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LETTER TO THE EDITOR

Partial structure factors of multicomponent alloys in the long-wavelength limit

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Abstract. With the aid of a functional equation the long-wavelength limits of partial structure factors of multicomponent systems are expressed in terms of compressibility and dilatation factors. This generalises similar formulae for a binary system discovered by Bhatia and Thornton.

In recent years substantial progress has been made in both theory and experiment in the study of the partial structure factors of binary alloys. In particular the formulae of Bhatia and Thornton (1970) which express the long-wavelength limits of partial structure factors in terms of thermodynamic quantities were applied successfully to Na–K alloys (Bhatia *et al* 1973). The formulae are useful not only for checking the consistency of experimental data but also for constructing proper models (Bhatia *et al* 1973, Bhatia and March 1975). Therefore we feel it appropriate to extend the formulae in anticipation of future applications to multicomponent systems.

The starting equation is (Bhatia and Ratti 1976)

$$\partial(\ln \rho_i)/c_j\partial(\beta\mu_j) = \delta_{ij}/c_i + a_{ij} - 1 \qquad (1)$$

where ρ_i, c_i and μ_i stand respectively for density, mole fraction and chemical potential of a multicomponent system containing n species of molecules. a_{ij} is the long-wavelength limit of a partial structure factor as defined, for example, in Bhatia *et al* (1973). From the chain rule of partial differentiation it follows that

$$\frac{\partial(\ln \rho_1, \ln \rho_2, \ldots, \ln \rho_n)}{\partial(\mu_1, \mu_2, \ldots, \mu_n)} = \frac{\partial(\ln \rho_1, \ln \rho_2, \ldots, \ln \rho_n)}{\partial(p, c_2, \ldots, c_n)} \frac{\partial(p, c_2, \ldots, c_n)}{\partial(\mu_1, \mu_2, \ldots, \mu_n)}. \qquad (2)$$

Using the definitions

$$K_T = \left(\frac{\partial \ln \rho}{\partial p}\right)_{T, c_2, \ldots, c_n} \qquad (3)$$

$$\delta_i = \left(\frac{\partial \ln \rho}{\partial c_i}\right)_{p, T, c_{j \neq i}} \qquad (4)$$

it is easy to show that the matrix elements of the first Jacobian on the right-hand side

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of (2) are given by

$$\frac{\partial(\ln \rho_i)}{\partial p}=K_T \tag{5}$$

$$\frac{\partial(\ln \rho_1)}{\partial c_i}=-c_1^{-1}+\delta_i, \qquad i\neq 1 \tag{6}$$

and

$$\frac{\partial(\ln \rho_i)}{\partial c_j}=\frac{\delta_{ij}}{c_i}+\delta_j, \qquad i\neq 1. \tag{7}$$

In equations (3) and (4) ρ denotes the total density, K_T is the isothermal compressibility and δ_i is a dilatation factor (Bhatia and Thornton 1970). The second Jacobian on the right-hand side of equation (2) is the inverse of $\partial(\mu_1, \mu_2, \ldots, \mu_n)/\partial(p, c_2, c_3, \ldots, c_n)$ whose matrix elements are easily obtained by partial differentiation using the standard thermodynamic relation:

$$\mathrm{d}g=-s\,\mathrm{d}T+\mathrm{d}p/\rho+\sum_{i=2}^{n}(\mu_i-\mu_1)\,\mathrm{d}c_i \tag{8}$$

where g and s are respectively specific free energy and entropy, p is the pressure. The results are

$$\partial\mu_1/\partial p=\left(1+\sum_{k=2}^{n}c_k\delta_k\right)\rho^{-1} \tag{9}$$

$$\partial\mu_1/\partial c_i=-\sum_{k=2}^{n}g_{ik}c_k, \qquad i\neq 1 \tag{10}$$

$$\partial\mu_i/\partial p=\left(1+\sum_{k=2}^{n}c_k\delta_k\right)\rho^{-1}-\delta_i/\rho, \qquad i\neq 1 \tag{11}$$

$$\partial\mu_i/\partial c_j=-\sum_{k=2}^{n}g_{jk}c_k+g_{ji}, \qquad i\neq 1,\ j\neq 1 \tag{12}$$

where g_{ik} stands for $\partial^2 g/\partial c_i\partial c_k$. Inverting the matrix to obtain the second Jacobian of equation (2). multiplying the two Jacobians on the right-hand side of equation (2) together and then substituting the results into equation (1) we obtain

$$\delta_{ij}/c_i+a_{ij}-1=\rho k_\mathrm{B}TK_T+\langle\delta|\mathbf{A}|\delta\rangle+\langle\delta|\mathbf{A}|j\rangle/c_j+\langle i|\mathbf{A}|\delta\rangle/c_i+\langle i|\mathbf{A}|j\rangle/c_ic_j \tag{13}$$

where bras and kets are vectors of $(n-1)$ components defined by

$$|\delta\rangle=\begin{pmatrix}\delta_2\\ \delta_3\\ \delta_4\\ \vdots\\ \delta_n\end{pmatrix},\qquad |2\rangle=\begin{pmatrix}1\\0\\0\\ \vdots\\0\end{pmatrix},\qquad |3\rangle=\begin{pmatrix}0\\1\\0\\ \vdots\\0\end{pmatrix},\ldots,\qquad |n\rangle=\begin{pmatrix}0\\0\\0\\ \vdots\\1\end{pmatrix} \tag{14}$$

$$|1\rangle=-|2\rangle-|3\rangle-\cdots-|n\rangle.$$

$|2\rangle, |3\rangle, \ldots, |n\rangle$ are unit vectors along the coordinate axes and the matrix $\mathbf{A}$ has an inverse which satisfies

$$(\mathbf{A}^{-1})_{i-1,j-1} = \beta g_{ij}. \tag{15}$$

Specialising the above three equations to a binary alloy one immediately recovers the equations of Bhatia and Thornton. Hence they are the generalisations that we search for.

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