On the estimation of SRO effects on surface segregation

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Abstract.   The free-energy concentration expansion method (FCEM) is introduced and applied to the elucidation of short-range order (SRO) effects on surface segregation in alloys. This statistical–mechanical analytical approach, based on the Ising model Hamiltonian energetics, is verified by Monte Carlo (MC) simulations. In particular, calculations performed for the (100) surface of fcc solid solution show that the FCEM agrees with MC results much better than the Bragg–Williams (BW) theory, including the prediction of an increase in equilibrium segregation level with temperature, associated with SRO/segregation competition. FCEM is quite accurate and simple to apply, demanding much less computational effort compared to MC simulations or the cluster variation method. It can replace the corresponding BW formulae in theoretical evaluation of various surfaces as well as bulk phenomena, allowing systematic studies of SRO effects in alloys.

Some recent experimental and theoretical efforts regarding equilibrium surface segregation phenomena in alloys emphasized distinct deviations from the common monotonic decrease of segregation level with temperature (Langmuir–McLean behaviour). Generally, this has been attributed to the role of interatomic interactions that induce short-range order (SRO) and long-range order (LRO) in both the alloy bulk and surface [1]. In particular, the competition between ordering and segregation can induce suppression of segregation and its entropy-driven recovery with increasing temperature due to compositional disordering. The resultant peaked segregation curve is possible both in ordered phases (e.g. in 'size-factor' intermetallics [2]), and above the order–disorder transition temperature in alloys with pronounced SRO [3, 4]. While surface segregation theories of the Bragg–Williams (BW) or 'mean-field' type can approximately account for LRO effects, estimation of SRO effects demands the adaptation of appropriate interatomic correlational approaches of equilibrium statistical mechanics or Monte Carlo simulations.

Traditional pair correlation theories, such as the Bethe–Peierls approximation [5, 6], the quasi-chemical method [7, 8] or the more elaborate cluster-variation method (CVM) [9–11], use much more complicated formulae for the alloy free energy than the BW theory. Furthermore, in the case of surface segregation even the simplest pair approximation explicitly includes a large number of intra-layer and inter-layer probabilities or SRO parameters, and of the corresponding equilibrium equations obtained by means of free-energy minimization [12–15]. Still more cumbersome and time consuming are higher-order approximations, when a tetrahedron of nearest-neighbour atoms is required as a basic cluster for correct description of fcc-based alloys [16–21]. Due to such computational complications associated with the presence of a surface, these correlation approximations have been less frequently used than the BW approach.

The alternative quantitative theory of SRO effects proposed by us recently [3], which is based on the inverse temperature expansion, accounted for experimental data concerning the unusual peaked temperature dependence of Al segregation in Ni–9% Al solid solution. However, as was noted [3], a problem can exist regarding the expansion convergence and the applicability of the truncated series. In the present work, multilayer segregation calculations based on a simple analytical formula derived from the infinite inverse-temperature series are compared to results of Monte Carlo simulations in order to verify the validity of the convenient new approach to SRO effects, including the possibility of peaked segregation–temperature dependence.

The Ising model Hamiltonian for an $A_c B_{1-c}$ alloy with a surface reads

$$H = \sum_p \left(\sum_{m \in p\text{-}plane} H_p \sigma_m \right) + \frac{1}{2} \sum_{\{mn\}} V_{mn} \sigma_m \sigma_n \qquad (1)$$

where the spin-like variables σ_m are equal to 1 (-1) if the site m is occupied by an atom of type A (B), the effective pair interaction is $V_{mn} = (V_{mn}^{AA} + V_{mn}^{BB} - 2V_{mn}^{AB})/2$, the 'layer field' H_p accounts for the difference in p-layer tensions between pure constituents and a possible size effect, and $H = \sum_{\{mn\}} \sum_{i,j} V_{mn}^{ij} p_m^i$ denotes a pair of lattice sites.

The alloy free energy can be written as the sum

$$F = F^{BW} + \Delta F^{SRO} \qquad (2)$$

where in the BW-type approximation

$$F^{BW} = kT \sum_p N_p(c_p \ln c_p + (1 - c_p) \ln(1 - c_p)) + \sum_p N_p H_p(2c_p - 1)$$

$$+ \frac{1}{2} \sum_{\{mn\}} V_{mn}(2c_m - 1)(2c_n - 1) \qquad (3)$$

and ΔF^{SRO} is the SRO related perturbation, which takes into account the non-randomness of the actual distribution of solute–solvent atoms in a solid solution (or in sublattices of ordered alloys). The SRO correction, expanded in inverse-temperature power series, is given by [22]

$$\Delta F^{SRO} = -kT \sum_{s=1}^{\infty} \frac{M_s}{s!} \left(-\frac{1}{kT} \right)^s \qquad (4)$$

where M_s are sth order cumulants.

In the dilute limit ($c_p, c \ll 1$) the infinite expansion (4) can be rearranged to a power series in lattice site concentrations c_m as mentioned briefly in our previous publication [3]. It should be noted that since change of signs of all the spinlike variables does not affect the interaction-related part of the Hamiltonian (1), the corresponding contributions to the free energy, including the SRO correction, should be symmetric with respect to A $\leftrightarrow$ B exchange. Therefore, an expansion parameter, $u_m = c_m(1 - c_m)$, which possesses the corresponding symmetry has been chosen. Truncation of the concentration expansion after the first non-zero term (of $u_m u_n$ order) yields the analytical formula of this 'free-energy concentration expansion method' (FCEM),

$$\Delta F^{SRO} = -kT \sum_{\{mn\}} c_m(1 - c_m)c_n(1 - c_n) \left(\exp\left(-\frac{2V_{mn}}{kT} \right) + \frac{2V_{mn}}{kT} - 1 \right) \qquad (5)$$

with the temperature-dependent multiplier representing the sum of the convergent infinite T^{-1} series. The pair occupation probability of lattice sites m and n by nearest-neighbour A atoms

(p_{mn}^{AA}), which deviates from the non-correlational value, $c_m c_n$, can be obtained by means of ΔF^{SRO} differentiation with respect to V_{mn},

$$p_{mn}^{AA} = c_m c_n - c_m(1 - c_m)c_n(1 - c_n)\left(1 - \exp\left(-\frac{2V_{mn}}{kT}\right)\right) \tag{6}$$

and the directly related solute–solvent atom pair probability is given by

$$p_{mn}^{AB} = c_m - p_{mn}^{AA}. \tag{7}$$

For the description of (100) surface segregation in fcc solid solution, chosen as a model system, the free energy (equation (2)), with the SRO correction given by equation (5), was minimized with respect to the near-surface layer concentrations of the solute A atoms, assuming nearest-neighbour interactions with ordering tendency ($V > 0$) and non-zero field for the outmost layer only ($H_{p>0} = 0$). The FCEM results were compared to grand canonical Monte Carlo computer simulations using the same values of the surface layer field relative to the nearest-neighbour effective pair interaction (H_0/V), and the standard Metropolis algorithm. The grand canonical ensemble has been used to better control the bulk concentration disregarding the magnitude of the segregation.

In the case of non-dilute solid solution ($c = 0.09$) the calculated results by FCEM and MC agree reasonably well even at low temperatures (figure 1(a), with mean relative deviation of ~2.5%), while the BW results are highly inaccurate except when correlations are weakened at relatively high temperatures. An expanded concentration scale (figure 1(b)) shows that both correlation approaches do predict the uncommon, SRO-induced, increase of segregation level with temperature (peaked segregation curve), depending mainly on the magnitude of H_0/V. As expected, the agreement between FCEM and MC improves for lower values of the alloy bulk concentration, and it becomes nearly perfect for a dilute alloy with $c = 0.01$, as is shown together with the deviating BW segregation plots in figure 1(c).

In order to elucidate SRO effects, solute–solvent pair occupation probabilities for nearest neighbours, p_{mn}^{AB}, have been calculated versus temperature (via equations (6) and (7)) for this structure with $H_0/V = 1.93$ and $c = 0.01$, 0.09 (figure 2). Due to the SRO-induced reduced solute atomic concentration at the surface in FCEM (figure 1), the corresponding pair probabilities are lower than those obtained in the non-correlation BW approximation. It should be further noted that for both the dilute and non-dilute cases the difference between the FCEM results and the MC simulations is much smaller than their deviation from the BW predictions, which decreases at relatively higher temperatures due to SRO weakening.

The accuracy of the proposed concentration expansion approximation was checked also by calculation of bulk properties, for which, again, it appears effective even beyond the dilute limit. In particular, according to the FCEM and MC-calculated fcc bulk partial phase diagram (described in more detail elsewhere [23]), the correct maximum of the $L1_2$–$A1$ order–disorder transition temperature near the stoichiometric composition $c = 0.25$ is predicted. For this composition, compared to the presumably accurate MC normalized transition temperature ($kT_c/V = 0.88$), the BW theory predicts an erroneous value (1.64 [24]), while the pair approximation predicts no phase change at all because of a poor representation of the disordered state for the fcc lattice [25]. In comparison, FCEM predicts $kT_c/V = 0.90$, which is between the quasi-chemical tetrahedron (0.82 [26]) and the CVM tetrahedron (0.96 [25]) values, and is closer to the MC result. Furthermore, in the FCEM (and MC) the concentrations of interest with respect to the above segregation calculations, $c = 0.01$–0.09, are in the region of a disordered solid solution. In particular, the corresponding normalized transition temperatures vary between ~0.0 and 0.2, while the BW calculations give for the same concentration range kT_c/V between ~0.1 and 0.8.
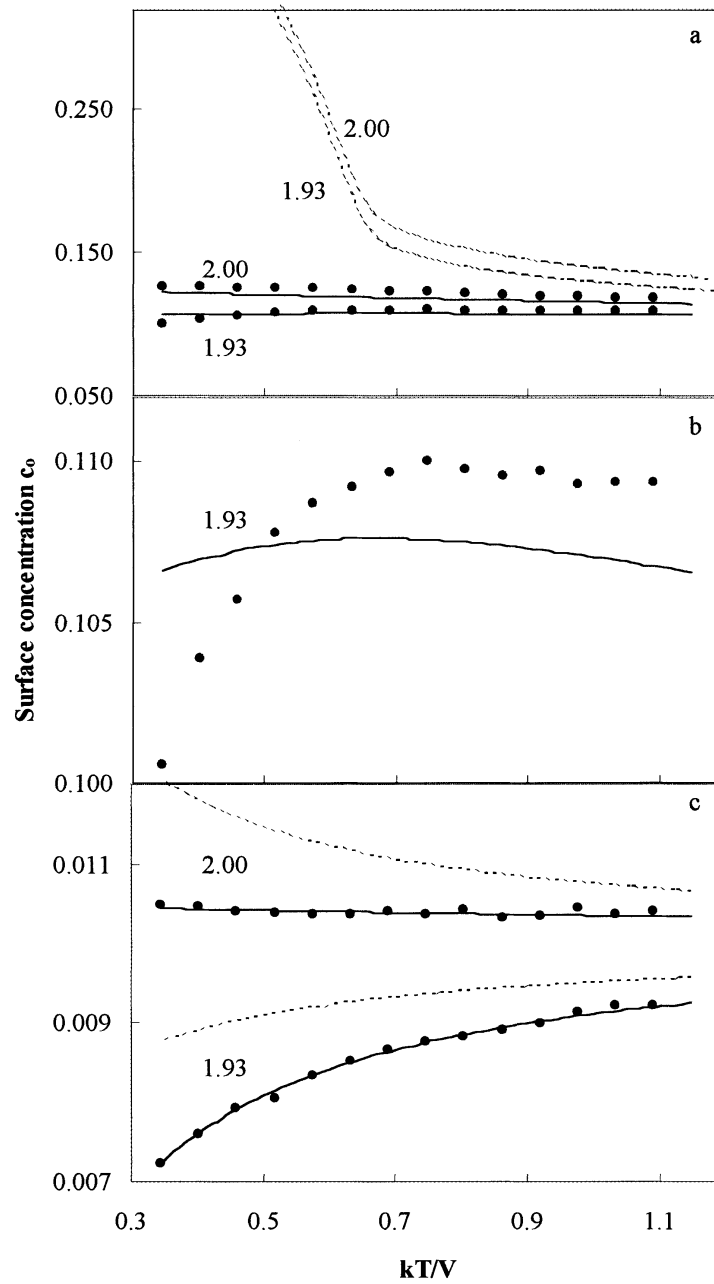
Figure 1. Calculated (100) surface solute concentrations for fcc solid solution with solute bulk concentration: $c = 0.09$ (a), (b), and $c = 0.01$ (c). Solid lines—the concentration expansion method (FCEM), circles—MC simulations, dotted lines (in (a), (c))—the BW approximation. The ratio of the surface field (H_0) to the effective interaction (V) is marked near the curves (note the change from solute to solvent segregation in (c)).

To summarize, the FCEM analytical correlation approximation developed for the free energy of dilute alloys has some practical advantages compared to the numeric MC computer
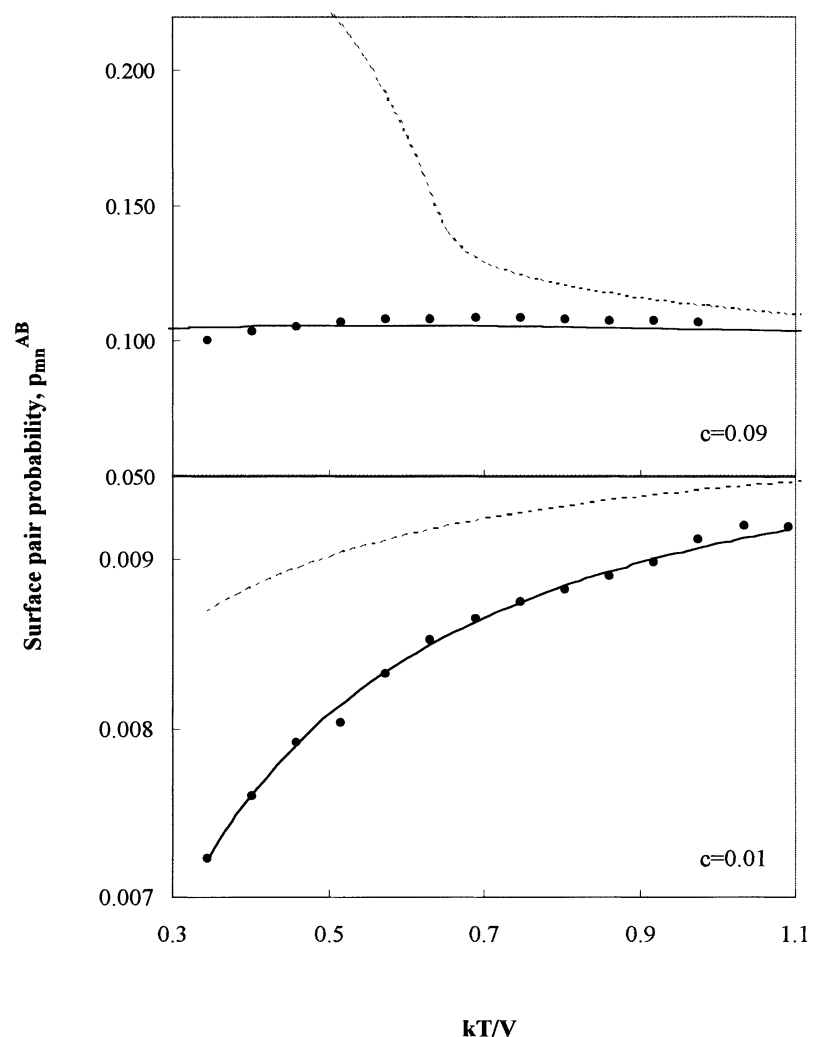
Figure 2. Calculated surface nearest-neighbour, solute–solvent pair probabilities, p_{mn}^{AB}, at the (100) surface of fcc solid solution: - - - - BW, ● ● ● ● MC, —— FCEM. In all calculations $H_0/V = 1.93$.

simulation approach or the CVM approximation, both demanding much greater computational effort. FCEM appears to give reasonable results even for non-dilute alloys, in spite of possible convergence problems. It can replace the corresponding, less accurate BW formulae in the prediction of various surface as well as bulk phenomena without any considerable complication of calculations. However, MC simulations are obviously more accurate than FCEM, and can furnish detailed atomistic information. Furthermore, in spite of the several calculated examples presented in this work, it cannot be claimed that FCEM is more accurate than the other correlation methods (CVM etc). Yet, as demonstrated here, using FCEM can furnish new perspective for systematic studies of SRO effects on surface segregation.

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