

THE MULTIDENSITY INTEGRAL EQUATION APPROACH IN THE THEORY OF COMPLEX LIQUIDS

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Recent development of the multi-density integral equation approach and its application to the statistical mechanical modelling of a different type of association and clusterization in liquids and solutions are reviewed. The effects of dimerization, polymerization and network formation are discussed. The numerical and analytical solutions of the integral equations in the multi-density formalism for pair correlation functions are used for the description of structural and thermodynamical properties of ionic solutions, polymers and network forming fluids.

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1. INTRODUCTION

Ten years ago I had a possibility to have in the Beke-tov building in Kharkiv the seminar about the modern state of liquid theory. On this seminar was A.I. Akhiezer. The subject was very interested for him. He put a lot of questions that was important for understanding of problems and development of theory. For the last ten years we try to expand the techniques developed in the theory of simple liquids to more complex liquids. This short review of our activity in this field I would like to devote to the unforgettable memory of A.I. Akhiezer.

The pair distribution function $g(r)$ plays central role in the modern liquid state theory. It establishes a bridge between microscopic properties modeling by interparticle interactions and macroscopical ones such as structure, thermodynamic, dielectric, kinetic and other properties. The essenceal progress in the liquid state theory for the last decades is connected with the development of the integral equation technique which is based on the analytical or numerical calculation of the pair distribution function $g(r)$ by the solution of the Ornstein-Zernike (OZ) equation within different closures: the Percus-Yevick (PY) approximation, the hypernetted chain (HNC) one, the mean spherical approximation (MSA) and its different modifications [1,2]. The background of such closure relations is connected with diagram analyses of the Mayer density expansions of the pair distribution function and their applicabilities are tested usually by comparison with computer simulation results.

However such inequal equation approach is efficient enough only for fluids having not so strong interparticle attraction and needs an essential improvements for a more complex fluids with strong interparticle attraction which can lead to the clustering of particles into pairs or larger groups such as chains, networks, self-assembling aggregates etc. Due to the clustering the δ -like intraparticle distribution function appears and the distribution function can be divided into the intra- and interparticle parts

$$g(r) = g^{intra}(r) + g^{inter}(r). \quad (1)$$

In addition, resulting from clusterization the corresponding running integration numbers

$$n(R) = 4\pi\rho \int_0^R g(r)r^2 dr, \quad (2)$$

which describes the average number of particles in the sphere of radius R surrounding one of them which is found in the center of this sphere, divides into bounded (intra) and nonbounded (inter) parts

$$n(R) = n_{intra}(R) + n_{inter}(R), \quad (3)$$

where ρ is the number density of particles.

Due to the saturation of bounding

$$n_{intra}(R) \leq n_{bond} \quad (4)$$

where the number of bonds n_{bond} is fixed. Specifically, for pairs $n_{bond} = 1$, for chains $n_{bond} = 2$, for network $n_{bond} = 4$ etc.

Since the clusterization is caused by the attraction part of interparticle interaction for the description of their contribution it is more convenient to use the activity expansions instead of density ones [3]. In particular, in order to reproduce the correct low-density limit for the fluids with strong clusterization, an infinite number of terms in the density expansion must be included, while only a few terms of the activity expansions are enough for this purpose [4,5]. Consider, for example, the series in the activity Z for the pressure P and density ρ terminated at n -th order terms

$$\begin{aligned} \beta P &= Z + b_2 Z^2 + b_3 Z^3 + \dots + b_n Z^n, \\ \rho &= Z \frac{\partial}{\partial Z} (\beta P) = Z + 2b_2 Z^2 + 3b_3 Z^3 + \dots + nb_n Z^n, \end{aligned} \quad (5)$$

where b_n is the attraction part of the n -th virial coefficient, $\beta = 1/(kT)$ is the inverse temperature. In result of the strong interparticle attraction $Z \leq 1$ and in the limit $Z \rightarrow 0, b_n \rightarrow \infty$

$$b_n Z^n = \frac{1}{n} \rho - \frac{Z}{n} - \frac{2}{n} b_2 Z^2 - \frac{3}{n} b_3 Z^3 - \dots - \frac{n-1}{n} b_{n-1} Z^{n-1} \rightarrow \frac{1}{n} \rho. \quad (6)$$

After elimination of Z from equations (5) we obtain the equation of state which will be changed from the ideal gas equation $\beta P/\rho = 1$ to the equation of ideal gas of pairs $\beta P/\rho = 1/2$, ideal gas of trimers $\beta P/\rho = 1/3, \dots$, and in general the ideal gas of n -mers $\beta P/\rho = 1/n$. Moreover the summation of the infinite series in (5) leads to the possibility of the self-assembling in the system. In approximation $b_n = b_2^{n-1}$ the expansions (5) reduce to the following form

$$\beta P = \frac{Z}{1 - b_2 Z}, \quad \rho = \frac{Z}{(1 - b_2 Z)^2}, \quad (7)$$

which is well known in the thermodynamical theory of micellization [6]. For this reason $Z = \rho_0$ can be identified with the monomer density of amphiphilic molecules and the divergence point $Z_c = \rho_c = 1/b_2$ has the sense of the critical micelle concentration (CMC).

From these considerations it might be expected that a theory which combines the activity and density expansions would be advantageous. The second and higher terms in the expansions (5) can be interpreted as the dimers density $\rho_1 = b_2 Z^2$, the trimers density $\rho_2 = b_3 Z^3, \dots$, n -mers density $\rho_{n-1} = b_n Z^n$ correspondingly. Such interpretation suggests the possibility of the description of clusterization by the introducing the multi-density formalism for this purpose. A consistent integral equation theory for this description of the clusterization in liquids has been proposed by Wertheim [7,8]. This is based on the multi-density formalism in which the description in terms of the activity and density expansions are combined.

The multidensity formalism was reformulated in order to treat the effects of clusterization in fluids with spherically symmetric attraction and it was applied for ionic liquids [5,9-19], chain and network forming fluids [20,21] for the treatment of the percolation phenomena in the network forming fluids [22], for the adsorption of associative fluids in porous media [23], for the description of electronic structure of associative fluids [24] etc. Short review of the development of the multi-density integral equation approach in the theory of complex fluids was done in [25].

The recent progress in the application of the multi-density integral equation approach to the modelling of a different type of association and clusterization in liquids and solution will be reviewed in this report. The general scheme of this approach in the framework of the two-density formalism with the applications to electrolyte and polyelectrolyte solutions will be considered in the second section. In the third section the possibility of the multi-density formalism for the description of polymerization and network formation are presented.

2. TWO-DENSITY APPROACHES: THE APPLICATION TO IONIC SOLUTIONS

The general idea of the multi-density formalism is connected with the separation of the potential of interparticle interaction $U(r)$ into the bonding and non-bonding parts

$$U(r) = U_{bond}(r) + U_{nonb}(r), \quad (8)$$

where $U_{bond}(r)$ is some short-range attractive interaction which includes at least the potential energy minimum of $U(r)$. The nonbonding part $U_{nonb}(r)$ includes a repulsive part and long-range tail of $U(r)$.

The diagrams appearing in the activity expansions for the one-point density are classified with respect to the number of associative bonds incident with the labelled white circle. Thus, the total number density of the system is separated into two densities, the density of nonbonding particles (monomers) ρ_0 and the density of bonding particles ρ_1 :

$$\rho(1) = \rho_0(1) + \rho_1(1). \quad (9)$$

Similarly the pair distribution function will be splitting into four terms

$$\begin{aligned} \rho(12) = & \rho(1)g(12)\rho(2) = \rho(1)g_{00}(12)\rho(2) \\ & + \rho(1)\hat{g}_{01}(12)\rho_0(2) + \rho_0(1)\hat{g}_{10}(12)\rho(2) \\ & + \rho_0(1)\hat{g}_{11}(12)\rho_0(2) \end{aligned} \quad (10)$$

or

$$g(r) = g_{00}(r) + \alpha \hat{g}_{01}(r) + \alpha \hat{g}_{10}(r) + \alpha^2 \hat{g}_{11}(r), \quad (11)$$

where $\alpha = \rho_0/\rho$ is the fraction of a nonbonding part of particles. In order to treat correctly the limit $\alpha \rightarrow 0$ it is advantageous to represent $g(r)$ in the form [26]

$$g(r) = g_{00}(r) + g_{01}(r) + g_{10}(r) + g_{11}(r). \quad (12)$$

Due to saturation of bonding the restriction only by pair formation leads to the self-consistent relation for α

$$1 = \alpha + 4\pi \alpha^2 \rho \int_0^\infty g_{00}(r) f_{as}(r) r^2 dr, \quad (13)$$

where $f_{as}(r) = \exp(-\beta U_{bond}(r)) - 1$ is the Mayer function for the associative interaction. At the sticky limit follows

$$f_{as}(r) = B\delta(r - R) \quad (14)$$

and the equations (13) can be rewritten in the form

$$\frac{1 - \alpha}{\alpha^2} = 4\pi \rho B R^2 g_{00}(R), \quad (15)$$

where R is diameter of particles and $g(R)$ is the contact value at $r = R$ of the pair distribution function.

The classification and topological reduction of the diagrams for pair correlation function leads to the Wertheim's modification of the OZ equation [7,8]

$$\mathbf{h}(r_{12}) = \mathbf{C}(r_{12}) + \rho \int d\vec{r}_3 \mathbf{C}(r_{13}) \mathbf{Xh}(r_{32}), \quad (16)$$

where the corresponding matrices have the following form:

$$\begin{aligned} \mathbf{h} = & \begin{pmatrix} h_{00} & h_{01} \\ h_{10} & h_{11} \end{pmatrix}, \quad \mathbf{C} = \begin{pmatrix} C_{00} & C_{01} \\ C_{10} & C_{11} \end{pmatrix}, \quad \mathbf{X} = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}, \\ h_{00} = & g_{00} - 1, \quad h_{01} = g_{01}, \quad h_{10} = g_{10}, \quad h_{11} = g_{11}. \end{aligned} \quad (17)$$

As usually, the equation (16) should be supplemented by closure relations. Among them we distinguish the associative HNC (AHNC) closure

$$\begin{aligned} g_{00} &= e^{-\beta U_{nonb} + t_{00}}, \\ g_{01} &= g_{00} t_{01}, \quad g_{10} = g_{00} t_{10}, \\ g_{11} &= g_{00} [t_{10} t_{01} + t_{11} + \alpha^2 f_{as}], \end{aligned} \quad (18)$$

where $t_{\alpha\beta} = h_{\alpha\beta} - C_{\alpha\beta}$;

the associative PY (PYA) closure

$$\begin{aligned} g_{00} &= e^{-\beta U_{nonb}} y_{00}, \quad g_{01} = e^{-\beta U_{nonb}} y_{01}, \\ g_{10} &= e^{-\beta U_{nonb}} y_{10}, \quad g_{11} = e^{-\beta U_{nonb}} (y_{11} + \alpha^2 f_{as} y_{00}), \end{aligned} \quad (19)$$

where $y_{\alpha\beta} = g_{\alpha\beta} - C_{\alpha\beta}$;

the associative MSA (AMSA) closure

$$\begin{aligned} h_{00}(r) &= -1, \quad h_{01} = h_{10} = h_{11} = 0 \text{ for } r < R \\ C_{00} &= -\beta U_{nonb}, \quad C_{01} = C_{10} = 0, \\ C_{11} &= \alpha^2 g_{00} f_{as} \text{ for } r \geq R. \end{aligned} \quad (20)$$

The analytical solution of AMSA for symmetrical ionic systems was obtained [9] and also generalized for nonsymmetrical case [12]. The essential feature of this result is connected with appearance of new the screening parameter Γ_B instead of the usual inverse Debye-Huckel

screening length $\kappa = \left(4\pi\beta \frac{e^2}{\epsilon} \sum_a Z_a^2 \rho_a \right)^{1/2}$. The param-

eter Γ_B depends from the fraction of free ions α and the sizes of ions R and is defined by

$$4(\Gamma_B R)^2 (1 + \Gamma_B R)^2 = (kR)^2 \frac{\alpha + \Gamma_B R}{1 + \Gamma_B R}. \quad (21)$$

The simple analysis of equation (21) suggests the consideration of two regimes [18], namely the weak ($\alpha \rightarrow 1$) and the strong ($\alpha \rightarrow 0$) association regimes.

The regime of the weak association is realized for

$$1 \geq \alpha \gg \frac{\Gamma_B R}{(1 + 2\Gamma_B R)}$$

and corresponds to the traditional MSA-MAL (mass action law) description of ion association [27] where equation (21) reduces to

$$4(\Gamma_B R)^2 (1 + \Gamma_B R)^2 = (kR)^2 \alpha. \quad (22)$$

In this regime only the electrostatic contribution from free ions is important and the electrostatic contribution from ionic pair can be neglected.

The regime of the strong association is realized for

$$0 \leq \alpha \ll \frac{\Gamma_B R}{1 + 2\Gamma_B R},$$

where equation (21) reduces to

$$4\Gamma_B R (1 + \Gamma_B R)^3 = (kR)^2 (1 - \alpha). \quad (23)$$

In this regime only electrostatic contribution from the ion pairs is important and the contribution from the free ions can be neglected.

The AMSA was applied for the description of thermodynamic properties of ionic solutions and it was

shown that it satisfactory reproduces the properties of nonaqueous electrolyte solutions of solvent of relative permittivities in range $20 < \epsilon < 36$ [18]. For ionic solutions of lower permittivity the AMSA was modified by including the effect of ion trimer and tetramers [19]. The possibility of such modification of AMSA is enough promising for the description and interpretation of thermodynamical and transport properties of nonaqueous electrolyte solutions with the enough low dielectric permittivity [28].

3. THE MULTIDENSITY APPROACHES: CHAIN AND NETWORK FORMATIONS

For the particles having more than one bonding state, the formation of chains, rings, networks and more complex aggregates is possible. Such aggregates can be considered as a collection of monomers (segments) bonded at asymmetric attraction sites. In general for the particles with M bonding sites the density is separated into 2^M densities of different bonding states. The diagram analysis leads to the generalized version of the OZ equation which has the form similar to (16) where in general case \mathbf{h} , \mathbf{C} , \mathbf{X} are the matrices $2^M \times 2^M$. In general $2^M - 1$ self-consistent relations are needed instead of the relation (13) for the pairing case. Some simplification can be connected with the approximation that the bond creation between two particles is independent of the existence of other bonds. As a result, the fraction of the particles that have $n \leq M$ bonded neighbors can be given by the binomial distribution

$$x_M^n = \frac{\rho_M(n)}{\rho} = \binom{M}{n} p^n (1-p)^{M-n}, \quad (24)$$

where $p = 1 - \alpha$, α is the fraction of particles nonbonded by one fixed site.

For example, for the particles with two attractive sites A and B (one is donor, the other is acceptor) the assumption (24) leads to the ideal chain approximation (ICA) [29] and $m = 1/\alpha$ can be considered as the mean chain length.

The analytical solution of the OZ-like equation in polymer PY (PPY) approximation for the chain forming fluids in ICA approximation for the case when bond length $L = R$ was obtained and discussed in [29]. The generalization of this result for the case $L \leq R$ was considered in [20]. In the ICA approximation the formation of the ring polymers is neglected. This approximation can be used to describe a system of chain polymers, polydisperse in length that is characterized by a prescribed mean chain length m . As example of such case the application of PPY theory for the description of the structure of liquid sulfur was discussed [30].

For the molecules with four attractive sites A , B , C and D (the two are donors and the two are acceptors) the assumption (24) leads to the ideal network approximation (INA) [21,22]. The analytical solution of the OZ-like equation for the network forming fluids in network

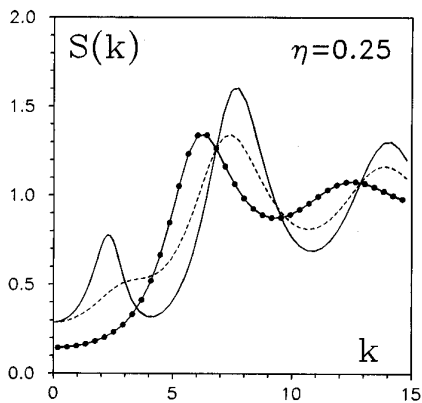


Fig. 1. The predicted from NPY-INA approximation structure factor of network forming fluids at $\eta = 0.25$ for different strength of bonding B_s : $B_s = 0$ (dotted line); $B_s = 0.1$ (dashed line); $B_s = 30$ (solid line)

PY (NPY) and INA approximation was done in [21]. The structure factor calculated for the model of associating hard spheres with four symmetrical bonding sites is presented in Fig. 1. It can be display the strong changes in $S(k)$ caused by increasing of association constant B_s . For the network forming fluid similar as for chain forming fluid [20] at small number region of k the pre-peak appears connected with the forming of relatively large clusters. Due to the correlation between them, the ordering in mesoscopic scale appears, so-called intermediate-range order [31].

The number of the bonding states of molecules can principally change the thermodynamic properties of fluids [25]. For example, the formation of finite m -mers leads to increasing of the liquid-gas critical temperature and the decreasing of critical density. For network forming fluids there are a new mechanism of critically connected with the network formation.

The multidensity integral equation theory was reformulated for studying connectedness properties in order to understand a peculiarity of the network forming fluids. The division of the potential of interparticle interaction into the blocked and connectedness parts

$$U(r) = U^+(r) + U^*(r) \quad (25)$$

leads to the similar separation also for the pair and direct correlation functions

$$\mathbf{h}(r) = \mathbf{h}^+(r) + \mathbf{h}^*(r), \quad \mathbf{C}(r) = \mathbf{C}^+(r) + \mathbf{C}^*(r). \quad (26)$$

The connectedness pair and direct correlation functions satisfy the OZ equation similar to (16). The mean cluster size is given by

$$S = 1 + \rho \int d\mathbf{r} h^+(r) \quad (27)$$

As the percolation transition is approached S increases and becomes infinite at the percolation threshold. The connectedness version of the OZ equation supplemented by the NPY-like closure and INA approximation was solved analytically [22]. In this approximation

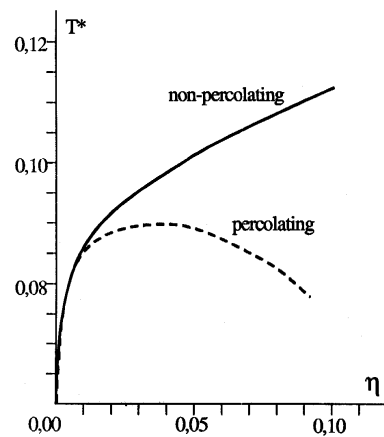


Fig. 2. The phase diagram of network forming fluid in NPY-INA approximation: the spinodal (broken line) and percolation (solid line) curves

$$S = \frac{4(4 + \alpha - 2\alpha^2)}{3(1 - 3\alpha)^2} \quad (28)$$

It is seen that $S \rightarrow \infty$ when $\alpha \rightarrow 1/3$. The spinodal (broken line) and percolation (solid line) curves in the coordinats the density $\eta = \frac{1}{6}\pi\rho R^3$ and the temperature

$T^* = (\beta\epsilon)^{-1}$ is presented in Fig. 2, ϵ is the square-well parameter of intersite bonding. The Fig. 2 shows that liquid phase including the critical point is inside the percolation region.

4. CONCLUSIONS

The characteristic features of numerous complex liquids are connected with associating the molecules into a different clusters caused by strong interparticle attraction. The starting point of the theory of such liquids is the combined cluster expansions for pair correlation function in which the activity expansions are used to describe the contribution of the bonding part of the interparticle interactions while the usual density expansion is used to describe of nonbonding part of interactions. The diagram analysis of these cluster expansions leads to the multi-density integral equation approach which is flexible enough to treat different associative features of liquids such as dimerization, polymerization, network formation, self-assembling etc.

The possibilities of the theory are tested by comparing with computer simulations. It is shown that the multidensity approach essentially improves the integral equation theory for ionic systems. The analytical solution of AMSA is useful for the description of thermodynamic and kinetic properties of nonaqueous electrolyte solutions in a wide range of ionic concentration specially for the solvents with enough low dielectric permittivity.

The multidensity integral equations are solved for polymerization and network formation cases. It is shown that structure factor for chain and network forming flu-

ids exhibits a peculiarity at small wave number connected with the forming of relatively large molecular clusters. The multidensity integral equation theory is reformulated for studying the connectedness properties of network forming fluids. The gas-liquid critical point is predicted to exist for network case, and a region of liquid state is inside the percolation region.

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