ORNSTEIN–ZERNIKE RELATION FOR A DISORDERED FLUID

By R. J. Baxter*

[*Manuscript received April* 4, 1968]

Summary

The Ornstein–Zernike equation for a homogeneous fluid relates the direct correlation function $c(r)$ and the indirect correlation function $h(r)$. In this paper it is shown that if $c(r)$ vanishes beyond a range R then a third function $Q(r)$ can be introduced which is related to $c(r)$ and $h(r)$ by equations that involve the functions only over the range $(0,R)$. The analytic solution of the Percus–Yevick approximation for hard spheres can then be obtained very simply and, as $c(r)$ normally tends rapidly to zero with increasing r, it is expected that the results should be of use in numerical calculations based on the Percus–Yevick, convolution-hypernetted chain, or similar approximations.

I. Introduction

The Ornstein–Zernike (OZ) relation (Ornstein and Zernike 1914) for a classical homogeneous fluid with central forces can be written as

$$h(r) = c(r) + \rho \int \mathrm{d}\boldsymbol{r}'\, c(r')\, h(\,|\,\boldsymbol{r}-\boldsymbol{r}'\,|\,)\,, \tag{1}$$

where r and r' are the magnitudes of the vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$, ρ is the particle density, $c(r)$ is the direct correlation function, and $h(r)$ is the indirect correlation function. If $g(r)$ is the radial distribution function then

$$h(r) = g(r) - 1\,. \tag{2}$$

Interest in the OZ relation has been stimulated by certain approximate relations between $c(r)$ and $g(r)$ that have been proposed. In particular, if $\phi(r)$ is the interparticle potential, k is Boltzmann's constant, and T is the temperature, the Percus–Yevick (PY) approximation (Percus and Yevick 1958; Percus 1962) supplements equations (1) and (2) with the relation

$$c(r) = \{1 - \exp(\phi(r)/kT)\}g(r)\,. \tag{3a}$$

Similarly, the convolution-hypernetted chain (CHNC) approximation (Van Leeuwen, Groenveld, and de Boer 1959; Meeron 1960; Morita and Hiroike 1960) supplements them with

$$c(r) = h(r) - \log g(r) - \phi(r)/kT\,. \tag{3b}$$

It is found that the function $c(r)$ tends to zero with increasing r much more rapidly than the function $h(r)$ (Goldstein 1955). In particular, the PY approximation (3a) predicts that $c(r)$ should vanish beyond the range of the potential, while the CHNC approximation (3b) predicts that $c(r)$ should be of order $\frac{1}{2}h^2(r)$

* Research School of Physical Sciences, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

when $h(r)$ is small. In the present paper it will be shown that when $c(r)$ vanishes beyond a range R equation (1) can be transformed so as to involve the function $h(r)$ only over the range $(0, R)$. As an example of the utility of this result it will be shown that the analytic solution of the PY approximation for hard spheres can be obtained very simply from the transformed equations. Further, the result should be of use in numerical calculations.

As far as the author is aware the equations obtained are new, but are related to the work of Wertheim (1964) and to a previous paper by the author (Baxter 1967). It is believed that the results and their derivation represent a considerable simplification of this previous work.

II. Derivation of Required Equations

Multiplying both sides of equation (1) by $\exp(\mathrm{i}\,\boldsymbol{k}.\boldsymbol{r})$ and integrating with respect to $\boldsymbol{r}$ over all space, it is found that

$$\tilde{h}(k) = \tilde{c}(k) + \rho\tilde{c}(k)\tilde{h}(k)\,, \tag{4}$$

where $\tilde{h}(k)$ and $\tilde{c}(k)$ are the three-dimensional Fourier transforms of $h(r)$ and $c(r)$ and depend only on the magnitude k of the vector $\boldsymbol{k}$. Using spherical polar coordinates about an axis along the vector $\boldsymbol{k}$, the angle integrations can be performed to give

$$\tilde{h}(k) = 4\pi k^{-1}\int_0^\infty \mathrm{d}r\,\sin kr\,r\,h(r)\,, \tag{5}$$

$$\tilde{c}(k) = 4\pi k^{-1}\int_0^\infty \mathrm{d}r\,\sin kr\,r\,c(r)\,. \tag{6}$$

From equation (4) it can be seen that

$$1+\rho\tilde{h}(k) = \{\tilde{A}(k)\}^{-1}\,, \tag{7}$$

where

$$\tilde{A}(k) = 1-\rho\tilde{c}(k)\,. \tag{8}$$

If the direct correlation function $c(r)$ vanishes beyond a range R, then the integration in equation (6) can be truncated at R. Integrating by parts and substituting the result in equation (8) gives

$$\tilde{A}(k) = 1-4\pi\rho\int_0^R \mathrm{d}r\,\cos kr\,S(r)\,, \tag{9}$$

where

$$S(r) = \int_r^R \mathrm{d}t\,t\,c(t)\,. \tag{10}$$

For a disordered fluid the integral on the right-hand side of equation (5) must be convergent for real k. Thus $\tilde{h}(k)$ is finite and from equation (7) it follows that $\tilde{A}(k)$ can have no zeros on the real k axis. When this is so it is shown in the Appendix that $\tilde{A}(k)$ can be factorized according to the equation

$$\tilde{A}(k) = \tilde{Q}(k)\tilde{Q}(-k)\,, \tag{11}$$

where the function $\tilde{Q}(k)$ is regular, has zeros only in the lower half-plane, and can be written in the form

$$\tilde{Q}(k) = 1 - 2\pi\rho \int_0^R \mathrm{d}r\, \mathrm{e}^{\mathrm{i}kr} Q(r)\,, \tag{12}$$

$Q(r)$ being a real function.

Substituting the forms (9) and (12) of $\tilde{A}(k)$ and $\tilde{Q}(k)$ into equation (11), multiplying by $\exp(-\mathrm{i}kr)$, and integrating with respect to k from $-\infty$ to ∞ gives

$$S(r) = Q(r) - 2\pi\rho \int_r^R \mathrm{d}t\, Q(t)\, Q(t-r)\,, \qquad 0 < r < R\,. \tag{13}$$

From equations (7) and (11) it follows that

$$\tilde{Q}(k)\,\{1 + \rho\tilde{h}(k)\} = \{\tilde{Q}(-k)\}^{-1}\,, \tag{14}$$

and from equation (5) the function $\tilde{h}(k)$ can be written as

$$\tilde{h}(k) = 2\pi \int_{-\infty}^{\infty} \mathrm{d}r\, \mathrm{e}^{\mathrm{i}kr} J(|r|)\,, \tag{15}$$

where

$$J(r) = \int_r^{\infty} \mathrm{d}t\, t\, h(t)\,. \tag{16}$$

Consider the effect of multiplying both sides of equation (14) by $\exp(-\mathrm{i}kr)$ and integrating with respect to k from $-\infty$ to ∞. The contribution from the right-hand side vanishes when $r > 0$ as the integration can then be closed round the lower half k plane, where $\tilde{Q}(-k)$ is regular, has no zeros, and tends to unity at infinity. Substituting the forms (15) and (12) of $\tilde{h}(k)$ and $\tilde{Q}(k)$ into the left-hand side of equation (14) and performing the integration, it follows that

$$-Q(r) + J(r) - 2\pi\rho \int_0^R \mathrm{d}t\, Q(t)\, J(|r-t|) = 0 \tag{17}$$

for $r > 0$, where the range of $Q(r)$ is extended by defining

$$Q(r) = 0 \qquad \text{for} \qquad r > R\,. \tag{18}$$

From equations (10) and (13) it can be seen that $Q(r) \to 0$ as $r \to R$ from below, so the definition (18) ensures that $Q(r)$ is continuous at $r = R$.

Equations (13) and (17) may be expressed in terms of $c(r)$ and $h(r)$, rather than $S(r)$ and $J(r)$, by differentiating them with respect to r. Using equations (10) and (16) and the fact that $Q(R) = 0$, it is found that

$$r\, c(r) = -Q'(r) + 2\pi\rho \int_r^R \mathrm{d}t\, Q'(t)\, Q(t-r) \tag{19}$$

for $0 < r < R$, and

$$r\, h(r) = -Q'(r) + 2\pi\rho \int_0^R \mathrm{d}t\, (r-t)\, h(|r-t|)\, Q(t) \tag{20}$$

for $r > 0$, where $Q'(r)$ is the derivative of $Q(r)$.

Although equation (20) is valid for all positive r, it is of particular interest when r is restricted to lie in the range $(0, R)$ for then it involves the function $h(r)$ only over this range. With this restriction, equations (19) and (20), together with the PY or CHNC approximations (3), form a closed set of equations for the functions $c(r)$, $Q(r)$, and $h(r)$ in the range $(0, R)$ within which $c(r)$ is nonzero. The PY approximation can be reduced to a form suitable for computation by Newton–Raphson techniques by using equations (2) and (3a) to express $h(r)$ explicitly in terms of $c(r)$. Using equation (19) it is then possible to express $h(r)$ in terms of $Q(r)$, and substituting this form for $h(r)$ into equation (20) gives a single equation for $Q(r)$.

The inverse compressibility equation of state is known to be given by

$$(kT)^{-1}\frac{\partial P}{\partial \rho}\bigg|_T = 1-\rho\int \mathrm{d}\boldsymbol{r}\, c(r) = 1-\rho\,\tilde{c}(0)\,, \tag{21}$$

where P is the pressure. From equation (8) the right-hand side of equation (21) is simply $\tilde{A}(0)$, which must be positive since $\tilde{A}(k)$ is required to have no zeros on the real axis and can be seen from equation (9) to tend to unity as k tends to infinity. Further, from the factorization (11) of $\tilde{A}(k)$, equation (21) can be written as

$$(kT)^{-1}\frac{\partial P}{\partial \rho}\bigg|_T = \{\tilde{Q}(0)\}^2\,, \tag{22}$$

so, if $Q(r)$ is known, $\tilde{Q}(0)$ can be evaluated from equation (12), giving the inverse compressibility as proportional to the square of a real parameter.

III. PY Approximation for Hard Spheres

The PY approximation for hard spheres of diameter R, which was first solved by Thiele (1963) and Wertheim (1963), can be expressed as

$$g(r) = 0\,, \qquad 0<r<R\,; \qquad\qquad c(r) = 0\,, \qquad r>R\,. \tag{23}$$

Thus $h(r)$ has the value -1 throughout the range $(0, R)$ within which $c(r)$ is nonzero. Substituting this value in equation (20) for $0<r<R$, it follows that

$$Q'(r) = ar+b\,, \qquad 0<r<R\,, \tag{24}$$

where a and b are constants determined by $Q(r)$.

Using the condition $Q(R) = 0$, $Q(r)$ can be obtained by integrating equation (24). Substituting the result into the expressions for a and b gives two linear equations that can be solved to give

$$a = (1+2\eta)/(1-\eta)^2\,, \qquad b = -\tfrac{3}{2}R\eta/(1-\eta)^2\,, \tag{25}$$

where

$$\eta = \tfrac{1}{6}\pi\rho R^3\,. \tag{26}$$

Thus $Q(r)$ is now a known function and $c(r)$ can be calculated from equation (19).

It is also possible to use equations (19) and (20) to obtain the analytic solution of the PY approximation for the adhesive hard spheres model (Baxter 1968). Indeed, some of the properties of this model, such as the fact that the inverse compressibility was found to be a perfect square, prompted the present work.

IV. Discussion

It has been shown that equations (19) and (20) can be of use in analytic calculations based on the Ornstein–Zernike relation. The same may be expected to be true of numerical calculations, for in these it is always necessary to truncate $h(r)$ and $c(r)$ at some range R. If the OZ relation is used directly then R must be large enough for $h(r)$ to be small, whereas if equations (19) and (20) are used it should be sufficient for $c(r)$ to be small. The equations are particularly applicable to the PY approximation for a potential of finite range, for then truncation errors can be completely avoided.

In Section II it was indicated that in the PY approximation the equations can be reduced to a single equation for $Q(r)$. The more natural function to calculate is not $Q(r)$ but rather its derivative $Q'(r)$. The fact that $Q'(r)$ is a linear function in the PY approximation for hard spheres, while $c(r)$ is a cubic, suggests that in general $Q'(r)$ may be an even smoother and better-behaved function than $c(r)$.

Once $Q(r)$, $h(r)$, and $c(r)$ are known in the range $(0, R)$, the values of $h(r)$ for $r > R$ can be obtained. One way to do this is to multiply both sides of equation (20) by $\exp(ikr)$ and integrate with respect to r from 0 to ∞, giving

$$\tilde{h}_+(k) = -\frac{1}{\tilde{Q}(k)} \int_0^R \mathrm{d}r\, \mathrm{e}^{ikr} \left(Q'(r) + 2\pi\rho \int_0^{R-r} \mathrm{d}t\, t\, h(t)\, Q(t+r) \right), \tag{27}$$

where $\tilde{h}_+(k)$ is the one-sided Fourier transform of $r\,h(r)$, that is,

$$\tilde{h}_+(k) = \int_0^\infty \mathrm{d}r\, \mathrm{e}^{ikr}\, r\, h(r)\,. \tag{28}$$

The right-hand side of equation (27) can be evaluated to give $\tilde{h}_+(k)$, and $h(r)$ can then be evaluated by inverting the Fourier transform (28).

Another way to obtain $h(r)$ is to invert the two-sided Fourier transform $\tilde{h}(k)$ given by equation (4). From an analytic viewpoint this method is more complicated, since both $\tilde{Q}(k)$ and $\tilde{Q}(-k)$ occur in the denominator of the expression for $h(k)$, while only $\tilde{Q}(k)$ occurs in the expression (27) for $\tilde{h}_+(k)$.

From equations (27) and (28), the condition that $Q(k)$ has zeros only in the lower half-plane implies that the integral on the right-hand side of equation (28) is convergent for all k with non-negative imaginary parts. It is possible that equations (19) and (20) may have solutions which violate this condition; such solutions must be discarded. In particular $\tilde{Q}(0)$ must be positive, for as $Q(k)$ is real and continuous on the positive imaginary axis and tends to unity at infinity, a negative value of $\tilde{Q}(0)$ implies that there is a zero on this axis.

The function $Q(r)$ can be eliminated from equations (19) and (20) to give the relation between $c(r)$ and $h(r)$ previously derived (Baxter 1967) and used in numerical calculations by Watts (1968). The complexity of this relation, together with the usefulness of $Q(r)$ in determining the long-range behaviour of $h(r)$, makes it more convenient to work with equations (19) and (20) directly.

V. Acknowledgments

The author is grateful to Professor K. J. Le Couteur for comments that led the author to seek the theorem given in the Appendix, and to Mr. W. A. Coppel for supplying pertinent references.

VI. References

Baxter, R. J. (1967).—*Phys. Rev.* **154**, 170.

Baxter, R. J. (1968).—Percus–Yevick equation for hard spheres with surface adhesion. *J. chem. Phys.* (in press).

Goldstein, L. (1955).—*Phys. Rev.* **100**, 981.

Krein, M. G. (1962).—*Am. math. Soc. Transl.* (2) **22**, 194.

Levin, B. Ja. (1964).—*In* "Distribution of Zeros of Entire Functions". Appendix V. (American Mathematical Society: Providence, Rhode Island.)

Meeron, E. (1960).—*J. math. Phys.* **1**, 192.

Morita, T., and Hiroike, K. (1960).—*Prog. theor. Phys., Kyoto* **23**, 1003.

Noble, B. (1958).—"Methods based on the Wiener–Hopf Technique." (Pergamon Press: London.)

Ornstein, L. S., and Zernike, F. (1914).—*Proc. Sect. Sci. K. ned. Akad. Wet.* **17**, 793.

Paley, R. E. A., and Wiener, N. (1934).—"Fourier Transforms in the Complex Domain." (American Mathematical Society: New York.)

Percus, J. K. (1962).—*Phys. Rev. Lett.* **8**, 462.

Percus, J. K., and Yevick, G. J. (1958).—*Phys. Rev.* **110**, 1.

Thiele, E. (1963).—*J. chem. Phys.* **39**, 474.

Van Leeuwen, J. M. J., Groenveld, J., and de Boer, J. (1959).—*Physica* **25**, 792.

Watts, R. O. (1968).—The Percus–Yevick equation applied to a Lennard–Jones fluid. *J. chem. Phys.* **48**, 50.

Wertheim, M. S. (1963).—*Phys. Rev. Lett.* **10**, 321.

Wertheim, M. S. (1964).—*J. math. Phys.* **5**, 643.

Appendix

The factorization theorem represented by equations (9), (11), and (12) can be found in the literature on Fourier transforms (Krein 1962, and associated references; Levin 1964). The derivation presented here is based on the Wiener–Hopf technique (Paley and Wiener 1934; Noble 1958).

Consider the behaviour of $\tilde{A}(k)$ in the complex k plane and set $k = x+\mathrm{i}y$. $\tilde{A}(k)$ is required to have no zeros on the real axis and from equation (9) it tends uniformly to unity as $|x| \to \infty$ in any strip $y_0 \leqslant y \leqslant y_1$. There thus exists a strip $|y| \leqslant \epsilon$ about the real axis within which $\tilde{A}(k)$ has no zeros.

As $\tilde{A}(k)$ is a Fourier transform over a finite interval it is regular throughout the complex plane. The function $\log \tilde{A}(k)$ is therefore regular within the strip $|y| \leqslant \epsilon$ and tends uniformly to zero as $|x| \to \infty$. Integrating round the strip and applying Cauchy's theorem it follows that when $|y| < \epsilon$

$$\log \tilde{A}(k) = \log \tilde{Q}(k) + \log \tilde{P}(k), \tag{A1}$$

where

$$\log \tilde{Q}(k) = \frac{1}{2\pi\mathrm{i}} \int_{-\mathrm{i}\epsilon-\infty}^{-\mathrm{i}\epsilon+\infty} \mathrm{d}k' \, \frac{\log \tilde{A}(k')}{k'-k}, \tag{A2}$$

$$\log \tilde{P}(k) = -\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{i}\epsilon-\infty}^{\mathrm{i}\epsilon+\infty} \mathrm{d}k' \, \frac{\log \tilde{A}(k')}{k'-k}. \tag{A3}$$

Negating k' in equation (A3) and using the fact that $\tilde{A}(k)$ is an even function, it can be seen that

$$\log \tilde{P}(k) = \log \tilde{Q}(-k). \tag{A4}$$

The function $\log \tilde{Q}(k)$ is regular in the domain $y > -\epsilon$, so it follows from equations (A1) and (A4) that when $|\, y \,| < \epsilon$

$$\tilde{A}(k) = \tilde{Q}(k)\,\tilde{Q}(-k), \tag{A5}$$

where $\tilde{Q}(k)$ is regular and has no zeros in the domain $y > -\epsilon$. This proves equation (11).

When $|\, x \,| \to \infty$ within the strip $|\, y \,| < \epsilon$ it follows from equation (A2) that $\log \tilde{Q}(k) \sim O(x^{-1})$, so that $\tilde{Q}(k) \sim 1+O(x^{-1})$. The function $1-\tilde{Q}(k)$ is therefore Fourier integrable along the real axis, and a function $Q(r)$ can be defined by

$$2\pi\rho\, Q(r) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}k \; \mathrm{e}^{-\mathrm{i}kr}\{1-\tilde{Q}(k)\}. \tag{A6}$$

From equation (A2) it can be seen that when k is real the complex conjugate of $\tilde{Q}(k)$ is $\tilde{Q}(-k)$, from which it follows that $Q(r)$ is a real function.

When $y \leqslant 0$, $\tilde{Q}(k)$ tends to unity as k tends to infinity. If $r < 0$, the integration in equation (A6) can therefore be closed round the upper half-plane, where $\tilde{Q}(k)$ is regular, giving

$$Q(r) = 0 \qquad \text{for} \qquad r < 0. \tag{A7}$$

The right-hand side of equation (A2) is a different analytic function of k according as y is greater than or less than $-\epsilon$. The analytic continuation of the function $\tilde{Q}(k)$ into the lower half-plane is therefore *not* given by equation (A2) but by equation (A5), that is,

$$\tilde{Q}(k) = \tilde{A}(k)/\tilde{Q}(-k), \tag{A8}$$

where equation (A2) can be used to evaluate $\tilde{Q}(-k)$ on the right-hand side of (A8).

As $\tilde{A}(k)$ is regular everywhere and $\tilde{Q}(-k)$ is regular and has no zeros for $y < \epsilon$, from equation (A8) the function $\tilde{Q}(k)$ is regular in this domain. Further, as $\tilde{Q}(-k) \to 1$ when $y \to -\infty$, it follows from equations (9) and (A8) that both $\tilde{A}(k)$ and $\tilde{Q}(k)$ grow exponentially as $\exp(\mathrm{i}kR)$ when y becomes large and negative. When $r > R$ the integration in equation (A6) can therefore be closed round the lower half-plane, giving

$$Q(r) = 0 \qquad \text{for} \qquad r > R. \tag{A9}$$

Inverting the Fourier transform in equation (A6), equations (A7) and (A9) give

$$\tilde{Q}(k) = 1 - 2\pi\rho \int_0^R \mathrm{d}r \; \mathrm{e}^{\mathrm{i}kr} Q(r), \tag{A10}$$

which is the desired equation (12).