

The Liquid-Amorphous Phase Transition Study On Silicon And Water In Supercooled Region

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Abstract— The silicon and water are the useful substances and their anomalous behaviour in supercooled region propose interest to study on these. The silicon in the form of amorphous state is widely used in solar cells as a semiconductor and its liquid form, on the other hand, is metallic in nature. The amorphous silicon is melted to a liquid by heating to a high temperature and then quenched rapidly to form crystalline silicon in laser annealing process. This process can be understood by the study of phase transition between the liquid and amorphous phase of silicon. In this work, we perform free energy calculations to understand the thermodynamics of liquid-amorphous transition of silicon modeled by an empirical potential known as the Stillinger-Weber (SW) potentials. In previous studies by using SW potential it has been shown that a sharp transition between liquid and amorphous occurs at 1060 K. A significant change in the structure has also been observed during the transition leading to a local tetrahedral structure of amorphous silicon. There is a debate that whether liquid and amorphous phases coexist at 1060 K just as in a normal first-order phase transition. In this study we have shown that the transition can be explained on the basis of entropy changes with respect to temperature, without invoking the concept of a coexistence temperature. Further, we also extended this study to supercooled water using the SW potential to understand the transitions of the liquid water to low density amorphous phases near the transition temperature ~202 K. Here, we found that at or near the transition temperature the entropy changes with temperature are significant. Our results are quite consistent with the simulation studies performed earlier and also are in qualitative agreement with some of the experimental observations.

Index Terms— Phase Transition, Gibbs Free Energy, NPT-MC Simulation.

1 INTRODUCTION

The Silicon and water are the most interesting substance because of their unusual behaviour and liquid state properties in supercooled region. It has been confirmed from the earlier study that these substance shows the tetrahedral like structure. The most observed phases of these substance are liquid (or melt), crystalline and amorphous phase [7,11].

The properties of liquid silicon and water in the supercooled states has importance to understand many industrial and natural processes [1]. In molecular simulation studies, it has been observed that the liquid silicon and water upon cooling at constant pressure undergo rapid change in the physical and structural properties such as the density, the diffusivity and the coordination number. These rapid changes in the supercooled region have been characterized broadly as liquid-amorphous transitions. To understand the phase behavior of these substance, the liquid-amorphous transition in silicon and water modeled by Stillinger Weber (SW) Potential [4] has been studied [10]. On the basis of initial molecular dynamics (MD) studies on SW silicon [11] it was found that the high density liquid (HDL) phase, at a sufficiently slow cooling rate, undergoes a sudden transition to a low density amorphous phase (LDA) at around 1060 K. We employ a recently developed thermodynamic integration method [2], [3] as a primary tool which enables the precise measurement of the excess Gibbs free energy (G^e) of the HDL phase with respect to the crystalline phase. In this work we perform computations of excess Gibbs free energy (G^e) of liquid phases relative to crystalline phases to understand the phase behaviour and thermodynamics of such transitions.

2 METHODOLOGY

In this study we used Stillinger-Weber (SW) model for silicon [4] and the monatomic model (mW) for water [5]. We have computed the free energy difference between two liquid states by thermodynamic integration method. The thermodynamic integration method connects directly the liquid and the solid phases of a binary mixture by a reversible path [4]. The state along the path are simulated by performing the isothermal isobaric ensemble (NPT) and the potential energy of the system has been computed. The fundamental equation for thermodynamic integration method is defined as:-

$$\Delta G = \int_0^1 d\lambda \left\langle \frac{\partial \phi}{\partial \lambda} \right\rangle$$

Where, λ is an integration path parameter and ΔG is the Gibbs free energy difference between two states. The potential energy (ϕ) in the above equation is defined as:-

$$\phi(\lambda) = \lambda \phi_L + (1 - \lambda) \phi_S$$

Where ϕ_L and ϕ_S represents the potential energy of the liquid and solid state respectively.

The Gibbs free energy difference along the three stages of the reversible path has been computed by the thermodynamic integration

$$\Delta G_i = \int_0^1 d\lambda_i \left(\frac{\partial G_i}{\partial \lambda_i} \right) = \int_0^1 d\lambda_i \left(\frac{\partial \phi_i}{\partial \lambda_i} \right) \quad (1)$$

Where (...) represent the isothermal-isobaric ensemble average at a given value of λ_i .

3 RESULTS AND DISCUSSION

We studied the liquid-amorphous phase transition of silicon and water in supercooled region. In case of SW silicon we found that the non-equilibrium states are generated at and below 1060 K [6] in NPT-MC simulations. We also found the rapid changes in average density and average energy of equilibrium liquid phases near 1060 K. We computed the Gibbs free energy (G^e) at different temperature for silicon and water at or near the transition temperature. The variation of Gibbs free energy with respect to temperature are shown in figure 1 and figure 2 for silicon and water respectively. The slope of the curve yields the excess entropy (S^e) of HDL phase with respect to crystalline phase for both silicon and water. The excess entropy (S^e) increases as temperature decrease to 1060 K and 202 K for silicon and water respectively. Based on the slope of G^e with respect to temperature (T) we found that the absolute entropy of non-equilibrium phases at 1060 K and 202 K is higher as compared to that of equilibrium phases at higher temperatures [6]. Our result possibly indicate instabilities in the underlying entropy surface $S(E,V)$ accessed by the liquid phases near 1060 K and 202 K. Further we analyse the monatomic potential model of water. In case of mW water we found the rapid changes in the properties near 202 K at zero pressure. At 197 K, we found that the several liquid phases with different average energies are generated in NPT-MC simulations. This is also a possible indication of instabilities in the underlying surface. The energy distributions corresponding to liquid phases near 202 K (mW water) and 1060 K (SW silicon) are further points to such instabilities. Thus our work broadly indicates the reason for the rapid change in properties of liquid silicon and water in supercooled region. Such properties include specific heat capacity which is turn to indicates large entropy fluctuations.

4 FIGURES

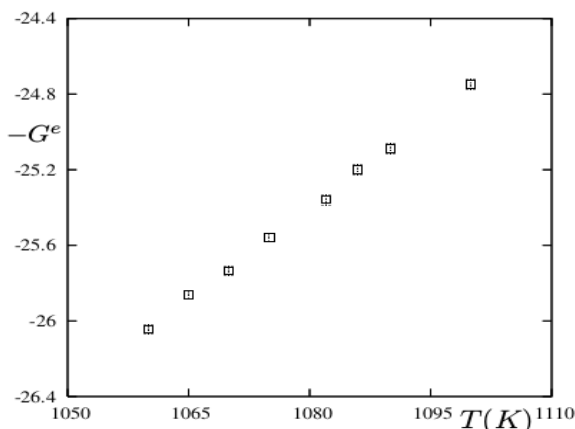


Figure 1: Variation of Gibbs free energy with respect to

temperature. The slope of the curve yields the excess entropy (S^e) of HDL phase with respect to crystalline phase. The S^e increases as temperature decrease to 1060 K.

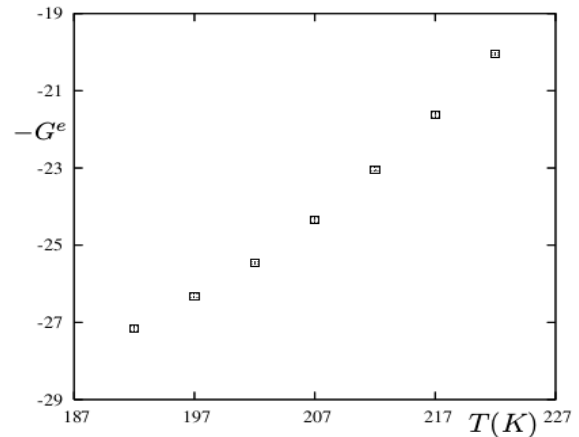


Figure 2: Variation of Gibbs free energy with respect to temperature. The slope of the curve yields the excess entropy (S^e) of HDL phase with respect to crystalline phase. The S^e increases as temperature decrease to 202 K.

5 CONCLUSION

The above observations indicate the possible presence of thermodynamic instabilities in the broad range of materials such as Germanium (Ge), Silicon (Si) and water which can be modeled by three-body potentials. The liquid-amorphous transitions in these materials does not shows the first order transition [7, 8, 9, 10], but are possibly driven by entropy changes. Further confirmation of these observation require more sophisticated models which we will be pursued in our future work.

ACKNOWLEDGMENT

I would like to acknowledge Dr. Pankaj A. Apte for his valuable suggestions and IIT Kanpur for providing the required facilities for this work.

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