

6. *Carnie S. L., Stell G.* Nonlinear field effects in magnetic systems // *Phys. Rev. B.*— 1982.— 26, N 3.— P. 1389—1402.
7. *Вакарчук И. А., Рудавский Ю. К., Понедилок Г. В.* Микроскопическая теория жидкого состояния системы магнитных атомов.— Киев.— 1980.— 40 с.— (Препр. / АН УССР. Ин-т теорет. физики; ИТФ-80-135Р).
8. *Вакарчук И. А., Рудавский Ю. К., Понедилок Г. В.* К проблеме жидкого ферромагнетика // *УФЖ.*— 1982.— 27, № 9.— С. 1414—1415.
9. *Вакарчук И. А., Рудавский Ю. К., Понедилок Г. В.* Микроскопическая теория аморфных и жидких ферромагнетиков // *Сб. трудов «Международный симпозиум по избранным проблемам статистической механики».* D-17-81-758.— Дубна, 1981.— С. 307—317.
10. *Вакарчук И. А., Рудавский Ю. К., Понедилок Г. В.* Теория жидких магнетиков // *ТМФ.*— 1984.— 58, № 3.— С. 445—460.
11. *Вакарчук И. А., Маргольц И. Ф.* Теория многосортных неупорядоченных магнетиков. Свободная энергия.— Киев, 1984.— 28 с.— (Препр. / АН УССР. Ин-т теорет. физики; ИТФ-83-163Р).
12. *Вакарчук И. А., Маргольц И. Ф.* К теории многокомпонентных неупорядоченных магнетиков // *ТМФ.*— 1987.— 72, № 3.— С. 462—476.
13. *Ахизер И. А., Ахизер И. Т.* Колебания ферромагнитной жидкости // *ЖЭТФ.*— 1984.— 86, № 1.— С. 120—124.
14. *Ахизер И. А., Ахизер И. Т.* Колебания жидких ненасыщенных ферромагнетиков // *ФТТ.*— 1987.— 29, № 7.— С. 2167—2169.
15. *Зубарев Д. Н.* Неравновесная статистическая термодинамика.— М.: Наука, 1971.— 415 с.
16. *Зубарев Д. Н.* Современные методы статистической теории неравновесных процессов // *Итоги науки и техники. Современные пробл. математики.*— 1980.— 15.— С. 131—220.
17. *Калашников В. П., Ауслендер М. И.* Макроскопические уравнения динамики магнетиков. I. Линейные неравновесные процессы // *ФММ.*— 1977.— 44, вып. 4.— С. 710—726.

Институт фізики конденсованих систем
АН України, Львів

Одержано 15.12.92

UDK 532/533;536;538.9

A. D. TROKHIMCHUK, O. A. PIZLO

OPTIMIZED CLUSTER THEORY FOR THE STRUCTURAL PROPERTIES OF MOLTEN IONIC SYSTEMS. MOLTEN PHASES OF AgI, Ag₂Se AND Ag₂S

The optimized cluster expansions are applied for the description of structural properties of the molten systems containing silver cations. The results for partial pair distribution functions and corresponding structure factors are presented. The coordination numbers are calculated. The detailed comparison with experimental and simulation data is given. It is shown that exponential approximations of OCE coincide quite well with HNC theory and simulation results.

1. Introduction

In the series of papers [1], a general scheme to construct optimized cluster expansions for liquid ionic systems has been presented. An interion interaction contains a short-range term due to steric repulsion and long-range Coulomb interaction. The former is considered as a reference system and the latter is treated by means of renormalized or screened potentials. The many-body correlations are allowed for at different levels of infinite series truncation. The method has been successfully used for the molten alkali halides. An analysis of the cation and anion size ratio on the structural correlations has been presented also.

Further insight into the applicability of the theory for other systems is the main aim of this paper. We can widen the scope and it is necessary to do that by changing the charge state of cations or anions and both of them.

One can consider doubly-charged small cations in order to study the molten alkaline-earth halides. It is clear that intensity of interactions due to the change of cations charge will increase essentially. The renormalized potentials will increase also and some problems can arise when one truncates the optimized cluster expansions at some step. We shall investigate that problem in the sub-

© A. D. Trokhymchuk, O. A. Pizlo, 1993

sequent paper. Here we shall deal with more favourable situation considering the systems with larger anions which possess larger charge.

We intend to study three systems containing silver cations, i. e. AgI, Ag₂Se, Ag₂S. The choice of the subject is stimulated both by theoretical interest due to its physical behaviour and a practical importance.

To the best of our knowledge there are some experimental results by the neutron diffraction method on isotopically enriched samples for these systems [2, 3]. Their structural and dynamic properties have been studied also by means of MD simulation [4, 5]. So the interaction potentials necessary for the theory are available. We shall not discuss the quality of the potential functions [6], but nevertheless have to note that these systems are often called semionic, or are characterized as the ones with mixed ion-covalent bonding with prevailing ionicity. Therefore, the Coulomb terms in the effective interaction potentials contain the noninteger values of ionic charges. We have to note finally that all these systems have superionic phase and we hope to eliminate different degree of the coordination of cation and anion subsystems at different temperatures in the molten phase too.

The method of calculation of the structure is directly taken from papers [1]. If any changes will be introduced we shall mention it.

2. Structural properties of molten AgI

The effective pair potentials were constructed by Parinello et al. and we have applied them from the ref. [7]:

$$\begin{aligned} U_{\text{AgAg}}(r) &= 0,014804/r^{11} + Z^2/r, \\ U_{\text{AgI}}(r) &= 114,48/r^9 - Z^2/r - 1,1736/r^6, \\ U_{\text{II}}(r) &= 446,64/r^7 + Z^2/r - 2,3472/r^4 - 6,9331/r^6. \end{aligned} \quad (2.1)$$

The unit of energy is 14,399 eV.

The set of results for structural properties of AgI, is presented in the Figs. 1—3. In order to provide comparison with experimental data we have

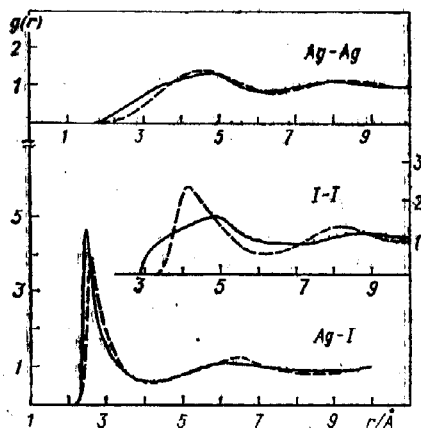


Fig. 1. Pair distribution functions for molten AgI at $T = 873$ K from HNC [7] (dashed) and OCE (full) calculations.

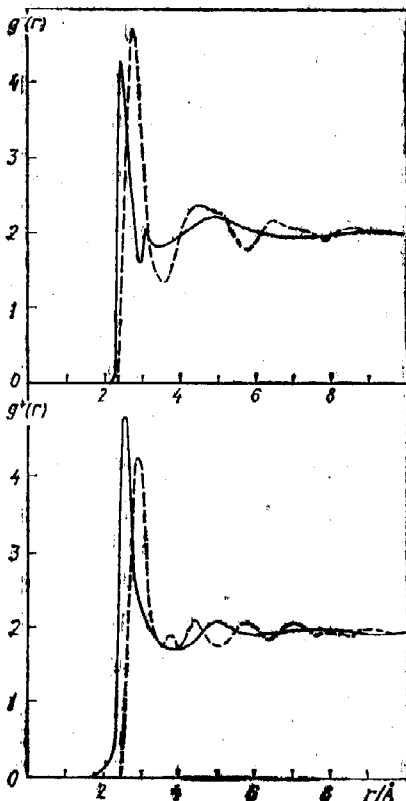


Fig. 2. Pair distribution functions $g_-(r)$ and $g_+(r)$ for molten AgI at $T = 873$ K from neutron diffraction experiments by Howe et al. [3] (dashed) and OCE theory (full).

calculated besides partial pair distribution functions their linear combinations defined as follows:

$$\begin{aligned} g_+(r) &= g_{+-}(r) + 0,9617g_{++}(r), \\ g_-(r) &= g_{+-}(r) + 1,0724g_{--}(r) \end{aligned} \quad (2.2)$$

and

$$g_T(r) = \sum_{ij} c_i c_j b_i b_j g_{ij}(r) / \bar{b}^2, \quad (2.3)$$

where $\bar{b} = \sum_i c_i b_i$, where c_i , b_i are respectively the concentration and scattering length of ions of species i .

The valency of ions in the potentials (2.1) is assumed to be noninteger, namely $Z = 0,6$. Therefore the effect of electrostatic interactions is weaker

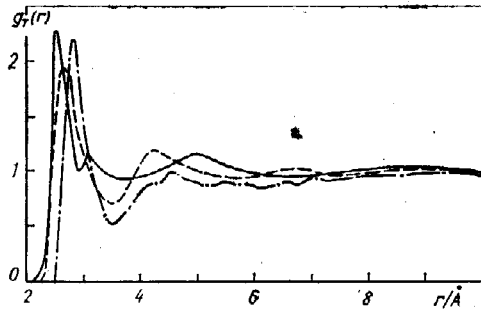


Fig. 3. Total pair distribution function (full) compared with HNC [2] (dashed) and neutron diffraction experiments by Howe [2] (dotted) molten AgI at $T = 873$ K.

if compared with the one for the molten alkali chlorides. The difference between the results of different exponential approximations is less essential. We have chosen the It1 approximation [1] to study the structural ordering in this system. It can be seen from the Fig. 1 that the p. d. fs. calculated by us are similar to the ones calculated within more elaborated HNC theory. The discrepancy between It1 and HNC is especially pronounced for the distribution function of large anions $g_{--}(r)$. In particular, the It1, similarly to MSA, EXP2, EXP3, does not reproduce

both the height and position of the first peak of $g_{--}(r)$ and oscillations are weaker than predicted by HNC. Actually, this is what we have expected from our theory. The polarizability effects are essentially important for AgI on the background of weaker electrostatic effects. However in our derivation of the p. d. fs [1] the polarizability effects in $U_{--}(r)$ have not been allowed for at all, neither in the description of the reference fluid nor in the renormalized potentials. Besides that, the point r_{+-}^* here have been chosen from the $U_{+-}(r)$ minimum contrarily to the potential energy minimum in the case of alkali chlorides. We feel that the additional attraction in $U_{--}(r)$ caused by the polarizability will really shift $g_{--}(r)$ peak to smaller distances and increase it height. In general, the study of polarizability effects need additional efforts and we will present it in the following papers.

After the p. d. fs, one can provide comparison with the quantities observed experimentally (see Figs. 2, 3). There are some discrepancies between the theory and experiment due to nonsatisfactory behaviour of $g_{--}(r)$, therefore we can consider these results for AgI as preliminary.

3. Structure of the Molten Ag_2Se , Ag_2S

In order to investigate structural properties of these interesting systems we have applied the potentials presented in [4]

$$\begin{aligned} U_{AgAg}(r) &= 0,2408/r^{11} + Z_{Ag}^2/r, \\ U_{AgSe}(r) &= 86,6614/r^9 - Z_{Ag}Z_{Se}/r - 0,7088 \exp[-r/4,43]/r^4, \\ U_{SeSe}(r) &= 220,1905/r^7 + Z_{Se}^2/r - 5,67 \exp[-r/4,43]/r^4. \end{aligned} \quad (3.1)$$

The results for molten Ag_2Se are presented in the Figs. 4—6. We have chosen for presentation the set of data calculated in EXP2 approximation. Even that simplified form provides very good description of the structural properties. The results obtained by us for the partial distribution functions

and structure factors coincide with corresponding ones from MD simulation [4]. One has to note that the total structure factor agree well with the experiment [4] (see Fig. 6).

Unfortunately we have not exact numbers for MD results in order to provide the comparison of curves in each figure.

While examining the set of potentials we have to mention the effects of polarizability included in $U_{\text{SeSe}}(r)$ similarly to the potential $U_{\text{II}}(r)$ for the

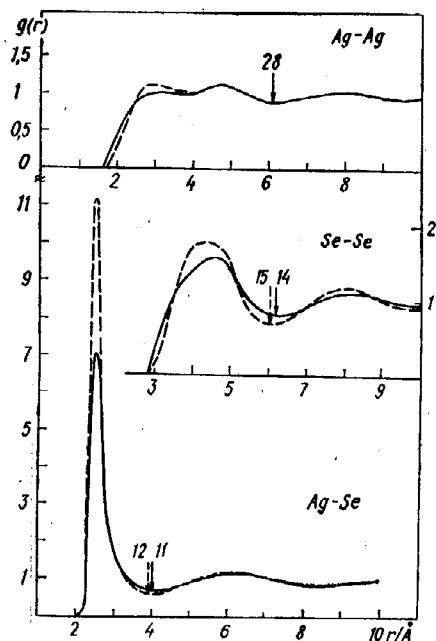


Fig. 4. Pair distribution functions and coordination numbers for molten Ag_2Se at $T = 123$ K (full) and $T = 804$ K (dashed)

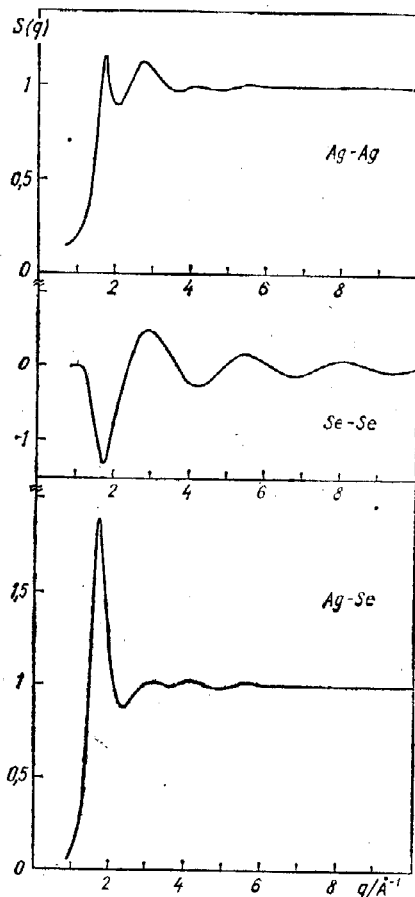


Fig. 5. Partial structure factors for molten Ag_2Se at $T = 123$ K.

previous case. The valency of ions is assumed here to be $Z_{\text{Ag}} = 0,45$ and $Z_{\text{Se}} = -0,90$ and so the electrostatic effects are essentially weaker than for 1-1 systems. One can expect then, that polarizability influences to high extent on the quality of results. However this is not true. Despite the similarity of size ratio in both cases ($\sigma_1/\sigma_{\text{Ag}} = 1,714$; $\sigma_{\text{Se}}/\sigma_{\text{Ag}} = 1,517$) the polarizability effects in this case do not influence the results. This happens due to the different respective concentrations N_+/N in both cases and obviously due to the different values of interactions strength parameters, namely $\beta^* = e^2 Z^2 / kT \sigma_+ = 39,48$ (for AgI) and $\beta^* = 60,68$ (for Ag_2Se).

We have examined different exponential approximations and have to state that EXP2 is the best for Ag_2Se . One has to be very careful while choosing the truncation step for the infinite series especially for the p. d. f. of smaller cations. This point has been already discussed in our previous paper.

One can see that the coordination numbers are reproduced well within EXP2 if compare them with MD simulation. It is very interesting for the system considered to study the coordination changes dependent on the temperature.

At the decreasing temperature the coordination of cation subsystem remains unchanged. On the contrary, the anion subsystem becomes more coordi-

nated, the height of $g_{\text{SeSe}}(r)$ first peak increases preserving its position. The oscillations of this function are amplified describing the tendency for more pronounced structure of anion subsystem.

We should like to note that in forthcoming paper our results for the three-particle distribution function will be shown. It is constructed at a higher level that superposition approximation and with EXP2 as an input. This function will provide then the bond angle distribution necessary to clarify the additional features of structure dependence on the temperature.

We do not discuss here the physical properties of Ag_2Se as a representative of fast-ion conductors because they are presented in details in [4]. Summariz-

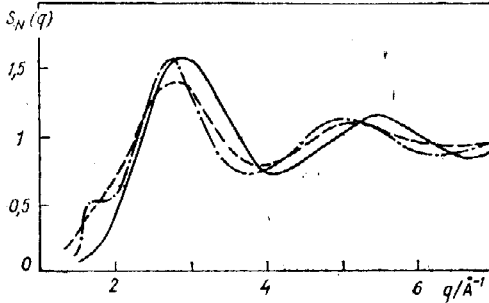


Fig. 6. Static structure factors $S_N(q)$ (full) compared with neutron diffraction experiment (dotted) and molecular dynamics results of Rino et al. [4] (dashed) for the molten Ag_2Se at $T = 1236$ K.

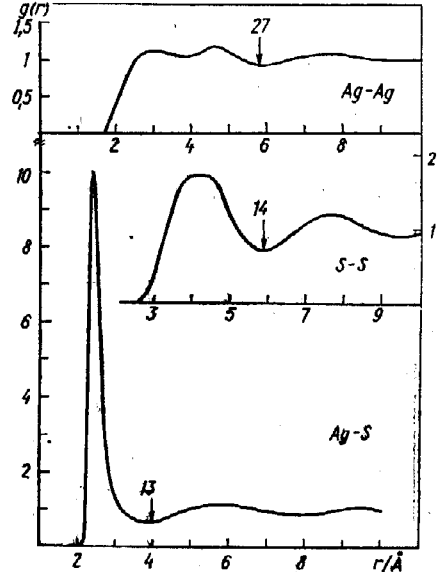


Fig. 7. Pair distribution functions and coordination numbers for the molten Ag_2S at $T = 873$ K.

ing, we stress that exponential approximation provide a correct description of structural properties for molten Ag_2Se .

The effective potentials for Ag_2S are very similar to the ones which were applied for other binary superionic conductors and look as follows [5]

$$U_{\text{AgAg}}(r) = 0,06042/r^7 + Z_{\text{Ag}}^2/r,$$

$$U_{\text{AgS}}(r) = 16,12/r^7 - Z_{\text{Ag}}Z_{\text{S}}/r - 0,66/r^4, \quad (3.2)$$

$$U_{\text{SS}}(r) = 346,3/r^7 + Z_{\text{S}}^2/r - 5,28/r^4.$$

The size ratio is chosen equal to $\sigma_{\text{S}}/\sigma_{\text{Ag}} = 1,46$, the valencies are $Z_{\text{Ag}} = 0,45$, $Z_{\text{S}} = -0,90$, and the strength of intercation interaction is characterized by the parameter $\beta^* = 85,28$. We have presented the results for partial pair distribution functions within EXP2 in the Fig. 7. Qualitatively the picture is very similar to the previous case, namely Ag_2Se . The anion subsystem even in the molten phase is more structured than the cation one. Unfortunately we have no the data of other theories and the experiment to provide direct comparison.

So, in this paper we have studied structural properties of the molten phases for three systems containing silver cations. It is shown that the optimized cluster expansions are applicable in all cases and provide qualitatively correct picture of the structure. Actually the theory of this kind can be used in future for the investigation of more complicated systems which contain larger number of ionic species. We think that the results obtained will be helpful to develop the theory of dynamic properties of ionic systems as well. Some of results discussed here were presented by us already in [8].

Acknowledgement

We are indebted to M. A. Howe for sending us the experimental results for AgI and fruitful discussions.

1. *Holovko M. F.*— Kiev, 1985.— 21 P.— (Prepr. / Acad. Sci. Ukr. SSR. Inst. Theor. Phys.: ITP-84-178P); *Holovko M. F., Pizio O. A., Trokhymchuk A. D.*— Kiev, 1988.— 44 P.— (Prepr. / Acad. Sci. Ukr. SSR. Inst. Theor. Phys.: ITP-87-155E); *Holovko M. F., Kriienke H.* // *Mol. Phys.*— 1989.— 68.— P. 967; *Pizio O. A., Protchykevich I. A., Pustai L. et al.* // *Rasplavy.*— 1990.— N 3.— P. 10.
2. *Howe M. A.* // Clarendon Laboratory University of Oxford-Ref. OUCI-89/3 Oxford.— 1989.— P. 192 (Ph. D. Thesis).
3. *Howe M. A., McGreevy R. L. and Mitchell E. W. J.* // *Z. Phys. B.*— 1986.— 62.— P. 15.
4. *Rino J. P., Hornos Y. M., Antoni G. A. et al.* // *J. Chem. Phys.*— 1988.— 89.— P. 7542.
5. *Vashista P., Ebbsjo I., Dejus R., Skold K.* // *J. Phys. C.*— 1985.— 18.— 1291.
6. *Bucher M.* // *Phys. Rev. B.*— 1984.— 30.— P. 947.
7. *Stafford A. J. and Silbert M.* // *Z. Phys. B.*— 1987.— 67.— P. 31.
8. *Trokhymchuk A. D., Pizio O. O.* // *Systems with Fast Ion Transport* / Eds. G. Schuster, K. Kunstler and H. Ullmann.— 1991.— 76.— P. 57—60.

Institute for the Physics of Condensed Matter
Svientsitskoho 1, 290011 Lviv, Ukraine

Received 15.12.92