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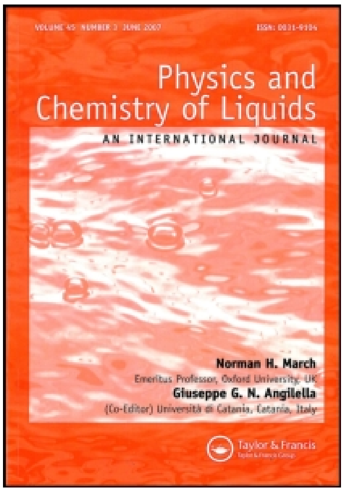

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Golden, K. I. and March, N. H.(1994) 'Liquid Structural Theories of Two- and Three-Dimensional Plasmas', Physics and Chemistry of Liquids, 27: 3, 187 — 193
To link to this Article: DOI: 10.1080/00319109408029524
URL: http://dx.doi.org/10.1080/00319109408029524

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Phys. Chem. Liq., 1994, Vol. 27, pp. 187–193
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LETTER

Liquid Structural Theories of Two- and Three-Dimensional Plasmas

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(Received 1 May 1993)

Following a treatment of a two-dimensional and one-component plasma (OCP) with a ln r interaction which possesses a Fourier transform, proposals are made for a generalized structural theory in three dimensions, based on a separation of the direct correlation function into a "long" and a "short" range part.

KEY WORDS: Three-atom correlation function, Liquid metals, One-component plasma.

In this Letter, previous progress[1–3] in formally solving the lowest-order member of the Born–Green–Yvon (BGY) hierarchy for an assumed pair potential $\phi(r)$ possessing a Fourier transform $\tilde{\phi}(k)$ will be applied and also generalized. The main application considered is a two-dimensional (2D) one-component plasma (OCP) with a ln r interaction, though an outline is also given of a proposed approach to a liquid structural theory for a three-dimensional plasma such as liquid Na or K near freezing. The generalization effected is to exhibit the r space 'shape' of a general structural theory, avoiding now the need for $\phi(r)$ to possess a Fourier transform.

We first carry out k-space calculations which assume that the pair potential $\phi(r)$ possesses the Fourier transform $\tilde{\phi}(k)$. This will set the stage for the calculations involving the more general non-Fourier transformable $\phi(r)$ below.

It can be shown[3] that $\tilde{\phi}(k)$ can be written in terms of the liquid structure factor $S(k)$, where $(1/n)[S(k) - 1] = \tilde{h}(k)$ is the Fourier transform of $g(r) - 1$: $g(r)$ is the pair correlation function. The somewhat formal result is[3]

$$\frac{\tilde{\phi}(k)}{k_B T} = -\frac{\tilde{E}(k)}{S(k)}, \tag{1}$$

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where $\tilde{E}(k)$ involves both the three-particle correlation function g_3 and the force $-\partial\phi(r)/\partial\mathbf{r}$. The **k**-space analysis of the BGY equation provides

$$\tilde{E}(k) = \tilde{h}(k) + \sum(\mathbf{k}), \tag{2}$$

where

$$\sum(\mathbf{k}) = \frac{1}{V}\sum_q \frac{\mathbf{k}\cdot\mathbf{q}}{k^2}\,\beta n\tilde{\phi}(q)\{\tilde{h}(|\mathbf{k}-\mathbf{q}|) + n\tilde{t}(\mathbf{k}-\mathbf{q},\mathbf{q})\}: \tag{3}$$

$\beta^{-1} \equiv k_BT.$ In Eq. (3), $\tilde{t}$ is the Fourier transform of t in the **r**-space expression

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

Generally to make progress in calculating $\sum(\mathbf{k})$, one must decouple g_3. In the case of the 2D OCP with $\ln r$ interaction, however, the pair function $g(r)$ has been calculated exactly by Jancovici[4] for a particular coupling strength $\Gamma = \bar{\beta}\bar{e}^2 = 2$($\bar{\beta}^{-1}$ and $\bar{e}$ are thermal energy per unit length and charge per unit length); Jancovici obtained $g(r) = 1 - \exp(-r^2/a^2)$, whence $S(k) = 1 - \exp(-k^2a^2/4)$; a is the 2D Wigner–Seitz radius. Consequently, for this particular reference liquid, $\tilde{E}(k)$ can be exactly calculated from Eq. (1) since $\tilde{\phi}(k) = 2\pi\bar{e}/k^2$. One obtains

$$-\frac{k^2}{2\pi\bar{e}^2\bar{\beta}}\,\tilde{E}(k) = S(k). \tag{4}$$

The left-hand side of Eq. (4) versus wavenumber ka is plotted in Figure 1 (see also Golden *et al.*[5]) The continuous curve shows the exact value of $\tilde{E}(k)$ given by Eq. (4) with $S(k) = 1 - \exp(k^2a^2/4)$. This can now be used as a standard for comparison in assessing the accuracy of two well known approximate theories.

The simplest approximation for $\tilde{E}(k)$ is to put $\sum(\mathbf{k}) = 0$ in Eq. (2) Then $n\tilde{E}(k) = S(k) - 1$, whence Eq. (1) simplifies to the well-known Debye–Hückel (DH) formula.

$$\beta n\tilde{\phi}(k) \approx -\tilde{c}(k); \tag{5}$$

$\tilde{c}(k) = 1 - 1/S(k)$ is the Fourier transform of the direct correlation function $c(r)$. This approximation evidently uses the asymptotic form for $c(r)$, namely $c(r) = -\beta\phi(r)$, outside its proper range of validity. Nevertheless, it is of interest to note the result

$$-\frac{k^2}{2\pi\bar{e}^2\bar{\beta}}\,\tilde{E}_{DH}(k) = \frac{k^2a^2}{4}\exp\left(-\frac{k^2a^2}{4}\right) \tag{6}$$

as the dash-dot-dash curve of Figure 1 (see also Ref. [5]).

Transcending the DH approximation, the hypernetted chain (HNC) formula is

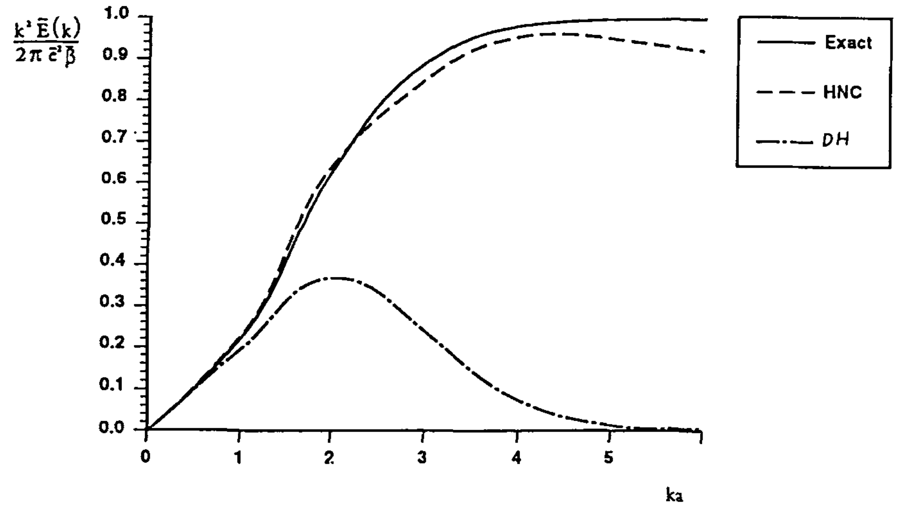

Figure 1 The function $[k^2/(2\pi\bar{e}^2\bar{\beta})]\tilde{E}(k)$ versus ka for the 2D OCP with ln r interaction potential. The solid curve is exact; the dash-dot-dash curve represents the Debye-Hückel approximation; and the dash curve represents the hypernetted chain approximation.

given by[3]

$$\tilde{E}_{HNC}(k) = -\frac{1}{n}\bar{\beta}\tilde{U}(k)S(k) - \frac{1}{n}\left[S(k) - 1\right]^2, \tag{7}$$

where

$$\begin{aligned}\bar{\beta}\tilde{U}(k) &= 2\pi n\int_0^\infty dr\,rJ_0(kr)\ln\left[1 - \exp\left(-\frac{r^2}{a^2}\right)\right] \\ &= \sum_{p=1}^{\infty}\frac{1}{p^2}\exp\left(-\frac{k^2a^2}{4p}\right)\end{aligned} \tag{8}$$

is calculated via the potential of mean force, $U(r)$, derived from the definition $g(r) = \exp[-\bar{\beta}U(r)]$ and the exact pair correlation function, $g(r) = 1 - \exp(-r^2/a^2)$, for the 2D OCP at $\Gamma = 2$. The formula for $-k^2\tilde{E}_{HNC}(k)/(2\pi\bar{e}^2\bar{\beta})$ which follows from Eqs. (7) and (8) is displayed as the dash curve in Figure 1.

Not surprisingly, the HNC result (7) fits better with the exact form (4) than the DH result (6) though neither tends at large k to a finite constant given by the exact theory. It is, of course, of considerable interest that for the value of $\Gamma = 2$ of the coupling strength, one has an exact test of the accuracy of approximate structural theories.

Up to this point, the structure of the BGY equation for potentials $\phi(r)$ which possess a Fourier transform has been exploited. But for a liquid like argon, the

Lennard-Jones 6–12 potential is a reasonable zeroth order approximation and this does not have a Fourier transform. Our purpose below is therefore to recast the theory into an **r** space form applicable to more general pair potentials.

To do so, let us start by subtracting $\beta\tilde{U}(k)$ from both sides of Eq. (1) and introducing the function $\tilde{F}(k) = n\tilde{E}(k) + \beta\tilde{U}(k)$. Taking the inverse transform of the result, one then obtains

$$\frac{\phi(r) - U(r)}{k_B T} \equiv -\frac{\Delta(r)}{k_B T} = -F(r) + n\int F(|\mathbf{r} - \mathbf{r}'|)c(r')d\mathbf{r}', \tag{9}$$

where $F(r)$ is evidently the inverse transform of $\tilde{F}(k)$. Below, Eq. (9) will be solved on the assumption that though $\phi(r)$ and $U(r)$ do not separately have Fourier transforms, the difference $\Delta(r)$ does.

With this assumed, the Fourier transform of Eq. (9) gives

$$\frac{\tilde{\Delta}(k)}{k_B T} = -\tilde{F}(k) + \tilde{F}(k)\tilde{c}(k). \tag{10}$$

The simplest application of Eq. (10) is now to relate to the often useful, though clearly approximate, HNC approximation. To motivate such a relation, we recall that at large r, $\phi(r) \to -k_B Tc(r)$ and $U(r) \to -k_B Th(r)$, whence

$$\frac{\phi(r) - U(r)}{k_B T} \equiv -\frac{\Delta(r)}{k_B T} \to h(r) - c(r);\ \underline{\text{large-r limit}}, \tag{11}$$

Guided by Eq. (11), we are led to write its small-k counterpart in the form

$$\frac{\tilde{\Delta}(k)}{k_B T} = [S(k) - 1] - \tilde{c}(k) + \delta(\Gamma);\ \underline{\text{small-}k\text{ limit}}, \tag{12}$$

where

$$\delta(\Gamma) = n\int d\mathbf{r}\ \ln g(r) + 1 - \beta\left(\frac{\partial p}{\partial n}\right)_T - S(0)\tilde{c}(0).$$

The k-independent $\delta(\Gamma)$ correction guarantees the *exactness* of Eq. (12) through $O(k^0)$; the coupling parameter, Γ, which was introduced above for the 2D OCP with $\ln r$ interaction, is generally defined to be the ratio of the average interaction energy to the thermal energy; e.g., $\Gamma = \beta(Ze)^2/a$ for the 3D ionic OCP with charge Ze. We note that in the weak coupling limit ($\Gamma \ll 1$), $\delta(\Gamma) = -\Gamma/4$ for the 2D OCP with ln r interaction. Eq. (12) is a valuable result for what follows.

We turn now to the "inverse" problem of classical liquid structure theory. The so-called "inverse" problem, namely the extraction of the pair potential $\phi(r)$ from diffraction measurements, was proposed by Johnson and March[6]. They recognized that the force (BGY) equation again provided the fundamental route. But then, decoupling of g_3 is required[1] which is often uncontrolled and violates the correct limiting result $c(r) \to -\beta\phi(r)$ at large r, and this does not permit the required accuracy to extract $\phi(r)$. Though the decoupling of g_3 has been bypassed in the work of Reatto[7] and co-workers, the price paid is to invoke computer simulation as the "corrector" in an iterative predictor-corrector technique. It remains of considerable importance to have a largely analytical solution of this inverse problem.

To this end, we outline a proposed solution by returning to the thermodynamically consistent decomposition of Kumar *et al.*[2] of the direct correlation function: they write $c(r) = c_p(r) + c_c(r)$, where $c_p(r)$ and $c_c(r)$ are the "potential" and "cooperative" parts. Keeping this decomposition in mind, Eq. (10) can be rewritten as

$$\tilde{c}_p(k) + \tilde{c}_c(k) = \frac{\beta\tilde{\Delta}(k)}{\tilde{F}(k)} + 1. \tag{14}$$

Kumar *et al.*[2] emphasized that the virial and compressibility routes to the equation of state were thermodynamically consistent, provided only that the cooperative part $c_c(k) \to 0$ as $k \to 0$; thus $\tilde{c}_p(k) \to \tilde{c}(k) = 1 - 1/S(k)$ in this limit. This property and the structure of Eq. (12) suggest rewriting the right-hand side of Eq. (14) as follows:

$$\begin{aligned}\tilde{c}_p(k) + \tilde{c}_c(k) &= 1 + \frac{[S(k) - 1 - \tilde{c}(k)] + \delta(\Gamma)}{\tilde{F}(k)}\\ &\quad + \frac{(\beta\tilde{\Delta}(k) - [S(k) - 1 - \tilde{c}(k)]) - \delta(\Gamma)}{\tilde{F}(k)}.\end{aligned} \tag{15}$$

Since we have now arranged the last term on the right-hand side of Eq. (15) to tend to zero as $k \to 0$ from Eq. (12), we propose the "closure" of the present theory by identifying $\tilde{c}_p(k)$ as the first two right-hand side terms of (15), whence

$$[\tilde{c}(k)]^2 = -\frac{\tilde{F}(k)}{S(k)}[1 - c_p(k)] - \frac{\delta(\Gamma)}{S(k)}. \tag{16}$$

The final step in reaching the proposed solution of the inverse problem is to combine Eqs. (16) and (10). One obtains

$$\beta\tilde{\Delta}(k) = \frac{[\tilde{c}(k)]^2 + \delta(\Gamma)[1 - \tilde{c}(k)]}{1 - \tilde{c}_p(k)} \tag{17}$$

with its **r**-space counterpart

$$\begin{aligned}\Delta(r) - n\int d\mathbf{r}'\Delta(r')c_p(|\mathbf{r} - \mathbf{r}'|)\\ = k_B T n\int d\mathbf{r}'c(r')c(|\mathbf{r} - \mathbf{r}'|) - k_B T\delta(\Gamma)c(r);\ \mathbf{r} \neq 0.\end{aligned} \tag{18}$$

Eq. (9), which is formally exact, and the approximate Eq. (18) represent the principal results of this Letter. Eq. (18) is expected to be especially accurate at large r because of the underlying requirement of thermodynamic consistency; at small r, it is less satisfactory. By contrast, the complementary HNC structure

$$\Delta(r) - n\int d\mathbf{r}'\Delta(r')c(|\mathbf{r}-\mathbf{r}'|) = k_BTn\int d\mathbf{r}'c(r')c(|\mathbf{r}-\mathbf{r}'|) \tag{19}$$

is more satisfactory at small r, but is less accurate at large r.

Of course, in applying Eq. (18) to extract $\phi(r)$, one has immediately to recall from Ref. [2] that $c_p(r)$ involves $\phi(r)$ itself as well as T, n and $g(r)$. Therefore, for a given thermodynamic state, $c_p(r)$ is uniquely determined in terms of $\phi(r)$ provided diffraction measurements on $S(k)$ and also its density derivative $\partial S(k)/\partial n$ are made. Thus with a starting approximation to $\phi(r)$, say $\phi_0(r)$, experimental data then determine completely the right-hand side of Eq. (18), and hence a first approximation $\beta\phi_1(r)$ since $-\beta U(r) = \ln g(r)$ is also known from the diffraction measurements. One then recalculates $c_p(r)$ with this reset approximation to $\phi(r)$, and iterates to self consistency.

The essential points of this Letter can be summarized as follows. The shape of classical liquid structure theory is determined by the solution of the force equation (1) [with (2)]. This leads to an $\mathbf{r}$ space theory in which the difference between the pair potential $\phi(r)$ and the potential of mean force $U(r)$, denoted throughout this Letter by $\Delta(r)$, is a central quantity for the theory. Provided that $\Delta(r)$ has a Fourier transform (FT) $\tilde{\Delta}(k)$, even when such FTs do not exist for $\phi(r)$ and $U(r)$ separately, one can write $\Delta(r)$ precisely as the difference between a function $F(r)$ and the convolution of this same function with the direct correlation function $c(r)$ as in Eq. (9).

If one makes contact, for example, with HNC approximation of classical liquid structure theory, then the FT of $F(r)$, is $\tilde{F}_{HNC}(k) = -[S(k)-1]^2$, where $S(k)$ is the liquid structure factor. Guided by the HNC structure for $\Delta(r)$ at large r, we formulate its small-k counterpart $\tilde{\Delta}(k)$ in a way which guarantees thermodynamic consistency at $k \to 0$. To set up a theory of $\tilde{F}(k)$ for all k, the thermodynamically consistent decomposition of $c(r)$ into the sum $c_p(r) + c_c(r)$ is finally invoked. A form of $\tilde{F}(k)$ and ultimately $\Delta(r)$ [Eq. (18)] is then proposed solely in terms of $c(r)$ and $c_p(r)$, the latter depending in an explicitly known way on $\phi(r)$, $g(r)$, and the density derivative of the pair function.

In summary, the 2D OCP has been considered within an exact liquid structural theory for one coupling strength $\Gamma = 2$. Comparison has been made with the Debye–Hückel and HNC approximations. Then, the shape of an $\mathbf{r}$ space theory avoiding the assumption that the pair potential $\phi(r)$ has a Fourier transform has been exposed. Finally, an outline proposal is presented, based on a separation of the direct correlation function $c(r)$ into "potential" and "cooperative" parts, which may well have application to three-dimensional plasmas such as liquid Na or K.

K.I.G. would like to thank Professor N. H. March and the Theoretical Chemistry Department at the University of Oxford for hospitality. K.I.G.'s contributions to this research have been partially supported by U.S. National Science foundation Grants

PHY-9115695 and INT-9215300, and by a visiting fellowship from the Institute of Advanced Studies at the Australian National University.

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