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Explanation for the configurational heat capacity of ordered phases

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Recently, an intriguing “W shape” has been reported for the curve of the configurational heat capacity versus composition. A typical result is shown in Fig. 1. This feature, in which the heat capacity is large both right at and far from stoichiometry, but is small just away from stoichiometry (Fig. 1), is found in both the cluster variation method and Bragg-Williams calculations for ordered phases. The heat capacity at a fixed composition with, e.g., the cluster variation method expressions for the heat capacity are derived. These expressions indicate that the W shape originates from the composition dependence of the order parameter. \[C_v = \left(\frac{\partial U}{\partial \eta}\right)^2 \left(\frac{T^2}{\partial \eta^2}ight).\] (4)

Equation (4) allows one to compute analytically the heat capacity at a fixed composition with, e.g., the cluster variation method. Hence, finite difference calculations with limited accuracy are not necessary.\(^1\)

In order to explain the composition dependence of \(C_v\), the \(\partial U/\partial \eta\) and \(\partial^2 F/\partial \eta^2\) are now examined. Quite generally, the internal energy can, to a good approximation, be written as a sum over pairwise interatomic interaction terms

\[U = - \sum_{a,b,i,j} W_{i,j}^{a,b} c_i^a c_j^b,\]

where \(W_{i,j}^{a,b}\) refers to the (positive) interaction between atomic species \(i\) and \(j\) on sublattices \(\alpha\) and \(\beta\), and where \(c_i^a\) is the \(\alpha\) sublattice concentration of the \(i\) species.

The concentration of the \(i\) species \(c_i\) is a sum over the sublattice concentrations, whereas the order parameter is a difference of sublattice concentrations. Therefore, \(U\) generally has a quadratic and \(\partial U/\partial \eta\) has a linear dependence on \(\eta\). From now on, for brevity, cases with two species only will be considered, so that the composition can be uniquely specified with a single parameter \(c = c_1\), however, the treatment is equally valid for cases with larger numbers of species.

When \(\eta\) is defined as a positive quantity, \(\partial \eta/\partial T\) is negative because the order will decrease as the temperature is raised. The energy is lowered by an increase of the order, and the free energy is at a minimum with respect to the order parameter, so that, indeed, Eq. (3) gives the correct sign. Without any approximation, and without reference to any particular model, the following expression for the heat capacity is derived:

\[C_v = \frac{\partial U}{\partial \eta} \left(\frac{T^2}{\partial \eta^2}\right).\] (3)

FIG. 1. Heat capacity \(C_v\) in units of \(k_B\) as a function of composition \(c\). Parameters: \(W = 20\), \(k_B T = 1.5\), see text.
Actual calculations bear this out, see Fig. 3, as for the case of $C$ wide to explain the sharp narrow peak that occurs in $C^\text{th}$ at not too high a temperature, the composition dependence of $U$ is proportional to $\rho \eta^2$, so that, its second derivative cannot produce the sharp peak in $C^\rho$. Hence, $\partial^2 S/\partial \eta^2$, only, remains. As a first order approximation of the entropy, the single site approximation can be used,

$$ S = -k_B \sum_{\alpha, i} c^\alpha_i \ln(c^\alpha_i). \quad (6) $$

The sublattice concentrations are linear functions of the composition and order parameter so that generally

$$ \frac{\partial^2 S}{\partial \eta^2} = -k_B \sum_{\alpha, i} \frac{(b^\alpha_i)^2}{c^\alpha_i}, $$

where $b^\alpha_i$ is given by $c^\alpha_i = c_i + b^\alpha_i$. Clearly, the entropy term can become very large when sublattice concentrations approach zero, as is the case at low temperature. Then, the entropy term is approximately proportional to the inverse of the smallest sublattice concentration. The smallest sublattice concentration is proportional to $\eta_{\text{max}} - \eta$ because when $\eta = \eta_{\text{max}}$ at least one sublattice concentration vanishes. Thus, in the limit that $\eta = \eta_{\text{max}}$,

$$ C^\rho = \eta^2 (\eta_{\text{max}} - \eta). \quad (7) $$

To understand the compositional dependence of Eq. (7), the order parameter must be examined more closely.

Notice that at stoichiometry, $\eta_{\text{max}}$ in Eq. (5) is nonanalytic. However, at nonzero temperature, when there is no phase transformation, such as in the interior of a single phase field, physical observables, such as $\eta$, are analytic. At stoichiometry, for $\eta = \eta_{\text{max}}$, sublattice concentrations are either zero or unity, which is entropically very unfavorable, see Eq. (6). The entropy forces a certain concentration of antisite defects. Therefore, sublattice concentrations deviate slightly from the extremal values. This lowers $\eta$ and causes a rounding of the $\eta(c)$ curve. Such a rounding causes the order parameter to deviate more from $\eta_{\text{max}}$ at stoichiometry than at other compositions just slightly away from stoichiometry, see Fig. 2.

The larger difference of $\eta_{\text{max}} - \eta$ at stoichiometry causes the sublattice concentrations there to be a little farther removed from zero so that $\partial^2 S/\partial \eta^2$ has a rather sharp maximum at stoichiometry, see Fig. 4. The second derivative of the free energy inherits this feature and has a sharp minimum at stoichiometry, and thus causes the sharp peak in $C^\rho(c)$. The peak is accentuated by the broader peak that occurs in $\partial U/\partial p$ term. Of course, the effect of the larger difference of $\eta_{\text{max}} - \eta$ at stoichiometry is immediately apparent in Eq. (7).
The sharp peak in $C_v$ thus, is explained in terms of sublattice concentrations. At finite temperature, at stoichiometry, a certain number of antisite defects exist. In a binary alloy of $A$ and $B$ atoms there are then equal numbers of $A$ atoms on the $\beta$ sublattice as $B$ atoms on the $\alpha$ sublattice. When some $A$ atoms are replaced by $B$ atoms, to make the alloy off-stoichiometric, the number of $B$ atoms on the $\alpha$ sublattice becomes bigger, but the number of $A$ atoms on the $\beta$ sublattice becomes smaller. Hence, introducing off-stoichiometric defects has made the smallest sublattice concentration smaller so that the entropy term becomes more negative, see Fig. 4. This effect is the main cause of the sharply peaked $C_v(c)$ curve.

When the temperature is lowered, the order parameter increases, and the smallest sublattice concentrations approach zero more closely. Therefore, at low temperatures the peak at stoichiometry in the $C_v$ curve becomes more pronounced.

Far from stoichiometry $C_v$ increases, see Fig. 1. This too, is readily apparent from the large difference $\eta_{\text{max}} - \eta$ seen in Fig. 2, and from Eq. (7). Far from stoichiometry the order breaks down because the internal energy term becomes small compared to the entropy term. Hence, both right at, and far from stoichiometry $\eta$ differs much more from $\eta_{\text{max}}$ than is the case just a little away from stoichiometry, see Fig. 2. Therefore, $C_v$ takes large values both at, and very far from stoichiometry.

A Bragg-Williams model has been used to explain the W shape of the configurational heat capacity versus the composition for ordered phases. It was shown that the heat capacity at low temperature with nearly optimal ordering is proportional to the difference of the maximal attainable order parameter and the actual order parameter. The maximal attainable order parameter has a singularity at stoichiometry, unlike the actual order parameter at nonzero temperature, so that the difference of the maximal attainable and actual order parameters has a peak at stoichiometry. At the compositional limit of the ordered state, the order breaks down and the actual order parameter differs much from the maximal attainable value, causing again an increase in the heat capacity. In terms of the sublattice concentrations it was explained that near stoichiometry, the heat capacity is proportional to the smallest sublattice concentration. When off-stoichiometric defects are introduced, on at least one sublattice, the concentration of antisite defects becomes very small, causing a minimum in the heat capacity just away from stoichiometry, as a consequence, at stoichiometry a maximum occurs.

Although, these results have been derived using a Bragg-Williams description, the relations between the various properties should be qualitatively model independent. As such, the peak in the heat capacity, and its origin, should be generally valid.

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