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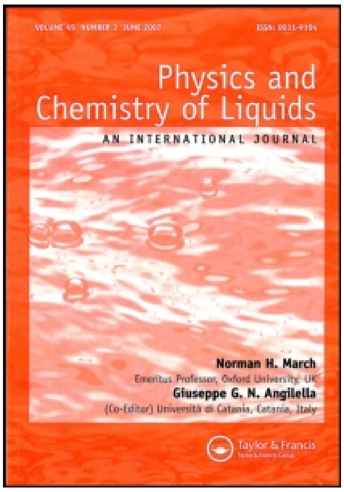

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Letter

Extraction of Force Laws from Measured Liquid Structure via Decoupling of Triplet Direct Correlation Function

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Extraction of a pair potential from measured structure data on monatomic liquids is proposed by combining work of Hernando and the writers with a recent decoupling of the triplet direct correlation function by Barrat *et al.*

Key Words: Pair potential, structure factor, inverse problem.

Since the proposal of Johnson and March[1,2], almost 25 years ago, to use approximate theories of liquid structure to invert $S(k)$, accessible from diffraction data, to extract a pair potential $\phi(r)$, there has been continuing interest in such a programme; an article by one of us[3] has surveyed recent progress.

The purpose of this Letter is to point out that, by combining work of Hernando[4] and the writers[5], in which triplet direct and total correlation functions, $c^{(3)}$ and $g^{(3)}$ respectively, are related, with a decoupling of $c^{(3)}$ proposed very recently by Barrat *et al*[6], a method of inversion emerges which promises to have considerable advantages over the use of earlier approximate integral equations.

It is again useful to start from the force equation[3], which, within an assumed pair potential framework reads:

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = \frac{-\partial\phi(r_{12})}{\partial \mathbf{r}_1} - \rho\int \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(r_{12})}\frac{\partial\phi(r_{13})}{\partial \mathbf{r}_1}\,d\mathbf{r}_3 \qquad (1)$$

with U as usual the potential of mean force. Clearly, if one obtains the pair function $g(r)$ by Fourier transformation of diffraction experiments measuring the liquid structure factor $S(k)$:

$$g(r) = 1 + \frac{1}{8\pi^3\rho}\int [S(k) - 1]\exp(i\mathbf{k}\cdot\mathbf{r})\,d\mathbf{k} \tag{2}$$

with ρ the number density in the liquid, then following references 1 and 2 one must input information relating to $g^{(3)}$ in order to extract $\phi(r)$ from Eqn. (1).

It has been known since the early work of Schofield[7] that $g^{(3)}$ can be related to the density derivative $\partial g/\partial\rho$ and the importance of such data has been previously stressed[8, 3]. Therefore, while in Ref. 5 a decoupling of the triplet direct correlation function $c^{(3)}$ was explicitly quoted, and related to the Kirkwood approximation combined with the convolution approximation of Ichimaru[9], a similar, but more quantitative generalization proposed by Barrat *et al*[6]; namely ($\mathbf{r}_1 \equiv 1$ etc)

$$c^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = t(12)t(23)t(31) \tag{3}$$

has the merit that t can be fixed by requiring that the exact relation between $\partial c(r)/\partial\rho$ and $c^{(3)}$ be satisfied. Specifically, knowledge of the density derivative $\partial c/\partial\rho$ of the Ornstein-Zernike direct correlation function $c(r)$ would be enough to permit the unambiguous determination of the function $t(r)$ in Eq. (3) through[6]

$$\frac{\partial c(r)}{\partial\rho} = t(r)\int t(r')t(|\mathbf{r} - \mathbf{r}'|)\,d\mathbf{r}'. \tag{4}$$

Given the approximation (3), with $t(r)$ determined empirically from Eq. (4), it remains only to utilize in Eq. (1) the relation between $g^{(3)}$ and $c^{(3)}$ discussed by Hernando[4] and the writers[5]. To illustrate the procedure, without going into detail that soon proliferates, we note that $\partial g/\partial\rho$, related to $g^{(3)}$, is given by[5]

$$\begin{aligned}\frac{\partial g^{(12)}}{\partial\rho} &= \int d3\; h(13)h(32) + \frac{\partial c(12)}{\partial\rho} \\ &\quad + 2\rho\int d3\; h(13)\frac{\partial c(32)}{\partial\rho} + \rho^2\int d3\int d4\; h(13)h(24)\frac{\partial c(34)}{\partial\rho}\end{aligned} \tag{5}$$

which illustrates one, admittedly limited, aspect of the relation between $g^{(3)}$ and $c^{(3)}$, with $h(r) = g(r) - 1$.

In summary, it is now feasible to build explicitly into the inverse problem of extracting $\phi(r)$ from $S(k)$ the density dependence of the two-body functions $g(r)$ and $c(r)$. Examples of the form of $t(r)$ in Eq. (3) have already been presented by Barrat *et al*[6].

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NOTE ADDED IN PROOF

The practical way to combine Eq. (1) with the approximate decoupling (3) is to resort to the three-body total correlation function, which has a Fourier transform

$$\tilde{h}^{(3)}(\mathbf{q}_1, \mathbf{q}_2) = S^{(3)}(\mathbf{q}_1, \mathbf{q}_2) + S(q_1) + S(q_2) + S(|\mathbf{q}_1 + \mathbf{q}_2|) + 2,$$

with $S^{(3)}$ given in Ref. 6. Equation (1) requires only the p harmonic of $g^{(3)}$ and this can be shown to lead to

$$\frac{\partial U}{\partial r} = \frac{\partial \phi}{\partial r} + \rho \int ds \, \frac{(h_1^{(3)}(r, s) + g_1(r, s))}{g(r)} \frac{\partial \phi}{\partial s},$$

with $h_1^{(3)}$ and g_1 the $l = 1$ projection of $h^{(3)}(\mathbf{r}, \mathbf{s})$ and $g(|\mathbf{r} - \mathbf{s}|)$, respectively.