Ornstein-Zernike Relation for a Fluid Mixture

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Baxter has shown that, when the direct correlation function vanishes beyond some range, the Ornstein-Zernike relation for a single-component fluid can be transformed into a form involving only the radial distribution function within the range. Baxter’s form is generalized to the case of a multicomponent fluid mixture. The derivation is given without using the assumption that the direct correlation functions are of finite range.

§ 1. Introduction

In a single-component fluid the direct correlation function $c(r)$ is related to the total correlation function $h(r)$ by the Ornstein-Zernike relation

$$h(r) = c(r) + \rho \int dr' c(r') h(|r-r'|), \quad (1.1)$$

where $r$ and $r'$ are the magnitudes of the position vectors $r$ and $r'$ respectively, and $\rho$ is the particle number density. The total correlation function $h(r)$ is defined in terms of the radial distribution function $g(r)$ by

$$h(r) = g(r) - 1. \quad (1.2)$$

As is well known, by introducing bipolar coordinates in Eq. (1.1), the Ornstein-Zernike relation is rewritten as

$$H(r) = C(r) + 2\pi \rho \int_{0}^{\infty} ds \int_{|r-r'|}^{s+r} dt C(s) H(t), \quad (1.1')$$

where

$$H(r) = rh(r) \quad (1.3)$$

and

$$C(r) = rc(r). \quad (1.4)$$

One of the reasons why we are interested in the Ornstein-Zernike relation is that certain approximate theories for classical fluids may be considered to give relations between $c(r)$, $g(r)$ and the pair interaction potential. These relations are supplemented by the Ornstein-Zernike relation. In the Percus-Yevick approximation, for example, $c(r)$ and $g(r)$ are determined by the Ornstein-Zernike relation together with the relation
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\[ c(r) = \{1 - e^{\phi(r)/kT}\} g(r), \]

where \( \phi(r) \) is the pair interaction potential, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. Another example is the hypernetted chain approximation, in which the above relation is replaced by

\[ c(r) = h(r) - \log g(r) - \frac{\phi(r)}{kT}. \]

Since the direct correlation function \( c(r) \) is usually considered to be much smaller than \( h(r) \) for large values of \( r \), we may be allowed to make an approximation that \( c(r) \) vanishes beyond some range \( R \). In such a case, however, we cannot use the approximation that \( h(r) = 0 \) for \( r > R \) unless \( R \) is chosen large enough. In the Ornstein-Zernike relation for \( r < R \), there appears the function \( h(r) \) with \( r \) in the range from 0 to \( 2R \). The relation for \( R < r < 2R \) involves \( h(r) \) with \( r \) in the range from 0 to \( 3R \) and so on. When we attempt to find \( h(r) \) and \( c(r) \) by means of the Percus-Yevick or the hypernetted chain approximation, the Ornstein-Zernike relation demands a knowledge of \( h(r) \) for all values of \( r \) for which \( h(r) \) is significant, even though \( c(r) \) may be negligible for the majority of these values. Therefore it will be useful to transform the Ornstein-Zernike relation into a form which includes \( h(r) \) only over the range from 0 to \( R \).

Recently such an attempt has been made by Baxter. Under the assumption that \( c(r) \) is of finite range, he has derived two forms of the Ornstein-Zernike relation. One of them has been applied by Watts to obtain the numerical solution of the Percus-Yevick equation and the hypernetted chain equation in the case of the Lennard-Jones interaction potential. Baxter has used the same form to solve analytically the Percus-Yevick equation for hard spheres with surface adhesion.

Baxter's first form is written as

\[ H(r) = C(r) + 2\pi \rho \int_0^r ds \int_0^s dt H(s) H(t) + 4\pi \rho \int_0^r ds \int_{|r-s|}^r dt C(s) H(t) \]

\[ + (2\pi \rho)^2 \int_0^r ds \int_0^r dt C(s) W(s, t), \quad (1.5) \]

where \( W(s, t) \) is defined by

\[ W(s, t) + W(t, s) = 0 \quad (1.5a) \]

and

\[ W(s, t) = \int_0^s du \int_{|t-u|}^{s-|t-u|} dv H(u) H(v) \quad \text{for } s > t. \quad (1.5b) \]

Baxter's second form is as follows:
\[ H(r) = -P'(r) + 2\pi \rho \int_r^\infty dtH(r-t)P(t) - 2\pi \rho \int_0^r dtH(t-r)P(t), \]
\[ C(r) = -P'(r) + 2\pi \rho \int_r^\infty dtP'(t)P(t-r), \]
\[ P(R) = 0, \]
where \( P'(r) \) is the derivative of \( P(r) \).

The purpose of the present paper is to generalize Baxter's forms of the Ornstein-Zernike relation to the case of a multicomponent fluid mixture. We consider an \( n \)-component system. Let \( c_{ij}(r) \) and \( h_{ij}(r) \) be the direct correlation function and the total correlation function between two particles of species \( i \) and \( j \), respectively \((i, j = 1, 2, \ldots, n)\). Then the Ornstein-Zernike relation generalized to the \( n \)-component system is written as
\[ H_{ij}(r) = C_{ij}(r) + 2\pi \int_0^\infty ds \int_{|s-r|}^{s+r} dt \sum_{k=1}^n \rho_k H_{kj}(t) C_{ik}(s), \]
or
\[ H_{ij}(r) = C_{ij}(r) + 2\pi \int_0^\infty ds \int_{|s-r|}^{s+r} dt \sum_{k=1}^n \rho_k C_{ik}(s) H_{kj}(t), \]
where
\[ C_{ij}(r) = r c_{ij}(r), \quad H_{ij}(r) = r h_{ij}(r), \]
and \( \rho_i \) is the number density of particles of the species \( i \). From the physical meaning of \( c_{ij}(r) \) and \( h_{ij}(r) \), they must be symmetric with respect to \( i \) and \( j \). Therefore, Eqs. (1.7) and (1.7') are equivalent to each other.

For simplicity of description, we introduce matrices \( C(r) \) and \( H(r) \) whose elements are given by
\[ \{C(r)\}_{ij} = 2\pi \sqrt{\rho_i \rho_j} C_{ij}(r) \]
and
\[ \{H(r)\}_{ij} = 2\pi \sqrt{\rho_i \rho_j} H_{ij}(r). \]

The Ornstein-Zernike relation Eq. (1.7) or Eq. (1.7') is now written as
\[ H(r) = C(r) + \int_0^\infty ds \int_{|s-r|}^{s+r} dt C(s) H(t), \]
or
\[ H(r) = C(r) + \int_0^\infty ds \int_{|s-r|}^{s+r} dt H(t) C(s). \]

It is clear that \( C(r) \) and \( H(r) \) are symmetric matrices, so that
\[ C^*(r) = C(r) \quad \text{and} \quad H^*(r) = H(r), \]
where \( H^* \) denotes the Hermitian conjugate of \( H \).
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where \( C^*(r) \) and \( H^*(r) \) are the transposed matrices of \( C(r) \) and \( H(r) \), respectively.

In § 2, Baxter's first form will be generalized. An equation similar to Eq. (1·5) will be obtained which is a necessary consequence of the Ornstein-Zernike relation, although the derivation is quite different from Baxter's. In § 3, Baxter's second form will be generalized. The derived equation is slightly different from Eq. (1·6), and gives a sufficient condition for the validity of the Ornstein-Zernike relation. In the derivation of both §§ 2 and 3, we need not assume that the direct correlation functions are of finite range. Some remarks will be given in § 4. In Appendix A, the method used by Baxter in deriving Eq. (1·5) will be generalized to the case of the fluid mixture by means of Laplace transforms. In Appendix B, we shall prove the symmetric property of some matrix appearing in § 3.

§ 2. Generalization of Baxter's first form

We define the matrix \( D(r) \) by

\[
D(r) = C(r) - H(r) + \int_0^\infty ds \int_t^{t+r} dt C(s) H(t)
\]

\[
+ \int_0^\infty ds \int_s^{s+r} dt \left\{ H(s) - C(s) - \int_0^\infty du \int_{[u-s]}^{u-s} dv H(v) C(u) \right\} H(t)
\]

\[
- \int_0^\infty ds \int_{[s-r]}^s dt H(t) \left\{ H(s) - C(s) - \int_0^\infty du \int_{[u-s]}^{u-s} dv C(u) H(v) \right\}.
\]

(2·1)

From the Ornstein-Zernike relation (1·12) or (1·12'), we have

\[
D(r) = 0. \quad (2·2)
\]

After elementary calculations, Eq. (2·1) is transformed into the following form:

\[
D(r) = C(r) - H(r) + \int_0^r ds \int_0^{r-s} dt H(s) H(t)
\]

\[
+ \int_0^r ds \int_{[s-r]}^s dt \left\{ C(s) H(t) + H(t) C(s) \right\}
\]

\[
+ \int_t^r dt \left\{ \int_t^\infty ds \int_0^{s-[u-t]} dv \int_0^{t-[u-t]} dv \right\} H(u) C(s) H(v).
\]

(2·3)

Because of Eq. (1·13), it is easy to see that the right-hand side of Eq. (2·3) is a symmetric matrix, so that

\[
D^*(r) = D(r). \quad (2·4)
\]

Equation (2·2) in which Eq. (2·3) is to be used for \( D(r) \) is the generalization of Baxter's first form to the case of the fluid mixture. As is seen from
the derivation, this equation is a necessary condition for the Ornstein-Zernike relation (1·12) or (1·12'). When a single-component system is considered under the assumption that \( C(r) \) vanishes for \( r > R \), Eq. (2·2) together with Eq. (2·3) reduces to Baxter's first form (1·5). In deriving Eq. (1·5), Baxter has adopted the "discrete approximation". It is seen from Appendix A that such an approximation is not necessary even if we proceed with Baxter's method. In Appendix A, the Laplace transform method is applied to the Ornstein-Zernike relation. The method in Appendix A leads to Eq. (1·5) in the case of the single-component fluid, but it is not sufficient to derive Eq. (2·2) for the fluid mixture.

\[ \text{§ 3. Generalization of Baxter's second form} \]

Let us consider a matrix \( P(r) \) which is a differentiable function of \( r \). We assume that \( P(r) \) vanishes sufficiently fast when \( r \) tends to infinity:

\[
\lim_{r \to \infty} P(r) = 0 .
\]

A matrix \( \hat{P}(r) \) is defined in terms of \( P(r) \) by

\[
\hat{P}(r) \equiv -P'(r) + \int_{0}^{r} dt P^*(t-r) P'(t) = -P'(r) + \int_{0}^{r} dt P^*(t) P'(t+r) ,
\]

where \( P'(r) \) and \( P^*(r) \) are the derivative and the transposed matrix of \( P(r) \), respectively. Then it is easily verified that the following identity holds:

\[
H(r) - \hat{P}(r) - \int_{0}^{r} ds \int_{|s-r|}^{s+r} dt \hat{P}(s) H(t) + \int_{0}^{r} dt \int_{s}^{r} ds [\hat{P}(s) - \hat{P}^*(s)] H(t+s) = 0 ,
\]

If \( P(r) \) satisfies the integro-differential equation

\[
H(r) + P''(r) - \int_{0}^{r} dt P(t) H(r-t) + \int_{0}^{r} dt P(t) H(t-r) = 0 ,
\]

Eq. (3·3) is rewritten as

\[
H(r) - \hat{P}(r) - \int_{0}^{r} ds \int_{|s-r|}^{s+r} dt \hat{P}(s) H(t) + \int_{0}^{r} dt \int_{s}^{r} ds [\hat{P}(s) - \hat{P}^*(s)] H(t+r) = 0 .
\]

Furthermore, if the matrix \( \hat{P}(r) \) is assumed to be a symmetric matrix, Eq. (3·5) reduces to the same form as the Ornstein-Zernike relation (1·12). Therefore, \( C(r) \) must be equal to \( P(r) \) and we have

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\[ C(r) = \tilde{P}(r) = -P'(r) + \int_{0}^{\infty} dt P^*(t-r) P'(t). \]  

(3.6)

Summarizing the above arguments, we can say as follows: If a solution \( P(r) \) of Eq. (3.4) under the condition Eq. (3.1) is found in terms of \( H(r) \) and if the solution gives the symmetric matrix \( \tilde{P}(r) \) which is defined by Eq. (3.2), then \( C(r) \) which is given by Eq. (3.6) and \( H(r) \) are connected with each other by means of the Ornstein-Zernike relation (1.12). The present authors have failed in proving generally that the solution of Eq. (3.4) gives the symmetric matrix \( \tilde{P}(r) \). In Appendix B, the symmetric property of \( \tilde{P}(r) \) is proved under the assumption that an iterative method is valid.

The above result is a generalization of Baxter's second form (1.6). When \( C(r) \) is assumed to be zero for \( r > R \), we can assume without loss of generality that \( P(r) \) vanishes for \( r \geq R \). In the case of a single-component fluid under such an assumption, it is easy to see that Eqs. (3.1), (3.4) and (3.6) reduce to Eq. (1.6).

\section*{§ 4. Concluding remarks}

In §§ 2 and 3, Baxter's forms of the Ornstein-Zernike relation for a single-component fluid have been generalized to the case of a multicomponent fluid mixture. It should be noted that the generalization has been made without using the assumption that the direct correlation functions are of finite range. Therefore, it may be said that Baxter's results have been generalized in such a sense even for a single-component fluid.

Although we have not explicitly stated the assumption that the integral

\[ \int dr \left| h_{ij}(r) \right| \]  

(4.1)

converges, this assumption will be necessary to justify the derivation in §§ 2 and 3. Since the direct correlation functions have not been assumed to be of finite range, the convergence of the integral

\[ \int dr \left| c_{ij}(r) \right| \]  

(4.2)

must also be assumed. We shall make no attempt to justify our results with mathematical exactitude. We believe, however, that the results are valid except for the critical region where both \( H(r) \) and \( C(r) \) may be of long range.

Our results are as useful as Baxter's forms when the direct correlation functions are of finite range. If all the direct correlation functions, \( c_{ij}(r) \)'s \( (i,j=1,2,\ldots,n) \), have a common range \( R \), the results obtained in §§ 2 and 3 have the forms including the \( h_{ij}(r) \)'s only for \( r < R \). It would be more preferable, however, to consider the case in which each direct correlation function \( c_{ij}(r) \) has its own range \( R_{ij} \). In such a case, it is desirable to derive an equation

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including \( h_{ij}(r) \) only for \( r < R_{ij} \). Investigations in this direction will be given in another paper.\(^7\)

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**Appendix A**

*Laplace transform version of Baxter's method*

In deriving Eq. (1·5), Baxter has used the "discrete approximation" in which the integral in Eq. (1·1') is replaced by a sum.\(^3\) Such an approximation will not be used here. We assume that the matrix \( C(r) \) which is defined by Eq. (1·10) is of finite range, so that

\[
C(r) = 0 \quad \text{for} \quad r > R, \tag{A·1}
\]

where \( R \) is some range. For convenience of calculations, we denote the integral involving \( C(r) \) simply as

\[
\int_R^r dr' C(r') = \int_R^\infty dr' C(r'). \tag{A·2}
\]

The integral (4·1) is assumed to converge.

Laplace transforms \( \tilde{H}(p) \) and \( \tilde{C}(p) \) of \( H(r) \) and \( C(r) \) are defined by

\[\tilde{H}(p) = \int_0^\infty dr e^{-pr} H(r) \quad \text{for} \quad \text{Re} \, p \geq 0\]  \tag{A·3}

and

\[\tilde{C}(p) = \int_0^\infty dr e^{-pr} C(r).\]  \tag{A·4}

From Eq. (A·1), \( \tilde{C}(p) \) is found to be an entire function of \( p \). Equation (1·12) is written by using Laplace transforms as

\[\tilde{B}(p) \tilde{H}(p) = \tilde{A}(p) \quad \text{for} \quad \text{Re} \, p \geq 0, \tag{A·5}\]

where

\[\tilde{B}(p) = E + \frac{1}{p} [\tilde{C}(p) - \tilde{C}(-p)], \tag{A·6}\]

\[\tilde{A}(p) = \tilde{C}(p) + \tilde{Q}(p), \tag{A·7}\]

and

\[\tilde{Q}(p) = \int_0^\infty ds \int_0^r dt \frac{1}{p} [e^{-p(s-t)} - e^{-p(s-t)}] C(s) H(t). \tag{A·8}\]
In Eq. (A·6), \( E \) denotes a unit matrix. As is seen from the definition, the matrices \( B(p) \), \( A(p) \) and \( Q(p) \) are entire functions of \( p \), and in particular \( B(p) \) has the property that
\[
B(p) = B(-p) = B^*(p). \tag{A·9}
\]

The analytic continuation of \( \hat{H}(p) \) into the left half-plane, \( \text{Re} \ p < 0 \), is given by means of Eq. (A·5) for \( \text{Re} \ p < 0 \). Then the symmetric property of \( \hat{H}(p) \) leads to the relation
\[
\hat{A}(p) B(p) = B(p) \hat{A}^*(p). \tag{A·10}
\]

Let us define a matrix \( \hat{S}(p) \) by
\[
\hat{S}(p) = \hat{H}(p) \hat{A}(-p). \tag{A·11}
\]

Using Eqs. (A·5), (A·9) and (A·10), we have
\[
\hat{S}^*(p) = \hat{A}^*(-p) \hat{H}(p) = \hat{A}^*(-p) \frac{1}{B(p)} \hat{A}(p) = \frac{1}{B(-p)} \hat{A}(-p) \hat{A}^*(p)
\]
\[
= \hat{H}(-p) \hat{A}(p) = \hat{S}(-p). \tag{A·12}
\]

From the definition, \( \hat{S}(p) \) is regular in the right half-plane including the imaginary axis. Furthermore, Eq. (A·12) shows that it is regular in the left half-plane also and hence \( \hat{S}(p) \) is an entire function of \( p \).

Let us now introduce two matrices \( \hat{F}(p) \) and \( \hat{r}(p) \) by
\[
\hat{F}(p) = \hat{A}(p) \hat{A}(-p) - B(p) \hat{S}(p) \tag{A·13}
\]

and
\[
\hat{r}(p) = \hat{A}(p) B(p) - B(p) \hat{A}^*(p). \tag{A·14}
\]

The matrix \( \hat{F}(p) \) is an entire function of \( p \) and it follows from Eqs. (A·5) and (A·11) that
\[
\hat{F}(p) = 0. \tag{A·15}
\]

The matrix \( \hat{r}(p) \) is an entire even function of \( p \). It is seen from Eq. (A·10) that
\[
\hat{r}(p) = 0. \tag{A·16}
\]

In order to find the inverse Laplace transform of \( \hat{F}(p) \), it is necessary to know the inverse Laplace transform of \( \hat{S}(p) \). Equation (A·11) is now rewritten as
\[
\hat{S}(p) = - \hat{H}(p) \hat{C}(p) + \hat{H}(p) \hat{F}(p), \tag{A·17}
\]

where
\[
\hat{F}(p) = \hat{Q}(p) + \hat{C}(p) + \hat{C}(-p) = \hat{F}(-p). \tag{A·18}
\]

Denoting the inverse Laplace transform of \( \hat{S}(p) \) and \( \hat{F}(p) \) by \( S(r) \) and \( F(r) \),
respectively, we obtain, from Eqs. (A·12) and (A·18),
\[ S^*(r) = S(-r) \quad \text{and} \quad F(r) = F(-r). \]  
(A·19)

Since
\[ H(r) = C(r) = 0 \quad \text{for } r < 0, \]  
(A·20)
the inverse Laplace transform of Eq. (A·17) is given by
\[ S(r) = \int_0^\infty dt H(t) F(r - t) = \int_0^\infty dt H(t - |r|) F(t) \quad \text{for } r < 0. \]  
(A·21)

With the aid of Eq. (A·19), we have
\[ S(r) = \int_r^\infty dt F^*(t) H(t - r) \quad \text{for } r > 0. \]  
(A·22)

The function \( F(r) \) is expressed, with the aid of Eq. (A·18), in terms of \( Q(r) \) and \( C(r) \), where \( Q(r) \) is the inverse Laplace transform of \( \hat{Q}(p) \). Although the explicit forms of \( S(r), Q(r) \) and \( F(r) \) are not written here, it is to be noted that they vanish when \( |r| > R \).

The inverse Laplace transforms of \( \hat{A}(p) \) and \( \hat{B}(p) \) can be obtained in a similar way. After elementary calculations we have from Eq. (A·13)
\[ F(r) = \int_r^\infty dt C(t) C(t - r) - \int_r^\infty dt C(t) H(t - r) 
+ \int_r^\infty dt \int_0^\infty du \int_0^{u-t} dv H(v) C(u) H(t - r) 
- \int_r^\infty dt \int_{t-r}^\infty du \int_0^{u-|t-r|} dv C(t) C(u) H(v) 
- \int_r^\infty dt \int_{t+r}^\infty du \int_0^{u-t-r} dv C(u) C(v) H(t) 
+ \int_r^\infty dt \int_{t-r}^\infty du \int_t^\infty dv C(u) C(v) H(v - t) C(v) 
+ \int_r^\infty dt \int_{t+r}^\infty du \int_t^\infty dv C(u) H(v - t) C(v) 
+ \int_r^\infty dt \int_t^\infty du \int_0^{u-t} dv \left\{ \int_{t-|t-r|}^\infty dw \int_0^{u-t-r} dx \right\} C(u) H(v) C(w) H(x) 
- \int_r^\infty dt \int_{t-r}^\infty du \int_0^{u-t} dv \int_0^{u-|t-r|} dw C(u) H(x) C(w) H(v - t) 
- \int_r^\infty dt \int_{t+r}^\infty du \int_t^\infty dv \int_0^{u-t} dw \int_0^{u-|t-r|} dx C(u) H(v - t) C(w) H(x) \]  
(A·23)
The inverse Laplace transform of \( \hat{\tau}(p) \) is written as

\[
\tau(r) = \hat{\tau}(-r) = -\int_0^\infty ds \int_{r+s}^\infty dt \{C(s)C(t) - C(t)C(s)\}
- \int_0^\infty ds \int_{r+s}^\infty dt \{C(t)H(s) - H(s)C(t)\}
+ \int_0^\infty dt \int_0^\infty du \int_0^{u-t} dv \left\{ \int_0^\infty dw + \int_{r+t}^\infty dw \right\}
\times \{C(u)H(v)C(w) - C(w)H(v)C(u)\} \quad \text{for } r > 0. \tag{A·24}
\]

Therefore, Eq. (A·16) leads to

\[
\tau(r) = 0. \tag{A·16'}
\]

By using Eq. (A·16'), it is shown that the right-hand side of Eq. (A·23) is rewritten as

\[
\Gamma(r) = \Gamma(-r) = \int_0^\infty dt C(t+r)D(t) \quad \text{for } r > 0, \tag{A·25}
\]

where \( D(r) \) is given by Eq. (2·3) in the text. Using Eq. (A·15), we have

\[
\int_0^\infty dt C(t+r)D(t) = 0 \quad \text{for } r > 0 \tag{A·26}
\]

or explicitly

\[
\int_0^{R-r} dt C(t+r)D(t) = 0 \quad \text{for } 0 < r < R. \tag{A·26'}
\]

In the case of a single-component fluid, the integrand in Eq. (A·26') is just a product of two functions. Then a mathematical theorem [see, for instance, E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford University Press, 1937), p.327.] shows that Eq. (A·26') leads to \( D(r) = 0 \) when \( 0 < r < R \). In other words, we get Baxter's first form (1·5). In the case of a fluid mixture, however, the integrand is a matrix product and hence Eq. (A·26') does not imply that \( D(r) \) vanishes. The reason why Eq. (2·2) is not a sufficient condition for the Ornstein-Zernike relation is that we must use Eqs. (A·12) and (A·16') to derive Eq. (A·26'). Although Eqs. (A·12) and (A·16) are derived from the Ornstein-Zernike relation, it is not clear whether they could be proved by using only the fact that \( D(r) = 0 \). The situation is similar also in the case of a single-component fluid, because Eq. (A·12) is still needed to derive Eq. (A·26'), though Eq. (A·16') is now an identity.

In order to obtain the form (2·1) of \( D(r) \), it would be useful to consider the following formula:

\[
\tilde{\Phi}(p) = \tilde{A}(-p) [\tilde{A}(p) - \tilde{B}(p) \tilde{H}(p)] + \tilde{B}(p) [\tilde{A}^*(p) \tilde{H}(p) - \tilde{S}^*(p)] = 0. \tag{A·27}
\]

The last equality follows from Eqs. (A·5) and (A·12). It is shown that the
inverse Laplace transform of Eq. (A·27) is expressed as

$$\Gamma_0(r) = \int_0^\infty dt C(t-r) D(t) = 0 \quad \text{for } r<0,$$

(A·28)

where the expression for $D(r)$ is given by Eq. (2·1).

**Appendix B**

*Proof of the symmetric property of $\tilde{P}(r)*

We now show with the aid of an iterative method that the matrix $\tilde{P}(r)$ appearing in § 3 is symmetric. Equation (3·5) in the text can be regarded as an integral equation for $\tilde{P}(r)$ if the symmetric matrix $H(r)$ is given. Let us consider an integral equation

$$\tilde{P}(r) = \lambda H(r) - \lambda \int_0^\infty ds \int_{|s-r|}^{s+r} dt \tilde{P}(s) H(t) + \lambda \int_0^\infty dt \int_t^\infty ds [\tilde{P}(s) - \tilde{P}^*(s)] H(t+r),$$

(B·1)

where $\lambda$ is a parameter. We assume that the integral equation (B·1) has a solution of the form

$$\tilde{P}(r) = \sum_{n=1}^\infty \lambda^n \tilde{P}_n(r).$$

(B·2)

Inserting Eq. (B·2) into Eq. (B·1), we have

$$\tilde{P}_1(r) = H(r)$$

(B·3)

and

$$\tilde{P}_{n+1}(r) = - \int_0^\infty ds \int_{|s-r|}^{s+r} dt \tilde{P}_n(s) H(t)$$

$$\quad + \int_0^\infty dt \int_t^\infty ds [\tilde{P}_n(s) - \tilde{P}_n^*(s)] H(t+r) \quad (n=1, 2, \ldots).$$

(B·3’)

It is easy to prove by the mathematical induction that the $\tilde{P}_n(r)$’s ($n=1, 2, \ldots$) satisfy the following relations:

$$\tilde{P}_n^*(r) = \tilde{P}_n(r)$$

(B·4)

and

$$\int_0^\infty ds \int_{|s-r|}^{s+r} dt \tilde{P}_n(s) H(t) = \int_0^\infty ds \int_{|s-r|}^{s+r} dt H(t) \tilde{P}_n(s).$$

(B·5)

Therefore the symmetric property of $\tilde{P}(r)$ has been proved if the series in Eq. (B·2) is convergent when $\lambda=1$.

**References**


2) J. M. J. Van Leeuwen, J. Groeneveld and J. de Boer, Physica 25 (1959), 792.