

# Self-diffusion coefficient of liquid germanium studied by a classical molecular-dynamics simulation

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**Abstract** The self-diffusion coefficients of liquid germanium for a wide range of temperature were calculated by a classical molecular-dynamics simulation. The interatomic potential was calculated by the pseudopotential perturbation theory. The results of the self-diffusion coefficient were compared with the experimental data.

The temperature dependence of the self-diffusion coefficient of the liquid germanium was investigated by a classical molecular-dynamics (MD) simulation. The interatomic potential was calculated by the pseudopotential perturbation theory, where the empty core pseudopotential due to Ashcroft and the local field correction by Ichimaru-Utsumi [1] were employed. The cut-off radius of the pseudopotential was 0.98 a.u. For the density of the system, the experimental values [2] were used. Though the experimental data of the density were obtained from 1223 to 1542 K, we used the fitting formula proposed by Nakanishi *et al.* [2] up to 2000 K as listed in table 1. With these data of the density the effective pair potentials  $\phi(r)$ 's were calculated at the five temperatures from 1253 to 2000 K and the results are shown in figure 1.

The MD simulations were carried out over 20000 steps with the time step of 2.4 fs for the five temperatures. We used  $N = 4096$  atoms in the cubic MD cells with periodic boundary conditions. The temperature is controlled by the Nosé thermostat. The cut-off length of the effective pair potential was 11 Å.

Table 1. The density of the liquid germanium [2].

$T$ (K)	mass density $\rho$ (g/cm <sup>3</sup> ) $\rho(T) = -4.42 \times 10^{-4} T(\text{K}) + 6.17$	number density $n$ (Å <sup>-3</sup> )
1253	5.62	0.0466
1400	5.55	0.0460
1473	5.52	0.0458
1700	5.42	0.0449
2000	5.29	0.0438

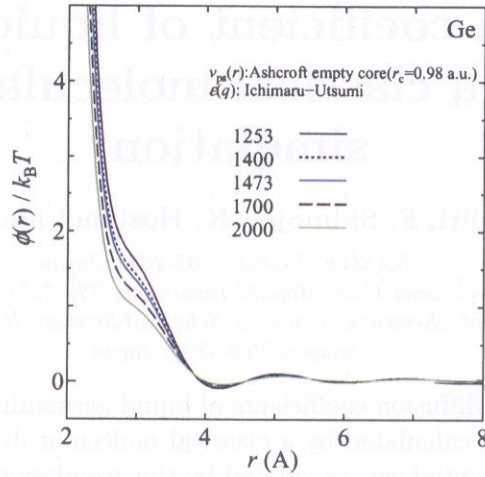


Figure 1. The effective pair potential of liquid germanium calculated by the pseudopotential perturbation theory with the empty core pseudopotential due to Ashcroft  $v_{ps}(r)$  and the local field correction for the dielectric screening function  $\epsilon(q)$  by Ichimaru-Utsumi [1].

The calculated structure factor  $S(Q)$  and the radial distribution function  $g(r)$  are shown in figures 2 and 3, respectively. A shoulder in the structure factor is well reproduced and the whole shape of the structure factor at 1253 K is in good agreement with the corresponding experimental data [3]. A characteristic feature in the radial distribution function is the small peak between the first and the second peaks. Though the position of this peak is slightly different from that of the experimental one, the calculated  $g(r)$  is also in good agreement with the experimental data [3]. With increasing temperature the height of the first peaks of both  $S(Q)$  and  $g(r)$  become lower while other parts of the structure are almost unchanged.

The mean-square displacement (MSD) of atoms is shown in figure 4. The MSD's are well fitted by the straight lines in the long time region,  $t > 1$  ps. The self-diffusion coefficients are calculated from the gradient of the fitted lines at each temperature. The velocity autocorrelation function  $Z(t)$  and its spectrum  $\tilde{Z}(\omega)$  are shown in figures 5 and 6, respectively. The velocity autocorrelation function does not show negative values, which means that the *cage effect* is small in liquid germanium.

The self-diffusion coefficient  $D$  can also be estimated from  $\tilde{Z}(0)$ . Since the MD simulations were performed for an enough long time, the values of  $D$  estimated from the gradient of the MSD in a long time region and from  $\tilde{Z}(0)$  are in excellent agreement with each other and the averaged values for each temperature are shown as the solid circles in figure 7. For comparison other calculated values [4, 5] and the experimental data [6, 7, 8] are also shown. Though near the melting temperature the all results are in reasonably agreement with each other, the temperature variation of our data is smaller than that of the other data.

When the temperature changes under a constant pressure, the density also changes. To separate the contribution from the temperature and the density to the self-diffusion coefficient, we carried out MD simulations from 1253 to 2000 K with the constant density at

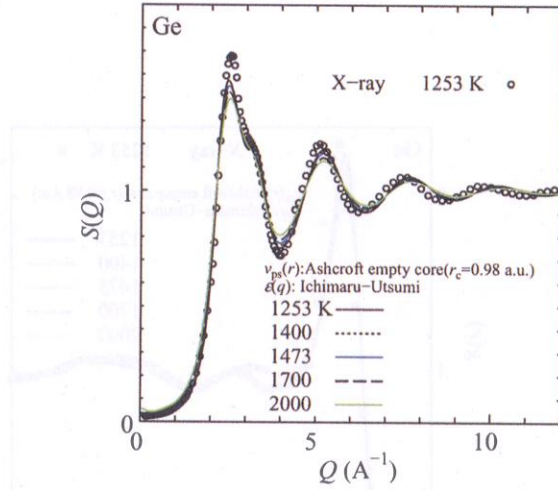


Figure 2. The structure factors of liquid germanium calculated by the present MD simulation and observed by the X-ray scattering experiment [3].

1253 K and also with the constant temperature of 1253 K varying the density. For saving the calculating cost, the MD simulations were performed in the small system of  $N = 1000$  atoms. The results are compiled in tables 2 and 3.

In this report the temperature dependence of the structure and the self-diffusion coefficient were studied with the effective pair potential and the MD simulation. Though it has been said that there exist chemical bonds in liquid germanium, we have shown that the structure and the self-diffusion coefficient near the melting point were well reproduced by the *pair* potential. To investigate the dynamic properties of liquid germanium in more detail, the study on the dynamic structure factor is now in progress.

Table 2. Temperature dependence of the self-diffusion coefficient  $D$  of liquid germanium at the constant density of  $\rho = 5.62$  (g/cm<sup>3</sup>) with the effective pair potential at 1253 K.

$T$ (K)	$\rho$ (g/cm <sup>3</sup> )	$D$ (10 <sup>-4</sup> cm <sup>2</sup> /s)
1253	5.62	1.27
1400	5.62	1.43
1700	5.62	1.76
2000	5.62	2.07

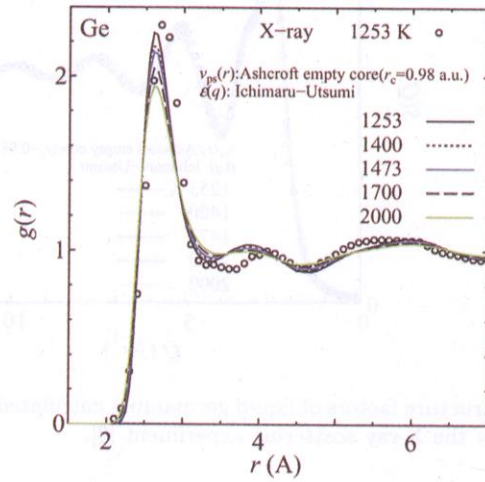


Figure 3. The radial distribution functions of liquid germanium by the present MD simulation and by the X-ray scattering experiment [3].

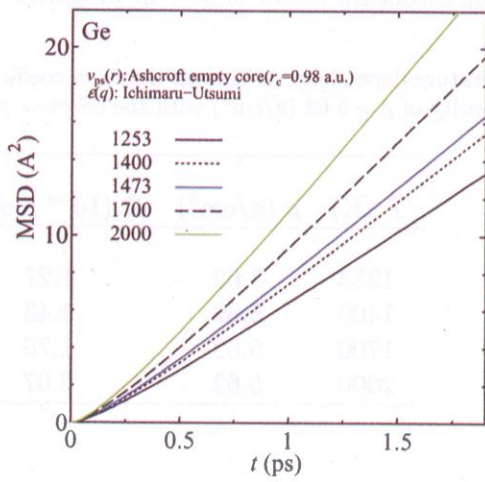


Figure 4. The mean-square-displacement (MSD) of atoms of liquid germanium.

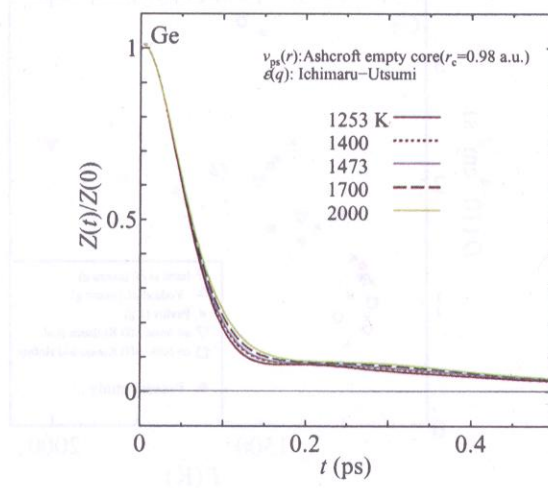


Figure 5. The velocity autocorrelation function of liquid germanium.

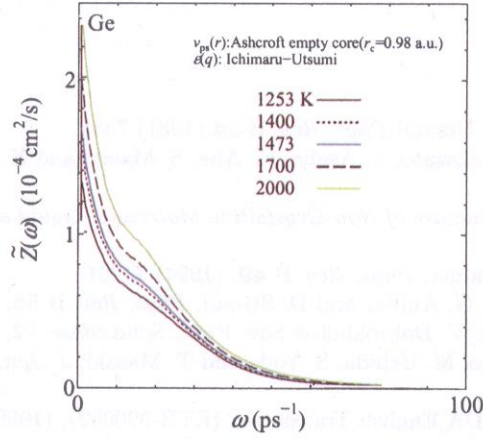


Figure 6. The spectrum of the velocity autocorrelation function.

Table 3. The density dependence of the self-diffusion coefficient  $D$  of liquid germanium at the constant temperature of 1253 K with the effective pair potential at 1253 K.

$T$ (K)	$\rho$ (g/cm <sup>3</sup> )	$D$ (10 <sup>-4</sup> cm <sup>2</sup> /s)
1253	5.62	1.27
1253	5.55	1.29
1253	5.42	1.37
1253	5.29	1.41

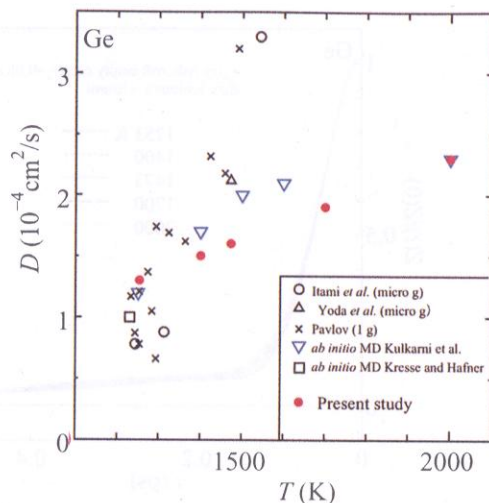


Figure 7. The self-diffusion coefficients of liquid germanium for a wide range of temperature. The solid circles show the present result. The other calculated and the experimental data are also shown.

## References

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