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# Direct Free Energy Minimization Methods: Application to Grain Boundaries [and Discussion]

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# Direct free energy minimization methods: application to grain boundaries

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A critical review is given of recently developed methods for determining the atomic structures and solute concentration profiles at defects in elemental solids and substitutional alloys as a function of temperature. Exact results are given for the effective force on an atom arising from the vibrational entropy in the quasiharmonic approximation and for the occupancy of a site in the pair potential approximation. An improved, approximate formula is given for the effective force arising from the vibrational entropy. The mean field approximation that is used in the alloy problem is compared with the auto-correlation approximation. It is shown that the better statistical averaging of the auto-correlation approximation leads to effective pair interactions that are temperature and concentration dependent.

## 1. Introduction

Kinetic, mechanical and electrical properties of grain boundaries in most (possibly all) materials vary markedly with temperature and purity of the specimen. In elemental bicrystals the excess vibrational entropy of an interface can drive grain boundary phase transformations. The introduction of minute quantities of impurities can result in strong grain boundary segregation and dramatic changes in grain boundary properties. The modelling of such processes entails the consideration of the appropriate free energy and its minimization with respect to the atomic coordinates and the local impurity concentration. This is a formidable task because of the *five dimensional* parameter space that characterizes the orientation of the boundary plane and the misorientation between the crystal lattices. Faced with such a task it is essential to focus on *trends in behaviour* and to avoid excessively detailed studies of a few rather special cases (for an example of such an approach see Sutton (1991)). In this paper I review some new methods that involve direct minimization of free energy functionals (Sutton 1989; LeSar *et al.* 1989; Najafabadi *et al.* 1991*a*, *b*). The much greater computational speed of these methods, compared with other available techniques (see Rickman & Phillpot 1991, and references therein), and the relative ease with which all excess thermodynamic state variables are obtained, offer the greatest feasibility for exploring trends in behaviour. My purpose is to give a more thorough discussion than has so far appeared of the approximations and physical assumptions involved in these new methods.

The essence of the 'direct methods' is (i) to write down a functional form for the free energy of the system, in terms of microscopic variables such as the average atomic coordinates and atomic site occupancies, at a given temperature, pressure and set of chemical potentials, and (ii) to minimize this functional form by using the derivatives of the free energy with respect to the microscopic variables. The

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computational effort is little more than that involved in a minimization of the energy of a system at 0 K, and standard steepest descent, conjugate gradient or variable metric energy minimization techniques may be used.

## 2. Direct free energy minimization in an elemental solid

Here the issue is the determination of the atomic structure and excess thermodynamic quantities of a grain boundary (or some other defect) in an elemental solid at an elevated temperature. Since atoms are vibrating we have to define what we mean by the atomic structure. This is true even at 0 K owing to the zero point energy. We mean the time averaged positions of the atoms, assuming that the system is in thermodynamic equilibrium, and assuming that diffusion does not take place. The time averaged structure is what is measured in an X-ray diffraction experiment for example. As the temperature changes the time averaged positions of the atoms change until the time averaged forces on them are zero. The time averaged forces vary with temperature because of the anharmonicity of the atomic interactions. The time averaged structure may be determined, therefore, by requiring that the time averaged force on each atom is zero. By ergodicity the time averaged value of a quantity is identical to the ensemble average. The ensemble average of the force on an atom is equal to the negative of the gradient of the ensemble free energy with respect to its position. Thus, by expressing the free energy of the system as a function of the average atomic coordinates, we can obtain the time averaged structure directly by simply minimizing the free energy with respect to the position of each atom (Sutton 1989; LeSar *et al.* 1989).

It is emphasized that it is assumed that each atom never leaves its own potential well. More precisely, the curvature of the potential energy of each atom, evaluated at its equilibrium position, is assumed to be positive definite, and therefore the system is mechanically stable. Thus no diffusion is allowed and the theory is therefore inapplicable to liquids, or to those solids or molecules where there are two adjacent minima in the potential energy (as a function of some coordinate in the system) separated by an energy barrier comparable to $kT$, no matter how close those minima are in configurational space. Such double potential wells are important in the low temperature thermodynamics of amorphous solids, and they may also exist at crystalline defects such as grain boundaries.

### *Rewriting the free energy*

In general, it is necessary to make an approximation in order to write down the free energy of the system as a function of the average atomic positions. In the harmonic approximation the potential energy is expanded to second order in the displacements of the atoms from their mean positions. Let $u_{i\alpha}$ be the displacement of atom $i$ in the $\alpha$ direction ($\alpha = x, y$ or $z$) from the equilibrium positions $\boldsymbol{r}_i$. The potential energy is given by

$$E_{\mathrm{p}} = E_{\mathrm{p}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) - \sum_{i\alpha} f_{i\alpha}\, \delta u_{i\alpha} + \tfrac{1}{2} \sum_{i\alpha} \sum_{j\beta} D_{i\alpha j\beta}\, u_{i\alpha} u_{j\beta}, \tag{2.1}$$

where $f_{i\alpha} = -\partial E_{\mathrm{p}}/\partial r_{i\alpha}$ and $D_{i\alpha j\beta} = \partial^2 E_{\mathrm{p}}/\partial r_{i\alpha} \partial r_{i\beta}$ are evaluated at the equilibrium positions. It follows that $f_{i\alpha}$ are all zero. The potential energy $E_{\mathrm{p}}$ is expressed either in terms of some interatomic potential, such as a sum of pair potentials or $N$-body potentials, or as the potential energy surface defined by an electronic structure calculation. Writing $u_{i\alpha}(t)$ as $u_{i\alpha}\,\mathrm{e}^{\mathrm{i}\omega t}$, the equations of motion may be expressed as follows:

$$\omega^2 \tilde{u}_{i\alpha} = \sum_{j\beta} \tilde{D}_{i\alpha j\beta}\, \tilde{u}_{j\beta}, \tag{2.2}$$

where $\tilde{u}_{i\alpha}$ is equal to $\surd(m_i)\,u_{id}$ and $\tilde{D}_{i\alpha j\beta}$ is equal to $D_{i\alpha j\beta}/\surd(m_i m_j)$, and $m_i$ is the mass of atom $i$. The eigenvalues $\omega_n^2$ may be determined by solving the secular determinant $\det(\omega^2 I - \tilde{D}) = 0$ and the normalized eigenvectors $\tilde{u}_{i\alpha}^{(n)}$ may then be obtained from (2.2) by setting $\omega^2$ equal to $\omega_n^2$. The total density of states is given by $Y(\omega^2) = \Sigma_n\, \delta(\omega^2 - \omega_n^2)$. The Helmholtz free energy is given by

$$F = E_{\mathrm{p}} + kT \int_0^\infty N(\omega) \ln\left[2 \sinh\left(\frac{h\omega}{4\pi kT}\right)\right] \mathrm{d}\omega, \tag{2.3}$$

where the density of states $N(\omega)$ is related to the density of states $Y(\omega^2)$ by $Y(w^2) = N(\omega)/2\omega$. The equilibrium position $i$ is given by the condition that $-\nabla_i F = 0$. From (2.3) for the free energy we see that there are two contributions to $-\nabla_i F$. The first is the temperature independent force due to the potential energy $-\nabla_i E_{\mathrm{p}}$. This is the force that we would consider in the absence of any vibratory motion of the atoms. The second contribution, $-\nabla_i(F - E_{\mathrm{p}})$, is temperature dependent and arises from the fact that the density of states changes as atom $i$ undergoes a virtual displacement because elements of the matrix $\tilde{D}$ change. This contribution is not zero even when $T = 0$ owing to the zero point motion of the atoms. The changes in the matrix $\tilde{D}$ as an atom is displaced are due to the anharmonicity of the potential energy $E_{\mathrm{p}}$. Thus, although the expansion of the potential energy is carried out to only second order in the atomic displacements, the matrix elements $D_{i\alpha j\beta}$ vary as the equilibrium atomic positions change because of higher order derivatives of the potential energy. For this reason we are really discussing quasiharmonic theory.

### *Expressions of the temperature dependent force*

Approximate solutions for $-\nabla_i(F - E_{\mathrm{p}})$ have appeared (Sutton 1989; LeSar *et al.* 1989), but before we outline them we give the *exact* solution. Using (2.2) and (2.3) it may be shown that

$$-\nabla_i(F - E_{\mathrm{p}}) = -\operatorname{tr} \rho \nabla_i \tilde{D}, \tag{2.4}$$

where tr denotes trace and the elements of the matrix $\rho$ are

$$\rho_{j\beta k\alpha} = \tfrac{1}{2} \sum_n \frac{E(\omega_n)}{\omega_n^2}\, \tilde{u}_{j\beta}^{(n)}\, \tilde{u}_{k\alpha}^{(n)*}. \tag{2.5}$$

The sum over $n$ is taken over all normal modes of the system and $E(\omega_n)$ is the internal energy associated with the $n$th normal mode:

$$E(\omega_n) = \frac{h\omega_n}{2\pi}\left(\frac{1}{2} + \frac{1}{\exp\,(h\omega_n/2\pi kT) - 1}\right). \tag{2.6}$$

It is clear from (2.4) that $-\nabla_i(F - E_{\mathrm{p}})$ is non-zero only if the potential has non-zero third derivatives and is therefore anharmonic. The force diverges if any normal mode frequency approaches zero, which indicates that the system must be mechanically stable to avoid such singularities. In (2.4) the $3N \times 3N$ matrix $\tilde{D}$ must be diagonolized where $N$ is the number of atoms in the cluster. If periodic boundary conditions are used $N$ is the number of atoms in the unit cell and the matrix $D$ has to be diagonolized at an appropriate number of $\boldsymbol{k}$-points in the Brillouin zone. The more approximate methods outlined below were developed to avoid the diagonalization of such large matrices. In the classical limit where $kT \gg h\omega/2\pi$ the free energy equation (2.3)) becomes

$$F_{\text{class}} = E_{\text{p}} + 3kT \ln\left[\left(\frac{h}{2\pi kT}\right)^{N} |\tilde{D}|^{\frac{1}{6}}\right] \tag{2.7}$$

and eqn. (2.4) becomes

$$-\nabla_i(F_{\text{class}} - E_{\text{p}}) = -\sum_n \tfrac{1}{2}kT\,\nabla_i \ln \omega_n^2 = -\tfrac{1}{2}kT\,\nabla_i \ln |\tilde{D}|, \tag{2.8}$$

where $|\tilde{D}|$ is the determinant of the $3N \times 3N$ matrix $\tilde{D}$.

### *Einstein models*

LeSar *et al.* (1989) approximate (2.7) with an Einstein model in which $|\tilde{D}|$ becomes a product of $N$ $3 \times 3$ determinants, $|\tilde{D}_k|$, one for each atom. They called this the 'local harmonic model', but I feel 'classical Einstein model' is more apposite. The matrix elements $\tilde{D}_{k\alpha k\beta}$ are found from the condition that the energy of the system is invariant with respect to a rigid translation:

$$D_{k\alpha k\beta} = -\sum_{j \neq k} D_{k\alpha j\beta}. \tag{2.9}$$

Thus the Einstein frequencies are determined by interactions with neighbouring sites (note the absence of tildas above the matrix elements in (2.9)), even though there is no dispersion in the Einstein approximation. In this approximation the free energy of the system in the classical limit becomes

$$F^{\text{E}}_{\text{class}} = E_{\text{p}} + 3kT \sum_{j=1}^{N} \ln\left[\frac{h|\tilde{D}_j|^{\frac{1}{6}}}{2\pi kT}\right]. \tag{2.10}$$

The equilibrium position of atom $i$ is determined by $-\nabla_i F^{\text{E}}_{\text{class}} = 0$, which is now straightforward to evaluate:

$$-\nabla_i F^{\text{E}}_{\text{class}} = -\nabla_i E_{\text{p}} - \tfrac{1}{2}kT \sum_j \nabla_i \ln |\tilde{D}_j|. \tag{2.11}$$

LeSar *et al.* (1989) compared the estimation of the Helmholtz free energy of a perfect Cu crystal using the above classical Einstein model with a Monte Carlo procedure in which the quasiharmonic approximation was not made. The copper crystal was modelled by a pairwise Morse potential truncated between the second and third neighbours. The two sets of results are indistinguishable. They also compared the vacancy formation free energy in the two methods. The errors range from 0 to 1.2% as the temperature is increased from zero up to about 75% of the melting point of the model for Cu. This agreement is perhaps surprisingly good in view of the approximations that are made in the classical Einstein model. Both the classical Einstein model and the Monte Carlo procedure yield incorrect free energies at temperatures below the Debye temperature of the model because they neglect the quantum freezing out of modes.

Najafabadi *et al.* (1991*a*) applied the classical Einstein model with embedded atom potentials for gold (Foiles *et al.* 1986) to simulate the structural evolution and excess thermodynamic properties of twelve (001) twist boundaries for temperatures between 0 and 700 K. Four of the twelve grain boundaries underwent first-order structural phase transitions as seen by the crossing of the free energy against temperature curves for the competing structures. The grain boundary linear thermal expansion coefficient varied with misorientation in a similar way to the excess grain boundary entropy.

### *Approaches based on the local atomic environment*

Sutton (1989) developed a different strategy in which neither the classical limit nor the Einstein approximation are assumed. Returning to the Helmholtz free energy in (2.3) we can always write the total density of states $N(\omega)$ exactly as a sum of local densities of states:

$$N(\omega) = \sum_{j=1}^{N} n_j(\omega) = 2\omega \sum_{j=1}^{N} y_j(\omega^2), \tag{2.12}$$

where the local density of states $y_j(\omega^2)$ is defined by

$$y_j(\omega^2) = \sum_{n} |\tilde{u}_j^{(n)}|^2 \delta(\omega^2 - \omega_n^2), \tag{2.13}$$

and the sum is over all $3N$ normal modes. The Einstein model approximates $y_j(\omega^2)$ by three delta functions. The strategy taken by Sutton (1989) was to approximate the local density of states by using information about the local atomic environment through the moments theorem and the known functional form of the local density of states at the band edges. By fitting more and more moments of the local density of states we obtain increasingly accurate approximations to the true density of states.

Let $M_j^{(p)}$ denote the $p$th moment of the local density of states $y_j(\omega^2)$:

$$M_j^{(p)} = \int_0^\infty y_j(\omega^2)\,\omega^{2p}\,\mathrm{d}\omega^2 = \int_0^\infty n_j(\omega)\,\omega^{2p}\,\mathrm{d}\omega = \mu_j^{(2p)}. \tag{2.14}$$

Thus, $M_j^{(p)}$ is equal to the $2p$th moment, $\mu_j^{(2p)}$, of the local density of states $n_j(\omega)$. Using the moments theorem (Cyrot-Lackmann 1968) the second moment of $n_j(\omega)$ is given by

$$\mu_j^{(2)} = M_j^{(1)} = \sum_{\alpha=1}^{3} \tilde{D}_{j\alpha j\alpha} = \nabla_j^2 E_{\mathrm{p}}/m_j. \tag{2.15}$$

The first moment $M_j^{(1)}$ was fitted to an assumed function form for the local density of states $y_j(\omega^2)$. In a three dimensional crystal the density of states must vary like the square root of $\omega^2$ at the band edges. The lower band edge is always at $\omega^2 = 0$, and the integral of $y_j(\omega^2)$ over the whole band must equal 3. The simplest choice of functional form for $y_j(\omega^2)$, satisfying these constraints, is the following:

$$y_j(\omega^2) = (6/\pi M_j^{(1)})\,[(M_j^{(1)})^2 - (\omega^2 - M_j^{(1)})^2]^{\frac{1}{2}}, \tag{2.16}$$

This form is a semi-elliptic density of states, which is non-zero between $\omega^2 = 0$ and $2M_j^{(1)}$, with the centre of gravity at $M_j^{(1)}$. The corresponding local density of states $n_j(\omega)$ is given by

$$n_j(\omega) = \frac{12\omega^2}{\pi(\mu_j^{(2)})^2}(2\mu_j^{(2)} - \omega^2)^{\frac{1}{2}}, \tag{2.17}$$

which is proportional to $\omega^2$ at low frequencies. At $T = 0$ K the Helmholtz free energy differs from the potential energy due to zero point motion. Taking the limit of $T = 0$ in (2.3) we obtain

$$F_{\text{zero}} = E_{\text{p}} + \frac{h}{4\pi}\sum_{j}\mu_j^{(1)} \approx E_{\text{p}} + 1.44\frac{h}{2\pi}\sum_{j}[\mu_j^{(2)}]^{\frac{1}{2}}. \tag{2.18}$$

Thus, at $T = 0$ K the Helmholtz free energy has the form of a Finnis–Sinclair potential (Finnis & Sinclair 1984), with the square root term arising from zero point motion. In an Einstein model the zero point energy of atom $j$ is $1.5h\omega_j^{\text{E}}/2\pi$. From (2.18) it follows that $\omega_j^{\text{E}} = 0.96[\mu_j^{(2)}]^{\frac{1}{2}}$.

At intermediate temperatures, where quantum freezing out of modes is still important, we must use the full form of the Helmholtz free energy, equation (2.3). In our second moment approximation this becomes

$$F = E_{\text{p}} + \sum_{i=1}^{N} F_i, \tag{2.19}$$

where
$$F_i = \frac{48kT}{\pi}\int_0^1 x^2(1-x^2)^{\frac{1}{2}}\ln\left[2\sinh\left(\tfrac{1}{2}c_i x\right)\right]\mathrm{d}x, \tag{2.20}$$

and
$$c_i = h[2\mu_i^{(2)}]^{\frac{1}{2}}/2\pi kT. \tag{2.21}$$

The free energy in (2.19) comprises the potential energy $E_{\text{p}}$ and a sum of *projections* $F_i$ of the vibrational free energy of the whole system onto individual sites. The projection is effected by the local densities of states, which are projections of the global density of states onto individual atomic sites. When $c_i$ is infinite the temperature is zero and $F$ reduces to $F_{\text{zero}}$ given in (2.18). At the other extreme limit where $c_i$ tends to zero we obtain the classical limit, which in our second moment model is given by

$$F_i^{\text{class}} = 3kT\left[\ln\left(\tfrac{1}{2}c_i\right) + \tfrac{1}{4}\right]. \tag{2.22}$$

Quantum effects begin to be important when $c_i \geqslant 1$. The temperature $\theta_i = h[2\mu_i^{(2)}]^{\frac{1}{2}}/(2\pi k)$ has the meaning of a local Debye temperature.

The vibrational entropy, internal energy and specific heat may be projected onto individual atomic sites (Sutton 1989). Expressions were also given for the mean square displacement $\langle u_i^2\rangle$ and a local Grüneisen parameter $\gamma_i$. The effective force acting on atom $i$ is given by

$$-\nabla_i F = -\nabla_i E_{\text{p}} - \sum_{j}\tfrac{1}{2}U_j\nabla_i(\ln\nabla_j^2 E_{\text{p}}), \tag{2.23}$$

where $U_j$ is the internal energy projected onto site $j$, which is given by

$$U_j = \frac{24kT}{\pi}c_j\int_0^1 x^3(1-x^2)^{\frac{1}{2}}\coth\left(\tfrac{1}{2}c_j x\right)\mathrm{d}x. \tag{2.24}$$

Sutton (1989) applied this second moment model to a study of the thermodynamic properties of the 22.06° twist boundary in gold. By far the most significant structural change with increasing temperature was the increase in the boundary expansion. A strong correlation (over 90%) was found between the local stiffness parameter $c_i$, equation (2.21) and the local hydrostatic pressure. Thus, compressed sites are associated with low contributions to the excess vibrational entropy, specific heat and mean square displacement and high (positive) contributions to the excess

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vibrational free energy and internal energy. Compressed sites are also well correlated (over 90%) with low Grüneisen constants.

### *Comparison of approaches*

Comparing (2.23) with the force in the classical Einstein model, equation (2.11), we see that the two are very similar in that the temperature dependent contribution is an $N$-body force which depends on the third derivatives of the potential energy. However, the determinant of $\tilde{D}_j$ is used in the local Einstein model, whereas the trace of $\tilde{D}_j$ is used in the second moment model. Thus, the off-diagonal elements of the $3\times 3$ matrix $\tilde{D}_j$ are taken into account in the local Einstein model, but not in the second moment model. The off-diagonal elements of $\tilde{D}_j$ describe the resistance of the local atomic environment to shear. Local shears are important modes of thermal excitation in open crystal structures (Barron *et al.* 1980). Local shears parallel to the plane of a grain boundary are also known to be important local modes of thermal excitation. A model that combines all the information contained in each matrix $\tilde{D}_j$ with a continuous density of states $y_j(\omega^2)$, displaying square root singularities at the band edges, would be preferable to both the classical Einstein model and the second moment model. This may be achieved by replacing the three delta functions representing the local density of states in the classical Einstein model by three semi-elliptic bands, one for each Einstein mode. The effective force on atom $j$ becomes

$$-\nabla_j F = -\nabla_j E_{\mathrm{p}} - \sum_{i=1}^{N}\sum_{\nu=1}^{3}\frac{U_{i\nu}}{2\omega_{i\nu}^2}\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} x_{i\beta}^{(\nu)}\, x_{i\alpha}^{(\nu)*}\,\nabla_j \tilde{D}_{i\alpha i\beta}, \qquad (2.25)$$

where $\omega_{i\nu}^2$ are the eigenvalues and $x_{i\alpha}^{(\nu)}$ are the eigenvectors of the $3\times 3$ matrix $\tilde{D}_i$ and $U_{i\nu}$ is the internal energy associated with the $\nu$th Einstein mode at atom $i$. In the high temperature limit, where $U_{i\nu}$ becomes $kT$, we recover (2.11) of the classical Einstein model. But at lower temperatures, where quantum effects reduce $U_{i\nu}$, we obtain a more accurate description of the forces and thermodynamic functions than in either the local Einstein model or the second moment model of Sutton (1989). Comparing (2.25) with the exact expression for the quasiharmonic effective force, (2.4), we see that the off-diagonal elements ($i \neq j$) of the matrix $\rho$ are ignored in (2.25). The incorporation of such intersite correlations would entail taking into account higher moments of the local densities of states.

## 3. Direct free energy minimization in a substitutional alloy

Consider a bicrystal containing A and B atoms. The interface may be of the homophase type, e.g. a grain boundary separating misoriented crystals of an AB alloy or an anti-phase boundary separating two ordered AB alloy crystals, or of the heterophase type, e.g. an interface separating crystals of (initially) pure A and pure B. Whatever the interface type it is assumed that a fixed number of atomic sites exists, which limits the treatment to substitutional alloys. It is not assumed that the positions of the atomic sites are fixed. The problem at hand is to determine the equilibrium distribution of A and B atoms in the vicinity of the interface, at a given temperature and pressure. The problem is still not fully defined until we specify whether the numbers of A and B atoms are fixed or whether the chemical potentials of A and B atoms are fixed. We assume the latter, since the crystals on either side of the interface act as large reservoirs of A and B atoms, at fixed chemical potentials $\mu_{\mathrm{A}}$ and $\mu_{\mathrm{B}}$, which can exchange atoms with the interfacial region.

Even at equilibrium there are fluctuations in the atomic structure and solute distribution. Thus, if we took two snapshots of the interface at different instants we might see different positions of solute atoms. But if we averaged the position and occupancy of each site over a large period of time we would expect, at equilibrium, to obtain convergent values. Thus the problem at hand addresses the time averaged atomic structure and solute distribution within the interface. The time averaged quantities, at equilibrium, are the expectation values for those quantities computed in the appropriate statistical ensemble. The present ensemble is a reduced grand canonical ensemble since the numbers of A and B atoms are not fixed, but no vacant sites are allowed. In principle we may regard the vacancies as a third alloy component, and thereby recover the grand canonical ensemble, but in practice there are difficulties associated with vacancies as described below.

### *Expressions for thermodynamic quantities*

Let $p_i$ denote the occupancy of site $i$ at a given instant in time. We set $p_i$ equal to 1(0) if site $i$ is occupied by a B(A) atom. Let the ensemble average of $p_i$ be $\langle p_i \rangle = c_i$. We call $c_i$ the occupancy of site $i$, with the understanding that it means the average occupancy of the site at equilibrium. The site occupancy is a number lying between 0 and 1. Let $\boldsymbol{R}_i$ be the position of site $i$ at any given instant and let the time average of $\boldsymbol{R}_i$ be $\langle \boldsymbol{R}_i \rangle = \boldsymbol{r}_i$. Our task is to find the site occupancies $\{c_i\}$ and positions $\{\boldsymbol{r}_i\}$ which minimize the grand potential of the system. We shall write down an expression for the grand potential in terms of the sets $\{c_i\}$ and $\{\boldsymbol{r}_i\}$ and demand that it is minimized with respect to these variables. These ideas first appeared in Gyorffy & Stocks (1983) and Lundberg (1987).

We express the grand potential, $\Omega$, as follows:

$$\Omega = F(\{c_i\}, \{\boldsymbol{r}_i\}) - TS_{\mathrm{c}} - \mu_{\mathrm{A}} N_{\mathrm{A}} - \mu_{\mathrm{B}} N_{\mathrm{B}}. \tag{3.1}$$

$F$ is the Helmholtz free energy of the ensemble excluding the configurational entropy:

$$F(\{c_i\}, \{\boldsymbol{r}_i\}) = U(\{c_i\}, \{\boldsymbol{r}_i\}) - TS_{\mathrm{v}}(\{c_i\}, \{\boldsymbol{r}_i\}), \tag{3.2}$$

where $U$ is the internal energy, including the vibrational contribution, and $S_{\mathrm{v}}$ is the vibrational entropy. In (3.1) the configurational entropy is denoted by $S_{\mathrm{c}}$. In the Bragg–Williams approximation for $S_{\mathrm{c}}$ we assume that the configurational entropy is that of an ideal (i.e. non-interacting) mixture of A and B atoms. This is an upper bound because the interactions introduce correlations between the occupancies of the sites which reduce the configurational entropy. In this approximation $S_{\mathrm{c}}$ is given by

$$S_{\mathrm{c}} = -k \sum_i c_i \ln c_i + (1-c_i) \ln (1-c_i), \tag{3.3}$$

$N_{\mathrm{A}}$ and $N_{\mathrm{B}}$ are the numbers of A and B atoms:

$$N_{\mathrm{A}} = \sum_i (1-c_i), \quad N_{\mathrm{B}} = \sum_i c_i. \tag{3.4}$$

Inserting (3.2)–(3.4) into (3.1) for $\Omega$ and minimizing with respect to $c_k$ we obtain

$$\frac{\partial F}{\partial c_k} + kT \ln \left( \frac{c_k}{1-c_k} \right) = \mu_{\mathrm{B}} - \mu_{\mathrm{A}}. \tag{3.5}$$

At equilibrium, therefore, the local chemical potential difference, $\mu_{\mathrm{B}}^k - \mu_{\mathrm{A}}^k$, which equals the left-hand side of (3.5), is the same at all sites and equal to $\mu_{\mathrm{B}} - \mu_{\mathrm{A}}$. The equilibrium condition involves the difference in chemical potentials $\mu_{\mathrm{B}}-\mu_{\mathrm{A}}$ because, in a substitutional alloy, equilibrium is attained by exchanging atoms between sites. The variation of the occupancy from site to site at a defect is a result of the variation of $\partial F/\partial c_k$. If $\partial F/\partial c_k \gg (\mu_{\mathrm{B}}-\mu_{\mathrm{A}})$ then site $k$ is occupied by an A atom almost all the time, and, conversely if $\partial F/\partial c_k \ll (\mu_{\mathrm{B}}-\mu_{\mathrm{A}})$ site $k$ is occupied by a B atom almost all the time.

### *Role of configurational entropy*

To illustrate the role of the configurational entropy let us ignore the vibrational entropy contribution so that the Helmholtz free energy, $F(\{c_i\}, \{\boldsymbol{r}_i\})$, reduces to the potential energy. We assume the potential energy may be represented by a sum of pair potentials. We denote the energy of interaction between an A atom at site $i$ and a B atom at site $j$ by $\epsilon_{ij}^{\mathrm{AB}} = \epsilon_{ji}^{\mathrm{AB}}$, with the understanding that $\epsilon_{ij}^{\mathrm{AB}}$ is a function of $|\boldsymbol{R}_i-\boldsymbol{R}_j|$. Similar symbols are used for A–A and B–B interaction. The hamiltonian of the system is given by

$$\mathscr{H} = \sum_{\substack{i,j\\ i\neq j}} p_i p_j \theta_{ij} + \sum_i (p_i \alpha_i + d_i^{\mathrm{A}}), \tag{3.6}$$

where

$$\left.\begin{aligned} \theta_{ij} &= \tfrac{1}{2}[\epsilon_{ij}^{\mathrm{BB}} + \epsilon_{ij}^{\mathrm{AA}} - 2\epsilon_{ij}^{\mathrm{AB}}], \\ \alpha_i &= \sum_{j\neq i} (\epsilon_{ij}^{\mathrm{AB}} - \epsilon_{ij}^{\mathrm{AA}}) - (\mu_{\mathrm{B}}-\mu_{\mathrm{A}}), \\ d_i^{\mathrm{A}} &= (\tfrac{1}{2} \sum_{j\neq i} \epsilon_{ij}^{\mathrm{AA}}) - \mu_{\mathrm{A}}. \end{aligned}\right\} \tag{3.7}$$

The connection between the grand potential and the hamiltonian is $\Omega = -kT\ln Z$ where $Z$ is the grand partition function, $Z = \operatorname{tr} \mathrm{e}^{-\beta\mathscr{H}}$, and $\beta = 1/kT$. To evaluate the trace we imagine the atom positions are temporarily frozen and consider all the states of the system characterized by the set of integers $p_1, p_2, p_3, \ldots$, each of which can be zero or one. We can obtain a useful identity for the expectation value $\langle p_k\rangle = c_k = \operatorname{tr} p_k \mathrm{e}^{-\beta\mathscr{H}}/Z$ by evaluating the trace in a particular way due to Callen (1963). The result (Balcerzak 1991) is

$$c_k = \langle p_k\rangle = \langle (1+\mathrm{e}^{\beta\gamma_k})^{-1}\rangle, \tag{3.8}$$

where $\gamma_k$ is the 'local field' at site $k$:

$$\gamma_k = \alpha_k + 2\sum_{j\neq k} p_j \theta_{jk}. \tag{3.9}$$

Equation (3.8) is useful because it is an identity against which standard approximations such as mean field theory and the auto-correlation approximation (AA) may be tested. In the mean field approximation (MFA) correlations between the occupancies on different sites are ignored and it is also assumed that $\langle p_j^n\rangle = \langle p_j\rangle^n$. In that case $c_k$ becomes

$$c_k = (1+\mathrm{e}^{\beta\gamma_k^{\mathrm{MFA}}})^{-1} \tag{3.10}$$

where

$$\gamma_k^{\mathrm{MFA}} = \alpha_k + 2\sum_{j\neq k} c_j \theta_{jk}. \tag{3.11}$$

The physical meaning of the local field is that it is the difference between the energy of replacing an A atom at site $k$ with a B atom, and $(\mu_{\mathrm{B}}-\mu_{\mathrm{A}})$. Comparing with the exact result (equations (3.8) and (3.9)), it is seen that the $\langle..\rangle$ brackets have been taken inside the exponent in the MFA. The grand partition function in the MFA, $Z^{\mathrm{MFA}}$, is readily evaluated for a given set of atomic positions and the following transparent form for the grand potential, $\Omega^{\mathrm{MFA}}$, may thus be obtained:

$$\Omega^{\mathrm{MFA}} = \tfrac{1}{2}\sum_{\substack{i,j\\ i\neq j}} (c_i c_j \epsilon_{ij}^{\mathrm{BB}} + [c_i(1-c_j)+c_j(1-c_i)]\,\epsilon_{ij}^{\mathrm{AB}} + (1-c_i)(1-c_j)\,\epsilon_{ij}^{\mathrm{AA}})$$
$$+kT\sum_i [c_i \ln c_i + (1-c_i)\ln(1-c_i)] - \mu_{\mathrm{A}}\sum_i (1-c_i) - \mu_{\mathrm{B}}\sum_i c_i. \quad (3.12)$$

The first term is the internal energy, which is obtained by replacing the site occupancy operators in the Hamiltonian, equation (3.6), by their expectation values. The second term is the contribution from the configurational entropy. The final term is the contribution from the chemical potentials of the A and B atoms. Thus, in the MFA each A or B atom is replaced by a *hybrid atom*, which varies in the degree of its A property or B property with the local atomic environment in a continuous and self-consistent manner. It is easily shown that minimization of the grand potential with respect to $c_k$ leads to (3.10). We may think of $-\partial\Omega/\partial c_i$ as a generalized force, conjugate to the site occupancy $c_i$. But in (3.10) the grand potential is also a function of all the atomic coordinates in the system, through the pair potentials. We should, therefore, minimize the grand potential with respect to all $4N$ variables, where $N$ is the total number of sites. In this way the atomic structure of the interface changes as the degree of segregation changes, for example because the chemical potential difference $\mu_{\mathrm{B}}-\mu_{\mathrm{A}}$ is changed.

### *Surface and interface segregation*

Najafabadi *et al.* (1991*b*) used embedded atom potentials (Foiles *et al.* 1986) in a MFA to model surface and interfacial segregation in a Cu–Ni solid solution alloy, and they included the vibrational entropy contribution in the classical Einstein model. The atomic mass associated with site $j$ was set equal to $c_j m_{\mathrm{B}} + (1-c_j)\,m_{\mathrm{A}}$, which is consistent with the notion that each site is occupied by a hybrid atom. The results of the simulations for the surface segregation profiles compared very well, layer by layer, with Monte Carlo simulations, using the same interatomic potentials, where the mean field, Bragg–Williams and classical Einstein approximation are not made. Three (001) twist boundaries were also studied with bulk alloy copper concentrations of 10, 50 and 90 at. %. The only significant disagreement with the Monte Carlo simulations was at the low bulk copper concentration, where the concentration of copper in the boundary plane was overestimated by 59% in the 10.4° boundary. However, the *trends* in the segregation profiles of the Monte Carlo results are well reproduced in all boundaries studied. Not only is this new approach much faster than Monte Carlo methods it enables excess thermodynamic state functions to be determined as an important by-product, and it offers much greater physical insight into the local environmental factors driving segregation.

If the composition of the interface is predicted to be quite different from that of the bulk, or if an ordered phase is predicted at the interface while the adjoining crystals remain compositionally disordered, the configurational entropy of the system will be reduced. In that case, since the Bragg–Williams approximation overestimates the configurational entropy, it may be said that the configurational entropy of the system is lower despite the Bragg–Williams approximation. The

Bragg–Williams approximation is therefore not a reason for concern except in those cases where the configurational entropy is predicted to increase, such as the compositional disordering of a grain boundary, or fault, in an ordered alloy.

### *Role of correlations*

The MFA is almost certainly more severe. Not only does this approximation ignore correlations in the occupancies of different sites but it also ignores self-correlations. Experience in magnetic systems (Balcerzak *et al.* 1990), indicates that inclusion of self-correlations gives the largest correction to the MFA. Self-correlations refer to the fact that $\langle p_j^n \rangle = \langle p_j \rangle$, rather than $\langle p_j^n \rangle = \langle p_j \rangle^n$ which is assumed in mean field theory. Using the pair potential model described above it is possible to include these self-correlations while continuing to ignore correlations on different sites. This is known as the auto-correlation approximation (AA) (see Balcerzak (1991) for a thorough discussion of the magnetic case).

Let us reconsider the grand partition function, and $\mathrm{e}^{-\beta\mathscr{H}}$ in the pair potential model, (3.6). It is useful to rewrite $\exp(-\beta\theta_{ij} p_i p_j)$ as follows:

$$\exp(-\beta\theta_{ij} p_i p_j) = 1 + p_i[\exp(-\beta\theta_{ij} p_j) - 1], \tag{3.13}$$

where we have used $p_i^n = p_i$. Inserting this expression for $\exp(-\beta\theta_{ij} p_i p_j)$ into $\mathrm{e}^{-\beta\mathscr{H}}$ we obtain

$$\mathrm{e}^{-\beta\mathscr{H}} = \prod_n \exp(-\beta(p_n \alpha_n + c_n^{\mathrm{A}})) \prod_i \prod_{j\neq i} (1 - p_i + p_i \exp(-\beta\theta_{ij} p_j)]. \tag{3.14}$$

This equation is still exact. In the MFA term $\exp(-\beta\theta_{ij} p_j)$ is replaced by $\exp(-\beta\theta_{ij} \langle p_j \rangle) = \exp(-\beta\theta_{ij} c_j)$. In the AA it is replaced by

$$\left.\begin{aligned} \langle \exp(-\beta\theta_{ij} p_j) \rangle &= \langle 1 + p_j(\exp(-\beta\theta_{ij}) - 1) \rangle \\ &= 1 + c_j(\exp(-\beta\theta_{ij}) - 1) = \exp-(\beta\xi_{ij} c_j), \end{aligned}\right\} \tag{3.15}$$

where $\xi_{ij}$ is defined by

$$\xi_{ij} = -(kT/c_j)\ln[1 + c_j(\exp(-\beta\theta_{ij}) - 1)]. \tag{3.16}$$

We can think of the $\xi_{ij}$ as effective interaction parameters which result from the improved treatment of the statistical averaging. Note that as $c_j \rightarrow 0$ then $\xi_{ij} \rightarrow kT(1 - \mathrm{e}^{-\beta\theta_{ij}})$, which tends to $\theta_{ij}$ as $T \rightarrow 0$. Also, as $c_j \rightarrow 1$ then $\xi_{ij} \rightarrow \theta_{ij}$. But for $0 < c_j < 1$ the effective pair potential $\xi_{ij}$ is less than $\theta_{ij}$. Clearly, the effective interaction parameters are dependent on temperature and the local concentration.

The 'local field', equation (3.11), the self-consistency condition (3.10), and the grand potential equation (3.12), are precisely the same in the auto-correlation approximation as in the MFA, except that where the interaction parameters $\theta_{ij}$ appear in the MFA they are replaced by the effective interaction parameters $\xi_{ij}$. We conclude that the only difference between the MFA and AA is the change in definition of the local field, with the interaction parameters $\theta_{ij}$ being replaced by effective interaction parameters $\xi_{ij}$, which are temperature and concentration dependent.

### *Role of relaxation*

Both the MFA and AA are expected to break down when there is extensive relaxation around solute atoms, due to a large size misfit for example, especially in the limit of small concentrations. (In practice the same comment applies also to Monte Carlo simulations but for different reasons.) For example, consider a single face centred cubic (FCC) crystal of A atoms containing vacant sites, in which atomic interactions are modelled by pair potentials $\epsilon_{ij}^{\mathrm{AA}}$. In this case the 'alloy' is between A atoms and vacancies and it is disordered. Rather than treating each site as being occupied ($p_i = 0$) or vacant ($p_i = 1$) the MFA treats all sites in the crystal as having the same vacancy occupancy $c$, which is determined by the following self-consistency condition:

$$c = 1/[1+\exp(\beta(\mu_{\mathrm{A}}-(1-c)\sum_{j\neq 1}\epsilon_{ij}^{\mathrm{AA}}))]. \tag{3.17}$$

(Although we are discussing the MFA here our remarks apply equally to the AA.) We have assumed that the vacancies are in thermal equilibrium so that their chemical potential is zero. The failure of the MFA in this case lies in the inadequacy of its description of the relaxation around each vacancy. In reality there is relaxation around each vacant site in the crystal which affects the formation energy to a significant degree. This relaxation renders sites that are occupied by atoms non-equivalent. The only form of relaxation that appears in the mean field theory is that the lattice parameter of the FCC crystal is altered very slightly, and all sites remain equivalent. Thus the mean field treatment essentially neglects the relaxation energy of each vacancy. Similarly the relaxation energy in any dilute AB alloy is underestimated in the MFA. In such cases the approximation will be most successful where the relaxation energy is small.

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## *Discussion*

P. A. Mulheran (*Harwell Laboratory, Didcot, U.K.*): As I understand it the Srolovitz method (and presumably your method also) is to calculate a local frequency to represent a whole phonon branch. When the atomic configuration is altered the phonon branches change and these changes are mirrored in the local frequencies. The way these frequencies are calculated by the Srolovitz group is reasonable provided that the interatomic forces are short-ranged and I assume that this comment also applies to your calculation. However if the forces are long-ranged as in ionic systems the correlations between the moving ions must be considered since long-range polarization fields contribute to the vibrational frequencies. This necessarily precludes the use of entirely localized modes. Nevertheless we can use the same concept provided that the ionic system has two-dimensional symmetry; we cannot work with point or line defects.

A. P. Sutton: The idea of both the local Einstein and the second moment models is to use information about local atomic environment to characterize the local vibrational spectrum. The information that is incorporated consists of certain local *second* derivatives of the potential energy, which, as you say, are often longer-ranged than the first derivatives of the potential energy.

Perhaps a greater concern might be the *averaging* over all the normal modes of the system that is done in both of these simple models. If particular modes dominate the vibrational properties of a defect then one would like to see them treated explicitly. This is done only in the exact expression for the force (within the quasiharmonic approximation) given in (2.4).

A. M. Stoneham (*Harwell Laboratory, Didcot, U.K.*): I think your exact theory could be used to check a further model. Temperature-dependent empirical potentials (i.e. refitted to crystal properties at each temperature) are used for defect studies. It is not clear that these are fully transferrable, and a check would be useful.

A. P. Sutton: Yes the exact formula, given in (2.4), would enable the consistency of the potentials fitted to properties measured at different temperatures to be tested.