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Inversion problem for dense classical liquids: The binary case

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A few years ago Levesque, Weis, and Reatto (LWR) [D. Levesque, J.-J. Weis, and L. Reatto, Phys. Rev. Lett. **54**, 451 (1985)] proposed an iterative procedure for the solution of the "inversion problem" of classical liquid state theory, i.e., the determination of an effective pair interaction from the pair structure. We present the generalization of this method to the binary case using in a first step computer simulation results instead of neutron-scattering data. We show that the LWR approach which is based on the modified hypernetted-chain approximation and on computer simulations also works successfully for two-component liquids even for rather high densities and nonadditive potentials. In order to guarantee a good accuracy of the simulation results and hence a satisfactory convergence of the procedure the number of particles of the minority component has to be sufficiently large for dilute systems.

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Although the first attempts to solve the so-called "inversion problem" of classical liquid state theory (by which we understand the determination of the pair interaction from the pair structure) date back to the 1960s and were proposed by Johnson *et al.* [1], it is only about ten years ago that one possible and satisfactory solution for this problem has been proposed by Levesque, Weis, and Reatto (LWR) [2, 3]. These authors have demonstrated that their algorithm is very reliable even near the triple point, i.e., in a region where the pair distribution function (PDF) $g(r)$ is known to be rather insensitive to the detailed shape of the (effective) two-body interaction $v(r)$. In a subsequent paper, Levesque and Weis and co-workers have applied their method to very accurate neutron-scattering results for the pair structure of liquid Ga [4]. Inversion schemes in the proper sense (i.e., without the usage of adjustable parameters) proposed earlier either fail in this region [5] or are not general enough to be applied to any liquid [6]. Furthermore, Dzugutov *et al.* [7] have used a different method to extract an effective pair potential from neutron-scattering data, which, however, should rather be referred to as a fitting procedure: they applied it to liquid Pb using a parametrized potential which is determined by fitting simulation results to the experimental data. However, up to now, none of the above mentioned methods has been generalized to the binary case.

The idea of the LWR method originally stems from an inversion scheme proposed by one of the authors to a related problem in the Jastrow theory of Bose quantum fluids [8]. The method is an iterative predictor-corrector algorithm: it starts from the pair structure [represented either by $g(r)$ or the static structure factor $S(q)$] which may be given, either from a *neutron-scattering* experiment, or—for testing reasons—from a *computer* experiment with a known potential; then a sequence of interatomic potentials $v^i(r)$ is constructed as follows: a trial pair interaction serves as a predictor; it is constructed—due to the lack of *exact* theories for the determination of the pair structure—by means of the modified hypernetted-chain (MHNC) relation [9], which is at present one of the most reliable liquid state methods. The subsequent corrector step is performed by means of a simulation which yields for this trial interaction the corresponding *exact* PDF. From the difference between this structure and the experimental structure an improved guess for the potential is constructed. This procedure is iterated until self-consistency between the trial and the initial pair structures is achieved. Convergence of this procedure turned out to be very fast [2, 3].

We present here the extension of an inversion procedure to the binary case and demonstrate that the generalization of the LWR procedure is in principle possible and that it yields reliable results also for two-component fluids. However, due to the increased number of parameters characterizing the binary system, the following problems may be foreseen: (i) if the concentration of the minority component is rather small, then the correlation functions of this component might not be accurate enough if the ensemble is not sufficiently large: statistical errors in the determination of the PDF will cause errors in the predicted potential which may accumulate over the iteration steps resulting in unrealistic and/or inaccurate results; (ii) realistic potentials as those of binary metal alloys sometimes show a rather pronounced degree of nonadditivity; a good convergence of the inversion scheme for highly nonadditive systems cannot be guaranteed *a priori*; (iii) finally, in the case of systems near the phase boundary, it may not be excluded that the sequence of potentials $v_{ij}^k(r)$ created during the procedure may "lead into" or "pass through" the phase-separation region.

The principal aim of this contribution is to demonstrate both accuracy and reliability of the procedure. We achieve this by producing "experimental" data in a computer experiment with a known interatomic potential and show that the proposed method is able to reproduce this set of interactions with good accuracy. To this end we proceeded as in the original papers [2, 3]: the experimental results for the pair structure stem from a computer experiment [molecular dynamics (MD)] for a given potential $v_{ij}^{\text{expt}}(r) = v_{ij}^0(r)$ and will be denoted by $g_{ij}^{\text{expt}}(r) = g_{ij}^0(r)$ $[S_{ij}^{\text{expt}}(q) = S_{ij}^0(q)]$. The systems we have chosen for this study are as follows.

TABLE I. Potential parameter ε_{ij}^* and σ_{ij} $(i,j=1,2)$ of the three LJ systems investigated (A, B, and C). ξ and α characterize the deviation of the potential parameters from the Lorentz-Berthelot rule (cf. text). c_1 is the concentration of species 1. The masses of atoms 1 (2) are those of Ar (Xe), i.e., 6.682×10^{-26} kg (2.180×10^{-25} kg), the mass density is for all systems 1874 kg m^{-3}. N is the number of particles in the MD simulation.

System	ε_{11}^*	ε_{12}^*	ε_{22}^*	ξ	σ_{11}/σ_{22}	σ_{12}/σ_{22}	α	c_1	N
A	0.4278	0.6278	0.8278	1.055	0.873	0.936	0	5/8	4000
B1	0.4278	0.6278	0.8278	1.055	0.873	0.936	0	1/10	4000
B2									6912
C	0.4278	0.7438	0.8278	1.250	0.873	0.880	−0.06	2/5	4000

(i) Lennard-Jones (LJ) mixtures with the known pair interaction

$$\beta v_{ij}^{\mathrm{expt}}(r) = \beta v_{ij}^{0}(r) = 4\varepsilon_{ij}^{*}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]. \qquad (1)$$

LJ potentials are characterized by the reduced energy parameters ε_{ij}^*, the distance parameters σ_{ij}, the concentrations c_i of species i, and a mass density ρ_m. The parameters of the LJ systems (denoted by A, B, and C) investigated are compiled in Table I. It also contains parameters ξ and α defined via $\varepsilon_{12}^* = \xi\sqrt{\varepsilon_{11}^*\varepsilon_{22}^*}$ and $\sigma_{12} = \frac{1}{2}(\sigma_{11}+\sigma_{22})(1+\alpha)$; they characterize the nonadditivity of a set of interactions $\mathbf{v}$ $[=\{v_{11}(r), v_{22}(r), v_{12}(r)\}]$, i.e., the deviation from the Lorentz-Berthelot rules ($\xi = 1$ and $\alpha = 0$).

(ii) A binary liquid metal alloy, which mimics $\mathrm{Cs_{70}K_{30}}$ at a temperature of 573 K and a mass density $\rho_m = 1488$ kg m^{-3} (for details cf. Ref. [10]). Potentials are given henceforward in thermal units, omitting for simplicity the usual asterisk.

Systems A, B1, and B2 are more or less additive mixtures; note that in system B the concentration of the minority component (species 1) is only 0.1. System C shows a rather strong nonadditivity, both with respect to the position and the depth of the minimum. The simulation of the corrector step of the procedure is a standard microcanonical MD simulation. We have considered in general 4000 particles; for system B2 additional calculations have been performed for a 6912-particle ensemble. The runs have been split up into two (A, B1, and C) or five (B2) independent runs, extending, on the whole, over 20 000 integration steps Δt ($= 5\times10^{-15}$ s); an energy conservation smaller than 0.1% over the entire run was required. The PDFs $g_{ij}(r)$ were determined in intervals of 20 Δt. Both the PDFs and the potentials $v_{ij}^k(r)$ were truncated

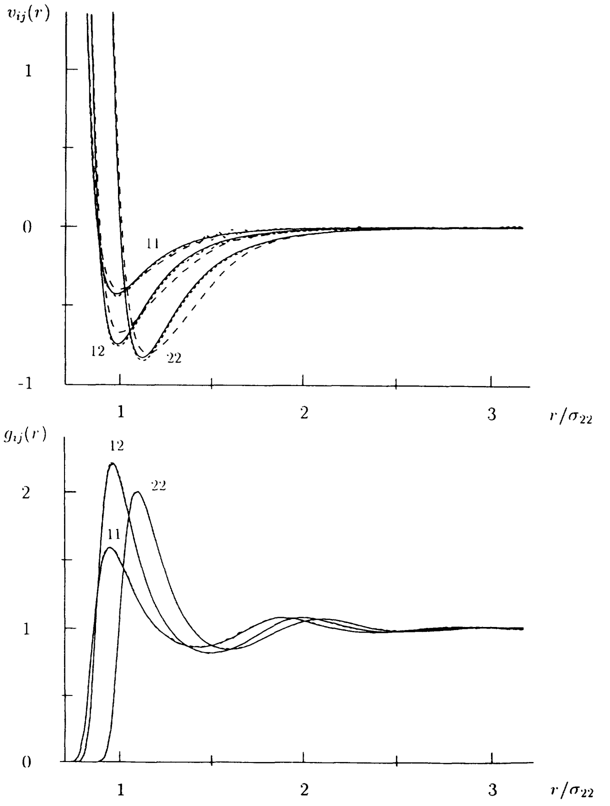

FIG. 1. Pair potentials $\mathbf{v}^k$ (top) and PDFs $g_{ij}^k(r)$ (bottom) for the nonadditive system C: comparison of the initial functions (k=0, full line) with the converged results (after k=12 iterations, dotted line); the broken line represent the first estimate (k=1) for the potentials.

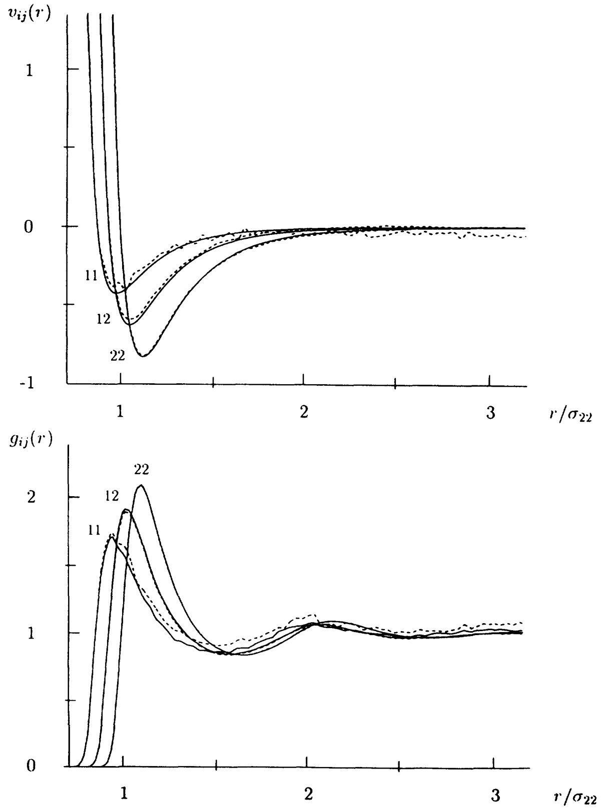

FIG. 2. Pair potentials $\mathbf{v}^k$ (top) and PDFs $g_{ij}^k(r)$ (bottom) for the (smaller) dilute system B1 (4000 particles): comparison of the initial functions (k=0, full line) with the results after k=12 iterations (dotted line).

at r_c (LJ: $r_c = 4\sigma_{22}$, liquid metals: $r_c = 18$ Å), "continuing" the PDFs beyond the cutoff radius via the usual Verlet prescription [11]

$$\begin{aligned} g_{ij}(r) &= g_{ij}^{\mathrm{sim}}(r)\ , \quad r < r_c \\ c_{ij}(r) &= -v_{ij}(r)\ , \quad r > r_c . \end{aligned} \tag{2}$$

The $c_{ij}(r)$ are the direct correlation functions, their Fourier transforms $\hat{c}_{ij}(q)$ are related via the well-known expressions with the partial structure factors $S_{ij}(q)$. Such an extension in r space is necessary to guarantee a sufficient accuracy of the Fourier transforms [from $g_{ij}(r)$ to $S_{ij}(q)$] and the determination of the $c_{ij}(r)$, which will be required in the recursive expression (see below).

The inversion scheme itself is based on the following formally exact relation:

$$g_{ij}(r) = \exp[-v_{ij}(r) + 1 + g_{ij}(r) - c_{ij}(r) + B_{ij}(r;\mathbf{v})]. \tag{3}$$

The bridge functions $B_{ij}(r;\mathbf{v})$—being far too complicated to be calculated—are replaced in the MHNC [9] by the bridge functions of a suitably chosen binary additive hard-sphere system [where they can be determined analytically within the Percus-Yevick (PY) approximation [12]]; this approach is justified by the "universality hypothesis" of Rosenfeld and Ashcroft [9].

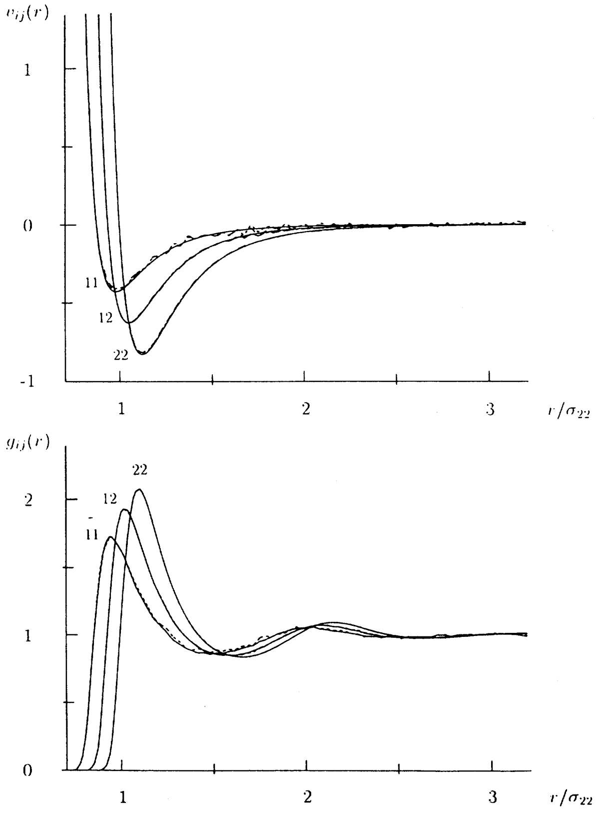

FIG. 3. Pair-potentials $\mathbf{v}^k$ (top) and PDFs $g_{ij}^k(r)$ (bottom) for the (larger) dilute system B2 (6912 particles): comparison of the initial functions (k=0, full line) with the converged results (after k=12 iterations, dotted line); the broken line (which coincides practically with the dotted line) marks the average over iterations 8 to 12 of the inversion procedure.

The iterative scheme starts from a set of trial potentials $\mathbf{v}^1$ which represents a first guess. The quality of this guess will of course have influence on the speed of convergence of the procedure. To investigate this influence we have constructed $\mathbf{v}^1$ from the $g_{ij}(r)$ via the PY relation (system A) or a generalized MHNC approximation using the Lado criterion [13] (systems B1, B2, and C). What now follows, i.e., the argumentation of how to construct the $\mathbf{v}^i$, is similar to the one-component case: a simulation for $\mathbf{v}^1$ yields a set of PDFs $g_{ij}^1(r)$, which—since $\mathbf{v}^1$ is only a predictor for $\mathbf{v}^0$—will of course differ from the $g_{ij}^{\mathrm{expt}}(r)$. Using the exact relation

$$v_{ij}^1(r) = 1 + g_{ij}^1(r) - c_{ij}^1(r) + B_{ij}(r;\mathbf{v}^1) - \ln[g_{ij}^1(r)] \tag{4}$$

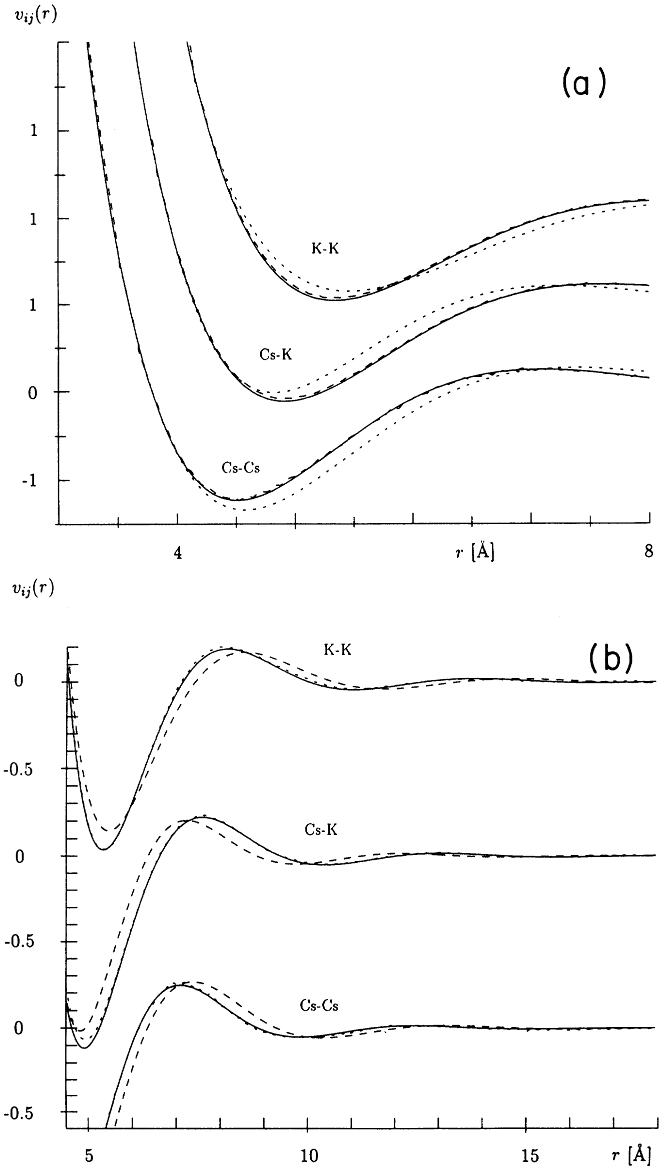

FIG. 4. Pair potentials $\mathbf{v}^k$ for the $\mathrm{Cs}_{70}\mathrm{K}_{30}$ alloy as labeled: (k=0)—full line, first guess; (k=1)—broken line; and converged result (k=8)—dotted line. (a) Region of the main minimum; (b) Friedel oscillations.

we can assume that the set of $B_{ij}(r;\mathbf{v}^1)$ represent rather good first approximations for the unknown $B_{ij}(r;\mathbf{v})$ in (3). Hence, replacing the $B_{ij}(r;\mathbf{v})$ in the exact relation (3) by their first estimates $B_{ij}(r;\mathbf{v}^1)$ yields an improved estimate $\mathbf{v}^2$ for the interaction $\mathbf{v}^0$, which we want to extract in this approach. Iterating this procedure, we obtain the recursive relation

$$v_{ij}^k(r) = v_{ij}^{k-1}(r) + \ln[g_{ij}^{k-1}(r)/g_{ij}^{\text{expt}}(r)] + c_{ij}^{k-1}(r) - c_{ij}^{\text{expt}}(r) - g_{ij}^{k-1}(r) + g_{ij}^{\text{expt}}(r), \qquad (5)$$

which is formally identical—except for the indices—with the expression of the one-component case. The $c_{ij}^k(r)$ are obtained from the simulation PDFs $g_{ij}^k(r)$ as mentioned above.

Our results may be summarized as follows: for systems A and C (with rather large minority concentrations) a fast convergence could be observed; after 12 iterations, a satisfactory agreement between the initial potentials $\mathbf{v}^0$ and $\mathbf{v}^{12}$ was found. Figure 1 shows the results for the potentials and the corresponding PDFs for system C (data for system A are of the same accuracy and are not displayed here). However, we found that an ensemble size of 4000 particles for the simulation step is absolutely necessary for a sufficiently high numerical accuracy. The situation is somewhat different for the dilute system B: a satisfactory convergence of the algorithm could only be obtained for the larger system B2 (6912 particles). For B1 (4000 particles), the statistical errors especially in $g_{11}^k(r)$ caused artificial wiggles in the pair interaction $v_{11}^{k+1}(r)$ of the subsequent iteration step; these artifacts accumulated in every iteration step so that after 12 iterations the results were by no means acceptable (see Fig. 2), while for system B2 a satisfactory convergence was obtained after 12 steps. Results for system B2 are displayed in Fig. 3: the statistical errors inherent to the simulation still cause small wiggles, which, however, have only minor influence on the resulting PDFs. We want to point out that no smoothing procedure whatsoever has been applied to the simulation data. A slight improvement of the results may again be obtained by averaging over several sets of potentials $\mathbf{v}^k$ as proposed by LWR [2].

We estimate that ~ 700 particles of the minority component are sufficient to guarantee a good accuracy and hence a satisfactory convergence of the algorithm; this is in agreement with LWR's results [2, 3] for the one-component case. The price for this accuracy requirement is, however, high: one simulation step for system B2 required a considerable amount of computing time even on a vector computer. Unfortunately, to the best of our knowledge, no experimental data for the full pair structure of binary rare gases (as a testing case for a binary LJ system) are available.

In Fig. 4 we display the results of the Cs-K alloy. Even though here the potentials are—measured in thermal units—stronger than in the LJ case, we obtain satisfactory convergence already after eight iteration steps, which proves the LWR scheme to be applicable to binary liquid metals, too. Note that also the characteristic Friedel oscillations are reproduced very accurately.

Concluding, we may say that the iterative inversion procedure proposed by LWR may be successfully generalized to binary systems (both in LJ and liquid metal systems): it works even for higher densities and for nonadditive interaction potentials. It is, however, much more "expensive" (regarding computer time) than in the one-component case, if we require the same degree of numerical accuracy. The only serious numerical problems occur for dilute systems: to guarantee a good accuracy at least ~ 700 particles of the minority component are required. Hence, for extremely dilute systems (concentrations less than ~ 0.05) the reliability of new numerical algorithms (as careful smoothing of the simulation data) has to be tested. These results along with more numerical details are planned to be published elsewhere.

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