

Anomaly melting transition of Silicon using Free Energy Analysis from Pseudo-supercritical Thermodynamic Path: A Molecular Dynamics Study

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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 still does not exist any generalized concept regarding this. Also, there are certain anomalies in silicon, which makes its melting and phase transition mechanism more difficult to understand and predict. In order to understand the phenomenon, 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. Melting of Silicon atoms is studied using Molecular Dynamics Simulation with the help of LAMMPS software. The only extensive property that remains constant during phase transformation is the Gibbs free energy. Using this beautiful property one can estimate true thermodynamics melting temperature. Estimation of Gibbs free energy is performed with the help of pseudo-supercritical reversible thermodynamic cycle along the help of multiple histogram reweighting diagrams. Heating and quenching processes is implemented on a system of Si atoms. An estimated melting temperature is determined from density hysteresis plot. The pseudo-supercritical reversible thermodynamic cycle is conducted at estimated temperature to determine free energy difference between solid-liquid phases. Supercritical path is constructed with the help of more than one reversible thermodynamic path. The sufficient and necessary condition is that there should not be presence of any first order phase transition and pressure remains unaltered at the beginning and at the end of the path. It is consisting of three steps, for each I performed NVT simulation varying coupling parameter. The value of coupling parameter varies from zero to one. The potential energy and density appear to be steady, indicating pre-melting. Melting temperature can be predicted using Gibbs free energy. Gibbs free energy calculation involve with thermodynamics integration and multiple histogram reweighting(MHR) method.

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

1. Introduction

Silicon is the very important element for the advancement of technology, due to widely used of silicon and its products in various fields of engineering and technology. Silicon is widely used as semiconductor. Exact mechanism of phase transformation of silicon becomes a challenging problem and remains unanswered[1-5].

Phase transition is reported for many pure materials including silica and silicon[6-8]. Transition point is obtained either pressure swinging or temperature swinging method[8-10]. Transition temperature can also be evaluated using specific heat capacity information[11, 12]. Another robust technique for determination of transition point is calculation of entropy[13, 14]. Conventional methods like density hysteresis plot, Lindemann parameter[5], non-Gaussian parameter[15], radial distribution function, structure factor, orientation order parameter etc are employed to predict the transition point of a material.

Solid to liquid transformation of Lennard-Jones(LJ) system under confinement is reported[16]. Transition point is determined on the basis of density hysteresis plot, Lindemann parameter, non-Gaussian parameter, radial distribution function, structure factor, orientation order parameter[16]. For determination of melting transition, Change in first and second coordination number is important too[15].

Most of the above-mentioned methods are not accurate to predict the melting transition[17]. Transition temperature of Lennard-Jones(LJ) and sodium Chloride(NaCl) is reported from free energy information[18]. Free energy is evaluated with the help of thermodynamic integration. The supercritical path is constructed using pseudo-supercritical path[17, 18]. Phase transformation from solid to liquid under slit[19, 20] and cylindrical confinement is studied using free energy analyses[21].

Melting in solids has been a difficult problem that has yet to be solved,[17] and predicting melting temperature is difficult. The phenomenon has been thoroughly investigated through studies of surfaces, lattice vibrations, missing atoms, grain boundaries, defects and[17] structure catastrophes[17] particularly those of Tallon and Cahn.

2. Methodology

In this work, I evaluate free energy difference between two phases during transitions. The inclusive technique is described elsewhere [17]. 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. Second is estimation of equation of state for the solid phase with respect solid reference state. Similarly for liquid phase is also

determined with respect to liquid reference state. Equation of states are generated using multiple histogram reweighting technique[21]. Third stage is the estimation of difference in free energy between solid-liquid at an estimated transition point[21]. Free energy computation is performed with the help of pseudo-supercritical transformation path. Then ultimately with the help of second and third steps evaluation of the transition point is done at zero energy difference[21]. That point is considered as true thermodynamic transition point.

2.1 Estimation of an estimated transition temperature

To detect an approximate transition temperature, gradually heat and quench simulations are performed. Quenching is performed from 3000K to 500K while heating is carried out from 500K to 3000K [21], 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[21].

2.2 Solid and liquid equation of state

The next stage is the formation of the Gibbs free energy. Gibbs free energy is expressed as a function of temperature for both phases with respect to their respective reference state temperature. This is performed over a small region around the estimated transition point at the constant pressure[21]. Using the free energy difference at the estimated transition point the pure phase relative equation of state curves can be altered to the solid-liquid free energy difference. This difference is expressed as a function of temperature. That curve is used to determine the true thermodynamic transition temperature. True thermodynamic transition point is point the free energy difference phases is zero[21]. This is carried out using multiple histogram reweighting(MHR) technique.

2.3 Computation of solid-liquid free energy difference at the estimated transition point

The Helmholtz free energy difference phases at an estimated transition point are estimated by constructing a reversible thermodynamic path. The path constructed between the solid and liquid phases. The thermodynamic reversible path is consisting of one or more reversible stages[21]. The free energy using pseudo-supercritical path is evaluated using renowned thermodynamic integration method:

$$\Delta A^{ex} = \int \left\langle \frac{dU}{d\lambda} \right\rangle_{NVT\lambda} d\lambda \quad (1)$$

where ΔA^{ex} is the difference in excess Helmholtz free energy, λ is the Kirkwood's coupling parameter. Generally, λ varies from zero up 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. Very short explanation of the stages is presented below with schematic diagram.

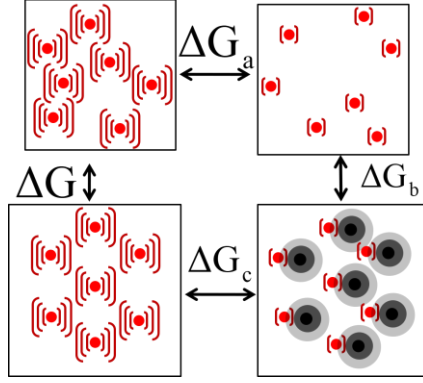


Figure : 1 The schematic presentation of the three stages pseudo-supercritical conversion path. (a) The liquid phase is transformed into a poorly interacting fluid by slowly decreasing the intermolecular interactions[18]. (b) Gaussian potential wells are located to the corresponding particles simultaneously the volume is enlarged to obtain a poorly interacting oriented state. (c) Gaussian wells are removed gradually while simultaneously intermolecular interactions are slowly brought back to its full strength to obtain a crystalline state.

1. Stage-a

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

$$U_a(\lambda) = [1 - \lambda(1 - \eta)]U_{inter}(r^N) \quad (2)$$

where $U_{inter}(\mathbf{r}^N)$ is the interatomic interaction energy due to location of all N particles[18]. The η is a scaling parameter. The value varies $0 < \eta < 1$. The first derivative of intermolecular relation produces:

$$\frac{\partial U_a}{\partial \lambda} = -(1-\eta)U_{inter}(r^N) \quad (3)$$

2. Stage-b

During second stage, liquid state volume is enlarged into solid state volume unlike other conventional substances. This stage is most complicated among the three stages. Hence, length of the simulation box (L_x , L_y and L_z) for a particular system dimension should be predetermined at the estimated transition point. That can be done from the MHR results or hysteresis diagram[18]. Liquid box dimension(H_l) is 21.28163 Å and solid phase dimension(H_s) is 21.81412Å. Greater solid phase dimension compare to liquid state dimension make the simulation more complicated. The changes in simulation dimension confirm that the liquid and solid state pressures remain unaltered during the thermodynamic path and at the end of stage-c, which is presented in Fig. 6. The potential energy on the basis of λ in this stage is represented following way:

$$U_b(\lambda) = \eta U_{inter}[r^N(\lambda)] + \lambda U_{Gauss}[r^N(\lambda), r_{well}^N(\lambda)] \quad (4)$$

where $\mathbf{r}^N(\lambda)$ and $\mathbf{r}_{well}^N(\lambda)$ are the representation of the positions of atoms and Gaussian wells respectively[18]. These coordinates are purely function of *coupling parameter* due to the change in simulation dimension. U_{Gauss} presents interatomic energy due to the attraction between the potential wells and corresponding particles. The relationship of Cartesian position of dimension, follow the same manner as did in literature[18].

$$H(\lambda) = (1 - \lambda)H_l + \lambda H_s \quad (5)$$

$$U_{Gauss}[r^N(\lambda), r_{well}^N(\lambda)] = \sum_{i=1}^N \sum_{k=1}^{N_{wells}} a_{ik} \exp[-b_{ik} r_{ik}^2(\lambda)] \quad (6)$$

$$-\frac{\delta U_{inter}}{\delta H_{xz}} = \sum_y P_{xy}^{ex} V H_{zy}^{-1} \quad (7)$$

3. Stage-c

Stage-c is last step of the pseudo-supercritical conversion method[18]. In this stage fully interacting solid configurationally phase is obtained. The interaction potential is presented of this final step in term of λ

$$U_c(\lambda) = [\eta + (1 - \eta)\lambda]U_{inter}(r^N) + (1 - \lambda)U_{Gauss}[r^N(\lambda), r_{well}^N(\lambda)] \quad (8)$$

And the derivative term can be written:

$$\frac{\partial U_c}{\partial \lambda} = (1 - \eta)U_{inter}(r^N) - U_{Gauss}(r^N, r_{well}^N) \quad (9)$$

2.4 Determination of transition point where ΔG is zero

The free energy ΔA^{ex} , between phases at the estimated transition point is evaluated by thermodynamic integration[18]. It is essential to transfer the Helmholtz free energy into the Gibbs free energy. It is obtained using the formulae given, $\Delta G = \Delta A^{ex} + \Delta A^{id} + P\Delta V$. The expression ΔA^{ex} is computed using reversible transformation path method. The second term ΔA^{id} is the contribution from ideality. Final term in the expression is work term due to change in volume from solid to liquid phase. Additionally, the histogram reweighting method produces two free energy curves. For the liquid phase, $[(\beta G)_{T_{1,l}} - (\beta G)_{T_{i,l}}]$ is known and for the solid phase $[(\beta G)_{T_{1,s}} - (\beta G)_{T_{i,s}}]$ [18], is known, where the term $(\beta G)_{T_{m,n}}$ signifies (βG) for the meta-stable phase n at the state point T_{em} [21]. Provided that T_{em} , an estimated transition temperature, is the state point where the thermodynamic integration[21] is performed[18], achieved the following:

$$[(\beta G)_{T_{1,l}} - (\beta G)_{T_{em,s}}] + [\beta(G_{T_{em,s}} - G_{T_{em,l}})] - [(\beta G)_{T_{i,l}} - (\beta G)_{T_{em,l}}] = [(\beta G)_{T_{1,s}} - (\beta G)_{T_{i,l}}] \quad (10)$$

Eq. 10 further can be rearranged as:

$$[(\beta G)_{T_{1,l}} - (\beta G)_{T_{em,s}}] + [\beta(G_{T_{em,s}} - G_{T_{em,l}})] + [(\beta G)_{T_{1,l}} - (\beta G)_{T_{i,l}}] - [(\beta G)_{T_{1,l}} - (\beta G)_{T_{em,l}}] = [(\beta G)_{T_{1,s}} - (\beta G)_{T_{i,l}}] \quad (11)$$

Where, all the terms except second term on the left side of Eq.11 is achieved using the multiple histograms reweighting technique. The second term is determined using three stages reversible thermodynamic path using thermodynamic integration.

3. Simulation Details and Software Work

3.1 Simulation Details and Potential Model

The NPT MD simulations are conducted with the help of LAMMPS[22]. Unit system of the simulation process is metal. The velocity-Verlet algorithm is deployed to integrate newton's 2nd law of motion. Integration time step (Δt) is 5fs. The temperature is monitored using a Nose'-Hoover thermostat. The pressure is monitored using Nose'-Hoover barostat. The time relaxation is of 100ps. Pressure relaxation is of 500ps. Number of particles are simulated around 512. The periodic boundary condition is applied in all three directions of the simulation box. During quenching, the initial liquid configurations are taken as ideal diamond structures at 3000k. 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. At the time of heating process, the last configuration of the quenching

simulation is initial co-ordinate of the heating system. Heating is also conducted same way as the quenching. The increment of temperature T is 25K for each NPT simulation. Process of heat supply is done until the solid has completely converted into liquid. Temperature range of heating is from 500k to 3000k until completely lost its crystallinity. The density is determined at every interval. Interaction potential of silicon is as follows:

$$E = U_{inter}(r^N) = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk}) \quad (12)$$

$$\varphi_2(r_{ij}) = A_{ij} \epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \quad (13)$$

$$\varphi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \exp \left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right) \quad (14)$$

Where φ_2 is two body interaction term whereas φ_3 is three body interaction term. The addition in the equations are through neighbors J and K of atom I in the range of truncation length a [22]. The A, B, p, and q parameters are used only for two-body interactions. The λ and $\cos \theta_0$ parameters are used only for three-body interactions. The ϵ , σ and a parameters are used for both two-body and three-body interactions. γ is used only in the three-body interactions, but is defined for pairs of atoms. The non-annotated parameters are unitless[22].

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

The Gibbs free energy difference between phases is determined at a single state point as per the methodology described in three stages. The true Thermodynamic transition point is estimated where Gibbs free energy difference of two phases reach zero. First, we select an estimated transition point, T_{em} . The two different types of *NPT* simulations are carried out using LAMMPS[22]. The velocity-verlet algorithm is employed throughout the process. Integration time step is $\Delta t = 5$ fs. The temperature is monitored using a Nose'-Hoover thermostat. The pressure is monitored using Nose'-Hoover barostat. The time relaxation is of 100ps whereas; pressure relaxation is of 500ps. The periodic boundary condition is applied in all the three dimensions. The constructions of equations of states for both phases are done employing multiple histogram reweighting diagrams. Histograms are generated from *NPT* simulations based on volume and potential energy of the system. Total 41 simulations are carried out for individual phase. The temperature is selected in accordance with eq.15.

$$T_i = T_{em} + \sum_{n=-20}^{20} n \Delta T \quad (15)$$

Where T_{em} is the expected transition point computed from the density vs. temperature plot hysteresis data; $\Delta T (= 10 \text{ }^\circ\text{K})$ is determined based on size of the with meta-stable region.

The initial configurations for both phases are used from previous simulation run. Sufficient equilibration, run around 200 ps, simulations is performed duration for 10ns. The standard reference temperatures are chosen at the minimum point, $T_i = T_{em} - 20 \Delta T$. Histograms are generated on the basis of potential energy and volume of system.

For the thermodynamic integration evaluation (during the three steps of pseudo-supercritical path) as shown in Fig. 1, simulations are carried employing *NVT ensemble* molecular dynamics with Nose'-Hoover thermostat algorithm. The value of Gaussian parameters are selected from Grochola[17]. The scaling parameter is constant at $\eta = 0.1$ [18]. The reversible thermodynamic path are initiated using a random initial co-ordinates system (i.e., $\lambda = 0$). These co-ordinates are

achieved during heating quenching simulations. After that for each λ initialization is done from its previous λ simulation[18]. Time step is fixed at 5 fs for all simulations. Total run time for each λ is 20 ns[21]. For the second stage, the last configuration of the stage-a is used. However, to achieve ultimate configuration another 512 atoms are situated on its corresponding lattice point[18]. The Gaussian potential wells are located to its corresponding lattice point[18]. The initial configuration for the third stage is taken from the heating run of hysteresis loop at T_{em} and the dummy atoms are created as described for the second stage. The way it is performed the pressure of the system remains constant before and after of the transformation path as in Fig. 4. Thermodynamic integration is performed employing the conventional ten, fifteen and twenty points Gauss-Legendre integration techniques[18]. Same technique is applied for all the stages[18].

4. Results and Discussions

In this section I shall discuss the output results of various parameters like density, potential energy, and Gibbs free energy difference between two phases.

4.1 Density

In this part I describe the nature of density of the Si system as for heating and quenching. Sharp density changed is observed for both the heating and quenching cases. That indicates first order phase transition. Hysteresis loop is rudimentary for first order phase transition. Density of silicon for different temperature is shown in Fig. 2. Potential energy also shows the similar kind of behavior. Metastable region is observed in middle portion of the hysteresis curve. Density shows an exceptional behavior at transition point compare to conventional substances. An estimated melting temperature is around 1600K. True melting temperature lies in this loop or adjacent to this meta-stable zone. The following data represents the variation of density with temperature around melting point temperature:

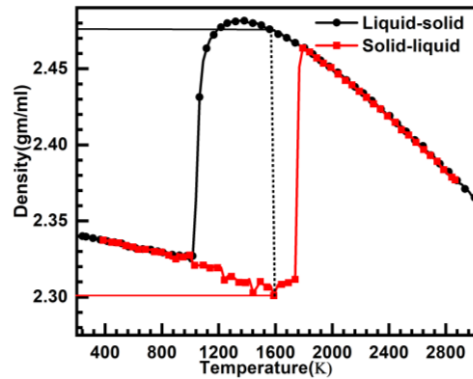


Figure 2: figure represents density as a function of temperature. Filled circle black in color for quenching the system whereas filled square for heating the system. Quenching and heating curves do not follow the same path which indicates first order transition. Hysteresis loop is clearly observed in density temperature plot. Metastable region is noticed middle of the curve and true transition point lies in this meta-stable region. Vertical dotted line indicates an estimated estimate transition point(T_{em}). Horizontal black line and red line indicate corresponding liquid density(2.477) and solid density(2.30) respectively. From where one can determine liquid phase as well as solid phase box dimension

4.2 Free energy

Helmholtz free energy difference between phases determine employing pseudo-supercritical path by constructing reversible thermodynamic paths [17]. NVT simulations are carried out at estimated melting temperature 1600K. Thermodynamics integration is performed using Gauss-quadrature integration scheme. Integration is carried out using 10, 15 and 20 points. No significance difference is observed due to difference in data points. Derivative of interaction potential energy with respect to λ presents in figure below. For the λ values they coincide as shown in Fig. 3. Fig. 5 and 6 represent stage-b and stage-c respectively.

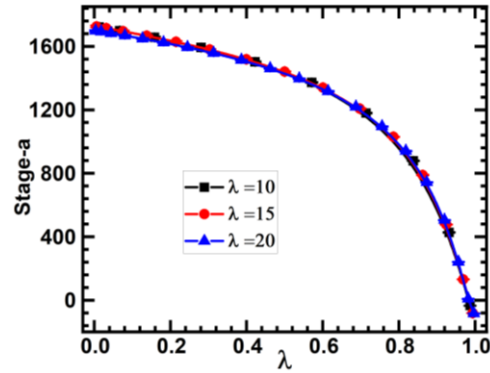


Figure: 3 $\langle \partial U_a / \partial \lambda \rangle_{NVT\lambda}$ as a function of λ for three λ values (10, 15 and 20) of Stage-a for pseudo supercritical path. Thermodynamic path is smooth and reversible, hence integrable. Errors are so small, it submerges with symbol. There is no significant difference among them for stage-a of pseudo-supercritical transformation path

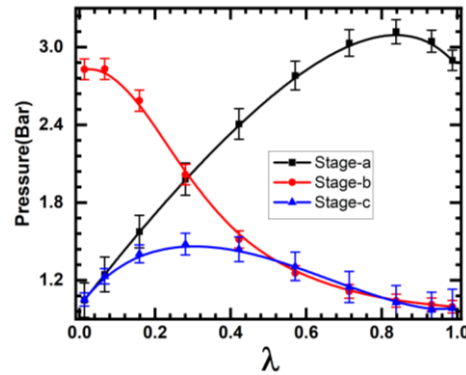


Figure : 4 Pressure at the start of stage-a and at the end of stage-c is constant. This is essential and the sufficient criteria for construction of the thermodynamic reversible paths..

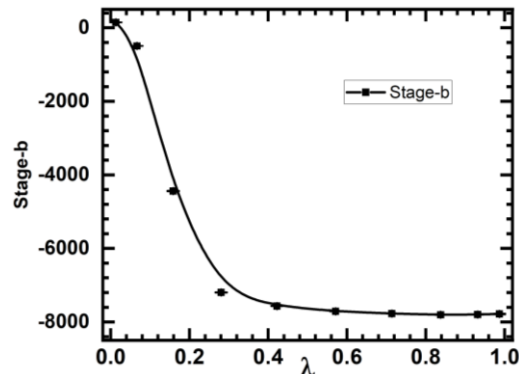


Figure :5 $\langle \partial U_b / \partial \lambda \rangle_{NVT\lambda}$ as a function of λ for ten λ of Stage-b values. Thermodynamic path is smooth and reversible, hence integrable. Error is so small it submerges with symbol.

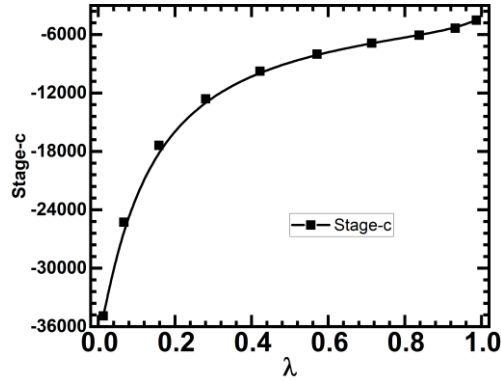


Figure :6 $\langle \partial U_c / \partial \lambda \rangle_{NVT\lambda}$ as a function of λ for three λ values for stage-c. Thermodynamic path is smooth and reversible, hence integrable.

Figure for all the stages are smooth and reversible, so we can easily integrate it. Results are reported in table 2 below. Using this free energy difference along with equation of state which is obtained from multiple histogram reweighting(MHR) method. The Gibbs free energy difference between two phases are converted into single reference state and presented in figure 10. True thermodynamic melting temperature is the point where ΔG is zero. From Fig. 7 it is clear that true thermodynamic transition point is around 1684°K.

Table: 2. Separation of the subscriptions to the Gibbs free energy difference between the two states $T= 1600^\circ\text{K}$ and $P= 1 \text{ Bar}$ for the silicon system(Stillinger-Weber Potential).

Free Energy Terms(eV)	
$A_s^{*ex} - A_l^{*ex}$	16600±100
$A_s^{*uu} - A_l^{*uu}$	-60073
$P^* \Delta V^*$	741.7546
$G_s^* - G_l^*$	-42731.2000±100

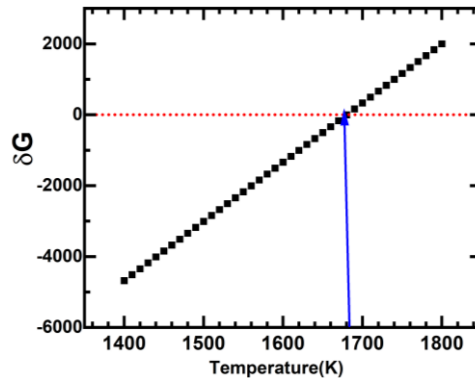


Figure : 7 ΔG as a function of T . Vertical arrow line blue in colour indicates solid-liquid transition point temperature or true thermodynamic transition temperature (T_m) of solid where Gibbs free energy difference, ΔG , between solid and liquid is zero.

5. Conclusion

Various methods have been employed and I have been successful in observing the phase transition of silicon, depending on various parameters. The density of silicon is known to be

2.32 g/cc. While simulating with decreasing temperature, this is the value was noted for density after the melting occurred at approximately at 1687 K.

Anomaly behavior is observed in density for silicon system, which make more complicated to implement pseudo-supercritical thermodynamic path.

Phase transition point is determined based on Gibbs free energy calculation. The construction of supercritical path is combination of three stages. For each step, thermodynamics integration is applied using 10, 15 and 20 points. The thermodynamics integration is insignificance with respect to number of data point, which is shown for stage-a. Estimated true thermodynamics melting temperature is around $1684^{\circ}\text{K} \pm 2^{\circ}\text{k}$, which is in good precision with experimental results. 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.

I have been successful in implemented pseudo-supercritical path to evaluate free energy difference between solid for complicated interaction potential model. Though, simulations are performed with a smaller number of particles. Simulations with large number of particles are important to observe the system size effect. In future I shall check the system size effect by varying number of simulated particles. One can apply this approach for other system both in bulk or confinement in future.

6. References

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