Free Energy Calculations of Hydrogen Clathrate
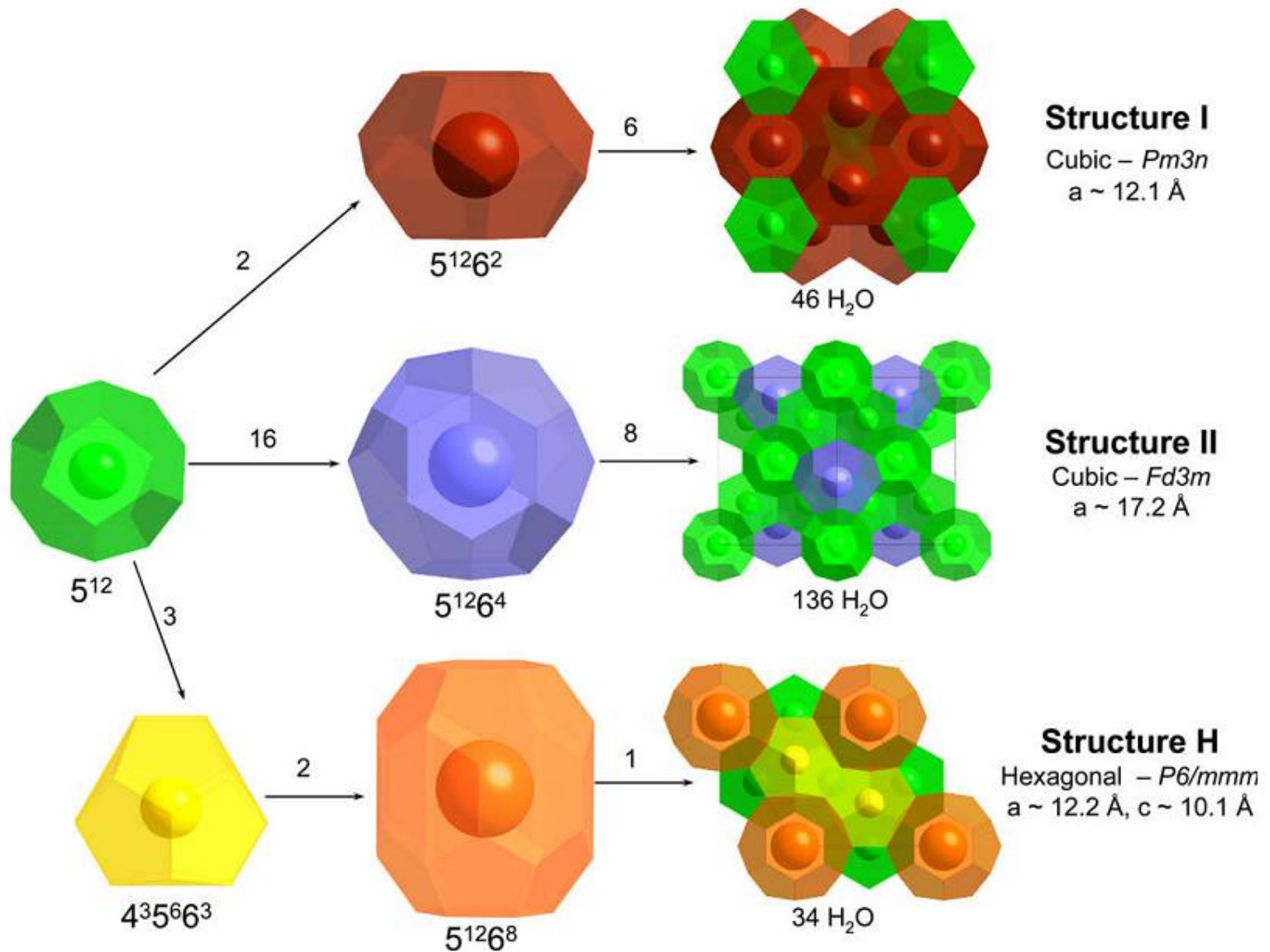
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Outline

- Introduction

- Free Energy Calculation

- Review of Lattice Dynamics (LD) of crystal

- LD of non-linear rigid molecular system

Introduction

- Clathrate hydrates are crystalline water-based solids physically resembling ice, in which small non-polar molecules (typically gases) with large hydrophobic moieties are trapped inside "cages" of hydrogen bonded water molecules.

Hydrate Structures

5^{12}

$5^{12}6^2$ 46 H$_2$O

Structure I
Cubic – $Pm3n$
a ~ 12.1 Å

$5^{12}6^4$ 136 H$_2$O

Structure II
Cubic – $Fd3m$
a ~ 17.2 Å

$4^3 5^6 6^3$

$5^{12}6^8$ 34 H$_2$O

Structure H
Hexagonal – $P6/mmm$
a ~ 12.2 Å, c ~ 10.1 Å

Free Energy calculations of hydrates

- The plan of computing the FE of hydrate with specific occupation of hydrogen molecules is as follows:

1. Calculate the harmonic free energy of "empty" hydrate at very low temperature (for harmonic approximation to be valid)

2. Get the FE of higher temperature using thermodynamic integration method.

3. Insert/Delete guest molecules (at constant T,P, μ_{H_2}) to get the equilibrium equilibrium H2 concentration.

4. Calculate the Gibbs free energy of that concentration using:

$$G = N_m \mu_m + N_w \mu_w^{(0)} - \int_{\mu_m^{(0)}}^{\mu_m} N_m \, d\mu_m'$$

5. Account for the Quantum effects of hydrogen and estimate the effect.

Lattice Dynamics of Crystals: Review

- The potential energy can be expanded in terms of atomic displacements **u**:

- $U(x_1, y_1, z_1 \ldots x_N, y_N, z_N) =$

$$\sum_{k\alpha} \left(\frac{\partial U}{\partial u_\alpha(k)} \right)_0 u_\alpha(k) + \sum_{\substack{kk' \\ \alpha\beta}} \left(\frac{\partial^2 U}{\partial u_\alpha(k) u_\beta(k')} \right)_0 u_\alpha(k) \, u_\beta(k') + \cdots HO$$
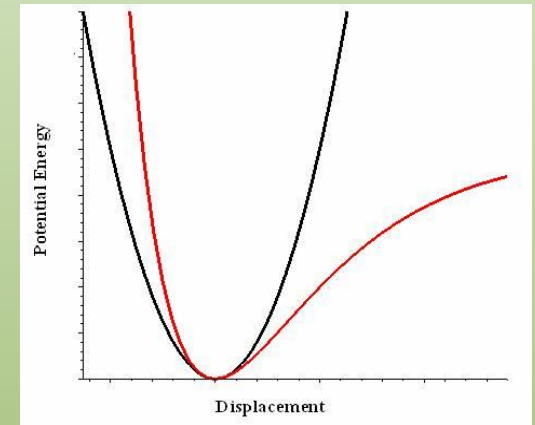
$\alpha, \beta = x, y, z$

$$u_\alpha(k) = \mathbf{r}_\alpha(k) - \mathbf{R}_\alpha(k)$$

$\left(\frac{\partial U}{\partial u_\alpha(k)} \right)_0 = 0$, at equilibrium.

$$U_{harmonic} = \sum_{\substack{kk' \\ \alpha\beta}} \Phi_{\alpha\beta}(k, k') \, u_\alpha(k) \, u_\beta(k')$$

$$\Phi_{\alpha\beta}(k, k') \equiv \left(\frac{\partial^2 U}{\partial u_\alpha(k) u_\beta(k')} \right)_0$$

Lattice Dynamics of Crystals: Review

$$U_{harm} = \sum_{\substack{kk' \\ \alpha\beta}} \Phi_{\alpha\beta}(k, k')\, u_\alpha(k)\, u_\beta(k')$$

$$U_{harm} = \mathbf{u}^T \, \mathbf{\Phi} \, \mathbf{u}$$

$\mathbf{\Phi}$ is 3N × 3N force constants matrix

$\mathbf{u}$ is 3N × 1 displacement vector

$$\mathbf{\Phi} \, \mathbf{v_i} = \lambda_i \mathbf{v_i}$$

Free energy:

$$A_{harm} = \frac{k_B T}{2} \sum_i^{3(N-1)} ln\left(\frac{\lambda_i}{2\pi k_B T}\right)$$

Molecular Crystal LD

- The molecular degrees of freedom can be separated into two modes:
  - External (rigid translational + rotational)
  - Internal (stretch, bend,…etc.)

- For rigid-molecules we have only external modes: $\mathbf{u}^t$ and $\mathbf{u}^r$

- $U(\{\mathbf{u}_1^t, \mathbf{u}_1^r\}, \dots, \{\mathbf{u}_N^t, \mathbf{u}_N^r\}) =$

$$\sum_{\substack{K\alpha \\ i=t,r}} \left(\frac{\partial U}{\partial u_\alpha^i(K)}\right)_0 u_\alpha^i(K) + \frac{1}{2} \sum_{\substack{KK' \\ \alpha\beta \\ i=t,r}} \left(\frac{\partial^2 U}{\partial u_\alpha^i(K)\partial u_\beta^{i'}(K')}\right)_0 u_\alpha^i(K)u_\beta^{i'}(K') + \cdots HO$$

$\alpha, \beta = x, y, z.$

At equilibrium, there is no net force or torque on a molecule, so

$$\left(\frac{\partial U}{\partial u_\alpha^i(K)}\right)_0 = 0 \quad \text{for } i = t, r$$

$$U_{harmonic} = \frac{1}{2} \sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{tt}(K,K')u_\alpha^t(K)u_\beta^t(K') + \frac{1}{2} \sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{tr}(K,K')u_\alpha^t(K)u_\beta^r(K')$$

$$\frac{1}{2} \sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{rt}(K,K')u_\alpha^r(K)u_\beta^t(K') + \frac{1}{2} \sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{rr}(K,K')u_\alpha^r(K)u_\beta^r(K')$$

Molecular Crystal LD

- In a matrix form (assume M molecules)

$$U_{harmonic} = \frac{1}{2}\mathbf{u}^T\mathbf{D}\mathbf{u}$$

$$= \frac{1}{2}\begin{bmatrix}\mathbf{u}^t & \mathbf{u}^r\end{bmatrix}\begin{bmatrix}\mathbf{D}^{tt} & \mathbf{D}^{tr} \\ \mathbf{D}^{rt} & \mathbf{D}^{rr}\end{bmatrix}\begin{bmatrix}\mathbf{u}^t \\ \mathbf{u}^r\end{bmatrix}$$

$\mathbf{D}^{ii'}$ is $3M \times 3M$ matrix

$\mathbf{u}^i$ is $3M \times 1$ vector

$$\mathcal{F} \equiv \begin{bmatrix}\mathbf{F} \\ \boldsymbol{\tau}\end{bmatrix} = -\begin{bmatrix}\mathbf{D}^{tt} & \mathbf{D}^{tr} \\ \mathbf{D}^{rt} & \mathbf{D}^{rr}\end{bmatrix}\begin{bmatrix}\mathbf{u}^t \\ \mathbf{u}^r\end{bmatrix}$$

$$\mathbf{F}_\alpha(K) = -\sum_{K'\beta}D^{tt}_{\alpha\beta}(K,K')u^t_\beta(K') - \sum_{K'\beta}D^{tr}_{\alpha\beta}(K,K')\,u^r_\beta(K')$$

$$\boldsymbol{\tau}_\alpha(K) = -\sum_{K'\beta}D^{rt}_{\alpha\beta}(K,K')u^t_\beta(K') - \sum_{K'\beta}D^{rr}_{\alpha\beta}(K,K')\,u^r_\beta(K')$$

Molecular force constants in terms of atomic ones!

External Vibrations in Complex Crystals

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The study of dispersion relations for external modes in molecular and complex ionic crystals is reviewed. The concept of external modes is introduced, so that the formal theory may be developed along the lines of standard Born–von Kármán formalism. The studies reported thus far in the literature are then surveyed against the background of the formal theory. The role of macroscopic electric fields in relation to external modes is next discussed, and the work of Kellermann is generalized to obtain Coulomb coefficients connected with external modes in complex ionic crystals. Finally, the group-theoretical aspects are considered, and the recent work of Maradudin and Vosko is extended to cover the external modes. A detailed illustrative example is also provided.

In this context, it is desirable to write formal expressions for $\phi_{\alpha\beta}{}^{ii'}(l\kappa; l'\kappa')$ in terms of the conventional Born–von Kármán constants $\phi_{\alpha\beta}(l\kappa k; l'\kappa'k')$. Such a connection is not easy to establish in the case in which molecules are regarded as nonrigid. In the case of rigid molecules, however, the relevant formulas are easily derived.

Molecular force constants in terms of atomic ones.

- The displacement of an atom k of molecule K is given by (to the first order)
- $\mathbf{u}(Kk) = \mathbf{u}^t(K) + \mathbf{u}^r(K) \times \mathbf{R}(Kk) + \cdots HO$

$$u_\alpha(Kk) = u_\alpha^t(K) + \sum_{\mu\nu} \varepsilon_{\alpha\mu\nu}\, u_\mu^r(K)R_\nu(Kk) + \cdots HO$$

$\varepsilon_{\alpha\mu\nu}$ is the Levi-Civita function ($\varepsilon_{\alpha\mu\nu} = 1$ if $\alpha\mu\nu = xyz, yzx$, or zxy, $\varepsilon_{\alpha\mu\nu} = -1$ if $\alpha\mu\nu = zyx, yxz$, or xzy, equals zero otherwise)

- So, we can assume that we have "atomic" system with harmonic energy

$$U_{harm} = \frac{1}{2} \sum_{\substack{kk'KK' \\ \alpha\beta}} \Phi_{\alpha\beta}(Kk, K'k')\, u_\alpha(Kk)\, u_\beta(K'k')$$

$$= \sum_{\substack{kk'KK' \\ \alpha\beta}} \Phi_{\alpha\beta}(Kk, K'k') \left\{ u_\alpha^t(K) + \sum_{\mu\nu} \varepsilon_{\alpha\mu\nu}\, u_\mu^r(K)R_\nu(Kk) \right\} \left\{ u_\beta^t(K') + \sum_{\mu\nu} \varepsilon_{\beta\gamma\delta}\, u_\gamma^r(K')R_\delta(K'k') \right\}$$

$$U_{harmonic} = \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} \left\{ \sum_{kk'} \Phi_{\alpha\beta}(Kk, K'k') \right\} u_\alpha^t(K) u_\beta^t(K')$$

$$+ \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} \left\{ \sum_{\substack{kk' \\ \gamma\delta}} \Phi_{\alpha\gamma}(Kk, K'k')\varepsilon_{\gamma\beta\delta}R_\delta(K'k') \right\} u_\alpha^t(K) u_\beta^r(K')$$

$$+ \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} \left\{ \sum_{\substack{kk' \\ \mu\nu}} \Phi_{\mu\beta}(Kk, K'k')\varepsilon_{\mu\alpha\nu}R_\nu(Kk) \right\} u_\alpha^r(K) u_\beta^t(K')$$

$$+ \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} \left\{ \sum_{\substack{kk' \\ \gamma\delta\mu\nu}} \Phi_{\mu\gamma}(Kk, K'k')\varepsilon_{\mu\alpha\nu}R_\nu(Kk)\ \varepsilon_{\gamma\beta\delta}R_\delta(K'k') \right\} u_\alpha^r(K) u_\beta^r(K')$$

Comparing it to

$$U_{harmonic} = \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{tt}(K, K') u_\alpha^t(K) u_\beta^t(K') + \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{tr}(K, K') u_\alpha^t(K) u_\beta^r(K')$$

$$+ \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{rt}(K, K') u_\alpha^r(K) u_\beta^t(K') + \frac{1}{2}\sum_{\substack{KK' \\ \alpha\beta}} D_{\alpha\beta}^{rr}(K, K') u_\alpha^r(K) u_\beta^r(K')$$

So, we can easily write the molecular force constant coefficients in terms of the regular atomic coefficients.

$$D^{tt}_{\alpha\beta}(K, K') = \sum_{kk'} \Phi_{\alpha\beta}(Kk, K'k')$$

$$D^{tr}_{\alpha\beta}(K, K') = \sum_{\substack{kk' \\ \gamma\delta}} \Phi_{\alpha\gamma}(Kk, K'k')\varepsilon_{\gamma\beta\delta}R_{\delta}(K'k')$$

$$D^{rt}_{\alpha\beta}(K, K') = \sum_{\substack{kk' \\ \mu\nu}} \Phi_{\mu\beta}(Kk, K'k')\varepsilon_{\mu\alpha\nu}R_{\nu}(Kk)$$

$$D^{rr}_{\alpha\beta}(K, K') = \sum_{\substack{kk' \\ \gamma\delta\mu\nu}} \Phi_{\mu\gamma}(Kk, K'k')\varepsilon_{\mu\alpha\nu}R_{\nu}(Kk)\,\varepsilon_{\gamma\beta\delta}R_{\delta}(K'k')$$

Or, in terms of matrix formulation

$$\mathbf{D}(K, K') = \begin{bmatrix} \mathbf{D}^{tt} & \mathbf{D}^{tr} \\ \mathbf{D}^{rt} & \mathbf{D}^{rr} \end{bmatrix}$$

$$= \sum_{kk'} \begin{bmatrix} \boldsymbol{\Phi} & \boldsymbol{\Phi}\mathbf{R}(K'k') \\ -\mathbf{R}(Kk)\boldsymbol{\Phi} & -\mathbf{R}(Kk)\boldsymbol{\Phi}\mathbf{R}(K'k') \end{bmatrix}$$

Where $\boldsymbol{\Phi} \equiv \boldsymbol{\Phi}(Kk, K'k')$ is the regular 3×3 atomic force constant matrix.

$$\mathbf{R}(Kk) = \begin{bmatrix} 0 & R_z(Kk) & -R_y(Kk) \\ -R_z(Kk) & 0 & R_x(Kk) \\ R_y(Kk) & -R_x(Kk) & 0 \end{bmatrix}$$

Dynamical Matrix Approach

- To get the eigen values needed for the harmonic free energy we need to diagonalize a matrix of dimensions 6MX6M.
- For big systems, the direct approach becomes inefficient.
- The symmetry of crystal structure can be utilized to solve this problem.
- The main idea is to assume the solution of the equation of motion

$$\mathbf{F}_\alpha(lK) = m(lK)\ddot{u}^t_\alpha(lK) = -\sum_{l'K'\beta} D^{tt}_{\alpha\beta}(lK, l'K')u^t_\beta(l'K') - \sum_{K'\beta} D^{tr}_{\alpha\beta}(lK, l'K')\, u^r_\beta(l'K')$$

$$\boldsymbol{\tau}_\alpha(lK) = \sum_{\beta} \mathbf{I}_{\alpha\beta}(lK)\ddot{u}^r_\beta(lK) = -\sum_{l'K'\beta} D^{rt}_{\alpha\beta}(lK, l'K')u^t_\beta(l'K') - \sum_{l'K'\beta} D^{rr}_{\alpha\beta}(lK, l'K')\, u^r_\beta(l'K')$$

- To be in the form

$$u^i_\alpha(lK) = U^i_\alpha(K, \mathbf{q})\; exp(-i[\mathbf{q}.\mathbf{r}(l) - \omega(\mathbf{q})t])$$

Where
$\mathbf{q}$ is the allowed wave vector of a given crystal (number of allowed wave vectors = # of unit cells),
$\mathbf{r}(l)$ is the position of cell l.

Dynamical Matrix Approach

- Plug this into the equation of motion, we get an eigen value equation on dimension of only one unit cell

$$\mathbf{D}_{dyn}(\mathbf{q})\mathbf{U}(\mathbf{q}) = \omega^2(\mathbf{q})\,\mathbf{M}\,\mathbf{U}(\mathbf{q})$$

$$\mathbf{M} = \begin{bmatrix} \mathbf{m(3mX3m)} & \mathbf{0} \\ \mathbf{0} & \mathbf{I(3mX3m)} \end{bmatrix}$$

- Where $\mathbf{D}_{dyn}(\mathbf{q})$ is the dynamical matrix of the system which has diminutions of $6m \times 6m$; where m is number of molecules in ONE unit cell (M=Lm; L=# of unit cells).

$$D^{ii'}_{dyn,\,\alpha\beta}(\mathbf{q}, KK') = \sum_{l'} D^{ii'}_{\alpha\beta}(lK, l'K')exp(-i[\mathbf{q}.\,\mathbf{r}(l')])$$

Therefore, the 6MX6M problem is now reduced to L smaller matrices, each of size 6mX6m.m

Harmonic FE of sI clathrate hydrate

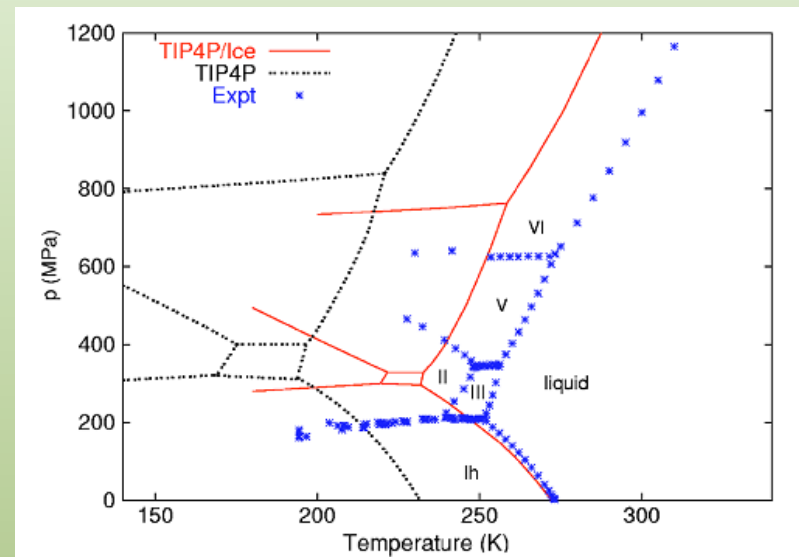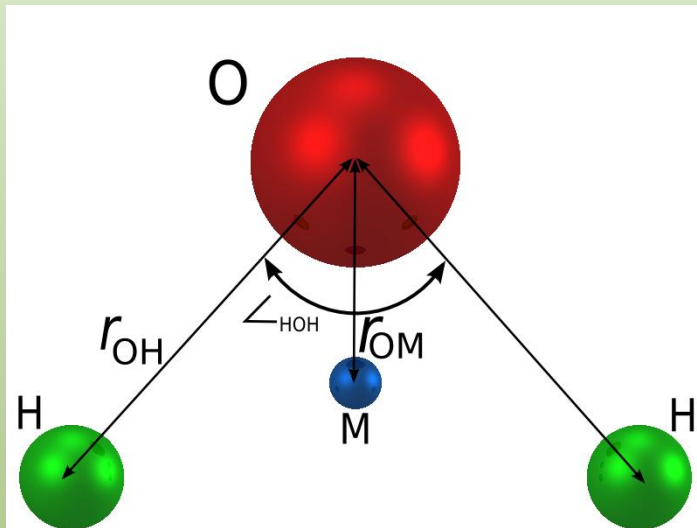- The potential model we will use is TIP4P/Ice

FIG. 1. The phase diagram of TIP4P/Ice (full lines) and TIP4P (dashed) compared to the experiment (stars). The labels mark the domain of stability of the ice phases in the experimental phase diagram.

r_{OH} (Å)	$\angle$HOH , deg	σ (Å)	ϵ/k (K)	q(O) (e)	q(H) (e)	q(M) (e)	r_{OM} (Å)
0.9572	104.52	3.1668	106.1	0	0.5897	-2q(H)	0.1577

Atomic force constant matrix of TIP4P/Ice

- Ewald Sum (ES) technique is used to solve the long range interaction problem of coulomb potentials.

U(coulomb)=U(real)+U(reciprocal)−U(self)

$$\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\sideset{}{'}\sum_{\boldsymbol{L_n}} Q_i Q_j \frac{\mathrm{erfc}(\alpha|\boldsymbol{r}_{ij}+\boldsymbol{L_n}|)}{|\boldsymbol{r}_{ij}+\boldsymbol{L_n}|} + \frac{2\pi}{V}\sum_{\boldsymbol{k}\neq 0}\frac{\exp(-k^2/4\alpha^2)}{k^2}\left|\sum_{i=1}^{N}Q_i\exp(j\boldsymbol{k}.\boldsymbol{r}_i)\right|^2 - \frac{\alpha}{\sqrt{\pi}}\left(\sum_{i=1}^{N}Q_i^2\right)$$

For rigid molecular system, we have to subtract the "Intramolecular" contribution of the "reciprocal" part (sine the ES formulation assumes **atomic** system).

$$U(Intra) = \frac{1}{2}\sum_{I=1}^{M}\sum_{ij}^{molecule\ I} Q_i Q_j \frac{\mathrm{erf}(\alpha|\mathbf{r}_{ij}|)}{|\mathbf{r}_{ij}|}$$

Atomic force constant matrix of TIP4P/Ice

The atomic force constants due to ES potential is given by:

D_{ij}(coulomb)=

$$D_{\mu\nu}^{ij} = D_{\mu\nu}^{ij}\text{ (real)}+D_{\mu\nu}^{ij}\text{(reciprocal)}-D_{\mu\nu}^{ij}\text{(self)}-D_{\mu\nu}^{ij}\text{(Intra)}$$

$D_{\mu\nu}^{ij}$(self)=0

$$D_{\mu\nu}^{ij}\text{(real)}=Q_iQ_j\left[\left(\frac{\text{erfc}(\alpha r_{ij})}{r_{ij}^3}+\frac{2\alpha}{\sqrt{\pi}}\frac{\exp(-\alpha^2 r_{ij}^2)}{r_{ij}^2}\right)\delta_{\mu\nu}\right.$$

$$\left.-\left(\frac{6\alpha}{\sqrt{\pi}}\frac{\exp(-\alpha^2 r_{ij}^2)}{r_{ij}^4}+\frac{4\alpha^3}{\sqrt{\pi}}\frac{\exp(-\alpha^2 r_{ij}^2)}{r_{ij}^2}+3\frac{\text{erfc}(\alpha r_{ij})}{r_{ij}^5}\right)r_{ij,\mu}r_{ij,\nu}\right]$$

$$D_{\mu\nu}^{ij}(reciprocal)=\frac{4\pi Q_iQ_j}{V}\sum_{\mathbf{k}\neq 0}\left(\frac{\exp(-k^2/4\alpha^2)}{k^2}\cos(\mathbf{k}\cdot\mathbf{r}_{ij})k_\mu k_\nu\right)$$

$$D_{\mu\nu}^{ij}(Intra)=Q_iQ_j\left[\left(\frac{\text{erf}(\alpha r_{ij})}{r_{ij}^3}-\frac{2\alpha}{\sqrt{\pi}}\frac{\exp(-\alpha^2 r_{ij}^2)}{r_{ij}^2}\right)\delta_{\mu\nu}\right.$$

$$\left.+\left(\frac{6\alpha}{\sqrt{\pi}}\frac{\exp(-\alpha^2 r_{ij}^2)}{r_{ij}^4}+\frac{4\alpha^3}{\sqrt{\pi}}\frac{\exp(-\alpha^2 r_{ij}^2)}{r_{ij}^2}-3\frac{\text{erfc}(\alpha r_{ij})}{r_{ij}^5}\right)r_{ij,\mu}r_{ij,\nu}\right]$$

Then …

- Once we get the harmonic FE of empty hydrate, we will use it as a reference for the thermodynamic integration (TI).

- We will use an efficient TI method called HTTI (Harmonically-Targeted TI).

- HTTI requires forces, so we will use MD simulation since we it moves all molecules at once. This makes using direct Ewald sum method a reasonable option (to avoid using the FFT methods).

Thank You