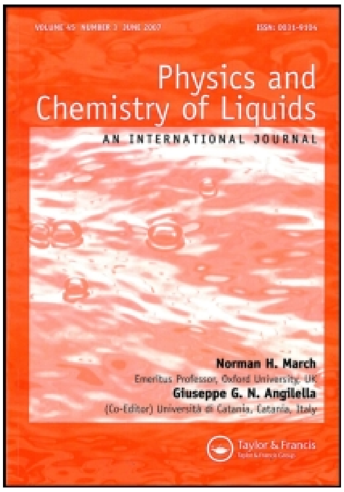

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Inversion of Structural Data for Effective Potentials in Dense Liquids and Colloids

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INVERSION OF STRUCTURAL DATA FOR EFFECTIVE POTENTIALS IN DENSE LIQUIDS AND COLLOIDS

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We address the inverse problem of obtaining microscopic interaction potentials from macroscopic structure, here in the context of liquid-like systems. The proposed method uses a perturbation-theoretic formalism and requires no *a priori* knowledge of the form of the potential. Very stable and rapidly converging potentials are obtained for widely different classes of fluids, and the results demonstrate the feasibility of inversion. The methodology can be extended to related problems in condensed matter physics and will aid in the analyses of structural data.

KEY WORDS: Inverse problem, effective potentials, liquids, colloids.

1 INTRODUCTION

The effective interparticle pair-potentials play a central role in the theories of fluids or fluid-like collection of particles (e.g., colloids) and govern the structure, the bulk properties and the nature of both bulk and interfacial phase transitions in very subtle ways. Consequently, numerous attempts have been made in recent years to determine at least the essential features of these potentials by a variety of theoretical and experimental methods[1-7]. One way to obtain such information is to fit the observed structure or other macroscopic properties to an assumed potential by trial-and-error. Alternatively, one can devise a *formal inversion method* based on a forward formalism which relates given pair-potentials to the structure or macroscopic properties. The method described in this paper falls under the latter category, known as 'the inverse problem'. Traditionally, statistical physics has concerned itself primarily with the evaluation of the macroscopic properties of matter from given interparticle potentials. In contrast, the inverse problem has received very limited (and, to this day, incomplete) attention. Indeed, the question of whether there is a one-to-one correspondence between structure and pair-potential itself is a non-trivial (and much debated) problem and needs to be properly addressed. Successful and reliable inversion

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methods, such as the one presented here, can greatly help to clarify this important question.

Recent attempts to extract effective potentials from structural data can be traced to the pioneering work of Johnson and March[1] which employed the integral equation theories based on the Percus–Yevick (PY) and the Hypernetted-Chain (HNC) closure schemes[7]. Because of the well-known inaccuracies of these approaches[7,8], current attempts have resorted to more sophisticated liquid-state theories. Jacobs and Andersen[2] have used the Weeks–Chandler–Andersen (WCA) perturbation theory in an attempt to fit the large-q (i.e., large-scattering-vector) part of theoretical structure factors of several model potentials to experimental ones. Formal inversion schemes based on a WCA *corrector* (see below) have been devised by Mitra and coworkers[3] and by us[6], but have met with only partial success. In an attempt to avoid the shortcomings of perturbation and integral equation theories, Madden and Rice[4] formulated a generalized mean-spherical approximation (GMSA) [that retains the strengths of those theories] and used it for inversion, which showed substantial improvements over integral equation approaches. Mitra's[3] use of a WCA corrector met with limited success for an inert gas (neon), but relied on fitting the tail of the potential to an empirical power-law form at each iteration of the inversion. The most successful inversion method available in the literature, by Reatto *et al.*[5], is based on a predictor that uses the Reference Hypernetted-Chain (RHNC) scheme[9], but requires molecular dynamics as corrector at each iteration (with its attendant need for extrapolation and smoothing of the derived structure). Nevertheless, Reatto *et al.*'s results establish the feasibility of achieving reliable inversion.

Our objective here is to formulate an inversion method that does *not* require any preconceived functional form for the potential *nor* any computer simulations for the corrector. It is also our objective to demonstrate that not only are the essential details of the interactions preserved in the structure, but they may, in fact, be recovered to a large extent if the inversion method places proper emphasis on the dominating features of the interaction potentials. In what follows, we present a self-consistent inversion scheme which uses the same theoretical formalism (in this case, the WCA perturbation theory[10]) both as a *predictor* [i.e., in the inversion route: $S(q)$ or $g(r) \rightarrow u(r)$] and as a *corrector* [i.e., in the forward route: $u(r) \rightarrow S(q)$ or $g(r)$].

2 PERTURBATION THEORY: AN OUTLINE OF THE FORWARD FORMALISM

We first outline the central features of the forward perturbation theory in order to place the inversion in proper context. The actual potential, $u(r)$, is first decomposed into a reference part and a perturbative part, $u_0(r)$ and $u_p(r)$, respectively, i.e.,

$$u(r) = u_0(r) + u_p(r) \tag{2.1}$$

One then chooses an effective hard-sphere diameter d, and thus a hard-sphere potential $u_d(r)$, which replaces $u_0(r)$ in Eq. (2.1) and defines the *trial potential*, i.e.,

$$u(r) \rightarrow u_T(r) \equiv u_d(r) + u_p(r). \tag{2.2}$$

The replacement of u_0 by u_d is needed for using the Optimized Cluster Theory (OCT)[10] in the WCA method. A number of options exists for the selection of d; the use of the following criterion due to Lado is known to lead to better predictions of the thermodynamic properties of the fluid[11,12]:

$$\int [\partial y_d(r)/\partial d]\{e^{-\beta u_0(r)} - e^{-\beta u_d(r)}\}\, d\mathbf{r} = 0, \tag{2.3}$$

where y_d is the well-known cavity function corresponding to u_d. Finally, in OCT, the trial structure factor is given by[10]

$$S_T(q) = S_d(q)/[1 + S_d(q)\rho\beta u_p(q)], \tag{2.4}$$

where ρ is the number density, $u_p(q)$ is the Fourier transform of an optimized $u_p(r)$ which is redefined inside the hard core in terms of a polynomial obtained by a well-known optimization prescription[10], and $S_d(q)$ is the structure factor of a hard-sphere fluid of diameter d. The radial distribution function in the so-called EXP-approximation can be written as

$$g_{\mathrm{EXP}}(r) = y_d(r)\exp[C_L(r) - u_0(r)], \tag{2.5}$$

where $C_L(r)$ is a renormalized potential[10].

3 THE INVERSION METHOD

In developing an inversion procedure one attempts to ensure structural consistency between the observed structure and the one derived from the extracted potential. Information from such requirements may then be used to obtain a more refined inverted potential. This is the essence of the predictor-corrector mechanism, which is used iteratively until the inverted potential converges. In order to impose structural consistency, we have chosen to compare $g(r)$ with $g_{\mathrm{EXP}}(r)$ of Eq. (2.5) since $g_{\mathrm{EXP}}(r)$ takes the softness of the real system into account in a much better way than $S_T(q)$.

As also noted by others[5], the choice of a correct iterative equation (or, a set of equations, as in our case) for the inversion is quite crucial. For our WCA-based inversion method, we propose the following set of equations:

i) Given a hard-sphere diameter d in the nth iteration, one first obtains the perturbation in the q-space, $u_p(q)$, corresponding to the given hard-sphere reference system by requiring that the trial structure factor $S_T(q)$ in Eq. (2.4) be equal to the 'observed' structure factor, $S_{\mathrm{obs}}(q)$.

$$\beta u_p(q) = [1/S_{\mathrm{obs}}(q) - 1/S_d^{(n)}(q)]/\rho. \tag{3.1}$$

ii) The Fourier transform of the renormalized potential $C_L(r)$ corresponding to the above perturbation follows from[12]

$$C_L(q) = -[S_d^{(n)}(q)]^2\beta u_p(q)/[1 + S_d^{(n)}(q)\rho\beta u_p(q)],$$

which, in view of Eq. (3.1), becomes

$$C_L(q) = -S_{\text{obs}}(q)S_d^{(n)}(q)\beta u_p(q). \tag{3.2}$$

iii) Finally, the *predictor* for $u^{(n+1)}(r)$ is given by ·

$$\beta u^{(n+1)}(r) = \ln\left[y_d^{(n)}(r)/g_{\text{obs}}(r)\right] + C_L(r) + \beta u_p(r). \tag{3.3}$$

Equation (3.3) is a consequence of Eqs. (2.1) and (2.5), with the requirement that $g_{\text{EXP}}(r)$ be equal to $g_{\text{obs}}(r)$.

iv) A new hard-sphere diameter can be calculated for the reference part of this $u^{(n+1)}(r)$ using the Lado criterion, Eq. (2.3). This diameter can then be used in Step (i) to obtain further improvements in $u(r)$ until convergence is achieved. This feedback, with its accompanying readjustment of $u_p(r)$ and $C_L(r)$ [here, using the forward WCA formalism implicit in Eqs. (3.1) and (3.2)], serves as the *corrector*.

As implicit in the statement leading to Eq. (3.1), this inversion scheme requires, as a starting point, nothing more than an initial estimate for d. A good estimate, for the given data, can be obtained as follows. One first rewrites Eq. (2.4) for $S_d(0)$ by substituting $S_{\text{obs}}(0)$ for $S_T(0)$:

$$S_d(q=0) = S_{\text{obs}}(q=0)/[1 - S_{\text{obs}}(q=0)\rho\beta u_p(q=0)] \tag{3.4}$$

Here, $u_p(q=0)$ can be estimated from the Fourier transform of $u_p(r)$ derived from a modified mean-spherical approximation

$$\begin{aligned} \beta u_p(r) &= -c(r_{\max}), \qquad \text{for } r \le r_{\max} \\ &= -c(r), \qquad \text{for } r > r_{\max} \end{aligned} \tag{3.5}$$

where $c(r)$ is the direct correlation function corresponding to the given data, and $r_{\max}$ is the location of its primary peak. Since the structure factor at $q = 0$ is related to the isothermal compressibility, d is now calculated from $S_d(0)$ using a suitable equation-of-state. Alternatively, one can start with a given initial potential and use the WCA decomposition, with Eq. (2.3) or (3.4), to obtain an initial d.

4 RESULTS

We now examine the performance of this inversion method for three widely different classes of fluids. The first is argon, for which excellent scattering data are available[13] and which has been used as a testing ground for several previous attempts at inversion[7]. The second is a *model* colloidal fluid with a complicated interaction potential (including a primary minimum *and* a secondary minimum) that has a hard core (of unit diameter), a weak Yukawa repulsion, a strong van der Waals attraction, and a steep Born-type repulsion near the core. These model colloids mimic liquid metals and metallic glasses in *some* respects[14]; more importantly, the effective interactions in such supramolecular fluids are of intrinsic interest for a number of reasons[15]. The last is a (relatively soft) Lennard-Jones (LJ) fluid at a reduced density of $\rho\sigma^3 = 0.38$, with a minimum of -0.1 kT in the potential.

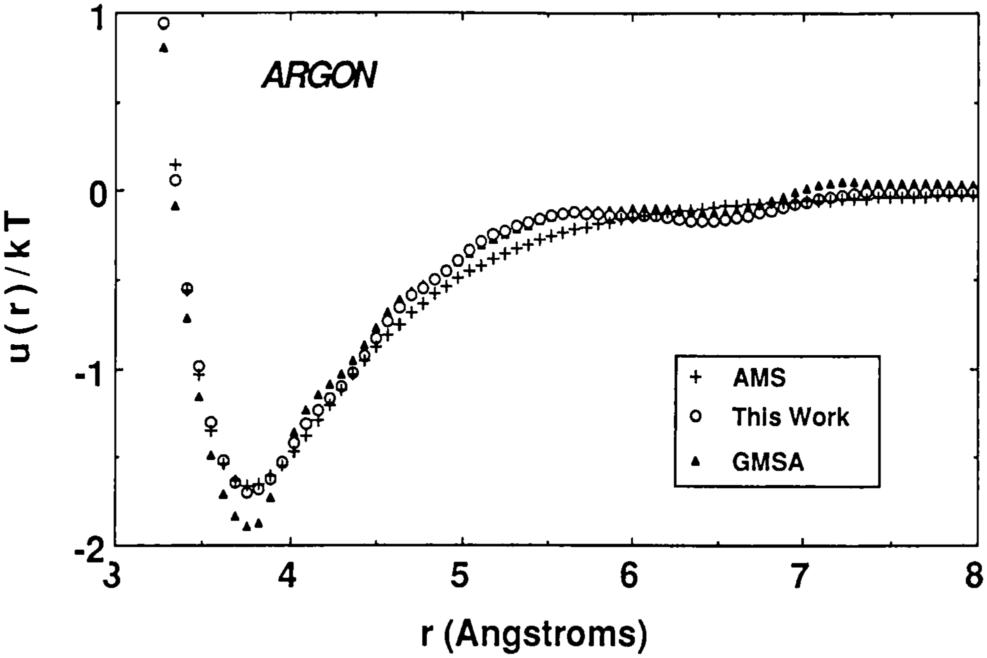

Figure 1 Effective potentials for argon (near the triple point) extracted from observed data[13], along with the Aziz-Maitland-Smith (AMS) potential[16].

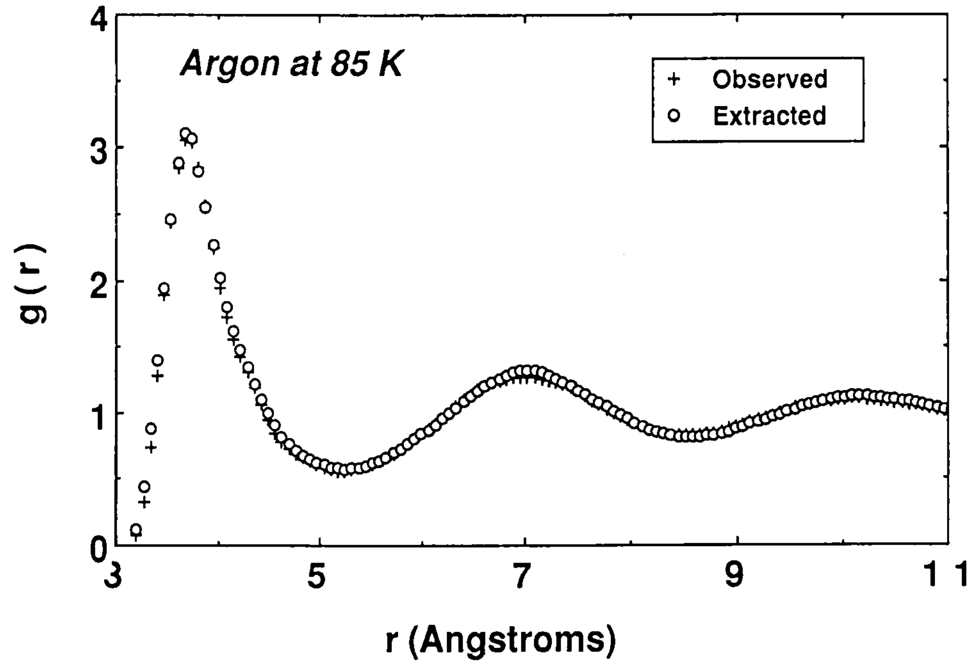

Figure 2 Radial distribution function, *g*(*r*), for our inverted potential in Figure 1, along with the corresponding experimental values[13].

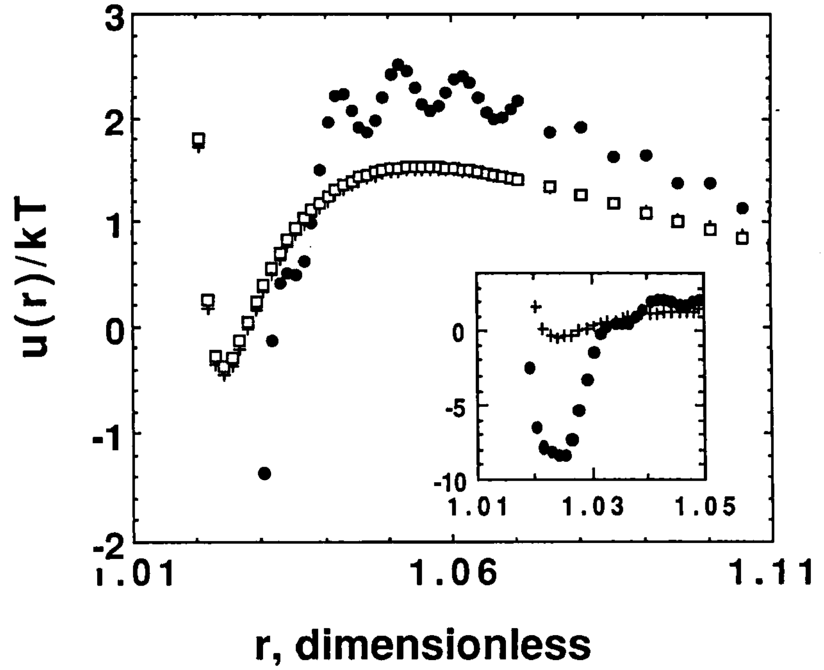

Figure 3 Details of the pair-potential near the primary minimum for the model colloid (r is in units of rigid-core diameter). See Figure 4 for explanation of symbols. The structure data used in the inversion are for a volume fraction of 0.4.

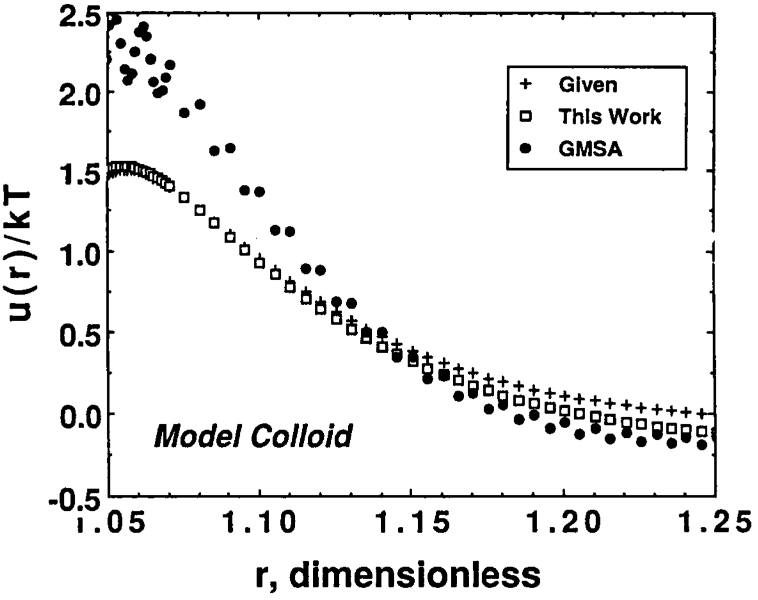

Figure 4 Potentials shown in Figure 3 for the model colloid, beyond the potential barrier.

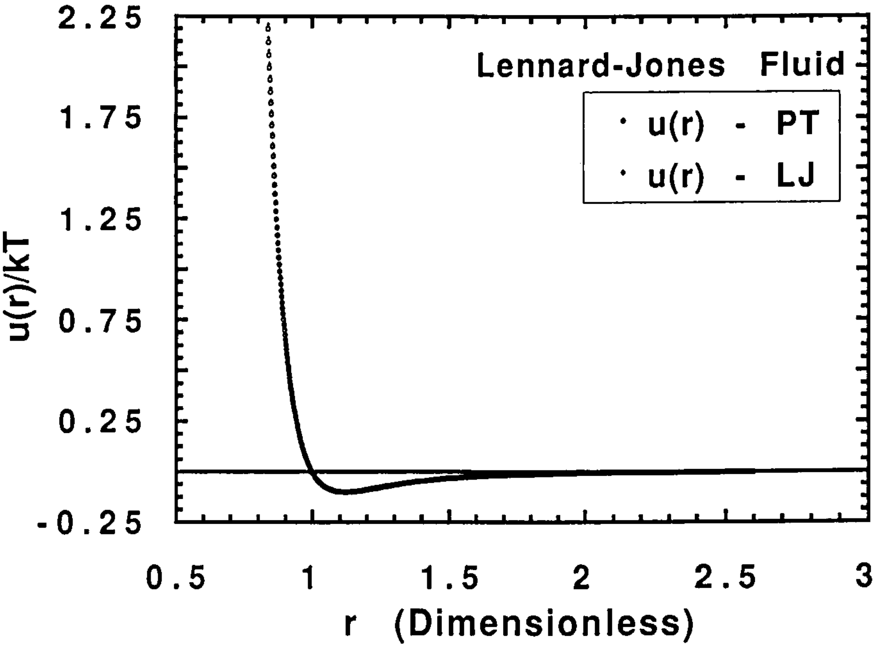

Figure 5 The inverted potential (denoted by 'PT') for a Lennard-Jones fluid with $\sigma = 1$, $\varepsilon = -0.1$ kT, and $\rho\sigma^3 = 0.38$ compared with the known LJ potential ('LJ').

Figures 1–5 illustrate the results obtained for the above three cases along with the known potentials. In the case of argon, we have chosen, for comparison, the Aziz-Maitland-Smith (AMS) potential[16], parametrized by Aziz and Chen[17]. The AMS potential is one of the most accepted potentials for argon [with essentially the same values of ε ($\varepsilon/k \approx 142$ K), $r_{\min}$ (≈ 3.76 Å), and σ (≈ 3.36 Å), as the other similarly useful argon potentials (e.g., the Barker–Fisher–Watts function or the Maitland-Smith BBMS function)[16]] and leads to good gas, liquid and solid properties when suitable three-body corrections are added. Figure 1 shows that these parameters for the extracted potential are in good agreement with those of the AMS potential, although, as one would expect, noticeable differences in $u(r)$ for $r > r_{\min}$ exist since the extracted potential is, in reality, an *effective* potential. The inversion converges rapidly (in about 10 iterations) to a precision better than 1 in 10^5. In addition, it is very robust, and the full (extended) data set of Yarnell *et al.* and truncated sets lead to essentially the same result shown in Figure 1. [It is important to note that the $g(r)$ supplied by Yarnell *et al.* is derived from the *full* $S(q)$-set. Therefore, the truncation of one data set does not eliminate the far-field information in the other.] The level of structural consistency obtained in this case can be seen from Figure 2, and these results can be improved further with the use of computer simulations to generate $g(r)$; however, we note that $g(r)$ from the extracted potential is not needed at any step for the subsequent corrector.

The results of the inversion in the case of the more complex colloidal potential are even more striking. The structure factor in this case was calculated from the known potential using RHNC, since we have found[18] that RHNC agrees very well with Monte Carlo results. As the method of generation of the data *excludes many-body potentials*, the inversion can be tested *without ambiguity* for its ability to reproduce the crucial features of the known *pair*-potential and for the effects of numerical artefacts. In addition, because of the very sharp change in the potential near the primary minimum, a finer step size in r is needed here, and this was guaranteed by generating a much larger data set (over 2000 points). Again, the inversion converges (Figures 3 and 4) within four iterations with a precision better than 1 in 10^7. Figures 3 and 4 also demonstrate the high degree of accuracy with which the shape and the potential barrier are reproduced in the inverted potential. However, the far-field values of $u(r)$ show a noticeable deviation because of the inaccuracy of the RHNC results for $S(q)$ as $q \to 0$ in this case.

In order to circumvent this, we have also tested the inversion for an LJ fluid with accurate Monte-Carlo-generated structural data. As Figure 5 illustrates, one can see excellent improvements in the extracted potential.

In each of the three cases, the iterates oscillate around the final result, with progressive and rapid convergence, and the convergence is *uniform* (i.e., independent of r). This is in marked contrast to the other inversion attempts reported in the literature (where monotonic drifts, non-uniform behavior, divergence, or almost chaotic jumps are observed). In order to place our inversion in proper perspective, we also compare our results with those of a GMSA-predictor, which has been shown earlier[4] to be reasonable for liquid sodium and potassium. Although, as previously established[4], GMSA does quite well for argon (see Figure 1), the quality of its predictions is less than acceptable for the colloidal potential (Figures 3 and 4). GMSA's failure is at least partly attributable to its reliance only on the 'observed' $c(r)$ beyond the global minimum. While a single-step inversion *is* convenient, Figures 3 and 4 illustrate that a predictor-corrector method is essential for more complicated potentials. A similar observation has also been made[5] about the single-step RHNC-predictor.

We emphasize that even with seemingly correct inversion equations the effects of numerical artefacts such as spurious far-field oscillations due to finite cut-offs in Fourier transforms can jeopardize the inversion from the outset. *Ad hoc* corrections, either through empirical fits to the extracted potential[3] or by other means[6], do not necessarily lead to convergence, stability nor expected potentials. We have also observed that an attempt to circumvent Fourier transforms in the predictor, as made by Schommers[19], fails badly for argon (at least when used with a WCA corrector); Schommers's method fails also for a Lennard-Jones fluid as already noted by Reatto *et al.*[5]. All of these highlight the fact that a proper formulation of inversion equations (especially, what information is passed between the predictor and the corrector at each stage, and *vice versa*) is very crucial and is *non*-trivial. Further, the notable success of our inversion method in the case of the model colloidal fluid suggests that it can be expected to do well for liquid metals where Friedel oscillations are important. The details of these, the influence of errors in data, and whether unambiguous potentials may be obtained in general will be addressed elsewhere.

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