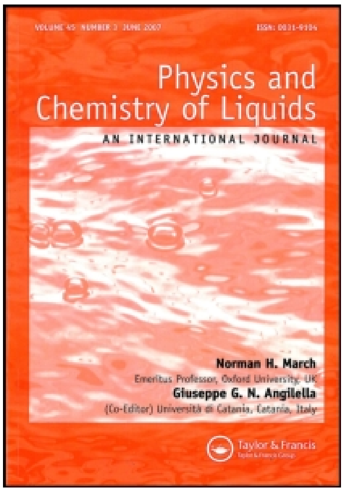

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The Influence of Medium-and Long-range Forces on the Structure of Binary Liquid Alloys I. Size Effects in Alkali Alloys

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The Influence of Medium- and Long-range Forces on the Structure of Binary Liquid Alloys

I. Size Effects in Alkali Alloys

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We present the first optimized random-phase (ORPA) calculation for the structure of liquid binary alloys, with an application to K-Rb and K-Cs alloys. We show that the inclusion of the medium- and long-range forces in the ORPA yields a marked improvement over calculations based on hard-sphere mixtures or soft repulsive forces only. However, for larger size differences and non-additive pairpotentials, the random-phase approximation produces a singularity in the partial structure factors, which is not completely eliminated through the optimization process.

PACS classification: 61.20Gy, 61.25 Mv, 61.20.Qg

Key Words: Random-phase calculation, liquid binary alloys, medium- and long range forces.

1 INTRODUCTION

The progress in liquid-metal theory over the last ten years has made it clear that a fully quantitative description of the structure of liquid metals is impossible without proper consideration of the long-range oscillatory interatomic forces. Of course the zeroth-order model of the structure of liquid metals is determined by the geometrical requirements of sphere packing, but this simplistic picture is substantially modified by the corrections for the "softness" of the repulsive interactions and for the long-range oscillatory forces characteristic for the

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interactions between the atoms in a metal. Evidence as to the importance of the long-range forces comes from computer simulations,[1–3] the numerical solution of one of the integral equations of the statistical theory of liquids,[4] and from thermodynamic perturbation theory.[5–8] If the corrections introduced by the long-range forces are rather small for the alkali metals, for polyvalent metals such as Ga, Ge or Sn they are strong enough to enforce a qualitative change in the liquid metal.

In a binary liquid alloy we would expect these effects to be even more pronounced, as it is now possible that the intermediate and long-range forces produce structural effects which do not compete with the short-range repulsions. Progress, however, has been rather slow. Only a few computer-simulations of liquid alloys have been presented up to now (see e.g. [9–11]), to our knowledge the application of the integral equation method to binary liquid alloys has not even been attempted as yet. The application of thermodynamic perturbation methods has remained essentially at the level of Gibbs-Bogoljubov variational calculations with a hard-sphere-mixture[12] or a symmetric hard-core-Yukawa mixture[13] as reference systems. Only very recently we have presented an extension of the blip-function expansion of Weeks, Chandler, and Andersen[14] to binary alloys.[15] The effect of the medium- and long-range oscillatory potentials upon the structure of binary alloys has not been investigated as yet.

In the present paper we present an extension of the optimized random-phase approximation to binary alloys, with an application to liquid K-Rb and K-Cs alloys. The results of the analytical calculations are compared with experimental diffraction data. We find that the long-range forces have a distinct effect upon the structure of these homovalent, nearly ideal mixtures.

2 FROM THE INTERATOMIC FORCE LAW TO THE STRUCTURE OF THE LIQUID ALLOY

Thermodynamic perturbation theory starts from a decomposition of the interatomic potentials $\Phi_{ij}(R)$ into a repulsive short-range part $\Phi^0_{ij}(R)$ and a long-range oscillatory part $\Phi^1_{ij}(R)$ according to (see also Figure 1)

$$\Phi_{ij}(R) = \Phi^0_{ij}(R) + \Phi^1_{ij}(R) \tag{1a}$$

$$\Phi^0_{ij}(R) = \begin{cases} \Phi_{ij}(R) - \Phi_{ij}(R_{ij}) & R < R_{ij} \\ 0 & R > R_{ij} \end{cases} \tag{1b}$$

$$\Phi^1_{ij}(R) = \begin{cases} \Phi_{ij}(R_{ij}) & R < R_{ij} \\ \Phi_{ij}(R) & R > R_{ij} \end{cases} \tag{1c}$$

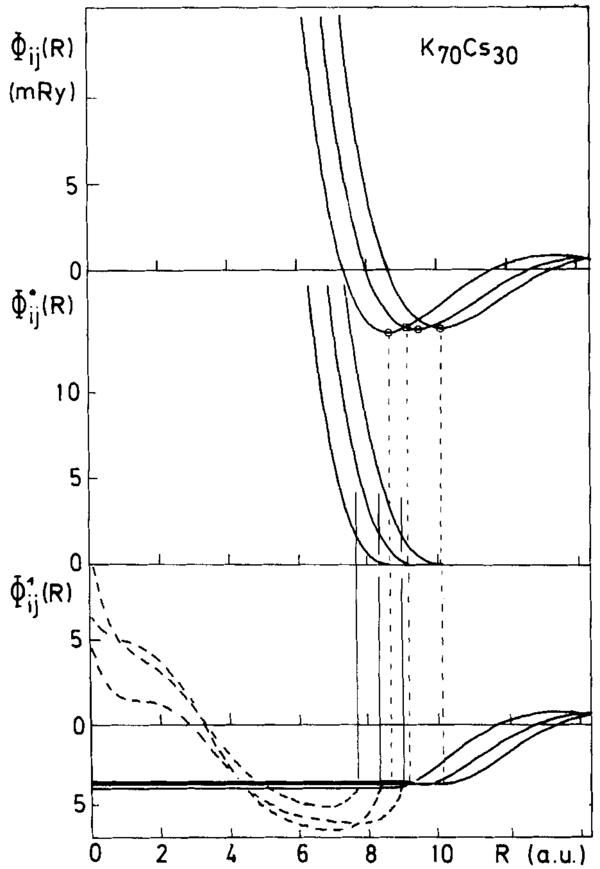

Figure 1 Separation of the effective interatomic interaction $\Phi_{ij}(R)$ into a short-range repulsive term $\Phi_{ij}^0(R)$ and a medium- and long-range term $\Phi_{ij}^1(R)$, illustrated at the example of a $K_{70}Cs_{30}$ alloy. The position of the first minimum in the potential is marked by an open circle. The distance at which the total potential Φ_{ij} is split into Φ_{ij}^0 and Φ_{ij}^1 is marked by the dashed vertical lines and the open square for the unlike-atom interaction $\Phi_{12}(R)$. The full vertical lines mark the effective hard-core diameters σ_{ij}, the dashed lines show the optimized potentials $\Phi_{ij}(R)$ for $r<\sigma_{ij}$, see Eq. (14) and text.

where R_{ij} is the position of the first minimum in $\Phi_{ij}(R)$. Any integral equation for the partial correlation function may be cast into the form of coupled Ornstein Zernike relations

$$h_{ij}(R_{12}) = c_{ij}(R_{12}) + \sum_{k=A,B} n_k \int c_{ik}(R_{13})h_{kj}(R_{32})d^3R_3, \qquad (2)$$

$$i,j = A, B$$

for the total correlation functions $h_{ij}(R)$ and the direct correlation functions $c_{ij}(R)$ (n_k is the partial number density), supplemented by closure conditions relating the $h_{ij}(R)$, $c_{ij}(R)$, and the pair potentials $\Phi_{ij}(R)$. In analogy to (1), the correlation functions are split into two parts,

$$h_{ij}(R) = h_{ij}^0(R) + h_{ij}^1(R) \tag{3a}$$

$$c_{ij}(R) = c_{ij}^0(R) + c_{ij}^1(R) \tag{3b}$$

Assuming for the moment that we know the solution of the purely repulsive Φ^0-system with the OZ-relations

$$h_{ij}^0(R_{12}) = c_{ij}^0(R_{12}) + \sum_{k=A,B} n_k \int c_{ik}^0(R_{13}) h_{kj}^0(R_{32}) d^3R_3, \qquad i,j = A, B \tag{4}$$

we can subtract the purely repulsive Φ_{ij}^0-couplings from both sides of Eq. (2) and derive a residual OZ-relation describing the effect of the long-range interactions

$$\begin{aligned} h_{ij}^1(R_{12}) = c_{ij}^1(R_{12}) + \sum_{k=A,B} n_k \Bigg\{ & \int c_{ik}^0(R_{13}) h_{kj}^1(R_{32}) d^3R_3 \\ & + \int c_{ik}^1(R_{13}) h_{kj}^0(R_{32}) d^3R_3 \\ & + \int c_{ik}^1(R_{13}) h_{kj}(R_{32}) d^3R_3 \Bigg\} \qquad i,j = A, B \end{aligned} \tag{5}$$

In the Weeks-Chandler-Andersen-method,[14] the free energy of the Φ_{ij}^0-system is expanded in terms of the differences in the Mayer-functions $f_{ij} \equiv \exp(-\beta\Phi_{ij}) - 1$ of the Φ_{ij}^0-system and those of a binary hard-sphere mixture of the same density and concentration and the diameters $\{\sigma\} = \{\sigma_{AA}, \sigma_{AB}, \sigma_{BB}\}$, $\beta = (k_B T)^{-1}$

$$\Delta f_{ij}(R) = \exp(-\beta\Phi_{ij}^0(R)) - \exp(-\beta\Phi_{\sigma_{ij}}). \tag{6}$$

In this approximation, the pair correlation functions of the repulsive system are given by

$$h_{ij}^0(R) = h_{\sigma_{ij}}(R) + B_{\sigma_{ij}}(R) \tag{7}$$

with the "blip-functions"

$$B_{\sigma_{ij}}(R) = \exp(\beta\Phi_{\sigma_{ij}}) g_{\sigma_{ij}}(R)\, \Delta f_{ij}(R) \tag{8}$$

For a one-component liquid, the effective hard-core diameter is determined from the condition $\int B_\sigma(R)d^3R = 0$.[14] The straightforward generalization to binary systems[25]

$$I_{ij} = \int B_{\sigma_{ij}}(R)d^3R = 0, \qquad i, j = A, B \tag{9}$$

determines the set $\{\sigma\} = \{\sigma_{AA}, \sigma_{AB}, \sigma_{BB}\}$ uniquely. However, for a general set of $\Phi_{ij}^0(R)$'s, the three conditions (9) can be met only for a non-additive ($\sigma_{AB} \neq (\sigma_{AA} + \sigma_{BB})/2$) reference system. For such non-additive hard-sphere mixtures, only approximate solutions for a rather restricted range of parameters are available.[16] Weaker conditions allowing to retain the additivity of the reference system have been proposed by Sandler:[17]

$$\sum_{i,j=A,B} c_i c_j |I_{ij}| = \text{Minimum} \tag{10a}$$

or

$$\sum_{i,j=A,B} |I_{ij}| = \text{Minimum} \tag{10b}$$

However, we have shown[15] that both conditions lead to partial structure factors $S_{ij}(q)$ that are unrealistic in the long wave-length regime. This difficulty may be resolved in the following way: we determine σ_{AA} and σ_{BB} by requiring $I_{AA} = I_{BB} = 0$. Then we adjust R_{AB} in such a way that for a given $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ we satisfy the condition $I_{AB} = 0$. Clearly there are two solutions $\tilde{R}_{AB}$ on either side of the minimnum R_{AB}, and we choose the one with $\tilde{R}_{AB} < R_{AB}$, so that the new $\Phi_{AB}^0(R)$ is again purely repulsive. This is equivalent to modify (1) in such a way that the repulsive system is purely additive (in the sense that condition (9) is satisfied for an additive reference system); an eventual non-additivity of the full potential is absorbed by the long-range forces $\Phi_{ij}(R)$. With the correlation functions of the repulsive system being approximated by hard-sphere correlation functions $h_{\sigma_{ij}}(R)$, the ORPA-closure conditions to the residual OZ-relations (5) are given by

$$h_{ij}^1(R) = 0 \qquad R < \sigma_{ij} \tag{11a}$$

$$c_{ij}^1(R) = -\beta\Phi_{ij}^1(R) \qquad R > \sigma_{ij} \tag{11b}$$

Andersen *et al.*[18] have shown that the set of coupled integral equations defined by Eqs (5) and (11) is equivalent to the variational conditions

$$\frac{\delta}{\delta\Phi_{ij}^1(R)} F^{\text{RPA}}[\Phi_{ij}^1(R)] = 0 \qquad R < \sigma_{ij}, i, j = A, B \tag{12}$$

where

$$F^{\mathrm{RPA}} = \frac{1}{2(2\pi)^3} \int d^3q \left\{ \mathrm{Tr}\left[\beta \sum_{k=A_1B} n_k \Phi^1_{ik}(k) S_{\sigma_{kj}}(k) \right] \right.$$
$$\left. - \ln \det\left[\delta_{ij} + \beta \sum_{k=A_1B} n_k \Phi^1_{ik}(k) S_{\sigma_{kj}}(k) \right] \right\} \qquad (13)$$

is the random phase contribution to the free energy.[18] This means that the ORPA requires the free energy to be stationary with respect to variations of $\Phi^1_{ij}(R)$ in the interior of the hard core. In (13) the $S_{\sigma_{kj}}(k)$ are the partial static structure factors of the reference system, and $\hat{\Phi}^1_{ik}(k)$ is the Fourier transform of the pair potential $\hat{\Phi}^1_{ik}(R)$ (we use $\tilde{f}$ for the Fourier transform of a function f). The solution of (12) defines an optimized potential $\Phi^{*1}_{ij}(R)$ given by

$$\Phi^{*1}_{ij}(R) = \begin{cases} \Psi_{ij}(R) & R < \sigma_{ij} \\ \Phi^1_{ij}(R_{ij}) & \sigma_{ij} < R < R_{ij}(\tilde{R}_{12}) \\ \Phi^1_{ij}(R) & R > R_{ij} \end{cases} \qquad (14)$$

The $\Psi_{ij}(R)$ are found numerically by expanding in a series of basis functions. In particular, the optimized potentials are expressed as

$$\Psi_{ij}(R) = \Phi^1_{ij}(R_{ij}) + \sum_{n=1}^{6} c^{(n)}_{ij}(R - \sigma_{ij})^n \qquad (15)$$

As $F^{\mathrm{RPA}}[\Phi^1_{ij}]$ is a positive definite functional of the Φ^1_{ij}, the solution of (12) corresponds to the absolute minimum in the 18-parameter space defined by (15) (by symmetry we have $c_{12} = c_{21}$). Combining (3), (7) and the solution of (12), we find for the pair correlation functions

$$h_{ij}(R) = h_{\sigma_{ij}}(R) + B_{\sigma_{ij}}(R) + h^1_{ij}(R) \qquad (16)$$

The solution of (12) defines the optimized potentials (14)—the interactions of the physical system however are still given by $\Phi_{ij}(R)$. Therefore, we are forced to define a new repulsive potential $\tilde{\Phi}^0_{ij}(R)$, solve the WCA again and we find a new set of effective hard-core diameters $\tilde{\sigma}_{ij}$. This has then to be used in the ORPA calculation. Clearly the whole procedure has to be repeated until a *self-consistent* separation of the total interatomic potential into a repulsive (short-range) part and an optimized long-range part has been achieved.[19] In the following we discuss the application of this scheme to K-Rb and K-Cs alloys.

3 THE STRUCTURE OF LIQUID K-Rb ALLOYS

The interatomic potentials used in this work are based on the pseudopotential formalism (empty-core model potentials[20] and the Ichimaru-Utsumi form of the screening function[21]) already used for the pure liquid alkali metals.[5] The K-Rb system has been selected for this study, because we expect it to be very close to an ideal-mixing behaviour, the ratio of the atomic radii being $R_{Rb}/R_K \sim 1.06$. Indeed we find for all compositions $\sigma_{12} \approx (\sigma_{11} + \sigma_{22})/2$, according to the criterion introduced above the pair potentials of the K-Rb system are "additive". In Figure 2 we study the partial structure factors of a $K_{50}Rb_{50}$ alloy at $T = 473$ K in the HS, WCA and ORPA approximations, Figure 3 shows the total neutron weighted structure factor. As for the pure alkali

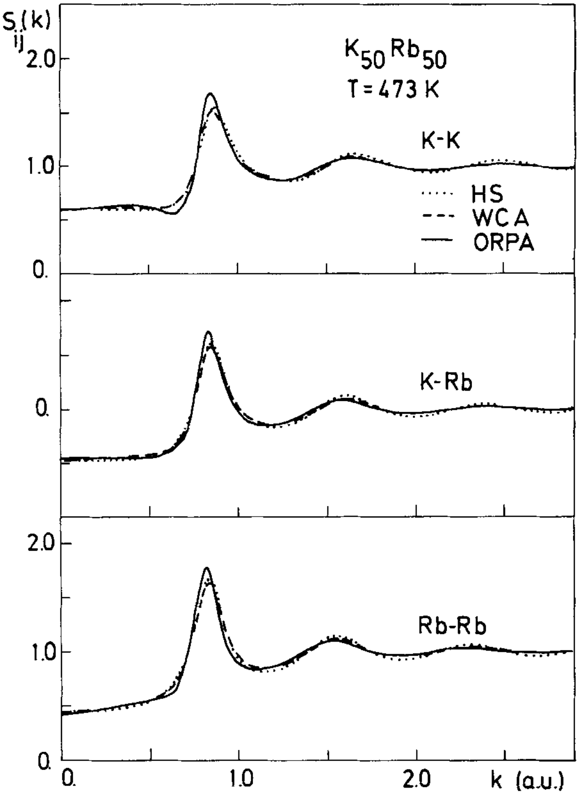

Figure 2 The partial static structure factors $S_{ij}(k)$ for a $K_{50}Rb_{50}$ alloy, evaluated in the hard-sphere, WCA-, and ORPA approximations.

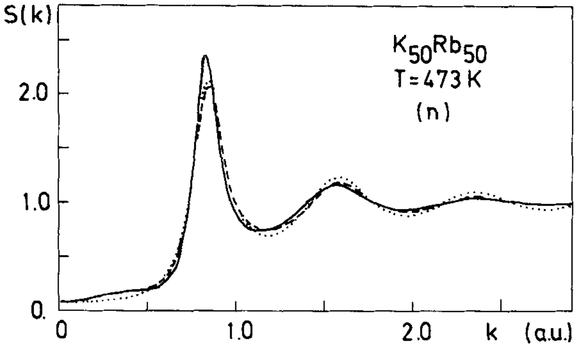

Figure 3 The neutron-weighted total static structure factor $S(k)$ for $K_{50}Rb_{50}$, calculated in the hard-sphere, WCA- and ORPA approximations.

metals we find that the WCA-corrections for the softness of the short-range repulsions damp the large-k oscillations of the structure factor, the inclusion of the medium- and long-range interactions in the ORPA provide a further damping, a slight shift of the maxima to smaller momentum transfers and a quite pronounced increase of the main peak. For the pure metals we have found that all this tends to improve the agreement with both computer-simulation and diffraction data. For the alloy no data for comparison are available, but we think that we can again conclude that the combined WCA + ORPA procedure yields a good description of the structure of liquid K-Rb alloys.

4 THE STRUCTURE OF LIQUID K-Cs ALLOYS

The ratio of the atomic radii of K and Cs is $R_{Cs}/R_K \simeq 1.15$, so we expect slight deviations from an ideal mixing behaviour. The K-Cs system has been studied extensively using X-ray and neutron diffraction.[22] In Figure 4 we compare the calculated X-ray weighted static structure factors for some selected alloys with experiment, Figure 5 presents a similar comparison with the neutron data.

In general we find that the inclusion of the "softness" corrections and of the medium- and long-range forces in the ORPA substantially improves the agreement with experiment. The oscillatory forces produce a sharpening of the main peak, and a dampening and a phase shift of the oscillations at larger momentum transfers. In the ORPA we

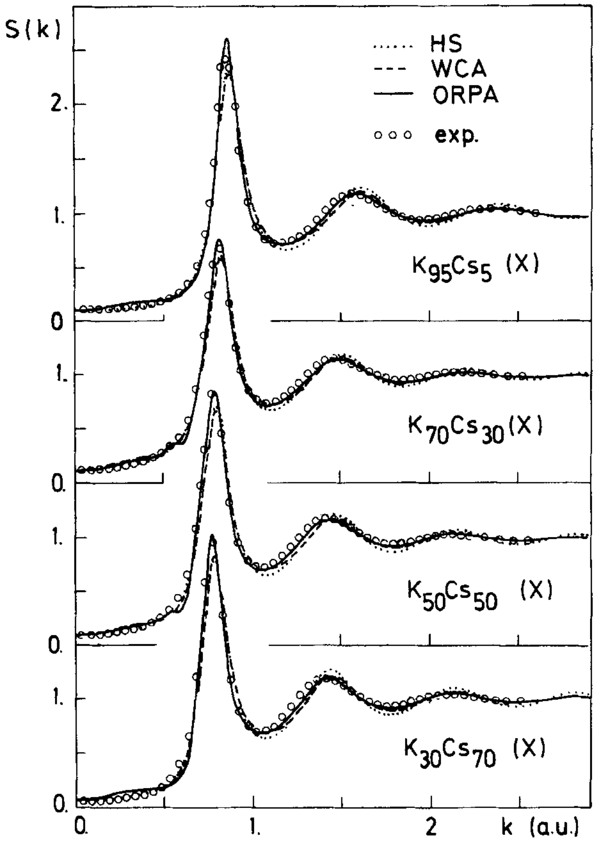

Figure 4 The X-ray weighted total static structure factors $S(k)$ for $K_{1-c}Cs_c$ alloys ($c = 0.05$, 0.30, 0.50 and 0.70), calculated in the hard-sphere, WCA- and ORPA approximations at $T = 373$ K. The open circles mark the experimental results of Alblas *et al.*[22]

obtain now a really good agreement with experiment, except for minor disagreements:

i) At the left side of the second peak, a small phase difference subsists even in the ORPA. The same discrepancy also appears in the pure metals, in thermodynamic perturbation calculation as well as in computer-simulation studies based on the same class of interatomic potentials (see the discussion in[5]), it represents most likely a short-coming of the linear screening approach to the calculation of the interatomic potentials.

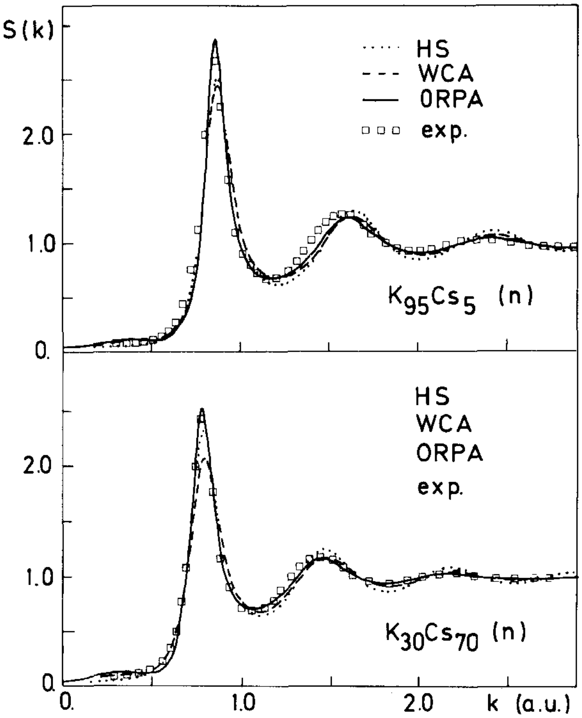

Figure 5 The neutron-weighted total static structure factors of $K_{95}Cs_5$ and $K_{30}Cs_{70}$ alloys at $T = 373$ K, evaluated in the hard-sphere, WCA- and ORPA approximations. The open squares mark the experimental results of Alblas *et al.*[22]

ii) A broad hump appears in $S(k)$ at small wave numbers ($q \simeq 0.3$ Å^{-1}). This is a well-known artefact of the WCA-expansion[5,14] and could in principle be eliminated by using the Jacobs-Andersen[23] partial resummation of higher order terms (but remember that this resummation has only a low-q validity[24]).

iii) In the X-ray structure factors of $K_{70}Cs_{30}$ and $K_{50}Cs_{50}$ alloys we observe a small irregularity near $q \simeq 0.6$ Å^{-1}, which does not appear in the neutron structure factor.

If we look at the partial static structure factors, we find a pronounced irregularity in the Faber-Ziman structure factors; in the Bhatia-Thornton structure factors it appears only in the concentration-fluctuation part $S_{cc}(q)$ (see Figures 6 and 7). This singularity is not related to the rather restricted basis set used in the variational calculation (see Eq. (15)), it appears already in the RPA before the optimization—even in a much more pronounced form (see Figure 6). The wiggle

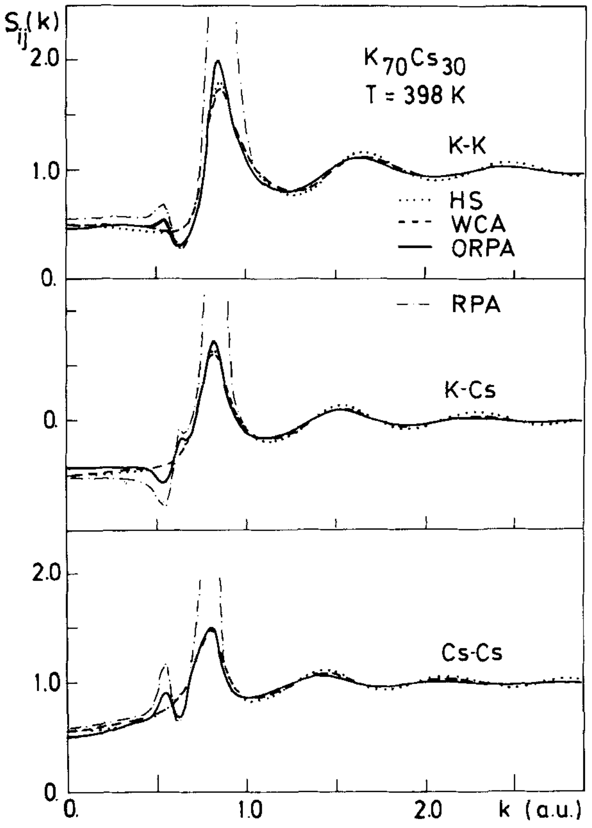

Figure 6(a) The partial Faber-Ziman static structure factors $S_{ij}(k)$ (i,j = K, Cs) for a $K_{70}Cs_{30}$ alloy at $T = 398$ K, calculated in the hard-sphere, WCA-, RPA, and ORPA approximations.

in the $S_{ij}(k)$ disappears if we return to the standard separation of the $\Phi_{ij}(r)$ (all three positions are separated at the position of the minima). In that case, however, the long-wave length form of the WCA-partial structure factors becomes unrealistic as discussed in [15]. Preliminary results indicate that the irregularity is even larger in Na-Cs alloys, due to the larger size-difference. Thus we conclude that we have not yet completely solved the problem of modelling the structure of a binary mixture with non-additive pair interactions, starting from an additive hard-sphere mixture. In our method the potentials are separated in such a way that only the $\Phi^1_{ij}(R)$ part is nonadditive. This allows us to obtain realistic WCA-partial structure factors, but introduces an asymmetry between the like-atom and the unlike-atom pair interactions. In

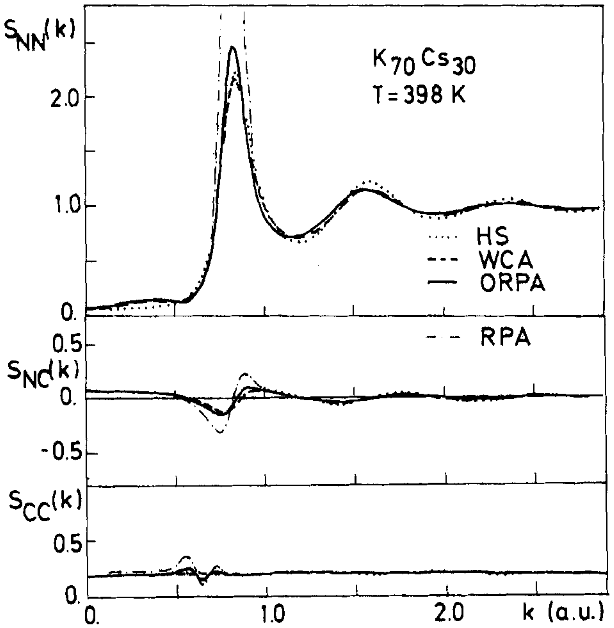

Figure 6(b) The Bhatia-Thornton static structure factors $S_{NN}(k)$, $S_{Nc}(k)$, and $S_{cc}(k)$ for a K_{70} Cs_{30} alloy at $T = 398$ K, calculated in the hard-sphere, WCA-, RPA and ORPA approximations.

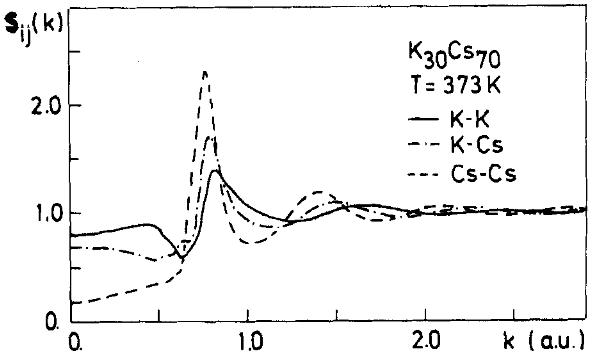

Figure 7 The partial Faber-Ziman static structure factors $S_{ij}(k)$ for a $K_{30}Cs_{70}$ alloy, calculated in the ORPA.

the random-phase approximation, this asymmetry produces a large singularity in the Faber–Ziman structure factors. The optimization procedure reduces the singularity, but cannot eliminate it completely.

5 CONCLUSIONS

We have presented the first optimized random-phase calculations for liquid binary alloys, with an application to K-Rb and K-Cs alloys. Even for these simplest alloys, the calculations show a marked improvement over binary hard-sphere models and calculations with soft repulsive forces, resulting in a very satisfactory agreement with the available diffraction data. For larger size differences, a weak singularity in the partial Faber–Ziman structure factors appears to the left of the main peak. This irregularity is a consequence of the non-additivity of the interatomic potentials.

Thus we conclude that the ORPA appears to be a very promising method for describing liquid binary alloys with a size ratio close to unity (this is confirmed by an investigation on Al-Ge alloys to be presented in a companion paper), but care must be exercised when dealing with larger size-factors.

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