FIZIKA VOLUME 10 SUPPLEMENT 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics
of Condensed Matter, Kruševac, September, 18-22, 1978

NUMERICAL CALCULATION OF THE INTERATOMIC POTENTIAL FOR SOME LIQUID METALS

M. Davidović, Dj. Jović and M. Živanović
"Boris Kidrič" Institute of Nuclear Sciences
Beograd, Yugoslavia

Abstract: Different approaches to calculation of the pair potential $\varphi(r)$ of some monoatomic liquid metals are discussed. With the knowledge of the measured static structure data from diffraction experiments, $\varphi(r)$ can be determined with the use of statistical theories. The inverting perturbation theory developed by Anderson, Chandler and Weeks can be used by iteration method in defining of the attractive forces in $\varphi(r)$. In this paper pseudopotential theories were applied in evaluation of the interatomic potential.

1. Introduction

Interatomic potential $\varphi(r)$ together with the correlation functions g(r), h(r) and c(r) is the most important parameter for a better understanding of the liquid state. For pure metals, the potential $\varphi(r)$, at any point within the medium, is supposed to be the sum of supersposable potentials $\varphi(r)=\sum_i \varphi(r-r_i)$, where the potential $\varphi(r-r_i)$ corresponds to the centre of the i-th ion. In general, $\varphi(r)$ can be devided into two parts, a short range very steep repulsive part $\varphi_r(r)$ and a long range attractive part $\varphi_a(r)$, as follows:

$$\varphi(r) = \varphi_r(r) + \varphi_a(r) \tag{1}$$

It is also known that the repulsive part of the potential can be determined by the large wave vector part of the structure factor $S(\varkappa)$, whereas the attractive part of the potential manifests itself by the small wave vector part of the structure factor. To get any detailed information on the interatomic potential and correlation function it is necessary to analyse $S(\varkappa)$ in a wide $\varkappa$-region. On the other hand, precise measurements of the static structure factor $S(\varkappa)^{1-3)}$ for the whole $\varkappa$-region are very difficult and a proper normalization of the measured $S(\varkappa)$ for small and large $\varkappa$-vector is a serious problem. This normalization can be performed using the relation[2,4)]

$$S(\varkappa) = \frac{[1-\rho K_B T \beta_B]\, S(\varkappa)_{exp} + S(\varkappa)_{exp} * \rho K_B T \beta_T - S(0)_{exp}}{S(\infty)_{exp} - S(0)_{exp}} \qquad (2)$$

where $\lim_{\varkappa \to 0} S(\varkappa)_{exp} = 1$, and in the limit $\varkappa \to 0$, $S(\varkappa)_{exp}$ becomes simple fluctuation of the mean density ρ, which is related to the isothermal compressibility β_T; β_T can be calculated knowing the velocity sound through the medium[5)]. The "best" value for $S(0)_{exp}$ can be chosen by minimization of the pair correlation function g(r) with respect to the hard core diameter σ[2)].

The correlation functions for liquid tin, lead and aluminium were calculated using Fourier transform of the measured structure factor [1,2,3)]. The pair correlation functions for values of r smaller than σ, for mentioned liquid metals, show the ripples which represent the errors of truncation and the statistical nature of the measured points in $S(\varkappa)$, Fig. 1.

Knowing the correlation functions g(r) and c(r) one can obtain the interatomic potential $\varphi(r)$ applying different theoretical approaches like statistical theories of Born and Green (BG), the Percus-Yevick (PY) and Hypernetted chain (HNC) theories and the perturbation theory.

If we assume a liquid metal as a two component system consisting of nearly free conduction electrons in which the ions are almost steady localized, the pseudopotential theory can be successfully used for calculation of interatomic potential $\varphi(r)$.

Other theoretical approaches to $\varphi(r)$, like Rahman's iterative method [6)] and a self-consistent scheme with a knowledge of the zeroth and fourth moment of the coherent scattering function $S(\varkappa, \omega)$[7,8)] are omitted in this paper.

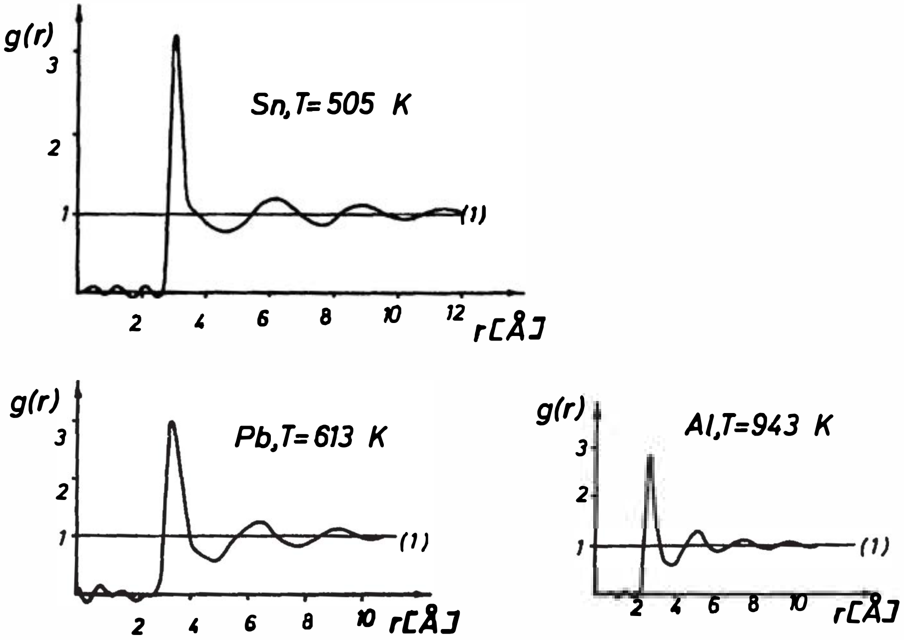

Fig. 1. Pair correlation functions for Sn, Pb and Al

2. Evaluation of interatomic potentials and discussion

If a direct calculation of the interatomic potential $\varphi(r)$ is to be calculated according to the statistical theory PY and HNC, it is necessary to make an expansion of the direct correlation function C(r)$^{9)}$. The best way to show the difference between the mentioned theories is the diagram technique, given by following equations $^{4,10)}$

$$c(r) = \bullet\!\!-\!\!\bullet + \rho \wedge + \frac{1}{2}\rho^2 \left\{ \left[2 \sqcap + 4 \boxslash + \boxtimes + \dots \right\} \right.$$
$$\cong h(r) - \mathrm{lug}(r) - \varphi(r)\beta \qquad \text{(HNC)} \qquad (3)$$

and

$$c(r) = \bullet\!\!-\!\!\bullet + \rho \wedge + \frac{1}{2}\rho^2 \left\{ \left[2 \sqcup + \boxtimes + \dots \right\} \right.$$
$$\cong g(r)\left[1 - e^{\beta\varphi(r)} \right] \qquad \text{(PY)} \qquad (4)$$

where the expressions that appear with ϱ^2 are truncated[11,12] in both equations. Diagram technique is well known[13,14] and we shall not discuss it in detail.

Both equations PY and HNC have been often used for the calculation of the pair potential $\varphi(r)$, but even for simple liquids, like liquid metals, the results are not always reliable[15]. The reason for that is probably the sensitivity of these theories due to unsatisfactory accuracy of the measured static structure factor, especially in determination of the slope in the front of the first maximum of the S(ϰ).

As it has been mentioned before, several thermodynamic properties of the highly dense system can be described if the repulsive part of the potential, equ. 1, is replaced by the hard core interatomic potential $\varphi_\sigma(r)$ and the attractive part of the $\varphi(r)$ is treated as a perturbation on the hard core part [16,17]. According to the hard sphere model the repulsive part of the real $\varphi(r)$ can be derived from the Taylor series[16]

$$a = a_T - \frac{1}{2}\beta\varrho^2\int Y_T(r)\Delta f(r)d^3r + \sum_{n=2} a_n \qquad (5)$$

where $a = -\frac{\beta\Delta F}{V}$ [16] and β is the reciprocal of the temperature and the Boltzmann constant, whereas F is the free energy. The first term, a can be evaluated by minimization of the function a, and using the random phase approximation (RPA) all quantities can be calculated by knowing the static structure data [17] where it is necessary to assume $\varphi_a(r)$ [18,9]

$$\beta\varphi_a(r) = -C(r) + \left[A(1) + A(2)u + A(3)u^2 + A(4)u^3 \ldots\right]$$

(6)

where $u = \frac{r}{\sigma}$ and coefficients A(1), ... are parameters which can be calculated by minimization of the free energy

$$\frac{\partial a}{\partial A(i)} = 0 \qquad (i = 1,2,3,4) \qquad (7)$$

The principal requirement in this calculation of $\varphi(r)$ is a satisfactory convergence for trial σ in equ. 6.

It was underlined in the beginning of this paper that the pair interaction potential $\varphi(r)$ can be calculated from various pseudopotentials and screening functions [19], e.g.

$$\varphi(r)=\frac{Z^2e^2}{r}\left[1-\frac{2}{\pi}\int_0^\infty F_N(\varkappa)\sin\varkappa\,d\varkappa\right] \tag{8}$$

where $F_N(\varkappa)$ is the normalised energy wave number characteristic $[F_N(0)=1]$. Using the Sham [20] and Heine and Abarenkov [21] expression for $F_N(\varkappa)$, with exchange and correlation effects between electrons suggested by Geldart and Vosko [22], and the screening function (9), we have calculated $\varphi(r)$ for Pb and Al.

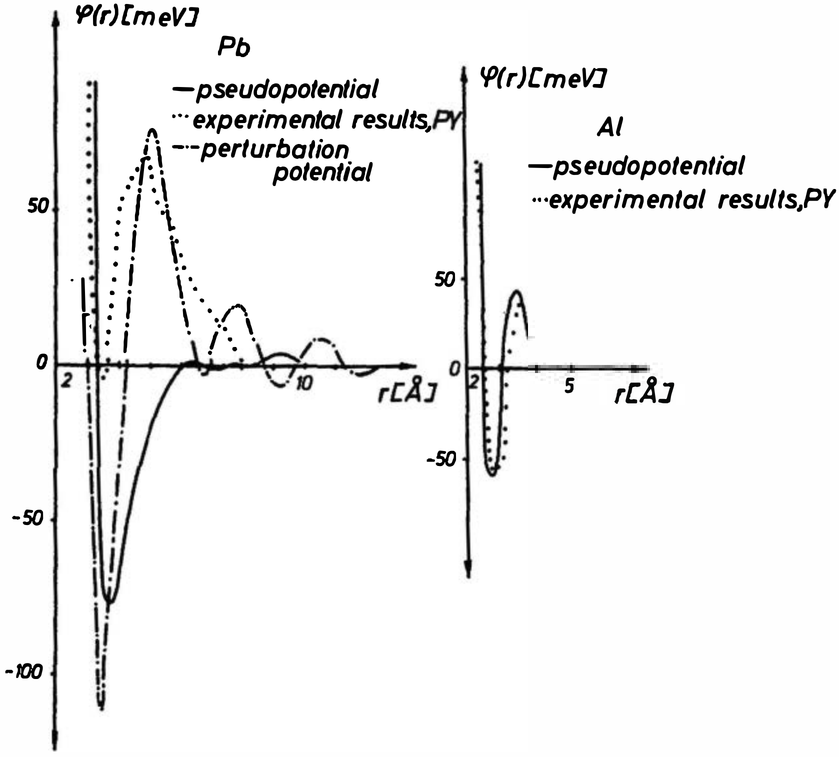

Fig. 2. The pair interaction potential $\varphi(r)$ for Pb and Al in the vicinity of the melting point.

In Fig. 2. calculated pair interaction potential $\varphi(r)$ of liquid lead and aluminium using pseudopotential theory, statistical theory PY and the perturbation theory have been compared. It is obvious from the Fig. 2 that there is a big discrepancy between different theoretical approaches to the interatomic potential $\varphi(r)$.

This work was supported by the Scientific Association of Serbia and partly by the Serbian Academy of Sciences and Art.

References

1) Dj. Jović and I. Padureanu, J.Phys.C 9 (1976) 1135.

2) U. Dahlborg, M. Davidović and K. E. Larsson, Phys.Chem.Liq. 6 (149) 1977.

3) Dj. Jović, I. Padureanu and S. Rapeanu, Inst.Phys.Conf.Ser. No. 30 (1977) 120.

4) Y. Marcus, Introduction to Liquid State Chemistry, John Wiley & Sons, London (1977).

5) A. V. Grosse, NYO-4176-6, GL (1970) 1970-14.

6. A. Rahman, Phys.Rev., All (1975) 2191.

7) N. K. Ailawadi and I. Naghizadeh, Ber.Bunsenges.Phys.Chem. 80 (1976) 708.

8) R. Bausal, P. K. Banerjee and N. K. Ailawadi, Phys.Rev., A17 (1978) 1156.

9) M. Davidović, Ph.D. Thesis, Department of Physics, Faculty of Natural Sciences and Mathematics, University of Belgrade (1978).

10) D. A. Johon, Molecular Physics. 21 (1971) 755.

11) C. Croxton, Introduction to Liquid State Physics, John Wiley & Sons, London (1975).

12) A. Barker and D. Henderson, Rev.Mod.Phys. 48 (1976) 587.

13) W. Brostow, Chem.Phys.Letts. 33 (1975) 387.

14) J. O. Hirshfelder and C. F. Curtiss, R. Byron Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, New York (1967).

15) D. Levesgue and L. Verlet, Phys.Rev.Lett. 20 (1968) 905.

16) H. C. Andersson, D. Chandler and J. D. Weeks, Advances in Chem.Phys. 34, I. Pirgogine and S. P. Rice eds., John Wiley & Sons, New York (1976).

17) K. S. Mitra and M. J. Gillou, J.Phys.C. 9 (1976) L515.

18) S. K. Mitra, private communication, 14/9 (1977).

19) W. Schommers, Zeischrift für Physik, B24 (1976) 171.

20) L. J. Shaw, Proc.Roy.Soc., A283 (1965) 33.

21) I. V. Abarenkov and V. Heine, Phyl.Mod. 12 (1965) 529.

22) W. Geldort and S. H. Vosko, Canad.J.Phys., 44 (1966) 2137.