Determination of Free Energy Difference between Anomaly Solid-Liquid Phase Transitions of Silicon using Pseudo-supercritical Thermodynamic Path: A Molecular Dynamics Study

Chandan K Das[*]

Department of Chemical Engineering, National Institute of Technology Rourkela
Rourkela, India-769008.
[*]Corresponding author E-mail:dasck@nitrkl.ac.in

Abstract: Silicon shows a very different trend while melting. Melting has remained a challenging subject from a long time. Especially, predicting the melting temperature of any solid substance still exists as a problem in many cases. Recently, various studies and new rules and set of parameters have simplified things, but its mechanism is yet to be studied properly and there does not exist any generalized concept regarding this. This work is an attempt to study the mechanism of free energy difference between solid-liquid. In order to understand the free energy difference, it is important to know the interaction potential governing the silicon system. Stillinger-Weber potential is a good model for Si atoms which takes into account two and three particle interactions. Heating and quenching processes is implemented on a system of Si atoms. Free energy gap connecting phases is estimated with the help reversible thermodynamic route. Supercritical path is constructed with the help of more than one reversible thermodynamic path. The best of my knowledge, this is first attempt to implement pseudo-supercritical reversible thermodynamic path for a system whose solid volume is higher than liquid volume at phase transition point.

Keywords: *Molecular Dynamics, LAMMPS, Hysteresis Loop, Pseudo-super-critical Path, Thermodynamic Integration*

1. Introduction

Phase transition is reported for many pure materials including silica and silicon. Transition point is obtained either pressure swinging or temperature swinging method. Transition temperature can also be evaluated using specific heat capacity information. Another robust technique for determination of transition point is calculation of entropy. Conventional methods like density hysteresis plot, Lindemann parameter, non-Gaussian parameter, radial distribution function, structure factor, orientation order parameter etc are employed to predict the transition point of a material.

Most of the above-mentioned methods are not accurate to predict the melting transition[1]. Estimated melting temperature is often higher compare to true melting temperature. Melting transition can be predicted more precisely using the knowledge of free energy. Transition temperature of Lennard-Jones(LJ) and sodium Chloride(NaCl) is reported from free energy information[2]. Free energy is evaluated employing thermodynamic integration. The thermodynamic route connecting solid-liquid is constructed employing reversible thermodynamic route[1,2]. Phase transformation from solid to liquid under slit[3,4] and cylindrical confinement is studied using free energy analyses[5].

In this work, I evaluate free energy gap connecting solid-liquid transitions. The best of my knowledge, this is first attempt to implement pseudo-supercritical reversible thermodynamic path for a system whose solid volume is higher than liquid volume at phase transition point. Moreover, due to very small density difference between two phases make the simulations more complicated. I present briefly the technique. (a) The liquid state is transformed into a poorly interacting liquid with the help of slowly decreasing the interatomic attractions. (b) Gaussian wells are located to the corresponding particles; simultaneously the volume is enlarged to obtain a poorly interacting oriented state. (c) Gaussian wells are removed gradually and simultaneously interatomic attractions are slowly brought back to its whole strength to obtain a crystalline state.

2. Methodology

In this work, I evaluate the free energy connecting solid-liquid state transition. The inclusive technique is described elsewhere[1]. The estimation of phase transition point from free energy analysis is combination of four stages. First step is evaluation of an approximate transition point from quenching and heating method. Free energy computation is performed with the help of pseudo-supercritical transformation path. Each step is exclusively elaborated below. Interaction potential of silicon[6] is as follows:

$$E = U_{inter}(r^N) = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk}) \qquad (1)$$

$$\varphi_2(r_{ij}) = A_{ij}\epsilon_{ij}\left[B_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right] exp\left(\frac{\sigma_{ij}}{r_{ij}-a_{ij}\sigma_{ij}}\right) \qquad (2)$$

$$\varphi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk}\epsilon_{ijk}[cos\theta_{ijk} - cos\theta_{0ijk}]^2 exp\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij}-a_{ij}\sigma_{ij}}\right) exp\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik}-a_{ik}\sigma_{ik}}\right) \qquad (3)$$

The φ_2 represents two particles interaction term. The φ_3 presents three particles attraction expression. The summation in the expression are overall neighbors J and K of atom I within a truncated length a[7]. The A, B, p, and q parameters employed for two-particles attractions. The λ and $cos\theta_0$ parameters are used only for three-particles attractions. The ϵ, σ and *a* parameters employed for both cases. γ is employed for three-particles

attraction. However, this is classified for pairs of atoms. The others extra parameters are dimensionless[7].

Table 1: Values of parameters used in SW potential(in metals unit)

A	B	P	Q	A	λ	γ	ε(eV)	σ(Å)
7.0495562	0.6022245	4	0	1.80	21.0	1.20	2.1672	2.0951

### 2.1 *Estimation of an estimated transition temperature*

To detect an approximate transition temperature, gradually heating and quenching simulations are performed for solid and liquid states, respectively[5], by employing *NPT* simulation at *P* = 1.0 bar. Afterwards, the estimated transition temperature is chosen within the metastable region at where a sudden change in the density is noticed[5].

2.2 *Computation of solid-liquid free energy gap at an estimated transition point*

The Helmholtz free energy gap connecting the solid and liquid states at an estimated transition point is estimated by forming a reversible way connecting the solid and liquid states with the help others reversible stages[5]. The free energy throughout the connecting route is evaluated using a known integration scheme:

$$\Delta A^{ex} = \int \langle \frac{dU}{d\lambda} \rangle_{NVT\lambda} \, d\lambda \tag{4}$$

while ΔA^{ex} is the gap in Helmholtz free energy. Kirkwood's coupling parameter is used by the symbol λ. Generally, λ changes in between 0 to 1. The value of $\lambda = 0$ system act as an ideal state[18]. The angled bracket is indication of ensemble average for a specific λ parameter[18]. The three stages pseudo-supercritical conversion method is represented in Fig. 1.
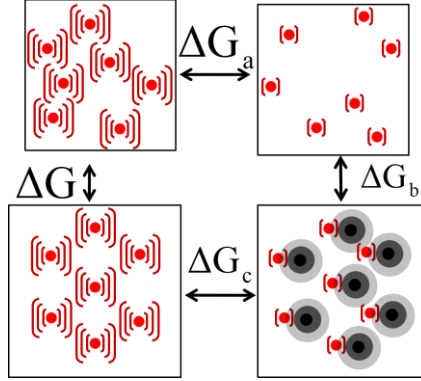
Figure : 1 presents the three stages pseudo-supercritical conversion route. (a) The liquid state is transformed into a poorly interacting liquid by slowly increasing the coupling parameter[18]. (b) Gaussian wells are located to the corresponding particles; simultaneously the volume is enlarged to obtain a poorly interacting oriented state. (c) Gaussian wells are removed gradually while coupling parameter is slowly increasing to bring back its full strength to obtain a crystalline state.

1. *Stage-a*

Initially, strongly attracted liquid state is transformed into a poorly interacting liquid using a coupling parameter λ, which controls interatomic potential[18] in the mentioned way:

$$U_a(\lambda) = [1 - \lambda(1 - \eta)]U_{inter}(r^N) \tag{5}$$

where $U_{inter}(\mathbf{r}^N)$ is the interatomic interaction energy due to location of all *N* particles[2]. The η is a scaling parameter. The value varies $0 < \eta < 1$. The first derivative of intermolecular interaction relation produces:

$$\frac{\partial U_a}{\partial \lambda} = -(1 - \eta)U_{inter}(r^N) \tag{6}$$

2. *Stage-b*

During second stage, volume of liquid state is enlarged to the volume of solid state unlike other conventional substances. Enlarge volume is clearly visible in Fig. 1. Hence, length of the simulation box (*L_x, L_y and L_z*) for a particular system dimension must be predetermined at the estimated transition point, either from the MHR results or hysteresis diagram. Liquid box dimension is 21.28163 Å(H_l) and solid phase dimension is 21.81412Å(H_s). The change in simulations' box dimension confirms that pressures remain unaltered at the start

of thermodynamic path and at the completion of stage-c, which is presented in Fig. 7. The interatomic interaction on the basis of λ in this stage is represented following way:

$$U_b(\lambda) = \eta U_{inter}[r^N(\lambda)] + \lambda U_{Gauss}[r^N(\lambda), r^N_{well}(\lambda)] \tag{7}$$

where $\mathbf{r}^N(\lambda)$ and $\mathbf{r}_{well}^{\ N}(\lambda)$ are the representation of the positions of atoms and Gaussian wells respectively[18]. U_{Gauss} presents interatomic potential because of the attraction in between the wells and corresponding particles(Eq.9). The values of parameters 'a' and 'b' are taken from Gochola's works[1]. $H(\lambda)$ denotes box dimension at any value of coupling parameter λ. Equation 8 represents change in box dimension for coupling parameter values.

$$H(\lambda) = (1 - \lambda)H_l + \lambda H_s \tag{8}$$

$$U_{Gauss}[r^N(\lambda), r^N_{well}(\lambda)] = \sum_{i=1}^{N} \sum_{k=1}^{N_{wells}} a_{ik} exp[-b_{ik}r^2_{ik}(\lambda)] \tag{9}$$

$$-\frac{\delta U_{inter}}{\delta H_{xz}} = \sum_y P^{ex}_{xy} V H^{-1}_{zy} \quad H(\lambda) = (1 - \lambda)H_l + \lambda H_s \tag{10}$$

Derived form of potential expression with respect to λ is

$$\frac{\partial U_b}{\partial \lambda} = -\sum_{x,y,z} V(\lambda)H^{-1}_{zy}(\lambda)\Delta H_{xz}\left(\eta P^{ex}_{xy} + \lambda P^{ex}_{Gauss,xy}\right) + U_{Gauss}[r^N(\lambda), r^N_{well}(\lambda)] \tag{11}$$

3. Stage-c

Stage-c is ultimate step of the pseudo-supercritical conversion method[2]. In this stage fully interacting solid configurationally phase is obtained. The interaction potential is presented of this final step in term of λ

$$U_c(\lambda) = [\eta + (1 - \eta)\lambda]U_{inter}(r^N) + (1 - \lambda)U_{Gauss}[r^N(\lambda), r^N_{well}(\lambda)] \tag{12}$$

And the derivative term can be rewritten:

$$\frac{\partial U_c}{\partial \lambda} = (1 - \eta)U_{inter}(r^N) + U_{Gauss}[r^N(\lambda), r^N_{well}(\lambda)] \tag{13}$$

3. Simulation Details

3.1 Atomic Potential Used

Stillinger-Weber Potential is a good model for Si. It considers both two-particle and three-particle interactions. The values of following parameters in metal units have been used. The potential of the silicon is provided in Eq. 1, 2 and 3. Parameters values are listed in Table. 1.

3.2 Simulation Details and Potential Model

The NPT MD simulations are conducted with the help of LAMMPS[7]. Integration time step (Δt) is 5fs for all type of simulations. The temperature is monitored using a Nose´–Hoover thermostat. The pressure is monitored using Nose´–Hoover barostat. The time relaxation is of 100ps. The pressure relaxation is of 500ps. Number of particles are simulated around 512. Cooling process is carried out gradually after each 5000,000 MD time steps. Change of temperature T is 25K for each NPT simulation. Temperature is dropped from 3000K to 500K with a decrement of 25K. Heating is also conducted same way as the quenching. Temperature range of heating is from 500K to 3000K. The Gibbs energy gap for connecting states is estimated at transition temperature using pseudo-super-critical path. For the reversible path evaluation (for the three steps of pseudo-supercritical path)as shown in figure 1, simulations are carried with *NVT* ensemble. The value of Gaussian parameters are selected in accordance with Grochola[1].

Simulations of Stage-a of the reversible thermodynamic path are initialized from a random initial co-ordinates of the particles. Total run time for each coupling parameter value is 20 ns[4]. During the stage-b of three stages, final co-ordinates of step-1 are the starting point. But, to achieve the Gaussian potential wells another 512 atoms are situated on its corresponding lattice point[2,8].

4. Results and Discussions

In this portion I try to describe output results of various parameters like density, potential energy and free energy with the change in temperature and coupling parameter(λ).

4.1 Density

In this part we describe the nature of density of the Si system as we perform heating and quenching. Quenching and heating path are not reversible, for this reason hysteresis loop is formed. That indicates first order phase transition. Density of silicon for different temperature is shown in figure 2. The plot clearly forms a hysteresis. This is an indication of first order phase change. Density plot shows anomaly behavior towards the phase transition. Metastable region is observed in middle portion of the hysteresis curve. True melting temperature lies in this loop.

4.2 Free energy

Helmholtz free energy difference between liquid-and solid phase is determined using pseudo-supercritical

path by constructing reversible thermodynamic paths[1]. Thermodynamics integration is performed using Gauss-quadrature integration scheme. At the beginning of the reversible path the interaction potential is changing according to Eq. 5. Integration is carried out using 10, 15 and 20 points. No significance difference is observed due to different data points. Derivative of interaction potential energy with respect to λ presents in Fig. 6 below. For the λ values they coincide as shown in figure 6. Figure 8 and 9 represent for stage-b and stage-c respectively. Figures for all the stages are smooth and reversible, so we can easily integrate it. The free energy difference connecting solid-liquid is around -59024.2454±10eV. Results are reported in Table 4 below.
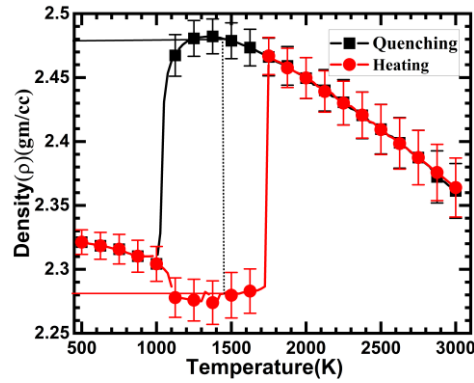

Figure 2: figure represents density vs. temperature plot. I skipped some intermediate points for better clarity. Filled square black in color presents for quenching the system whereas filled circle for heating the system. Quenching and heating curves do not follow the same path which indicates first order transition. Vertical dotted line indicates an estimated estimate transition point(T_{em})(1450 °K). Horizontal black line and red line indicate corresponding liquid density(2.477) and solid density(2.850) respectively to determine liquid phase and solid phase box dimension.
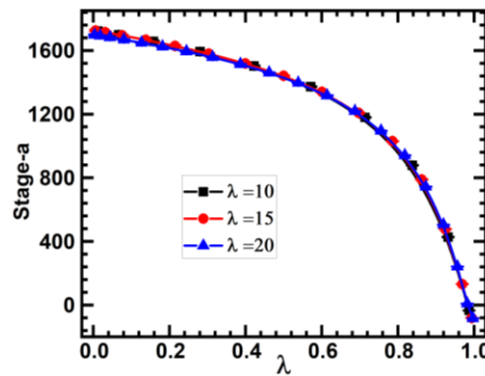

Figure: 6 $\langle \partial U / \partial \lambda \rangle_{NVT\lambda}$ *as a variable of λ for three λ types values(10,15 and 20) of Stage-a for pseudo supercritical path . Thermodynamic path is smooth and reversible, hence integrable. Error is so small it submerges with symbol. There is no significant difference among them for stage-a of pseudo-supercritical transformation path*
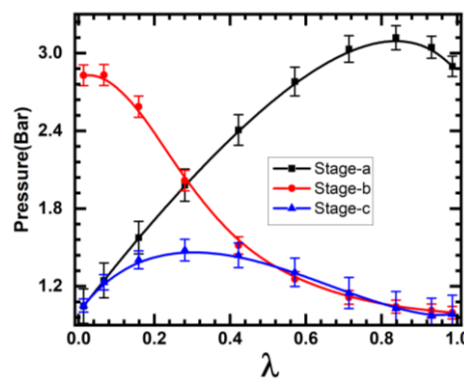

Figure : 7 Pressure at the start of stage-a and at the end of stage-c is constant. This is essential and the sufficient criteria for construction of the thermodynamic reversible paths..
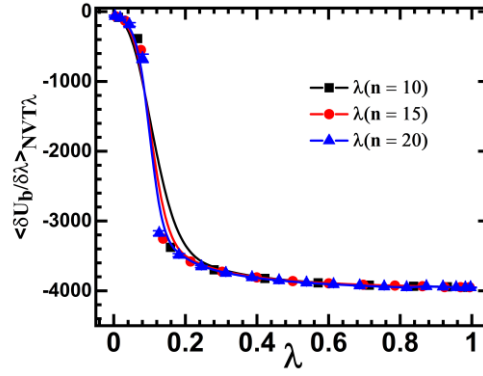
Figure : 8 $\langle \partial U / \partial \lambda \rangle_{NVT\lambda}$ as a variable of λ for ten λ of Stage-b values. Thermodynamic path is smooth and reversible, hence integrable. Error is so small it submerges with symbol.
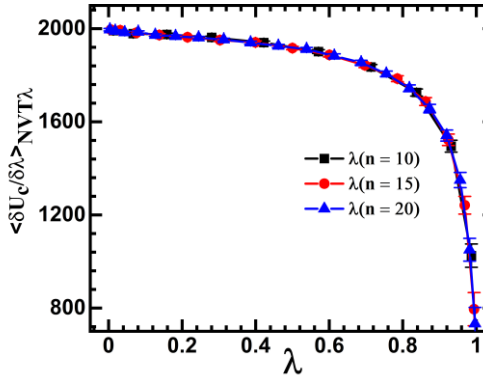

Figure : *9 $\langle \partial U / \partial \lambda \rangle_{NVT\lambda}$ as a variable of λ for three λ values for stage-c. Thermodynamic path is smooth and reversible, hence integrable.*

Table: 4. Separation of the subscriptions to the gap in Gibbs free energy connecting the two states T= 1450 °K .The pressure is maintained at P= 1 bar for the silicon(Stillinger-Weber Potential).

Free Energy Terms(eV)	
$A_s^{*ex} - A_l^{*ex}$	307±10
$A_s^{*\iota u} - A_l^{*\iota u}$	-60073
$P^* \Delta V^*$	741.7546
$G_s^* - G_l^*$	-59024.2454±10

5. Conclusion

Various methods have been employed   and we have been   successful in observing   the phase transition of silicon, depending on various   parameters.

Also, keeping in mind the traditional meaning of solid to liquid phase transition, the jump in potential energy is also used to indicate the melting stage of any substance. This jump is seen at 1700-1800 K for decreasing temperature   and 2400-2500 K for increasing temperature. Anomaly behavior is observed in density for silicon system, which make more complicated to implement pseudo-supercritical thermodynamic path.

Estimation of the Gibbs free energy is performed with the help of pseudo-supercritical reversible thermodynamic cycle. The construction of supercritical path is combination of three stages. For each step of thermodynamics integration is applied using 10, 15 and 20 points. The thermodynamics integration is insignificance with respect to number of data points. Accuracy of determined melting temperature from free energy analysis is better comparing any other methods. This is a very clear indication   of how the break-down of lattice occurs on heating a substance.

6. References

1. Grochola, G., *Constrained fluid λ-integration: Constructing a reversible thermodynamic path between the solid and liquid state.* J. Chem. Phys., 2004. **120**: p. 2122.
2. Eike, D.M., J.F. Brennecke, and E.J. Maginn, *Toward a robust and general molecular simulation method for computing solid-liquid coexistence.* J. Chem. Phys., 2005. **122**: p. 014115.

3. Das, C.K. and J.K. Singh, *Effect of confinement on the solid-liquid coexistence of Lennard-Jones Fluid.* J. Chem. Phys., 2013. **139**(17): p. 174706.
4. Das, C.K. and J.K. Singh, *Oscillatory Melting Temperature of Stockmayer Fluid in Slit Pores.* J. Phys. Chem. C., 2014. **118**(36): p. 20848−20857.
5. Das, C.K. and J.K. Singh, *Melting transition of Lennard-Jones fluid in cylindrical pores.* J. Chem. Phys., 2014. **140**(20): p. 204703-1 - 204703-9.
6. Stillinger, F.H. and T.A. Weber, *Computer simulation of local order in condensed phases of silicon.* Phys. Rev. B, 1985. **31**(8): p. 5262-5271.
7. J, P.S., *Fast Parallel Algorithms for Short–Range Molecular Dynamics.* J. Comp. Phys., 1995. **117**: p. 1-9.
8. Das, C.K. and J.K. Singh, *Melting transition of confined Lennard-Jones solids in slit pores.* Theor Chem Acc, 2013. **132**: p. 1351.