Pair Interaction from Structural Data for Dense Classical Liquids

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We show that deduction of the pair interaction from structural data for simple liquids is feasible even under the triple-point condition. We use an iterative predictor-corrector method based on the modified hypernetted-chain equation and on simulation. We show that simulation can give enough accuracy to test inversion schemes.

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The determination of the interatomic interaction in the condensed phases of matter is of fundamental importance and this explains the attention that in the physics of liquids has been devoted to the so-called inverse problem, i.e., the deduction of the interatomic interaction starting from measured structural data as obtained from scattering experiments. It is believed that in a monatomic liquid, there is a one-to-one correspondence between the structure factor for density fluctuations $S(q)=\langle\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\rangle/N$, where $\rho_{\mathbf{q}}$ is the $\mathbf{q}$ component of the microscopic density fluctuation, and the pair interaction $v(r)$. If in the system many-body forces are present, as in general they are, this $v(r)$ has the role of an effective two-body interaction and it will be state dependent.

Starting with the pioneering work of Johnson, Hutchinson, and March,[1] this inverse problem has a long history but it is still in an inconclusive stage. The theoretical methods that have been used have not been seriously tested and widely different results have been obtained from the same data.[2] It has become evident that scattering data of very high precision, at least of order of 1% in absolute accuracy, are required over a wide range of momentum transfer q. It is clear that what is an asset[3] in the direct problem, i.e., the insensitivity in a dense fluid of the radial distribution function (rdf) $g(r)$ to the exact shape of $v(r)$, works against us in the inverse problem.

The simulation of model fluids is ideally suited to test whether a theory is adequate for this purpose: Using the rdf obtained from a simulation one should be able to recover the interaction used in that computation. However, since the simulation results are statistical in nature, this is a meaningful test only if the statistical noise of simulation is small enough. The purpose of this work is twofold. On one hand, we show that simulation results can give a rdf accurate enough to test theories. On the other hand, we show that an inversion scheme that has been proposed by one of us[4] and applied to a related problem in the Jastrow theory of Bose quantum fluids[5] is successful in the extraction of the pair interaction with good accuracy. This scheme is based on the modified hypernetted chain (MHNC) equation and on simulation. We find that methods[6,7] recently used are inadequate.

We have considered two model systems. The first is the Lennard-Jones (LJ) fluid, $v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, a prototype of a simple dielectric fluid under triple-point conditions $\rho\sigma^3=0.84$ and $k_BT/\epsilon=0.75$. The second is a model potential v_{Al} for aluminum.[8] Here we are not interested in the extent to which this model is realistic for Al, but it was chosen because v_{Al} is very different from the potentials of simple fluids; it has strong structure at short distance, followed by many small oscillations at larger distance (see Fig. 2 below).

For the LJ system we have performed three independent runs, one molecular-dynamics simulation of 6800 integration steps with a cutoff on $v(r)$, $r_c/\sigma=4$, and two molecular-dynamics simulations of 16 800 integration steps with $r_c/\sigma=2.5$. All our simulations are for 864-particle systems. The $g(r)$ provided by these runs have typical differences of 0.3% for $r/\sigma\sim 1$ becoming of order 0.01% at larger distances. When $g(r)$ is obtained by averaging over subsets of 1600 integration steps, fluctuations in $g(r)$ of order 1% are observed. The effect of these fluctuations of $g(r)$ in the inversion problem is studied by the MHNC equation.[9] This starts from the formally exact relation

$$\beta v(r)=g(r)-1-c(r)-\ln\{g(r)\}+E(r/v), \quad (1)$$

where $\beta=(k_BT)^{-1}$, c is the usual Ornstein-Zernike (OZ) direct-correlation function, and $E(r)$ is the so-called bridge function which is known only as an infinite series in a cluster expansion. The HNC approximation[3] consists in the statement $E(r)=0$, whereas the MHNC one[9] corresponds to writing $E(r)=E_{\mathrm{HS}}(r,\eta)$ where $E_{\mathrm{HS}}(r,\eta)$ is the bridge function of hard spheres at a suitable packing fraction $\eta=\pi\rho d^3/6$. Usually (1) is solved with respect to $g(r)$ for a given $v(r)$. However, if we know $g(r)$ of a certain system then (1) gives $\beta v(r)$ if we have a criterion for choosing η. This

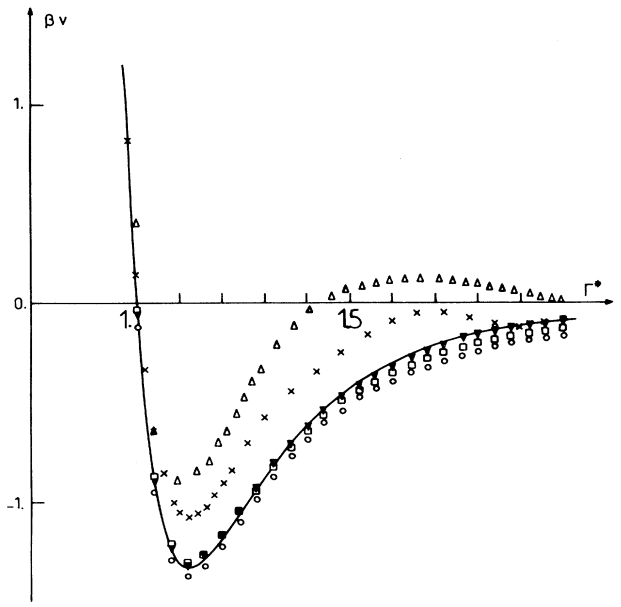

FIG. 1. Potentials from inversion procedure for the LJ system. Solid line, exact βv_{LJ}; open triangles, βv_{13} from Schommers's procedure; crosses, open circles, open squares, and solid triangles, βv_0, βv_5, βv_9, and average βv over iterations 8–12 of our inversion procedure ($r^* = r/\sigma$).

can be obtained by solving the equation

$$\int d^3r[g(r) - g_{\mathrm{HS}}(r,\eta)]\frac{\partial E_{\mathrm{HS}}(r,\eta)}{\partial d} = 0, \qquad (2)$$

where g_{HS} is the hard-sphere rdf. This condition[10] derives from an extremum condition for the free energy in the MHNC approximation. Both g_{HS} and E_{HS} are known quantities from simulation and parametrized forms are available from Verlet and Weis.[11] Then (1), (2), and the OZ relation form a closed set of equations which can be solved for $\beta v(r)$.[12] The $\beta v(r)$ extracted in this way from the simulation with a cutoff $r_c = 4\sigma$ is plotted in Fig. 1 where it is called $\beta v_0(r)$. It is clear that MHNC, which is considered to be one of the most accurate integral equations, is not adequate for the inversion procedure: The minimum of βv is underestimated by 30% and a spurious additional structure appears at larger distance. In spite of this result, the MHNC can be used to see how much the extracted βv is modified when rdf's coming from different simulation runs are used. Even if MHNC is approximate, these deviations should be essentially independent of this approximation. With use of the rdf of the three long runs, the extracted βv show deviations that at most are of order 0.02–0.04 and almost no change ($\ll 1\%$) in the position of the minimum of βv. These deviations increase by a factor of 3 if the shorter runs are used. Similar results are obtained for the Al model potential studied at density $\rho = 0.0527$ atom/Å^3 and $T = 1051$ K. v_{Al} is cut off at $r_c = 8.81$ Å (see Fig. 2). Thus, first, the potential obtained by MHNC reproduces only the main features of the exact $v(r)$, and, second, the rdf calculated from independent runs of 2000 integration steps [or 2000 moves/particle for Monte Carlo (MC) simulation], can be accurate enough to test theories for the inversion procedure. The uncertainties on the extracted βv from these rdf will be 0.04–0.08 and the positions of the extrema will be precisely obtained if an inversion procedure better than MHNC is used.

Other integral equations like Percus-Yevick and Born-Green (BG) are known to give very poor results,[2] as does a modified BG equation,[13] which includes the lowest-order correction to the superposition approximation. Mixed integral equations[14] have been

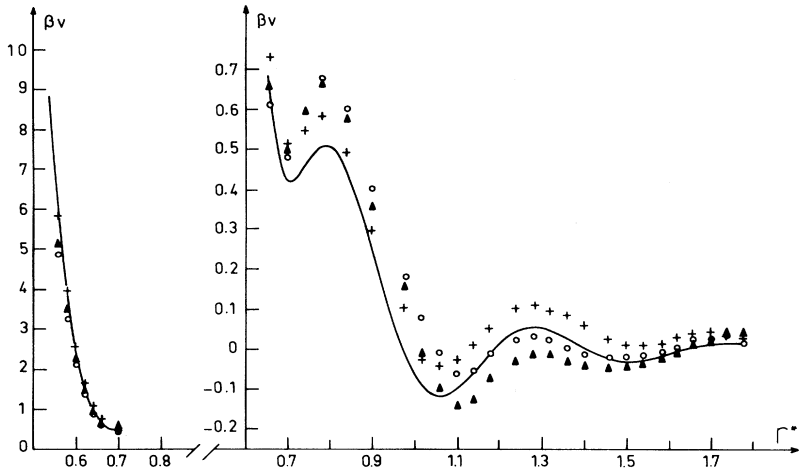

FIG. 2. Potentials from our inversion procedure for Al. Solid line, exact βv_{Al}; circles, βv_0; crosses, βv_1; triangles, βv_2 [$r^* = r/(4.234$ Å$)$].

used to extract βv but their accuracy has not been tested and, in any case, have serious difficulty in the treatment of liquid metals. This permits the conclusion that no integral equation for $g(r)$ is accurate enough and of wide applicability for the extraction of βv for very dense systems.

Our approach to the inverse problem is based on an iterative predictor-corrector method.[4] As a predictor we use the MHNC equation as discussed above. Thus, given a $g(r)$, we obtain a potential which we call $\beta v_0(r)$. This, however, is now considered only as a first estimate of the interaction. As a corrector we perform a simulation with $\beta v_0(r)$. This generates the "exact" rdf $g_0(r)$ corresponding to $\beta v_0(r)$. The difference $\Delta g_0(r) = g(r) - g_0(r)$ is nonzero because the prediction is not exact, but now the predictor can be used again to obtain a new estimate $\beta v_1(r)$ of the interaction and the procedure can be repeated until the difference $\Delta g_i(r)$ is small enough, in this case the accuracy being limited by the statistical fluctuations of the $g_i(r)$ obtained by simulation, i.e., by the length of the simulation. MHNC can be used to obtain these subsequent estimates βv_i of the interaction by approximating $E(r/v)$ for the unknown $v(r)$ not with E_{HS} but with $E(r/v_{i-1})$, which can be extracted from (1) when $g_{i-1}(r)$ (and the corresponding c_{i-1}) is known. This gives[4]

$$\beta v_i(r) = \beta v_{i-1}(r) + g(r) - g_{i-1}^{(r)} + \ln[g(r)/g_{i-1}^{(r)}] + (2\pi)^{-3}\rho^{-1}\int d^3q\, e^{i\mathbf{q}\cdot\mathbf{r}}[S^{-1}(q) - S_{i-1}^{-1}(q)], \tag{3}$$

where the OZ relation has been used to express $c(r)$ in terms of $S(q)$. This iterative scheme requires no *a priori* knowledge of $v(r)$ and no other information than $g(r)$ and its Fourier transform $S(q)$.[12]

A similar iterative predictor-corrector method has been proposed for the first time by Schommers[7] but his scheme is based on the assumption that the function $y(r) = g(r)\exp[\beta v(r)]$ does not change when $v(r)$ is varied. We have tested Schommers's scheme using $g(r)$ for the LJ system at $\rho\sigma^3 = 0.84$ and $k_{\mathrm{B}}T/\epsilon = 0.75$ and we find that it does not converge to the correct answer. We have followed that scheme for thirteen iterations and for the last three iterations the deviations $\Delta g = g - g_i$ were below the statistical errors of the simulation so that the computation was considered as converged. As can be verified in Fig. 1, βv_{13} is very different from the LJ potential. This result is not too surprising because $y(r)$ has a significant variation when $v(r)$ is varied.

On the contrary our predictor-corrector scheme based on MHNC has a good convergence property. First it was applied to the LJ potential with our simulation result with $r_c = 4\sigma$ as input $g(r)$. A cutoff of v_i at 3σ was used for the first six iterations after which the computation could be considered as converged. The resulting βv_6 is in good agreement with the LJ potential (see Fig. 1) but the minimum is overestimated by 0.04. In order to see if this could be due to the cutoff used, six additional runs have been performed with $r_c = 4\sigma$. The $\beta v_i(r)$ obtained in these last runs oscillate around the correct value with deviations ~ 0.05–0.15 which is what is expected from the effect of the statistical error on the simulated $g(r)$ (runs of 1200 moves/particle have been done and 2400 moves/particle for the last two iterations); $\beta v_i(r)$ for the last five iterations can be considered as independent estimates of the potential so that as a final prediction of the potential[5] we take the average of these last five iterations. At distances $r > 2.5\sigma$ where βv_{LJ} is less than 0.02, βv_i show some small oscillations around zero.

Our method converges very well, too, in the case of the Al potential model and we have performed four iterations. Some of the results are shown in Fig. 2. Positions of the extrema of βv are reproduced with very high accuracy and the values of βv at these extrema are reproduced with an uncertainty ~ 0.08 which again reflects statistical uncertainty of the simulations. Notice that now the positions even of very weak structure in v are stable under iteration and do not show the erratic behavior of the LJ case. This seems to make possible a discrimination between weak structure in v due to noise from the real ones.

In conclusion we have demonstrated that inversion of structural data even under the triple-point condition is feasible with our iterative predictor-corrector method (the application of the method to the LJ system at $\rho\sigma^3 = 0.65$ and $k_{\mathrm{B}}T/\epsilon = 1.036$ gives also excellent results). However, the result is meaningful only if the starting structural data is accurate enough. The method shows a very fast convergence even for highly structured potentials. Positions of the structures in $v(r)$ are very easily obtained, whereas the accuracy of the absolute values is a function of the length of simulation. At the same time we have shown that simulations provide structural data that are accurate enough to test inversion schemes. On the basis of this analysis we conclude that the deduction of the effective interparticle interaction for real fluids will be feasible when the experimental scattering data of the higher quality allowed by the new radiation facilities become available.

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