Electron Trapping in Amorphous Silicon - A Quantum Molecular Dynamics Study*

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ELECTRON TRAPPING IN AMORPHOUS SILICON - A QUANTUM MOLECULAR DYNAMICS STUDY

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ABSTRACT

Quantum molecular dynamics (QMD) simulations provide the real-time dynamics of electrons and ions through numerical solutions of the time-dependent Schrödinger and Newton equations, respectively. Using the QMD approach we have investigated the localization behavior of an excess electron in amorphous silicon at finite temperatures. For time scales on the order of a few picoseconds, we find the excess electron is localized inside a void of radius ~ 3 Å at finite temperatures.

INTRODUCTION

In amorphous silicon (a-Si) electron mobility measurements [1] reveal thermally activated behavior above 150 K with the activation energy around 0.14 eV. The microscopic understanding of localization and transport of electrons and holes in amorphous systems requires the knowledge of the real-time dynamics of quantum particles at finite temperatures.

In 1987 a new simulation technique, namely called quantum molecular dynamics (QMD), was proposed [2]. The QMD method provides the numerical solutions of the time-dependent Schrödinger and Newton equations for quantum and classical particles in mixed quantum-classical systems at finite temperatures. Since the QMD approach provides the real-time dynamics of quantum particles, it allows the study of the microscopic behavior of quantum particles in materials.

In this paper we discuss the QMD algorithm and the results for the localization behavior of an excess electron in a-Si.

QUANTUM MOLECULAR DYNAMICS ALGORITHM

For the discussion of the QMD algorithm, let us consider the situation where an electron is interacting with an ensemble of atoms. This situation occurs in the electron mobility measurements where the motion of an electron injected into a material is monitored under the influence of an electric field. Excess electron in molten salts [2], water [3], or inert gases [4] are examples of the situation we have considered. The atoms behave as classical particles if

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their de Broglie wave length is small compared to the average interatomic spacing. The time-dependent Schrödinger equation for the electron reads,

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = H\psi(\mathbf{r},t) ; H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r},\{\mathbf{R}_l(t)\}) , \quad (1)$$

where $\psi(\mathbf{r},t)$ is the electron wave function, m is the electron mass, and $\hbar$ is the Planck constant. In Eq. (1), $\{\mathbf{R}_l(t)\}$ denote the positions of the atoms and $V(\mathbf{r},\{\mathbf{R}_l(t)\})$ is the interaction potential between the electron and the atoms. Formally, the solution of Eq. (1) can be written as,

$$\psi(\mathbf{r},t+\Delta t) = \mathbb{T} \exp\left(-\frac{i}{\hbar} \int_t^{t+\Delta t} H dt'\right) \psi(\mathbf{r},t) , \quad (2)$$

where Δt is a discrete time interval and $\mathbb{T}$ is a time-ordering operator. Using the split-operator method [5], the above equation becomes

$$\psi(\mathbf{r},t+\Delta t) = \exp\left(-i\frac{\Delta t}{2\hbar} V(\mathbf{r},\{\mathbf{R}_l(t)\})\right) \exp\left(i\Delta t \frac{\hbar^2 \nabla^2}{2m}\right) \exp\left(-i\frac{\Delta t}{2\hbar} V(\mathbf{r},\{\mathbf{R}_l(t)\})\right) \psi(\mathbf{r},t) + O[(\Delta t)^3] , \quad (3)$$

for sufficiently small Δt .

Assuming the adiabatic dynamics for classical particles, the equations of motion for classical atoms evolve from,

$$M_l \frac{d^2 \mathbf{R}_l(t)}{dt^2} = -\nabla_l U(\{\mathbf{R}_l(t)\}) - \nabla_l \int V(\mathbf{r},\{\mathbf{R}_l(t)\}) |\psi(\mathbf{r},t)|^2 d\mathbf{r} , \quad (4)$$

where M_l is the mass of the classical atom- l and $U(\{\mathbf{R}_l(t)\})$ is the interaction energy among the classical atoms.

The QMD simulations involve simultaneous solutions of Eqs. (3) and (4). To implement this algorithm, the simulation box is divided into a regular grid on which the values of the electron wave function and the potential $V(\mathbf{r},\{\mathbf{R}_l(t)\})$ evolve in time. First $\psi(\mathbf{r},t)$ is multiplied by $\exp(-i\Delta t \frac{V(\mathbf{r},\{\mathbf{R}_l(t)\})}{2\hbar})$ and the result, $\zeta(\mathbf{r})$, is operated upon by the free-particle propagator - the kinetic-energy operator. In bulk materials, the discrete fast Fourier transforms (FFT) can be used to implement this step efficiently:

$$\exp\left(i\Delta t \frac{\hbar^2 \nabla^2}{2m}\right) \zeta(\mathbf{r}) = \sum_{\mathbf{k}} \exp\left(-i\Delta t \frac{\hbar^2 \mathbf{k}^2}{2m}\right) \zeta(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) . \quad (5)$$

Multiplying the left-hand side with $\exp(-i\Delta t \frac{V(r, \{R_l(t)\})}{2\hbar})$, one obtains the wave function at time $t+\Delta t$. Repeated application of the three steps provides the time evolution of the wave function. The simplest algorithm for solving Newton equations for classical particles is [6]

$$R_l(t+\Delta t) = 2R_l(t) - R_l(t-\Delta t) + (\Delta t)^2 \frac{d^2 R_l(t)}{dt^2} + O[(\Delta t)^4]. \quad (6)$$

RESULTS AND DISCUSSION - AN EXCESS ELECTRON IN AMORPHOUS SILICON

We have investigated the localization behavior of an excess electron in a-Si using the QMD approach. In our simulations the silicon atoms interact via the Stillinger-Weber potential [7]. Luedtke and Landman [8] have shown the MD results for the static structure factor, the bond-angle distribution, and phonon density of states, based on this potential are in very good agreement with experiments on a-Si.

The excess electron-silicon atom effective potential is determined from the self-consistent electronic-structure calculations in the density functional formalism. In our calculations we use the Bachelet, Hamann, and Schlüter (BHS) [9] pseudopotential for the electron-ion interaction. The electron-electron interactions include the Hartree term and Ceperley-Alder exchange-correlation formalism [10] parameterized by Perdew and Zunger [11]. We first perform the self-consistent calculation for a system of 54 ions, described by the BHS nonlocal pseudopotential, and 216 valence electrons with ionic positions taken from a random network model of a-Si [12]. Next we introduce the excess electron and a uniform, positive background into the system. From the participation ratio, $\frac{1}{\Omega \int |\phi_i(r)|^4 dr}$, where $\phi_i(r)$ is the excess electron wave function and Ω is the volume of the MD cell, the length scale for the excess electron corresponding to the extent of localization can be obtained. The total energy difference of the two systems gives the energy scale of the excess electron.

The excess electron-silicon atom effective potential has a repulsive core due to Coulomb and Pauli exclusion effects and, in addition, it includes the polarization effects due to charge distortion of the silicon atom. The effective potential is of the form,

$$V(r) = A \exp[-(\frac{r}{r_a})^2] [1 - s(r, r_a)] - \frac{\alpha}{2r^4} s(r, r_c), \quad (7)$$

where $s(r, r_a) = [1 - \exp(-(\frac{r}{r_a})^2)]^6$ is a cutoff function with radius r_a , and the parameter α is taken to be the electronic polarizability of Si atom. The effective potential has only three parameters - r_a , r_c , and the strength (A) of the interaction. To determine these parameters, an excess electron was injected into the a-Si network. The silicon-silicon interaction is described

by the Stillinger-Weber potential and the electron-silicon interaction by the effective potential. The parameters in the effective potential are optimized so that the energy of the excess electron and its participation ratio agree with the energy difference and the participation ratio from the aforementioned electronic structure calculations.

The QMD calculations were performed on a 512 silicon-atom system. The system was first thermalized at 5000 K, for a long period of time (~ 10 picoseconds). Then the temperature of the system was reduced by 1000 K until it reached 2000 K. At each temperature the system was thermalized for at least 10 picoseconds before further cooling. The system at 2000 K was quenched to 1500, 1000, 600, and then 300 K. Again at each temperature the system was thermalized for a long time before cooling it to the next lower temperature. To simulate an excess electron in these systems, a gaussian wave packet was introduced into the a-Si system. For a fixed configuration of Si atoms, the gaussian wave packet was propagated in imaginary time until it reached the ground state. Subsequently, the electronic wave function and the positions of the silicon atoms were allowed to evolve in real-time with a time step of 1.21×10^{-17} seconds. The combined system was thermalized for at least 1 picosecond and then the QMD calculations were performed for an additional 2 picoseconds. The calculated correlation functions were found to be independent of the initial conditions.

FIGURE 1. The electron-silicon radial distribution function, $G(r)$, at 300 K.

To investigate the localization behavior of the excess electron in a-Si, we show in Fig. 1 the electron-silicon radial distribution function, $G(r)$. The radial distribution function is measured relative to the center-of-mass of the electron wave packet. Since $G(r) = 0$ up to ~ 3 Å, which indicates that the electron is localized inside a void of radius of 3 Å. In addition, we find that the void is surrounded by a ring of seven silicon atoms. In higher-temperature amorphous states at 600 and 1000 K, the electron is still trapped inside a void although the structural arrangements of silicon atoms around the electron changes with temperature.

In summary, we have applied the QMD technique to study the localization behavior of an excess electron in a-Si at finite temperatures. It is found that the excess electron is trapped inside a void of radius $\sim 3\text{\AA}$ at 300K. At higher temperatures (600 and 1000 K) the localization behavior of the electron does not change although the structural arrangements of silicon atoms change.

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