Thermodynamically Consistent Theory of Classical Liquid Structure and Inverse Problem of Extracting Pair Potential

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Thermodynamically Consistent Theory of Classical Liquid Structure and Inverse Problem of Extracting Pair Potential

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The direct correlation function $c(r)$ is divided into two parts, following the work of Kumar *et al.* One part, $c(r)_{\text{potential}} \equiv c_p(r)$, contributes the entire compressibility and decays at large r as $-\phi(r)/K_B T$, with $\phi(r)$ the density independent pair potential. The definition of $c_p(r)$ as $-\phi(r)/K_B T\{(1/6\rho r^2)\partial^2/\partial\rho\partial r[\rho^2 r^3 g(r)]\}$ is motivated by the condition of thermodynamic consistency, and for a hard core liquid leads to $c_p(r)$ small inside an atomic diameter.

The second part $c(r)_{\text{cooperative}} \equiv c_c(r)$ is not expressible simply in terms of $\phi(r)$ and the pair function $g(r)$, and is expected to differ in range between condensed rare gases and liquid metals say. Also, for a given liquid like argon, $c_c(r)$ can be shorter or longer range than $c_p(r)$ depending whether one is near the triple point, or near critical conditions. At the critical point, or alternatively in the presence of a collective mode as in liquid Rb, the long-range behaviour of $c_c(r)$ can be dominated by cooperative effects.

To illustrate the theory, fluid argon well away from the critical point is considered. Here, it is argued that $c_c(r)$ has the following properties: (i) it is short range compared with $c_p(r)$, (ii) it is near to the direct correlation function for hard spheres inside an atomic diameter σ, and (iii) it has Ornstein-Zernike form $e^{-\kappa r}/r$ for $r > \sigma$.

The present work demonstrates the importance of knowledge of the density derivative $\partial g(r)/\partial r$ as well as $g(r)$ in extracting density independent pair potentials from diffraction data.

I   INTRODUCTION

In early work, Johnson and March[1,2] attempted to extract pair force laws from the measured structure factor $S(k)$ of simple liquids. Some emphasis was placed in their work on the approximate structure theory based on the Kirkwood superposition approximation for the three-body function

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$g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, which results in this being replaced by a product of pair functions $g(r)$. However, this so-called Born–Green theory is seriously inconsistent thermodynamically and one manifestation of this is that the widely accepted asymptotic, large r, relation

$$c(r) = -\frac{\phi(r)}{K_B T}, \tag{1.1}$$

with $c(r)$ the Ornstein–Zernike direct correlation function and $\phi(r)$ the pair potential, can often be badly violated.[3] The relation (1.1) is valid near the triple point of simple liquids like argon, but is known to be inappropriate as the critical point is reached. Nevertheless the recent study of critical point behaviour of simple fluids by Kumar et al.[4] has provided the motivation for the present work. We therefore summarize in the following section the relevant part of their argument, which has to do with the thermodynamic consistency of the two routes to the equation of state, via first the compressibility expressed in terms of $\int c(r)\,\mathbf{dr}$ and secondly the virial expression for the pressure.

2   DIVISION OF c(r) INTO POTENTIAL AND COOPERATIVE CONTRIBUTIONS

As mentioned above, Kumar et al.[4] compared the result

$$\left(\frac{\partial P}{\partial \rho}\right)_T = K_B T[1 - \tilde{c}(0)] : \tilde{c}(0) = \rho \int c(r)\,\mathbf{dr}, \tag{2.1}$$

with that obtained by differentiating the virial expression for the pressure P, namely

$$P = \rho K_B T - \frac{\rho^2}{6}\int g(r)r\,\frac{\partial\phi(r)}{\partial r}\,\mathbf{dr} \tag{2.2}$$

with respect to the fluid number density ρ. They were then led, rather directly, to the result that $c(r)$ can be written as a sum of two contributions

$$c(r) = c_{\text{potential}}(r) + c_{\text{cooperative}}(r) \equiv c_p(r) + c_c(r). \tag{2.3}$$

They gave the explicit expression

$$c_p(r) = -\frac{\phi(r)}{K_B T}\left\{\frac{1}{6\rho r^2}\frac{\partial^2}{\partial\rho\,\partial r}[\rho^2 r^3 g(r)]\right\} \tag{2.4}$$

which is readily shown to contribute the entire asymptotic form (1.1) at sufficiently large r. It clearly then has the range of the pair potential $\phi(r)$.

No such complete expression exists for the "cooperative' contribution $c_c(r)$. However, we have in mind that, as the critical point is approached, say in fluid argon, $c_c(r)$ must eventually become long range, and then dominate the potential term $c_p(r)$ at sufficiently large r. Or again, in liquids where collective effects are known to play a role, e.g. in quantal liquid helium four at $T = 0$, or in liquid Rb, the cooperative term $c_c(r)$ can be expected again to dominate the potential contribution at sufficiently large r.

2.1   Case of 'hard core' fluid like argon

In addition to the large r behaviour of the two contributions to $c(r)$ discussed above, it seems clear from the form of Eq. (2.4) that, at least for a 'hard core' liquid like argon, $c_p(r)$ must rapidly become small inside an atomic diameter. Then the separation in Eq. (2.3) becomes rather directly comparable to that employed by Woodhead-Galloway et al.,[5] $c_p(r)$ being analogous to their long-range contribution, while almost the entire contribution to $c(r)$ within the core comes from $c_c(r)$. Thus, roughly speaking, and to be illustrated by a simple model in Section 3, $c_c(r)$ is reminescent of the hard-core direct correlation function inside an atomic diameter, though one must recall that

$$\int c_c(r)\, \mathrm{d}\mathbf{r} \equiv 0 \qquad (2.5)$$

and that, therefore, $r^2 c_c(r)$ must have at least one node. This point will again be illustrated in Section 3 below.

To press the analogy with the work of Woodhead-Galloway et al. for fluid argon, $\phi(r) \sim c_6/r^6$ at large r if we neglect retardation, and therefore from Eqs. (1.1) and (2.3) it follows that, far from the critical point, $c_c(r)$ falls off with distance more rapidly than r^{-6} at large r.

For this example of fluid argon, we note therefore that, without invoking any decoupling of $g^{(3)}$ such as referred to above, the asymptotic result (1.1) can be kept intact provided only that $c_c(r)$ is short-range compared with $\phi(r)$. The price to be paid according to Eqs. (2.3) and (2.4) is that the density dependence of the pair function now enters the theory, and this is natural enough when one recalls the fact that $\partial g(r)/\partial \rho$ can be written explicitly in terms of the three-body correlation function[6] $g^{(3)}$. Indeed, as shown in Appendix 1; the potential part $c_p(r)$ of $c(r)$, can be expressed entirely in terms of $g^{(3)}$, without density derivatives, with evidently no decoupling involved. Of course, it is quite another matter to write an explicit expression for $c_c(r)$: which should occasion no surprise because the examples of liquid helium four and liquid Rb referred to above show that very different phenomena can be involved: in these two examples relatively independent density fluctuations, or phonon-like behaviour, leading to long-range correlations.

However, in fluid argon far from the critical point, the Fourier transform $c_c(k)$ of $c_c(r)$ has the small k expansion

$$\tilde{c}_\gamma(k) = \text{const} \cdot k^2 + \cdots, \tag{2.6}$$

as will be discussed further in Section 3 below. In this connection, the Fourier transform of $c(r)$ itself is known for fluid argon far from the critical point to have the small k expansion[7,5]

$$\tilde{c}(k) = \tilde{c}(0) + c^{(2)}k^2 + c^{(3)}k^3 + \cdots \tag{2.7}$$

and, as we have stressed already via Eq. (2.5), $c_c(r)$ does not contribute to $c(0)$. Neither does $c_c(r)$ affect the k^3 term in Eq. (2.7), this coming entirely[7] from the asymptotic form $\phi(r) \sim -c_6/r^6$.

3   APPROXIMATE THEORY OF DIRECT CORRELATION FUNCTION $c(r)$ IN TERMS OF POTENTIAL PART $c_p(r)$ AND $S(k)$

To proceed further, we have either to make decoupling assumptions on $g^{(3)}$, which the Born–Green theory shows to be difficult or return to the Ornstein–Zernike relation relating $h(r) = g(r) - 1$ and $c(r)$ through

$$h(r) = c(r) + \rho \int h(r')c(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}'. \tag{3.1}$$

We choose this latter route, since we have separated $c(r)$ into a long-range part $c_p(r)$ and, near the triple point of a liquid like argon, a short-range part $c_c(r)$. Hence from Eq. (3.1) we can write

$$c(r) = h(r) - \rho \int h(r')c_p(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}' - \rho \int h(r')c_c(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}'. \tag{3.2}$$

Now it is clear that in the second convolution integral, since $c_c(r)$ is short range compared with $h(r)$, we can Taylor expand $h(r')$ around the point r to find

$$c(r) = h(r) - \rho \int h(r')c_p(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}'$$

$$- \rho h(r) \int c_c(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}' - \frac{\rho^2}{6} \nabla^2 h(r) \int |\mathbf{r} - \mathbf{r}'|^2 c_c(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}'. \tag{3.3}$$

But our choice of $c_p(r)$ made $\int c_c(r)\, d\mathbf{r}$ vanish according to Eq. (2.5) and if we denote the second moment of $c_c(r)$ by $c_c^{(2)}$:

$$c_c^{(2)} = -\frac{\rho^2}{6} \int r^2 c_c(r)\, d\mathbf{r} \tag{3.4}$$

then we find

$$c(r) = h(r) - \rho \int h(r')c_p(|\mathbf{r} - \mathbf{r}'|)\, \mathrm{d}r' + \nabla^2 h(r)c_c^{(2)}. \tag{3.5}$$

Assuming we can neglect the higher-order terms in the Taylor expansion which is certainly true at large r or small k, we can now Fourier transform Eq. (3.5) to find

$$\tilde{c}(k) = \tilde{h}(k) - \tilde{h}(k)\tilde{c}_p(k) - k^2\tilde{h}(k)c_c^{(2)} \tag{3.6}$$

or

$$\tilde{c}(k) = \tilde{h}(k)[1 - \tilde{c}_p(k) - k^2 c_c^{(2)}]. \tag{3.7}$$

In this approximation, knowledge of the second moment $c_c^{(2)}$ defined by Eq. (3.4) is all that is required about the short-range part $c_c(r)$ in the small k expression (3.7).

3.1   Hard core contribution to $c_c(r)$

As already stressed, $c_p(r)$ is small inside an atomic diameter for a hard core fluid. Hence $c_c(r)$ represents $c(r)$ almost entirely for $r < \sigma$, and in argon can be usefully approximated, say, by the Percus–Yevick hard sphere result, $c_{HS}(r)$, which is zero for $r > \sigma$.

For $r > \sigma$, we take the form

$$c_c(r) = A\, \frac{\exp(-r/l)}{(r/l)} \tag{3.8}$$

where l is determined completely by the second moment $c_c^{(2)}$ in Eq. (3.4). Evidently, from Eq. (2.5) we must have

$$\int_{r<\sigma} c_{HS}(r)\, \mathrm{d}\mathbf{r} + \int_{r>\sigma} c_c(r)\, \mathrm{d}\mathbf{r} = 0 \tag{3.9}$$

which relates the zero moment of $c_{HS}(r)$ to the second moment $c_c^{(2)}$, i.e. to l in Eq. (3.8).

We note that, in the above modelling of $c_c(r)$, there is a marked discontinuity at $r = \sigma$, due to the hard sphere assumption. If we take this discontinuous function, and Fourier transform it we shall find undamped oscillations at large k. Damping these with a factor like $e^{-\alpha k^2}$ will smooth the discontinuity in r space, α being a measure of the softness of the core.

C

4 SUMMARY

In this paper, we have proposed a structural theory of classical fluids based on the decomposition of the direct correlation function into two parts, $c_p(r)$ and $c_c(r)$ in Eq. (2.3). $c_p(r)$ is fixed explicitly in terms of structure and potential by Eq. (2.4) and the important new feature of the present treatment is that the density dependence of the liquid structure factor enters the theory. No closed expression is available for $c_c(r)$, at present, and so it will have to be modelled in a way appropriate to each different physical system.

However, for a hard core fluid like argon, available evidence points to the fact that $c_c(r)$ can be rather well represented by the Percus–Yevick hard sphere approximation $c_{HS}(r)$ for r inside an atomic diameter and by a short-range Ornstein–Zernike form proportional to $e^{-r/l}/r$ for $r > \sigma$; the range l being determined by the second moment of $c_c(r)$.

Calculations are now being planned to test the model proposed here for $c_c(r)$ for dense liquid argon, using the computer simulation studies of Verlet.[8] These, of course, have the merit that both $\phi(r)$ and $g(r)$, together with the density dependence of the structure factor, are all available and hence, in principle, knowledge of both $c(r)$ and $c_p(r)$ will allow $c_c(r)$ to be extracted and compared with the theoretical model proposed in Section 3 of the present paper. Once our proposal for $c_c(r)$ is tested and, if necessary, refined, we intend to proceed to use the present approach to reopen the inverse problem posed by Johnson and March.[1,2] What is abundantly clear from the present paper both in the main text and in the considerations of Appendix 2, is that experiments such as those of Egelstaff et al.[9] on the density dependence of the liquid structure factor will have an important role in successfully extracting quantitative pair potentials from experimental diffraction data. We are also considering extensions of the present approach to treat density dependent potentials in simple liquid metals and to mixtures.

Acknowledgement

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Appendix 1

RELATION BETWEEN POTENTIAL PART OF DIRECT CORRELATION FUNCTION AND THREE-ATOM CORRELATIONS

The potential part $c_p(r)$ of the direct correlation function $c(r)$ defined by Eq. (2.4) can be written explicitly in the form

$$c_p(r) = -\frac{\phi(r)}{K_B T}\left[g(r) + \frac{r}{3}\frac{\partial g(r)}{\partial r} + \frac{\rho}{2}\frac{\partial g(r)}{\partial \rho} + \frac{\rho r}{6}\frac{\partial}{\partial r}\frac{\partial g(r)}{\partial \rho} \right] \quad \text{(A1.1)}$$

In this equation, we can now insert the result[6] for the density derivative of the pair function in terms of the three-atom correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, namely

$$\rho\frac{\partial g(r_{12})}{\partial \rho} = -2g(r_{12})\tilde{c}(0) + \frac{\rho}{S(0)}\int [g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g(r_{12})]\,d\mathbf{r}_3 \quad \text{(A1.2)}$$

and hence we can express $c_p(r)$ in terms of $g(r)$, $\phi(r)$ and $g^{(3)}$ without density derivatives.

However, use of the above expression for $c_p(r)$ to close the Ornstein–Zernike Eq. (3.1) in an approximate theory of structure (which will also involve a modelling of $c_c(r)$), utilizing the equations of BBGKY–hierarchy to eliminate the derivatives with respect to r, will eventually require decoupling of higher order correlation functions in terms of $g(r)$. Decoupling of $g^{(3)}(r)$ will also be necessary, in order to extract information about the interatomic pair potential $\phi(r)$ from available structural evidence, when the change of the structure with density is not known.

Appendix 2

COMPRESSIBILITY RELATED TO PRESSURE P AND TO DENSITY DERIVATIVE OF PAIR FUNCTION

It is clear from Eq. (2.2) that we can relate $(\partial P/\partial \rho)_T$ to P and to density derivatives. Thus

$$\left(\frac{\partial P}{\partial \rho}\right)_T = K_B T - \frac{\rho}{3}\int g(r)r\frac{\partial \phi(r)}{\partial r}\,d\mathbf{r} - \frac{\rho^2}{6}\int \frac{\partial g(r)}{\partial \rho} r \frac{\partial \phi(r)}{\partial r}\,d\mathbf{r}. \quad \text{(A2.1)}$$

Using Eq. (2.2) to eliminate the first integral on the right-hand-side of Eq. (A2.1) we find

$$\left(\frac{\partial P}{\partial \rho}\right)_T = K_B T - \frac{2(P - \rho K_B T)}{\rho} - \frac{\rho^2}{6} \int \frac{\partial g(r)}{\partial \rho} r \frac{\partial \phi(r)}{\partial r} d\mathbf{r}$$

$$= \frac{2P}{\rho} - K_B T - \frac{\rho^2}{6} \int \frac{\partial g(r)}{\partial \rho} r \frac{\partial \phi(r)}{\partial r} d\mathbf{r}. \qquad (A2.2)$$

Clearly the density derivative of $g(r)$ is important at the critical point where $(\partial P/\partial \rho)_T$ is zero, for otherwise we should get $P/\rho K_B T|_{\text{crit point}} = \frac{1}{2}$ whereas for argon a value of ~ 0.28 is observed. The considerations of the present paper point strongly to the importance of $\partial g(r)/\partial \rho$ in dense liquids over a wide range of thermodynamic conditions.