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MASTER EQUATION APPROACH TO THE CONFIGURATIONAL KINETICS OF NONEQUILIBRIUM ALLOYS: EXACT RELATIONS, H-THEOREM, AND CLUSTER APPROXIMATIONS

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The fundamental master equation for probabilities of various atomic distributions over lattice sites in an alloy is used to develop the theoretical description for the alloy configurational kinetics. Exact equations for temporal evolution of local concentrations and correlators as well as for the nonequilibrium alloy free energy are presented. Methods for the approximate treatment of these equations are discussed.

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Problems of theoretical description of nonequilibrium statistical systems attract attention in many areas of physics. For equilibrium systems, such description is given by the Gibbs distribution and the statistical thermodynamics, but for the states far from equilibrium, the similar standard approaches are not available. Elaboration of such approaches is of particular interest for the cofigurational alloy kinetics, the atomic distribution evolution in nonequilibrium alloys. The microstructure and macroscopic properties of such alloys, e.g. strength and plasticity, depend crucially on their thermal and mechanical history, for example, on the transformation kinetic path during phase transformations. A number of theoretical approaches have been proposed in that field, see e.g. [1-4]. However, these approaches either treat the uniform alloy case [1] which excludes from consideration most applications of interest, or use various unclear approximations, e.g. extrapolation of linear Onsager equations for weakly nonequilibrium states to the nonlinear region of states far from equilibrium [2,3], which can result in significant errors [5-7].

Recently [5-7] we supposed to describe the nonequilibrium alloy kinetics using the fundamental master equation for probability P to find the occupation number set $\{n_i\} = \alpha$, for example, in the binary alloy A-B, where $n_i = n_i^{\mathrm{A}} = 1$ if atom A is at site i, and $n_i = 0$ otherwise:

$$dP(\alpha)/dt = \sum_{\beta}[W(\alpha,\beta)P(\beta) - W(\beta,\alpha)P(\alpha)] \equiv \hat{S}P \qquad (1)$$

while $W(\alpha,\beta)$ is the $\beta \to \alpha$ transition probability.

Accepting for probabilities W in (1) the "thermally activated atomic exchange model" [1,8,9], we can express the transfer matrix $\hat{S}$ in (1) via the microscopic inter-site jump probabilities w_{kl} (see [9] for details),

$$w_{kl} = \omega_{kl} \exp[-\beta(E^s_{kl} - \hat{E}^{in}_{kl})] \equiv \gamma_{kl} \exp(\beta \hat{E}^{in}_{kl}) . \qquad (2)$$

Here ω_{kl} is the attempt frequency, $\beta = 1/T$ is the reciprocal temperature, E^s_{kl} is the saddle point energy, γ_{kl} is the configurationally independent factor in the jump

probability, and $\hat{E}_{kl}^{in}$ is the initial (before jump) configurational energy of jumping atoms. Let us write the total configurational Hamiltonian H as

$$H = \sum_{\alpha} \varphi_i^{\alpha} n_i^{\alpha} + \frac{1}{2} \sum_{i\alpha, j\beta} v_{ij}^{\alpha\beta} n_i^{\alpha} n_j^{\beta} + \frac{1}{3!} \sum_{i\alpha, j\beta, k\gamma} v_{ijk}^{\alpha\beta\gamma} n_i^{\alpha} n_j^{\beta} n_k^{\gamma} + \dots \tag{3}$$

where index α, β or γ corresponds to the A- or B-species atom, and quantities φ_i^{α} are possible external fields (which are present only if not all alloy sites are equivalent). Then the operator E_{kl}^{in} in (2) can be written as the formal variational derivative of the hamiltonian (3)

$$E_{kl}^{in} = \delta H/\delta n_k^{\mathrm{B}} + \delta H/\delta n_l^{\mathrm{A}} - \delta^2 H/\delta n_k^{\mathrm{B}} \delta n_l^{\mathrm{A}} \equiv \hat{v}_k^{\mathrm{B}} + \hat{v}_l^{\mathrm{A}} - \hat{v}_{kl}^{\mathrm{BA}} \tag{4}$$

where the third term corresponds to substraction of the "double-counted" interaction between atom A at site l and atom B at site k. Let us note that in terms of the operators $n_i = n_i^{\mathrm{A}}$ (i.e. after eliminating operators $n_i^{\mathrm{B}} = n_i' = 1 - n_i$) the Hamiltonian (3) takes the form

$$H = v_0 + \sum_i \varphi_i n_i + H^{int} = v_0 + \sum_i \varphi_i n_i + \sum_{i>l} v_{il} n_i n_l + \sum_{i>l>m} v_{ilm} n_i n_l n_m + \dots \tag{5}$$

where v_0, φ_i and $v_{i\dots l}$ are linearly expressed via φ_i^{α} and $v_{i\dots l}^{\alpha\dots\gamma}$. For example, for the pair interaction v_{il} we have

$$v_{il} = (v^{\mathrm{AA}} - 2v^{\mathrm{AB}} + v^{\mathrm{BB}})_{il} + \sum_k (v^{\mathrm{BBB}} - v^{\mathrm{BBA}} - v^{\mathrm{BAB}} + v^{\mathrm{BAA}})_{kil} + \dots \tag{6}$$

Let us now multiply eq. (1) by operators n_i, $n_i n_j$, $\dots n_i n_j \dots n_k$ and sum both sides of these relations over all number sets $\{n_i\}$, i.e. over all configurational states. Then we obtain the set of equations for averages $< n_i n_j \dots n_k > \equiv g_{ij\dots k}$, in particular, for the average occupation $c_i = < n_i > = g_i$:

$$dg_{ij\dots k}/dt = < n_i n_j \dots n_k \hat{S} > \tag{7}$$

where $< (\dots) > = \mathrm{Tr}\{(\dots)P\}$ means averaging over the distribution P, the solution of eq. (1). Using eqs. (1), (2) and the explicit expresssion for $\hat{S}$, given in [9], we can rewrite (7) as

$$\frac{dg_{ij\dots k}}{dt} = \sum_{s\neq i,j,\dots k; i\neq j\neq\dots k} < (n_i' n_s \gamma_{is} e^{\beta E_{is}^{in}} - n_s' n_i \gamma_{si} e^{\beta E_{si}^{in}}) n_j \dots n_k > + \{i \to j, \dots, k\} \tag{8}$$

where $\{i \to j, \dots k\}$ denotes the sum of expressions obtained from the first term of (8) by index permutation.

Since n_i and $n_i' = 1 - n_i$ are the projecton operators: $n_i^2 = n_i$, $(n_i')^2 = n_i'$, $n_i n_i' = 0$, the most general expression for the distribution function $P\{n_i\}$ in (1) can be written as

$$P\{n_i\} = \exp(\Omega + \sum_i \lambda_i n_i - Q) \tag{9}$$

where the correlative, or "quasiinteraction" term Q is

$$Q = \sum_{i>j} a_{ij} n_i n_j + \sum_{i>j>k} a_{ijk} n_i n_j n_k + \dots \tag{10}$$

For what follows it is convenient to rewrite eqs. (8) in the form more symmetrical with respect to permutation of indices i and s. To this end we make following manipulations (used in [10,9]). We perform summation over all values of n_s (i.e. $n_s = 0$ and $n_s = 1$) in the first term of eq. (8), and similarly over all values of operator n_i in the second term. Then we formally restore summation over n_s in the first term introducing the projection operator n'_s (since summation over n_s with this factor is equivalent to multiplying all the n_s-dependent terms by unity), and similarly restore summation over n_i with the factor n'_i in the second term. Then eqs. (8) take the following symmetrical form

$$dg_{ij\ldots k}/dt = \sum_{s,\ i\neq j\ldots\neq k} \gamma_{is} < (\exp D_{is} - \exp D_{si})\, n'_i n'_s n_j \ldots n_k > + \{i \to j, \ldots k\} \quad (11)$$

where $D_{is} = \beta(\hat{v}_i^{\mathrm{B}} + \hat{v}_s^{\mathrm{A}} - \hat{v}_{is}^{\mathrm{BA}}) + \lambda_s - Q_s$; $Q_s = \delta Q/\delta n_s$ means the formal variational derivative of the quasihamiltonian Q (10) over n_s, analogous to that in eq. (4), and we took into account the $i \to s$ symmetry of the configuration independent factor γ_{is} in the jump probability. From the formal point of view relations (11) provide a generalization of similar eqs. (7b) in [10] or (11) in [9] to a more general case of the non-stationary substitution alloy (but for the "closed" system, in particular, in the absence of irradiation).

Let us divide operator D_{is} in eqs. (11) into parts D_{is}^+ and D_{is}^- being symmetrical and antisymmetrical in indices i and s. To simplify formulas, let us suppose the "double-counted" term v_{is}^{BA} in (11) to be symmetric in indices i and s (as it is, for example, when interatomic interactions are purely pairwise). Then D_{is} in (11) is written as $D_{is} = D_{is}^+ + D_{is}^-$, where

$$D_{is}^+ = \frac{1}{2}\beta\left[(\hat{v}^{\mathrm{B}} + \hat{v}^{\mathrm{A}})_i + (\hat{v}^{\mathrm{B}} + \hat{v}^{\mathrm{A}})_s - 2\hat{v}_{is}^{\mathrm{BA}}\right] + \frac{1}{2}[(\lambda_i + \lambda_s) - (Q_i + Q_s)], \quad (12a)$$

$$D_{is}^- = \frac{1}{2}\beta\left[(\hat{v}^{\mathrm{B}} - \hat{v}^{\mathrm{A}})_i - (\hat{v}^{\mathrm{B}} - \hat{v}^{\mathrm{A}})_s\right] - \frac{1}{2}[(\lambda_i - \lambda_s) - (Q_i - Q_s)]. \quad (12b)$$

Using expressions (4)-(6) for operators $\hat{v}$ and H we can rewrite expression (12b) for D_{is}^- in a more transparent form

$$D_{is}^- = \frac{1}{2}\left[(\lambda_s + \beta\varphi_s) - (\lambda_i + \beta\varphi_i) + (Q_i - \beta H_i^{int}) - (Q_s - \beta H_s^{int})\right] \quad (13)$$

where $H_i^{int} = \delta H^{int}/\delta n_i$ is the variational derivative of the interaction Hamiltonian (5). Then kinetic equations (11) take the final form convenient for both general discussions and approximate treatments

$$\frac{d}{dt} < n_i n_j \ldots n_k > = \sum_{s,\ i\neq j\ldots\neq k} \gamma_{is} \left\langle e^{D_{is}^+} n'_i n'_s \left(e^{D_{is}^-} - e^{-D_{is}^-}\right) n_j \ldots n_k \right\rangle + \{i \to j, \ldots k\}. \quad (14)$$

The expression in round brackets in (14) has evidently meaning of the "generalized driving force" (GDF) that deterinines trends in the atomic distribution evolution, while its prefactor plays role of the generalized mobility. To make the expression for GDF more transparent, we can take into account that the average value of fields φ_i in the Hamiltonian (5), $\bar{\varphi} = \sum_i \varphi_i/N_s$ (where N_s is the total number of lattice sites), has no physical meaning, reducing to an unessential

constant because of the atom number conservation. So we can put $\bar{\varphi} = 0$. Then it is convenient to re-define parameters λ_i in (9), separating their mean value $\lambda = \sum_i \lambda_i / N_s$, i.e. using instead of λ_i the difference $\psi_i = \lambda - \lambda_i$. Then in eqs. (13), (14) for GDF the constant λ cancels, while the stationary equilibrium form of $P(n_i)$ (9) corresponds to the Gibbs distribution with $\psi_i = \beta\varphi_i$ and $a_{i\ldots j} = \beta v_{i\ldots j}$. The constant λ determines the total particle number $N = \sum_i n_i$ and has meaning of the reduced chemical potential $\beta\mu$.

Eqs. (14) make it possible to define the "nonequilibrium free energy" having a fundamental property to not increase under spontaneous evolution of the system, similarly to the Boltzmann's not decreasing entropy. The derivation is similar to that given in [5] in the mean-field approximation (MFA), but now it is exact. Let us multiply eqs. (14) for $dg_i/dt = dc_i/dt$ by $(-\tilde{a}_i) = \lambda_i + \beta\varphi_i$ and sum them over i, eqs. (14) for dg_{ij}/dt by $(-\tilde{a}_{ij}) = \beta v_{ij} - a_{ij}$ and sum them over all $i > j$, eqs. for $g_{ij\ldots k}$ by $(-\tilde{a}_{ij\ldots k}) = \beta v_{ij\ldots k} - a_{ij\ldots k}$ and sum them over all $i > j > \ldots > k$, etc. Then we sum all these equations. If we denote for brevity

$$\xi_{mi} = \exp\{ \sum_{i_2 > \ldots > i_m} \tilde{a}_{ii_2\ldots i_m} n_{i_2} \ldots n_{i_m} \} \tag{15}$$

then the resulting relation can be written as

$$dF/dt = -\frac{1}{2} \sum_{is} < A_{is} n_i' n_s' (\Pi_i - \Pi_s) \ln \frac{\Pi_i}{\Pi_s} > . \tag{16}$$

Here $\Pi_i = \exp(-\lambda_i + Q_i - \beta\varphi_i - \beta H_i^{int})$ is the product of all ξ_{mi}: $\Pi_i = \prod_m \xi_{mi} = \xi_{1i}\xi_{2i}\ldots\xi_{N_s i}$, the positive quantity A_{is} is related to the operators D_{is}^+ and Π_i as: $A_{is} = \gamma_{is} \exp(D_{is}^+)(\Pi_i \Pi_s)^{\frac{1}{2}}$, and the "generalised free energy" F is defined by the differential relation

$$dF = -\sum_{m=1}^{N_s} \sum_{i_1 > \ldots > i_m} \tilde{a}_{i_1\ldots i_m} dg_{i_1\ldots i_m} = d < \beta H > + \sum_i \lambda_i dc_i - \sum_{i > \ldots > k} a_{i\ldots k} dg_{i\ldots k} . \tag{17}$$

Since summand in the rhs of eq. (16) is not-negative (and is similar in its form to that arising in proofs of the H-theorem for entropy), the relation (16) shows that the quantity F has the fundamental property to not increase under spontaneous evolution of the system.

To clarify the physical meaning of the free energy F we note that the normalizing constant Ω for the distribution (9), or the "generalised grand canonical potential"

$$\Omega = -\ln \mathrm{Tr} \exp(\sum_i \lambda_i n_i - Q), \tag{18}$$

according to its definition (18) obeys the relations

$$\partial\Omega/\partial\lambda_i = -c_i, \qquad \partial\Omega/\partial a_{i\ldots j} = g_{i\ldots j} . \tag{19}$$

Thus the basic differential relation for Ω ("the first law of thermodynamics") is

$$d\Omega = -\sum_i c_i d\lambda_i + \sum_{i > \ldots > j} g_{i\ldots j} da_{i\ldots j} . \tag{20}$$

Therefore, if we define the thermodynamical potential $\tilde{F}$ via the Legendre's transformation of Ω

$$\tilde{F} = \Omega + \sum_i \lambda_i c_i - \sum_{i>\ldots>j} a_{i\ldots j} g_{i\ldots j}, \tag{21}$$

the first law of thermodynamics for it takes the form

$$d\tilde{F} = \sum_i \lambda_i dc_i - \sum_{i>\ldots>j} a_{i\ldots j} dg_{i\ldots j}\,. \tag{22}$$

Comparing eqs. (22) and (17) we see that the free energy F is simply related to the thermodynamic potential $\tilde{F}$ (22):

$$F = \tilde{F} + < \beta H >= \Omega + \sum_i (\lambda_i + \beta\varphi_i)c_i + < \beta H^{int} - Q > \,. \tag{23}$$

Using the generalised chemical potential λ and the "full" quasihamiltonian $Q_f = \sum_i \psi_i n_i + Q$, we can also rewrite eq. (23) in a more transparent form

$$F = \Omega + \lambda N + (< \beta H > - < Q_f >)\,. \tag{24}$$

Eqs. (16), (23), (24) show, in particular, that in terms of the distribution (9), its evolution to equilibrium is described by the following relations: $\lambda \to \mu$, $\psi_i \to \beta\varphi_i$, $a_{i\ldots j} \to \beta v_{i\ldots j}$. The relaxation times τ for the processes described by these relations can be rather different. Usually they seem to obey the inequalities $\tau(\lambda), \tau(\psi_i) \gg \tau(a_{i\ldots j})$ [5-7], but these points need further studies.

Eqs. (14) can also be used for approximate approaches to the alloy kinetics description. These approaches correspond to various approximations in calculations of averages in the rhs of eqs. (14). The simplest approach is MFA that neglects all intersite correlations, which also implies neglecting the interaction renormalizations $a_{i\ldots j} - \beta v_{i\ldots j}$. Therefore, in the MFA one considers evolution of only mean site occupations $< n_i >= c_i$, and eqs. (14) become the mean-field kinetic equations (MFKE) discussed in [5-7]:

$$dc_i/dt = 2\sum_s M_{is} \sinh\,[(\partial F/\partial c_s - \partial F/\partial c_i)/2]\,. \tag{25}$$

Here $F = F\{c_i\}$ is the MFA expression for the free energy (23) presented in [5], while M_{is} is the generalized mobility in the MFA : $M_{is} = \gamma_{is}\{c_i c_i' c_s c_s' \exp(\beta u_i + \beta u_s)\}^{1/2}$, where $c_i' = 1 - c_i$, $u_i = v_i^{\mathrm{A}}\{c_j\} + v_i^{\mathrm{B}}\{c_j\}$, and $v_i^{\mathrm{A}}\{c_j\}$ or $v_i^{\mathrm{B}}\{c_j\}$ are obtained from the operators $\hat{v}_i^{\mathrm{A}}\{n_j\}$ or $\hat{v}_i^{\mathrm{B}}\{n_j\}$ in eq. (4) by the substitution: $n_j \to c_j$.

In spite of its relative simplicity, MFKE in many cases is sufficient for treatments of kinetic problems, and it was used for studies of a number of interesting phenomena [2,5,6]. However, for some problems, e.g. those connected with the $L1_2$ and $L1_0$ type orderings in the FCC lattice, MFA is known to be insufficient. In treating equilibrium thermodynamics these difficulties stimulated elaboration of more refined, cluster approximations, the known cluster variation method (CVM) [11,12], and also its simplified version, the cluster field method (CFM) [13]. Later CVM has been generalised to treat kinetics of uniform alloys [1]. However, for nonuniform alloys, the kinetic cluster equations suggested so far [4] seem to be not fully consistent, as their stationary solutions don't turn into the thermodynamic cluster results.

Eqs. (14) are just suitable for the cluster treatments, particularly for the CFM approach. The CFM corresponds to neglecting the interaction renormalization effects within the clusters considered: in writing distributions of type (9) for each of clusters one puts $a_{i\ldots j} = \beta v_{i\ldots j}$ [13]. Therefore, the CFM treatment of kinetic problems should correspond to similar neglecting such renormalizations due to kinetic effects, i.e. putting $a_{i\ldots j} = \beta v_{i\ldots j}$ in eqs. (9), (14). Thus the "cluster field kinetic equations" (CFKE) have the same form (25) as MFKE, but both the free energy $F\{c_i\}$ and the mobility $M_{is} = \gamma_{is} < n_i' n_s' \exp D_{is}^{+} >$ should be calculated using the CFM. The stationary solutions of these equations correspond to the thermodynamical equilibrium conditions $\partial F/\partial c_i = \text{const}$, so the solutions automatically agree with the thermodynamic results for same level of approximations, unlike the equations suggested in [4].

Methods for the CFM calculations of both the operator products $< n_i \ldots n_j >$ entering M_{is} and the free energy $F\{c_i\}$ for inhomogeneous allloys have been described earlier [13] and are simple enough. In particular, for the 2-cluster, or "pair" approximation of CFM (coinciding with that of CVM) $F\{c_i\}$ is calculated analytically [13], thus kinetic calculations in this approximation should be as feasible as those in MFA [5–7].

In the CVM, one should calculate some of renormalizations $a_{i\ldots j} - \beta v_{i\ldots j}$, as well as the corresponding averages $g_{i\ldots j}$ [11,12]. The resulting kinetic equations for $c_i(t)$ and $g_{i\ldots j}(t)$ can be derived similarly to CFKE. However, these equations look cumbersome and don't seem to be suitable for applications to nonuniform alloys.

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