

From Atoms to Materials: Predictive Theory and Simulations

Week 5 – Homework solution 3

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Charge equilibration

Q.1.1

- Di-atomic molecule

$$E(\{q_i\}) = \underbrace{\sum_{i < j} \frac{q_i q_j}{R}}_{\text{Coulomb.}} + \sum_i \underbrace{\left(\chi_i q_i + \frac{1}{2} H_i q_i^2 \right)}_{\text{EA / IP}} \checkmark$$

Charge equilibration

Q.1.1

- Di-atomic molecule

$$E(\{q_i\}) = \sum_{i < j} \frac{q_i q_j}{R} + \sum_i \left(\underbrace{\chi_i q_i}_{\text{EA}} + \underbrace{\frac{1}{2} H_i q_i^2}_{\text{IP}} \right)$$

Coulombic interaction

Total electrostatic: EA and IP

$$E(\{q_i\}) = 14.4 \frac{q_\alpha q_\beta}{R} + \underbrace{\chi_\alpha q_\alpha + \chi_\beta q_\beta}_{\text{EA}} + \underbrace{\frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\beta^2}_{\text{IP}}$$

- Di-atomic molecule

$$E(\{q_i\}) = 14.4 \frac{q_\alpha q_\beta}{R} + \chi_\alpha q_\alpha + \chi_\beta q_\beta + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\beta^2$$

- Chemical potential

$$\mu = \frac{\partial E}{\partial q_\alpha}$$

- Di-atomic molecule

$$E(\{q_i\}) = 14.4 \frac{q_\alpha q_\beta}{R} + \chi_\alpha q_\alpha + \chi_\beta q_\beta + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\beta^2$$

- Chemical potential

$$\mu = \frac{\partial E(\{q_i\})}{\partial q_\alpha}$$

$$\rightarrow \mu = 14.4 \frac{q_\beta}{R} + \chi_\alpha + H_\alpha q_\alpha$$

- Di-atomic molecule

$$E(\{q_i\}) = 14.4 \frac{q_\alpha q_\beta}{R} + \chi_\alpha q_\alpha + \chi_\beta q_\beta + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\beta^2$$

- Neutral total charge $q_\alpha = -q_\beta$ ✓

- Di-atomic molecule

$$E(\{q_i\}) = 14.4 \frac{q_\alpha q_\beta}{R} + \chi_\alpha q_\alpha + \chi_\beta q_\beta + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\beta^2$$

- Neutral total charge $q_\alpha = -q_\beta$

$$E(\{q_i\}) = -14.4 \frac{q_\alpha^2}{R} + \chi_\alpha q_\alpha - \chi_\beta q_\alpha + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\alpha^2$$

$$\frac{\partial E}{\partial q_\alpha} = 0$$

- Di-atomic molecule

$$E(\{q_i\}) = 14.4 \frac{q_\alpha q_\beta}{R} + \chi_\alpha q_\alpha + \chi_\beta q_\beta + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\beta^2$$

- Neutral total charge $q_\alpha = -q_\beta$

$$E(\{q_i\}) = -14.4 \frac{q_\alpha^2}{R} + \chi_\alpha q_\alpha - \chi_\beta q_\alpha + \frac{1}{2} H_\alpha q_\alpha^2 + \frac{1}{2} H_\beta q_\alpha^2$$

$$\frac{\partial E(\{q_i\})}{\partial q_\alpha} = 0 \Leftrightarrow q_\alpha = \frac{\chi_\beta - \chi_\alpha}{H_\alpha + H_\beta - 2 \frac{14.4}{R}}$$

Charge equilibration

Q.1.4

- Di-atomic molecule NaCl ✓

$$q_{Na} = \frac{\chi_{Cl} - \chi_{Na}}{H_{Na} + H_{Cl} - 2\frac{14.4}{R}}$$

$$q_{Na} = 0.92e$$

Thermal conductivity

Q.2.1

- MD simulation

$$\tau = 0.002 \times 120,000 = 240 \text{ ps}$$

1 Input → **2 Simulate**

Input Model | Energy Expression | Driver Specification

Thermalization run before thermal conductivity calculation?: ☒ **yes**
Temperature equilibration run before thermal conductivity calculation?: ☐ **no**

Thermalization Run

Ensemble: NVT
Temperature: 300K
Pressure: 0atm
Number of MD steps: 1000

Temperature Equilibration Run

Ensemble: NVT
Temperature: 300K
Pressure: 0atm
Number of Loops: 5
Number of MD Steps in Each Loop: 5000

Thermal Conductivity Calculation

Ensemble: NVT
Temperature: 300K
Pressure: 0atm
MD Time Step: 0.002ps
Number of MD Steps: 120000
Swapping Frequency (Steps): 100

Periodic Tasks

Write to Trajectory (Steps): 20000
Write to Temperature File (Steps): 10000

Data Analysis

Start Averaging Time (Steps): 20000

Thermal conductivity

Q.2.2

- MD simulation

1 Input → 2 Simulate

Input Model | Energy Expression | Driver Specification

Create your own structure?: ☒ yes

Superlattice Structure

Number of Unit Cells in One Bin: 1

Number of Unit Cells along x: 5

Number of Unit Cells along y: 5

Periodic Units

Lattice Parameter (Angstroms): 5.43

Material 1: Si

Number of Bins along z: 10

Material 2: Ge

Number of Bins along z: 0

Heatbaths: Si

Number of Bins along z: 3

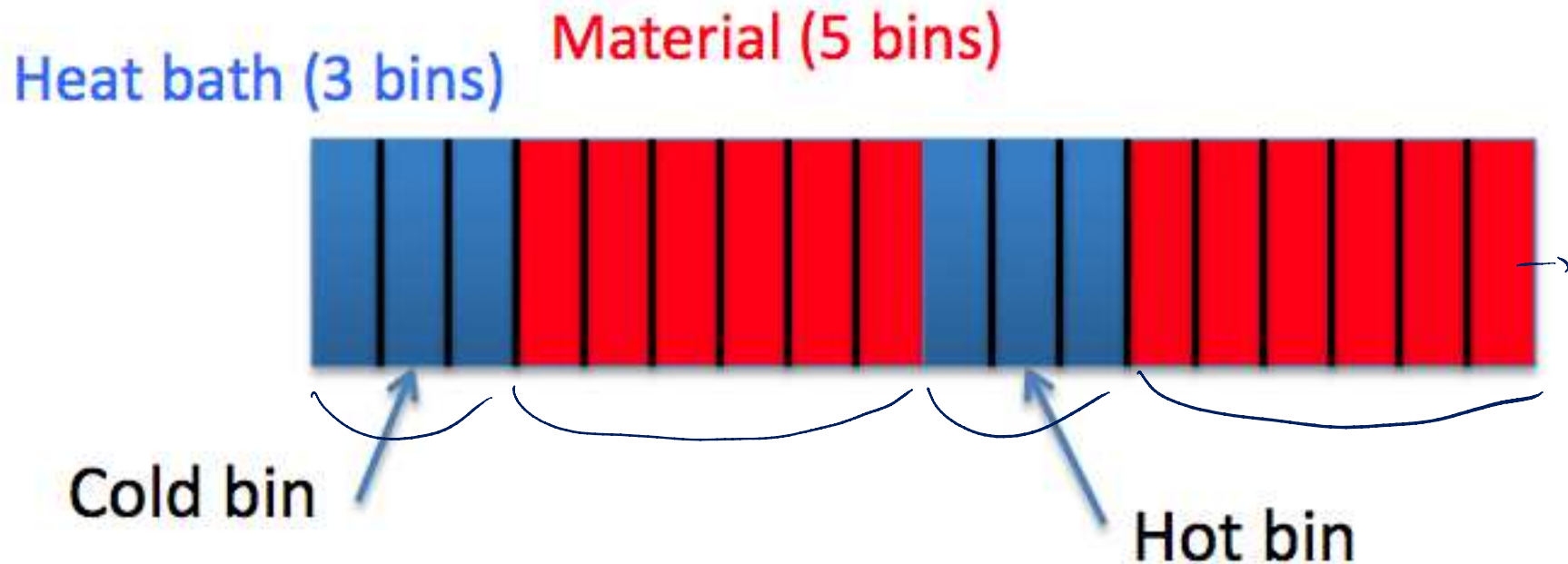
Number of Periods along z: 1

$$L_{x,y} = 5 \times 5.43$$
$$= 27.15 \text{ \AA}$$

Thermal conductivity

Q.2.3

- MD simulation



- Simulation transport direction (10 bins)

$$L = (10 + 3) \times 2 \times 5.43 = 141.18 \text{ \AA}$$

Thermal conductivity

Q.2.4

- MD simulation

Result: Thermal Conductivity

3 bins ✓

```
Thermal Conductivity including Material and Contacts: 1.65454 (W/mK)
Material Thermal Conductivity: 2.47298 (W/mK) from layer 3 ~ 5
KE: 4030.56000 Kcal/mol
Lx: 29.48301 Angstroms
Ly: 29.48168 Angstroms
Time: 200.00000 ps
Total Bin Number: 12
Number of Heatbath: 3
```

Thermal conductivity increases
Limiting the mean free path of phonons

Result: Thermal Conductivity

5 bins ✓

```
Thermal Conductivity including Material and Contacts: 2.18315 (W/mK)
Material Thermal Conductivity: 2.58948 (W/mK) from layer 3 ~ 7
KE: 4054.77630 Kcal/mol
Lx: 29.48602 Angstroms
Ly: 29.48528 Angstroms
Time: 200.00000 ps
Total Bin Number: 16
Number of Heatbath: 3
```

Result: Thermal Conductivity

10 bins ✓

```
Thermal Conductivity including Material and Contacts: 3.52272 (W/mK)
Material Thermal Conductivity: 5.40600 (W/mK) from layer 3 ~ 12
KE: 4019.45450 Kcal/mol
Lx: 29.49334 Angstroms
Ly: 29.49295 Angstroms
Time: 200.00000 ps
Total Bin Number: 26
Number of Heatbath: 3
```