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Integral-equation approach to the structure of liquid binary alkali-metal alloys

Gerhard Kahl
Institut für Theoretische Physik, Technische Universitat Wien, Wiedner Hauptstrasse 8 - 10, A-1040 Wien, Austria
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We present a comprehensive study of the structure of liquid binary alkali-metal alloys using integral-equation techniques. As in the one-component case we find that the soft-mean-spherical approximation is definitively superior to the hypernetted-chain approximation for such potentials, having a harshly repulsive short-ranged part and an oscillating long-ranged part. We find very good agreement with other liquid-state theories (perturbative methods and computer experiments) and good agreement with experimental scattering data, the differences being due to the simple model potential used (Ashcroft empty-core potential). By truncating the interactions at increasing distances (until recovering the full potential), we reveal the strong influence of the long-ranged parts of the interaction on the structure. We finally present an attempt to include thermodynamic self-consistency, being for the case of liquid metals a delicate problem that—for the moment—may not be solved exactly.

I. INTRODUCTION

Among the usual techniques used to determine the structure and thermodynamics of liquid systems, the integral-equation methods have been rediscovered during the last few years. They are defined by the Ornstein-Zernike (OZ) relation, together with a nonlinear closure relation, relating the potential and the structure functions in a functional way. Such standard or "conventional" closures are the hypernetted chain (HNC), the Percus-Yevick (PY), or soft-mean-spherical approximation (SMSA) (see Ref. 1 for an overview). The revival of these methods is due to two facts: one is the development of two powerful and efficient algorithms[2,3] for solving nonlinear integral equations (in the binary case we have to solve a set of three coupled equations); the other reason is the reintroduction of the old idea of interpolating closure relations.[4,5] Such an interpolation enables us to eliminate the old problem of thermodynamic inconsistency, i.e., the discrepancy occurring in general between different equations of state (EOS's) when using approximative liquid-state theories. This inconsistency may also be encountered – as a consequence of the approximations made in the derivation of their closure relations – at the conventional integral equations. The parametrized (or interpolated) integral equations are characterized by closure relations which are – by means of one or more parameters – functional interpolations between two conventional closure relations. The parameter(s) is (are) then chosen in such a way to force thermodynamic self-consistency (TSC) (see below). Among these integral equations, the modified HNC (MHNC) (Refs. 6–8) and the HMSA (Ref. 9) (being an "interpolation" of HNC and SMSA) represent in the one-component case powerful liquid-state techniques. Both of them have proven in applications to a great variety of liquid one-component systems[10–12] their reliability. Comparing the results with other liquid state methods (perturbation theories and computer experiments) we obtain very good agreement, i.e., results within the uncertainty of present-day computer simulations; however, the integral equations have nowadays the advantage of being much less time consuming than other methods. MHNC and HMSA are therefore well-established and reliable liquid-state theories.

Proceeding to the binary case, we are restricted – at least for the moment– to the HMSA, the MHNC being ruled out due to technical reasons (discussed in detail in Sec. II). Studies on model potentials (Lennard-Jones, soft spheres[9] and Morse potentials featuring an H-H_2 mixture[13]) show extremely good agreement with computer experiments even under high-pressure and/or high-temperature conditions.

Our main interest is focused on realistic systems, such as metal alloys, salts and metal–molten-salt solutions. Their potentials differ from those of model systems in two important aspects: their interactions are long ranged (Friedel oscillations) and explicitly density dependent (which shall cause some additional troubles, discussed below). What concerns salts and metal–molten-salt solutions a number of applications have been done.[14–16] For liquid metals there exists – to the best of our knowledge – only one study, in which $\mathrm{Li}_{61}\mathrm{Na}_{39}$ – a separating system – was treated within the HNC framework.[17] Although the authors obtain qualitative agreement, this choice seems to us to be somewhat problematic. Due to a further characteristic deficiency of conventional integral equations, one closure relation may be applied successfully only for a certain class of potentials. HNC is known to be a very reliable method for Coulombic potentials but not for metallic systems (as we shall demonstrate in Sec. III). Besides that treating a system near the phase separation is always a delicate task.

The aim of this contribution is therefore to demon-

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strate that integral-equation approaches may also be applied successfully to determine the structure of liquid binary alloys. As a testing system we have chosen the K-Cs alloy (i) being one of the rare binary systems which have been investigated experimentally in detail[18] and (ii) which allows us (as an alloy of alkali metals) at least to *try* to include TSC (cf. Sec. III D). We compare the SMSA and the HNC with other liquid-state theories (perturbation theories and computer experiments) as well as with experiment. As in the one-component case we find very good agreement with other liquid-state theories and good agreement with experiment. The differences in the latter case may largely be attributed to the simple prescription of how to construct the potentials: we use an Ashcroft empty-core pseudopotential[19] and Ichimaru-Utsumi's[20] expression for the exchange-correlation corrections. We confirm that the HNC yields unsatisfactory results for such a system.

We have then investigated the influence of the long-range parts of the potential on the structure and find for distances as large as 52 a.u. that their influence is not negligible. We finally present an *attempt* to include TSC. If we want to treat this problem exactly we have to be aware of two facts: (i) as noted above, the interactions used in metallic systems are explicitly density dependent, therefore the pressure EOS contains – compared to the model-potential case – additional terms; (ii) if we want to be exact up to second order in the pseudopotential in the compressibility EOS we would have to take into account three- and four-body correlation functions, especially the latter ones being practically unknown. Taking into account only the first aspect and neglecting the second one is neither correct nor satisfactory. We therefore propose to proceed as in the model-potential case[9,10,13] (and as we also did in the one-component case[11,12] obtaining satisfactory results). We think that this is the most honest compromise to tackle the problem in a *first* approximation and want to point out explicitly that this is just an *attempt* and may only be regarded as a first step towards a fully TSC treatment. Here, after having constructed the potentials we neglect the density dependence of the potential, i.e., we create exactly the same situation as in a computer experiment, where the atoms are *not* influenced by the density fluctuations either. From the electronic point of view such an approximation may be justified – among the metals – only for the alkali metals, where the neglected contributions are the smallest[21] ($\simeq 5\%$).

This paper is organized as follows. In Sec. II we provide the reader with the necessary theoretical tools; Sec. III first presents a comparison of the different integral-equation results (SMSA, HNC) with perturbation theory, which is followed by a comparison of the SMSA data with experimental neutron- and x-ray-scattering results. In Sec. III C we make a systematic investigation of the influence of the long-range parts of the potential on the structure and finally present in Sec. III D our attempt to include at least partly TSC. The paper is concluded by a summary.

II. THEORETICAL TOOLS

A. Conventional integral equations

Integral equations are based on the OZ relation, which reads for the N-component case

$$h_{ij}(r) = c_{ij}(r) + \sum_k c_k n \int h_{ik}(\mathbf{r}')c_{kj}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' , \qquad i,j,k = 1,\dots,N. \tag{1}$$

The $h_{ij}(r)$ and the $c_{ij}(r)$ are the total and the direct correlation functions, c_k is the concentration of the kth component, and n is the number density of the system. To make these $N(N+1)/2$ equations with $N(N+1)$ unknown functions $h_{ij}(r)$ and $c_{ij}(r)$ solvable, we have to add $N(N+1)/2$ closure relations, relating in a functional way for each pair i, j the pair potentials $\Phi_{ij}(r)$ with the $c_{ij}(r)$ and $h_{ij}(r)$:

$$F(\Phi_{ij}, h_{ij}, c_{ij}) = 0. \tag{2}$$

These relations are simplifications of diagrammatic developments[1] of the exact statistical-mechanics expressions of the pair-correlation functions $g_{ij}(r) = h_{ij}(r) + 1$. As examples of such (conventional) closure relations (2) we present here the expressions of the HNC and the SMSA; for an overview we refer the reader again to Ref. 1:

$$g_{ij}(r) = \begin{cases} \exp[-\beta\Phi_{ij}(r) + h_{ij}(r) - c_{ij}(r)] \ \ (\text{HNC}), & (3) \\ \exp[-\beta\Phi_{1,ij}(r)][1 + h_{ij}(r) - c_{ij}(r) - \beta\Phi_{2,ij}(r)] \ \ (\text{SMSA}) & (4) \end{cases}$$

where the $\Phi_{1,ij}(r)$ and $\Phi_{2,ij}(r)$ are the repulsive and attractive parts of the potentials $\Phi_{ij}(r)$ in the sense of Weeks, Chandler, and Andersen[22] (WCA) and $\beta = 1/k_BT$. Provided by one of the closure relations (2), the OZ relation (1) may be solved numerically by an iterative algorithm.[2,3]

Liquid-state theories, based on a closure relation such as (2) normally have two deficiencies. (i) If we calculate one thermodynamic quantity (e.g., the isothermal compressibility χ_T) by means of different EOS's (compressibility, pressure, or energy route) we shall obtain different results, unless we do not have an *exact* liquid-state theory. Since we have to make some approximations in the derivation of the closure relations (2) the integral-equation methods are not exact theories. Consequently the EOS's are no longer consistent, i.e., the methods are thermodynamically inconsistent. This lack is inherent not only to the integral equations but to all liquid-state theories except for the computer simulations. (ii) Each of these closure relations have – due to information that was neglected in their derivation – some weak points depending on the potential of the system: without going into details (we refer the reader to Ref. 1), HNC, e.g., turns out to be a very reliable method for Coulombic systems, whereas for strongly repulsive potentials with long-range parts (as liquid metals) PY or SMSA should preferentially be used.

The revival of the integral-equation technique during the last years is mainly due to the development of two very efficient algorithms for solving nonlinear integral equations[2,3] (reducing the number of iterations necessary for solutions drastically) and the rediscovery of the old idea of "interpolating" between two "conventional" closure relations.[4,5]

We use in our study a powerful implementation of Gillan's algorithm,[2,23] which concerns the numerical solution, to solve the coupled integral equations (1); for details of the method we refer the reader to Ref. 2. In q and r space we use a grid of 512 points ($\Delta r/a = 0.05$, where a is the Wigner-Seitz radius), Fourier transforms are performed by the fast Fourier technique.

B. Parametrized integral equations

A lot of possible formulations exist for the parametrized integral equations (see again Ref. 1 for an overview). In our studies on pure metals[11,12] we have used two of them, the MHNC (Refs. 6–8) and the HMSA (Ref. 9), whose closures are given by

$$g_{ij}(r) = \exp[-\beta\Phi_{ij}(r) + h_{ij}(r) - c_{ij}(r) + B_{ij}(r)] \quad \text{(MHNC)}, \tag{5}$$

$$g_{ij}(r) = \exp[-\beta\Phi_{1,ij}(r)]\left(1 + \frac{\exp\{[h_{ij}(r) - c_{ij}(r) - \beta\Phi_{2,ij}(r)]f_{ij}(r,\alpha_{ij})\} - 1}{f_{ij}(r,\alpha_{ij})}\right) \quad \text{(HMSA)}. \tag{6}$$

The functions $B_{ij}(r)$ in the closure relation (5) of the MHNC are the so-called bridge function. If we could calculate them exactly, (5) would represent an exact closure relation; however, these functions are extremely complicated to be evaluated. Using the "universality argument" of Rosenfeld and Ashcroft[7] (which was substantiated recently[24]) the true $B_{ij}(r)$ may be replaced for an application of the MHNC in a good approximation by those of a suitably chosen hard-sphere (HS) system, $B_{ij}^{\rm HS}(r)$. The diameters have to be adjusted to force consistency between the EOS's. The functions $B_{ij}^{\rm HS}(r)$ may be determined analytically (i.e., within a reasonable amount of computing time) only for the case of an *additive* hard-sphere system (taking profit of the analytic solution of the PY equation[25]), but not for a general system; this, however may represent – what concerns the potentials of realistic systems – a drastic restriction:[13,26] most of the realistic systems are nonadditive (sometimes to a rather strong degree), which is also reflected in the structure functions. Several attempts have been made to circumvent these difficulties, trying to use the analytic expressions of the one- and two-component HS case, but none of them are completely satisfactory solutions[14,27] and leave the application of the MHNC to binary systems somewhat problematic. Thus we are limited – for the moment, until further progress is done – to the HMSA, giving results as good as those of the MHNC for the one-component case.[11,12]

The functions $f_{ij}(r,\alpha_{ij})$ in (6) are called mixing (or crossover[28]) functions. They depend both on the distance r and the parameters α_{ij} and trigger the degree of contributions of the two conventional integral equations (in this case SMSA and HNC). A typical choice is

$$f_{ij}(r,\alpha_{ij}) = 1 - \exp(-\alpha_{ij} r), \tag{7}$$

where the α_{ij} are restricted to positive values. In the limits $\alpha_{ij} \to \infty$ and $\alpha_{ij} \to 0$ we recover the conventional closure relations (3) and (4). Here we shall determine the α_{ij} by forcing agreement of the pressure and compressibility EOS's. The compressibility in the long-wavelength approach (LW) $\chi_T^{\rm LW}$ reads for a binary case and constant-volume condition:[9]

$$(nk_BT\chi_T^{\rm LW})^{-1} = 1 - \sum_{i,j} c_i c_j n \hat{c}_{ij}(0), \tag{8}$$

where the caret denotes the Fourier transform. On the other hand, in the homogeneous-deformation approach (HD) the pressure P and $\chi_T^{\rm HD}$ are related via

$$P = nk_BT - \sum_{i,j} \frac{c_i c_j}{2} n^2 \int g_{ij}(r) \frac{r}{3} \frac{d\Phi_{ij}(r)}{dr} d\mathbf{r}, \tag{9}$$

$$\left(\frac{\partial n}{\partial P}\right)_{V,T} = n\chi_T^{HD}. \tag{10}$$

Since in our case there is only one consistency requirement to match [equality of (8) and (10)] we put $\alpha_{ij} = \alpha$ for all i and j. A rescaling (following Bernu *et al.*[29]) is necessary only for strongly nonadditive systems.[13]

C. The potentials

For the potentials $\Phi_{ij}(r)$ we proceed as in our former studies on the same system [perturbative approach using the Weeks-Chandler-Andersen (WCA) approximation[22] for the repulsive parts of the potentials and the optimized random-phase approximation[30] (ORPA) for the attractive parts of the potentials[31,32]]. Each system investigated is characterized by its density n (or equivalently its atomic volume Ω; for the alloy we use a linear interpolation of the Ω values of the pure metals), temperature T, and concentration c_i, which are taken from experimental studies.[18,33] Again we use local Ashcroft empty-core potentials[19] (we take exactly as in the ORPA approach the following values for the core radii r_c: r_{K}=1.2012 Å, r_{Cs}=1.4393 Å), assuming that the r_c's remain unchanged on alloying. For the local-field correction $G(q)$ we take Ichimaru-Utsumi's expression;[20] the density dependence is expressed via the density parameter r_s which reads for our series of alloys

$$r_s = \left(3\frac{\Omega}{4\pi}\right)^{1/3}. \tag{11}$$

a (the Wigner-Seitz radius mentioned above) is defined as the quantity r_s in atomic units. For brevity we do not reproduce here the formulas for how to calculate the effective interactions $\Phi_{ij}(r)$ since they are well known by now. We refer the reader to Ref. 32 for an extensive discussion.

We point out that we used in our former study on liquid potassium[12] a slightly different value for r_{K}, which was adjusted to neutron-scattering data just above the melting point; anyway we have found out that the small difference (2%) between the two values has only minor influence on the results. Here we rather stick to the r_c values given above to enable an exact comparison with our former WCA-ORPA results.

Finally we would like to note that eventual disagreement of theoretical and experimental results might be due to the following simplifications made in the construction of the interactions of the systems: (i) the use of a simple local pseudopotential, (ii) the choice of $G(q)$ (which is nowadays anyway the most reliable expression available), and (iii) the linear concentration dependence of Ω.

III. RESULTS

We performed SMSA and HNC calculations for the ten different systems, which were investigated in detail in an experimental study[18] at a temperature of 373 K; the input parameters for each system are compiled in Table I together with the values for χ_T, calculated in the two different approaches using the pressure and the virial EOS's. Figure 1 depicts these values demonstrating the degree of thermodynamic inconsistency of the integral-equation approaches: it is rather large for HNC and quite small for the SMSA. Table I also contains for the sake of completeness the data of the pure metals.

A. Comparison of different liquid-state theories

We present results for the partial structure factors $S_{ij}(q)$ which are obtained from the $g_{ij}(r)$ via the well-known expressions

$$S_{ij}(q) = \delta_{ij} + \sqrt{c_i c_j}\, n \int [g_{ij}(r) - 1] \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}. \tag{12}$$

We compare in a first step results obtained from the WCA-ORPA (using a nonadditive hard-sphere reference system[26]) and those obtained from the integral-equation approaches: the agreement, as demonstrated in Fig. 2, where we have depicted SMSA and WCA-ORPA, is good. This agreement is more astonishing since both the concept as well as the mathematical tools used by those two liquid-state methods are completely different. Not only do the positions of the maxima and the minima coincide, but also the low-q behavior agreement is surprisingly good. Even small details, such as the shoulder in the main-peak of $S_{22}(q)$ for c = 0.7 are reproduced exactly (for a detailed discussion of this shoulder, cf. Sec. III C). Differences in the region of about 0.3 a.u. are due to the well-known "spurious hump," an artifact of the WCA approach.

We now turn to a comparison of the different integral-equation approaches (SMSA and HNC). As may be seen from Fig. 3 where we compare these two methods the well-known deficiencies of the HNC for this kind of po-

TABLE I. Density-input data for the series $\mathrm{K}_c\mathrm{Cs}_{1-c}$ at a temperature of 373 K. Ω is the atomic volume [obtained by linear interpolation between the Ω-values of the pure metals (Ref. 33)] and a is the Wigner-Seitz radius. The χ_{T}'s are the respective values of the compressibility, calculated via the LW or the HD route, within the HMSA and HNC.

$c = c_{\mathrm{K}}$	Ω (a.u.)	a (a.u.)	$\chi_{T,\mathrm{HD}}^{\mathrm{HNC}}$	$\chi_{T,\mathrm{LW}}^{\mathrm{HNC}}$	$\chi_{T,\mathrm{HD}}^{\mathrm{SMSA}}$	$\chi_{T,\mathrm{LW}}^{\mathrm{SMSA}}$
0.00	829.236	3.083 87	0.0349	0.1011	0.0389	0.0443
0.20	770.390	3.009 27	0.0348	0.1049	0.0387	0.0457
0.29	743.909	2.974 93	0.0350	0.1064	0.0389	0.0461
0.30	740.967	2.970 45	0.0350	0.1065	0.0389	0.0462
0.40	711.544	2.930 60	0.0352	0.1078	0.0392	0.0469
0.50	682.121	2.889 64	0.0353	0.1085	0.0394	0.0466
0.60	652.697	2.847 47	0.0353	0.1083	0.0396	0.0473
0.70	623.274	2.804 02	0.0352	0.1070	0.0396	0.0471
0.80	593.851	2.759 19	0.0349	0.1046	0.0394	0.0462
0.875	571.784	2.724 58	0.0345	0.1020	0.0390	0.0454
0.95	549.717	2.689 07	0.0340	0.0988	0.0384	0.0441
1.0	535.005	2.676 58	0.0357	0.1040	0.0408	0.0469

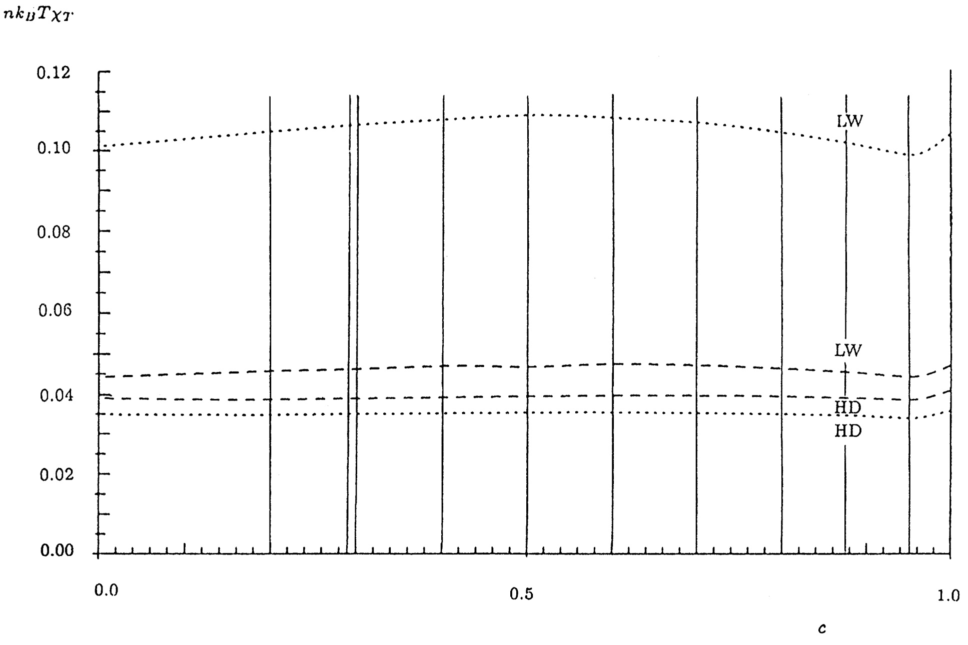

FIG. 1. Dimensionless isothermal compressibility ($nk_BT\chi_T$) of K_cCs_{1-c} as a function of concentration c at a temperature T=373 K. Symbols: dotted curves represent HNC, broken lines SMSA results. LW and HD denote the different EOS's (see text), vertical lines represent the systems investigated.

tential are demonstrated: an overestimation of the compressibility (see also Fig. 1) as we shall also see in comparison with experiment (Sec. III B), a strong dampening of the peaks and a large phase shift of the oscillations are observed. An additional repulsive potential, as it is represented by the "bridge functions" within the MHNC framework would be able to correct for this (see our results for the one-component case[11,12]). But as noted already above there is little chance at the moment for a possible application of the MHNC for binary systems.

We have also made computer simulation calculations for K-Cs systems on which we shall report in Sec. III D.

B. Comparison with experimental results

Since we have seen that the comparison of SMSA results with WCA-ORPA data is very satisfactory and since we know in turn that good agreement between perturbation theory and experiment holds,[26,31] it would be redundant to show the integral-equation results together with the experimental data for the complete concentration series. We have picked out three concentrations and display the results in Fig. 4. Of course, all discussions about the comparison between integral equations and WCA-ORPA for the $S_{ij}(q)$ also hold for the composite structure factor, defined as

$$S(q) = \frac{1}{< f^2 >} \sum_{i,j} \sqrt{c_i c_j} f_i(q) f_j(q) S_{ij}(q), \qquad (13)$$

where the $f_i(q)$ are the atomic scattering factors and $< f^2 >= c_1 f_1^2(q) + c_2 f_2^2(q)$; we just note that within the integral-equation approach the spurious hump (produced by the WCA) of course does not exist and that the height of the main peak is somewhat reduced. The phase shift between experiment and *all* liquid state theories used still remains. When using potentials constructed in this way, we find the same problems using any of the reliable liquid-state theories (WCA-ORPA, TSC integral equations, or computer simulations). It is by now well established that it is due to the simplifications made in the construction of the potential, i.e., the simple Ashcroft empty-core potential[19] and the local-field corrections.[20]

C. The influence of the long-range part of the potentials on the pair structure

Looking at Fig. 2 we remark on the rising part of the main peak of the partial structure factor $S_{22}(q) = S_{\mathrm{CsCs}}(q)$, a shoulder, especially pronounced for the concentration $c = 0.7$. This phenomenon is most pronounced in the intermediate concentration range but may be observed to a weaker extent for all concentrations: both for Cs-rich alloys (where this shoulder is largely covered by the rising part of the large main peak) and for K-rich alloys [where $S_{22}(q)$ is – due to the dilution – near unity]. $c = 0.7$ seems to us to be a good system to make a closer investigation into this effect. First, Figs. 2 and 3 confirm that this effect is *not* an artifact of the integral-equation method, since it occurs (with remarkable accuracy) for the WCA-ORPA (a little bit less pronounced) as well as for the SMSA and HNC. Assuming that this effect may be caused by the long-ranged attractive forces we proceed as follows. We take the potential $\Phi_{22}(r)$ [having found out that the long-ranged parts of $\Phi_{11}(r)$ and $\Phi_{12}(r)$ have no influence on this effect] and mark the minima and maxima at positions r_L (cf. Fig. 5 and Table II). We then construct a series of potentials $\bar{\Phi}_{22,L}(r)$, defined as

$$\bar{\Phi}_{22,L}(r) = \begin{cases} \Phi_{22}(r), & r \leq r_L \\ \Phi_{22} \exp[-\xi(r - r_L)], & r > r_L, \end{cases} \tag{14}$$

thus erasing the long-range forces beyond r_L. For ξ we have taken the value 10, guaranteeing a sufficiently rapid decay. We then solve the SMSA for each system defined by $\{\Phi_{11}(r), \bar{\Phi}_{22,L}(r), \Phi_{12}(r)\}$ for different L values.

The effect of this procedure on $S_{11}(q)$ and $S_{12}(q)$ is negligible from $L = 3$ onwards (except for small differences in the low-q behavior) and is no longer observable for $L \geq 4$ [cf. Figs. 6(a) and 6(d)]. The same holds for the pair-correlation functions $g_{11}(r)$ and $g_{12}(r)$: for $L > 4$ ($r_4 \simeq 25$) a slight phase shift may be observed only for $r > 52$ a.u. (i.e. five times the nearest-neighbor distance). Note that the distance of the onset of the differences is

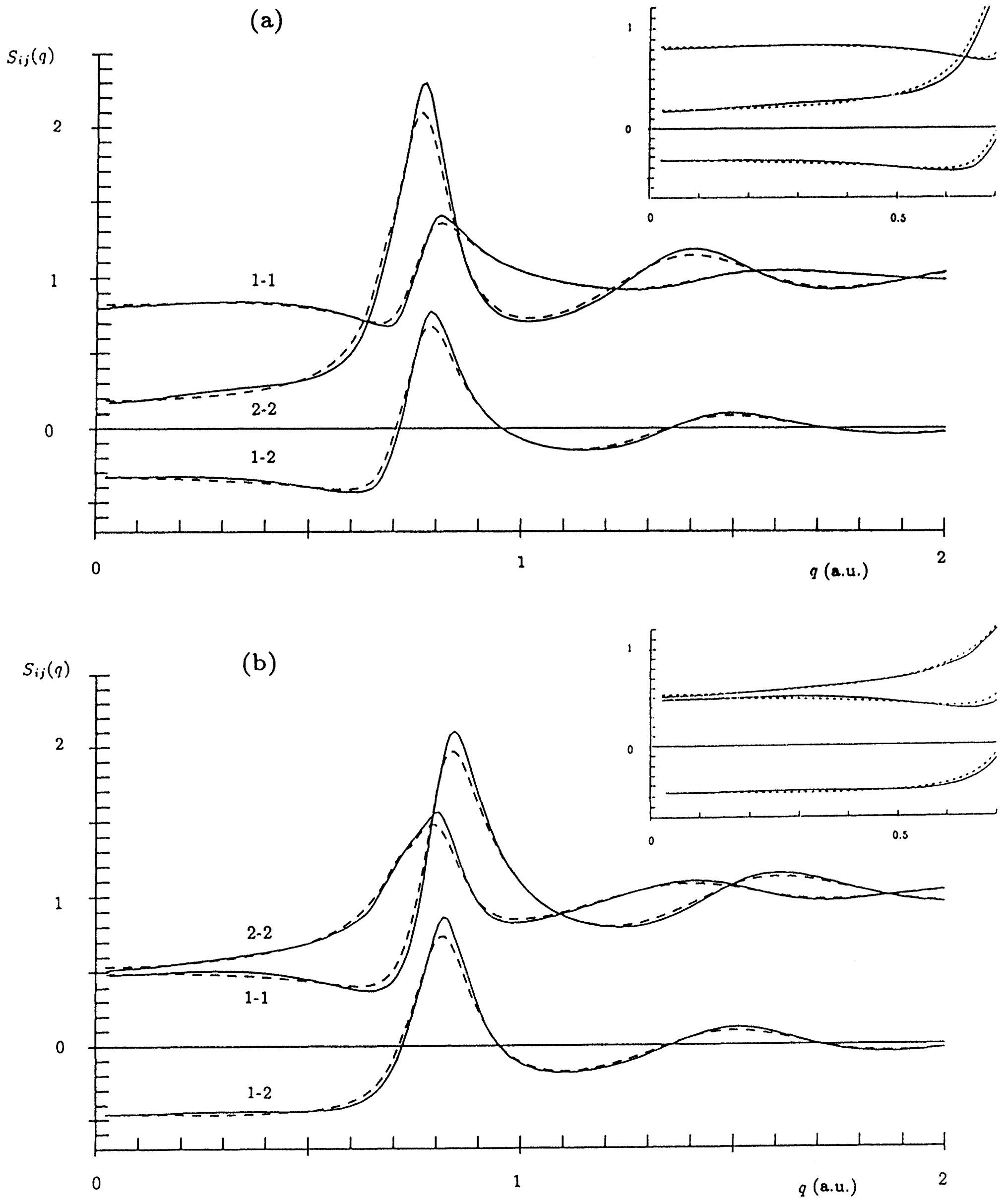

FIG. 2. Partial structure factors $S_{ij}(q)$ of K_cCs_{1-c} as a function of q at a temperature T=373 K for two different concentrations (a) c=0.30 and (b) c=0.70 . Solid lines represent ORPA results from Ref. 26, the dashed curves are SMSA results. The inset shows the low-q behavior.

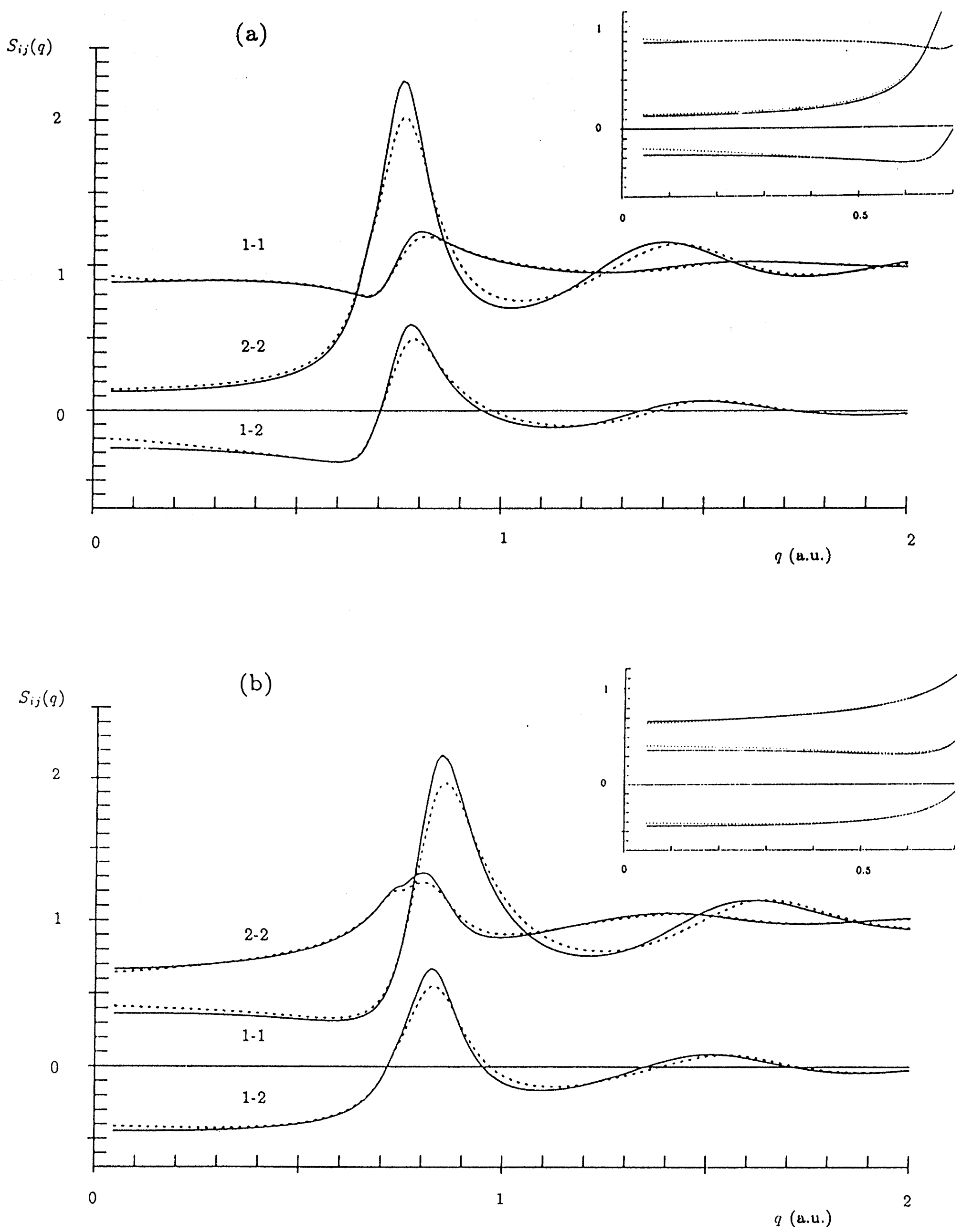

FIG. 3. Partial structure factors $S_{ij}(q)$ of K_cCs_{1-c} as a function of q at a temperature T=373 K for two different concentrations (a) c=0.20 and (b) c=0.80 . Solid lines represent SMSA results, the dotted lines HNC results. The inset shows the low-q behavior.

TABLE II. r_L values from whereon the potential $\Phi_{22}(r)$ is dampened in order to study long-range effects of the interaction on the structure [cf. text and (14)].

L	2	3	4	5	6	8	10	15
r_L (a.u.)	15.102	20.136	24.905	29.674	33.914	42.922	51.665	73.391

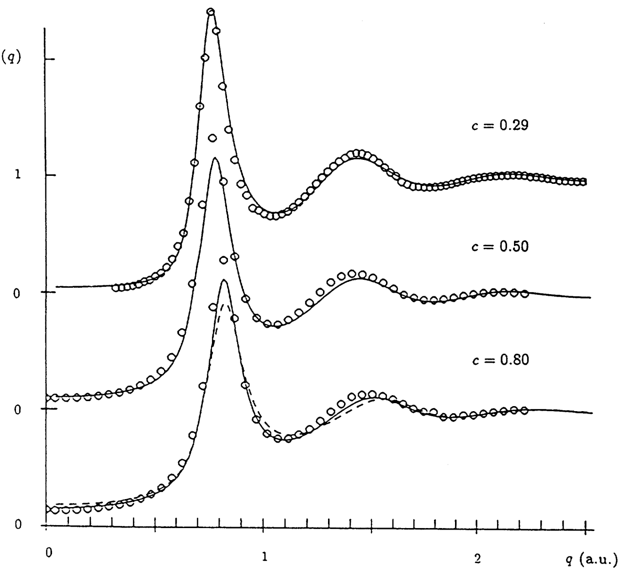

FIG. 4. Composite structure factor $S(q)$ [Eq. (13)] of K_cCs_{1-c} as a function of q at a temperature of 373 K. Symbols represent experimental scattering data of Ref. 18 (c=0.5 and 0.8, x rays; c=0.29, neutrons); curves represent theoretical results: solid lines are SMSA results, whereas the HNC data are represented by the dashed curve (only for one concentration).

more than twice the distance r_4 (from whereon the potential is modified). (Since the effects are rather minor and the panels for the pair-correlation functions require a lot of space we do not present these results in a separate figure.)

For the 2-2 component the situation is different: $S_{22}(q)$ has a symmetric main peak up to $L = 6$, then the shoulder observed for the full system starts to form slowly; for $L = 10$ differences between the full potential and $\bar{\Phi}_{22,10}(r)$ are negligible and only for $L = 15$ ($r_L \simeq 73$ a.u.) do we obtain the same result as for the full potential [cf. Fig. 6(b)]. What concerns $g_{22}(r)$ is that r_L triggers directly the influence of $\bar{\Phi}_{22,L}(r)$ on $g_{22}(r)$ for $r > r_L$, i.e., we obtain nearly perfect agreement between the pair-correlation functions of $\Phi_{22}(r)$ and of $\bar{\Phi}_{22,L}(r)$ for $r < r_L$, whereas remarkable differences are observed beyond this distance (cf. Fig. 7).

Obviously the long-ranged parts of the potential $\Phi_{22}(r)$ force the larger Cs atoms in a distorted structure. The asymmetric peak – interpreted as the superposition of two symmetric ones – points towards two preferred nearest-neighbor distances, the ratio of which is $\simeq 1.1$, independent of the concentration. Only when these long-ranged parts of the interactions are truncated by means of the above-mentioned method these atoms may be arranged in a completely relaxed structure, resulting in a symmetric peak ($L \leq 5$). The effect becomes more striking as the concentration of the Cs atoms becomes smaller: then the choice for these few atoms where to be placed is more restricted than in the case where they represent the majority component: in this case they can arrange themselves more easily according to their potential, the effect is less pronounced but does not vanish completely.

The integral equations are an ideal means to study this effect (we extend all integrations up to $\simeq 75$ a.u.): they are the fastest methods among the usual liquid-state theories and enable us to manipulate the input-potential deliberately and obtain results within a reasonable amount of computing time. Although it would be very interesting to study this effect by means of computer simulations, we doubt if we could obtain – using the usual ensemble size of about 2000 particles – reasonable results by this method since the parts of those potentials which cause this effect would be outside the simulation box.

D. An attempt to include thermodynamic self-consistency

We now present an *attempt* towards inclusion of TSC. If we treat metallic systems we must not forget that the potentials are – in contrast to model potentials – explicitly density dependent, bringing along the following consequences:

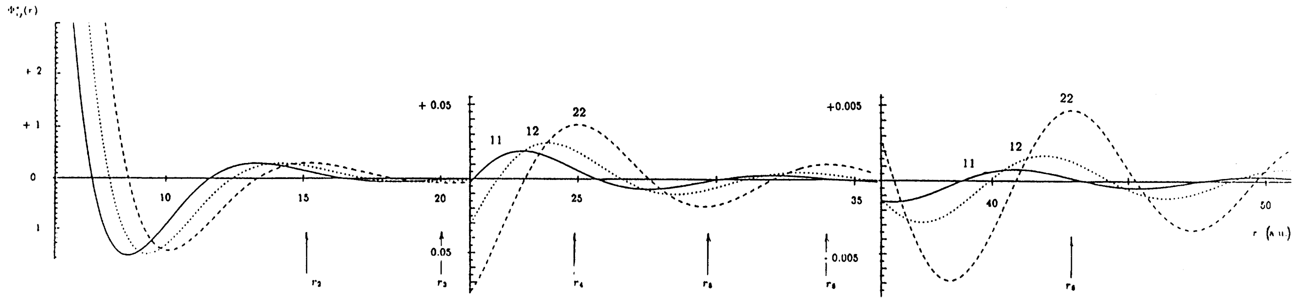

FIG. 5. Reduced interatomic potentials $\Phi^*_{ij}(r) = \beta\Phi_{ij}(r)$ for $K_{70}Cs_{30}$ (1-1, solid line; 1-2, dotted line; and 2-2 dashed line). The vertical arrows indicate the positions r_L from where the long-range parts of the interaction $\Phi_{22}(r)$ are dampened (cf. text and Table II).

(i) Switching to the one-component case, the expression for the pressure (9) has to be replaced by

$$P = nk_BT - \frac{n^2}{6}\int g(r)\frac{r}{3}\frac{\partial\Phi(r)}{\partial r}d\mathbf{r} + \frac{n^2}{2}\int g(r)n\frac{\partial\Phi(r)}{\partial n}d\mathbf{r} -\frac{1}{6}nr_s\frac{\partial}{\partial r_s}\Phi_{\rm BS}(r=0) - n\frac{r_s}{3}\frac{\partial E_{\rm EG}}{\partial r_s}. \qquad (15)$$

The last three terms in (15) are new compared to (9) and have to be taken into account for the HD route when calculating the isothermal compressibility [via (10)]. $\Phi_{\rm BS}$ is the band-structure energy and we refer the reader for its explicit form to Ref. 32; $E_{\rm EG}$ contains the contribution of the electron gas, and its explicit form depends on the local-field correction $G(q)$.

(ii) To obtain TSC between pressure and compressibility EOS's by including terms up to second order in pseudopotential we need three- and four-particle correlation functions. Only for the three-particle correlation

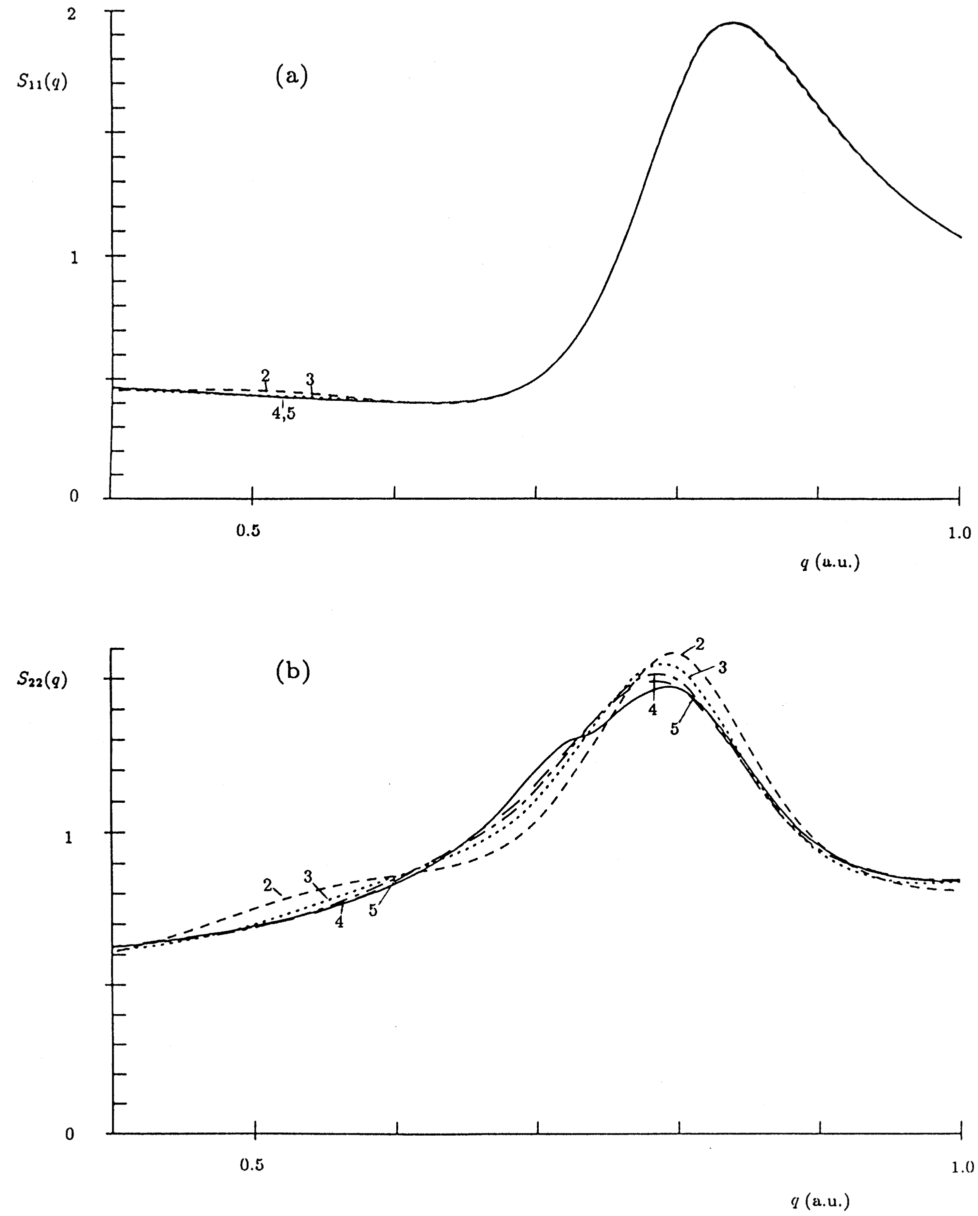

FIG. 6. Partial structure factors for the $K_{70}Cs_{30}$ alloy, using the potential $\bar{\Phi}_{22,L}(r)$. (a) and (d) are the results for $S_{11}(q)$ and $S_{12}(q)$; the solid line represents results using the full potential $\Phi_{22}(r)$, other symbols for results obtained by using $\bar{\Phi}_{22,L}(r)$: - - - -, L=2; ······, L=3; – · –, L=4; – – –, L=5. (b) and (c) are the results for $S_{22}(q)$; for the symbols for panel (b) see (a); for panel (c) - - - -, L=6; ······, L=8; – · –, L=10; and – – –, L=15.

functions are suitable theories known;^{34} about the four-particle function we know practically nothing.

Since the exact treatment of the problem is not possible, differences (in addition to those caused by the thermodynamic inconsistency) between the two EOS's will occur, which will be called a lack of electronic inconsistency (EOS).

Since we think it is neither correct nor physically sound to treat (i) exactly but neglect the consequences of (ii), we propose the following approach (that results in a separation of TSC and ESC): we use also for the metal case the pressure formulation of Eq. (9), thus neglecting the density dependence of the interactions once they are constructed. We are well aware that this assumption is a crude approximation, yet the situation is not so bad as it might seem: in fact we create the same situation which we encounter in computer experiments. Also there the atoms see – when getting moved according to their equations of motion – the same potential, despite the fact that it should vary according to the local particle density. Once the potential has been constructed (using the average particle density) it remains the same for the whole run and for every particle. Consequently computer experiments are TSC but not ESC. And this situation is the same if we neglect for the integral-equation approach in the TSC requirement the explicit density dependence.

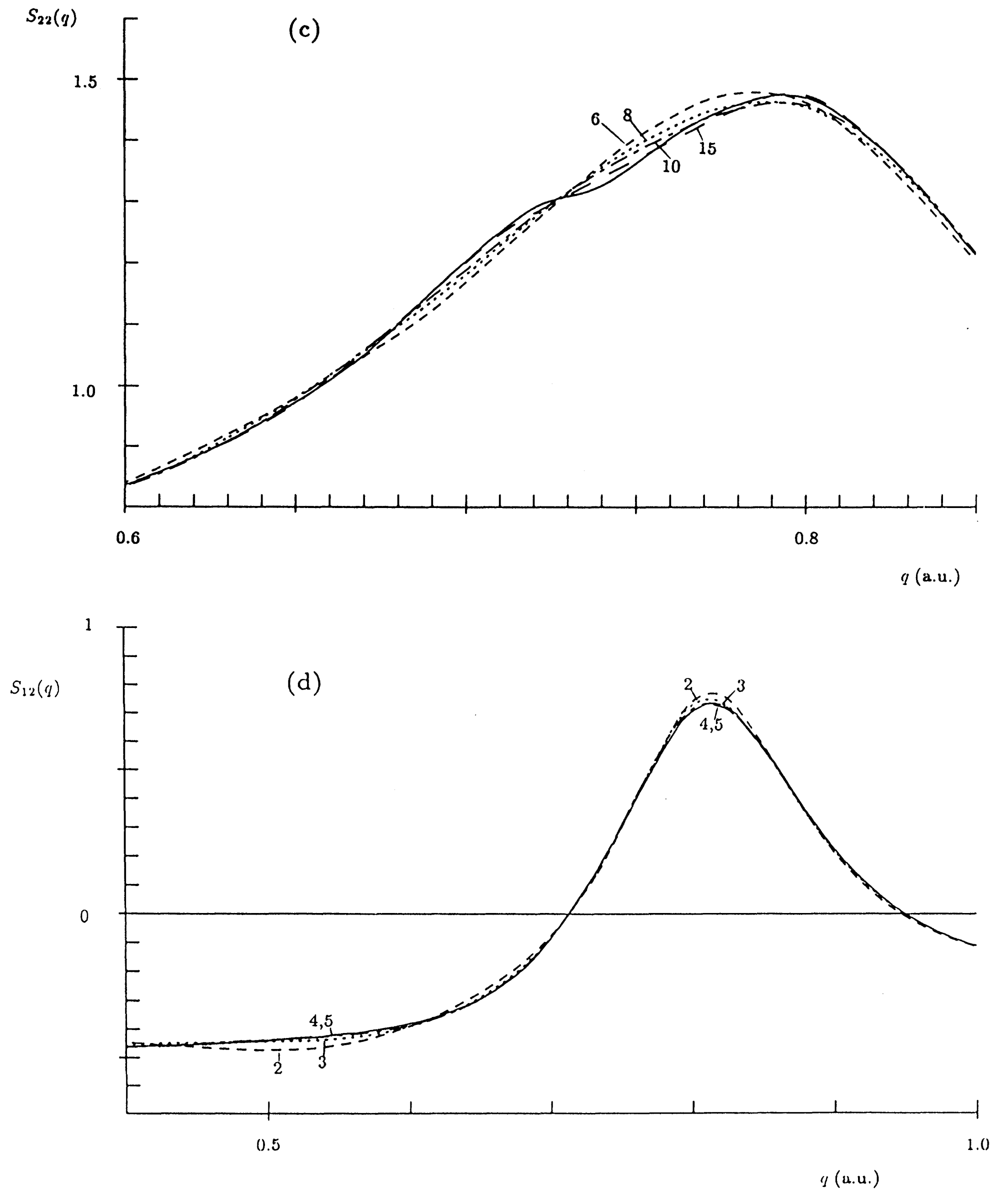

FIG. 6. (*Continued*).

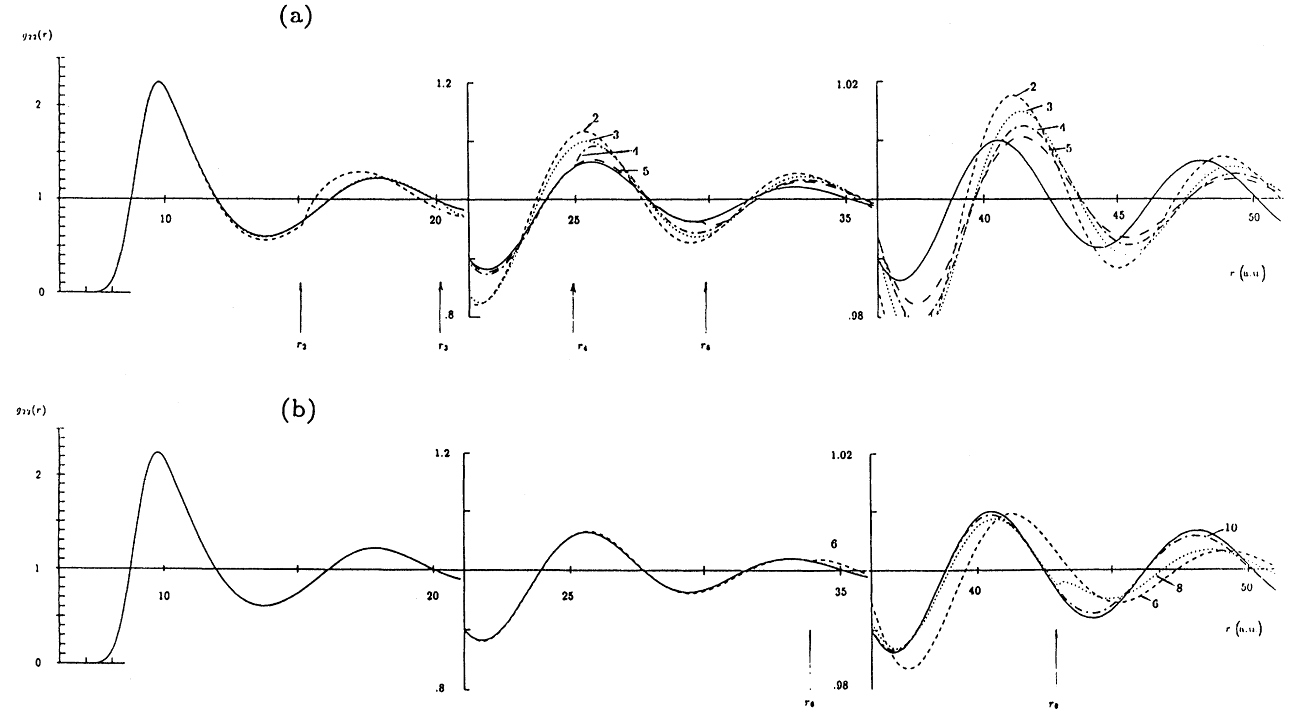

FIG. 7. Pair-correlation function $g_{22}(r)$ for the $K_{70}Cs_{30}$ alloy, using the potential $\bar{\Phi}_{22,L}(r)$. In terms of the symbols, 7(a) corresponds to 6(b) and 7(b) corresponds to 6(c). The vertical arrows indicate the positions r_L (cf. Fig. 5 and Table II). Note the different vertical scales.

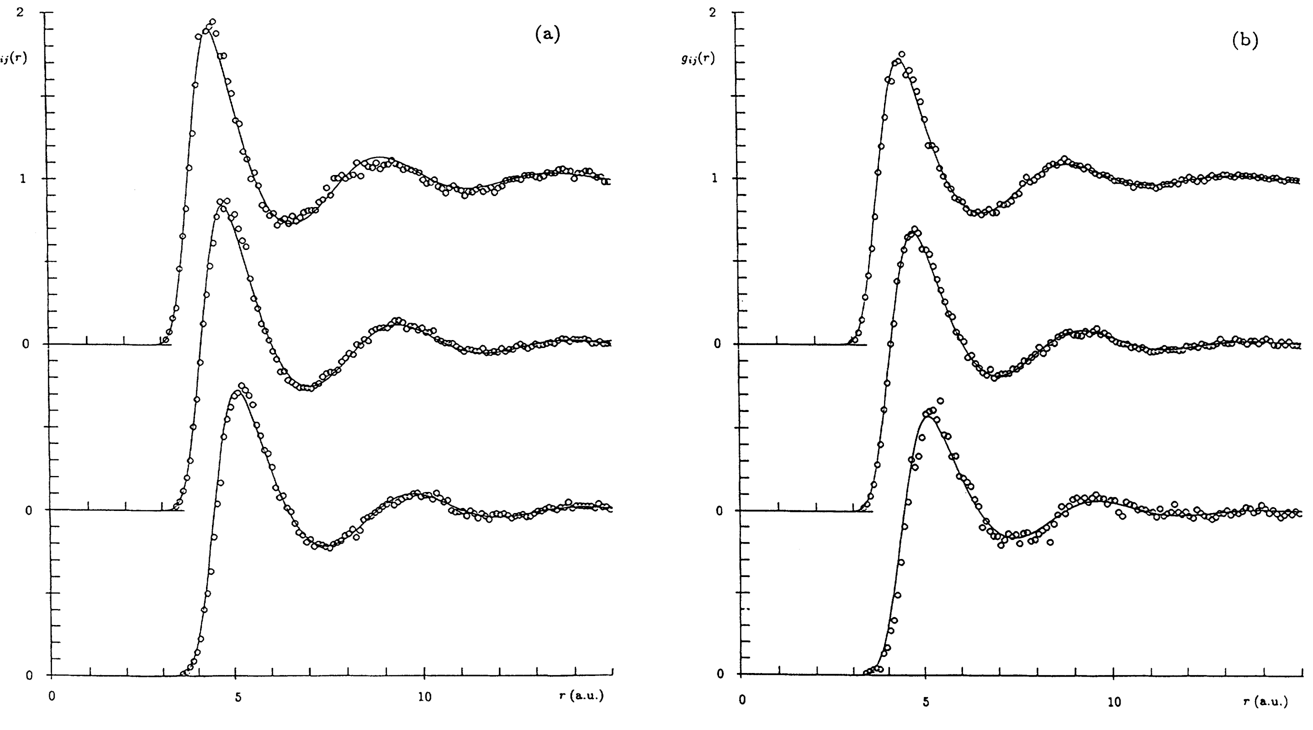

FIG. 8. Comparison of the pair-correlation functions $g_{11}(r)$, $g_{12}(r)$, and $g_{22}(r)$ (from top to bottom) for systems (a) A and (b) B (for parameters cf. Table III): solid line, HMSA; symbols, computer simulation.

TABLE III. Potential parameters for the systems A and B. See also caption of Table I.

System	$c = c_K$	Ω (a.u.)	a (a.u.)	T (K)	αa	$\chi_{T,\mathrm{HD}}^{\mathrm{HNC}}$	$\chi_{T,\mathrm{LW}}^{\mathrm{HNC}}$	$\chi_{T,\mathrm{HD}}^{\mathrm{SMSA}}$	$\chi_{T,\mathrm{LW}}^{\mathrm{SMSA}}$	χ_T^{HMSA}
A	0.4	948.703	3.060 23	773	0.05	0.2041	0.1077	0.1315	0.1249	0.1291
B	0.7	759.074	2.994 46	973	0.15	0.1548	0.2502	0.1899	0.1699	0.1846

This assumption has also lead to very satisfactory results in the one-component case.[11,12]

From the electronic point of view it may be shown that the neglected terms may contribute – depending on the metal – up to 30%. However these contributions amount up to only 5% for the pure alkali metals (which we assume to hold also for their alloys) which also justifies this attempt.

The most sound comparison of these TSC methods is of course against computer simulations. Looking at the compressibility values of Table I we see, that in the α range of $[0, \infty]$ (corresponding to [HMSA, HNC]) no intersection of the virial and the compressibility EOS's as a function of α is possible (a similar phenomenon was also observed in the one-component case for systems near the melting point.[11,12]) We have therefore constructed two additional systems (denoted by A and B) at higher temperatures, for which TSC could be obtained. The density input data were taken from experiment,[33] their parameters are compiled together with the thermodynamic results in Table III. However no experimental scattering data are available for these two systems. Computer experiments were performed on a 1372-particle system, using toroidal boundary conditions and a time increment of $\delta t = 2 \times 10^{-15}$ s.[35] Typical runs took about 2–3000 steps for melting and equilibration and about as many for production. Pair-correlation functions are based on averages over about 40 independent configurations.

Agreement with computer experiments (Fig. 8) is excellent, demonstrating very clearly that the different groups of liquid-state theories have nowadays achieved the same level of numerical accuracy.

Concluding we want to point out that this subsection should rather be regarded as a first attempt to include TSC in metallic systems. We also think that this way of approximation is more acceptable than treating self-consistency in a hybrid way, i.e., including all terms in the pressure EOS (15) but not in the compressibility EOS.

IV. CONCLUSIONS

In this paper we have presented an integral-equation (SMSA and HNC) approach to the structure of liquid binary metallic (alkali-metal) systems. The potentials show – in contrast to simple model potentials – the well-known long-ranged oscillations which turn out to have an important influence on the structure. We have tested our results against experimental scattering results for the series $\mathrm{K}_c\mathrm{Cs}_{1-c}$ and find that agreement for the SMSA is very good, except for the usual phase shift of the second peak in the total structure factor. This discrepancy always occurs (independent of the liquid-state theory) in both the one- and the two-component case; it may be attributed to the simplifications made in the construction of the potentials. We find that the HNC is not an appropriate liquid-state theory for metallic systems (having a harshly repulsive and a long-ranged oscillating potential). Comparing the results with the perturbative WCA-ORPA method, we obtain excellent agreement within numerical accuracy: all details of the structure functions are reproduced exactly. This demonstrates very impressively the fact that any of the three large groups of liquid-state theories (perturbative theories, integral-equation methods, and computer simulations) at their most sophisticated level show the same degree of reliability, despite the fact that they are based on completely different concepts. Studying the influence of the long-range parts of the interactions on the structure we find out that especially the long-range parts of the Cs-Cs interaction are extremely important for the forming of the structure. The Cs atoms are forced by the long-range forces into distorted structures with two preferred distances (with a ratio of about 1.1).

We have tried to implement TSC, separating ESC and TSC by creating a computer simulation situation, neglecting in a first approximation the density dependence of the potentials in the expressions of the EOS's. TSC was obtained by forcing agreement between pressure and compressibility EOS's. Agreement with computer simulations (where the atoms do not see the density dependence of the potentials either, once they are constructed) is very good. We can conclude that the HMSA is also for the case of realistic systems – as liquid metals – a reliable liquid-state theory.

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