

Comparative Simulation Study of Vacancy Diffusion in MgO and Ne Crystals in Very High Pressures

Project Representative

Mitsuhiro Toriumi Japan Agency for Marine–Earth Science and Technology/ Graduate School of Frontier Science,
University of Tokyo

Author

Mitsuhiro Toriumi Japan Agency for Marine–Earth Science and Technology/ Graduate School of Frontier Science,
University of Tokyo

MD simulations with Born-Mayer type pairwise potential on MgO vacancies pair were conducted to obtain the Newtonian viscosity of lower mantle. The results are such that the viscosity of the upper half portion in the lower mantle shows uniform structure but in the lower half it rapidly decreases to the core mantle boundary by two order of magnitude.

To clarify the reason of viscosity lowering in the deep lower mantle, we performed this year the experiments MD calculations of vacancy mobility in Ne solids using Lenard-Jones type pairwise potential. The results indicate that the viscosity lowering is responsible for the long term electrostatic force but not short term force. Thus, the actual lower mantle rheology should also show the viscosity lowering in the deepest lower mantle.

Keywords: vacancy diffusion, MgO, Ne solid, lower mantle, pairwise potential

1. Introduction

The aim of this research program is to obtain the mechanical behavior of earth's materials in the conditions ranging from shallow crust to deep mantle by means of the following simulations studies; (1) dislocation and vacancy structure and dynamics in MgO and MgSiO₃ in the lower mantle conditions using molecular dynamics method of several different type pairwise potentials, (2) water structure and the physical properties in earth's materials using ab initio simulation, (3) shear zone structure and dynamics involving mineral reaction, water migration, localization, crack formation using granular system simulation. This year, we intend to perform long term time studies and the one million basic cell simulation studies of vacancy diffusion in MgO in very high pressure conditions for evaluation of the Newtonian viscosity of the lower mantle, and to conduct the vacancy diffusion in Ne fcc solids to compare the mechanism responsible for the viscosity lowering in deep lower mantle condition in MgO crystal. These materials are constructed by typical Lennard-Jones type potential in contrast with MgO by Born-Mayer type one.

2. Results

We investigated the molecular dynamic simulation of Ne solids to construct a neutral vacancy and to relax to the stable structure. Then it moves random walk from the initial position. The mean square distance of this random walk of the vacancy is temperature compensated diffusivity. The size

of the basic cell reaches three thousands atoms. This type of simulation required in the estimation of very high pressure viscosity of these solids is to consider the density of vacancy, because equilibrium densities of them depend on applied stress are very small low stress conditions. To conduct the simulation, the relaxation time is needed to be several nanoseconds. Even using the ES, it is impossible to conduct the precise simulation of vacancy random walk for the relaxation process of vacancy migration need enough time.

Thus, the author (Ito) made a new algorithm utilizing table update method of near atomic position and velocities. As a result the n^2 calculation changes down to the $n^{1.5}$ power calculation, so that the times required for the 20 nanosecond relaxation experiments are possible in the evaluation of the Newtonian viscosity. In addition, the time studies for relaxation of vacancy are conducted and then it is concluded that the 20 ns experiments show enough narrow range of diffusivity compared with 4 ns experiments.

The MD experiments of Ne fcc solids with pairwise potential of Lennard-Jones type were carried out in the range from 1500 to 3000 K and 80 to 200 Gpa. The potential terms of Ne fcc crystals used here are the same as those by Kittel (1972) as shown in Fig. 1. The results are shown in Fig. 2, indicating that the diffusion coefficients of various temperatures from 1500 to 3000 K decrease monotonously from 80 to 200 Gpa. This means the monotonous increase of Newtonian viscosity derived by the vacancy diffusion. The increase of diffusion

Ne solid;
Lennard-Jones type potential $U(r_{ij}) = 4 \epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$

MgO
Born-Mayer type potential $U_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r^6}$

	$\epsilon [10^{-16} \text{erg}]$	$\sigma [\text{\AA}]$
Ne	50	2.74
Ar	167	3.4

Fig. 1 The difference in the potential type between MgO and Ne crystals with fcc structure. The parameters for Ne solid are cited from Kittel (1972).

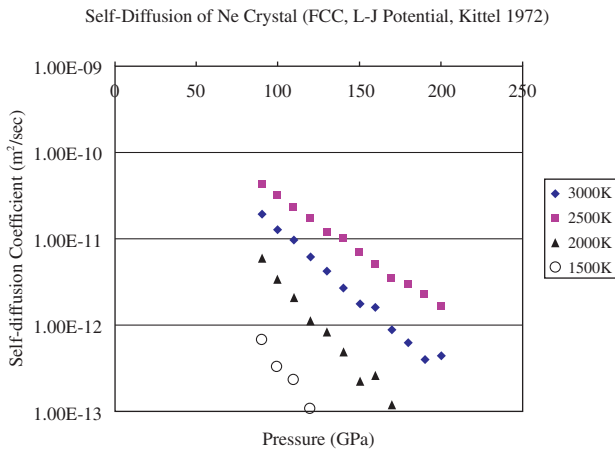


Fig. 2 Diffusion coefficient D (m^2/sec) as a function of pressure (GPa) in the range from 1500 to 3000 K. The profiles of the diffusion coefficient show constantly decreasing with pressure in the very high pressure conditions.

coefficients at the constant pressure conditions are derived reasonable activation enthalpy of this vacancy diffusion. These results indicate sharply that the activation volume of the vacancy diffusion in Ne fcc crystals is nearly constant in the wide range of pressure and temperature conditions.

The viscosity of the Ne solids can be defined as the derivatives of strain rate by stress. The strain rate and stress relation is commonly called as the constitutive law, and it should be classified into the linear law and non-linear law. The latter is the power law creep in general. The linear type is Newtonian creep and representative model of the solid materials is the diffusion creep. This type of creep is governed by the lattice diffusion along the paths of grain boundary or of volume. In this case, the flow law of the Nabarro-Herring creep can be formulated as follows;

$$d\epsilon/dt = AVD\sigma / RTd^2$$

where $A = 13.3$ and $V = 2.44 \times 10^{-5} \text{ m}^3/\text{mol}$, and D and d are diffusion coefficient and grain size, respectively. In this

case, the Newtonian viscosity of the Ne solids is controlled by the diffusion of vacancy as shown in the earlier sections.

4. Viscosity lowering in the lower mantle

In order to evaluate the viscosity lowering of MgO in the deep mantle, the comparative study between the Born-Mayer type and Lennard-Jones type potentials in solids was carried out in MgO and Ne crystals. The difference between these potential types comes from the ionic bonding in MgO, that is the electrostatic potential which is effective in the long distance. The short term forces are the Born type exponential and the short term repulsive one and the Van der Waals potential. The results show that the diffusion coefficients in Ne solids decrease monotonously with increasing pressure under the constant temperature conditions. It indicates that the activation volume in vacancy diffusion is positive and keeps nearly constant until 200 GPa.

On the other hand, previous studies of vacancy diffusion in MgO indicates that the diffusion coefficients decrease until 70 GPa and then they increase with increasing pressure reaching 150 GPa as shown in Fig. 3. Therefore, the activation volume changes from positive to negative value with increasing pressure under constant temperatures.

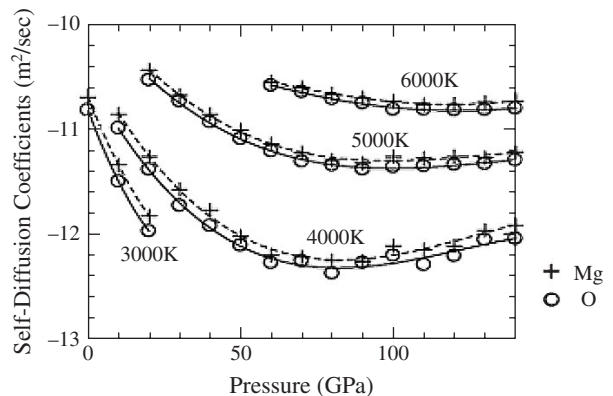


Fig. 3 Diffusion coefficient as a function of pressure in MgO cited from Toriumi (2004).

The difference of the pressure-dependence between Ne and MgO solids, therefore is responsible for the potential terms of them, because of the same basic cell of fcc structure of them. The long term force by electrostatic potential exists in MgO but in Ne solid the potentials are basically short term ones. Then we consider that the negative activation volume term of diffusion in high pressure conditions in MgO is derived from the long term force. This is important in the context that the long term force is enough evaluated from the pairwise potential though the short term potential should be required for ab initio MD simulations for multi-body effects (Tsuneyuki, 2002). Consequently, we can conclude that viscosity lowering in the deep mantle predicted in the previous simulation studies is available for the real earth mantle.

5. Conclusions

We conducted the MD simulations with pairwise potentials on MgO vacancies pair and Ne vacancies to compare the

viscosity change with pressure corresponding to the difference in potential types. The results are such that the viscosity lowering should be derived from the long term electrostatic potential term in MgO. It suggests strongly that the MD simulation of viscosity in MgO with pairwise potential can be available for the lower mantle conditions and that the viscosity lowering with pressure in the deep mantle is well simulated without ab initio MD calculations.

References

- Kittel, C., Introduction to Solid State Physics, John Wiley & Sons, New York, 766p, 1972.
- Toriumi, M., Numerical simulation of physical properties of earth materials. Annual report of the Earth Simulator Center, 2003-2004, 101-103, 2004.
- Tsuneyuki, S., Quantum localization of hydrogen atoms in solids, Current Opinion in Solid State and Materials Science 6, 147-151, 2002.

地球物質の数値計算科学的物性評価

プロジェクト責任者

鳥海 光弘 海洋研究開発機構・東京大学新領域創成科学研究科

著者

鳥海 光弘 海洋研究開発機構・東京大学新領域創成科学研究科

分子動力学法による格子拡散型の変形に対する直接計算を2つの異なるタイプの2体ポテンシャルで比較することにより、マントル下部におけるMgO結晶の粘性率低下の原因を同定することを目的として、Ne結晶のMD拡散係数を200GPaまで求めた。実験の結果は温度が1500–3000Kにおいて、いずれも一定温度における空孔の拡散係数は超高压において、圧力とともに減少する結果を得た。すなわち、空孔拡散における活性化体積はほぼ一定で正の値であることが示された。

MgOの空孔拡散係数は約70GPaまでは減少するが、それより高压では急速に増加することが明らかにされている。拡散係数の圧力依存性のこの差異はMgOにおける2体ポテンシャルのうち、静電ポテンシャル項、すなわち長距離相互作用項によっていると判断された。これは長距離相互作用であるため、第一原理計算で大きく効いてくる短距離相互作用とは切りはさすことができ、したがって、2体ポテンシャルのMD法による拡散係数の圧力による増加は正しくマントル下部の物性を現していると判断してよいだろう。

このことから下部マントル深部の条件で推定されたニュートン粘性率が一桁から2桁程度減少するという前報告の結論は十分支持されると思われる。

キーワード：流動則, 粘性率, 2体ポテンシャル, Ne, 下部マントル