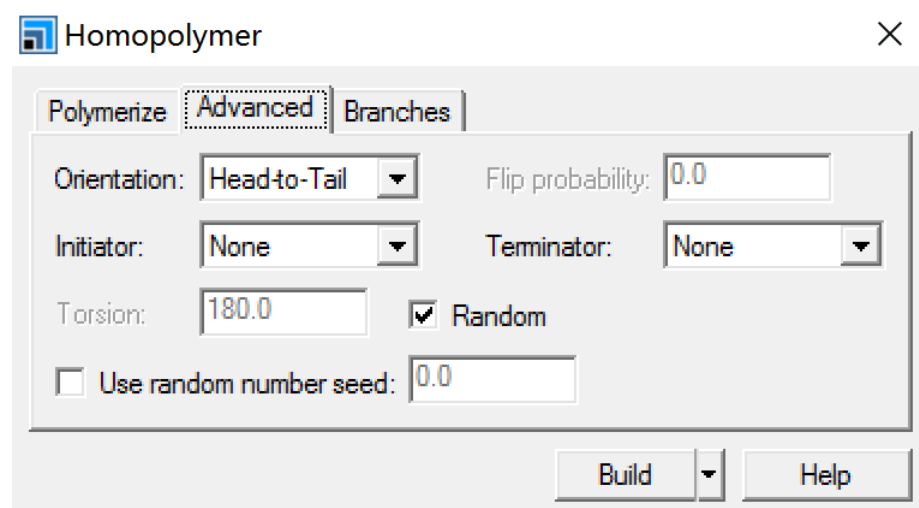
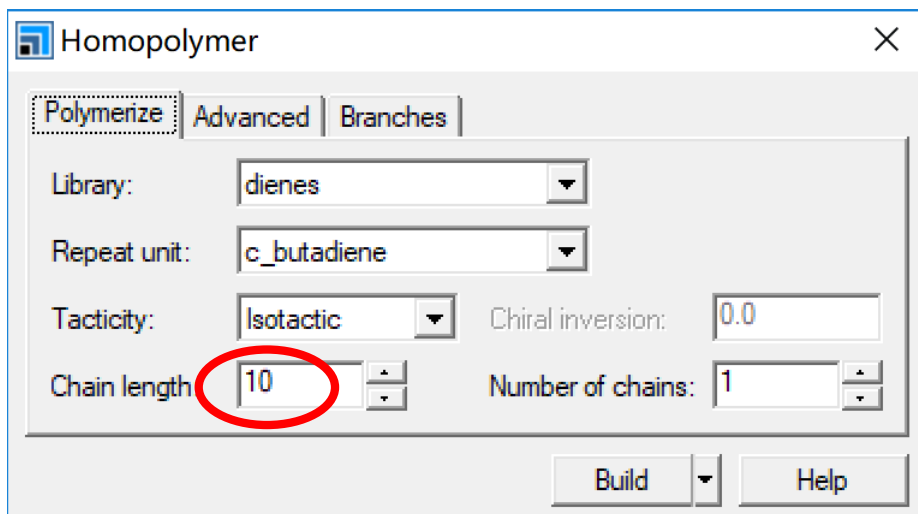


# 11月25日上机实习安排

使用MS软件Forcite模块完成气体CH<sub>4</sub>在聚合物  
poly(cis-1,4-butadiene) (PBD)中的扩散研究

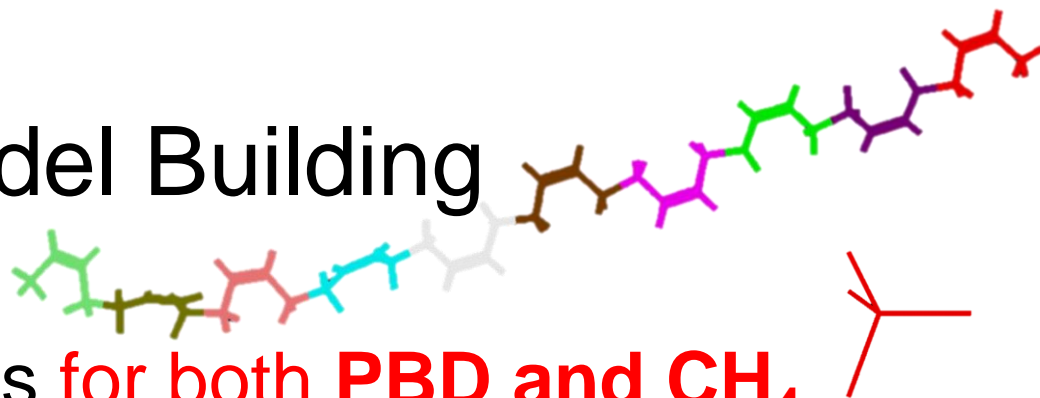
# Model Building

➤ **PBD chain generation** (Build → Build Polymers → Homopolymer)

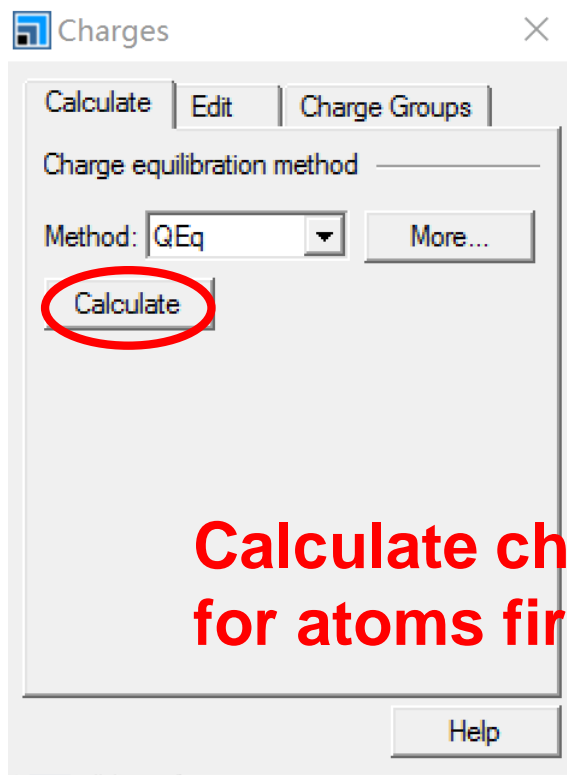


➤ CH<sub>4</sub> molecule (eg: from GaussView)

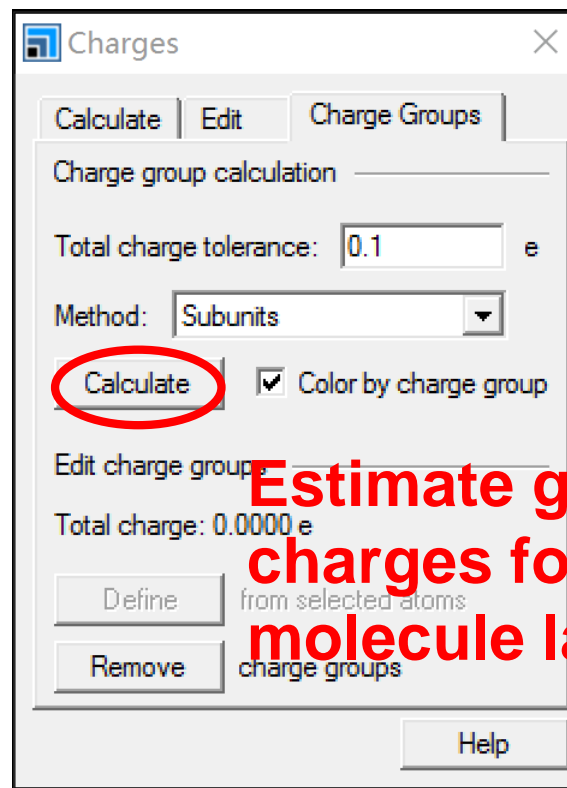
# Model Building



➤ Modify → Charges for both **PBD** and **CH<sub>4</sub>**



**Calculate charges  
for atoms first**



**Estimate group  
charges for whole  
molecule later**

# Model Building

➤ Use the Forcite module to type FF **(COMPASS)** and charges **(Use current)**:

1. PBD:

✓ **h** for H atoms

✓ **c4** for single-bond C atoms

✓ c3= for double-bond C atoms

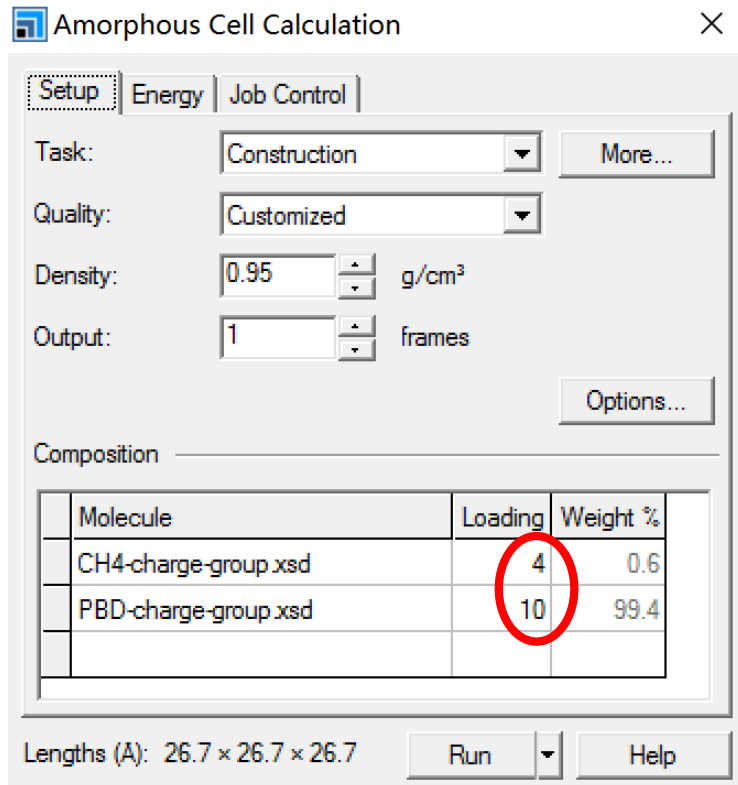
2. CH<sub>4</sub>:

✓ **h** for H atoms

✓ **c40** for C atom

# Model Building

## ➤ Generate amorphous cell



Amorphous Cell Calculation

Setup | Energy | Job Control

Task: Construction More...

Quality: Customized

Density: 0.95 g/cm<sup>3</sup>

Output: 1 frames

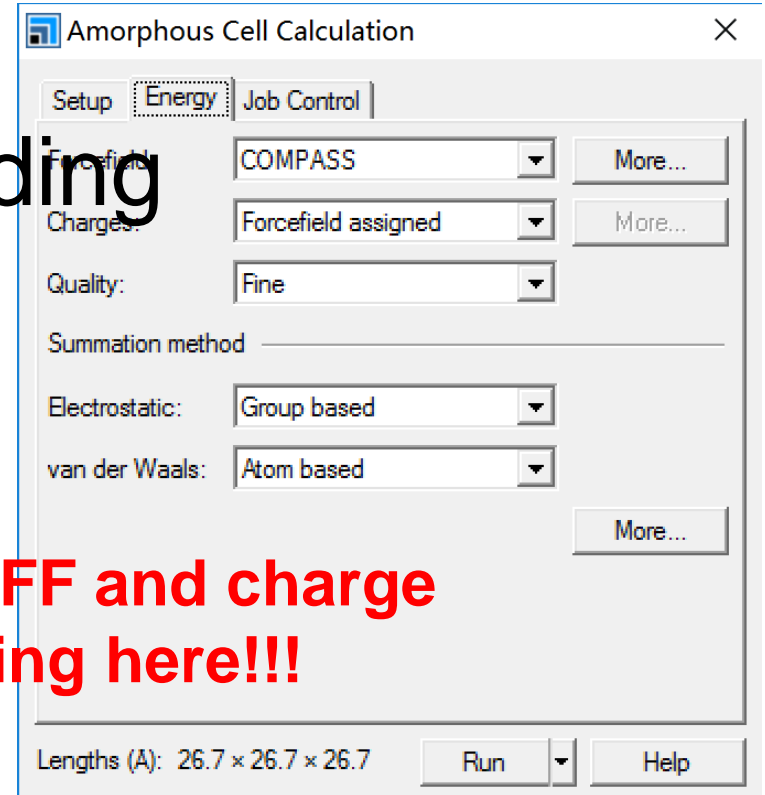
Options...

Composition

Molecule	Loading	Weight %
CH4-charge-group.xsd	4	0.6
PBD-charge-group.xsd	10	99.4

Lengths (Å): 26.7 × 26.7 × 26.7 Run Help

**No FF and charge typing here!!!**



Amorphous Cell Calculation

Setup | Energy | Job Control

Forcefield: COMPASS More...

Charges: Forcefield assigned More...

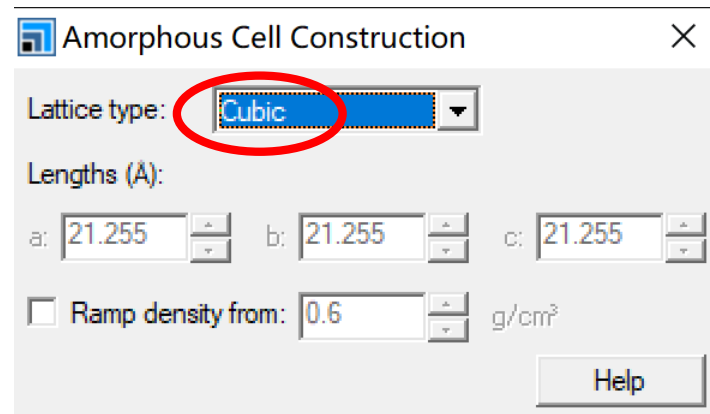
Quality: Fine

Summation method

Electrostatic: Group based

van der Waals: Atom based More...

Lengths (Å): 26.7 × 26.7 × 26.7 Run Help



Amorphous Cell Construction

Lattice type: Cubic

Lengths (Å):

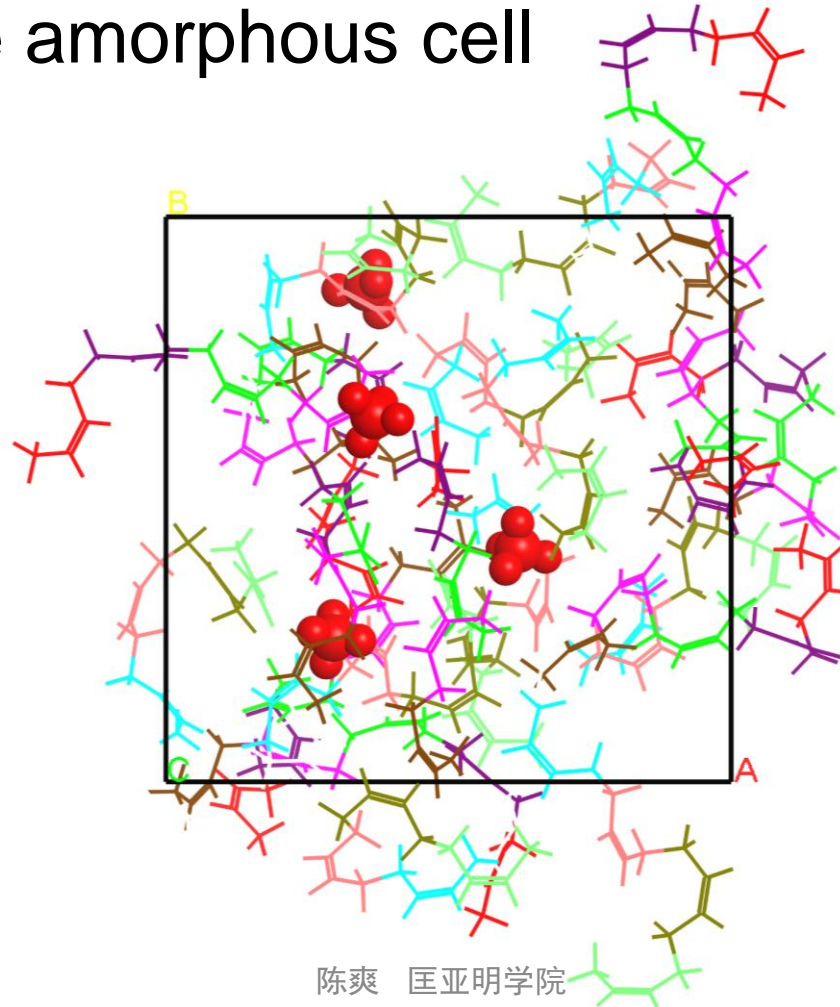
a: 21.255 b: 21.255 c: 21.255

☐ Ramp density from: 0.6 g/cm<sup>3</sup>

Help

# Model Building

➤ Generate amorphous cell



# MD Simulations

## ➤ Geometry optimization

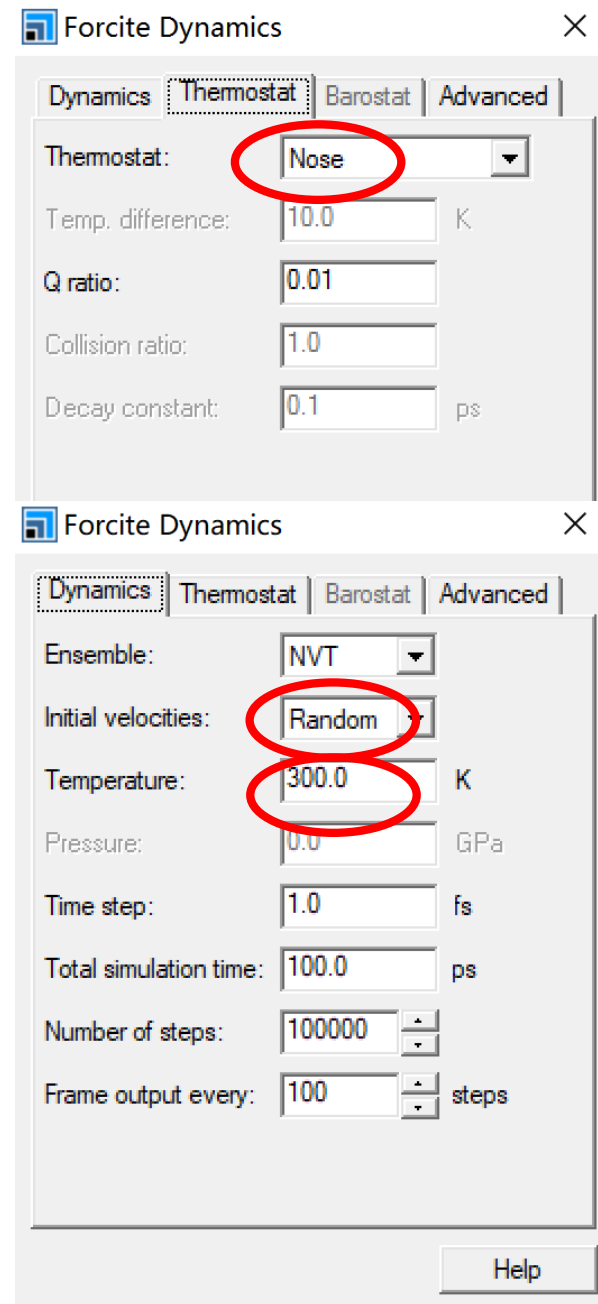
- ✓ FF: compass (no typing here !!!)
- ✓ Electrostatics & vdW: group based

## ➤ NVT ensemble

- ✓ Quality: Fine
- ✓ 100 ps

## ➤ NVE ensemble

- ✓ 100 ps



# MSD Estimation by Forcite Analysis

- Open **\*.xtd file** and select 4 CH<sub>4</sub> molecules
- Edit Sets → New... → set 4 methanes as a set (name this set)
- Forcite Analysis for Mean Square Displacement (**set Length: 500 frames**)
- Export data
- Estimate the slope of MSD-*t* curve to calculate self-diffusion coefficients (*D*s)



# Mean Square Displacement（均方位移）

MD计算系统中的原子由起始位置不停移动，每一瞬间各原子的位置皆不相同。以 $\vec{r}(t)$ 表示时间 $t$ 时粒子的位置，则粒子位移平方的平均值成为均方位移即

$$\text{MSD} = R(t) = \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle$$

式中括号表示平均值。

依据统计原理，只要粒子数目足够多，计算时间足够长，系统的任一瞬间均可当作时间的零点，所计算的平均值应相同。

因此，由储存的轨迹计算均方位移应将各轨迹点视为零点。

# Mean Square Displacement (均方位移)

设MD计算共收集了 $n$ 步轨迹，各部的位置向量分别为 $\vec{r}(1), \vec{r}(2), \dots, \vec{r}(n)$ ，通常将此轨迹分为相等数目的两部分，计算均方位移时，每次计算 $R(t)$ 皆取 $n/2$ 组数据的平均。将轨迹分为：

$$\vec{r}(1), \vec{r}(2), \dots, \vec{r}(n/2) \quad \vec{r}(n/2+1), \vec{r}(n/2+2), \dots, \vec{r}(n)$$

设步数的时间间隔为 $\delta t$ ，因此任一瞬间均可视为零点，故均方位移为：

$$R(\delta t) = \frac{|\vec{r}(2) - \vec{r}(1)|^2 + |\vec{r}(3) - \vec{r}(2)|^2 + \dots + |\vec{r}(n/2+1) - \vec{r}(n/2)|^2}{n/2}$$

$$R(2\delta t) = \frac{|\vec{r}(3) - \vec{r}(1)|^2 + |\vec{r}(4) - \vec{r}(2)|^2 + \dots + |\vec{r}(n/2+2) - \vec{r}(n/2)|^2}{n/2}$$

# Mean Square Displacement (均方位移)

...

$$R(m\delta t) = \frac{|\bar{r}(1+m) - \bar{r}(1)|^2 + |\bar{r}(2+m) - \bar{r}(2)|^2 + \cdots + |\bar{r}(n/2+m) - \bar{r}(n/2)|^2}{n/2}$$

...

$$R(n\delta t/2) = \frac{|\bar{r}(1+n/2) - \bar{r}(1)|^2 + |\bar{r}(2+n/2) - \bar{r}(2)|^2 + \cdots + |\bar{r}(n/2+n/2) - \bar{r}(n/2)|^2}{n/2}$$

上式均为计算某一个粒子的均方位移，如计算系统中所有粒子的均方位移则需对粒子数再平均。

得到MSD- $t$ 曲线后，如果二者关系随着 $t$ 的增大呈线性，可根据Einstein扩散定律，求粒子的自扩散系数：

$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle |r(t+t_0) - r(t_0)|^2 \rangle}{t}$$