# Effective Pair Potentials of Liquid Silicon and Gallium Estimate from Experimental Structure Factor Data

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(Received September 7, 2001: final form October 3, 2001)

**ABSTRACT**

The effective pair potentials of liquid Si and Ga have been calculated from measured structural data by applying the modified hypernetted-chain equation coupled with predictor-corrector method. The calculation was also made for liquid Na for comparison. The effective pair potential of liquid Si indicates the ledge-type repulsive core part with weak attractive feature, whereas the long range oscillatory behavior, similar to the typical liquid metals, is clearly observed in liquid Ga. The usefulness of the effective pair potentials presently obtained for three liquid metals was confirmed by reproducing the structural behavior and self-diffusion and visocity coefficients, as well.

## 1. INTRODUCTION

The general profile of the structure factor $S(Q)$ of most liquid metals is known to be well described by the hard-sphere model /1/. On the other hand, the structure factors of some non-simple polyvalent liquid metals such as Ge, Sn, Ga and Si show a small hump on the higher wave-vector side of the first peak. This particular feature could not be explained by such a simple hard-sphere theory.

Some theoretical approaches to the structure of polyvalent metals suggest that the hump of the structure factor is attributed to the screened core-polarization effect /2/. Although the general profiles of liquid polyvalent metals are known to be described by the pair potentials derived from the simple empty-core pseudo-potential. The recent works on liquid Ge and Sn /3/ suggest that the structural features of these elements are rather sensitive to the part of the pair potential around the second peak of the pair distribution functions, in contrast to the simple liquid metal case in which the structural feature is almost determined by the part of the pair potential near the first peak region. However, these methods involve some physical assumptions and still face serious difficulties with very complicated systems such as liquid Ga and Si.

For this reason, in this work, the "predictor-corrector" procedure proposed by Reatto *et al.* /4/ was utilized in order to estimate the effective pair potentials of liquid Ga and Si from experimental structural data. The effective pair potentials obtained in this way should include automatically the particular structural features of liquid of interest, by taking into account more precisely the many-body correlation.

Self-diffusion and viscosity coefficients were also calculated using the small-step diffusion theory of Rice and Kirkwood /5/, in order to test the usefulness of the effective pair potentials obtained.

## 2. FUNDAMENTALS OF DATA PROCESSING

The utilized method for estimation of the effective pair potential of simple liquid is well known and has been described in detail /3,4/. Thus, for convenience, only some essential points are given below.

### 2.1 Effective pair potential

A diagrammatic expansion for the pair distribution function $g(r)$ of a single component liquid, provided that the particles interact through two-body additive potentials $u(r)$, leads to the following equation,

$$g(r) = \exp\left[-\frac{u(r)}{k_B T} + h(r) - c(r) + B(r)\right], \qquad (1)$$

where $h(r) = g(r) - 1$ and $k_B$ is the Boltzmann constant and $T$ the absolute temperature. Direct correlation function $c(r)$ is defined through the following Ornstein-Zernike relation,

$$h(r) = c(r) + \rho \int h(|r - r'|) \cdot c(r') \mathrm{d}^3 r', \qquad (2)$$

where $\rho$ is number density. $B(r)$ is called a bridge function, corresponding to a sum of the contribution of all elementary graphs in a cluster expansion.

By means of these equations, when the experimental structural data are given, the effective pair potential can be estimated through the following equation,

$$u(r) = k_B T[h(r) - c(r) - \ln g(r) + B(r)]. \qquad (3)$$

The simplest way to solve this inverse problem is to set $B(r)=0$ (hypernetted-chain (HNC) approximation). However, this is not suitable to obtain the pair potentials from measured structural data, because $B(r)$ could not be neglected in near neighbor region for dense liquids.

In terms of the proposed "predictor-corrector" method /4/, starting from an initial estimation for the effective pair potential (for instance HNC approximation) it is possible to obtain an improved estimation for the effective pair potential, by substitution of estimation of $B(r)$ into Eq.(3) through iterative procedure as follows:

$$\frac{u_i(r)}{k_B T} = \frac{u_{i-1}(r)}{k_B T} + [g(r) - g_{i-1}(r)] + \ln\left[\frac{g(r)}{g_{i-1}(r)}\right] + (2\pi)^{-3}\rho^{-1}\int d^3 Q e^{-iQr}\left[\frac{1}{S(Q)} - \frac{1}{S_{i-1}(Q)}\right] \qquad (4)$$

where $g(r)$ and $S(Q)$ refer to the experimental pair distribution function and experimental structure factor, respectively. Number density values utilized in this work are listed in Table 1 for further convenience.

**Table 1**
Number density of liquid Si, Ga and Na utilized in this work.

| Element | Si | Ga | Na |
|---|---|---|---|
| Temperature (K) | 1733 | 323 | 378 |
| Number density ($nm^{-3}$) | 54.2 | 52.5 | 24.3 |

### 2.2 Self-diffusion and viscosity coefficients

In terms of the small-step diffusion theory by Rice and Kirkwood /5/ the following expression gives the self-diffusion coefficient for one component liquid.

$$D = \frac{k_B T}{\zeta^H + \zeta^S + \zeta^{SH}}, \qquad (5)$$

where $\zeta^H$, $\zeta^S$ and $\zeta^{SH}$ are the friction coefficients corresponding to the repulsive hard-part interaction, the soft-part interaction between neighboring atoms and the cross-effect between the hard and soft forces in the pair potential, respectively.

$$\zeta^H = \frac{8}{3}\rho g(\sigma)\sigma^2\sqrt{m k_B T}, \qquad (6)$$

$$\zeta^S = \left[\frac{4\pi m\rho}{3}\int_0^\infty \nabla_r^2 u^S(r) g(r) r^2 \mathrm{d}r\right], \qquad (7)$$

$$\zeta^{SH} = -\frac{1}{3}\rho g(\sigma)\sqrt{\frac{m}{\pi k_B T}}\int_0^\infty [(Q\sigma)\cos(Q\sigma) - \sin(Q\sigma)]\tilde{u}^S(Q)\mathrm{d}Q, \qquad (8)$$

where $\rho$ is the number density of atoms, $\sigma$ is the effective hard sphere diameter, $g(\sigma)$ the value of the

pair distribution function at $r = \sigma$, $m$ the atomic mass and $\tilde{u}^S(Q)$ is the Fourier transform of the soft part of the pair potential which is defined as follows:

$$u(r) = u^H(r) + u^S(r) \tag{9}$$

$$\begin{aligned} u^H(r) &= \infty \text{ and } u^S(r) = 0 \qquad r \le \sigma \\ u^H(r) &= 0 \text{ and } u^S(r) = u^{eff}(r) \qquad r \ge \sigma \end{aligned} \tag{10}$$

Also, the viscosity might be estimated through following equation /6/.

$$\eta = \frac{2\pi}{15}(m/k_B T)^{1/2}\rho^2 \int_0^\infty g(r)\frac{du(r)}{dr} r^4 dr . \tag{11}$$

## 3. RESULTS AND DISCUSSION

For liquid Si at 1733 K and Ga at 323 K, the structure factor data measured extremely down to 0.5 $nm^{-1}$ by means of transmission geometry are available /7/. Thus, the initial estimation of the pair potential was deduced by hyper-netted chain (HNC) equation from the completed data set of structure factor. Then the "predictor-corrector" method was utilized coupled with a Monte Carlo (MC) simulation technique as predictor stage and the modified hyper-netted chain (MHNC) equation as corrector stage. MC simulation was carried out with 1728 particles corresponding to the cell size of $L^3 = 3.162^3$ $nm^3$ for liquid Si at 1733 K, $L^3 = 3.205^3$ $nm^3$ for liquid Ga at 323 K and $L^3 = 4.302^3$ $nm^3$ for liquid Na at 378 K.

The results for the effective pair potentials obtained in this work are presented in Fig. 1 together with those for liquid Na at 378 K for reference. Figure 2 shows the experimental pair distribution functions for these three liquid metals in comparison with the results from MC simulation using the effective pair potentials presently obtained. Figure 3 provides the resultant structure factors for liquid Si, Ga and Na given by Fourier transform of the simulated pair distribution functions together with the experimental data. The effective pair potential of liquid Na obtained in this work was found to reproduce well the experimental structural data. On the other hand, we observe deviation from the experimental data in the cases of both liquid Si and Ga, especially in the width of the first peak of their pair distribution functions.

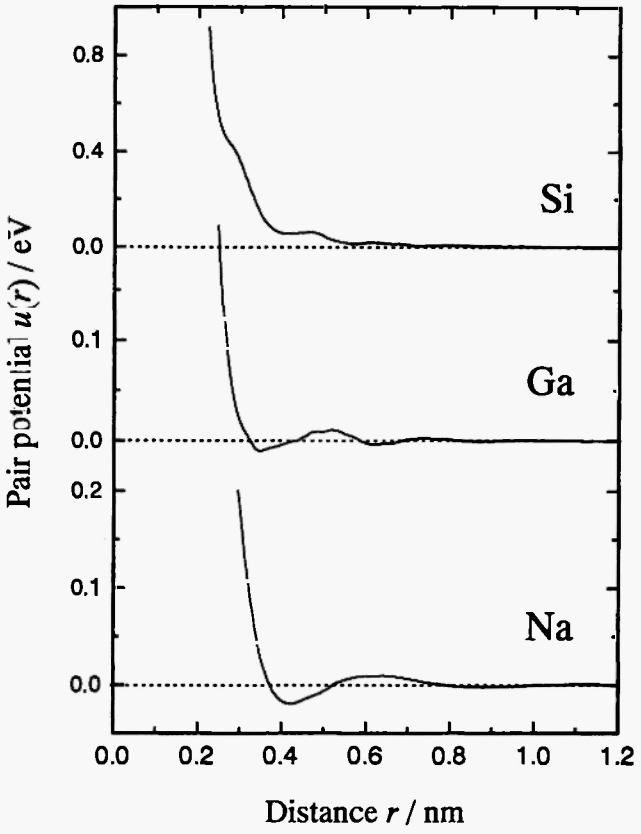


**Fig. 1:** Effective pair potentials of liquid Si, Ga and Na estimated from the experimental structure factor data.

Although the peak height of the structure factor is not considered to be important for determining the effective pair potentials /8/, the difference between the calculated values and the experimental data should be stressed. Nevertheless, the effective pair potentials of liquid Si and Ga obtained in this work reproduce well the particular structural features characterized by a small hump on the higher wave vector side of the first peak in the structure factor.

It may be worth noting that the behavior of the structure factor of liquid Si presently obtained is very close to the theoretically predicted case by using the pseudo-potential theory of metals /9/. The effective pair

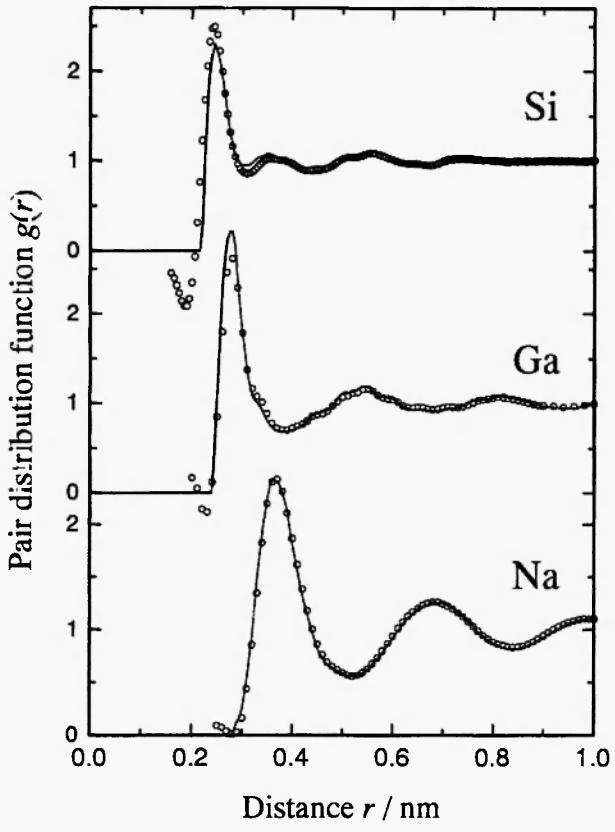


Fig. 2: Experimental pair distribution function (open circles) of liquid Si, Ga and Na in comparison with those of Monte Carlo simulation with the effective pair potentials obtained in this work (solid line).

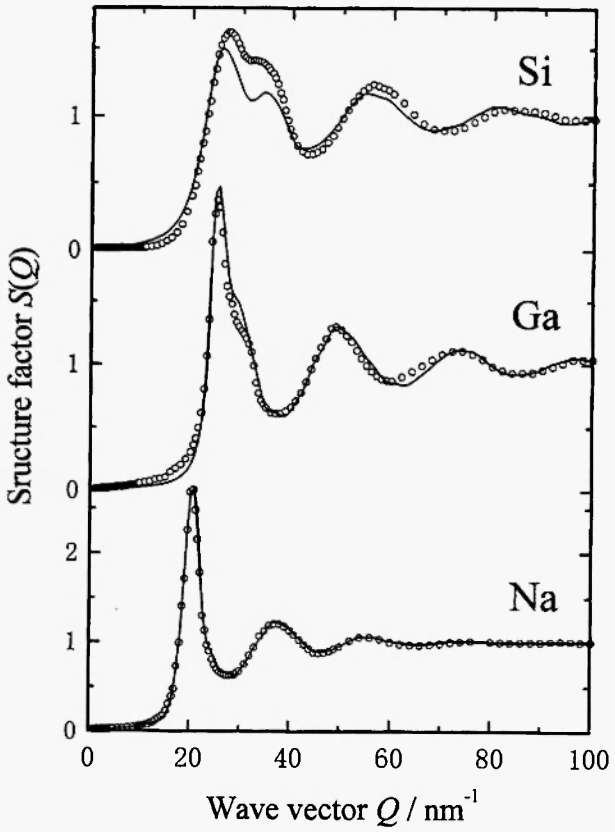


Fig. 3: Structure factor of liquid Si, Ga and Na (solid line) given by Fourier transform of the simulated pair distribution functions in comparison with the experimental data (open circles).

potential of liquid Si is characterized by the ledge-type feature in the repulsive core part within the first coordination shell and the attractive interaction is also recognized in the range of the second coordination shell. Such specific features in the effective pair potential might be related to particular properties and structure of liquid Si. On the other hand, the effective pair potential of liquid Ga obtained in this work rather shows the typical long range oscillatory behavior, as shown in Fig.3. This result is not close to the pseudo-potential case for trivalent metals including Ga /10/.

It must be noted here that the method employed in this work for estimating the effective pair potential using the MHNC equation is not a unique mathematical procedure. Nevertheless, the effective pair potentials obtained in this work are considered to be, at least, in a sense of necessary condition at best by reproducing the experimental structural data using computer simulation, although they might not be sufficient condition.

The calculated values of friction, self-diffusion and viscosity coefficients are summarized in Table 2 together with some available reference data. In this work the position on the rising curve at the height of 30% of the first peak of the pair distribution function was chosen for the value of the effective hard-sphere diameter.

The present results for friction coefficients are found to be comparable with those of other liquid metals /11/.

**Table 2**
Comparison of the calculated values for friction, self-diffusion and viscosity coefficients with the reference data of liquid Si, Ga and Na.

| Element | Si | | Ga | | Na | |
|---|---|---|---|---|---|---|
| | cal. | ref. | cal. | ref. | cal. | ref. |
| $\zeta^H$ (kg $s^{-1}\times10^{-12}$) | 0.48 | - | 0.53 | - | 0.16 | - |
| $\zeta^\delta$ (kg $s^{-1}\times10^{-12}$) | 0.49 | - | 1.04 | - | 0.64 | - |
| $\zeta^{\delta H}$ (kg $s^{-1}\times10^{-12}$) | 0.39 | - | 0.31 | - | 0.06 | - |
| $D$ ($m^2$ $s^{-1}\times10^{-9}$) | 18 | 19[12] | 2.36 | 1.6[14] | 6.0 | 4.2[14] |
| $\eta$ (m Poise) | 21.2 | 5.3[13] | 22.3 | 18.1[15] | 9.3 | 7 0[16] |

Both self-diffusion and viscosity coefficients of three liquid metals estimated in this work agree rather well with the reference values /12-16/. This includes the self-diffusion coefficient of liquid Si, which is close to the values ($D = 20 \sim 26$ x $10^{-9}$ $m^2/s$) by molecular dynamic (MD) simulation /17/. However, the present authors maintain the view that the reasonable agreement between calculation and the reference data should be considered only as one piece of evidence for suggesting the usefulness of the effective pair potentials presently obtained.

## 4. CONCLUDING REMARKS

The effective pair potentials of liquid silicon and gallium have been estimated in order to gain insight into the particular structural features of these elements in the liquid state. The result for liquid Ga indicates the long range oscillatory behavior, characteristic for liquid metals, whereas the effective pair potential of liquid Si is described by the ledge-type repulsive core part with weak attractive feature. These effective pair potentials estimated from the experimental structure factor data are found to reproduce the reference values of self-diffusion and viscosity coefficients. However, the origin of unusual behavior detected in liquid Si cannot be certainly identified yet just from the presently available information.

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