Linear singlet equation in the surface phenomena physics

Yu Agrafonov and I Petrushin
Department of Physics, Irkutsk State University, 1 Karl Marx St., 664003 Irkutsk, Russia
E-mail: agrafonov@physdep.isu.ru

Abstract. We consider difficulties and algorithms of numerical solution of nonlinear equations of statistical physics of liquids. Analysis of nonlinear singlet equations of the surface phenomena in liquids is carried out. To solve Fredholm integral equations of second kind we compare the known algorithms and evaluate their application for linear singlet equation.

1. Introduction
Statistical physics of liquids bases on Born-Green-Yvon-equations infinite system (or chain) of equations for \( l \)-particle distribution functions. This system is equivalent to equations for one- and two-particle distribution functions, which may be written as Ornstein–Zernike (OZ) integral equations. The kernel of integral equations is expressed by infinite functional series of irreducible diagrams, which depends on distribution functions.

For isotropic systems we can summarize some of the terms in equation for two-particle distribution function and reduce it to approximate integral equation for the binary correlation function, but the precision of such approximation is hard to estimate. When describing the surface phenomena in liquids it’s hard to summarize the diagrams in equation for one-particle function. To solve this problem one can apply singlet approximation, which precision is also unknown.

In our previous study [1] we suggested to define infinite series for direct correlation functions in particular way to cancel nonlinearity and reduce singlet equation to linear integral equation in form of Fredholm integral equations of the second kind. This linear integral equation can be solved by the number of methods, which are reviewed also in that study.

2. Integral equations and structure of liquid
Statistics of the considered molecular system is based on Born-Green-Yvon-equations system (also known as BGY hierarchy) for \( l \)-particle functions and on \( G_{l,...,l}=\{r_i,...,r_l\} \) for ensemble of identical particles, where \( l=1,...,N \) \((N\to\infty)\). These particles interact with each other through potential \( \Phi_{ij}(r_{ij}) \), where \( r_{ij}=|r_i-r_j| \) is the distance between centers of particles \( i \) and \( j \).

The BGY-equations system may be transformed to equations for one- and two-particle distribution functions, which may be written as OZ [1, 2]:

\[
\omega_l = nG_2C^{(1)}_{12}d(2) + \mu, \quad h_{12} = C^{(2)}_{12} + nC^{(2)}_{13}h_{23}d(3). \tag{1}
\]

All higher order functions can be expressed by these two functions. Here we integrate on coordinates of \( i \)-particle, where \( d(i)=dr_i \), \( n \) is a density. Due to its positive value one-particle
distribution function may be expressed as \( G = \exp(-\Phi_i (kT)^{-1} + \omega_i) \), where \( \Phi_i \) is potential energy in external field; \( \omega_i \) is one-particle thermal potential; \( \mu \) is chemical potential, which is defined by condition of passing to isotropic system in absence of external forcefield. The binary correlation function \( h_{ij} = [\exp(-\Phi_{ij} (kT)^{-1} + \omega_{ij}) - 1] \) is expressed via direct particles interaction \( \Phi_{ij} \), and indirect interaction \( \omega_{ij} \). Direct correlation functions \( C_{ij}^{(k)} \)

\[
C_{ij}^{(1)} = h_{ij} - \omega_{ij} - \frac{1}{2} h_{ij} (\omega_{ij} + M_{ij}^{(1)}) ; \quad C_{ij}^{(2)} = h_{ij} - \omega_{ij} + M_{ij}^{(2)}
\]

(2)

are expressed by infinite functional series of irreducible diagrams \( M_{ij}^{(1)} \) and \( M_{ij}^{(2)} \), which depends on distribution functions. Usually we have to take into account only these terms which can be summarized and omit the others. As a result, we get the closure – the relation between direct and the binary correlation function. Applying the closure reduces the OZ equation to the number of nonlinear integral equations, which can be solved numerically. It’s hard to methodically estimate the precision of such approximation; the only way is to compare the results with numerical experiment data (Monte-Carlo or molecular dynamics modelling). The most popular closures are: hypernetted (HNC), Perkus–Yevick (PY), Rogers–Young (RY), and Martynov–Sarkisov (MS).

For spherically symmetric systems one-particle distribution function is equal to one \( (G_i (r) = 1, \omega_i (r = 0)) \) and two-particle distribution function depends only on distance between particles \( h_{12} (r_1, r_2) = h_{12} (r_{12}) \). As a result, first equation of (1) reduces to evaluating chemical potential \( \mu = \ln a = const \). The second equation (1) determines the binary correlation function \( h_{12} (r_{12}) \), which can be evaluated by number of methods [9]. We should note that in PY equation direct correlation function is \( C_{ij}^{(2)} (r_{12}) = h_{12} - (\exp(\omega_{12}) - 1) \) and nonlinearity reduces from exponential to quadratic. In particular for hard spheres system the analytical solution is possible [4].

For systems with axial symmetry, such as a liquid near a hard surface, functions \( G_i (r_i), G_{12} (r_1, r_2) \) describe microstructure of the substance and allow to get all of the thermodynamic parameters (f. e. adsorption and surface tension). Analytical solution for one-particle distribution is possible only for particular cases: one- and two-dimensional system [5]. In general, solving the equations (1-2) for many variables functions numerically is hard problem and requires a lot of computational costs. One can simplify this task using boundary value \( C_{12}^{(1,0)} (r_{12}) \) for direct correlation function \( C_{12}^{(1)} (r_1, r_2) \). In this case, depending on closure used for evaluating (2) we get various nonlinear integral equations for one-particle distribution function depending on one variable (particle distance from the surface). All singlet approximations produce the equations of the same type (which are differ into kernel). All of these equations contain non-linear terms and have to solve numerically, but not require much computational power. Numerical approaches and algorithms of solving are reviewed in [6-8]. Methodical precision of singlet equations is unknown and must be evaluated by comparing with the results of numerical experiment data (Monte-Carlo or molecular dynamics modelling). In any case, numerical experiment is only way to verify the results and estimate the precision. We suggest to study the singlet equation further: define infinite series for direct correlation functions in particular way to cancel nonlinearity and reduce singlet equation to linear integral equation, which can be solved numerically. This approach we suggested for 3-dimensional hard sphere system near hard surface [3].

In the first equation of the system (1) direct correlation function expressed as

\[
C_{12}^{(1)} (r_{12}, z_1, z_{12}) = C_{12}^{(1,0)} (r_{12}) + C_{12}^{(1)} (r_{12}, z_1, z_{12}),
\]

(3)
where $C_{12}^{(1,0)}(r_{12})$ previously evaluated using known value of the binary correlation function $h_{12}(r_{12})$. Here we used cylindrical coordinates, where $r_{12}^2 = \rho_{12}^2 + z_{12}^2$, $z_{12} = \|z_2 - z_1\|$ and the origin located at the hard surface. We redefine all $S_{12}^{(l)}(r_{12}, z_1, z_{12})$ irreducible diagrams in particular way, so

$$n \int G_{s} S_{12}^{(l)}(r_{12}, z_1, z_{12}) d(2) = \omega_l(z_1) - (e^{\eta(z_1)} - 1). \quad (4)$$

Assuming this we write one-particle equation (1) as

$$(e^{\eta(z_1)} - 1) - 2\pi n \int dz_2 (e^{\eta(z_2)} - 1) \int r_{12} dr_{12} C_{12}^{(1,0)}(r_{12}) = -2\pi n \int dz_2 \int z_{12} r_{12} dr_{12} C_{12}^{(1,0)}(r_{12}), \quad (5)$$

where we use the hard sphere interaction potential and $G_s = \exp(\omega_l)$. This is the linear integral equation in form of Fredholm integral equations of the second kind. This linear integral equation can be solved analytically, if the kernel and the right part can be expressed analytically. For the 3-dimensional hard sphere system near hard surface with PY approximation we got the analytical solution [3]. For other closures one needs to get numerical solution of (5), but this procedure is rather simple than solving (1) for the many variables.

3. Algorithms and difficulties on numerical solutions of nonlinear equations of surface liquid physics

The binary correlation function, which is a part of the kernel and right term of the equation (5) – is a solution of representative nonlinear equation. The form of the solution depends on potential energy in external field, temperature and pressure. The Ornstein–Zernike (OZ) equation for the binary correlation function for $h(r)$ is a convolution and can be solved via Fourier transform. Evaluation of Fourier components is based on expanding the function $F(r) = r(h(r) - c(r))$ into the basis functions, Newton–Raphson combination and direct iterations. We should continue the iterations while reaching required precision. The convergence of iteration procedure depends on chosen density of the system as the starting point (initial approximation). Labik and Malijevsky [9, 10] suggested the rapid convergent method for solving the OZ equation with spherically symmetric interaction potential. Using the Perkus–Yevick and HNC approximation for hard sphere system and Lennard–Jones (LJ) liquid shows the rapid convergency of this method. The other advantages of this method – low sensitivity to initial approximation and relatively simple algorithm.

For molecular systems with more complex interaction potential method of Labik–Malijevsky cannot be applied: the integral equations are not the convolution. The binary correlation function $h_{12}(\mathbf{r}_1, \mathbf{r}_2)$ depends here of six or more arguments. Numerical solutions for many variables’ equations are hard and requires a lot of computation power [11-13]. So, there are high need for suitable approaches, approximations and algorithms. The other way here is to carry out numerical experiments at supercomputer centers and extract local microstructure from the raw experimental data [14].

4. Fredholm equations

Numerical solutions of Fredholm integral equations of the second kind are widely studied in past years. In particular, systematic description of solutions, approaches and algorithms of linear Fredholm integral equations of the second kind available in reviews [15-21]. Some of the numerical algorithms for solving nonlinear Fredholm integral equations of the second kind [22, 23] are very close by idea to singlet equations. Numerical algorithms for solving singular Fredholm integral equations are of special interest [24]. Probably to evaluate the binary correlation function $h_{12}(\mathbf{r}_1, \mathbf{r}_2)$ one can use the methods for numerical solution of many dimension Fredholm integral equations or neural network approaches [25-27].
5. Numerical solution for linear singlet equation

At first, using Labik–Malijevsky algorithm we solve OZ equation for hard sphere system with LJ potential: starting from ideal gas density until the phase transition of liquid–crystal. The same approach we use for LJ liquid taking into account temperature dependency. Using solutions of these two equations we can evaluate direct correlation function $C_{12}(r_{12})$. The numerical solution of singlet equation (5), which is Fredholm integral equation of the second kind, can be done with one of the methods described above.

As result we get local microstructure of boundary layers of liquid. To estimate the advantages and weaknesses of suggested approach one should compare this result with the numerical solution of singlet equation [6]. Next, we can evaluate direct correlation function of ideal glass by replica method [28]. This approach allows to study thin amorphous layers.

6. Conclusion

All equations applied in liquid and surface phenomena physics are approximate. Its methodical precision is usually unknown and the only way to evaluate it – to compare the results with numerical experiment data. We suggest an approach for statistical physics of surface phenomena: contribution of irreducible diagrams into infinite series for direct correlation functions may be evaluated in particular way to cancel nonlinearity. The result is singlet linear equation – integral Fredholm equation of second kind. For some classes of equation’s kernel analytical solution is possible, but in general it should be solved numerically. The great advantage here: complexity of this task is rather simple than for nonlinear equations. However, methodical precision must be evaluated by comparing with the results of numerical experiment data, but then we can compare the precision of equations. Another advantage of singlet equation: it can be generalized to study thin amorphous layers, which has vast application in technical and nanoscience.

Acknowledgements

We are grateful to Gavriluk A. A. for the interest to our study. The work is supported by the Russian Foundation for Basic Research (grant 18-02-00523a) and partially supported by the Ministry of Education and Science of the Russian Federation as part of State Task no. 3.1941.2017/PCh.

References

[1] Agrafonov Yu V and Petrushin I S 2020 Bull. Russian Acad. of Sci.: Physics 84 783
[2] Martynov G A 1997 J. Chem. Phys. 106 6095
[3] Vompe A G and Martynov G A 1997 J. Chem. Phys. 106 6095
[4] Wertheim M S 1963 Phys. Rev. Lett. 10 321.
[5] He Y, Rice S and Xu X 2016 J. Chem. Phys. 145 234508
[6] Tikhonov D A, Kiselyov O E, Martynov G A and Sarkisov G N 1999 J. Mol. Liquid. 82 3
[7] Agrafonov Yu V and Petrushin I S 2015 Physics Procedia 71 364
[8] Agrafonov Yu V and Petrushin I S 2016 J. Phys. Conf. Ser. 747 012024
[9] Labik S, Maliljevsky A and Vonka P 1985 Molecular Physics 56 709
[10] Maliljevsky A and Labik S 1987 Molecular Physics 60 663.
[11] Germain P and Amokrane S 2019 Phys. Rev. E 100 042614
[12] Zhou S 2014 Abstract and Applied Analysis 2014 751209
[13] Zhou S and Solana J R 2018 Molecular Physics 116 491
[14] Westen T and Gross J 2017 J. Chem. Phys. 147 014503
[15] Chen Z and Jiang W 2012 Applied Mathematics Letters 25 1131
[16] Ezzati R and Mokhtari F 2012 Int. J. of Phys. Sci. 7 1578
[17] Hatamzadeh-Varmazyar S and Masouri Z 2019 Int. J. Ind. Math. 11 79
[18] Mohammad M 2019 Symmetry 11 854
[19] Voytishek A and Shipilov N 2017 AIP Conf. Proc. 1907 030015
[20] Pandaa S, Marthaa S C and Chakrabartib A 2017 Appl. Math. and Comp. 271 102
[21] Maleknejad K and Nosrati Sahlan M 2010 Int. J. of Comp. Math. 87 1602
[22] Bazm S and Babolian E 2012 Commun. Nonlinear Sci. Numer. Simulat. 17 1215
[23] Hashmi M S, Khan N, and Iqbal S 2012 Appl. Math. and Comp. 218 10982
[24] Beyrami H, Taher L and Katayoun M 2016 J. of Comp. and Appl. Math. 300 385
[25] Heydari M, Avazzadeh Z, Navabpour H and Loghmani G B 2013 Appl. Math. Modelling 37 432
[26] Liang F and Lin F-R 2010 Appl. Math. and Comp. 216 3073
[27] Effati S and Buzhabadi R 2020 Neural Comp. and Appl. 21 843
[28] Bomont J M, Hansen J P and Pastore G 2014 J. Chem. Phys. 141 174505