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Note

Solution of Ornstein–Zernike Integral Equations for Lattice Gases

I. INTRODUCTION

Thermodynamic and structural properties of fluids are routinely routinely studied by solving the Ornstein–Zernike equation for the radial distribution function employing an approximate closure such as the hypernetted chain (HNC) approximation or the Percus–Yevick approximation. For electrolyte solutions [1] the HNC equations are particularly successful and the primitive model of charged hard spheres in a structureless medium is well understood. There is a solid state analogue of this electrolyte model, the coulomb lattice gas, which is of current interest in several problems of point defects in ionic solids. An extension of analytic methods from electrolyte theory [2], and numerical studies of integral equations [3, 4] have both been used in attempts to understand the properties of systems exhibiting superionic conductivity [2, 4], and other simpler systems [3]. We shall first outline the problems which have been previously found in solving integral equations on a lattice where we are concerned with lattice summations rather than integrations, and then outline a useful solution to the problem.

For the electrolyte solution studies [5] an important time saving is obtained by using the fast Fourier transform (FFT) to calculate the convolution integral, and a simple Picard iteration procedure is used to solve the equations. The slow convergence of the iteration is a limiting factor [6]. The situation is poorer for the lattice gas since the Fourier transforms are 3-dimensional and the advantages of using the one dimensional FFT are lost. Routine use of Fourier transforms for related defect problems [7] convinces us that there is little gain in Fourier transformation in the present context. A recent advance in electrolyte solution studies [8] has greatly improved the convergence by coupling the Picard iteration with a Newton–Raphson (NR) iteration on a smaller grid. A simplified version of this method has been used for lattice defect studies [3] with the summations performed in real space. Only very limited results were obtained because of poor convergence. Here we present a much more successful scheme using only the NR method at all points in which the convolution sums are evaluated using a table of lattice wiehgts. Taken together, these refinements greatly reduce the computer time and substantially increase the area of the phase diagram for which solutions can be obtained.

In the next section we first outline the method used for the convolution lattice

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summations and then describe its use to solve the HNC equations for a 2-component lattice gas of equal and opposite charges on an fcc lattice. In the final section we describe calculations using parameters appropriate to a model of defects in AgCl. Sample results are presented and compared with previous calculations [3] in order to evaluate the relative performance of the method.

II. METHOD

For a 1-component fluid the Ornstein–Zernike equation,

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

together with an approximate expression for the direct correlation function, $c(|\mathbf{r}|)$, in terms of $h(|\mathbf{r}|)$ and the pair potential, $u(|\mathbf{r}|)$, gives an integral equation which may be solved for $h(|\mathbf{r}|)\equiv g(|\mathbf{r}|)-1$. Here, $g(|\mathbf{r}|)$ is the pair correlation function, $\rho=N/V$ is the number density, and the integration is over the total volume V. Equation (1) applies to a lattice gas when $\mathbf{r}$ and $\mathbf{r}'$ are restricted to be lattice vectors, the integration sign is interpreted as a summation over all vectors $\mathbf{r}'$ for a crystal of B lattice sites, and ρ is interpreted as a site fraction (N/B). The lattice vectors $\mathbf{r}$ and $\mathbf{r}'$ can be zero; since two atoms cannot be assigned to the same site $h(|\mathbf{r}|=0)=-1$. We consider only cubic-based lattices.

We can rewrite Eq. (1) in a more convenient form. For any vector $\mathbf{R}$ which connects two sites which are lth nearest-neighbours we denote the distance $|\mathbf{R}|$ by r_l, with r_0 corresponding to $\mathbf{R}=0$. We will refer to the index l of r_l as the shell number since each atom is in the lth neighbour shell of the other. In Eq. (1), let $|\mathbf{r}|=r_i$. To do the summation over $\mathbf{r}'$ we first sum over all sites for which $|\mathbf{r}'|=r_j$ and then repeat this for all possible different values of $|\mathbf{r}'|$, i.e., sum over all j. Let $w_{k(i,j)}$ denote the number of sites encountered such that $|\mathbf{r}-\mathbf{r}'|=r_k$ when we sum over all the vectors for which $|\mathbf{r}'|=r_j$. The OZ equation can then be written in the form

$$h(r_i)=c(r_i)+\rho\sum_{j=0}\sum_{k}h(r_j)\,w_{k(i,j)}c(r_k). \tag{2}$$

The weights $w_{k(i,j)}$ may be calculated separately and a suitable table of results incorporated in the program to solve the OZ equation.

The calculation of the weights follows straightforwardly from the definition. For a given shell i, in Eq. (2), pick any convenient representative vector $\mathbf{r}$ of magnitude r_i. Then for each shell j $(j=1,2,\dots,n)$ generate all vectors $\mathbf{r}'$ of magnitude r_j, calculate the corresponding vectors $\mathbf{r}-\mathbf{r}'$, and sort them according to length to determine to which $w_{k(i,j)}$ each contributes. The process is repeated for $i=1,2,\dots,n$. Here n is the neighbour separation beyond which $h(r)$ is assumed zero in solving the OZ equation. There are two well-known points about the geometry of lattices [9] to note here.

(i) Lattice vectors are conventionally written in the form

$$\mathbf{r} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \tag{3}$$

where $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ are basis vectors and (l_1, l_2, l_3) are integers. It is important to remember when calculating the weights that there may be several sets of 3 positive integers which, with their permutations and with sign changes, generate vectors of the same length, e.g. (4, 1, 1) and (3, 3, 0) in the fcc lattice.

(ii) It is more convenient, in computing terms, to tabulate the shell numbers l rather than the actual distances r_l, since one will wish to represent the correlation functions as 1-dimensional arrays labelled by shell number. The relation between r_l and l needs care. In calculating weights it is convenient to use dimensionless lengths $\bar{r}_l$ defined by

$$\bar{r}_l = (r_l/a)^2/2, \tag{4}$$

where a is the lattice spacing. For the first few nonzero shell numbers $l = 1, 2,...,$ corresponding to first neighbour separation, second neighbour separation,..., one has $\bar{r}_l = l$. However, it sometimes happens that there are no neighbours at any separation r_l such that $\bar{r}_l$ defined by (4) is equal to a particular integer. The smallest integers $\bar{r}_l$ for which this occurs in the fcc lattices are 14 and 30. This is called the phenomenon of "empty shells" in the literature [9]. In the storage and use of weights it is important to use the shell numbers l, which is just the set of integers without gaps, rather than the reduced distances $\bar{r}_l$ which are convenient in calculating the weights. If this is not done the NR routine becomes unnecessarily complicated. Similar remarks apply to other cubic-based lattices [9].

TABLE I

The Weights $w_{k(i,j)}$ for the fcc Lattice, Indexed to Pairs of Shells as in Eq. (2).

(i, j)	$w_{k(i,j)}$	$k(i, j)$
(1, 1)	1, 4, 2, 4, 1	0, 1, 2, 3, 4
(1, 2)	2, 2, 2	1, 3, 5
(1, 3)	4, 2, 4, 4, 4, 2, 4	1, 2, 3, 4, 5, 6, 7
(2, 1)	4, 4, 4	1, 3, 5
(2, 2)	1, 4, 1	0, 4, 8
(2, 3)	4, 8, 8, 4	1, 3, 7, 9
(3, 1)	2, 1, 2, 2, 2, 1, 2	1, 2, 3, 4, 5, 6, 7
(3, 2)	1, 2, 2, 1	1, 3, 7, 9
(3, 3)	1, 2, 2, 2, 1, 4, 4, 1, 2, 2, 2, 1	0, 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12

As an illustration, Table I gives weights and shell numbers for the first three shells of the fcc lattice. For the calculations detailed below the table contained 93 shells. It is important to have the entries in the table in a suitable order, so that they can be accessed in sequence, hence keeping computation time to a minimum. The order used is illustrated in Table I. For the actual table the first 93 entries are for $i=1$ with $j=1, 2,..., 93$. These are followed by the corresponding entries for $i=2, 3,..., 93$ with all values of j in each case. In this way the contributions to the sum over j in Eq. (2) are evaluated in the correct order without having to search for the correct entry in the table.

In order to illustrate the main calculation we consider a simple model system. The two components, labelled 1 and 2, occupy an fcc lattice in equal concentrations ρ (site fraction). The energy of interaction between pairs of particles is assumed to be coulombic, and such that two particles cannot occupy the same site:

$$\begin{gathered} u_{11}(r_i) = u_{22}(r_i) = -u_{12}(r_i) = e^2/Dr_i, \qquad i = 1, 2,..., n \\ u_{11}(0) = u_{22}(0) = u_{12}(0) = \infty, \end{gathered} \tag{5}$$

where D is the dielectric constant. It follows by symmetry that there are only two independent correlation functions which we denote by $h_1(r)$ and $h_2(r)$, where

$$h_1(r) \equiv h_{11}(r) = h_{22}(r) \text{ and } h_2(r) \equiv h_{12}(r) = h_{21}(r). \tag{6}$$

Using a similar notation for other functions the Ornstein–Zernike equations for the two component system can be written as follows

$$\begin{gathered} \gamma_1(r_i) = \rho \sum_{j,k} w_{k(i,j)}[h_1(r_j)\, c_1(r_k) + h_2(r_j)\, c_2(r_k)] \\ \gamma_2(r_i) = \rho \sum_{j,k} w_{k(i,j)}[h_1(r_j)\, c_2(r_k) + h_2(r_j)\, c_1(r_k)], \end{gathered} \tag{7}$$

where

$$\gamma_\alpha(r_i) = h_\alpha(r_i) - c_\alpha(r_i), \qquad \alpha = 1, 2 \tag{8}$$

The hypernetted chain approximation,

$$\begin{gathered} c_\alpha(r_i) = \exp[-u_\alpha(r_i)/k_B T + \gamma_\alpha(r_i)] - \gamma_\alpha(r_i) - 1 \\ h_\alpha(r_i) = \exp[-u_\alpha(r_i)/k_B T + \gamma_\alpha(r_i)] - 1, \end{gathered} \tag{9}$$

converts Eqs. (7) to two equations in two unknowns, γ_1 and γ_2. The equations can be solved by the NR method. Given a set of initial estimates $\gamma_\alpha^{[1]}(r_i)$ which yield new values $\gamma_\alpha^{[2]}(r_i)$ calculated from the right hand sides of Eqs. (7), then the set of new estimates $\gamma_\alpha^{[3]}$ is given by

$$\gamma_\alpha^{[3]}(r_i) = \gamma_\alpha^{[1]}(r_i) - \sum_{\beta=1,2} \sum_j (J^{-1})_{\alpha i,\beta j} [\gamma_\beta^{[1]}(r_j) - \gamma_\beta^{[2]}(r_j)], \tag{10}$$

where the recipe for the Jacobian matrix is

$$J_{\alpha i,\beta j} = \delta_{\alpha,\beta}\delta_{i,j} - \partial\gamma_\alpha^{[2]}(r_i)/\partial\gamma_\beta^{[1]}(r_j). \tag{11}$$

It is straightforward to differentiate equations (7) and obtain expressions for the derivatives, e.g.,

$$J_{1i,1j} = \delta_{i,j} - \rho \sum_k w_{k(i,j)} \{h_1(r_j)\, h_1(r_k) + [h_1(r_j) + 1]\, c_1(r_k)\}. \tag{12}$$

Both the new values $\gamma_\alpha^{[2]}(r_i)$ and the elements $J_{\alpha i,\beta j}$ are straightforward to compute using the table of weights. The NR iteration was terminated when $\xi \leqslant 10^{-5}$, where

$$\xi = \sum_{i=0}^{n} \sum_{\alpha=1,2} |\gamma_\alpha^{[3]}(r_i) - \gamma_\alpha^{[1]}(r_i)|/(2n+2). \tag{13}$$

III. Sample Results and Discussion

In this Section we present typical results for the coulomb lattice gas model described above. The dielectric constant and lattice spacing used correspond to AgCl and were the same as in an earlier study [3]. Silver chloride doped with divalent cations contains a lattice gas of cation vacancies and divalent cations on the fcc silver sublattice. At separations greater than about three lattice spacings the defect interactions are coulombic, but the present model takes them as coulombic at all separations. The model plays the same role as is played by the model of charged hard spheres in a continuum in electrolyte theory; it is the simplest useful model.

The calculated correlation functions may be used to calculate some of the thermodynamic properties of the lattice gas directly. The following expressions give the activity coefficients [3], $f = f_1 = f_2$, the compressibility χ_T of the lattice gas expressed as the reduced inverse compressibility $S^{-1} = (2\rho k_B T\chi_T)^{-1}$, and the configurational energy per point defect, E_c:

$$\ln f = \rho \sum_{\alpha=1,2} \sum_i w_i \{\tfrac{1}{2} h_\alpha(r_i)\, \gamma_\alpha(r_i) - c_\alpha(r_i)\},$$

$$S^{-1} = \left\{1 + \rho \sum_{\alpha=1,2} \sum_i w_i h_\alpha(r_i)\right\}^{-1}$$

$$E_c/k_B T = \tfrac{1}{2}\beta\rho f(T) \sum_{\alpha=1,2} \sum_i w_i g_\alpha(r_i)\, u_\alpha(r_i), \tag{14}$$

where w_i is the number of lattice sites in shell i (and occurs in the previous tabulation of weights since $w_{i(0,i)} = w_i$), and

$$f(T) = 1 + T\left(\frac{\partial \ln D}{\partial T}\right) \tag{15}$$

arises from the temperature dependence of the dielectric constant. A useful check on the quality of the solutions of the HNC equations is provided by the electrical neutrality and second moment conditions [1, 3],

$$\begin{aligned} \Delta_0 &= 1 + \rho \sum_i w_i[h_1(r_i) - h_2(r_i)], \\ \Delta_2 &= 1 + (\kappa^2\rho/6) \sum_i w_i r_i^2[h_1(r_i) - h_2(r_i)], \end{aligned} \tag{16}$$

where κ is the Debye–Hückel screening constant, defined by $\kappa^2 = 4\pi e^2\rho/Dk_BTa^3$. The moment defects Δ_0 and Δ_2 would be zero for exact solutions of the HNC equations.

We present results for the above quantities at 250° C for several values of ρ in Table II; results from the earlier study [3] are included for comparison. We note that in the present work the moment defects Δ_0 and Δ_2 are smaller in nearly every case and for concentrations up to 0.05 the values compare favourably with dilute

TABLE II

Thermodynamic Results for the Lattice Gas Model with AgCl Parameters at 250°C for Various Concentrations ρ.

ρ	Δ_0	Δ_2	$-\ln f$	S^{-1}	$-E_c/k_BT$
0.005	0.019	0.079	1.660	0.604	3.286
	−0.088	−1.625	1.694		
0.01	0.009	0.044	1.991	0.580	3.839
	−0.025	−0.477	2.004		
0.02	0.001	0.014	2.332	0.566	4.415
	−0.026	−0.013	2.334		
0.03	−0.001	−0.003	2.527	0.568	4.758
	−0.005	−0.045	2.531		
0.04	−0.002	−0.018	2.659	0.577	5.002
	−0.006	−0.058	2.665		
0.05	−0.003	−0.043	2.755	0.590	5.192
0.10	−0.019	−0.486	2.998	0.693	5.787

Note. At each ρ the first line refers to the present work and the second line to an earlier study [3].

electrolyte solutions, for which values of $\Delta_0 = 0.005$ and $\Delta_2 = 0.1$ are acceptable. For $\rho = 0.1$, corresponding to 1/5 of the sites occupied by defects, and for higher concentrations the moment defects are larger; we have been unable to find information on them for fluids at comparable concentrations. We also note that the agreement of our $\ln f$ with earlier values [3] is good; the slight difference at the lowest concentration is almost certainly due to very slow convergence in the earlier method.

The superior quality of the results is accompanied by very substantial savings in computer time. The earlier study [3] adapted a method [8] for fluids; it used an NR refinement of the correlation functions for the shortest lattice spacings followed by a Picard iterative refinement at all separations. The process was dominated by the slow convergence of the Picard iterations, which essentially refined the tails of the correlation functions. In the present work we applied the NR technique at all separations. The disadvantage of the method is that it involves the inversion of larger matrices, of order n^2, where n is the number of shells for which the $h_\alpha(r_i)$ are computed. This can lead to large demands on storage and CPU time but if storage is available then it is feasible when coupled with use of the table of weights method to carry out the lattice summations efficiently. It is important that the weights are calculated separately and are stored in a suitable order so that they can be accessed without having to search a table; this is much more efficient than the earlier method [3] for the convolution lattice summations. The gains in efficiency are illustrated by the results above which were obtained using a maximum of $n = 93$ shells, as in the earlier study by Allnatt and Allnatt [3]. They reported that 1600–2000 iterations were required with a CPU time of about 1–30s per iteration. The present technique required 10–30 iterations with a CPU time of 20–80s per iteration.

Finally, the superior convergence of the NR technique has allowed us to examine a much wider range both of thermodynamic states and of defect models. For example, for the model used above we have obtained solutions up to concentrations of $\rho = 0.4$ at 200°C, 250°C, and 400°C whereas earlier studies were limited by poor convergence to $\rho \leqslant 0.05$ and temperatures of 250°C and above. A number of new features appear in the new range, including highly structured correlation functions similar to those found in the charged hard sphere fluid [6] at comparable concentrations. A few concentrations were studied to as low as 170°C; evidence for multiple solutions arising from different starting points was found. This corresponds to region C of Larsen and Friedman [6] where the HNC approximation is unreliable. We have also been able to study a more realistic model of defects in AgCl which employs theoretical non-coulombic interaction energies up to and including the third neighbour separation and coulombic interactions at larger separations. The lack of smoothness in the variation of defect interaction energy with distance for this more realistic type of model was found in the earlier work to cause problems which are now much reduced. A full presentation of these results will be made in a future paper.

In conclusion, we have presented a technique for solving Ornstein–Zernike integral equations for lattice gases which is simpler and more efficient than those employed earlier. It makes the range of calculations accessible for lattice gas models

much more comparable to that available for fluids and is proving valuable in the study of lattice defects in systems with coulombic interactions.

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