}$ and $\bar{\gamma}_{0\mathbf{k}}^{\alpha\beta}$ tend to zero as k^2 in the limit $\mathbf{k}\to 0$, then

$\sigma_0^{cc}(\mathbf{k}\to 0)\equiv\sigma_{cc}$ for the systems considered here (assumed completely homogeneous) are determined by the ratios of the expansions of the coefficients of Eq. (31) for small k:

$$\sigma_{cc}=\frac{\alpha_+^t\varphi_c-\alpha_-\sigma_{\eta c}-\alpha_-^{12}\zeta_-}{\alpha_+}+\chi\frac{\alpha_{t-}^{11}\varphi+\alpha_{t-}^{12}\varphi^u-\alpha_-\sigma_{\eta\eta}-\alpha_-^{12}\zeta_+}{\alpha_+}-\chi\sigma_{\eta c}. \quad (33)$$

Here $\varphi_c=\beta v_0$, the quantities φ, φ^u, $\sigma_{\eta c}$, and $\sigma_{\eta\eta}$ are the same as in Eqs. (25) and (30), $\chi=K_0^{\eta c}/K_0^{cc}$, and, to within a common factor proportional to k^2, α_+ and α_- are the expansions of $A_+(\mathbf{k})=A_{\mathbf{k}}^{cc}$ and $A_-(\mathbf{k})=A_{\mathbf{k}}^{c\eta}$ for small k:

$$\alpha_+=\alpha_{cc}=\rho_{11}^t\cosh(y+\eta\varphi^u)+\rho_{11}^{\mathrm{b}}\cosh y+\sqrt{q}[\rho_{12}^t(1+\delta\cosh\eta\varphi)+\rho_{12}^b(\delta+\cosh\eta\varphi)], \quad (34a)$$

$$\alpha_-=\alpha_{c\eta}=\rho_{11}^t\sinh(y+\eta\varphi^u)+\rho_{11}^b\sinh y\sqrt{q}\,(\rho_{12}^t\delta-\rho_{12}^{\mathrm{b}})\sinh\eta\varphi, \quad (34b)$$

where

$$y=\frac{1}{2}\ln\left(\frac{c_1c_1'}{c_2c_2'}\right),\quad q=\frac{1}{1+2\delta\cosh\eta\varphi+\delta^2},$$

$$\rho_{\alpha\beta}^t=\exp(c\varphi_c^u)\sum_{\mathbf{r}}r^2\gamma_{\mathbf{r}}^{\alpha\beta},\quad \rho_{\alpha\beta}^{\mathrm{b}}=\sum_{\mathbf{r}}r^2\Gamma_{\mathbf{r}}^{\alpha\beta},$$

and we have allowed for the cubic symmetry of the lattice. The quantities $\alpha_{t-}^{\alpha\beta}$, α_-^{12}, or α_+^t in (33) stand for the terms α_- or α_+ in Eqs. (34) that incorporate $\rho_{\alpha\beta}{}^t$, $\rho_{12}^{t,b}$, or all $\rho_{\alpha\beta}^t$, respectively.

Using Eqs. (16) and (26), we can show that χ in (33) is equal to the derivative of the order parameter η with respect to concentration c on the stationary curve (26). To this end we note that if the matrix equation (16) is written as $(\sigma_{2\mathbf{k}}+\xi)K_{\mathbf{k}}=1$, where the ξ matrix is $1/cc'$, the ηc-component of this equation at $\mathbf{k}=0$ makes it possible to express ξ in terms of the ratio of elements of matrix $\sigma+\xi$, which, according to Eqs. (30) and (26), can be written in the form of the c-derivative of the implicit function $\eta(c,h)$ defined by Eq. (26):

$$\chi=\frac{K_{\eta c}}{K_{cc}}=-\frac{\sigma_{\eta c}+\xi_-}{\sigma_{\eta\eta}\xi_+}=-\frac{(\partial f/\partial c)_{\eta,h}}{(\partial f/\partial\eta)_{c,h}}=\left(\frac{d\eta}{dc}\right)_h, \quad (35)$$

where $\xi_\pm=1/2c_1c_1'\pm 1/2c_2c_2'$ [the link employed here between the functions $\sigma_{\eta\mu}$ (30) and the derivatives of the first term in (26) is, as shown below, a consequence of the general relations (24)]. Thus, Eq. (30) and (34) together with the SSS equation (26) determine all three functions $\sigma_2^{\mu\nu}(\mathbf{k}=0)=\sigma_{\mu\nu}(c,h)$, which are needed for finding the thermodynamic potentials via the RDF (24).

Note that for the model of a symmetric alloy ($\varphi^u=\varphi_c^u=0$), examined by Martin *et al.*[5–7], in which the thermal and ballistic hopping is assumed to occur only between neighboring sites, the quantities ρ_{11}^t and ρ_{11}^b *in Eqs.* (34) *vanish* (*and at* $v_c=0$, which was the case in Refs. 5–7, the total σ_{cc} vanishes, too). In view of this, the features of thermodynamics associated with the second term in (33) and discussed below are absent in the models examined in Refs. 5–7. We note also that if instead of completely homogeneous systems (discussed in the present paper) we take alloys whose $\eta(\mathbf{r})$ and $c(\mathbf{r})$ slowly vary in space, Eq. (31) transforms into a differential relation linking $\eta(\mathbf{r})$, $c(\mathbf{r})$, and $\sigma(\mathbf{r})$.

4.2. Free-energy calculation

In integrating RDF (24), one must bear in mind that the field h and the occupation numbers $c_\mu=\{c_c,c_\eta\}=\{c,\eta\}$, which enter into the expressions for σ_n, are not independent in stationary conditions; rather, they are related via Eq. (26), so that h in (24) must be expressed in terms of c_μ according to this equation. We denote, by analogy with the quantities $a_n^{\alpha_1\dots\alpha_n}$ in (23), the values of the Fourier components of the effective interactions (13) $\sigma_n^{\mu_1\dots\mu_n}(\mathbf{k}_1,\dots,\mathbf{k}_{n-1})$ for all $\mathbf{k}_i=0$ by $\sigma_n^{\mu_1\dots\mu_n}$. If the quasi-interactions a_n are independent of h [as they are in the absence of radiation, when $a_n=\beta V_n$, with V_n from (1)], these $\sigma_n^{\mu\dots\nu}$, according to (13), are simply partial derivatives of σ_0 in (23) with respect to c_μ, or $\sigma_n^{\mu\dots\nu}=\partial^n\sigma_0/\partial c_\mu\dots\partial c_\nu$. Thus, we can verify the absence of dependence on h in the $a_{\mu\dots\nu}$ by verifying the RDF and the cross-differentiation relations (CDR) between different $\sigma_n^{\mu\dots\nu}$, such as $\partial\sigma_{\mu\nu}/\partial c_\lambda=\partial\sigma_{\mu\lambda}/\partial c_\nu$.

To do this, we must start with Eqs. (14) for many-particle interactions $\sigma_n^{\mu\dots\nu}$ with $n\geqslant 3$. Here it is convenient to employ a diagrammatic technique, similar to the one developed in Ref. 11 for spin Hamiltonians. For the lowest MFA in the diagrammatic representation of Eqs. (14) for correlators of rank n one must retain only the "n-leg" diagrams that do not contain closed loops.[11] For small values of quasimomenta ($\mathbf{k}_i\to 0$; the case considered here), certain simplifications [similar to those used in the "pair" equations (28)–(33)] emerge in the Fourier components of these equations.

We denote the quantities $a_n^{\mu_1\dots\mu_n}$ in (23) or $\sigma_n^{\mu_1\dots\mu_n}$ in (13) in which at least one of the indices μ_i is equal to η by $a_{n,\eta}$ or $\sigma_{n,\eta}$, the same quantities with all the indices μ_i equal to c by $a_{n,c}$ or $\sigma_{n,c}$, and the contributions to the expression (23) for σ_0 of all the terms containing $a_{n,\eta}$ or $a_{n,c}$ by Q_η or Q_c. In the absence of radiation ($\Gamma=0$) the quantity Q_η in our model is equal to $\frac{1}{2}\varphi\eta^2$, while the function $Q_c=\frac{1}{2}\varphi_c c^2$ depends on neither h or η. For $\Gamma\neq 0$ the quasi-interactions $a_{n,\eta}$ and $a_{n,c}$ depend on the field h differently.

We say that the (n,η)-equation is the Fourier component with small $\mathbf{k}_i\to 0$ of Eqs. (14), $dg_{\mathbf{k}_1,\dots,\mathbf{k}_{n-1}}^{\mu_1\dots\mu_n}/dt=0$, in which at least one of the indices μ_1, $\mu_2,\dots,\mu_n$ is equal to η, and that the (n,c)-equation is a similar equation with all indices $\mu_1=\dots=\mu_n=c$. In the (n,η)-equation, as in the $(2,\eta)$-equations (29), we can directly set $\mathbf{k}_i=0$, thus obtaining a nontrivial formula for $\sigma_{n,\eta}$. This leads to considerable simplifications, most vividly illustrated by the diagrammatic technique. As a result these (n,η)-equations are again reduced to a system of homogeneous linear equations similar to (29) for certain "cumulants," that is, combinations of the quantities $\sigma_{m,\eta}$ with $m \leqslant n$ and the potentials φ and φ_c^u with coefficients equal to products of $n-1$ correlators $K_0^{\eta\mu}$. Setting these cumulants equal to zero yields a recurrence formula expressing $\sigma_{n,\eta}$ in terms of $\sigma_{m,\eta}$ with $m<n$.

We performed these calculations for $n=3$ and found the quantities $\sigma_{3,\eta}=\{\sigma_{\eta cc},\sigma_{\eta\eta c},\sigma_{\eta\eta\eta}\}$. The relations obtained, together with (30), show that all the RDF and CDR incorporating $\sigma_{2,\eta}$ and $\sigma_{3,\eta}$ are valid. For instance, $\partial\sigma_{\eta c}/\partial\eta=\partial\sigma_{\eta\eta}/\partial c$ (as Eqs. (30) show), $\sigma_{\eta c\eta}=(\partial\sigma_{\eta c}/\partial c)_\eta$, and $(\partial\sigma_{\eta\eta c}/\partial c)_\eta=(\partial\sigma_{\eta\eta c}/\partial\eta)_c$. The possibility of generalizing these results to $\sigma_{n,\eta}$ with higher values of n seems obvious. Thus, the $\sigma_{n,\eta}$ apparently satisfy both RFD and CDR. As noted earlier, this implies that the $a_{n,\eta}$ on the SSS line (26) are independent not only of the occupation numbers c (or η) for a given h but also of the field h. This makes it possible to find the total contribution Q_η of the quasi-interactions $a_{n,\eta}$ to σ_0 (23) and the quantity $\sigma_{1,\eta}=\partial Q_\eta/\partial\eta$ by a simple integration of Eqs. (30) with respect to c or η with the second variable constant:

$$\sigma_{1,\eta}(c,\eta)=\frac{1}{2}\ln\frac{\delta+e^{\sigma\varphi}}{\delta+e^{-\eta\varphi}}, \tag{36a}$$

$$Q_\eta(c,\eta)=\int_0^\eta \sigma_{1,\eta}(c,x)dx. \tag{36b}$$

Employing Eqs. (36) and (26) and the MFA relations $\exp(\lambda_\alpha-\sigma_1^\alpha)=c_\alpha/c'_\alpha$ between the "effective chemical potentials of the sublattice" $\lambda_\alpha=\lambda-a_1-h_\alpha$ and the σ_1^α (related to $\sigma_{1,\eta}$ by the formula $\sigma_1^1-\sigma_1^2=2\sigma_{1,\eta}$), we can obtain an equation for the effective fields h_1 and h_2 in the sublattices entering into Eq. (22): $h_2-h_1=2h$. Putting the insignificant constant h_1+h_2 to zero, we see that the fields h_α in our model retain their "unrenormalized" values $\beta(\psi_\alpha^{\mathrm{A}}-\phi_\alpha^{\mathrm{A}})$ from (1), with $\psi_\alpha^{\mathrm{A,B}}$ specified at the beginning of Sec. 4.

Writing σ_0 in (22) as $Q_\eta+Q_c$, we can represent the free energy F per site as the sum of the "concentration" interactions F_c and a term F_r that is a "regular" function of η, that is, $F=F_c+F_r$, where

$$F_c=a_0+a_1c+Q_c, \tag{37a}$$

$$F_r(c,\eta,h)=Q_\eta-S_{\mathrm{MFA}}-h\eta, \tag{37b}$$

with

$$S_{\mathrm{MFA}}=\tfrac{1}{2}(c_1\ln c_1+c_2\ln c_2+c_1'\ln c_1'+c_2'\ln c_2').$$

For ordinary nonirradiated alloys the function $F_c=\frac{1}{2}\varphi_c c^2$ depends on neither η nor h, and the equilibrium value of $\eta=\eta(c,h)$ in the employed MFA can be found either from the self-consistency equation $\eta=\frac{1}{2}\langle n_1-n_2\rangle$ or by minimizing the expression (37b) for $F_r(\eta,c,h)$ as a function of the independent variable η (i.e., considering the set of macrononequilibrium states with arbitrary η): $(\partial F_r/\partial\eta)_{c,h}=0$. Equations (36) and (37b) show that, similarly, for $\Gamma\neq0$ the SSS equation (26) coincides with the condition of the minimum of the "regular" contribution F_r to F. Hence, if the "concentration" terms F_c or Q_c under radiation (as without radiation) are independent of h or η, the thermodynamics of ordering is similar for $\Gamma\neq0$ and $\Gamma=0$.

However, Eqs. (33) and (34) show that for $\Gamma\neq0$ the terms $\sigma_{n,c}$ and their contribution to the free energy Q_c have a strong and peculiar dependence on h or η. First, (30) and (33) show that the CDR $\partial\sigma_{cc}/\partial\eta=\partial\sigma_{\eta c}/\partial c$ is not satisfied, so that the $a_{n,c}$, in contrast to $a_{n,\eta}$, must depend on h (and apparently may have hysteresis, that is, be many-valued functions of h for certain T and Γ, like the order parameter $\eta(h)$). This unusual behavior of the "concentration" components $a_{n,c}$ makes it desirable to check whether they obey the general RDF (24),

$$\left(\frac{d\sigma_{n-1,c}}{dc}\right)_h=\sigma_{n,c}, \tag{38}$$

that is, to verify that for a given field h the quasi-interactions $a_{nc}(h)$ on the SSS line (26) in our model and approximations is indeed independent of the mean occupation number c.

As noted earlier, to verify Eqs. (38) we must find the many-particle interactions $\sigma_{n,c}$ with $n\geqslant3$ using the general equations (14). For a disordered phase with $h=0$ these equations in MFA prove to be fairly simple. For instance, it is quite easy to obtain the formula (16) in Ref. 8 for $\sigma_3(\mathbf{k},0)$, which confirms the RDF (24) at $n=2$ for arbitrary $\mathbf{k}$. Employing the diagram technique and considering the case of an interstitial alloy to simplify the formulas we have proved the validity of Eq. (38) in a disordered alloy for any n by demonstrating that the recurrence relation between σ_{n+1} and σ_n, derived by applying the diagrammatic technique, is equivalent to this RDF. Generalization to the case of a substitution alloy only complicates the intermediate formulas. Thus, for disordered alloys (i.e., $h=\eta=0$), the RDF (38) and, hence, the independence of the quasi-interactions $a_{n,c}$ on c have been proved in general form.

For ordered phases the (n,c)-equations (14) and their solutions $\sigma_{n,c}$ become more cumbersome. This reflects the fact that they describe more complex contributions to F corresponding to correlated fluctuations of concentration and the order parameter. To illustrate the general form of these equations we present the $(3,c)$-equation, which yields $\sigma_{3,c}$ for an interstitial alloy:

$$\begin{aligned}&a_+(K\sigma_{3c}K)_{cc}+\alpha_-(K\sigma_{3\eta}K)_{cc}-\alpha_+^t[(\bar\sigma K)_{cc}^2+(\bar\sigma K)_{\eta c}^2]\\&\quad-\alpha_+^b[(\sigma K)_{cc}^2+(\sigma K)_{\eta c}^2]-2\alpha_-^t(\bar\sigma K)_{cc}(\bar\sigma K)_{\eta c}\\&\quad-2\alpha_-^b(\sigma K)_{cc}(\sigma K)_{\eta c}+2(KR_{3c}^t\bar\sigma K+KR_{3c}^b\sigma K)_{cc}\\&\quad+[(\alpha^t\bar\sigma+\alpha^b\sigma+r)K]_{c\eta}(KV_{3\eta}K)_{cc}=0.\end{aligned} \tag{39}$$

Here the subscripts following the parentheses signify that we must take the appropriate matrix element of the product of matrices inside the parentheses; σ_{3c}, $\sigma_{3\eta}$, $R_{3c}^{t,b}$, and $V_{3\eta}$ stand for rank-2 matrices corresponding to rank-3 matrices with one fixed index: $\sigma_{3c}^{\mu\nu}=\sigma_{c\mu\nu}$, etc.; $\bar\sigma_{\mu\nu}=\sigma_{\mu\nu}-\beta v^{\mu\nu}$, where $v^{cc}=v_0$, $v^{\eta\eta}=v^\eta$, and $v^{c\eta}=v^{\eta c}=0$; $r_{cc}=\alpha_-^{12}\zeta_-$ and $r_{c\eta}=\alpha_-^{12}\zeta_+$; and $\alpha_\pm$ and $\zeta_\pm$ are the same as in Eqs. (32)–(34) and $\alpha^t_\pm$ and $\alpha^b_\pm$ stand for the "thermal" and "ballistic" parts of $\alpha_\pm$, as they do in (32)–(34). The matrix elements $R^{\mu\nu}_{3c}$ are given by the following expressions:

$$\begin{aligned} R^{cc}_{3c}=R^{\eta\eta}_{3c}&=\tfrac{1}{2}(\alpha_+\zeta_+ +\alpha_-\zeta_-), \\ R^{c\eta}_{3c}=R^{\eta\,c}_{3c}&=-0\,\tfrac{1}{2}(\alpha_+\zeta_- +\alpha_-\zeta_+). \end{aligned} \tag{40}$$

The quantities V_3 have the meaning of "total" three-particle interactions consisting of the "direct" effective interaction σ_3 and the "kinematic" interaction S_3 similar to the so-called kinematic interaction of the spin z-components S^z_i in spin systems.[11] Using the results of Ref. 11, we can show that the matrix elements $S^{\mu\nu}_{3\eta}=S_{\eta\mu\nu}$ are equal to the third derivatives of the entropy S_{MFA} in Eq. (37b) with respect to the occupation numbers c_μ. As a result we obtain

$$V^{\mu\nu}_{3\eta}=V_{\eta\mu\nu}=\sigma_{\eta\mu\nu}+\frac{\partial^3 S_{\mathrm{MFA}}}{\partial\eta\partial c_\mu\partial c_\nu}. \tag{41}$$

Equation (39) illustrates the general structure of (n,c)-equations: their solutions $\sigma_{n,c}$ include powers of the ratio $K^{\eta c}_0/K^{cc}_0=\chi=(d\eta/dc)_h$ up to the $(n-1)$st. This corresponds to the fact that in the lowest MFA the diagrammatic representation of Eqs. (14) has the form of a "Cayley tree," that is, a collection of n-leg diagrams without closed loops. Physically this reflects the validity of the RDF (38) in accordance with the structure of $\sigma_{2,c}$ given by (33).

Equation (39) makes it possible to express $\sigma_{3,c}$ explicitly in terms of $\alpha_\pm$, $\zeta_\pm$, $\sigma_{3,\eta}$, $\sigma_{\mu\nu}$, and χ. Differentiating expression (33) for $\sigma_{2,c}$, after performing straight-forward but lengthy computations [which use the RDF for $\sigma_{n,\eta}$ and Eqs. (35)], confirms Eq. (38) for $n=3$. Since the result, in which a vast number (more than a hundred) of terms of different types on both sides of the equation coincide, cannot be accidental, we assume that this equation confirms the RDF (38) for all values of n (although we have not proved this formally for $n\geqslant 4$).

Thus, to determine the contribution Q_c to (23), we can use RDF (38) at a constant h and the expression (38) for σ_{cc}. Here we must bear in mind that σ_{cc} in (33) also incorporates the term $\sigma^r_{cc}=\partial^2 Q_\eta/\partial c^2$, which should be subtracted when finding Q_c. Using also Eqs. (37) and (36), we arrive at the following expressions for the total free energy $F=F_c+F_r$ and the chemical potential $\lambda=(dF/dc)_h$:

$$\lambda(c,h)=\int_{c_{\mathrm{ls}}}^{c}\sigma^{\alpha}_{cc}(x,h)\,dx+\frac{1}{2}\ln\frac{c_1c_2}{c'_1c'_2}+a_1, \tag{42a}$$

$$F(c,h)=\int_{c_{\mathrm{ls}}}^{c}\lambda(x,h)\,dx+a_0, \tag{42b}$$

where $\sigma^{\alpha}_{cc}=\sigma_{cc}+\chi\sigma_{\eta c}$ is the sum of the first two terms in Eq. (33).

Let us discuss the choice of the limits of integration and the constants a_0 and a_1 in Eqs. (42). As noted earlier, for the single-phase alloy considered here these constants have no observational meaning and cannot be found solely from the conditions that (4) and (10) be time-independent. However, in the physically interesting case of $h=0$ the existence of both an ordered phase and a disordered phase (which has $\eta=0$) is possible, and the differences Δa_0 and Δa_1 in a_0 and a_1 between these phases are important for the condition (9) that these phases be in equilibrium. We determine Δa_0 and Δa_1 from the physical assumption about the "maximum smoothness" of the variation of the free energy $F(\eta)$ as the order parameter η tends to zero. The geometric locus of points in the (c,T) plane at which $\eta(c,T)\to 0$ is the ordering spinodal curve (OSC), whose equation is obtained by requiring expression (27) to vanish. For this reason in Eqs. (42) for the λ and F of the ordered phase we select the lower limit of integration to lie on the left branch of the spinodal curve, $c_{\min}=c_{\mathrm{ls}}(T)$, and the values of a_0 and a_1 are determined from the continuity of $F(c,\eta)$ as $\eta\to 0$ (i.e., on the left and right OSC branches), with the values $F_{\mathrm{d}}(c)$ corresponding to the disordered phase:

$$F(c_{\mathrm{ls}})=F_{\mathrm{d}}(c_{\mathrm{ls}}),\quad F(c_{\mathrm{rs}})=F_{\mathrm{d}}(c_{\mathrm{rs}}), \tag{43}$$

where $c=c_{\mathrm{rs}}$ corresponds to the right branch of the ordering spinodal curve (at a given value of T).

4.3. Properties of the thermodynamics of ordering

Let us discuss the physical consequences of Eqs. (42). First we note that the chemical potentials of the ordered and disordered phases, λ and λ_{d}, calculated here in the MFA, cannot generally be matched continuously on the OSC, so that in the (c,R) plane the function $\lambda(c,T)$ formally has discontinuities $\Delta\lambda=\lambda-\lambda_{\mathrm{d}}$ on the OSC $c=c_{\mathrm{ls}}(T)$ and $c=c_{\mathrm{rs}}(T)$. This suggests the presence of similar discontinuities as $\eta\to 0$ in the effective interactions $\eta_{n,c}$ (determining the total F and λ as series of the form (17) of Ref. 8), which is illustrated by the expression (33) for σ_{cc}. For small η the quantity α_- in (34b) is proportional to η, while $\chi=d\eta/dc$ increases like $1/\eta$. Hence as $\eta\to 0$ the value of σ_{cc} does not transform into the value of σ^{d}_{cc} for the disordered phase (corresponding to the first term in (33) at $\eta=0$) but has a discontinuity proportional to Γ.

The presence of such discontinuities as $\eta\to 0$ appears to be a result of approximations inherent in MFA; using more consistent approaches should probably smooth out such discontinuities. As is well known, the MFA cannot be used in the immediate vicinity of second-order transition points, that is, close to the OSC. Even if the interaction range r_0 is large, the MFA becomes invalid for $\tau<r_0^{-6}$ (or $\tau<|v(\mathbf{r})/v(\mathbf{k}_{\mathrm{s}}|^2)$, where τ characterizes the closeness to OSC, for instance, $\tau=(c-c_{\mathrm{ls}})/c_{\mathrm{ls}}$ (see Ref. 11). Physically, the MFA does not allow for the fact that the order parameter η does not emerge uniformly over the entire macroscopic sample; rather, it emerges as an $\eta(\mathbf{r})$ inside correlated regions of size $r_{\mathrm{c}}(\tau)$, even in the absence of macroscopic ordering. This nonuniformity of the initial stage of ordering is not taken into account in MFA. Allowing for these effects of local ordering in a proper manner may be expected to smooth out the above-noted discontinuities for values of τ of the order of r_0^{-6}, a region where MFA breaks down. We also note that if in Eq. (31) the **k** are small but finite, the value of χ in an expression for $\sigma_{2\mathbf{k}^{cc}}$ similar to (33) is replaced near the OSC by a factor of the form

$$\eta K_{\mathbf{k}}^{\eta\eta} \sim \frac{\eta}{k^2+r_c}^{-2},$$

where we have dropped insignificant numerical factors. Hence, the second term in (33) varies with k and τ in this region like $\sigma^2/(k^2+r_c^{-2})$, which corresponds to the interaction

$$\sigma_{cc}(\mathbf{r}) \sim \frac{\eta^2}{r} \exp\left(-\frac{r}{r_c}\right)$$

for large values of r. Thus, the discontinuities reflect the emergence at small η and large r_c of peculiar long-range interactions, which must become modified and smoother owing to the local-ordering effects mentioned above.

Since we cannot use the MFA in the immediate vicinity of the OSC, the above assumption that the $F(c)$ and $F_{\mathrm{d}}(c)$ calculated in the MFA can be matched continuously on the OSC is generally unjustified. Thus, within the present framework in which only homogeneous systems are considered we cannot exclude the possibility of finite discontinuities on the OSC in not only the values of λ calculated in the MFA but also in the values of the free energy F, that is, $\Delta F_{\mathrm{MFA}} = F - F_{\mathrm{d}} \neq 0$ (this fact leads to phase diagrams and conclusions even more unusual than those discussed below). At the same, in proving the inevitability of discontinuities on OSC for the chemical potential λ_{MFA} we can omit the critical region $\tau < r_0^{-6}$. To do this, we consider the particular case of a symmetric substitution alloy, in which the asymmetric potentials u_{ij} are zero. For such an alloy the expressions for F in both ordered and disordered phases can be chosen symmetric under interchange of c' and c, that is, in the form of the function $F = F(cc')$ and $F_{\mathrm{d}} = F_{\mathrm{d}}(cc')$, so that both derivatives,

$$\lambda = \frac{\partial F}{\partial c}, \quad \lambda_{\mathrm{d}} = \frac{\partial F_{\mathrm{d}}}{\partial c},$$

vanish at $c = c' = \frac{1}{2}$. Then, integrating the difference $\Delta\sigma_{cc} = \sigma_{cc} - \sigma_{cc}^{\mathrm{d}}$ via RDF (38) from $c = \frac{1}{2}$ to values of c close to the OSC, we obtain the value of the finite discontinuity $\Delta\lambda_{\mathrm{MFA}}$, always remaining within the range of applicability of our formulas, $\tau > r_0^{-6}$.

The presence of such discontinuities $\Delta\lambda$ (which we assume to be smoothed out in a narrow range $\tau \sim r_0^{-6}$ near the OSC) leads to remarkable features of the thermodynamics of such ordering. Their nature depends on the sign of the discontinuities $\lambda_{\mathrm{l}} = \Delta\lambda(c_{\mathrm{ls}})$ and $\lambda_{\mathrm{r}} = \Delta\lambda(c_{\mathrm{rs}})$. If $\Delta\lambda_{\mathrm{l}} < 0$ (or $\Delta\lambda_{\mathrm{r}} > 0$), the ordered-phase free energy $F(c)$ for $c > c_{\mathrm{ls}}$ near the OSC lies below $F_{\mathrm{d}}(c)$ (in the vicinity of the point $c = c_{\mathrm{ls}}$; see Fig. 2). This means that a common tangent to $F(c)$ and $F_{\mathrm{d}}(c)$ can be constructed in the ordinary manner, which suggests that the phase-equilibrium equations (9) have solutions describing the formation of layers in the alloy. Hence, for $\Delta\lambda_{\mathrm{l}} < 0$ and $\Delta\lambda_{\mathrm{l}} < 0$ ordering is accompanied by striation for all values of the ballistic-mixing parameter Γ. This striation mechanism differs from the one examined by Bellon and Martin,[6] who discussed bifurcation of the solution of Eq. (26) for η, a process that emerges only for large $\delta \geqslant \frac{1}{2}(\sqrt{3}+1)$.

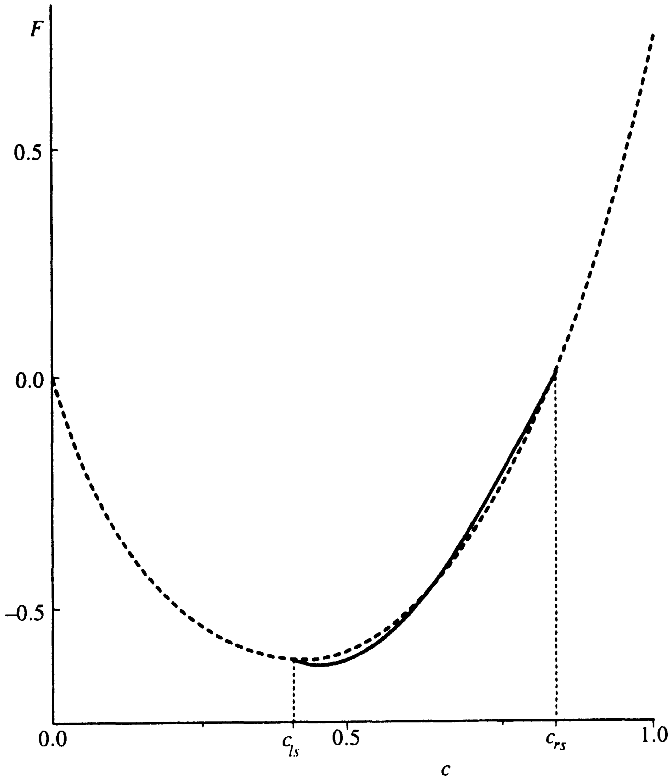

FIG. 2. The free energies $F(c)$ for the ordered phase (solid curve) and $F_{\mathrm{d}}(c)$ for the disordered phase (dashed curve) calculated at $T = 0.45 T_0$ for the model corresponding to Fig. 1c.

The opposite case, $\Delta\lambda_{\mathrm{l}} > 0$ or $\Delta\lambda_{\mathrm{r}} < 0$ (in the vicinity of point $c = c_{\mathrm{rs}}$; see Fig. 2), is more unusual. Here the free energy near the OSC increases rather than decreases during ordering, as it does in ordinary phase transitions. This seems to contradict the minimization of F discussed earlier. Since we have $F(\eta) > F(0) = F_{\mathrm{d}}$, this principle would seem to imply that the system must choose from the solutions of the time-independence equation (26) the one that corresponds to $\eta = 0$, that is, remain disordered even if a solution with $\eta \neq 0$ is possible. However, for values of c and T lying inside the OSC the disordered phase is locally unstable: for **k** close to $\mathbf{k}_{\mathrm{s}}$ the denominator of the correlator $K(\mathbf{k})$ in (16) passes through zero, which indicates spontaneous generation of concentration waves with these **k**. At the same time, for an ordered phase with $\eta \neq 0$ the presence of such instabilities is not obvious, so that this phase, can occur (say, as a metastable phase). States with $F(\eta) < F(0)$ we will call frustrated. Figure 1 shows that such states are possible within sizable intervals of values of c and T.

The possible existence of frustrated phases poses the question of feasible limits on the application to open systems of the principle that the free energy is minimized. For instance, in deriving this principle in Sec. 2 we used the "generalized ergodic hypothesis," that is, we assumed that for given external parameters η and number of particles N the statistical properties of a stationary state are determined completely. We also implicitly used a similar assumption that the time evolution of a macrononstationary state is independent of the way such a state is prepared for given values of the number of atoms in the subsystems, N_a, and so one. Applying these assumptions to open systems requires more careful analysis. Moreover, the experience in studies of open systems of another type, spin glasses, shows that the principle that F be a minimum should be formulated for such systems with certain reservations, which are unnecessary in the case of equilibrium systems. For instance, Binder and Young[15] suggested formulating this principle for spin glasses as the "principle that F be a minimum among locally stable states," states that remain stable under infinitely small perturbations. In our case a similar reservation is necessary in order to define a "local-stationary state of a subsystem," a concept used in deriving the minimality of F in Sec. 2. Thus, frustrated states in our model can serve as another example pointing to the necessity of similar limited formulations of the principle that F be minimized when this principle is applied to nonequilibrium or open systems.

If the existence of such a "limited" principle minimum F that allows for the presence of homogeneous frustrated phases is acknowledged, we can discuss the question of the possible existence of inhomogeneous, "less frustrated" states, which have an advantage in F over homogeneous phases. This seems to be quite possible in our problem, in which the properties of the thermodynamics are closely linked to a sharp dispersion in the effective interactions at small **k**. To illustrate this possibility we assume that such an inhomogeneous state (possibly random) can be described by a free energy F of the Ginzburg–Landua form, which incorporates the "quasilocal" order parameter η and the characteristic value k_c of the wave vector. Replacing, the quantity χ in (33) by the factor $\kappa K_{\mathbf{k}}^{\eta\eta}$ for finite k (in accordance with the above estimate) we can suggest instead of (37) and (42) the following expression for F:

$$F=\frac{1}{2}(k_c^2-\tau)\eta^2+\frac{1}{4}b\eta^4+\Delta\int_0^\tau\frac{(\tau-x)\eta^2(x)dx}{k_c^2-x+3b\eta^2(x)}, \tag{44}$$

Here we have dropped all insignificant terms and factors Δ (assumed small) is proportional to the ballistic-mixing parameter Γ, and we have not allowed for the presence of possible MFA discontinuities $\Delta\lambda_{\mathrm{MFA}}$ and ΔF_{MFA} (which would only increase the emerging inhomogeneity). Minimizing F in k_c, we obtain

$$\eta^2\simeq\frac{\tau}{b},\quad k_c^2\sim\tau\exp\left(-\frac{4}{\Delta}\right).$$

Thus, a state with a mesoscopically large inhomogeneity range k_c^{-1} has an advantage in F, that is, is less frustrated than a homogeneous state. Notwithstanding the obvious crudeness of such an estimate, it can illustrate a tendency toward formation of inhomogeneous phases in the presence of ballistic mixing. The presence of a general tendency of this kind in the models considered here may be correlated with the experimental indications that some irradiated alloys contain peculiar inhomogeneous structures whose properties strongly vary with temperature and conditions of irradiation.[2–4]

5. CONCLUSION

Our study shows that applying ordinary assumptions and methods of statistical physics to a description of ordering in open systems carried out on the model of an irradiated alloy leads to certain difficulties with the principle that the free energy be a minimum for stationary homogeneous systems and also to unusual features of phase equilibria. As noted above, these difficulties could indicate a tendency toward forming inhomogeneous and/or nonstationary states within certain ranges of radiation parameters. Such tendencies have been noticed in other systems (see, e.g., Ref. 15). Further studies of these aspects require generalizing the applied methods to both inhomogeneous stationary states and nonstationary, kinetic, processes. The methods described in Ref. 8 and in this paper apparently allow for such generalizations.

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1) Note the misprints in the similar formulas (9) and (10) in Ref. 8: the quantities $q_i=\langle\partial\hat{Q}/\partial h_i\rangle$ in these formulas must be replaced with $-q_i$.

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