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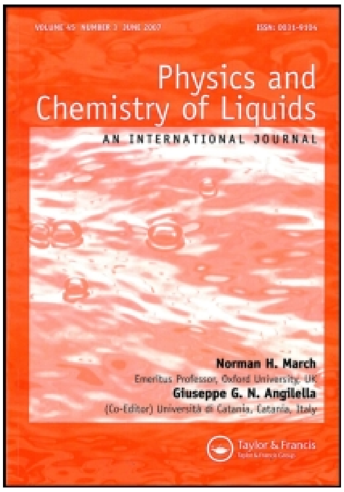

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Thermodynamic Consistency and Classical Liquid Structural Theory

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THERMODYNAMIC CONSISTENCY AND CLASSICAL LIQUID STRUCTURAL THEORY

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For classical liquids, with density-independent pair potentials $\phi(r)$ which possess a Fourier transform, a full study is made of the Born–Green-Yvon equation which links pair correlations, via the three-particle correlation function g_3, with the potential. It is shown that the shape of classical liquid structural theory is thereby determined, the pair potential $\phi(r)$ being given as the difference between a function in r space involving both g_3 and $\phi(r)$, and a convolution of this same function with the Ornstein–Zernike direct correlation function. Into this equation, a decomposition of the direct correlation function is inserted, which is designed to retain thermodynamic consistency between virial and compressibility routes to the equation of state, when approximations to g_3 are introduced, as is presently inevitable in analytical work. Some aspects of the procedure proposed are illustrated using the example of the two-dimensional one-component plasma with an interaction satisfying Poisson's equation in two dimensions.

KEY WORDS: Direct and three-particle correlation functions.

1 INTRODUCTION

Classical structural theories of liquids are, by now, rather numerous. Most of these can be thought of as invoking two basic relations:

1) The definition of the direct correlation function $c(r)$, due to Ornstein and Zernike (see Eq. (2.1) below) and

2) The so-called force equation, or equivalently that member of the Born–Green–Yvon (BGY) classical statistical mechanical hierarchy which relates the pair correlation function $g(r)$ and the three-body function $g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ via the (assumed) density-independent pair potential $\phi(r)$.

In relation to (1) above, it is generally accepted by workers in the field that, far from the critical point, $c(r)$ is related to $\phi(r)$ at sufficiently large r by[1,2]

$$c(r) = -\phi(r)/k_B\mathrm{T};\ \text{large } r \text{ limit.} \tag{1.1}$$

Any acceptable liquid-state theory must therefore contain Eq. (1.1) as a limiting case.

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With regard to point (2) above, closure of the BGY hierarchy is generally accomplished by 'decoupling' g_3 in terms of $g(r)$, the earliest decoupling in $\mathbf{r}$ space being that of Kirkwood[3]:

$$g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g(r_{12})g(r_{23})g(r_{31}). \tag{1.2}$$

Unfortunately, though useful for some purposes, the insertion of Eq. (1.2) into the force equation referred to in point (2) above leads to a theory relating $g(r)$ to $\phi(r)$ which is not quantitative, and in particular does not satisfy the limiting requirement (1.1).

Turning next to a central theme of the present paper, namely thermodynamic consistency, it is generally to be expected that, once g_3 is approximated as in Eq. (1.2), for example, different routes to thermodynamics lead to different predictions. This difficulty was addressed by Kumar *et al.*[4], who pointed out that thermodynamic consistency between the virial and compressibility routes to the equation of state could be maintained by dividing the direct correlation function into two parts:

$$c(r) = c_p(r) + c_c(r). \tag{1.3}$$

These workers then demonstrated that with the choice of the 'potential' part $c_p(r)$ as

$$c_p(r) = -\frac{\phi(r)}{k_B T}\frac{1}{6r^2 n}\frac{\partial^2}{\partial n\,\partial r}[n^2 g(r) r^3], \tag{1.4}$$

then thermodynamic consistency in the above sense was ensured provided only that the 'cooperative' part of $c_c(r)$ satisfied

$$\int c_c(r)\,\mathrm{d}\mathbf{r} = 0. \tag{1.5}$$

The expression (1.4) for $c_p(r)$ is known to be valid both for pair potentials falling off faster than $1/r^3$ in neutral liquids and for the one-component plasma (OCP). For the latter system, it is the charge-compensating background which validates (1.4), even with $\phi(r)$ satisfying Laplace's equation[5].

With the points (1) and (2) above, plus thermodynamic consistency, as guidelines, we shall now set out some general considerations on the shape of an acceptable liquid structure theory. In section 2 immediately below, an $\mathbf{r}$ space treatment of the force equation will be provided, motivated by the early work of Hutchinson[6,7]. Section 3 will then be concerned with the form of the same approach, but with the admittedly restrictive assumption that the pair potential $\phi(r)$ possesses a Fourier transform. In this case, the shape of the theory is shown to be settled by the force equation; though, of course, as set out above, to make the theory quite specific in the sense of providing and explicit relation between pair potential and structure factor, assumptions must be made about the three-body piece of the general theory. Section 4 returns to the still important problem of extracting a pair potential from diffraction measurements of the liquid structure factor, while section 5 constitutes a summary plus some proposals for further work. In an Appendix the example of a two-dimensional one-component plasma with *lnr* interaction is considered in some detail as an example to illustrate the present treatment.

2 r SPACE TREATMENT OF BGY (FORCE) EQUATION

Let us start by making points (1) and (2) above fully quantitative. First, the Ornstein–Zernike direct correlation function $c(r)$ for a liquid of atomic number density n is defined by

$$h(r) = c(r) + n \int h(r')c(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}' \tag{2.1}$$

where $h(r) = g(r) - 1$. This Eq. (2.1) can be solved directly for the Fourier transform $\tilde{c}(k)$ of $c(r)$, the result being quoted in Eq. (3.12) below.

Turning to the so-called force equation referred to in point (2), this reads:

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} + n \int \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} \frac{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(r_{12})}\, d\mathbf{r}_3. \tag{2.2}$$

In this equation, $U(r)$ is the potential of mean force. For the classical liquids which are our sole concern in the present work, this is related by the Boltzmann form

$$g(r) = \exp(-U(r)/k_B T) \tag{2.3}$$

to the pair correlation function $g(r)$.

Hutchinson[6,7] appears to have been the first to exploit the expansion of g_3 in Legendre polynomials. If we adopt the notation $\mathbf{r} = \mathbf{r}_{31}$, $\mathbf{R} = \mathbf{r}_{21}$, $\mathbf{r} \cdot \mathbf{R} = rR \cos\theta$, then taking the scalar product of Eq. (2.2) with the unit vector $\hat{\mathbf{r}}_{12}$ yields, with $\beta = (k_B T)^{-1}$:

$$-\frac{\partial g(R)}{\partial R} - \frac{\beta \partial \phi(R)}{\partial R} g(R) = n\beta \int d\mathbf{r}\, g_3(\mathbf{R}, \mathbf{r}) \cos\theta \frac{\partial \phi(r)}{\partial r}. \tag{2.4}$$

Making next the Legendre polynomial expansion already referred to in the form

$$g_3(\mathbf{R}, \mathbf{r}) = g_3(R, r, \cos\theta) = \sum_{l=0}^{\infty} Q_l(R, r) P_l(\cos\theta) \tag{2.5}$$

the cos $\theta(= P_1(\cos\theta))$ term in Eq. (2.4) removes by orthogonality all the terms in Eq. (2.5), on integration, except $l = 1$, to yield

$$-\frac{\partial g(R)}{\partial R} - \frac{\beta\partial\phi}{\partial R}\,g(R) = \frac{4\pi n\beta}{3}\int_0^\infty dr\, r^2\,\frac{\partial\phi(r)}{\partial r}\,Q_1(R, r). \tag{2.6}$$

Reinserting $U(R)$ from Eq. (2.3) into Eq. (2.6), one then finds

$$\frac{\partial}{\partial R}\,[U(R) - \phi(R)] = \frac{4\pi n}{3}\int_0^\infty dr\, r^2\,\frac{\partial\phi(r)}{\partial r}\,\frac{Q_1(R, r)}{g(R)}. \tag{2.7}$$

Integration can now be formally achieved as

$$\phi(R) = U(R) + \frac{4\pi n}{3}\int_0^\infty ds\, s^2\,\frac{\partial\phi(s)}{\partial s}\,F(R, s) \tag{2.8}$$

where

$$F(R, s) = \int_R^\infty dt\,\frac{Q_1(t, s)}{g(t)}. \tag{2.9}$$

We shall return to Eq. (2.8) at the end of the following section.

3 k-SPACE FORM OF THE FORCE EQUATION

The above argument rests only on the force equation and its solution and not on the existence of Fourier transforms of the potential $\phi(r)$ or of the potential of mean force $U(r)$. However, if it is assumed that $\phi(r)$ has a Fourier transform, then it will now be shown that a good deal of insight can be added to the above discussion.

Replacing $U(r_{12})$ in Eq. (2.1) by, essentially, $ln g(r)$ from Eq. (2.2), one can take as starting point for the Fourier development below the equivalent form of the force equation:

$$\frac{\partial g(r_{12})}{\partial \mathbf{r}_1} = -\beta g(r_{12})\frac{\partial\phi(r_{12})}{\partial \mathbf{r}_1} - n\int d\mathbf{r}_3\,\frac{\partial\phi(r_{13})}{\partial \mathbf{r}_1}\,g_3(\mathbf{r}_{12}, \mathbf{r}_{32}); \quad \beta = (k_B T)^{-1}. \tag{3.1}$$

The next step then is to Fourier analyze the three-particle correlation function g_3 as

$$g_3(\mathbf{r}_{12}, \mathbf{r}_{32}) = \frac{1}{V^2}\sum_{\mathbf{p},\mathbf{p}'}\tilde{g}_3(\mathbf{p}, \mathbf{p}')\exp(i\mathbf{p}\cdot\mathbf{r}_{12})\exp(i\mathbf{p}'\cdot\mathbf{r}_{32}). \tag{3.2}$$

With the admittedly restrictive assumption that $\phi(r)$ has a Fourier transform, we can also write

$$\phi(r_{13}) = \frac{1}{V} \sum_{\mathbf{q}} \tilde{\phi}(q) \exp(i\mathbf{q} \cdot r_{13}). \tag{3.3}$$

Forming the integral term in Eq. (3.1), one finds

$$\int d\mathbf{r}_3 \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} g_3(\mathbf{r}_{12}, \mathbf{r}_{32}) = \frac{i}{V^2} \sum_{\mathbf{q},\mathbf{p}} \mathbf{q}\tilde{\phi}(q)\tilde{g}_3(\mathbf{p}, \mathbf{q}) \exp[i(\mathbf{p} + \mathbf{q}) \cdot \mathbf{r}_{12}]. \tag{3.4}$$

The Fourier transform of Eq. (3.1) then takes the form

$$\mathbf{k}[\delta_{\mathbf{k}} V + \tilde{h}(k)] = -\frac{1}{V} \sum_{\mathbf{q}} \mathbf{q}\beta\tilde{\phi}(\mathbf{q})[V\delta_{\mathbf{k}-\mathbf{q}} + \tilde{h}(|\mathbf{k} - \mathbf{q}|) + n\tilde{g}_3(\mathbf{k} - \mathbf{q}, \mathbf{q})], \tag{3.5}$$

where $\tilde{h}(k)$ is the Fourier transform of the total correlation function $h(r) = g(r) - 1$.

3.1 *Rewriting of three-particle correlation function g_3*

To motivate the rearrangement of Eq. (3.5) below, let us first separate out from g_3 the total correlation functions h and t by writing

$$g_3(\mathbf{r}_{12}, \mathbf{r}_{32}) = 1 + h(r_{12}) + h(r_{32}) + h(r_{13}) + t(\mathbf{r}_{12}, \mathbf{r}_{32}). \tag{3.6}$$

Then Eq. (3.5) can readily be shown to take the form

$$\tilde{h}(k) = -\frac{1}{1 + \beta n\tilde{\phi}(k)} \left[\beta\tilde{\phi}(k) + \frac{1}{V} \sum_{\mathbf{q}} \frac{\mathbf{k} \cdot \mathbf{q}}{k^2} \beta\tilde{\phi}(q) \times \{\tilde{h}(|\mathbf{k} - \mathbf{q}|) + n\tilde{t}(\mathbf{k} - \mathbf{q}, \mathbf{q})\} \right]. \tag{3.7}$$

The liquid structure factor $S(k)$ is then related to $\tilde{h}(k)$ by

$$S(k) - 1 = n\tilde{h}(k) \tag{3.8}$$

so that Eqs. (3.7) and (3.8) provide a direct **k** space relation between potential $\tilde{\phi}(k)$, structure factor $S(k)$ and the part t of the three-particle correlation function separated out in Eq. (3.6). What we shall emphasize below is that, without making an approximation to t as yet, Eq. (3.7) already fixes the general 'shape' that a correct liquid structure theory, based on a model where the pair potential $\phi(r)$ has a Fourier transform, must take. All subsequent approximations should then be inserted in a form which (a) preserves this shape and (b) whenever possible also ensures thermodynamic consistency.

3.2 Form of equation for the potential: introduction of direct correlation function $c(r)$

To expose in the simplest fashion the shape of the theory based on Eq. (3.7), let us define the summation over q appearing there as

$$\Sigma(k) = \frac{1}{V}\sum_{\mathbf{q}} \frac{\mathbf{k}\cdot\mathbf{q}}{k^2}\,\beta\tilde{\phi}(q)\{\tilde{h}(|\mathbf{k}-\mathbf{q}|) + n\tilde{t}(\mathbf{k}-\mathbf{q},\mathbf{q})\} \tag{3.9}$$

Then Eq. (3.7) can be 'solved' for the potential $\tilde{\phi}(k)$ as

$$\frac{\tilde{\phi}(k)}{k_B T} = -\frac{[\tilde{h}(k) + \Sigma(k)]}{S(k)} \equiv -\frac{\tilde{E}(k)}{S(k)} \tag{3.10}$$

where evidently the quantity $\tilde{E}(k)$ is defined by

$$\tilde{E}(k) = \tilde{h}(k) + \Sigma(k). \tag{3.11}$$

3.2.1 **r** *space form of pair potential in terms of direct correlation function* To put Eq. (3.10) into **r** space, one notes from the Ornstein–Zernike definition of $c(r)$ in Eq. (2.1) that

$$\frac{S(k)-1}{S(k)} = \tilde{c}(k). \tag{3.12}$$

Hence, writing $1/S(k)$ appearing in Eq. (3.10) as $(1 - \tilde{c}(k))$, Eq. (3.10) becomes

$$\frac{\tilde{\phi}(k)}{k_B T} = -\tilde{E}(k) + \tilde{c}(k)\tilde{E}(k). \tag{3.13}$$

Inverting the Fourier transform in this equation, and noting that the final, product, term in Eq. (3.13) becomes a convolution in **r** space, one is led to the main result of the above analysis of the force equation as

$$\frac{\phi(r)}{k_B T} = -E(r) + n\int c(r')E(|\mathbf{r}-\mathbf{r}'|)\,\mathrm{d}\mathbf{r}'. \tag{3.14}$$

This Eq. (3.14) reflects the general 'shape' of classical structural theory for the case when $\phi(r)$ has a Fourier transform; Eqs. (3.10) and (3.14) being then equivalent forms of the theory.

This is now the point at which to return to the thermodynamically consistent decomposition in Eqs. (1.3)–(1.5). Eqs. (3.10) and (3.12) then lead to

$$\frac{\tilde{\phi}(k)}{k_B T} = -\tilde{E}(k)[1 - \tilde{c}_p(k) - \tilde{c}_c(k)] \tag{3.15}$$

and

$$\frac{\phi(r)}{k_B T} = -E(r) + n\int c_p(r')E(\mathbf{r}-\mathbf{r}')\,\mathrm{d}\mathbf{r}' + n\int c_c(r')E(\mathbf{r}-\mathbf{r}')\,\mathrm{d}\mathbf{r}'. \tag{3.16}$$

What is to be stressed about this form of Eq. (3.14) is that $c_p(r)$, from Eq. (1.4), already builds in derivatives of $g(r)$ with respect to density n, as well as r derivatives. Since it is known from the early work of Schofield[8] that integrals on g_3 are related to $\partial g(r)/\partial n$, one has in this way already inserted some limited knowledge about g_3 into Eq. (3.16), even before committing oneself to an approximate form for $E(r)$.

3.3 *Relation to Fourier transform of potential of mean force*

The **r** space treatment of section 2 did not, of course, need any assumptions about the existence of Fourier transforms of $\phi(r)$ and $U(r)$. But it is now of interest to assume this, and to recast Eq. (2.8) into a form which can be compared with Eq. (3.10). From Eq. (2.8) one can then write

$$\tilde{\phi}(k) - \tilde{U}(k) = \frac{4\pi n}{3}\int_0^\infty \mathrm{d}s\, s^2 \frac{\partial\phi(s)}{\partial s}\tilde{F}(k, s). \tag{3.17}$$

Direct comparison of Eqs. (3.17) and (3.10) then yields

$$\tilde{E}(k) = -S(k)\tilde{U}(k) + \frac{4\pi n}{3} S(k)\int_0^\infty \mathrm{d}s\, s^2 \frac{\partial\phi(s)}{\partial s}\tilde{F}(k, s). \tag{3.18}$$

This is therefore an alternative form for the three-body piece E into which approximations for g_3 can be introduced. In this context, it is worth noting that by taking the *ln* of Eq. (2.3) and writing $g = 1 + h$, one can expand the *ln* to find the approximation

$$-\frac{\tilde{U}(k)}{k_B T} = \tilde{h}(k) - \frac{1}{2V}\sum_q \tilde{h}(\mathbf{k}-\mathbf{q})\tilde{h}(q) + \cdots. \tag{3.19}$$

This form will be useful to insert in Eq. (3.18) for comparison with another approximation to be introduced below.

4 RELATION TO INVERSE PROBLEM OF EXTRACTING PAIR POTENTIAL $\phi(r)$ FROM DIFFRACTION MEASUREMENTS OF LIQUID STRUCTURE

It is now attractive to view Eq. (3.16) as a starting point for extracting a potential $\phi(r)$ from diffraction measurements on liquid structure; this defines the so-called inverse problem posed in the work of Johnson and March[9]. While using computer simulation within the framework of an iterative predictor-corrector method to bypass the need to approximate g_3, Reatto and co-workers[10] have brought this inverse problem to full fruition for liquid Na near freezing[11], it remains of considerable interest to use classical liquid structure theories to perform this inversion for other cases. Equation (3.16), we propose, may be the basis for this for $\phi(r)$'s which have Fourier transforms, such as those given by pseudopotential theories of effective ion–ion interactions in simple liquid metals like the alkalis.

4.1 *Zeroth order approximations*

Though it is not the purpose of the present paper to investigate this inverse problem in any numerical detail, it is relevant here to mention, as possible starting points in a future numerical study of Eq. (3.16), what zeroth order approximations might be available.

The simplest procedure which comes to mind is then to suppose that one has experimental data not only for $S(k)$, and hence $g(r)$, but also for the density derivative $\partial g/\partial n$. From $S(k)$ one can construct $c(r)$ by Fourier transform of Eq. (3.12). But one can also obtain $c_p(r)$ from the experimental data mentioned above. If $c_c(r) = c(r) - c_p(r)$ thereby constructed from experiment were found to be small, one could immediately extract a useful approximation to $\phi(r)$ from Eq. (1.4), by also inserting experimental data for $c_p(r) \simeq c(r)$ on the left-hand side.

If, however, as one will normally expect to find, $c_c(r)$ extracted from experiment is not sufficiently small to be neglected, at least it will be shorter range than $c_p(r)$, since Eq. (1.4) already tends to $-\phi(r)/k_BT$ at large r (see also further confirmation from the example presented in the Appendix). Under these conditions, the Ornstein–Zernike idea of Taylor expanding $E(\mathbf{r}')$ about the point $\mathbf{r}$ and retaining low-order gradient contributions only may afford a useful way of handling the last term (only!) in Eq. (3.16) in subsequent applications. But then, one has to ask as to the form of $E(r)$ to insert in Eq. (3.16).

4.1.1 *Possible approximations to $E(r)$* Putting $c_c(r) = 0$ as a zeroth-order approximation leads to a potential $\phi(r)$ directly from Eq. (1.4). This approximation is clearly consistent with the requirement (1.5) for thermodynamic consistency. Thus it is of interest to ask what are the implications for choice of $E(r)$ consistent with this assumption. In principle, this question is readily answered by combining Eq. (3.16), after putting $c_c(r) = 0$, with Eq. (1.4). This leads to an integral equation to determine this 'zero order' approximation, say $E_0(r)$. If (see also Eq. (A2) of the Appendix) we write Eq. (1.4) in terms of a function $J(r)$, then one finds immediately:

$$-\frac{c_p(r)}{J(r)} = -E_0(r) + n\int c_p(r')E_0(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}'. \tag{4.1}$$

Inserting $c_p(r)$ using $c(r)$, as well as $J(r)$, from experiment yields an integral equation to solve for E_0. It is then tempting to estimate the size of the omitted term involving $c_c(r)$ in Eq. (3.16) by inserting the approximation $E \simeq E_0$. Unfortunately, however, if this term proves to make a sizeable correction to $\phi(r)$ from Eq. (3.16), one will need to refine $E_0(r)$. Therefore it is useful to consider another route to $E(r)$ afforded by currently still useful liquid state theories.

While the most elementary choice $E(r) \simeq h(r)$, which amounts to putting $\Sigma = 0$ in Eq. (3.11), or $J(r) = 1$ in Eq. (4.1), leads back to the relatively crude random phase approximation, one might choose as an alternative starting point to $E_0(r)$ discussed above the hypernetted chain (HNC) approximation. This corresponds to writing the equation for $\phi(r)/k_BT$ in the form

$$\frac{\phi(r) - U(r)}{k_BT} = h(r) - c(r) = n\int c(r')h(\mathbf{r} - \mathbf{r}')\,d\mathbf{r}' \tag{4.2}$$

In k space this becomes

$$\frac{\tilde{\phi}(k) - \tilde{U}(k)}{k_BT} = \tilde{c}(k)\tilde{h}(k). \tag{4.3}$$

This is readily shown to be equivalent to the choice of $E(r)$ in Eq. (3.14) as having Fourier transform

$$-\tilde{E}^{(k)}_{\mathrm{HNC}} = \frac{S(k)\tilde{U}(k)}{k_BT} + [S(k) - 1]^2 \tag{4.4}$$

Again, this choice would allow experimental input into Eq. (3.16), not only through $c_p(r)$ but also through $E(r)$, since all the quantities appearing in Eq. (4.4) are accessible from diffraction measurements of $S(k)$ for the state under consideration.

5 SUMMARY AND PROPOSALS FOR FURTHER WORK

The main results of the present work are embodied in the equivalent Eqs. (3.10) and (3.14). These settle the 'shape' of the classical liquid structural theory. Inevitably, for analytical work as opposed to computer simulation, the function $E(r)$ appearing in Eq. (3.14) will have to be approximated in general. However, for the two-dimensional OCP with *lnr* interaction, and for the particular coupling strength $\Gamma = 2$, $\tilde{E}(k)$ is completely determined by the pair function of Jancovici plus the Fourier transform of the *lnr* interaction. This may be important for the future in allowing a fully quantitative assessment of the usefulness of specific decoupling approximations for the correlation function g_3.

It should be cautioned, however, that definite restrictions apply to the central Eqs. (1.4) and (3.14). Eq. (1.4), derived by Kumar *et al.* from the requirement of thermodynamic consistency, is based on a density-independent pair potential description. However, for the BGY (force) equation itself, no such constraint exists.

Let us reiterate also that Eq. (3.14) has been derived on the assumption that $\varphi(r)$ has a Fourier transform. In insulating liquids like argon, one should therefore return to the fully **r** space treatment of section 2, with the central Eq. (2.8) derived there. However, whereas the potential $\varphi(R)$ is roughly described by a Lennard-Jones 6-12 law, the potential of mean force $U(R)$, derived say from the measured pair function $g(r)$ using Eq. (2.3), exhibits pronounced oscillations. There must evidently be massive cancellation, in this liquid, in Eq. (2.3) for $\varphi(R)$, between $U(R)$ and the contribution involving $F(R, s)$, which in turn comes from g_3. It follows that accurate representation of g_3 is essential in such a case. It might therefore already be interesting, when suitable measurements of $g(r)$ under pressure become available, to contemplate using Eq. (1.4) directly, with $c_p(r) \simeq c(r)$ assumed, and experimental data inputted for $c(r)$. But we suspect from the example of the two-dimensional OCP in the Appendix that Eq. (1.4) 'overscreens' the potential $\varphi(r)$ at small r, and so such an analysis may not be quantitative deep in the core. However, the bowl of the potential, as well as its tail, might be quantitatively represented already, and, after all, $\varphi(R)$ is reflected directly in $U(R)$ deep in the core.

Finally, though simple metals like liquid Na have density-dependent potentials, it will be of interest for the future, because in pseudopotential representations $\varphi(R)$ does have a Fourier transform, to relate the basic structural Eqs. (3.10) and (3.14) to such electron theory considerations. This should lead in such a case to much deeper insight into the form of $\tilde{E}(k)$. We plan numerical studies on both the homogeneous electron liquid (classical OCP in three dimensions) and on liquid Na, using the present study as the starting point.

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APPENDIX *D*-DIMENSIONAL GENERALIZATIONS AND EXAMPLE OF TWO-DIMENSIONAL ONE-COMPONENT PLASMA (OCP)

As Rashid *et al.*[5] point out, the generalization to D dimensions of the potential part $c_pr)$ of $c(r)$ can be effected as

$$c_p(r) = -\frac{\phi(r)}{k_B T}\frac{1}{2Dr^{D-1}}\frac{\partial^2}{\partial n\,\partial r}\left[n^2 r^D g(r)\right]. \tag{A1}$$

This result evidently reduces to Eq. (1.4) for $D = 3$. The limiting form (1.1) follows in D dimensions also from Eq. (A1) at sufficiently large r. Equation (A1) is valid for the two-dimensional OCP with $\varphi(r) \propto ln r$, to be discussed below.

A1 Two-dimensional OCP with Coulomb interaction satisfying Poisson's equation

Writing $c_pr)$ in Eq. (A1) for $D = 2$ as

$$c_p(r) = -\frac{\phi(r)}{k_B T}J(r) \tag{A2}$$

and utilizing the result of Jancovici[12] for coupling strength $\Gamma = \bar{\beta}\bar{e}^2 = 2$, ($\bar{e}$ and $\bar{\beta}$ being the charge and thermal energy per unit length), namely

$$g(r) - 1 = h(r) = -\exp\left(-\pi n r^2\right) \tag{A3}$$

one finds the result for J in Eq. (A2) as

$$J(r) = 1 + h(r)\left[1 - 2\pi n r^2 + \frac{\pi^2 n^2 r^4}{2}\right]. \tag{A4}$$

Thus, in addition to any nodes in $\varphi(r)$, $c_p(r)$ has nodes arising from $J(r)$ at

(a) $r = 0$ since $h(r = 0) = -1$

and

(b) r_n given by

$$1 + h(r_n)\left[1 - 2\pi n r_n^2 + \frac{(\pi n r_n^2)^2}{2}\right] = 0. \tag{A5}$$

Evaluating $c_c(r = 0)$ from the Ornstein–Zernike relation (2.1) yields also

$$-1 = c_c(r = 0) + \int h(r)c_p(r)\,d\mathbf{r} + \int h(r)c_c(r)\,d\mathbf{r}. \tag{A6}$$

Inspection of the plot of Rashid *et al.*[5] shows that $c_c(r = 0) \sim -1$, ie., the sum of the two integrals is small. The first integral is, in fact, calculable from Eqs. (A2), (A4) and (A3) but we shall not give further detail.

For the present example, we note that the long wavelength behaviour of $S(k)$ can be calculated from the compressibility rule and fluctuation-dissipation theorem to be

$$S(k) \simeq \frac{k^2}{K_D^2} - \frac{k^4}{K_D^4}\left(1 - \frac{\Gamma}{4}\right): \quad k \to 0, \tag{A7}$$

which is derivable from Eq. (A3) for the special case $\Gamma = 2$. Here K_D denotes the Debye wave number: $K_D^2 = 2\pi \bar{e}^2 n \bar{\beta}$.

Furthermore, the total correlation function $h(r)$ can be obtained at small r as

$$h(r) = -1 + (r/R)^\Gamma; \quad r \to 0 \tag{A8}$$

which again is compatible with Jancovici's result (A3) for the case $\Gamma = 2$. In Eq. (A8), R is related directly to the areal density n.

Some progress can be made with the summation $\Sigma(k)$ introduced in the main text. When Eq. (3.9) is combined with the decoupling approximation (A11) below, the long wavelength formula is found to be

$$\Sigma(k) = -\frac{k^2}{8\pi n^2} \equiv \frac{\Gamma k^2}{4K_D^2}: \quad k \to 0. \tag{A9}$$

This reproduces the exact result (A.7) when substituted into Eq. (3.7) via (3.9).

To conclude the Appendix, however, let us return to the central question of the three-particle piece of the BGY equation for all k. This is subsumed into $\tilde{E}(k)$, which in turn is related to the Fourier transform of the pair interaction potential $\varphi(r)$ by Eq. (3.10). We note here that since the present model is characterized by

$$\tilde{\varphi}(k) = \frac{2\pi \bar{e}^2}{k^2} \tag{A10}$$

then

$$-\frac{k^2}{2\pi \bar{e}^2}\tilde{E}(k) = S(k). \tag{A11}$$

But for $\Gamma = 2$, $S(k) - 1$ is given by the Fourier transform of Eq. (A3), and hence $\tilde{E}(k)$ is known in exact form for this particular coupling strength $\Gamma = 2$. This is what one is led to from the BGY equation, once both $\tilde{\phi}(k)$ and $S(k)$ are known.

As to the three-particle correlation function itself, and in particular the part denoted by t in the main text, a useful closure approximation is given in this model problem by

$$t(\mathbf{k} - \mathbf{q}, \mathbf{q}) = h(\mathbf{k} - \mathbf{q})h(q) + h(\mathbf{k} - \mathbf{q})h(k) + h(q)h(k) + nh(\mathbf{k} - \mathbf{q})h(q)h(k). \tag{A12}$$

Though, of course, Eq. (A12) is certainly approximate for a general coupling strength Γ, it can be shown that it satisfies the compressibility sum rule for all Γ. In the same context, it is worthy of note that in this same model one has the exact result[13,14] for the pressure p:

$$\frac{\bar{\beta} p}{n} = 1 - \frac{\Gamma}{4} \tag{A13}$$

One expects that the decomposition of $c(r)$ into $c_p(r)$ in Eqs. (A2) and (A4) at $\Gamma = 2$ and $c_c(r)$, subject only to Eq. (1.5), will lead back to Eq. (A13) for $\Gamma = 2$.