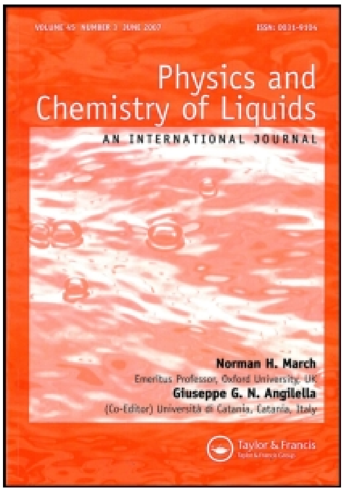

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Some Tests of a Thermodynamically Consistent Decomposition of Fluid Direct Correlation Functions

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A study is made of the decomposition of a fluid direct correlation function into two parts, $c(r) = c_p(r) + c_c(r)$ with c_p determined by the potential, and c_c representing cooperative effects, in two situations:

i) A two-dimensional Coulomb plasma with coupling constant $\Gamma = 2$.

ii) A condensed rare gas state near the triple point. In each case, $c_p(r)$ is determined by (a) the pair potential $\phi(r)$, (b) the pair function $g(r)$ and (c) the density and spatial derivatives of $g(r)$.

In case (i) the 'correction' $c_c(r)$ to $c_p(r)$ is small outside a suitably chosen core radius. Case (ii) is somewhat less decisive, partly because of inaccuracies in the experimental data. However, it seems probable that $c_p(r)$ approaches $c(r)$ at large r in a more complicated manner than in example (i).

1 INTRODUCTION

It has become increasingly clear that tractable and useful theories of liquids involve the direct correlation function $c(r)$ in an intimate way. However, all available simple integral equations describing relations between $c(r)$, the pair potential $\phi(r)$ and the pair function $g(r)$ are known to suffer from varying degrees of thermodynamic inconsistency. This is also true of the simplest approach with a degree of realism, namely the mean spherical approxima-

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tion, in which the direct function $c(r)$ is assumed to be related to $\phi(r)$ right into some core diameter σ say, according to

$$c(r) = \frac{-\phi(r)}{k_B T} \qquad r > \sigma. \tag{1.1}$$

This relation (1.1) is, however, known to be valid for sufficiently large r for thermodynamic states sufficiently far from the critical region in simple insulating liquids like Ar, or in the absence of collective modes such as exist in liquid Rb.

For reasons of consistency between virial and long-wave compressibility results, we proposed in earlier work[1,2] to divide $c(r)$ into two parts, namely

$$c(r) = c_p(r) + c_c(r). \tag{1.2}$$

The 'potential' contribution $c_p(r)$ was again chosen to embody the asymptotic condition (1.1) at sufficiently large r. The new feature of the choice of $c_p(r)$, however, was that it involved the density derivative $\partial g(r)/\partial\rho$ of the pair function. This latter point is physically appealing because the exact integral equation of classical statistical mechanics[3] relating potential ϕ and structure $g(r)$ involves the three-particle correlation function g_3. This correlation function is known to be related, in turn, to the density derivative of $g(r)$.[4]

So far, no closed theory of the 'correction' $c_c(r)$ in the Eq. (1.2) exists. However, $c_p(r)$ contributes the whole of the isothermal compressibility calculated from $c(r)$, which implies

$$\int c_c(r) d^d r = 0 \tag{1.3}$$

where the 'volume' integration has to be carried out in the appropriate dimensionality d for the system under examination.

The outline of the present paper is then as follows. In Section 2 immediately below, we treat the two-dimensional Coulomb plasma at a coupling strength $\Gamma = 2$ where everything is known analytically.[5] Hence c_p, c_c and c can all be exhibited precisely. Section 3 is concerned with Ar near its triple point, while the Appendix deals briefly with the dilute regime of Kr. Section 4 constitutes a summary of the main conclusions from this study.

2 DECOMPOSITION OF *c(r)* FOR THE STATE $\Gamma = 2$ OF TWO-DIMENSIONAL PLASMA

In d-dimensions, the formula for the 'potential' part $c_p(r)$ of the direct correlation function can be written

$$c_p(r) = \frac{-\phi(r)}{k_B T} \frac{1}{2d\rho r^{d-1}} \frac{\partial^2}{\partial\rho\, \partial r} [\rho^2 r^d g(r)]. \tag{2.1}$$

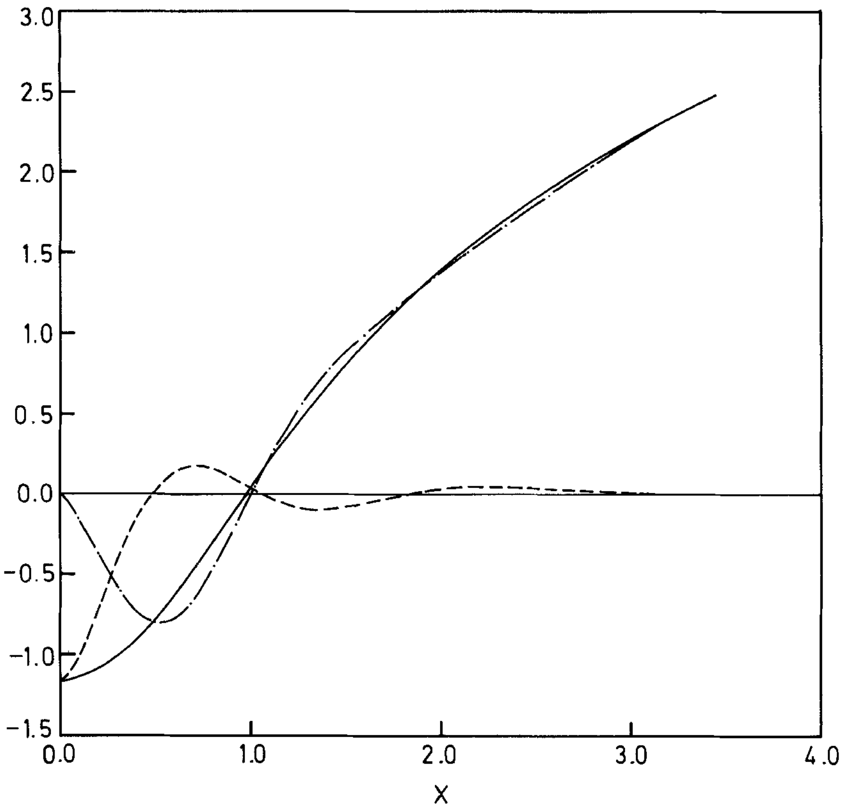

FIGURE 2.1 Plots of the direct correlation function $c(x)$ ——, the potential part $c_p(x)$ — • — • — and the correction to the potential part $c_c(x)$ — — — as a function of x for a two-dimensional Coulomb plasma with coupling constant $\Gamma = 2$.

This formula (2.1) can be written for pair potentials decaying faster than r^{-d} in d-dimensions for neutral systems. In overall neutral plasmas, however, the charge-compensating background validates Eq. (2.1) even with $\phi(r)$ as a solution of Laplace's equation in d-dimensions.

For the special state $\Gamma = 2$, the pair function $g(r)$ of the two-dimensional Coulomb plasma has the closed form[5]

$$g(r) = 1 - \exp(-\pi\rho r^2) \tag{2.2}$$

and hence, writing the independent variable $x = r(\pi\rho)^{1/2}$,

$$c_p(x) = 2\ln x\left\{1 - \exp(-x^2)\left[1 - 2x^2 + \frac{x^4}{2}\right]\right\}. \tag{2.3}$$

Using the Ornstein–Zernike convolution relating $g(r)$ and $c(r)$ yields, from Eq. (2.2) the result[6]

$$c(x) = -2\gamma - \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \zeta(n+1) x^{2n}. \tag{2.4}$$

where γ is Euler's constant and ζ denotes Riemann's function.

Figure 2.1 shows $c(x)$, $c_p(x)$ and $c_c(x)$ calculated for $\Gamma = 2$ from Eqs (2.4), (2.3) and (1.2) respectively. It is plain that, outside a 'core' region corresponding approximately to $x = 1$, $c(x)$ is well approximated by the potential part $c_p(x)$. However, for $x < 1$, $c_c(x)$ rapidly becomes of comparable or greater importance than $c_p(x)$. At $x = 0$, $c_c(x) = c(x)$. In connection with the degree of agreement between $c_p(x)$ and $c(x)$ beyond $x = 1$, it should be noted that, in fact the mean spherical approximation (1.1) reproduces $c(x)$ more accurately into smaller x than does $c(x) \cong c_p(x)$. Nevertheless, $c_p(x)$ soon approaches $-\phi/k_B T$ in this example.

Of course, the ultimate usefulness of the decomposition (1.2) will rest on whether c_c can be usefully approximated from theory or modelled. As to the latter, it is oscillatory and rapidly damped, decreasing by 3 orders of magnitude from $x = 0$ to $x = 3$.

3 CONDENSED RARE GAS PHASE NEAR TRIPLE POINT

As a second example, we briefly record the results of an analysis we have carried out of liquid Ar data[7] near the triple point.

Unlike the previous case, where analytical formulas were available, we meet here immediately the problem of handling data of limited accuracy.

Raveché and Mountain[8] have used the diffraction data of Mikolaj and Pings[9] to calculate numerically the density derivative of $g(r)$. We have used the same data, with the Lennard–Jones 6–12 potential $\phi(r)$ with parameters $\sigma = 3.405$ Å and $\varepsilon/k_B = 119.8$ K taken from Mikolaj and Pings,[10] to calculate $c_p(r)$ and the result is shown in Figure 3.1. The direct correlation function $c(r)$ also shown.

The subtraction of these two curves leaves a 'noisy' form of $c_c(r)$ that we have also recorded in the figure. However, we have the impression that it is of a considerably more complex structure than that found in the previous example.

It is clear that decisive conclusions for thermodynamic states near the triple point must await more accurate data, either from diffraction experiments or from computer simulation, which enable accurate numerical differentiation to be carried out to obtain both spatial and density derivatives of $g(r)$.

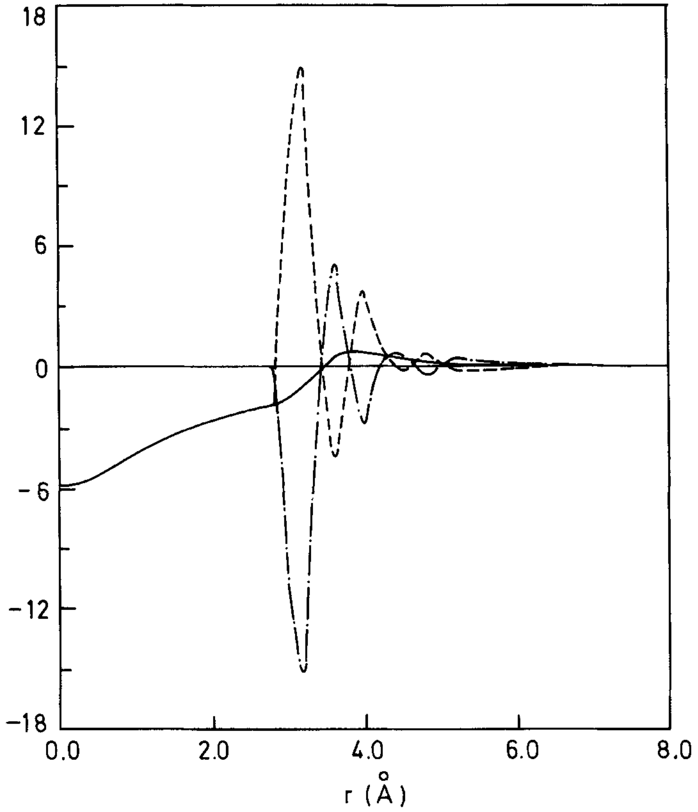

FIGURE 3.1 Plots of the direct correlation function $c(r)$ ———, the potential part $c_p(r)$ — •— • — and the correction to the potential part $c_c(r)$ — — — as a function of position r for a dense Argon fluid. Experimental data[7] are used to obtain these curves.

4 SUMMARY AND CONCLUSIONS

Of the two examples considered here, the two-dimensional Coulomb plasma is definitely encouraging from the point of view of a decomposition of the direct correlation function which immediately ensures thermodynamic consistency. The 'correction' to the precisely defined potential contribution $c_p(r)$ is small outside the core though this correction $c_c(r)$ is entirely dominant in $c(r)$ near $r = 0$ for the Coulomb plasma. It is difficult to be decisive for the second example of dense fluid Ar near its triple point, though our impression is that $c_c(r)$ is more important, and more complex in this case. Better data is clearly called for to draw final conclusions in this thermodynamic regime. The treatment of the dilute gas regime in the Appendix shows that the decomposition is to be used only for dense states or when cooperative effects are expected.

One important point made earlier is worth finally reemphasizing. The present study makes it rather clear that structural theories based on a single density are unlikely to be quantitatively successful, thermodynamic consistency being bound up with the force equation relating g, ϕ and the three-particle function g_3. It seems plain to us that g_3 at a particular density is not to be usefully approximated in terms of $g(r)$ solely at that density.

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Appendix Dilute rare gas states

In this Appendix we are concerned with the regime of low densities, where correlation functions can be developed usefully in a power series in ρ.[11] Defining the Mayer function $f(r)$ as usual by

$$f(r) = e^{-\phi/k_BT} - 1 \tag{A.1}$$

we have

$$c(r) = f(r) + O(\rho) \tag{A.2}$$

while

$$g(r) = f(r) + O(\rho). \tag{A.3}$$

Using the definition (2.1) for $d = 3$, we readily obtain

$$c_p(r) = \ln(f+1)\left[f + 1 + \frac{r}{3}\frac{\partial(f+1)}{\partial r}\right] + O(\rho). \tag{A.4}$$

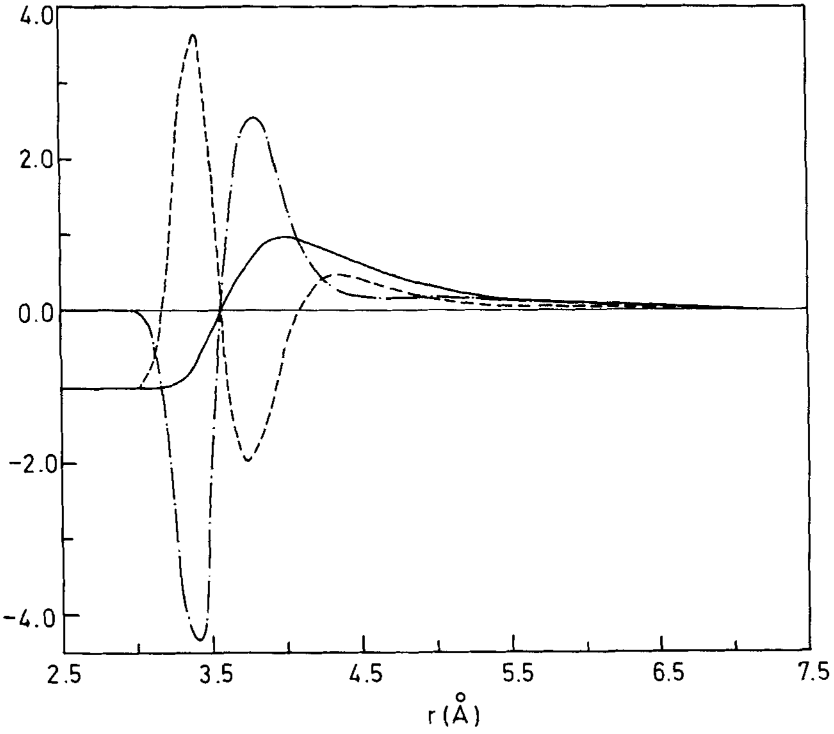

FIGURE A.1 Same as Figure 3.1 but for dilute Krypton fluid.

It follows immediately that the 'correction' $c_c(r)$ is

$$c_c(r) = f - \ln(f+1)\left[f + 1 + \frac{r}{3}\frac{\partial(f+1)}{\partial r}\right] + O(\rho). \tag{A.5}$$

After some manipulation, it can be shown that the form exhibited explicitly in Eq. (A.5) does indeed satisfy the sum rule (1.3). It is relevant here to mention the early work of Nijboer and van Hove[12] who studied thermodynamic consistency in the context of the virial expansion.

Figure A.1 shows the plots of $c(r)$, $c_p(r)$ and $c_c(r)$ using a Barker *et al.*[13] potential at 297 K for Kr. The conclusions are that both $c_p(r)$ and $c_c(r)$ contribute substantially to $c(r)$. No advantage appears to be gained here from the division of $c(r)$: this procedure should clearly be restricted to dense fluids and/or regimes where cooperative or critical effects are expected on physical grounds.