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HNC-Type Approximation for Transport Processes in Electrolytic Solutions

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On the basis of the diffusion approach in the theory of transport processes of electrolytic solutions we introduce a "direct correlation force" as a generalization of the direct correlation function in equilibrium. Starting from an approximation for the three-particle distribution function we derive a HNC (hypernetted chain)-type equation for calculation of binary distribution functions in nonequilibrium. The derivation is consistent with equilibrium theory.

KEY WORDS: Transport processes; electrolytic conductance; diffusion approach; direct correlation force; HNC equation.

1. INTRODUCTION

The equilibrium HNC-equation for the two-particle distribution function F_{ab} is perhaps the best existing approximation which describes interionic structure and therefore the excess properties of electrolytic solutions.$^{(1)}$ F_{ab} (12) denotes the probability of finding an ion of species a in the volume element $d\mathbf{r}_1$ and the ion of species b in $d\mathbf{r}_2$ which is given by

$$F_{ab}(1,2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,V^{-2}$$

Comparison with Monte Carlo studies indicates that the HNC-distribution function is relatively correct and yields good thermodynamic functions from strong to moderately associating electrolytes at all solute concentrations. The success of the HNC approximation in equilibrium strongly

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suggests the analog of HNC for transport processes should be constructed.(2,3) Our approach is based on (a) the diffusion approximation for the BBGKY hierarchy(4–8) and (b) the definition of a nonequilibrium direct correlation force in the framework of the diffusion approximation.(7–9)

2. THE DIRECT CORRELATION FORCE IN THE DIFFUSION APPROXIMATION

Let us consider an isothermal electrolyte. The diffusion flow of particles of species a is then given by

$$\mathbf{J}_a = n_a\left(e_a\mathbf{E} + \mathbf{K}_a^{\mathrm{rel}} + \mathbf{K}_a^{\mathrm{el}}\right)/R_a \tag{1}$$

where n_a denotes the particle density N_a/V, e_a their electric charge, $\mathbf{E}$ the external electric field, and $\mathbf{K}_a^{\mathrm{rel}}$ the relaxation force and $\mathbf{K}_a^{\mathrm{el}}$ the electrophoretic force, which are given by

$$\mathbf{K}_a^{\mathrm{rel}}(1) = -\sum_b n_b \int \nabla_1 \psi_{ab}(12) F_{ab}(12)\, d\mathbf{r}_2 \tag{2}$$

$$\mathbf{K}_a^{\mathrm{el}}(1) = R_a \sum_b n_b \int L_{ab} \cdot \left(e_b\mathbf{E} + \mathbf{K}_b^a\right) F_{ab}\, d\mathbf{r}_2 \tag{3}$$

$$\mathbf{K}_a^b(12) = -\nabla_1 \psi_{ab}(12) - \sum_c n_c \int \nabla_1 \psi_{ac}(13)\left(F_{abc}(123)/F_{ab}(12)\right) d\mathbf{r}_3 \tag{4}$$

Here ψ_{ab} is the potential of average force between two ions at infinite dilution which we assume to be known. L_{ab} is the electrophoretic or friction tensor,(3,5,8,10) and $\mathbf{K}_a^b$ the mean interionic force, which contains the three-particle distribution function F_{abc}. R_a is a friction coefficient.

For the p.d.f. we may write the continuity equation

$$(\partial/\partial t)F_{ab} + \nabla_1 \cdot \mathbf{j}_a^b + \nabla_2 \cdot \mathbf{j}_b^a = 0 \tag{5}$$

where $\mathbf{j}_a^b$ is the mean flow of ions of species a at $\mathbf{r}_1$ assumed that the ion b is fixed at $\mathbf{r}_2$. In the diffusion approximation $\mathbf{j}_a^b$ is given by (neglecting hydrodynamic couplings)

$$\mathbf{j}_a^b = F_{ab}\mathbf{u}_{ab}/n_a n_b = \left(\overline{\mathbf{K}}_a F_{ab} + F_{ab}\overline{\mathbf{K}}_a^b - kT\nabla_1 F_{ab}\right)/R_a \tag{6}$$

Here $\overline{\mathbf{K}}_a$ is the effective external force, taking into account the feedback of relaxation force and given by

$$\overline{\mathbf{K}}_a = e_a\mathbf{E} + \mathbf{K}_a^{\mathrm{rel}} \tag{7}$$

This relaxation force we subtract from the mean interionic force $\mathbf{K}_a^b$

$$\overline{\mathbf{K}}_a^b = \mathbf{K}_a^b - \mathbf{K}_a^{\mathrm{rel}} \tag{8}$$

This interaction contribution is the most complicated part of the vector flow field (6) because it contains the three-particle distribution F_{abc}. Therefore it is necessary to consider a full hierarchy of flow equations$^{(5)}$ together with the corresponding continuity equations. In order to get a formal closed system of equations which can be solved, e.g., by Fourier transforms, let us define an effective force, the direct correlation force $\mathbf{C}_{ab}$, by

$$F_{ab}\overline{\mathbf{K}}_a^b = \mathbf{C}_{ab} + \sum_c n_c \int \mathbf{C}_{ac} h_{cb}\, d\mathbf{r}_3 \tag{9}$$

Introducing this definition in Eq. (6) the two-particle flow can be expressed by $\mathbf{C}_{ab}$:

$$\mathbf{j}_a^b = \left(\overline{\mathbf{K}}_a F_{ab} - kT\nabla_1 F_{ab} + \mathbf{C}_{ab} + \sum_c n_c \int \mathbf{C}_{ac} h_{cb}\, d\mathbf{r}_3\right)/R_a \tag{10}$$

This equation is the nonequilibrium analog of the Ornstein–Zernike relation. The pair-correlation function $h_{ab} = F_{ab} - 1$ and the direct correlation force are in the diffusion approximation connected by the continuity equation:

$$\begin{aligned}(\partial/\partial t)h_{ab} = \nabla_1 \cdot \left(kT\nabla_1 h_{ab} - \mathbf{C}_{ab} - \sum_c n_c \int \mathbf{C}_{ac} h_{cb}\, d\mathbf{r}_3 - (1 + h_{ab})\overline{\mathbf{K}}_a\right)/R_a \\ + \nabla_2 \cdot (a \leftrightarrow b, 1 \leftrightarrow 2) \qquad (11)\end{aligned}$$

In equilibrium $\operatorname{rot}\mathbf{C}_{ab} = \mathbf{0}$ and therefore we can write

$$\mathbf{C}_{ab}^0 = kT\nabla c_{ab}^0 \tag{12}$$

where c_{ab}^0 is the well-known direct correlation function. In this case from (10) follows the Ornstein–Zernike relation:

$$h_{ab}^0 = c_{ab}^0 + \sum_c n_c \int d\mathbf{r}_3\, c_{ac}^0 h_{cb}^0 \tag{13}$$

($\mathbf{K}_a^{\text{rel}}$ is zero in that case.)

Therefore our definitions are consistent with the equilibrium direct correlation formalism.

In order to formulate the appropriate boundary conditions for the problem (11) at small distances let us assume that the potential possesses a hard core;

$$\psi_{ab} = V'_{ab} + V_{ab}, \qquad \begin{aligned} V'_{ab} &= \infty, \qquad \text{if} \quad r < R_{ab} \\ V'_{ab} &= 0, \qquad \text{if} \quad r > R_{ab} \end{aligned}$$

Then the Fuoss–Kelbg boundary conditions read

$$(\mathbf{r}_1 - \mathbf{r}_2) \cdot \left[\mathbf{j}_a^b(2,1) - \mathbf{j}_b^a(1,2)\right] = 0, \qquad \text{if} \quad |\mathbf{r}_1 - \mathbf{r}_2| = R_{ab} \tag{14}$$

It is easy to find a formal solution of (11) by Fourier transforms. To simplify the calculations we restrict the considerations to binary electrolytes and weak external fields ($\mathbf{K}_a = e_a\mathbf{E}$). Therefore we have in this case

$$h_{ab} = h^0_{ab} + h^1_{ab}, \qquad \mathbf{C}_{ab} = kT\nabla c^0_{ab} + \mathbf{C}^1_{ab} \tag{15}$$

where h^1_{ab} and $\mathbf{C}^1_{ab}$ are the first deviations from the equilibrium functions. Furthermore, we find in the stationary case $(\partial/\partial t)F_{ab} = 0$

$$h^1_{11} = h^1_{22} = 0 \quad \text{and} \quad \mathbf{C}^1_{11} = \mathbf{C}^1_{22} = 0$$

With this relations Eq. (11) can be solved in Fourier space. The result is

$$h^1_{12}(k) = \Big[(e_1w_1 - e_2w_2)h^0_{12}(k)\mathbf{E} + \Big[1 + w_1n_2h^0_{22}(k) + w_2n_1h^0_{11}(k)\Big]\mathbf{C}^1_{12}(k)\Big]\cdot\mathbf{k}\beta/\Big[k^2D(k)\Big] \tag{16}$$

Here are

$$D(k) = 1 - n_1w_1c^0_{11}(k) - n_2w_2c^0_{22}(k)$$

and

$$w_1 = R_2/(R_1 + R_2), \qquad w_2 = R_1/(R_1 + R_2), \qquad \beta = 1/kT$$

The formal solution given here will satisfy the boundary conditions if the integration constant in $\mathbf{C}^1_{ab}$ is chosen in an appropriate way. This is not a trivial task.

The problem in this theory is to find $\mathbf{C}_{ab}$, which means we have to solve equation (9) in a given approximation for the average force $\overline{\mathbf{K}}^b_a$ or F_{abc}. Let us first study the limit of very small concentrations. In this limit we have

$$\overline{\mathbf{K}}^b_a = -\nabla\psi_{ab} + O(n)$$

and find from (9)

$$\mathbf{C}_{ab} = -(1 + h_{ab})\nabla\psi_{ab} \tag{17}$$

with the equilibrium solution

$$c^0_{ab} = \exp(-\beta\psi_{ab}) - 1 \tag{18}$$

For the deviations from equilibrium we get

$$\mathbf{C}^1_{ab} = h^1_{ab}\nabla(-\psi_{ab}) \tag{19}$$

The boundary condition has in the limit of small concentrations the simple form

$$(\partial/\partial r)h^1_{12}(r,\vartheta) = \beta E\exp(-\beta\psi_{12})\cos\vartheta(e_1R_1 - e_2R_2)/(R_1 + R_2), \quad \text{if} \quad r = R_{12} = R \tag{20}$$

This very simple relation may be used as a zeroth approximation to the condition (14) even at finite (not-too-large) concentrations.

In order to demonstrate the whole procedure let us give finally the solution in the limit of small densities which satisfies the boundary conditions. We obtain[(6)]

$$
\begin{aligned}
h^1_{12}(r,\vartheta) = {} & \exp\left[-\beta V'_{12}(r)\right](e_1 - e_2)\,\beta E \\
& \times \cos\vartheta((T+1)(\exp(1/r)(1-2r)+1+2r)/(T-1) \\
& + \exp(1/r)(1+2r)-1-2r)/8
\end{aligned}
\tag{21}
$$

$$
\begin{gathered}
T = \exp(-b)(1+b+b^2/2), \qquad 1 = -e_1 e_2 \beta / D_0, \quad b = 1/R \\
\beta \mathbf{C}^1_{12}(r,\vartheta) = h^1_{12}(r,\vartheta) 1 \cdot \mathbf{r}/r^2
\end{gathered}
\tag{22}
$$

The well-known Onsager solution for h^1_{ab} which is obtained in the case $R_{ab} \to 0$ $(\psi_{ab} = e_a e_b / D_0 r)$ follows from Eq. (16) with the further relations

$$c^0_{ab} = -\beta\psi_{ab} \quad \text{and} \quad \mathbf{C}^1_{ab} = \mathbf{0} \qquad \text{(Ref. 14)}$$

3. THE CLOSURE RELATION

In order to get higher approximations in the calculation of the direct correlation force, we have to look for closure relations for the hierarchy of distribution functions. This means tractable approximations for $F_{abc}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ in terms of pair-distribution functions or equivalently a second relation between $\mathbf{C}_{ab}$ and F_{ab}. Let us first use a simple procedure which is based on the analogy to equilibrium HNC theory where the closure relations reads

$$c^0_{ab} = F^0_{ab} - 1 - \ln F^0_{ab} - \beta\psi_{ab} \tag{23}$$

By a formal extension of this relation to nonequilibrium we would obtain

$$\beta \mathbf{C}_{ab} = \nabla h_{ab} - \nabla \ln(1 + h_{ab}) - \beta \nabla \psi_{ab} = \nabla c_{ab} \tag{24}$$

However, this equation cannot be correct for two reasons: (1) It implies a direct correlation force free of rotational parts $(\operatorname{rot} \mathbf{C}_{ab} = \mathbf{0})$. (2) Equation (24) is in evident contradiction to (19), because in the limit $n_a \to 0$ it follows from (24) that

$$\beta \mathbf{C}^1_{ab} = \nabla \left\{ h^1_{ab} \left[1 - \exp(\beta\psi_{ab}) \right] \right\} \tag{25}$$

Let us consider now a more satisfactory statistical derivation of HNC approximations for transport processes which is based on a paper by Verlet[(12)] on the HNC approximation for equilibrium distribution functions.

In order to do this we have for a given approximation for F_{abc} and therefore for $\overline{\mathbf{K}}^b_a$ to solve Eq. (9). We use an approximation for F_{abc} which can be obtained from the Meeron–Salpeter representation of F_{abc} in a cluster series of two-particle distributions[(13)]:

$$F_{abc} = F_{ab}F_{bc}F_{ac}\left(1 + \sum_d n_d \int d\mathbf{r}_4\, h_{ad}h_{bd}h_{cd} + \cdots\right) \tag{26}$$

Now we introduce the approximation (26) in the definition of $\bar{\mathbf{K}}_a^b$ by Eq. (8) and get

$$\begin{aligned}
&F_{ab}(12)\bar{\mathbf{K}}_a^b(12)\\
&\quad = F_{ab}(12)\left[-\nabla_1\psi_{ab}(12)\right] + F_{ab}(12)\sum_c n_c \int d\mathbf{r}_3\, h_{bc}(23)\\
&\qquad \times\Big\{\left[-\nabla_1\psi_{ac}(13)\right]F_{ac}(13)\\
&\qquad\quad + \sum_d n_d \int d\mathbf{r}_4\; F_{ad}(14)\left[-\nabla_1\psi_{ad}(14)\right]h_{ac}(13)h_{dc}(43)F_{bd}(24)\Big\}
\end{aligned} \tag{27}$$

Using this approximation in Eq. (9) we get

$$\begin{aligned}
&\mathbf{C}_{ab}(12) + \sum_c n_c \int d\mathbf{r}_3\, \mathbf{C}_{ac}(13)h_{cb}(32)\\
&\quad = -\nabla_1\psi_{ab}(12)F_{ab}(12)\\
&\qquad + F_{ab}(12)\sum_c n_c \int d\mathbf{r}_3\, F_{ac}(13)\left[-\nabla_1\psi_{ac}(13)\right]F_{bc}(23)\\
&\qquad + F_{ab}(12)\sum_{c,d} n_c n_d \int\!\!\int d\mathbf{r}_3\, d\mathbf{r}_4\, F_{ad}(14)\left[-\nabla_1\psi_{ad}(14)\right]\\
&\qquad \times h_{ac}(13)h_{dc}(43)h_{bc}(23)F_{bd}(24)
\end{aligned} \tag{28}$$

In addition we use in the n^2 term the approximations $F_{ab} = 1$ and $F_{bd} = 1$. Then the following solution can be obtained:

$$\begin{aligned}
\mathbf{C}_{ab}(12) = {}& -\nabla_1\psi_{ab}(12)F_{ab}(12)\\
& + h_{ab}(12)\sum_c n_c \int d\mathbf{r}_3 \left[-\nabla_1\psi_{ac}(13)\right]F_{ac}(13)h_{bc}(23)
\end{aligned} \tag{29}$$

$$F_{ab}(12)\bar{K}_a^b = -\nabla_1\psi_{ab}(12)F_{ab}(12) + F_{ab}(12)\sum_c n_c \int d\mathbf{r}_3\, \mathbf{C}_{ac}(13)h_{bc}(23) \tag{30}$$

It is easy to eliminate $\bar{\mathbf{K}}_a^b$ with the help of Eq. (9). The result is then

$$\mathbf{C}_{ab} = -\nabla_1\psi_{ab}F_{ab} + h_{ab}\sum_c n_c \int d\mathbf{r}_3\, \mathbf{C}_{ac}h_{bc} \tag{31}$$

Equation (31) is the nonequilibrium analog of the HNC closure. As we can verify immediately from Eqs. (12) and (13) follows in the equilibrium case directly Eq. (23). But we may derive this result also in another way: Utilizing the nonequilibrium Ornstein–Zernike relation (10), we get a useful relation for the two-particle flow without integral terms:

$$\left(R_a \mathbf{u}_a^b - \bar{\mathbf{K}}_a\right) h_{ab} = \mathbf{C}_{ab} - kT \nabla_1 F_{ab} + kT \nabla_1 \ln F_{ab} + \nabla_1 \psi_{ab} \tag{32}$$

This equation is a second relation between h_{ab} and $\mathbf{C}_{ab}$ which may be used instead of Eq. (31). Together with the equation of continuity (11) and the nonequilibrium Ornstein–Zernike equation (10) we get a closed system of equations for the determination of the correlation functions h_{ab} of the ions in electrolyte solutions in nonequilibrium situations. To get (23), we have to take into account (12) and the fact that $\mathbf{u}_a^b = \mathbf{K}_a = \mathbf{0}$ in equilibrium. Then integrating (32) and recall from the boundary conditions at infinity that the integration constant must be zero, we arrive at the equilibrium HNC closure. Still we have to answer the question how the boundary conditions (14) or (20), respectively, can be satisfied. This is possible at least in two ways:

(i) The Fourier transform in Eq. (16) is chosen in such a way that the boundary condition (b.c.) is fulfilled, i.e., an appropriate integration pathway is to be found.

(ii) The normal Fourier transform with the usual pathway of integration is used; however, a homogeneous solution of the following equation,

$$(\partial/\partial t) h_{12}^1(12) = \nabla_1 \cdot \left(-\nabla_1 h_{12}^1(12) + n_1 \int d\mathbf{r}_3\, \nabla_1 c_{11}^0(13) h_{12}^1(32)\right)/R_1$$
$$+ \nabla_2 \cdot \left(-\nabla_2 h_2^1(21) + n_2 \int d\mathbf{r}_3\, \nabla_2 c_{22}^0(23) h_{21}^1(31)\right)/R_2 \tag{33}$$

is added to Eq. (16). The stationary solution with the appropriate symmetry reads

$$h_{12}^1(\mathbf{k}) = \left[(e_1 w_1 - e_2 w_2) c \mathbf{E} \cdot \mathbf{k}\right] / \left[k^2 D(k)\right] \tag{34}$$

where c is a free constant which may be used to fit the b.c. We note that in this approach the MSA discussed earlier$^{(9)}$ is obtained by the assumption $\mathbf{C}_{12}^1 \equiv 0$.

4. CONCLUSIONS

This paper is devoted to the problem of finding a nonequilibrium analog of the well-known HNC approximation in equilibrium. This problem has no unique solution, we have presented here one possibility which seems to be the most natural extension of the equilibrium relations. A general solution of the problem stated in Eqs. (10), (11), and (31) or (32) with the b.c. (14) requires considerable numerical effort and should be fulfilled with the help of fast Fourier transforms as in equilibrium.$^{(1)}$ Only in the limit of small densities explicit answers are found in an analytical way. Calculations in both directions are in progress. We will report about the results in a following paper.

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