сообщения
объединенного
института
ядерных
исследований
дубна

E14-92-79

I.Padureanu[1], Gh.Rotarescu[1], I.Popescu[1],
O.E.Kudryashov[2], I.E.Ovchinnikov[2]

ON THE STRUCTURE AND ATOMIC MOTIONS IN LIQUID SODIUM

---

[1] Institute of Atomic Physics, Bucharest, Romania
[2] Institute of Physics of Latvian Academy of Sciences,
Riga, Latvia

1992

Падуреану И. и др. E14-92-79

О структуре и движениях атомов
в жидком натрии

Получены микроскопические структурные функции жидкого натрия в области температур T = 100–600°C с использованием приближения твердых сфер и нейтронных дифракционных данных при малых волновых векторах Q. При помощи этих данных были получены корреляционные функции продольных токов, автокорреляционная функция скоростей и спектр частот на основе динамических моделей: обобщенного среднего поля, вязкоупругого поля и функции памяти.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1992

Padureanu I. et al. E14-92-79

On the Structure and Atomic Motions
in Liquid Sodium

The microscopic structure function for liquid Na in the temperature range T = 100°C–600°C from the hard sphere approach and neutron diffraction data at the low momentum transfer measurements are obtained. These data are used within the mean field, viscoelastic and memory function approach theories to derive the self and effective current longitudinal correlation function and its spectral function.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1992

INTRODUCTION

In this paper are presented the results concerning the static structure factor S(Q), and the radial distribution function g(r) in the liquid sodium as well as the temperature influence on these microscopic properties in the range 100°C - 600°C. The results are based on a hard sphere approach. The parameters needed in a such as approach are obtained from neutron diffraction experiments performed in the region of the small momentum transfer. The structure data were used in the theoretical dynamic models based on the mean field theory |1|, viscoelastic theory |2| and the memory function approach |3| to determine the dynamic structure factor $S_c(Q,\omega)$ for correlated atomic motions. A three pole approximation model is used for self motion via $S_1(Q,\omega)$.

The total dynamic function $S(Q,\omega)$ was compared to the experimental results at T=413K |4|. It is concluded that good agreement is obtained between the theory and experiment.

Therefore, the theoretical $S_c(Q,\omega)$ and $S_1(Q,\omega)$ could be considered as the real components for coherent and incoherent scattering in liquid sodium for all investigated temperature.

As the neutron scattering on liquid sodium does not involve the isotopic effects, the experimental separation of $S_c(Q,\omega)$ and $S_1(Q,\omega)$ is not possible.

Based on the above conclusion we have analyzed further the temperature dependence of the longitudinal current correlation functions on $J_1(Q,\omega)$ and $J_c(Q,\omega)$.

From $J_1(Q,\omega) = (\omega^2/Q^2)S_1(Q,\omega)$ the frequency spectrum of the velocity self correlation function:

$$\Phi(t) = \langle V(0)V(t)\rangle / \langle V(0)^2\rangle$$

and finaly $\Phi(t;T)$ is also obtained. In addition to the structure data $S(Q;T)$, $g(r;T)$ a Lennard Jones pair interaction potential in the dinamical models is used.

The present analysis is a continuation of the investigation of the liquid sodium performed by us in the papers |4, 5, 6,7|.

EXPERIMENTAL MEASUREMENTS. THE HARD SPHERE APPROACH

The inelastic neutron scattering experiments on liquid sodium performed at the IBR-2 reactor in JINR Dubna [4] have been continued at the VVR-S reactor in IAP Bucharest by neutron diffraction. The latter measurements were recorded at various temperatures in the region of the low wave vector transfer $0.3Å^{-1} \le Q < \le 1.5Å^{-1}$.

Using the conclusion of other papers [8] we also deduced that for values of $Q \le 1/4Q_0$, (where Q_0 corresponds to the first maximum) S(Q) is equal to its value at $Q \cong 0$ within the experimental errors.

For liquid sodium $Q_0 \cong 2Å^{-1}$ [9] $Q/4 = 0.5Å^{-1}$ and the value of $S(0) \cong S(0.5Å^{-1})$. The experimentally determined value of S(0) has been used within the hard sphere approach to obtain the packing density of hard sphere, η, as a function of temperature. As it is known for

$$Q \to 0: S(Q \to 0) = (1-\eta)^4/(1+2\eta)^4. \qquad (1)$$

The structure factor S(Q) for simple liquid can be obtained as a rigorous solution of the Percus-Yevick theory (P-Y) [10] for the case of a hard sphere pair interaction potential $\Phi(r)$.

The solution of the (P-Y) integral equation is :

$$S(Q_1)=[1-nC(Q_1)]^{-1} \qquad (2)$$

where n is the atomic density, $Q_1=Q\sigma$, σ is the diameter of the hard sphere and $C(Q_1)$ the direct correlation function.

$$C(Q_1)=-4\pi\sigma^3\int_0^1 dx\, x^2[\sin(Q_1x)/Q_1x](\alpha+\beta x+\gamma x^3). \qquad (3)$$

The parameters σ, α, β, γ are calculated from the packing density η:

$$\eta=\pi/6n\sigma^3;\ \alpha=(1+2\eta)^2/(1-\eta)^4;\ \beta=-6\eta(1+\eta/2)^2/(1-\eta)^4; \qquad (4)$$
$$\gamma=1/2\eta(1+2\eta)^2/(1-\eta)^4.$$

The structure factor S(Q;T) obtained in the temperature range 100°C- 600°C is shown in Fig.1. As one can see agreement between the hard sphere data and experimental ones is quite good. The effect of the attractive part of the potential is small at any Q value between $0.2Å^{-1}$ and $9Å^{-1}$ corresponding to wave lengths from 30Å to 0.6Å. For $Q>7Å^{-1}$ the experimental possibilities are limited while the theoretical modeling indicates the existence of the atomic order at higher Q- values.

TEMPERATURE DEPENDENCE OF THE RADIAL DISTRIBUTION FUNCTION

As the simple liquids metals are isotropic systems, the radial distribution function $g(r,T)=g(|r|,T)$.

The static structure factor S(Q) is correlated with g(r) by the relation:

$$S(Q,T)=1+(4\pi n/Q)\int[g(r,T)-1]r \sin Qr\, dr . \qquad (5)$$

To obtain g(r) correctly, S(Q;T) should be obtained over a large range of Q values to get the limit S(Q;T) ->1.

This is very difficult experimentally and, therefore, the Fourier transformation of the experimental data between the Q_{min} and Q_{max} limits is affected by errors.

Theoretical determination of S(Q) allows one to avoid this difficulties. In Fig.2 the radial distribution function g(r;T) is shown.

From the intersection of g(r;T) with r-axis the temperature dependence of the parameter $\sigma(T)$ is obtained. This parameter was used in the Lennard Jones pair interaction potential for dynamics calculations.

DYNAMIC STRUCTURE FACTOR CALCULATION

The scattering function $S_c(Q,\omega)$ has been obtained from three theoretical models. These models do not involve an adjustable parameter. The input data are S(Q;T), g(r;T) and the potential $\Phi(r;T)$. We write down here the main formulae used for calculation. According to the model of the Pathak-Singwi [1] dynamic structure factor $S_c(Q,\omega)$ is given by the relation.

$$S_c(Q,\omega)=\frac{-K_BT}{\pi n\omega}\;\frac{X''_{sc}(Q,\omega)}{[1-\Psi(Q)X'_{sc}(Q,\omega)]^2+[\psi(Q)X''_{sc}(Q,\omega)]^2}\,. \qquad (6)$$

All functions depending on (Q,ω) variables are obtained from the structure data. The main quantity to be calculated is the potential dependent part of the fourth order momentum of $S(Q,\omega)$, named $P_4(Q)$.

$$P_4(Q)=\int drg(r)[1-\cos(Qr)]/Q^2(Q\nabla)^2\Phi(r) \qquad (7)$$

$$\langle\omega^4\rangle=Q^2K_BT/M^2S(Q)[3K_BT+nP_4(Q)]\,.$$

The second model used for $S_c(Q,\omega)$ is proposed in the paper |2|. According to the approach described in this paper $S_c(Q,\omega)$ is calculated as follows:

$$S_c(Q,\omega)=\frac{Q^2K_BT}{\pi M}\;\frac{\tau(Q)[a(Q)-b(Q)]}{\omega\tau(Q)[\omega^2-a(Q)]^2+[\omega^2-b(Q)]^2} \qquad (8)$$

where $a(Q)=3K_BTQ^2/M - nQ^2P_4(Q)/M$

$b(Q)=Q^2K_BT/MS(Q)$

$1/\tau(Q)=2/\sqrt{\pi}\,[a(Q)-b(Q)]^{1/2}$.

Another theory proposed in the paper |3| gives for $S_c(Q,\omega)$ the following relation:

$$S_c(Q,\omega)=\frac{1}{\pi}\;\frac{\omega_0^2\Omega^2S(Q)K'_c(\omega)}{[\omega^2+\omega\Omega^2K''_c(\omega)-\omega_0^2]^2+[\omega\Omega^2K'_c(\omega)]^2} \qquad (9)$$

$$\Omega^2(Q)=\omega_1^2-\omega_0^2;\quad \omega_0^2=K_BTQ^2/MS(Q);\quad \omega_1^2=\langle\omega^4\rangle/\langle\omega^2\rangle\,.$$

The functions $K'_c(\omega)$, $K''_c(\omega)$ depend on the structure data, and these quantities have their usual meanings.

To calculate the function $S_1(Q,\omega)$ corresponding to the self motion, we have used the model of the paper [11].

$$S_1(Q,\omega)=\frac{1}{\pi}\;\frac{\tau(Q)\delta_1\delta_2}{\{\omega\tau(Q)(\omega^2-\delta_1-\delta_2)\}^2+(\omega^2-\delta_1)^2} \qquad (10)$$

$\delta_1 = \langle\omega^2\rangle = Q^2K_BT/M$

$\delta_2 = 2\langle\omega^2\rangle+\Omega^2$

$\Omega^2=\frac{n}{M}\int drg(r)\frac{d^2\Phi}{d^2r^2};\quad \tau(Q)=1/\xi\sqrt{\delta_2};\quad \xi=2/\sqrt{\pi}$

there Ω can be regarded as the oscillation frequency sodium atoms.

The total scattering function is obtained from the relation:

$$S(Q,\omega)=[\sigma_c\,S_c(Q,\omega)+\sigma_1S_1(Q,\omega)]/(\sigma_1+\sigma_c) \qquad (11)$$

where σ_1,σ_c are the total cross sections for incoherent and coherent scattering.

A first comparison of these calculations with the experimental data from inelastic neutron scattering on sodium at T=413K has already been performed in the paper |4|. All three models for $S_c(Q,\omega)$ give rather closed results.

LONGITUDINAL CURRENT CORRELATION FUNCTIONS

The longitudinal current correlation functions $J_1(Q,\omega)$ and $J(Q,\omega)$ have been obtained from the relations.|12|

$$J_1(Q,\omega)=\frac{\omega^2}{Q^2}\,S_1(Q,\omega) \qquad (12)$$

$$J(Q,\omega)=\frac{\omega^2}{Q^2}\,S(Q,\omega)\,.$$

In Fig.3 are shown the functions $J_1(Q,\varepsilon),(\varepsilon=\hbar\omega)$ for various temperatures and in Fig.4 are shown $J(Q.\varepsilon)$ calculated from the three models for $S_c(Q,\omega)$ at $Q=1.9\text{Å}^{-1}$. The function $J_1(Q,\omega)$ in Fig.3 is not normalized by the weight $\sigma_1/(\sigma_1+\sigma_c)$ while in Fig.4 the effective current correlation function $J(Q,\varepsilon)$ is obtained according to the relation.

$$J(Q,\varepsilon)=\sigma_1/(\sigma_1+\sigma_c)J_1(Q,\varepsilon)+\sigma_c/(\sigma_1+\sigma_c)J_c(Q,\varepsilon). \qquad (13)$$

The function $J_i(Q,\varepsilon)$ has a small maximum located at the energy transfer ε=3meV and a second one at ε=15meV. These details are observed at T=100°C. A relatively significant dependence on temperature is observed.

Thus with an increase of the temperature the first maximum disappears slowly. The second maximum is shifted to the smaller Q values. Unfortunately, we cannot compare our results with other authors, because the existing data are obtained for temperature not far from the melting point and are not tabulated.

In the paper ¦12¦ are plotted the results on liquid sodium at T=400K compared to the molecular dynamic calculations.

An approximate estimation leads to the conclusion that our results for T=400K are in agreement with the results presentedin paper ¦12¦ except the conclusion that the peak at ε=3meV is on resolution effect.

THE FREQUENCY SPECTRUM AND VELOCITY SELF CORRELATION FUNCTION

The frequency distribution spectrum of the velocity self correlation function is obtained from the incoherent scattering function according to the relation

$$p(\varepsilon)=\frac{2M}{\hbar K_B T}\lim_{Q\Rightarrow 0} J_1(Q,\varepsilon)=\frac{2M}{\hbar K_B T}\lim_{Q\Rightarrow 0}\frac{\varepsilon^2}{Q^2}S_1(Q,\varepsilon). \qquad (14)$$

The results obtained by the extrapolation method at various temperatures are shown in Fig.5. A maximum at 12-13 meV is present in $p(\varepsilon)$ for temperatures not far melting point. This maximum coincided with the main maximum observed in $J_1(Q,\varepsilon)$ for T=100°C. The comparison of $p(\varepsilon)$ for T=125°C with that of the paper ¦12¦ at T=400K shows good agreement. The small differences observed may be are due to $p(\varepsilon)$ determined in paper ¦12¦ as the limit Q->0 is taken equally with $J_1(Q,\varepsilon)$

for Q=0.69Å^{-1}. The temperature dependence of $p(\varepsilon)$ is very significant. It consists in the successive shifting of the position of the main peak, ε_m, to smaller ε as T increases. This behavior can be seen from Fig. 5a.

As T increases a better location of the main peak in $p(\varepsilon)$ is also observed. From $p(\varepsilon)$ we have calculated the velocity self correlation function $\Phi(t)$ according to the relation:

$$\Phi(t)=\frac{<v(t)v(0)>}{<v(0)>^2}=\int p(\varepsilon)\cos\omega t dt. \qquad (15)$$

In Fig.6 is shown the temperature dependence of $\Phi(t)$. At the lower temperatures not far from the melting point $\Phi(t)$ has a complicated behavior.

It decreases rapidly from t=0 at $t=0.1*10^{-12}$s becomes negative. After that it slowly oscillates in the field of the surrounding atoms (as in a "cage") with the frequency corresponding to the ε_m observed in the frequency spectrum.

At a given t inside this "cage" there is an ordered structure given by the radial distribution function g(r). The fluctuations in the atomic surrounding the cage lead to the break up of the initial order. During this process our atom in the "cage" loses its initial velocity due to the collision. Correlation of the velocity depends on the temperature. At temperature as high as T=600°C, $\Phi(t)$ has an exponential behavior $\Phi(t)= e^{-t/\tau}$ with the relaxation time τ.

CONCLUSIONS

The neutron diffraction data measured at low momentum transfer are used within the formalism of a hard sphere to obtain the static structure factor S(Q) and theradial distribution function g(r) over the temperature range T=100°C-600°C.

From the comparison with the X-ray measurements it is concluded that a hard sphere formalism gives rather a good description of S(Q) as a function of T (the packing density depends of T).

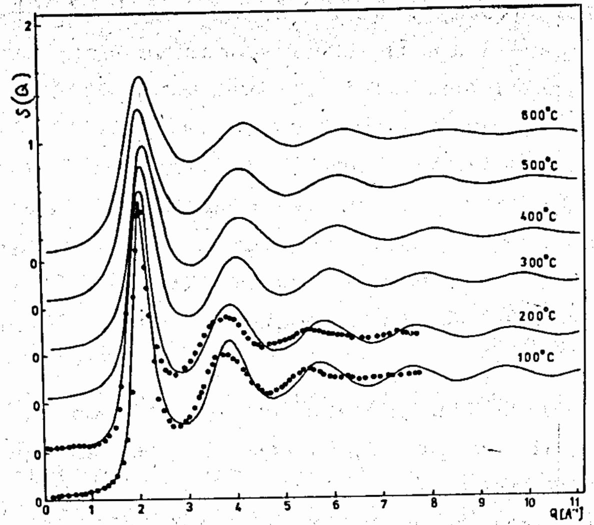

Fig. 1. The temperature dependence of the static structure factor S(Q;T). The full points represent the experimental data from the paper |9| obtained by X-ray diffraction at T=100°C and T=200°C.

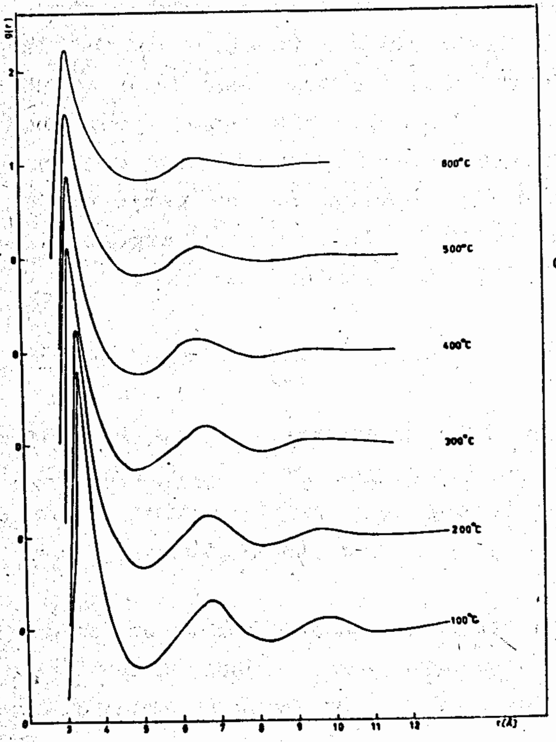

Fig. 2. The temperature dependence of the radial distribution function g(r;T) obtained from the Fourier inversion of S(Q;T).

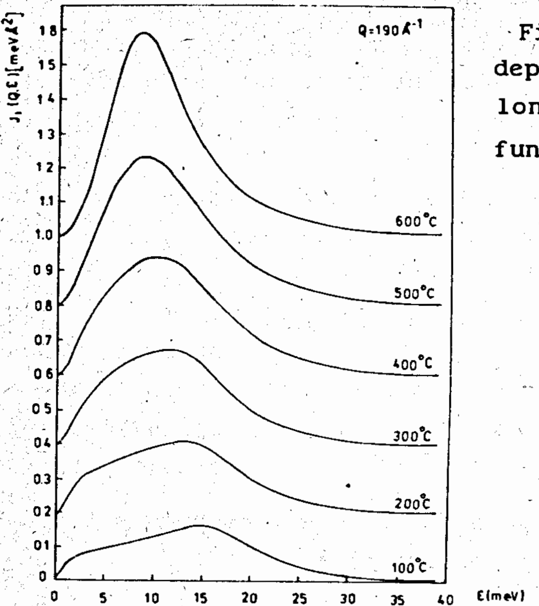

Fig. 3. The temperature dependence of the selfcurrent longitudinal correlation function for $Q=1.9Å^{-1}$.

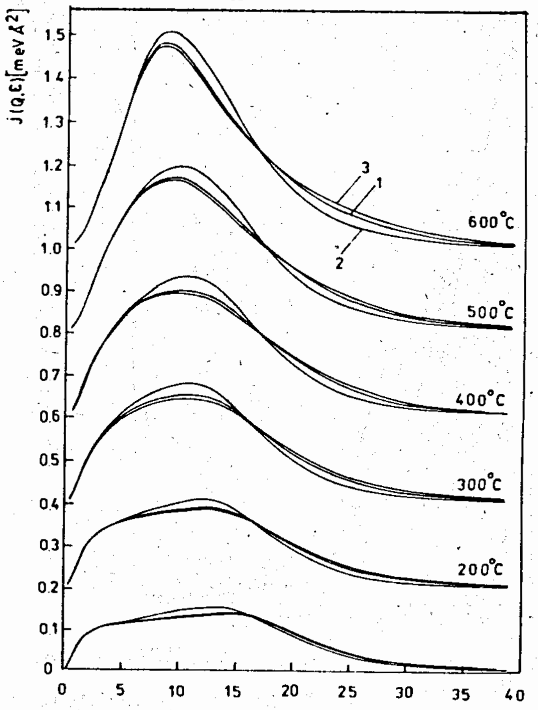

Fig. 4. The temperature dependence of the effective-current longitudinal correlation function for $Q=1.9Å^{-1}$.
1. model AZR 2. model Lovesey 3. model P-S.

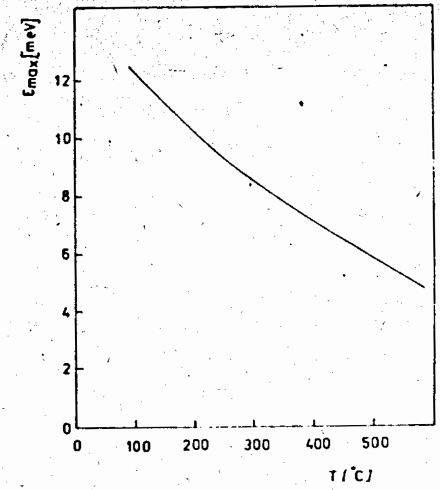

Fig. 5. The temperature dependence of the frequency spectra on the velocity selfcorrelation function.

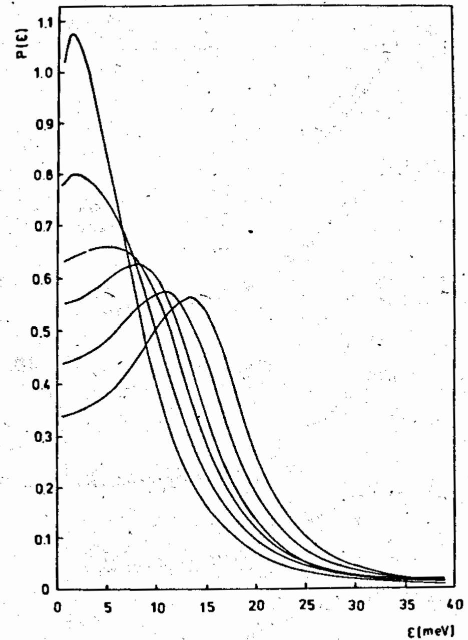

Fig. 5a. The temperature dependence of the position of the main peak, ε_m, on the frequncy spectrum $p(\varepsilon)$.

The dynamic structure functions are calculated from various models having as input data $S(Q)$ and $g(r)$ and compared with the experimental measurements by inelastic neutron scattering. It is concluded that $S_1(Q,\omega;T)$ and $S_c(Q,\omega;T)$ obtained in this way, can be considered the coherent and the incoherent components of the total scattering function $S(Q,\omega)$.

The longitudinal current correlation functions obtained from the dynamic structure functions are in good agreement with the measurement and with molecular dynamic calculations for T there where they exist.

The frequency distribution function $p(\varepsilon)$ and the velocity self correlation function show a rather sensitive dependence on temperature.

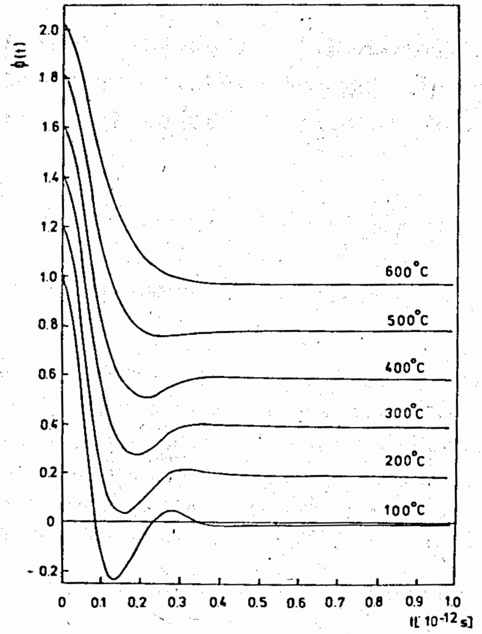

Fig. 6. The temperature dependence of the velocity selfcorrelation function $\Phi(t)$.

REFERENCES

|1| Pathak K.M., Singwi K.S., Phys. Rev. 1970, A2, p.2427
|2| Lovesey S.W., J. Phys. C, 1971, 4, p. 3057
|3| Ailawadi A. et al., Phys. Rev. 1971, A4, p. 1616
|4| Rapeanu S., Padureanu I., Rotarescu G, Ion M., Novicov A.G., Fomichov N.K., Phisyca Scripta, 1984, 29, p.721
|5| Padureanu I., Rapeanu S., Rotarescu Gh., Rev. Roum. Phys. 1978, 23, p.121
|6| Padureanu I., Rapeanu S., Rotarescu Gh., Rev. Roum. Phys. 1977, 22, p.931
|7| Padureanu I., Rapeanu S., Ion M., Rev. Roum. Phys. 1989, 34, p.657
|8| Egelstaff P.A. et al, Phys. Lett., 1966, 21, p. 286
|9| Greenfield A.J., Wellendorf J.; Phys. Rev. A, 1971, 4, p. 1607
|10| Percus J.K., Yevick G.J., Phys. Rev., 1958, 110, p.1
|11| Lovesey S.W., J. Phys. C, 1973, 6, p. 1856
|12| Kinell T., et al J.Phys. F., 1985, 15, p. 1033

Received by Publishing Department
on February 27, 1992.