

Liquid gallium-lead spinodal calculation from effective potentials

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Some homogenous binary liquid alloys present segregation when the temperature decreases. In the homogenous liquid alloys the structure factor increases at low angles when the temperature decreases and diverges at $q=0$ when the critical temperature is reached. This segregation is characterized in real space by a preference to homo coordination from a certain interatomic distance to large distances. In the calculation of the structure factor from effective potentials, the quantities which become infinite are linked to a determinant which becomes zero and is easier to study than a divergence. We correlate the study of the zero of the determinant to the calculated total and partial structure factors of the demixing alloy. This method using interatomic potentials fitted on the structure of pure metals permits to calculate very low angle structure factors (where numerical simulation fails), for the first time to our knowledge, to construct the spinodal of the gallium-lead liquid alloy.

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I. INTRODUCTION

Segregation in binary alloys is a phenomenon about which great interest has been shown. A thorough-going review has been done by Sommer and Singh.¹ The phenomenon appears at low angles by a divergence of the total structure factor. This divergence appears at higher angles in the Bhatia and Thornton² concentration-concentration partial structure factor $S_{CC}(q)$. In real space the segregation corresponds to a preference for homo coordination especially in the first nearest neighbor cell. Ruppertsberg and Knoll³ have highlighted this divergence experimentally for lithium-sodium liquid alloys. The main general structural relationship in simple liquids is the Ornstein Zernicke equation.⁴ This equation links, in real space, the total correlation function $h(r)$ to the direct correlation function $c(r)$ added to a convolution of the direct correlation function $c(r)$ with the function $h(r)$ weighted by the density [Eq. (4.22) of March and Tosi's book⁵]. In reciprocal space this equation is the same but the convolution product is changed into a simple product, which permits writing a scalar relation between the functions $h(q)$ and $c(q)$ [Eq. (4.17) of Ref. 5]. The structure of a binary liquid alloy is given by the three partial structure factors (indices 11, 12, 22). The same kind of equation exists in alloys but the relation between the $h_{ij}(q)$ and the $c_{ij}(q)$ functions are written with a matrix relationship using a determinant $D(q)$. The $h_{ij}(q)$ are obtained after the inversion of the $c_{ij}(q)$ matrix. With this approach, due to Stroud,⁶ the divergence of the total structure factor corresponds to the node at $q=0$ of the $c_{ij}(q)$ matrix determinant. This method explains the segregation in terms of direct correlation function $c_{ij}(q)$ and allows as well an easier approach to this phenomenon by the study of a quantity which tends towards zero. We used this method to calculate the structure of the gallium-lead liquid alloy near the miscibility gap. Simple step potentials such as Silbert-Young potentials⁷ are used to model the structure of the alloy. This very simple and physical potential

is described by only three parameters. The gallium-gallium and lead-lead partial potential in the alloys are supposed to be those of the pure metal. The corresponding parameters are fitted to the experimental structure factors of the pure metals at different temperatures. For liquid gallium, the structure factor has been measured by Bellissent⁸ and for liquid lead by Dalhborg.⁹ We study the determinant $D(q)$ at $q=0$ as function of the gallium concentration by varying a parameter [step of the potential $v_{12}(r)$] characterizing the gallium-lead interaction. The determinant exhibits a minimum at a certain concentration. Increasing the step parameter decreases the value of the minimum. Two quantities (gallium concentration and step value) cancel one times the determinant at the “critical temperature T_c .” The total and the Bhatia-Thornton $S_{CC}(q)$ partial structure factors are calculated at this critical temperature and gallium concentration. The segregation appears clearly by the divergence of the Bhatia-Thornton $S_{CC}(q)$ partial structure factor, and of the total structure factor (but at much smaller angles). The fact that the combination of pair correlation functions $g_{11}(r)+g_{22}(r)-2g_{12}(r)$ is positive at large distances is a proof of the homo-coordination. The spinodal curve is constructed from the study of the zeros of the determinant as functions of concentration. All parameters are temperature dependent. The parameters of the effective gallium-lead potential are obtained from the effective gallium-gallium and lead-lead effective potentials by an adapted Lorentz-Berthelot rule also used by Ali, Osman, and Singh.¹⁰ For each concentration, we scan the temperature, which cancels the determinant. That allows us to construct the spinodal.

Section II presents the theoretical formalism. It is divided into two parts. Section II A recalls some basic relations between structure and thermodynamics. Section II B deals with the structure and its relationships with effective potentials used to define and discuss the determinant which is the key to our work. In Sec. III A, we explain how to build the different effective potentials in the alloy, in order to obtain seg-

regation. The consistency of this method is shown by the structure factors and pair correlation functions study. We explain why the divergence does not appear in the total structure factor with a classical spectrometer. In Sec. III B, we use this method to construct the spinodal curve of the gallium-lead liquid alloy. Then, we provide our conclusion.

II. THEORY

A. Structure factors and pair correlation functions

With a spectrometer, one measures a total alloy structure factor $S_{\text{tot}}(q)$ that can be related to three complementary sets

of partial structure factors:¹¹ the Ashcroft-Langreth¹² ones [Eq. (1)], the Faber-Ziman¹³ ones [Eq. (2)], and the Bhatia-Thornton ones² [Eq. (4)]:

$$S_{\text{tot}}(q) = \frac{c_1 b_1^2 S_{11}(q) + 2\sqrt{c_1 c_2} b_1 b_2 S_{12}(q) + c_2 b_2^2 S_{22}(q)}{c_1 b_1^2 + c_2 b_2^2}, \quad (1)$$

where c_1, c_2, b_1, b_2 are, respectively, the concentrations and the neutron scattering lengths of each metal. $S_{ij}(q)$ are the Ashcroft-Langreth partial structure factors.¹² We also have

$$S_{\text{tot}}(q) - 1 = \frac{c_1^2 b_1^2 (a_{11}(q) - 1) + 2c_1 c_2 b_1 b_2 (a_{12}(q) - 1) + c_2^2 b_2^2 (a_{22}(q) - 1)}{c_1 b_1^2 + c_2 b_2^2}. \quad (2)$$

The $a_{ij}(q)$ are the Faber-Ziman partial structure factors.¹³ They are connected to the partial pair correlation functions $g_{ij}(r)$ by

$$g_{ij}(r) - 1 = h_{ij}(r) = \frac{1}{2\pi^2 \rho_0 r} \int_0^\infty q (a_{ij}(q) - 1) \sin(qr) dq, \quad (3)$$

where ρ_0 is the average number density.

The total structure factor $S_{\text{tot}}(q)$ can also be written

$$S_{\text{tot}}(q) = \frac{(c_1 b_1 + c_2 b_2)^2 S_{NN}(q) + 2(c_1 b_1 + c_2 b_2)(b_1 - b_2) S_{NC}(q) + (b_1 - b_2)^2 S_{CC}(q)}{c_1 b_1^2 + c_2 b_2^2}. \quad (4)$$

The functions $S_{NN}(q)$, $S_{NC}(q)$, and $S_{CC}(q)$ are the Bhatia-Thornton partial structure factors.² The concentration-concentration structure factor $S_{CC}(q)$, characteristic of chemical order, represents the fluctuations around the mean value $c_1 c_2$ and can be written as a function of the Faber-Ziman partial structure factors

$$S_{CC}(q) = c_1 c_2 (1 + c_1 c_2 (a_{11}(q) + a_{22}(q) - 2a_{12}(q))). \quad (5)$$

The Fourier transform of $[S_{CC}(q)/(c_1 c_2) - 1]$ is given by

$$\begin{aligned} & \frac{1}{2\pi^2 \rho_0 r c_1 c_2} \int_0^\infty q \left(\frac{S_{CC}(q)}{c_1 c_2} - 1 \right) \sin(qr) dq \\ &= g_{11}(r) + g_{22}(r) - 2g_{12}(r) \\ &= \frac{g_{CC}(r)}{(c_1 c_2)^2}. \end{aligned} \quad (6)$$

The quantity $g_{11}(r) + g_{22}(r) - 2g_{12}(r)$ is the difference between homo-coordination and hetero-coordination and indicates the nature of the chemical order in the alloy. Bhatia and Thornton have shown that the low q limit of $S_{CC}(q)$ is connected to the Gibbs function of the alloy by the relationship²

$$S_{CC}(0) = N k_B T \left(\frac{\partial^2 G}{\partial c^2} \right)_{T,P,N}^{-1}. \quad (7)$$

They have also determined the low q limits of their other partial structure factor, which can be written by the following equalities:

$$S_{NN}(0) = \rho_0 k_B T \chi_T + \delta^2 S_{CC}(0) \text{ and } S_{NC}(0) = -\delta S_{CC}(0), \quad (8)$$

where the number χ_T is the isothermal compressibility. The number k_B is the Boltzmann constant and T the temperature in Kelvin. Here δ is the dilatation factor and is equal to

$$\delta = \frac{1}{V} \left(\frac{\partial V}{\partial c} \right)_{T,P,N}. \quad (9)$$

When the alloy presents a phase separation like Li-Na,³ then $S_{CC}(0) \rightarrow \infty$ on the spinodal curve. For an ideal solution $S_{CC}(0) \approx c_1 c_2$ (Li-Ca).¹⁴ On the contrary, for an hetero coordinated alloy, the thermodynamic limit $S_{CC}(0)$ is lower than $c_1 c_2$ and the $S_{CC}(q)$ curve presents a prepeak at a q value [$q \approx 1.8 \text{ \AA}^{-1}$ for Mn-Sb (Ref. 15)] lower than the peaks of the pure components which cancel themselves.

The low q limit of the (measured) total structure factor $S_{\text{tot}}(q)$ can be written from Eqs. (4) and (8) by the equation

$$S_{\text{tot}}(0) = \frac{(c_1 b_1 + c_2 b_2)^2}{c_1 b_1^2 + c_2 b_2^2} \times \left\{ \rho k_B T \chi_T + \left[\delta - \frac{b_1 - b_2}{c_1 b_1 + c_2 b_2} \right]^2 S_{CC}(0) \right\}. \quad (10)$$

Only the Bhatia-Thornton partial structure factor $S_{CC}(0)$ in Eq. (10) can become infinite but it is weighted by the term

$$A = \left[\delta - \frac{b_1 - b_2}{c_1 b_1 + c_2 b_2} \right].$$

In certain circumstances, it is possible that the term A may be near 0 hiding the divergence of the total (and experimental) structure factor $S_{\text{tot}}(q)$.

B. Relations between the structure and the potential

In the alloys, the correlation functions are related by $g_{ij}(r) = h_{ij}(r) - 1$ and are given by the Ornstein-Zernicke equation⁴

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^2 \rho_k \int_0^\infty c_{ik}(|\mathbf{r} - \mathbf{r}'|) h_{kj}(r) d^3 \mathbf{r}' \quad i, j = 1, 2, \quad (11)$$

where ρ_k is the average number density of k type atoms. The $c_{ij}(r)$ are the direct correlation functions between i and j particles, the second term of formula (11) describes the correlation between i and j through all atoms in the alloy. This equation can be written in the q momentum space:

$$h_{ij}(q) = c_{ij}(q) + \sum_{k=1}^2 \rho_k c_{ik}(q) h_{kj}(q) \quad i, j = 1, 2. \quad (12)$$

Many equations can be used to link approximately the correlation functions to the ion-ion potentials $v_{ij}(r)$. For simple ion-ion effective potentials, it is convenient to use the Percus-Yevick equation,¹⁶

$$c_{ij}(r) = g_{ij}(r) \left(1 - \exp \frac{v_{ij}(r)}{k_B T} \right). \quad (13)$$

The pure liquid metals structure has often been calculated numerically by using the pseudopotential method. To our knowledge, the direct correlation functions have been calculated analytically for alloys only for very simple potentials: hard sphere potentials by Ashcroft and Langreth,¹² Silbert-Young⁷ potentials by Gopala Rao¹⁷ and Yukawa potentials by Hafner *et al.*¹⁸ (but only with equal hard sphere diameters). Some alloy structures have been calculated numerically by RPA from model-pseudopotentials, for example, by Hoshino and Young.¹⁹ Structure factors can also be calculated by numerical simulation. The pair correlation functions are calculated until a maximum distance value which depends on the size of the simulation box. It is not possible to calculate very small angle structure factors. Indeed, the cut off Q of the structure factor corresponds to a simulation box whose side size must be greater than $(4\pi/Q)$.

For a hard sphere pair potential, the function $c_{ij}(r)$ was determined for alloys by Lebowitz²⁰ and used by Ashcroft and Langreth¹² [Eq. (14)]. The Silbert-Young potential⁷ permits correction to the hard sphere potential (which is the main effect) either by an attraction or by a repulsion between i and j particles. For hard spheres we have

$$v_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij} \\ 0 & r > \sigma_{ij} \end{cases}, \quad (14)$$

$$-c_{ij}^{\text{HS}}(r) = \begin{cases} a_i & \lambda_{ij} > r > 0 \\ a_{ij} + b_{ij}r + dr^3 + \frac{f_{ij}}{r} & \lambda_{ij} < r < \sigma_{ij} \\ 0 & \sigma_{ij} < r \end{cases}.$$

The σ_{ii} are defined as being the hard sphere diameters of the i th type metallic ion in the alloy, the σ_i are defined as being the hard sphere diameters of the pure metal. We also use

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \quad \lambda_{ij} = (\sigma_{jj} - \sigma_{ii})/2, \quad (15)$$

$$a_{ij} = (a_i + a_j)/2, \quad \text{and} \quad b_{ij} = (b_i + b_j)/2.$$

(Some calculations with nonadditive spheres have been also published.) For the alloys, the $c_{ij}(r)$ functions of the Silbert-Young pair potential have been given by Gopala Rao and Satpathy,¹⁷

$$v_{ij}(r) = \begin{cases} \infty & \sigma_{ij} > r \\ \varepsilon_{ij} & \sigma_{ij} < r < A_{ij}\sigma_{ij} \\ 0 & A_{ij}\sigma_{ij} < r \end{cases} \quad (16)$$

$$c_{ij}(r) = \begin{cases} c_{ij}^{\text{HS}}(r) & \sigma_{ij} > r \\ -v_{ij}(r)/(k_B T) = -\varepsilon_{ij}/(k_B T) & \sigma_{ij} < r < A_{ij}\sigma_{ij} \\ 0 & A_{ij}\sigma_{ij} < r \end{cases}.$$

For the potential, we take the σ_{ij} and A_{ij} parameters as determined generally by using the Lorentz-Berthelot interpolation rule,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad A_{ij}\sigma_{ij} = \frac{A_{ii}\sigma_{ii} + A_{jj}\sigma_{jj}}{2}, \quad \varepsilon_{ij} = \pm \sqrt{\varepsilon_{ii}\varepsilon_{jj}}. \quad (17)$$

A strong chemical order can transgress the Lorentz-Berthelot rule. The correct choice of the parameters will be discussed later. The Lorentz-Berthelot calculation of ε_{12} cannot give the segregation. It needs a modification of the interpolation rule presented in Sec. III B, Eq. (23).

The direct $c_{ij}(r)$ pair correlation functions are simply linked to the effective potentials $v_{ij}(r)$. The $c_{ij}(q)$ are easy to calculate. For the alloy Eq. (12) can be written¹² by the matrix form

$$\begin{pmatrix} S_{11}(q) & S_{12}(q) \\ S_{12}(q) & S_{22}(q) \end{pmatrix} = \begin{pmatrix} 1 - \rho_1 c_{11}(q) & -\sqrt{\rho_1 \rho_2} c_{12}(q) \\ -\sqrt{\rho_1 \rho_2} c_{12}(q) & 1 - \rho_2 c_{22}(q) \end{pmatrix}^{-1}. \quad (18)$$

So the terms $S_{ij}(q)$ are obtained by inversion of this matrix whose determinant is given by the following equation:

$$\begin{aligned} D(q) &= \begin{vmatrix} 1 - \rho_1 c_{11}(q) & -\sqrt{\rho_1 \rho_2} c_{12}(q) \\ -\sqrt{\rho_1 \rho_2} c_{12}(q) & 1 - \rho_2 c_{22}(q) \end{vmatrix} \\ &= 1 - \rho_1 c_{11}(q) - \rho_2 c_{22}(q) + \rho_1 \rho_2 (c_{11}(q)c_{22}(q) - c_{12}(q)^2). \end{aligned} \quad (19)$$

In case of phase separation the partial structure factor becomes infinite at the limit $q=0$, thus the determinant $D(q)$ is equal to zero at $q=0$. This will be checked in the next section and is used to construct the spinodal of the gallium lead liquid alloy. The calculation of $D(q=0)$ needs to know the limit at $q=0$ of the three $c_{ij}(q)$ functions, which depend on the parameters $(\sigma_{ij}, A_{ij}, \varepsilon_{ij})$ of three effective partial step pair potentials. Thus $D(q=0)$ is a function of these parameters. It will be necessary to calculate the dilatation factor δ . We write, by using the relationships between the Bhatia-Thornton and Ashcroft-Langreth partial structure factors, the dilatation factor δ [Eq. (8)] as a function of $c_{ij}(0)$,

$$\begin{aligned} \delta &= -\frac{c_1 c_{11}(0) - c_2 c_{22}(0) + (c_2 - c_1) c_{12}(0)}{\rho_0^{-1} - c_1^2 c_{11}(0) - c_2^2 c_{22}(0) - 2c_1 c_2 c_{12}(0)} \\ &(\rho_1 = c_1 \rho_0 \text{ and } \rho_2 = c_2 \rho_0). \end{aligned} \quad (20)$$

III. RESULTS AND DISCUSSION

A. Search of the critical concentration

The parameters of the components in the alloy are taken to be the same as the parameters of the pure components at the same temperature. The pure metal density is compiled by Crawley²¹ as a function of temperature in the form: $d_i = a_i - b_i(T - T_{Mi})$, where T_{Mi} is the melting temperature of the i th metal. For gallium the different parameters $[\sigma_{11}(T), A_{11}(T), \varepsilon_{11}(T)/(k_B T)]$ have been determined at different temperatures: 326 K and 959 K by a fit to the accurate experimental structure measured by Bellissent *et al.*⁸ Then we obtain for gallium the following temperature dependent parameters:

$$\begin{aligned} \sigma_{11}(T) &= (2.62709 - 1.37418 \cdot 10^{-4} T) \text{ \AA}, \\ A_{11}(T) &= 2.94929 + 2.94059 \cdot 10^{-4} T, \\ \varepsilon_{11}(T)/(k_B T) &= R_{11}(T) = (70.33 + 0.04667 T)/T. \end{aligned} \quad (21)$$

For lead the different parameters $[\sigma_{22}(T), A_{22}(T), \varepsilon_{22}(T)/(k_B T)]$ have been determined at the temperatures equal to 613 K and 1163 K by a fit to the experimental structure measured by Dahlborg *et al.*⁹ For lead the temperature dependent parameters are the following:

$$\sigma_{22}(T) = (3.15112 - 1.21235 \cdot 10^{-4} T) \text{ \AA},$$

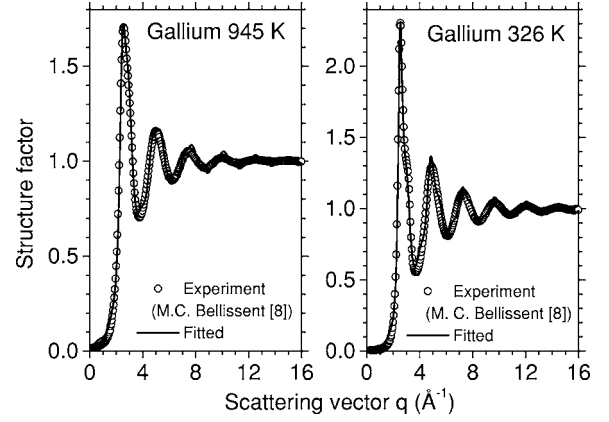


FIG. 1. Experimental (Ref. 8) and step potential fitted structure factors of pure gallium at 326 K and 959 K.

$$A_{22}(T) = 1.89311 + 1.76116 \cdot 10^{-4} T, \quad (22)$$

$$\varepsilon_{22}(T)/(k_B T) = R_{22}(T) = (172.26 - 0.05456 T)/T.$$

For the two pure metals the effective ion-ion potentials are repulsive. This is compatible with the nature of the gallium potential obtained from the structure by Bellissent *et al.*⁸ and calculated for lead by Dahlborg *et al.*⁹ In Figs. 1 and 2, we present the experimental and the fitted step potential structure factors for gallium and lead. The agreement is good for both pure metals.

We assume that σ_{12}, A_{12} , are given by the Lorentz-Berthelot rule [formula (17)]. So, they are also temperature dependent. We leave only one parameter $\varepsilon_{12}/(k_B T)$ free to be chosen. Our work is based on the fact that this parameter is determined in order to ensure the divergence of the structure factor at the critical temperature $T_C = 879.15$ K given by Massalski *et al.*²² From a technical point of view, we calculate $\varepsilon_{12}/(k_B T)$ which gives $D(q=0)=0$ at the critical temperature T_C . To calculate $R_{12}(T_C) = \varepsilon_{12}/(k_B T_C)$, we study the behavior of $D(q=0)$ versus the gallium concentration c_1 and the ε_{12} value. The curve in Fig. 3 displays a minimum, which is equal to zero, at the critical temperature, only for one pair $[c_1, \varepsilon_{12}/(k_B T_C)]$. The value of the critical gallium concentra-

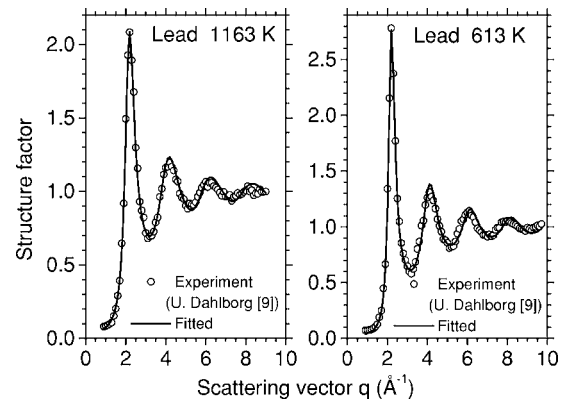


FIG. 2. Experimental (Ref. 9) and step potential fitted structure factors of pure lead at 613 K and 1163 K.

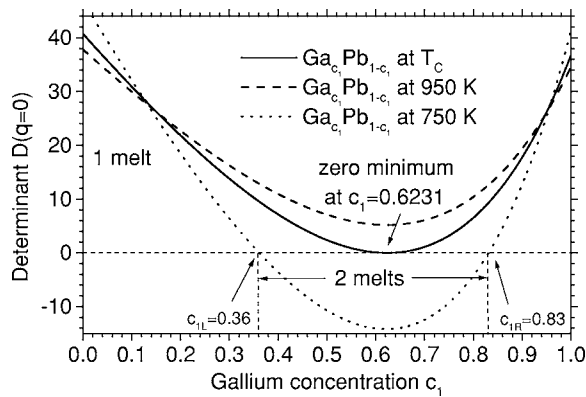


FIG. 3. Determinant $D(q=0)$ versus gallium concentration c_1 . For $\varepsilon_{12}/(k_B T) = 0.199464$, the minimum is equal to zero at the critical gallium concentration of 62.31% and a critical temperature of $T_C = 879.15$ K (Ref. 22). Two other curves have been calculated in the homogeneous ($T = 950$ K) and two melts temperature ($T = 750$ K) ranges.

tion c_1 is 62.31 at. %, while the experimental one, given by Massalski's book, is equal to 56 at. %. The critical parameter at the critical temperature and concentration $R_{12}(T_C) = \varepsilon_{12}/(k_B T_C)$ is precisely equal to 0.199464. We check that the determinant is equal to zero only at $q=0$ for this value. When the determinant becomes negative at this concentration, we observe a divergence at a value q_0 different from zero. Two divergences of the structure factor appear, one tends to $+\infty$ (at $q=q_0+\varepsilon$) and the other to $-\infty$ (at $q=q_0-\varepsilon$). The solutions are unphysical and the system recovers its stability by the phase separation. The calculation of $D(q)$ presents numerical problems very near $q=0$. Thus, we use a q^6 expansion of the determinant to get $D(q=0)$. In Fig. 4, we show that this approximation is accurate at q values lower than 0.3 \AA^{-1} .

With these parameters at the critical temperature and gallium concentration we have calculated the total structure factor $S_{\text{tot}}(q)$ and the Bhatia-Thornton partial structure factor $S_{CC}(q)$ (Fig. 5). The divergence appears very clearly in the Bhatia-Thornton partial structure factor, but not in the total

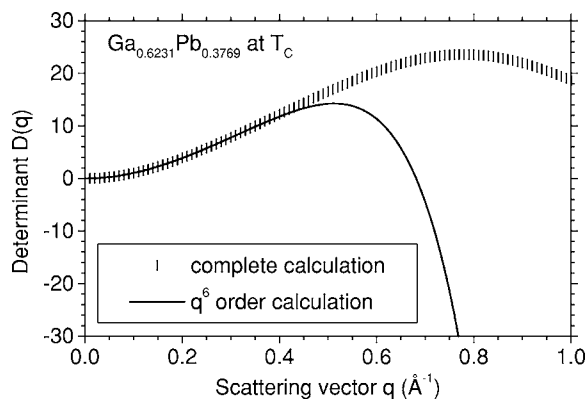


FIG. 4. Determinant $D(q)$ at our critical gallium concentration and temperature of the $\text{Ga}_{0.6231}\text{-Pb}_{0.3769}$ liquid alloy. Vertical bars correspond to exact calculation and the full line to the q^6 order calculation used near $q=0$ and at $q=0$.

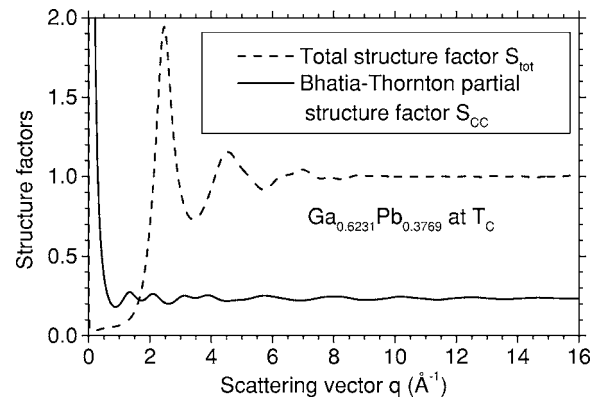


FIG. 5. Total structure factor $S_{\text{tot}}(q)$ and concentration concentration partial structure factor $S_{CC}(q)$ for $\text{Ga}_{0.6231}\text{-Pb}_{0.3769}$ liquid alloy at the critical temperature T_C .

structure factor. The value of the coefficient δ calculated from Eq. (20) is equal to -0.279 , while the term $(b_1 - b_2)/(c_1 b_1 + c_2 b_2)$ is equal -0.262 for our calculated critical concentration [the gallium and lead neutron scattering lengths are, respectively, equal to 7.288 fm and 9.405 fm (Ref. 23)]. The term

$$A = \left[\delta - \frac{b_1 - b_2}{c_1 b_1 + c_2 b_2} \right]$$

is very small -0.017 and is squared in Eq. (10). It is essentially impossible to get and to observe experimentally with high angle spectrometers the divergence of the total structure factor $S_{\text{tot}}(q)$ at low q . The divergence (Fig. 6) appears at very low q in the range $[0; 0.05] \text{ \AA}^{-1}$ like that observed in preliminary experimental results by Kaban, Pohlers, and Hoyer²⁴ using a very small angle spectrometer. These authors have observed experimentally the divergence on the total structure factor with the small-angle neutron scattering (SANS) of the GKSS Research Centre in der Helmholtz Gemeinschaft (experimental report GeNF SANS-2 in December

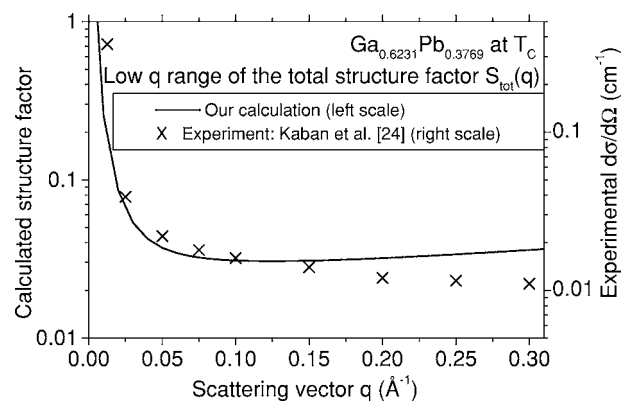


FIG. 6. Very small q range of the calculated total structure factor $S_{\text{tot}}(q)$ (full line) compared to the experimental value measured by Kaban (Ref. 24). The scale of the calculated total structure factor is on the left-hand side. The experimental differential cross section is on the right-hand side. The origin of the scales have been chosen in order to make roughly comparison between them.

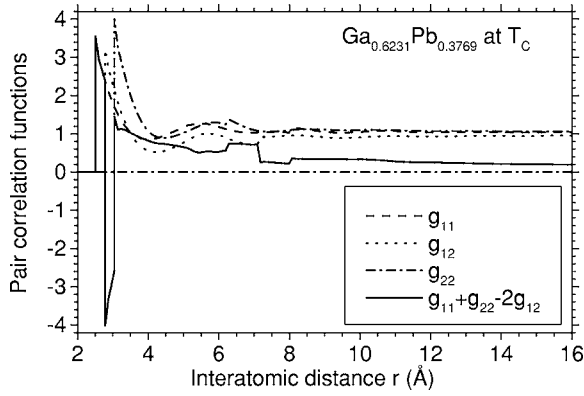


FIG. 7. Partial pair correlation functions $g_{ij}(r)$ and total pair correlation function $g_{11}(r)+g_{22}(r)-2g_{12}(r)$ obtained from our model for $\text{Ga}_{0.6231}\text{-Pb}_{0.3769}$ liquid alloy at the critical temperature T_C .

2003). To our knowledge it is the first time that a very low angle structure factor is calculated from interatomic potentials. The agreement can be considered as good taking account the experimental errors and the crudeness of the model. In Fig. 7, we have plotted the calculated pair partial correlation functions $g_{11}(r)$, $g_{22}(r)$, $g_{12}(r)$ and the total $g_{11}(r)+g_{22}(r)-2g_{12}(r)$ function. In real space the segregation is illustrated by the fact that the function $g_{11}(r)+g_{22}(r)-2g_{12}(r)$ is always positive beyond the interatomic distance $r=3.05$ Å and does not oscillate around zero. This is a clear indication of the homo coordination. Our calculations are also consistent with the Hoshino criterion²⁵ that is also filled: the homo coordination tendency is characterized by the fact that the first peaks of $g_{11}(r)$ and $g_{22}(r)$ are higher than that of $g_{12}(r)$. The model is consistent and will be used to construct the spinodal of the phase diagram.

B. Spinodal construction curve

A study of the determinant at $q=0$ versus the concentration of gallium and temperature has been done. All the temperature dependent parameters must be known. We take the parameters determined previously [$\sigma_{11}(T)$, $A_{11}(T)$, $\varepsilon_{11}/(k_B T)$, $\sigma_{22}(T)$, $A_{22}(T)$, $\varepsilon_{22}/(k_B T)$, $\sigma_{12}(T)$, $A_{12}(T)$]. The physical meaning of the terms $R_{ij}(T)=\varepsilon_{ij}/(k_B T)$ is the ratio of the (negative or positive) energy step of the ion-ion effective potential by the ions kinetic energy. It increases when the temperature decreases. The kinetic energy is proportional to the temperature T of the alloy.

For $R_{12}(T)=\varepsilon_{12}/(k_B T)$, we used an empirical law already used by Ali, Osman, and Singh,¹⁰

$$\varepsilon_{12}(T) = Cte\sqrt{\varepsilon_{11}(T)\varepsilon_{22}(T)}, \quad (23)$$

then by dividing by $k_B T$, the $R_{12}(T)$ parameterization becomes

$$R_{12}(T) = Cte\sqrt{R_{11}(T)R_{22}(T)}, \quad (24)$$

where the constant $Cte=1.4886$ has been calculated in order to obtain precisely $R_{12}(T=T_C)=0.199464$, calculated in the

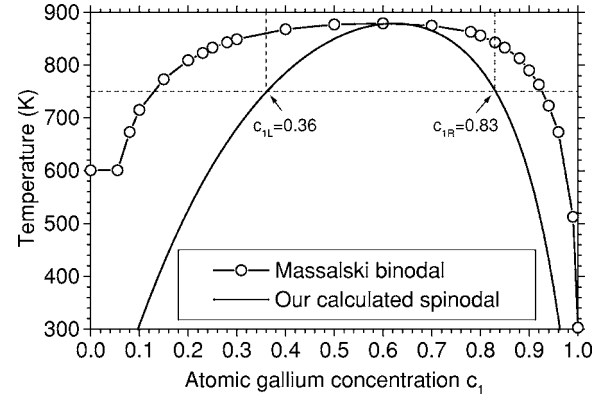


FIG. 8. Phase diagram of the $\text{Ga}_{c_1}\text{Pb}_{1-c_1}$ alloy. The binodal curve is given in Massalski (Ref. 22) (circles) and the spinodal curve is calculated in the frame of our model (full line).

previous section. Now all the temperature dependent parameters [$\sigma_{ij}(T)$, $A_{ij}(T)$, $\varepsilon_{ij}(T)/(k_B T)$] are determined. In Fig. 3, we have added two curves representing the determinant $D(q=0)$ versus the concentration calculated for two temperature 950 K (greater than T_C) and 750 K (lower than T_C). For the temperature of 950 K, the determinant $D(q=0)$ never becomes zero on the whole concentration range, it exists as only one melt. For the temperature of $T=750$ K the determinant $D(q=0)$ becomes zero two times for two concentration c_1 values ($c_{1L}=0.36$ and $c_{1R}=0.83$) which correspond to those of the spinodal. Between these values, the determinant is negative; it corresponds to the region where phase separation occurs (two melts). To construct the spinodal, we search for each gallium concentration c_1 the temperature which cancels the determinant $D(q=0)$. All these points correspond to the spinodal curve. Our calculated spinodal and the Massalski's binodal curve are represented in Fig. 8. We have reported the values $c_{1L}=0.36$ and $c_{1R}=0.83$ of Fig. 3 at 750 K. The spinodal curve is under the binodal curve as expected. It reaches the binodal curve at the critical temperature.

IV. CONCLUSION

We have calculated very low angle structure factors from analytical effective potentials. We applied them to explain the divergence of the structure factor at $q=0$ in accord with the spinodal concept. We applied successfully this concept to liquid gallium lead alloy and construct for the first time, to our knowledge, the spinodal curve from a partial effective potential.

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