Comment on "Thermal vacancies in random alloys in the single-site mean-field approximation"

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This comment concerns the contribution of configurational mixing entropy to the change in the total Gibbs free energy in the process of vacancy formation and the consequent effect on the thermal equilibrium vacancy concentration in multicomponent alloys. A different derivation is shown than that in [Phys. Rev. B **93**, 134115 (2016)], correcting an error that may come from using Gibbs free-energy per site. The derivation is further generalized to systems beyond binary alloys.

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According to Eq. (3) in Ref. [1], the vacancy formation free energy per site is defined as

$$G_{\text{vac}} = c_v \bar{G}_f - T S_{\text{conf}}. \tag{1}$$

Here, $\bar{G}_f$ is the effective vacancy formation free energy without considering the configurational entropy, and S_{conf} is the configurational entropy of an alloy with vacancies. For a binary AB alloy with vacancies,

$$S_{\text{conf}} = -k_B(c_v \ln c_v + c_A \ln c_A + c_B \ln c_B), \tag{2}$$

where $c_A = c(1 - c_v)$, $c_B = (1 - c)(1 - c_v)$, $c = \frac{c_A}{c_A + c_B}$, and $c_A + c_B + c_v = 1$. c_A, c_B, and c_v are the concentrations of A, B, and the vacancy, respectively.

To derive the equilibrium vacancy concentration at a given temperature T, Eq. (1) was minimized with respect to c_v in Ref. [1], yielding an equilibrium vacancy concentration,

$$c_v = \exp\left(-\frac{\bar{G}_f + k_B T S_{\text{all}}}{k_B T}\right) \equiv \exp\left(-\frac{\tilde{G}_f}{k_B T}\right), \tag{3}$$

where $S_{\text{all}} = -k_B[c \ \ln \ c + (1 - c)\ln(1 - c)]$. Equation (3) is exactly the same as Eq. (5) in Ref. [1]. Note that, in Ref. [1], the Boltzmann constant k_B was contained in the reduced temperature T.

The above formulation predicts an additional configurational entropy contribution $T S_{\text{all}}$ in the vacancy formation free energy. It implies that "the alloy configurational entropy can substantially reduce the concentration of vacancies in alloys." For example, in an equiatomic binary AB alloy, the equilibrium vacancy concentration will be reduced by a factor of 2 compared to that in a pure metal. The same effect was expected to hold for multicomponent alloys (e.g., high entropy alloys) with more pronounced reductions in the equilibrium vacancy concentrations.

We found that the above derivation is inaccurate due to the fact that it extremizes the Gibbs free energy per site. In the Gibbs representation (fixed N_A, N_B, P, and T), nature minimizes the total Gibbs free energy (G_{total}) of the system, or equivalently, the Gibbs free energy per atom or mole $N = N_A + N_B$, not the Gibbs free energy per site. N_A and N_B are numbers of A and B atoms, respectively. Although the number of atoms and the number of sites are often identical, making the distinction between them unimportant, this distinction matters for the case of vacancy formation as the number of sites is not constant under the process of vacancy formation. By the formation of one vacancy, the total number of each type of atom is conserved, whereas the total number of lattice sites increases by one. More generally, a system with N atoms (where $N = N_A + N_B$ for our binary example) and N_v vacancies has the number of sites $N_{\text{sites}} = N + N_v$.

To correct the derivation, we follow the same approach as in Ref. [1] but work with the total Gibbs energy. We also generalize the result to consider the equilibrium concentration of an arbitrary species 1 in a system with n total species. The system is open to species 1 and otherwise closed with respect to the other species. This general approach includes where species 1 represents a vacancy in the process of vacancy formation. We start with a system with N_{sites} lattice sites occupied randomly by N_i atoms of species i and define

$$c_i = \frac{N_i}{N_{\text{sites}}}. \tag{4}$$

Defining $c'_{i\neq 1} = \frac{N_i}{\sum_{j=2}^{n} N_j}$, we have $c_{i\neq 1} = (1 - c_1)c'_{i\neq 1}$. Note that $N_{\text{sites}} = \sum_{i=1}^{n} N_i$. The per site configurational entropy of the system is as follows:

$$S_{\text{conf}} = -k_B \sum_{i=1}^{n} c_i \ln(c_i). \tag{5}$$

This can be rewritten in the convenient form

$$\begin{aligned} S_{\text{conf}} &= -k_B\left(c_1 \ln(c_1) + \sum_{i=2}^{n} (1 - c_1)c'_i \ln[(1 - c_1)c'_i]\right) \\ &= -k_B\left(c_1 \ln(c_1) + (1 - c_1)\ln(1 - c_1) \right. \\ &\quad \left. + (1 - c_1)\sum_{i=2}^{n} c'_i \ln(c'_i)\right). \end{aligned} \tag{6}$$

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Note that this expression is a quite useful general decomposition of the ideal mixing entropy per site of a multicomponent system. It can be interpreted as showing that the total mixing entropy is a sum of the terms one would get for a binary system by mixing species 1 with species "not 1" (treated as identical), and the terms one would get by mixing the remaining species on the fraction of lattice sites not occupied by species 1. If we assume that, except for species 1, all species mix ideally and the reference states for all species are the unmixed states from which we are mixing, then the total Gibbs free energy is

$$G_{\text{total}} = N_1\mu_1^0 + N_{\text{sites}}k_BT[c_1\ln(c_1) + (1-c_1)\ln(1-c_1)] + (1-c_1)N_{\text{sites}}k_BT\sum_{i=2}^{n}c_i^{'}\ln(c_i^{'}). \quad (7)$$

Note that $N_{\text{sites}}(1-c_1)$ is the total number of atoms in the system that are not type 1 so that the last term is actually independent of N_1. For a system open for species 1 and closed for all other species as for the case of vacancy formation in an alloy, $N_{\text{sites}}(1-c_1)$ is actually a constant. For the same reason, $c_{i\neq 1}^{'} = \frac{N_i}{\sum_{j=2}^{n}N_j}$ is also a constant, and so is its summation [i.e., S_{all} in Eq. (3) above]. Therefore, Eq. (7) shows that, with the assumptions above, the multicomponent alloy free energy can be written in the form of a free energy for a system consisting of a species of type $A = 1$ and a fictitious species of type $B =$ "not type 1" plus a constant term independent of the concentration of species 1. We can solve for equilibrium concentration of species 1 by setting its chemical potential in the system equal to an external value μ_1^*, which gives the equation,

$$\left(\frac{\partial G_{\text{total}}}{\partial N_1}\right)_{T,P,\,N_{i\neq 1}} = \mu_1^*. \quad (8)$$

Equation (8) must be applied with all numbers of atoms fixed except that of species 1 and, therefore, with a changing number of lattice sites. The derivate in Eq. (8) will yield the exact same results as for a pure system of types A and B that have ideal mixing and a reference state for B equal to the unmixed state, i.e., the standard formula,

$$\frac{c_1}{1-c_1} = \exp\left(-\frac{\mu_1^0-\mu_1^*}{k_BT}\right). \quad (9)$$

If species 1 is a vacancy, then one traditionally sets $\mu_1^* = 0$ and $\mu_1^0 = \bar{G}_f$, which is the vacancy formation free energy. Taking the low concentration limit gives

$$c_1 = c_v = \exp\left(-\frac{\bar{G}_f}{k_BT}\right), \quad (10)$$

which is the usual expression for vacancies. This result shows that the thermodynamics governing vacancies concentration under ideal mixing assumptions is not impacted by the number of other species in the system, and it takes the same form as it would for a simple unary system. More generally, we see that, under ideal mixing assumptions, for any species 1, its mixing thermodynamics is the same in a binary system with one species 2 as in a multicomponent system with species $j = 2, \ldots, n$.

Our derivation, here, concerns only the mixing entropy contribution. We note that $\bar{G}_f$, the formation free energy, will be different for a multicomponent than that for a unary system thereby leading to a different vacancy concentration as has been shown in Ref. [1].

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[1] A. V. Ruban, Thermal vacancies in random alloys in the single-site mean-field approximation, Phys. Rev. B **93**, 134115 (2016).