Extended integral-equation theories for Lennard-Jones fluids

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There are two general sources of error in any statistical theory of the fluid state: limitations in the intermolecular potential-energy function and defects in the model equations which relate microscopic properties to those in the bulk. However, since the properties of a model system such as the Lennard-Jones (LJ) fluid is known exactly from computer experiments, the inadequacies in a proposed theory of fluid are better exposed by performing calculation for the model system. We report here the performance of our extended integral-equation theory1,2.

Much of recent work on higher-order approximations to integral-equation theories which derive from the Ornstein-Zernike (OZ) equation can be classified into two groups. In the first group are semi-empirical closure relations which approximate the bridge function as some simple, analytical function of the cavity function, y(r)14. The second approach, pioneered by Attard3,6 uses inhomogeneous fluid theory to achieve a higher-order approximation at the level of first-order closures2,10. In the first approach, although very good results are obtained at liquid-like densities, the converse is true at low gas densities. The second method out-performs the first-order PY and HNC theories; it is in fact equivalent to the older and cumbersome PY2 and HNC2 methods of Varlet11 and Wertheim12 in that it is exact at the level of the additive 4th virial coefficient. A demerit of the latter method, however, is that it requires considerable computer resources for its realization.

We are motivated to develop a theoretically based, accurate and computationally inexpensive equation of state method at sub-critical gas densities which may lead to useful results at high density states. The virial equation of state which might be considered an alternative approach to an integral-equation method may encounter convergence problems at the higher density of our region of interest.

Background Theory

For a homogeneous and isotropic fluid of number density ρ and at temperature T, the OZ equation defines the direct correlation function:

\[ \gamma_{12} = \rho \int \left[ y_{13} + c_{13} \right] f_{23} \, d\mathbf{r}_3; \] … (1)

where, the following shorthand was used to write equation (1), \( \gamma(r_{12}) = \gamma_{12} \), etc and where \( \gamma_{12} = h_{12} - c_{12} \) is the chain function. It is well-known that Eq. (1) by itself does not provide numerical values for correlation functions since there are two functions which are defined by that one equation. To achieve the latter objective one traditionally postulates a closure which enables \( \gamma \) to be solved for13.

In the spirit of the PY theory, a convenient standing point from which to derive a viable closure is the exact relation.
In Eq. (2), \( f_{12} \) is the Mayer function, \( e_{12} = 1 + f_{12} \) is the Boltzmann factor and \( d_{12} \) is the tail function. Equation (2) is not a viable closure, essentially because a subset of \( d_{12} \), known as the bridge function, has elements which are independent graphs and infinite in number. However, we have recently developed an efficient procedure for calculating terms in \( d_{12} \) up to third-order in its power series expansion in density. Consequently, rather than set \( d_{12} = 0 \) as in the first-order PY theory, we replace \( d_{12} \) by the calculated terms in the infinite series. Hence,

\[
c_{12} = \left[ 1 + y_{12} \right] f_{12} + e_{12} d_{12} \quad \ldots (2)
\]

where,

\[
d_{12}^{(n)} = \sum_{k=1}^{n} \rho^k d_k; \quad n \leq 3 \quad \ldots (4)
\]

It is clear that one obtains different versions of the extended theory depending as to the number of terms employed in Eq. (4). In our calculations, when \( d_{12}^{(n)} \) is set equal to zero, one recovers the PY theory; we designate this scheme as EPY1; when \( n = 2 \), the resulting closure is referred to as EYP2 and EPY3 is that which is obtained when \( n = 3 \). For a LJ fluid \( d_1 = 0 \); however, this is no longer true in real fluids.

Two other closure relations proposed by others were implemented to enable comparisons to be made with the various EPY theories. Many years ago Rowlinson proposed the following empirical relations,

\[
d_{12} = \frac{1}{2} \rho^2 \int f_{13} f_{14} f_{23} f_{24} g_{34} d\mathbf{r}_3 d\mathbf{r}_4 \; \ldots (5)
\]

where, \( g \) is the radial distribution function. Equation (5) is exact at the level of \( d_{12}^{(2)} \) but contains some higher graphs.

When Eq. (5) is used in place of \( d_{12}^{(n)} \), we denoted such a procedure as PYR. Duh and Henderson put forward the following approximation to the bridge function, \( E(r) \).

\[
E(r) = \begin{cases} 
\frac{s^2(s^2 + 9)}{3(s^2 + 3)(s^2 + 3)}, & s \geq 0 \\
\frac{1}{2} s^2, & s < 0 
\end{cases} \quad \ldots (6)
\]

In the above equation \( s = s(r) = [\gamma(r) - \beta \phi_a] \); where, \( \phi_a \) is related to the attractive portion of a realistic pair-potential function. The approximate theory resulting from Eq. (6), which is within the unique functionality theory, we shall call DHH.

In this paper, we confine our study to fluids modelled by the LJ potential function:

\[
\phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right];
\]

where, \( \varepsilon \) is an energy parameter and \( \sigma \) is the corresponding distance parameter.

Solution of the integral equations

While we are aware of the algorithms based on Newton’s method for solving integral-equations and did experiment with the version due to Gillan earlier in our work, we eventually preferred the Picard iteration in direct space. The latter method is too well-known to warrant a detailed description here but we do mention some details which bear directly on our work; additional details are in ref. (1).

All correlation functions are first discretized up to a maximum distance, \( r^*_{\text{max}} \), in \( N \) equal panels of width, \( \delta r^* \); where, \( r^* = r/\sigma \). Along an isotherm we solve for \( \gamma \) according to the Picard iteration, starting from the zero-density, perfect-gas state, and proceeding to a density which is slightly greater than the desired maximum density. The functions \( d_{12}^{(n)} \) are calculated according to the procedure described previously. In addition to accelerating convergence by mixing known iterates, we accelerated the convergence of the Picard iteration at a given density by extrapolating from lower densities using a two-point or three-point Lagrange formula; this is because along an isotherm correlation functions are not strong functions of density.

Convergence was presumed to have occurred when

\[
\left[ \frac{1}{N} \sum_{i=0}^{N} (\gamma_i^{(k)} - \gamma_i^{(k-1)})^2 \right]^{1/2} \leq 10^{-6}
\]

and

\[
|\gamma_i^{(k)} - \gamma_i^{(k-1)}| \leq 10^{-5}; \quad i = 0, \ldots, N
\]

Radial integration was carried out to \( r^*_{\text{max}} = 9 \), with panel width, \( \delta r^* = 0.015 \). A number of tests were
performed to ensure the reliability of our result. We compared our result for $g_{12}$ at the state $T^* = 1.5$ and $\rho^* = 0.6$ with that of Throop and Bearman. An indirect test was performed by calculating the second, $B$, and third, $C$, virial coefficients of a LJ fluid; since,

$$\frac{1}{RT} \left( \frac{\partial p}{\partial \rho} \right)_T = 1 + 2B\rho + 3C\rho^2 + \ldots$$

Our results were in very good agreement with those of Baker et al. Finally, as a check on the accuracy of the present calculations, the following parameters in the program were independently varied: (i) changing $\delta r^*$ from 0.015 to 0.01; (ii) changing $r_{max}$ from 9 to 12; and (iii) changing the number of density steps from 30 to 40. For the first-order PY theory at the fluid state $T^* = 1.5$, $\rho^* = 0.6$, none of these changes had a significant effect on the value of the compression factor, $Z = \rho/\rho_{RT}$.

**Derived thermodynamic properties**

If one defines a dimensionless inverse isothermal compressibility:

$$\frac{1}{\chi} = \frac{1}{RT} \left( \frac{\partial p}{\partial \rho} \right)_T$$

the compression factor may be calculated at a given density from:

$$Z = \frac{1}{\rho_n} \int_0^{\rho_n} \left( \frac{1}{\chi} \right)_T d\rho_n; \quad \ldots (8)$$

where $\rho_n$ is the amount-of-substance density. In terms of the direct correlation function, Eqs (7) and (8) give the result:

$$Z = \frac{1}{\rho_n} \int_0^{\rho_n} \left[ 1 - 4\pi N_A \rho \int_0^\infty r^2 C(r) dr \right] d\rho_n \quad \ldots (9)$$

Equation (9) is a consequence of the so-called compressibility route to properties and while most of our calculations of $Z$ followed Eq. (9); it was necessary for comparative purposes to deduce $Z$ from the virial route, namely:

$$Z = 1 - \frac{\rho}{\rho_{RT}} \int r_2 \phi_{12} dr_2; \quad \ldots (10)$$

with, $\phi_{12} = d\phi_{12}/dr_{12}$ . When $Z$ is calculated according to Eq. (10), we shall denote it as VPE.

**Results and Discussion**

**Structural properties**

In Fig. 1 we compare the performances of the various closures with the Monte Carlo simulation of Llano-Restrepo and Chapman at $\rho^* = 0.4$ and $T^* = 1.5$. We note that EPY2 produced the best values of $g_{12}$.

**Fig. 1**—Radial distribution functions of a LJ fluid calculated from various integral-equation theories for state ($\rho^* = 0.4$, $T^* = 1.5$).
and that these are in good agreement with the data of ref. (21) but observe the discrepancies which exist at the first and second nearest-neighbour distances. The unexpected superior performance of EPY2 relative to EPY3 is further confirmed at the isothermal ($T^*=1.5$) densities $\rho^*=0.6$ and 0.8 ref. (1). However, the good performances of some EPY closures which Fig. 1 seemingly depicts must be viewed against the fact that the simulation in ref. (21) was done with 133 particles and that the LJ potential was truncated at $r^*=2.5$. The results for the state $T^*=1.5$, $\rho^*=0.6$ is shown in Fig. 2.

The unknown function in all integral-equation theories is $E(r)$; in Fig. 3 we show the approximations to this function given by the various closures at $T^*=1.5$ and $\rho^*=0.4$ together with the simulation data from ref. (21).

While DHH is particularly good at separations inside of the potential core, EPY3 produced rather good results at intermediate separations. However, the core region of a pair-potential function contributes little to most thermodynamic properties; a notable exception being the chemical potential$^2$.

A fundamental concept in the PY theory is that the function $d(r)$ may be easier to deduce than $E(r)$; we compare the result of the theory EPY3 for the former function at the state $\rho^*=0.4$, $T^*=1.5$ with the data of Llano-Restrepo and Chapman in Fig. 4.

The Maitland-Smith potential$^23$ simulates two-body dipole-quadrupole and quadrupole-quadrupole dispersion energy with the parameter $\nu$, Eqs (11) and (12).

$$\phi(r) = \frac{\varepsilon}{n-6} \left[ 6 \left( \frac{r_m}{r} \right)^n - 9 \left( \frac{r_m}{r} \right)^6 \right]; \quad \ldots \ (11)$$

with,

$$n = m + \nu \left( \frac{r}{r_m} - 1 \right); \quad \ldots \ (12)$$

In Eqs (11) and (12), $r_m$ is the position of the potential minimum; $m$ and $\nu$ are shape parameters. In Fig. 5 we show the function $E_{12}^{(3)}$ calculated from EPY3 for three values of $\nu$; this plot suggests that the bridge function might be rather sensitive to the shape of the well-region of a pair-potential, and not just the attractive section as presumed in current formulations of the unique functionality hypothesis.

**Thermodynamic properties**

The compression factor of a LJ fluid is calculated along a number of isotherms using the various closures discussed above and these results are compared with a virial equation of state truncated after the 5th coefficient$^{20}$ and the molecular dynamics results of Johnson et al.$^{24}$ The result for $T^*=1.2$ is shown in Fig. 6; the saturation density corresponding to this temperature is $\rho^*=0.0985$, ref. (25), indicating

![Fig. 2—Radial distribution functions of a LJ fluid calculated from various integral-equation theories for the state ($\rho^*=0.6, T^*=1.5$)](image-url)
Fig. 3—Approximate bridge function of a pure LJ fluid calculated from the integral-equation theory EPY3. The fluid state is 
\((\rho^*=0.4, T^*=1.5)\)

Fig. 4—Approximate tail function for a pure LJ fluid calculated from the integral-equation theory EPY3. The fluid state is 
\((\rho^*=0.4, T^*=1.5)\)
that the maximum density shown in Fig. 6 is well inside the meta-stable two-phase region.

In Fig. 7 isothermal ($T^* = 1.2$) compression factors from various closures are compared with the virial series of ref. (20); this is shown as a deviation plot. This plot, as well as giving indirect confirmation of the accuracy of our calculations provides some evidence that, provided the virial series does converge at this temperature, the unique functionality approximation DHH may not be very accurate at sub-critical gas densities. Figures 8-10 show further results of compression factor values; one sub-critical isotherm ($T^* = 1.3$) and two super-critical temperatures ($T^* = 1.4$ and 2.5).

The thermodynamic inconsistency, which results when the compressibility and virial routes are used to calculate $Z$, are shown in Figs 11-14. In Figs 11 and 12 the closure EPY2 is used for both routes and these are compared with the DHH closure and the simulation data of ref. (24). In Figs 13 and 14 the
Fig. 7—Deviations of calculated $Z$ from the virial equation of state of Barker et al.\textsuperscript{29} $\Delta Z = Z_{\text{calculated}} - Z_{\text{virial}}$, the temperature is $T^* = 1.2$.

Fig. 8—The equations of state of a pure LJ fluid for the isotherm $T^* = 1.3$, calculated from various theories.
Fig. 9—The equations of state of a pure LJ fluid for the isotherm $T^*=1.4$, calculated from various methods

Fig. 10—The equation of state of a pure LJ fluid for the isotherm $T^*=2.5$, calculated from various theories
Fig. 11—Thermodynamic inconsistency in the equations of state of a pure LJ fluid at $T^*=1.4$. VPE = virial pressure equation, CES = compressibility equation; closure EPy2 was used for both routes. The filled circles are the MD data of ref. [24].

Fig. 12—Thermodynamic inconsistency in the equation of state of a pure LJ fluid at $T^*=2.5$. VPE = virial pressure equation, CES = compressibility equation of state; the closure EPy2 was used for both routes.
Fig. 13—Thermodynamic inconsistency in the equation of state of a pure LJ fluid at $T^* = 1.4$ when calculated from EPY1 and EPY2. $v =$ virial route; $c =$ compressibility route. The filled circles are the MD results of ref. [24].

Fig. 14—Thermodynamic inconsistency in the equation of state of a pure LJ fluid at $T^* = 2.5$ as calculated from EPY1 and EPY2. $v =$ virial route, $c =$ compressibility route. Filled circles are the MD results of ref. [24].
inconsistency in the closure EPY2 is compared with that from the corresponding first-order PY theory (EPY1).

Conclusion
At the lowest density studied here (ρ*=0.4) which, while corresponding to a supercritical state, is greater than ρc*, the values of g12 for a LJ2 fluid calculated according to the closure EPY2 is very good. Even at the higher density ρ*=0.6, this is nearly 2ρc*, the g12 calculated with EPY2 remains quite good; however, we note the substantial errors which now exist in the region of the first peak. The approximations to the functions E12 and d12 afforded by the EPY closures are generally poor inside of the potential core and at long-range.

Contrary to the results for a fluid of hard spheres, more cluster diagrams do not necessarily lead to a better approximation or theory. Apropos of the foregoing claim was the superior performance of the original PY theory when compared to HNC for non-ionic fluids. Here, we observe that, overall, EPY2 led to a more effective theory of fluids than EPY3. Attempts were made to form a Pade' approximant using the known coefficients in d12; these were abandoned due to the occurrences of spurious poles and zeroes.

Of the two functions E12 and d12, it would appear from results obtained here that d12 is simpler in structure and may be easier to deduce; a conclusion which is consistent with the spirit of the first-order PY theory.

It appears a reasonable conclusion to say that an equation of state derived from EPY2 ought to provide a very accurate (that is, to current experimental uncertainties) representation of volumetric and caloric thermodynamic properties of a one-component fluid on the gas side of the thermodynamic surface. Consequently, discrepancies existing in this region between integral-equation theory and real fluid properties suggests strongly that more attention should be expended on the functional representation of pair interactions and the contribution of many-body forces to properties at the level of four-molecule clusters. This conclusion may not extend to properties, like chemical potential, which depend on the region inside of the potential core. Conversely, the unique functionality theory DHH is not expected to lead to thermodynamic properties of high accuracy on the vapour-side of the thermodynamic surface; this is so, because many properties are insensitive to the core region of a pair-potential function.

References