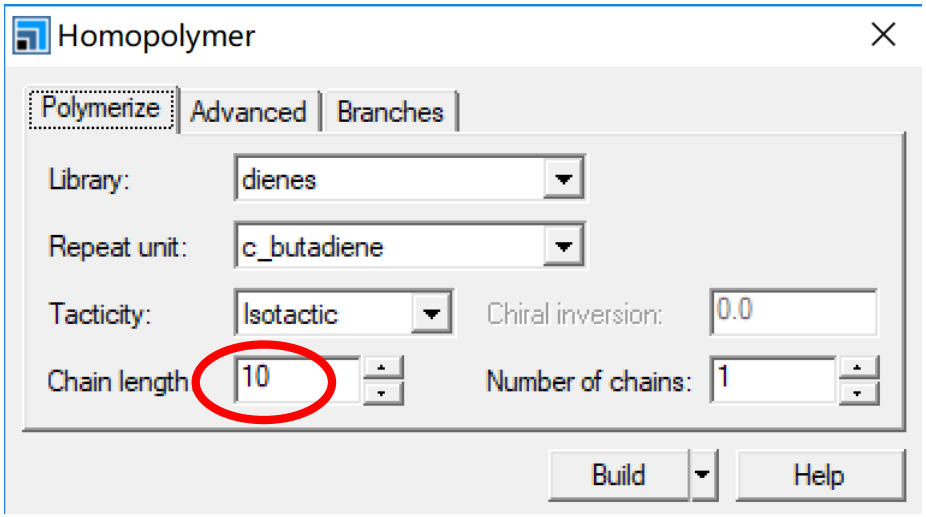
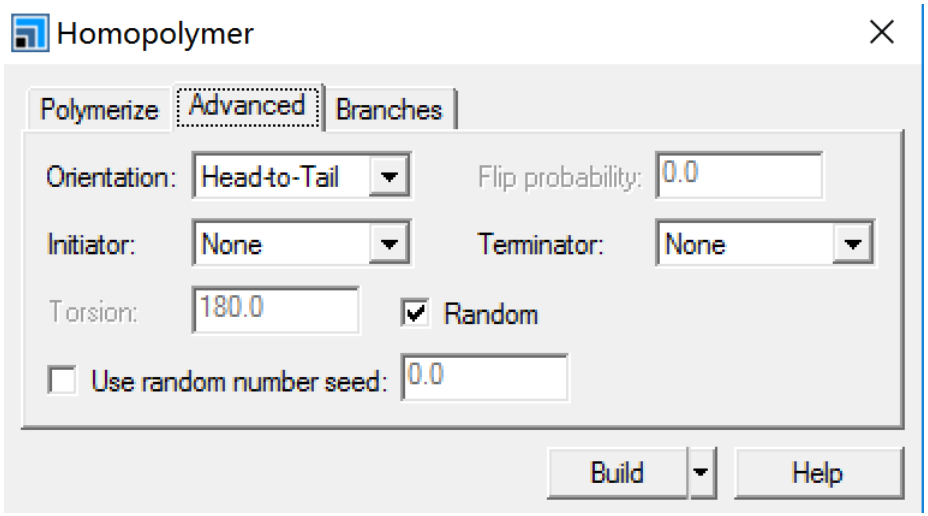
# 11月25日上机实习安排

使用MS软件Forcite模块完成气体$CH_4$在聚合物poly(cis-1,4-butadiene) (PBD)中的扩散研究

# Model Building

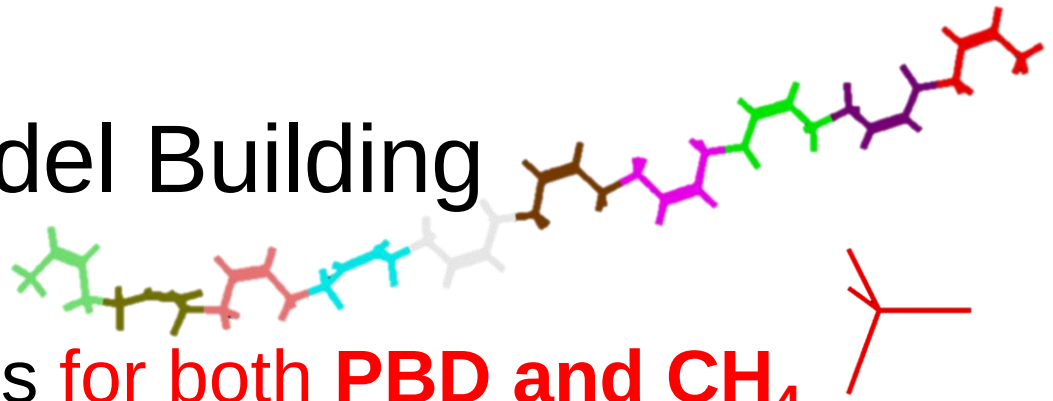
- **PBD chain generation** (Build → Build Polymers → Homopolymer)



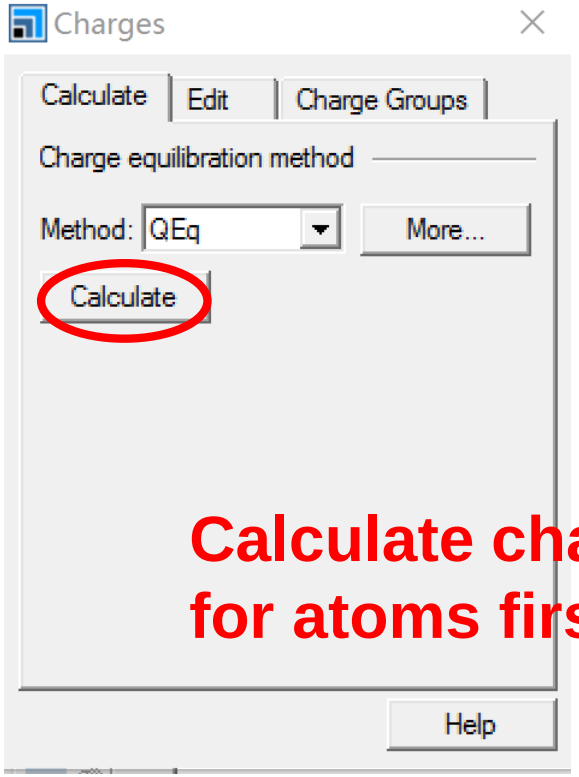




- $CH_4$ molecule (eg: from GaussView)

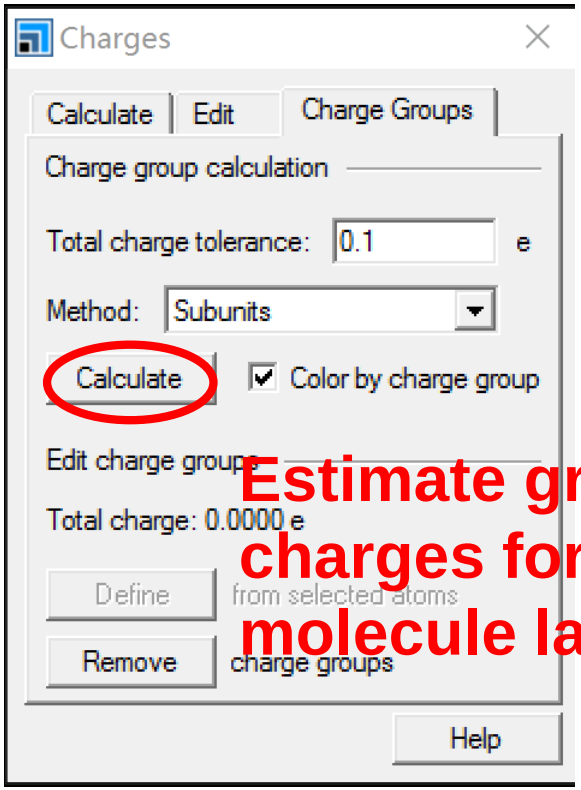
# Model Building



➢Modify → Charges for both **PBD and $CH_4$**




**Calculate charges for atoms first**



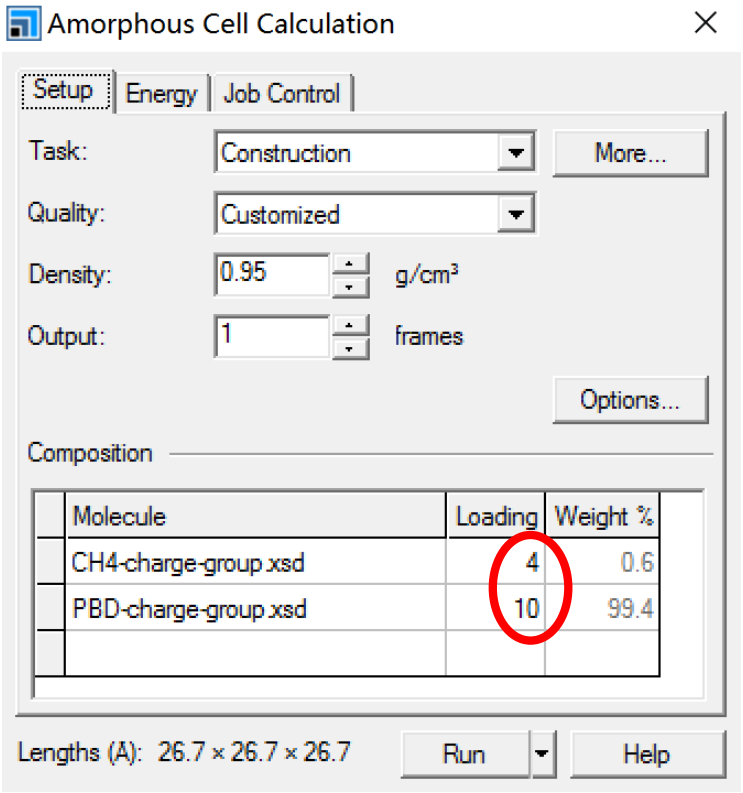

**Estimate group charges for whole molecule later**

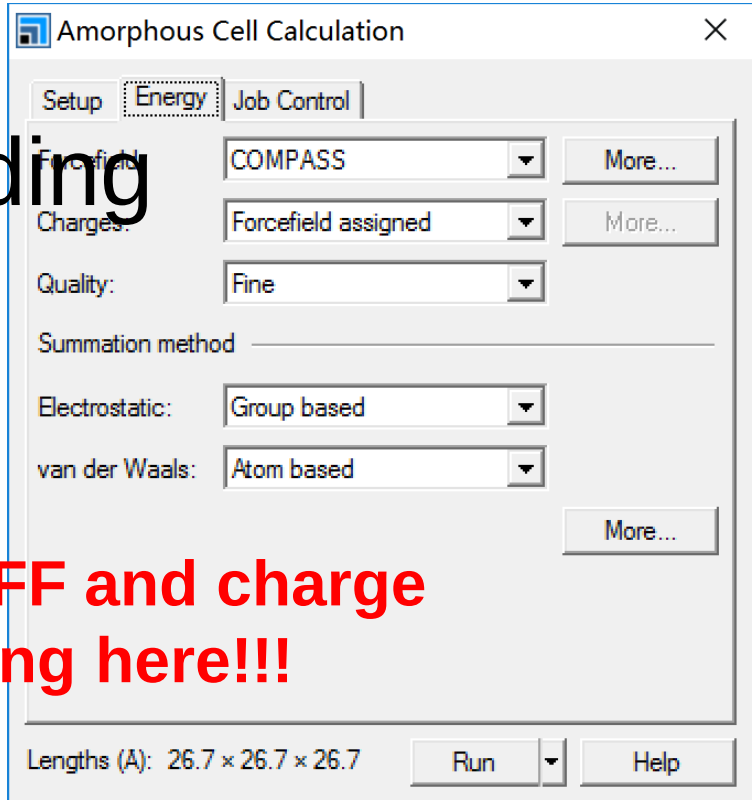
# Model Building

- 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. $CH_4$:
     - ✓**h** for H atoms
     - ✓**c40** for C atom

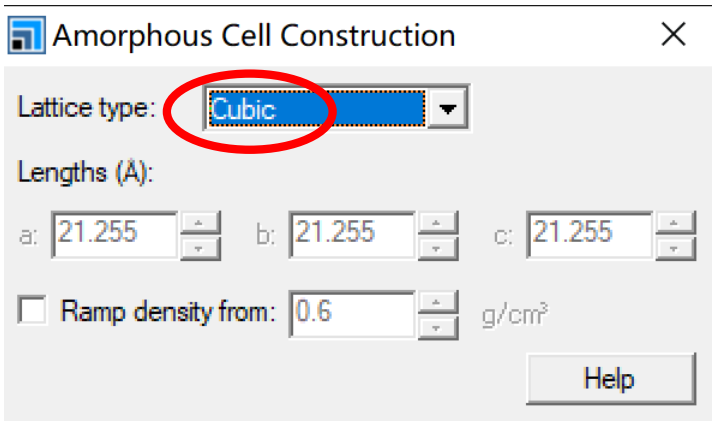
# Model Building

- Generate amorphous cell



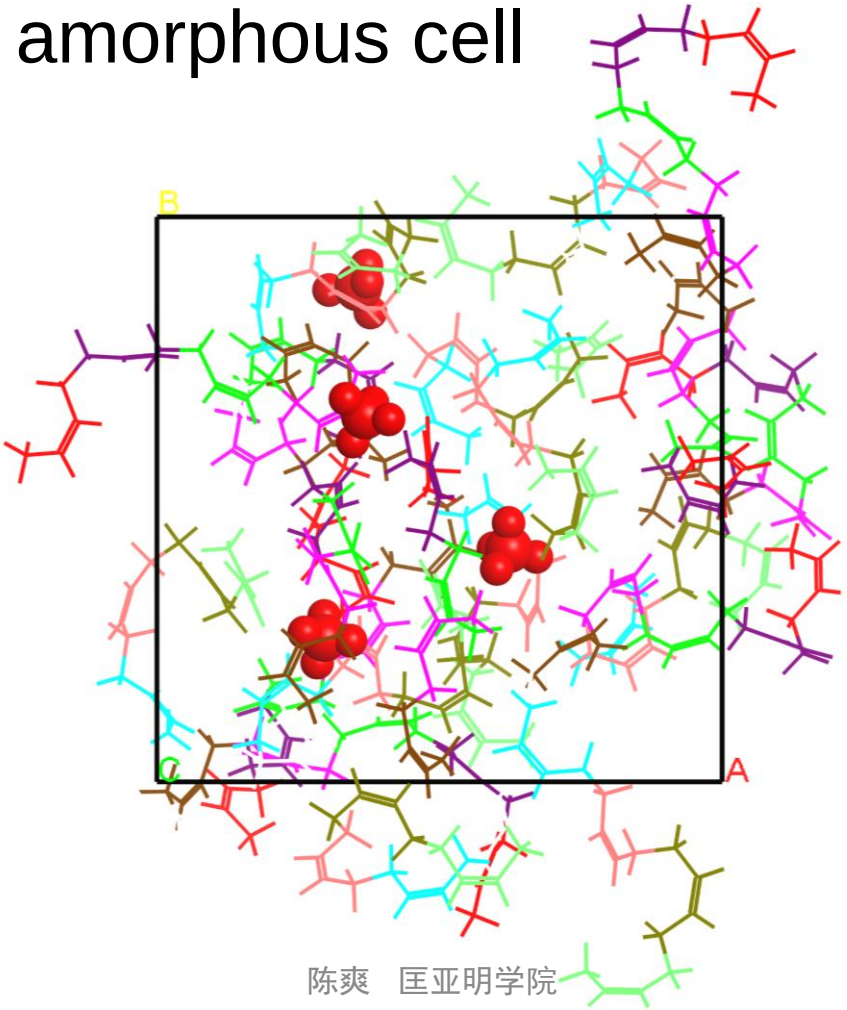




**No FF and charge typing here!!!**



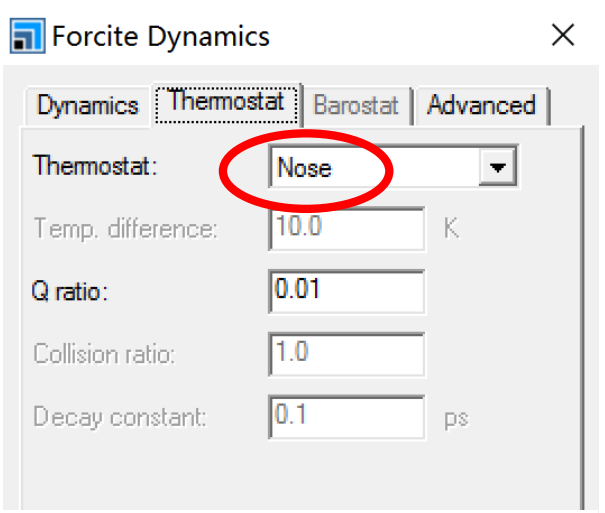
# Model Building

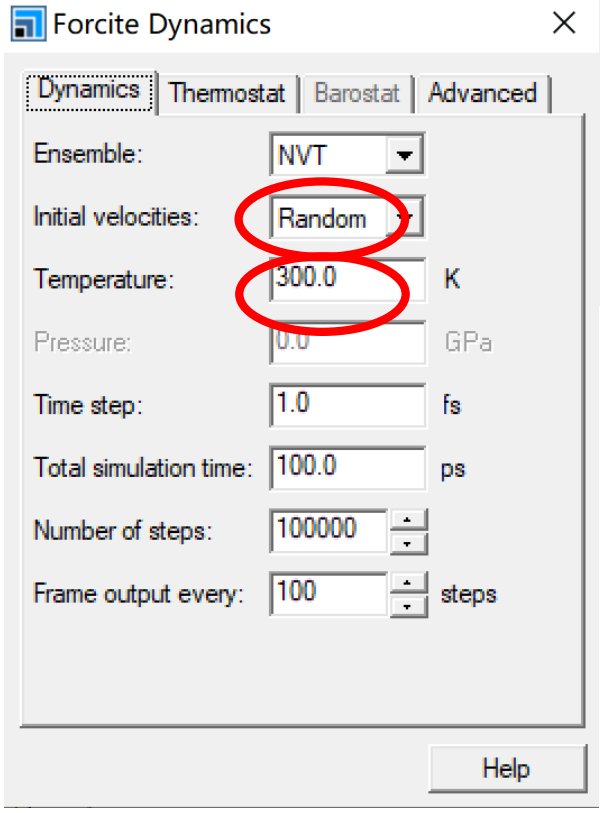
- Generate amorphous cell

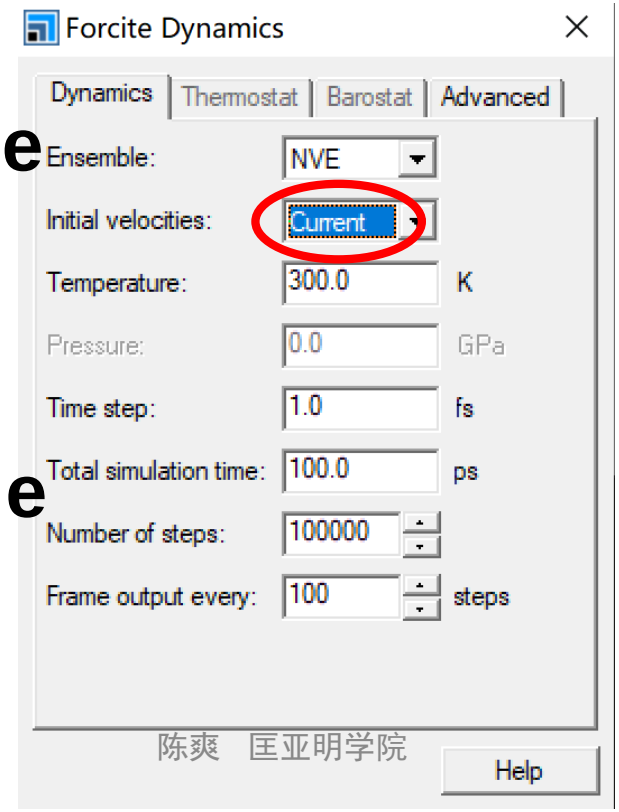


# MD Simulations

- **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 $CH_4$ 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$\vec{r}\left(t\right)$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

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

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 $\vec{r}(1)$，$\vec{r}(2)$，…,$\vec{r}(n)$，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：

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

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：

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

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

# Mean Square Displacement（均方位移）

…

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

…

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

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：

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