



## Relaxation of thermal concentration fluctuations in ternary liquids

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### ABSTRACT

Many small-angle neutron experiments have proven that concentration fluctuations develop in liquid alloys. The present work is devoted to the study of the relaxation of these concentration fluctuations. The mathematics associated with the analysis is close to the normal mode treatment of lattice vibrations. When applied to a ternary liquid exhibiting strong heteroatomic bonding between two components having high atomic mobilities, a long-lived clustering mode of relaxation and a short-lived substitutional mode are defined. It is found that the long-lived clustering relaxation mode is generated from a concentration fluctuation which is also the most probable. This gives physical meaning to the so-called 'clustering' in liquids where atomic cohesion is governed by metallic bonding. The possible influence of these long-lived clusters on crystalline nucleation is also discussed.

### §1. INTRODUCTION

Recently a new mechanism of nucleation in the undercooled liquid alloys has been proposed and applied to binary systems presenting a tendency to phase separation (Cini *et al.* 2000). This homophase fluctuation-mediated (HFM) mechanism of nucleation consists of two consequent steps.

- (i) First, thermal homophase concentration fluctuations generate small regions where the composition is close to that of the expected crystalline nucleus.
- (ii) Then, polymorphous (or partitionless) nucleation occurs, at a frozen composition, in the prepared region.

It has been found that the average lifetime of thermal concentration fluctuations is significantly greater than the transient time required for the establishment of stationary polymorphous nucleation inside relevant fluctuations.

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A fundamental point at the basis of this model remains the importance of the relaxation time of those nucleant fluctuations. In fact, relaxation of concentration fluctuations in a liquid containing  $\nu$  components is a superposition of  $\nu - 1$  processes, each of them being characterized by its own relaxation time (Kirkaldy 1975, Gusak and Zakarov 1979, Gusak and Gurov 1994). The mathematics associated with this analysis are close to the classical normal-mode treatment of lattice vibrations, but in the present application the transformation to normal fluctuation modes appears to be not unitary.

Among the ensemble of relaxation modes, one can expect that some fluctuations relax more slowly than others. If so, the HFM mechanism of nucleation is favoured in the corresponding directions in concentration space, particularly when these concentration directions are close to the stoichiometry of expected nucleating compounds.

The present work is focused on the normal-mode analysis applied to the relaxation of thermal concentration fluctuations. For simplicity the study is limited to a ternary liquid.

## §2. CONCENTRATION FLUCTUATION MODES: GENERAL ASPECTS

The average mole fractions of a ternary liquid 1–2–3 are given by  $c_1$ ,  $c_2$  and  $c_3 = 1 - c_1 - c_2$ .  $\delta c_1(t, x)$  and  $\delta c_2(t, x)$  designate the concentration fluctuations of components 1 and 2 respectively. The relaxation of these concentration fluctuations, which is a function of time  $t$  and distance  $x$ , obeys the usual Fick law:

$$\frac{\partial}{\partial t} \begin{pmatrix} \delta c_1 \\ \delta c_2 \end{pmatrix} = \nabla \left[ \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \cdot \nabla \begin{pmatrix} \delta c_1 \\ \delta c_2 \end{pmatrix} \right], \quad (1)$$

where  $D_{11}$ ,  $D_{12}$ ,  $D_{22}$  and  $D_{21}$  are the classical diffusion coefficients. The corresponding fluxes are such that  $J_i = -nD_{nk} \nabla c_k$ , where  $n$  is the number of atoms per unit volume.

For small fluctuations, the interdiffusion coefficients in the matrix  $\hat{\mathbf{D}}$  are taken constant, so that

$$\frac{\partial c_i}{\partial t} = \sum_{k=1}^2 D_{ik} \nabla^2 \delta c_k, \quad (2)$$

where  $i$  and  $k$  designate the components.

Some linear transformation (non-unitary in general) diagonalizing the diffusivity matrix is defined. New parameters  $u_n$  representing linear combinations of concentration fluctuations with constant coefficients  $a_{ij}$  (defining a matrix  $\hat{\mathbf{a}}$ ) are introduced:

$$u_n = \sum_i (\hat{\mathbf{a}}^{-1})_{ni} \delta c_i. \quad (3)$$

When condensed in a matrix form, equation (3) can be written  $\hat{u} = \hat{\mathbf{a}}^{-1} \hat{\mathbf{D}} \delta \hat{c}$ . The sign  $\hat{\phantom{x}}$  denotes matrix for  $\hat{\mathbf{a}}$  and  $\hat{\mathbf{D}}$  and row for  $\hat{u}$  and  $\delta \hat{c}$ .

Using the parameters  $u_n$ , equation (2) becomes

$$\frac{\partial}{\partial t} (\hat{u}) = (\hat{\mathbf{a}}^{-1} \hat{\mathbf{D}} \hat{\mathbf{a}}) \nabla^2 (\hat{u}). \quad (4)$$

The matrix  $\hat{\mathbf{a}}$  is chosen so that  $\hat{\mathbf{a}}^{-1}\hat{\mathbf{D}}\hat{\mathbf{a}}$  is diagonal:

$$\hat{\mathbf{a}}^{-1}\hat{\mathbf{D}}\hat{\mathbf{a}} = \hat{\mathbf{D}}_0 \equiv \begin{pmatrix} D^{(1)} & 0 \\ 0 & D^{(2)} \end{pmatrix}. \tag{5}$$

As can easily be shown, this diagonalization determines the eigenvalues  $D^{(1)}$  and  $D^{(2)}$  and the ratios  $a_{21}/a_{11}$  and  $a_{12}/a_{22}$  such that

$$D^{(1)}, D^{(2)} = \frac{D_{11} + D_{12}}{2} \pm \left( \frac{(D_{11} + D_{12})^2}{4} - \det \hat{\mathbf{D}} \right)^{1/2} \tag{6}$$

$$\begin{aligned} \frac{a_{21}}{a_{11}} &= \frac{D^{(1)} - D_{11}}{D_{12}} = \frac{D_{21}}{D^{(1)} - D_{22}}, \\ \frac{a_{12}}{a_{22}} &= \frac{D^{(2)} - D_{22}}{D_{21}} = \frac{D_{12}}{D^{(2)} - D_{11}}, \end{aligned} \tag{7}$$

where  $\det \hat{\mathbf{D}} = D_{11}D_{22} - D_{12}D_{21} = D^{(1)}D^{(2)}$ . The coefficients  $a_{11}$  and  $a_{22}$  can be taken to be arbitrary and in fact, do not influence the results. For simplicity, one can choose them to be equal to unity.

The diagonalization means that the parameters  $u_1$  and  $u_2$  behave as relaxing independently; this leads to

$$\frac{\partial u_1}{\partial t} = D^{(1)} \nabla^2 u_1, \quad \frac{\partial u_2}{\partial t} = D^{(2)} \nabla^2 u_2. \tag{8}$$

The corresponding relaxation times are such that  $\tau^{(1)} = l^2/6D^{(1)}$  and  $\tau^{(2)} = l^2/6D^{(2)}$ , where  $l$  is the characteristic size of the fluctuation region (referring to the HFM nucleation mechanism,  $l$  corresponds to the critical radius of a spherical crystalline embryo). Note that relaxation of the concentration fluctuations is a linear combination of  $u_1$  and  $u_2$  such that

$$\delta c_1 = a_{11}u_1 + a_{12}u_2, \quad \delta c_2 = a_{21}u_1 + a_{22}u_2.$$

Let us consider an initial fluctuation (at time  $t = 0$ ) of Gaussian type with dispersion  $l^2$ :

$$\begin{aligned} \delta c_1(0, x) &= \frac{A_1}{(2\pi l^2)^{1/2}} \exp\left(-\frac{x^2}{2l^2}\right), \\ \delta c_2(0, x) &= \frac{A_2}{(2\pi l^2)^{1/2}} \exp\left(-\frac{x^2}{2l^2}\right). \end{aligned} \tag{9}$$

Then the initial distribution of the parameters  $u_1$  and  $u_2$  is given by the following relation:

$$u_i(0, x) = \frac{B_i}{(2\pi l^2)^{1/2}} \exp\left(-\frac{x^2}{2l^2}\right)$$

with

$$B_i = a_{i1}^{-1}A_1 + a_{i2}^{-1}A_2,$$

$i$  designates component 1 or 2.

Solving the Fick equations for infinite  $x$  space, one obtains

$$\begin{aligned}
 u_i(t, x) &= \int_{-\infty}^{\infty} \frac{\exp [-(x-x')^2/4D^{(i)}t]}{(4\pi D^{(i)}t)^{1/2}} u_i(0, x') dx' \\
 &= \frac{B_i}{[2\pi(2D^{(i)}t + l^2)]^{1/2}} \exp \left( -\frac{x^2}{2(l^2 + 2D^{(i)}t)} \right). \tag{10}
 \end{aligned}$$

The average value of  $u_i$  in the interval  $(-l, l)$  is taken as a measure of the relaxation of the fluctuation:

$$\bar{u}_i(t) = \frac{1}{2l} \int_{-l}^l u_i(t, x) dx. \tag{11}$$

This leads to

$$\bar{u}_i(t) = \frac{1}{2} B_i \operatorname{erf} \left( \frac{1}{[2(1 + 2D^{(i)}t/l^2)]^{1/2}} \right). \tag{12}$$

Then, relaxation of the concentration fluctuations  $\delta c_1$  and  $\delta c_2$  obeys the following formulae:

$$\begin{aligned}
 \delta \bar{c}_1(t) &= a_{11} \bar{u}_1(t) + a_{12} \bar{u}_2(t) \\
 &= \underbrace{\frac{a_{11}(a_{11}^{-1}A_1 + a_{12}^{-1}A_2)}{2}}_{K_{11}} \operatorname{erf} \left( \frac{1}{[2(1 + 2D^{(1)}t/l^2)]^{1/2}} \right) \\
 &\quad + \underbrace{\frac{a_{12}(a_{21}^{-1}A_1 + a_{22}^{-1}A_2)}{2}}_{K_{12}} \operatorname{erf} \left( \frac{1}{[2(1 + 2D^{(2)}t/l^2)]^{1/2}} \right), \tag{13} \\
 \delta \bar{c}_2(t) &= \underbrace{\frac{a_{21}(a_{11}^{-1}A_1 + a_{12}^{-1}A_2)}{2}}_{K_{21}} \operatorname{erf} \left( \frac{1}{[2(1 + 2D^{(1)}t/l^2)]^{1/2}} \right) \\
 &\quad + \underbrace{\frac{a_{22}(a_{21}^{-1}A_1 + a_{22}^{-1}A_2)}{2}}_{K_{22}} \operatorname{erf} \left( \frac{1}{[2(1 + 2D^{(2)}t/l^2)]^{1/2}} \right).
 \end{aligned}$$

Equations (13) determine the evolution path of fluctuations in the concentration space. The direction of the relaxation can be represented in the Gibbs triangle by the tangent to the path as shown schematically in figure 1. The expression for the tangent to the path is deduced from equations (13):

$$\begin{aligned}
 \tan \alpha &= \frac{\partial(\delta \bar{c}_2)/\partial t}{\partial(\delta \bar{c}_1)/\partial t} \\
 &= \frac{K_{21}D^{(1)}(1 + 2D^{(1)}t/l^2)^{-3/2} \exp [1/2(1 + 2D^{(1)}t/l^2)]}{K_{11}D^{(1)}(1 + 2D^{(1)}t/l^2)^{-3/2} \exp [1/2(1 + 2D^{(1)}t/l^2)]} \\
 &\quad + \frac{K_{22}D^{(2)}(1 + 2D^{(2)}t/l^2)^{-3/2} \exp [1/2(1 + 2D^{(2)}t/l^2)]}{K_{12}D^{(2)}(1 + 2D^{(2)}t/l^2)^{-3/2} \exp [1/2(1 + 2D^{(2)}t/l^2)]} \tag{14}
 \end{aligned}$$

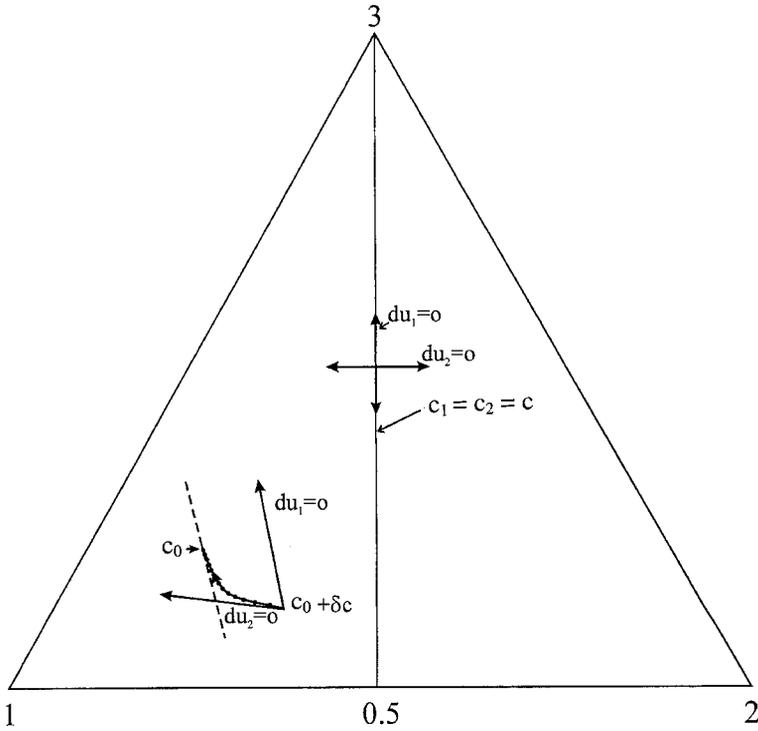


Figure 1. Gibbs triangle for a ternary system 1–2–3 where a schematic trajectory of a relaxing concentration fluctuation from  $c_0 + \delta c$  to  $c_0$  is represented (left-hand part of the figure). The kinetic curve of relaxation along this trajectory is displayed by full circles at identical time intervals. Note that the represented diffusion path is not S shaped since the trajectory does not result from a classical diffusion couple but from a change in composition in the limited volume of initial fluctuation. Along section  $c_1 = c_2 = c$ ,  $du_2 = 0$  is the direction of the substitutional mode and  $du_1 = 0$  corresponds to the clustering mode when atomic mobility of component 3 is very small.

Let us consider the limiting cases  $t \rightarrow 0$  and  $t \rightarrow \infty$ .

(i) For short times, the direction of the path can be written

$$(\tan \alpha)_{t=0} \approx \frac{K_{21} + K_{22}D^{(2)}/D^{(1)}}{K_{11} + K_{12}D^{(2)}/D^{(1)}}. \quad (15)$$

(ii) For long times the direction of path becomes

$$(\tan \alpha)_{t \rightarrow \infty} \approx \frac{K_{21}(D^{(2)}/D^{(1)})^{1/2} + K_{22}}{K_{11}(D^{(2)}/D^{(1)})^{1/2} + K_{12}}. \quad (16)$$

A link between these tangents with independent modes is expected. To check this, the particular limiting case where  $D^{(2)} \ll D^{(1)}$  (which means that the second mode is much slower than the first mode) is studied.

Then, at the beginning ( $t \approx 0$ ), one has from equations (16) and (13)  $\tan \alpha_0 \approx K_{21}/K_{11} = a_{21}/a_{11}$ . This means that

$$\left. \frac{dc_2}{dc_1} \right|_{t \rightarrow 0} = \frac{a_{21}}{a_{11}} \quad (17a)$$

or

$$\begin{aligned} a_{21} dc_1 - a_{11} dc_2 &= \frac{-a_{21}^{-1}}{\det \hat{\mathbf{a}}^{-1}} dc_1 - \frac{a_{22}^{-1}}{\det \hat{\mathbf{a}}^{-1}} dc_2 \\ &= -\frac{1}{\det \hat{\mathbf{a}}^{-1}} du_2 \\ &= 0. \end{aligned} \quad (17b)$$

Thus, for short times,  $du_2 \approx 0$ , so that the composition point moves along the line of constant  $u_2$ . For long times, it follows from equations (16) and (13) that

$$\tan \alpha_\infty \approx \frac{K_{22}}{K_{12}} = \frac{a_{22}}{a_{12}} \quad (18a)$$

or

$$\left. \frac{dc_2}{dc_1} \right|_{t \rightarrow \infty} = \frac{a_{22}}{a_{12}} = -\frac{a_{11}^{-1}}{a_{12}^{-1}}, \quad du_1 = a_{11}^{-1} dc_1 + a_{12}^{-1} dc_2 = 0. \quad (18b)$$

At the end of the relaxation, the composition point tends to move along the line of constant  $u_1$  (figure 1). It appears that relaxation proceeds in two steps: first, relaxation of the fast mode ( $u_2$  constant) and, then, relaxation of the slow mode ( $u_1$  constant). A representation of this effect is given in figure 1 where equal time intervals are noted by full circles on the schematic evolution path of a fluctuation relaxation between  $c_0 + \delta c$  and  $c_0$ . To illustrate the above-mentioned formalism, the following example is treated.

### § 3. 'CLUSTERING' AND 'SUBSTITUTIONAL' MODES IN TERNARY LIQUIDS WITH STRONG HETEROATOMIC BONDING BETWEEN TWO COMPONENTS

Let us consider a ternary liquid ABC with strong heteroatomic bonding between components A and B. In the following, 1 designates component A, 2 component B and 3 component C.

The sub-regular solution approximation is used with average coordination number  $z$ , and interchange energies  $\lambda_{ik_{i \neq k}} = z[\varepsilon_{ik} - (\varepsilon_{ii} + \varepsilon_{kk})/2]$  ( $\varepsilon_{ik}$  are the nearest-neighbour pair energies between the  $i$ th and  $k$ th species; they are negative; heteroatomic bonding between components  $i$  and  $j$  yields negative  $\lambda_{ik}$ ).

The flux of each component, in the laboratory reference frame, is equal to

$$J_i = j_i + nc_i \omega \quad (19)$$

with

$$j_i = -nL_i \nabla \mu_i = -n \frac{cD_i^*}{\theta} \nabla \mu_i, \quad \theta = kT.$$

$L_i$  is the corresponding Onsager coefficient,  $D_i^*$  is the tracer diffusivity of  $i$  and  $\mu_i$  is the chemical potential of the  $i$ th component.  $\omega$  is a drift velocity, determined by the condition  $\sum_1^3 J_i = 0$  which yields

$$\omega = -\frac{1}{n} \sum_1^3 j_i. \quad (20)$$

In equation (19), the cross-terms caused by the vacancy wind described by Manning (1968) have been neglected. Using equations (19) and (20) and finding the chemical potentials  $\mu_i$  from the standard expression for the Gibbs energy of regular solutions, the explicit forms of the diffusivity matrix elements are found to be

$$\begin{aligned}
 D_{11} &= (1 - c_1)D_1^* \left( 1 - \frac{c_1}{\theta} [\lambda_{12}c_2 + \lambda_{13}(c_3 - c_1 + 1) - \lambda_{23}c_2] \right) + \dots \\
 &\quad + c_1c_2 \frac{D_2^*}{\theta} [-\lambda_{21}(1 - c_2) + \lambda_{23}(1 - c_2) + \lambda_{13}(c_3 - c_1)] \\
 &\quad + c_1D_3^* \left( 1 - \frac{c_3}{\theta} [\lambda_{31}(1 - c_3 + c_1) + \lambda_{32}c_2 - \lambda_{12}c_2] \right), \\
 D_{12} &= -(1 - c_1)c_1 \frac{D_1^*}{\theta} [-\lambda_{12}(1 - c_1) + \lambda_{13}(1 - c_1) + \lambda_{23}(c_3 - c_2)] \\
 &\quad - c_1D_2^* \left( 1 - \frac{c_2}{\theta} [\lambda_{21}c_1 + \lambda_{23}(c_3 - c_2 + 1) - \lambda_{13}c_1] \right) \\
 &\quad + c_1D_3^* \left( 1 - \frac{c_3}{\theta} [\lambda_{31}c_1 + \lambda_{32}(1 - c_3 + c_2) - \lambda_{12}c_1] \right), \quad (21) \\
 D_{21} &= -c_2D_1^* \left( 1 - \frac{c_1}{\theta} [\lambda_{12}c_2 + \lambda_{13}(c_3 - c_1 + 1) - \lambda_{23}c_2] \right) \\
 &\quad - (1 - c_2)c_2 \frac{D_2^*}{\theta} [-\lambda_{21}(1 - c_2) + \lambda_{23}(1 - c_2) + \lambda_{13}(c_3 - c_1)] \\
 &\quad + c_2D_3^* \left( 1 - \frac{c_3}{\theta} [\lambda_{13}(1 - c_3 + c_1) + \lambda_{32}c_2 - \lambda_{12}c_2] \right), \\
 D_{22} &= c_2c_1 \frac{D_1^*}{\theta} [-\lambda_{12}(1 - c_1) + \lambda_{13}(1 - c_1) + \lambda_{23}(c_3 - c_2)] \\
 &\quad + (1 - c_2)D_2^* \left( 1 - \frac{c_2}{\theta} [\lambda_{21}c_1 + \lambda_{23}(c_3 - c_2 + 1) - \lambda_{13}c_1] \right) \\
 &\quad + c_2D_3^* \left( 1 - \frac{c_3}{\theta} [\lambda_{31}c_1 + \lambda_{32}(1 - c_3 + c_2) - \lambda_{21}c_1] \right).
 \end{aligned}$$

Owing to the complexity of these expressions and in order to proceed further, simplifications are required. As we are concerned with strong heteroatomic bonding between species 1 and 2,  $\lambda_{13}$  and  $\lambda_{23}$  are neglected in comparison with  $\lambda_{12} = \lambda$ , that is  $|\lambda_{13}|, |\lambda_{23}| \ll |\lambda_{12}| = |\lambda|$ .

Furthermore, the following limiting cases concerning atomic mobilities are studied.

### 3.1. Low atomic mobility of component 3

First, let us treat the case where the atomic mobilities of components 1 and 2 are taken to be equal and much larger than that of component 3.  $D_3^*$  is neglected with respect to  $D_1^* = D_2^* \equiv D^*$ , that is

$$D_3^* \ll D_1^* = D_2^* \equiv D^*.$$

With these simplifications, equations (21) are reduced to

$$\begin{aligned}\frac{1}{D^*}D_{11} &= 1 - c_1 - \frac{\lambda}{\theta}c_1c_2(2 - c_1 - c_2), \\ \frac{1}{D^*}D_{12} &= -c_1 + \frac{\lambda}{\theta}c_1[(1 - c_1)^2 + c_1c_2], \\ \frac{1}{D^*}D_{21} &= -c_2 + \frac{\lambda}{\theta}c_2[(1 - c_2)^2 + c_1c_2], \\ \frac{1}{D^*}D_{22} &= 1 - c_2 - \frac{\lambda}{\theta}c_1c_2(2 - c_1 - c_2).\end{aligned}\tag{22}$$

The eigenvalues have the following form:

$$\begin{aligned}D^{(1)}, D^{(2)} &= D^* \left( \frac{1 + c_3}{2} \left( 1 - 2c_1c_2 \frac{\lambda}{\theta} \right) \right. \\ &\quad \left. \pm \frac{1 + c_3}{2} \left\{ \left( 1 - 2c_1c_2 \frac{\lambda}{\theta} \right)^2 - \frac{4c_3}{(1 + c_3)^2} \left[ 1 - 2c_1c_2 \frac{\lambda}{\theta} - c_1c_2c_3 \left( \frac{\lambda}{\theta} \right)^2 \right] \right\}^{1/2} \right).\end{aligned}\tag{23}$$

Let us consider the particular case where  $c_1 = c_2 \equiv c$ ,  $c_3 = 1 - 2c$  with  $0 < c < \frac{1}{2}$ . Diagonalization is provided by taking

$$\hat{\mathbf{a}} = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}.$$

The expressions for the diffusivities of the independent modes become of the forms

$$D^{(1)} = D^* \left( 1 - c \frac{\lambda}{\theta} \right),\tag{24a}$$

$$D^{(2)} = D^* \left( 1 - 2c + c(1 - 2c)^2 \frac{\lambda}{\theta} \right).\tag{24b}$$

The corresponding directions in the composition space are determined in the following way:  $du_2 = 0$  yields  $a_{21}^{-1}dc_1 + a_{22}^{-1}dc_2 = 0$  and thus

$$\frac{dc_2}{dc_1} = -\frac{a_{21}^{-1}}{a_{22}^{-1}} = \frac{a_{21}}{a_{11}} = \frac{D^{(1)} - D_{11}}{D_{12}} = -1,\tag{25}$$

$$dc_2 = -dc_1;$$

$du_1 = 0$  gives  $a_{11}^{-1}dc_1 + a_{12}^{-1}dc_2 = 0$  and thus

$$\frac{dc_2}{dc_1} = -\frac{a_{11}^{-1}}{a_{12}^{-1}} = \frac{a_{22}}{a_{12}} = \frac{D_{21}}{D^{(2)} - D_{22}} = +1,\tag{26}$$

$$dc_2 = dc_1.$$

From equation (25) the first mode  $D^{(1)}$  means ‘substitutional fluctuations’ (see figure 1), where the concentration of component 2 changes only to the extent of component 1, leaving the concentration of component 3 undisturbed. It is seen from equations (24a) and (24b) that, when  $\lambda < 0$ , the first mode  $D^{(1)}$  is faster (note that

$D^{(2)} < D^{(1)}$  in the whole concentration range  $0 < c < \frac{1}{2}$ ). In fact, the high diffusivities of components 1 and 2 favour exchange between components 1 and 2, leaving the concentration of species 3 unchanged. The absence of concentration gradient in  $c_3$  with the supposed low mobility of component 3 ( $D_3^* \approx 0$ ) means that the mobile components 1 and 2 are responsible for the faster substitutional mode. This latter kinetic argument is consistent with equations (24 a) and (24 b) where  $D^{(1)}$  is formally greater than  $D^{(2)}$  when  $\lambda > 0$ . Note that, the more negative  $\lambda$  is (the stronger 1–2 heteroatomic bonding), the faster is the diffusion rate of the ‘substitutional mode’ and the faster is the relaxation of fluctuations towards equiatomic concentration.

The second mode, where the concentration of each pair of interacting components 1–2 changes simultaneously ( $dc_2 = dc_1$ ) in the direction leaving the ‘stoichiometry’ constant is designated as a ‘clustering mode’ (see figure 1). In fact, the occurrence of this clustering mode induces a significant variation in the concentration  $c_3$  such that  $\delta c_3 = -2 \delta c_1$  but, owing to the small atomic mobility of component 3, the resulting relatively high gradient in  $c_3$  is unable to generate a significant relaxation flux. Thus, it is understood from a physical point of view that the clustering mode is the slower. Again this is in complete agreement with equations (24) provided that  $\lambda < 0$ . The more negative  $\lambda$  is, the greater is the ratio of the relaxation time  $\tau_{\text{slow}}^{(2)}$  of the slow mode (clustering mode) to the relaxation time  $\tau_{\text{fast}}^{(1)}$  of the fast mode (substitutional mode). This ratio is given by

$$\frac{\tau_{\text{slow}}^{(2)}}{\tau_{\text{fast}}^{(1)}} = \frac{D^{(1)}}{D^{(2)}} = \frac{1 - c\lambda/\theta}{1 - 2c + c(1 - 2c)^2\lambda/\theta}. \tag{27}$$

The ratio  $\tau_{\text{slow}}^{(2)}/\tau_{\text{fast}}^{(1)}$ , as a function of  $c$ , is represented in figure 2 for different values of  $\lambda/\theta$ . The following features are found. For  $\lambda/\theta > -6.56$ ,  $\tau_{\text{slow}}^{(2)}/\tau_{\text{fast}}^{(1)}$  increases mono-

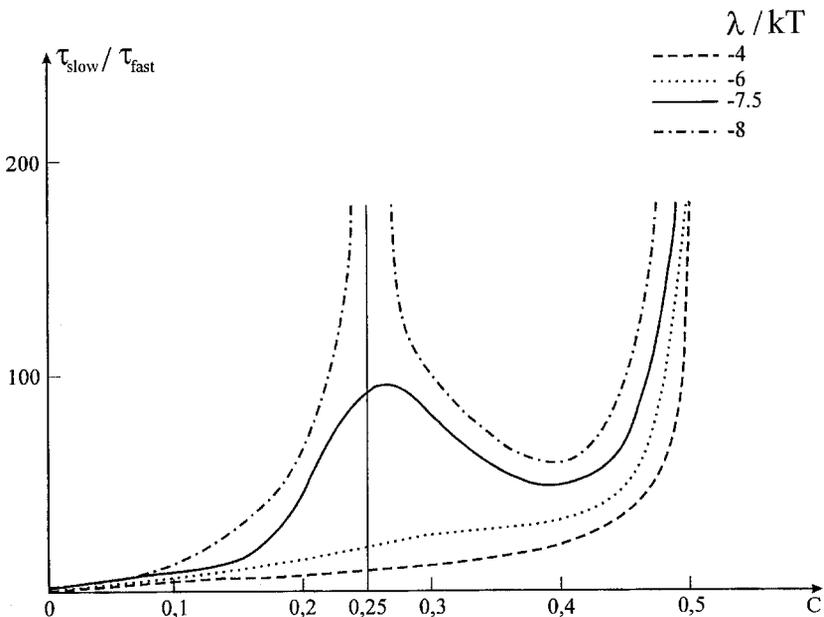


Figure 2. Representation of the ratio  $\tau_{\text{slow}}/\tau_{\text{fast}}$  versus concentration  $c_1 = c_2 = c$  for different values of  $\lambda/kT$ . Phase separation is obtained when  $\lambda/kT < -8$ .

tonically with increasing concentration  $c$ . For  $\lambda/\theta < -6.56$  there is a maximum  $\tau_{\text{slow}}^{(2)}/\tau_{\text{fast}}^{(1)}$  at around  $c = \frac{1}{4}$ . When  $\lambda/\theta = (\lambda/\theta)_{\text{critical}} = -8$ ,  $\tau_{\text{slow}}^{(2)}/\tau_{\text{fast}}^{(1)}$  diverges at  $c = \frac{1}{4}$  ( $D^{(2)} = 0$ ). When  $\lambda/\theta < -8$ , there are two values of  $c$ , namely  $c_1$  and  $c_2$ , for which  $D^{(2)} = 0$ ;  $c_1$  and  $c_2$  are such that

$$c = \frac{1 \pm (1 + 8\lambda/\theta)^{1/2}}{4}. \quad (28)$$

When  $c_1 < c < c_2$  phase separation occurs in the liquid phase ( $D^{(2)} < 0$ ). The critical temperature for phase separation is such  $T_c = -\lambda/8R$ . (Note that the expression for  $T_c$  is quite different from that obtained for a binary liquid exhibiting a tendency to phase separation ( $\lambda > 0$ ) which, for a strictly regular solution, is  $T_c = \lambda/2R$ .)

When  $c$  tends towards  $\frac{1}{2}$ , (i.e. to the binary liquid 1-2),  $D^{(2)}$  tends towards zero; this yields a diverging ratio  $\tau_{\text{slow}}^{(2)}/\tau_{\text{fast}}^{(1)}$  at  $c = \frac{1}{2}$ . As expected, when approaching this limit, the substitutional mode  $D^{(1)}$  becomes the only mode describing relaxation in the binary system 1-2.

Furthermore, it can be checked that the determinant associated with the thermodynamic matrix, namely

$$\begin{pmatrix} \frac{\partial^2 g}{\partial c_1^2} & \frac{\partial^2 g}{\partial c_1 \partial c_2} \\ \frac{\partial^2 g}{\partial c_2 \partial c_1} & \frac{\partial^2 g}{\partial c_2^2} \end{pmatrix}$$

( $g$  is the molar Gibbs energy of the liquid) is equal to zero at the same concentrations as given by equation (28).

Consequently, the above-mentioned 'substitutional' and 'clustering' modes have significance not only from a kinetic viewpoint but also from a thermodynamic viewpoint. It has been shown (Gusak and Zakharov 1979) that the transformation matrix  $\hat{\mathbf{a}}$  diagonalizing the diffusion matrix diagonalizes the thermodynamic matrix as well:

$$\hat{\mathbf{a}}^{-1} \hat{\mathbf{g}} \hat{\mathbf{a}} = \hat{\mathbf{g}}_0 = \begin{pmatrix} g^{(1)} & 0 \\ 0 & g^{(2)} \end{pmatrix}. \quad (29)$$

Note that in the general case the matrix  $\hat{\mathbf{a}}$  is not unitary, but in the present symmetric case ( $c_1 = c_2$ ) it becomes

$$\hat{\mathbf{a}} = \frac{1}{2^{1/2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}, \quad \hat{\mathbf{a}}^{-1} = \frac{1}{2^{1/2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}. \quad (30)$$

In the present application the following expressions for  $g^{(1)}$  and  $g^{(2)}$  are obtained:

$$\begin{aligned} \frac{1}{\theta} g^{(1)} &= \frac{2}{c(1-2c)} - 2\frac{\lambda}{\theta}, \\ \frac{1}{\theta} g^{(2)} &= \frac{2}{c(1-2c)} + 2\frac{\lambda}{\theta}. \end{aligned} \quad (31)$$

The probability of arbitrary homophase fluctuation in some region containing  $N$  atoms is classically given by

$$P \propto \exp \left( -\frac{N}{2\theta} \sum_i^2 \sum_k^2 g_{ik} \delta c_i \delta c_k \right),$$

an expression which can be easily transformed into the following form:

$$P \propto \exp\left(-\frac{N}{2\theta}g^{(1)}(u_1)^2\right) \exp\left(-\frac{N}{2\theta}g^{(2)}(u_2)^2\right). \quad (32)$$

This means that the above-mentioned parameters  $u_1$  and  $u_2$  fluctuate independently not only in the kinetic features but also in the thermodynamic features.

The mean-squared fluctuation is found to be larger for the ‘clustering mode’ when  $\lambda < 0$ ;  $\langle u_2^2 \rangle > \langle u_1^2 \rangle$  with:

$$\begin{aligned} \langle u_2^2 \rangle &= \frac{2\theta}{Ng^{(2)}} = \frac{1}{N} \frac{1}{1/c(1-2c) + \lambda/\theta}, \\ \langle u_1^2 \rangle &= \frac{2\theta}{Ng^{(1)}} = \frac{1}{N} \frac{1}{c(1-2c) - \lambda/\theta}. \end{aligned} \quad (33)$$

Note that, when  $\lambda/\theta < -8$ , the range covered by the ‘clustering mode’ tends to infinity for the concentrations given by equation (28).

It is noteworthy that the ‘clustering mode’, which has been found to be more slowly relaxing, appears to be also more probable. This result means that strong heteroatomic bonding in undercooled multicomponent liquids may favour the formation of ‘long-lived concentration fluctuations’, which can be considered as defining clustering effects in liquids where atomic cohesion is governed by metallic bonding. The relatively great probability of formation of these clusters together with their long lifetime act to enhance the HFM nucleation mechanism, particularly when an expected nucleating compound has nearly the same composition as that of the clusters.

It is notable that, in the case where  $\lambda > 0$  (repulsing interaction between 1 and 2) with the previous hypothesis concerning the atomic mobilities ( $D_3^* \ll D_1^* = D_2^* = D^*$ ), the substitutional mode would become the slower. Such a mode would classically lead to phase separation for large  $\lambda/\theta$ . In this latter case, phase separation would be initiated by homoatomic clustering.

### 3.2. High atomic mobility of component 3

It is also of interest to study the opposite limiting case, where the mobilities of atoms 1 and 2 are negligibly small compared with that of atoms 3:  $D_3^* \gg D_1^* = D_2^* = D^*$ .

In this case and keeping the condition of very strong heteroatomic bonding between components 1 and 2 ( $|\lambda_{13}|, |\lambda_{23}| \ll |\lambda_{12}| = |\lambda|$ ) it is found from equations (21) that

$$D_{11} \approx cD_3^* \left(1 + c(1-2c)\frac{\lambda}{\theta}\right) = D_{12} = D_{21} = D_{22}.$$

The expressions for the independent modes are

$$D^{(1)} \approx D_3^* 2c \left(1 + (1-2c)\frac{\lambda}{\theta}\right), \quad D^{(2)} \approx 0.$$

Again the mode  $D^{(2)}$  appears to be the slow mode, but in this case the physical meanings of the modes change. With

$$\hat{\mathbf{a}} = \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \quad \text{and} \quad \hat{\mathbf{a}}^{-1} = \frac{1}{2} \begin{pmatrix} 1 & +1 \\ -1 & 1 \end{pmatrix}$$

it can be found that, for the first mode,  $du_2 = 0$ , which leads to  $dc_1 = dc_2$  (the first mode corresponding to  $D^{(1)}$  now means clustering instead of substitution) and, for the second mode,  $du_1 = 0$ , which yields  $dc_1 = -dc_2$  (the second slow mode corresponding to  $D^{(2)}$  now means substitution). Thus, in the case of a highly mobile 'solvent' (component 3) and low mobility of strongly interacting solutes 1 and 2 the clustering mode is short lived and the substitutional mode is long lived; this situation is the opposite of that obtained with mobile species 1 and 2.

This last result appears to be reasonable as, for clustering fluctuations ( $dc_1 = dc_2 \equiv dc$ ), the concentration of the mobile component 3 changes to a maximal extent;  $dc_3 = -2dc$ , so that the resulting gradient  $\nabla c_3$  is significant; this effect added to large  $D_3^*$  pulls the system back rather quickly (fast relaxation). On the contrary for substitutional fluctuations ( $dc_1 = -dc_2$ ) the concentration of component 3 remains undisturbed,  $dc_3 = 0$ . As  $\nabla c_3 = 0$ , the resulting flux is certainly very small (this flux is not rigorously equal to zero as the flux depends formally on the gradient of chemical potential); this leads to a long relaxation time owing to the low mobilities of components 1 and 2.

#### §4. CONCLUSION

This study has been mainly devoted to the analysis of the relaxation of concentration fluctuations in ternary liquid alloys. Two normal modes of concentration fluctuations have been found to characterize the relaxation of fluctuations. Application to specific cases allows us to obtain a clear physical meaning of the eigenvalues corresponding to these modes. For example, when two components exhibit a strong heteroatomic bonding together with high atomic mobilities, a slower clustering mode is defined. It has also been found that the long-lived clustering fluctuations also have a maximum probability of being formed. This allows physical definition of clustering in metallic liquids.

In a multicomponent liquid containing  $\nu$  components, the relaxation of concentration fluctuations is described by  $\nu - 1$  normal modes. The particular strong chemical order between some components can generate long-lived clustering fluctuations whose relaxation is described by the corresponding normal mode. When the compositions of clusters are close to the concentration of expected nucleating compounds in the undercooled liquid, the HFM mechanism of nucleation is particularly favoured. This allows us to understand why the bulk glass-forming ability from the liquid state is particularly sensitive to the average composition of the alloy (Inoue *et al.* 1990, Pecker and Johnson 1993, Busch *et al.* 1995).

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