

Supporting information for:
Effects of Finite Size and Proton Disorder on
Lattice-Dynamics Estimates of the Free Energy
of Clathrate Hydrates

Sabry G. Moustafa, Andrew J. Schultz, and David A. Kofke*

*Department of Chemical and Biological Engineering, University at Buffalo, The State
University of New York, Buffalo, NY 14260-4200, USA*

E-mail: kofke@buffalo.edu

*To whom correspondence should be addressed

Atomic-to-molecular force-constants transformation

The molecular force constants, $\phi_{\alpha\beta}^{ii'}(l\kappa; l'\kappa')$ can be evaluated in terms of the forces on the atoms (or interaction sites) making up the rigid molecule, using the framework originally developed by Venkataraman and Sahni,^{S1} and corrected by others in subsequent work.^{S2,S3} The necessary molecular derivatives (both rotational and translational) are expressed as appropriate sums involving the corresponding derivatives applied to the interaction sites, which can be evaluated analytically. This approach is far preferable and faster compared to (a not uncommon) one based on numerical differentiation of the molecules' positions and orientations. Defining $\phi_{\alpha\beta}(l\kappa k; l'\kappa' k')$ as the atomic force-constant corresponding to the interaction between atoms k and k' on the molecules $l\kappa$ and $l'\kappa'$, the relevant molecular force-constant equations can be rewritten in a tensor form as follows^{S1-S3}

$$\phi^{tt}(l\kappa; l'\kappa') = \sum_{kk'} \phi(l\kappa k; l'\kappa' k') \quad (1a)$$

$$\phi^{tr}(l\kappa; l'\kappa') = \sum_{kk'} \phi(l\kappa k; l'\kappa' k') \mathcal{R}(\kappa' k') \quad (1b)$$

$$\phi^{rt}(l\kappa; l'\kappa') = \sum_{kk'} \mathcal{R}^T(\kappa k) \phi(l\kappa k; l'\kappa' k') \quad (1c)$$

$$\begin{aligned} \phi^{rr}(l\kappa; l'\kappa') &= \sum_{kk'} \mathcal{R}^T(\kappa k) \phi(l\kappa k; l'\kappa' k') \mathcal{R}(\kappa' k') \\ &+ \delta_{ll'} \delta_{\kappa\kappa'} \sum_k [\mathbf{X}(\kappa k) \cdot \mathbf{F}(l\kappa k) \mathbf{I}_3 - \mathbf{X}(\kappa k) \otimes \mathbf{F}(l\kappa k)] \end{aligned} \quad (1d)$$

where $\mathbf{F}(l\kappa k)$ is the the force on atom k associated with molecule κ in cell l . Also \mathcal{R} is an anti-symmetric matrix defined as

$$\mathcal{R}(\kappa k) = \begin{pmatrix} 0 & X_z & -X_y \\ -X_z & 0 & X_x \\ X_y & -X_x & 0 \end{pmatrix} \quad (2)$$

where the X_α is the α coordinate of the position of atom k with respect to the CM of molecule κ .

The atomic-to-molecular transformations of the force-constants above can be directly used for interaction between two distinct molecules because it consists of atomic force constants between distinct atoms (which can be expressed as second derivatives). However, for molecular self terms, the transformation can be divided into self and non-self atomic terms as follows

$$\phi^{tt}(l\kappa; l\kappa) = \sum_k \phi(l\kappa k; l\kappa k) + \sum_{k \neq k'} \phi(l\kappa k; l\kappa k') \quad (3a)$$

$$\begin{aligned} \phi^{tr}(l\kappa; l\kappa) &= \sum_k \phi(l\kappa k; l\kappa k) \mathcal{R}(\kappa k) \\ &+ \sum_{k \neq k'} \phi(l\kappa k; l\kappa k') \mathcal{R}(\kappa k') \end{aligned} \quad (3b)$$

$$\begin{aligned} \phi^{rt}(l\kappa; l\kappa) &= \sum_k \mathcal{R}^T(\kappa k) \phi(l\kappa k; l\kappa k) \\ &+ \sum_{k \neq k'} \mathcal{R}^T(\kappa k) \phi(l\kappa k; l\kappa k') \end{aligned} \quad (3c)$$

$$\begin{aligned} \phi^{rr}(l\kappa; l\kappa) &= \sum_k \mathcal{R}^T(\kappa k) \phi(l\kappa k; l\kappa k) \mathcal{R}(\kappa k) \\ &+ \sum_{k \neq k'} \mathcal{R}^T(\kappa k) \phi(l\kappa k; l\kappa k') \mathcal{R}(\kappa k') \\ &+ \sum_k [\mathbf{X}(\kappa k) \cdot \mathbf{F}(l\kappa k) \mathbf{I}_3 - \mathbf{X}(\kappa k) \otimes \mathbf{F}(l\kappa k)] \end{aligned} \quad (3d)$$

where $\phi(l\kappa k; l\kappa k)$ is the self atomic force-constant tensor of atom k ; which is given by the sum rule as follows

$$\phi(l\kappa k; l\kappa k) = - \sum_{\substack{l'\kappa'k' \\ \kappa' \neq \kappa}} \phi(l\kappa k; l'\kappa'k') \quad (4)$$

Atomic Hessian matrix of TIP4P water model

The atomic force-constant coefficient between atom k in cell l and atom k' in cell l' is defined as^{S4-S6}

$$\phi_{\alpha\beta}(lk; l'k') \equiv \left(\frac{\partial^2 U}{\partial u_\alpha(lk) \partial u_\beta(l'k')} \right)_0 \quad (5)$$

where it is assumed that the two atoms are different; *i.e.* non-self (Eq. (4) is used for self-terms). For clarity, lk and $l'k'$ atoms will be called i and j for the rest of this section.

The potential energy of the TIP4P water model can be decomposed into U_{LJ} , for Lennard-Jones O-O interactions, and U_{coul} for the Coulomb interactions between the other atoms; then

$$U = U_{\text{LJ}} + U_{\text{coul}} \quad (6)$$

Let us now start with the second derivatives of the LJ potential,

$$u_{ij,m} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij,m}} \right)^{12} - \left(\frac{\sigma}{r_{ij,m}} \right)^6 \right] \quad (7)$$

which is defined as

$$U_{\text{LJ}} = \sum_{i < j} \sum_m u_{ij,m} + \frac{1}{2} \sum_i \sum_{m \neq 0} u_{ii,m} \quad (8)$$

where $\mathbf{r}_{ij,m} = \mathbf{r}_i - \mathbf{r}_j + \mathbf{R}_m$, where \mathbf{R}_m is m 's supercell coordinate, which is defined in terms of the supercell lattice vectors, \mathbf{a}_i , as follows

$$\mathbf{R}_m = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3, \quad m_i = 0, 1, 2, \dots$$

Here, i and j sum over Lennard-Jones sites (oxygen atoms) in the supercell. The force on atom i is given as a first-derivative of (8) as follows

$$\mathbf{F}_i = - \sum_{\substack{j=1 \\ j \neq i}} \sum_m \frac{u'_{ij,m}}{r_{ij,m}} \mathbf{r}_{ij,m} \quad (9)$$

where, $u'_{ij,m}$ is the first derivative of $u_{ij,m}$. The respective $\alpha\beta$ component of the second derivative of ij atoms pair is given by

$$\phi_{\alpha\beta}^{LJ}(i, j) = \sum_m \left[\frac{v_{ij,m} - w_{ij,m}}{r_{ij,m}^4} r_{ij,m,\alpha} r_{ij,m,\beta} - \frac{v_{ij,m}}{r_{ij,m}^2} \delta_{\alpha\beta} \right] \quad (10)$$

where $v_{ij,m} \equiv r_{ij,m} u'_{ij,m}$, $w_{ij,m} \equiv r_{ij,m}^2 u''_{ij,m}$ and $\delta_{\alpha\beta}$ is the Kronecker delta function.

The long-range Coulomb interaction is treated using the Ewald summation (ES) method.^{S7,S8} The ES potential energy of a molecular system modeled as point charges (*e.g.* TIP4P) is given by

$$U = U_{\text{real}} + [U_{\text{rec}} - U_{\text{intra}}] - U_{\text{self}} \quad (11)$$

where U_{real} and U_{rec} are the ES in the real and reciprocal spaces, respectively, and U_{self} is the correction for the self interactions. Since in the standard ES method the reciprocal summation assumes only point charges, then an additional term, $-U_{\text{intra}}$, has to be added to cancel out the intramolecular interactions considered in U_{rec} . The ES energy contributions are given by

$$U_{\text{real}} = \sum_{\substack{i < j \\ i, j \notin \text{same mol.}}} \sum_m Q_i Q_j \frac{\text{erfc}(\alpha r_{ij,m})}{r_{ij,m}} + \frac{1}{2} \sum_i \sum_{m \neq 0} Q_i^2 \frac{\text{erfc}(\alpha r_{ii,m})}{r_{ii,m}} \quad (12a)$$

$$U_{\text{rec}} = \frac{2\pi}{V} \sum_{\mathbf{G} \neq 0} \frac{\exp[-(G/2\alpha)^2]}{G^2} \left| \sum_{j=1} Q_j e^{i\mathbf{G} \cdot \mathbf{r}_j} \right|^2 \quad (12b)$$

$$U_{\text{self}} = \frac{\alpha}{\sqrt{\pi}} \sum_{j=1} Q_j^2 \quad (12c)$$

$$U_{\text{intra}} = \sum_{\substack{i < j \\ i, j \in \text{same mol.}}} Q_i Q_j \frac{\text{erf}(r_{ij})}{r_{ij}} \quad (12d)$$

where α is an adjustable parameter (not to be confused with the coordinate summation index), Q_j is the charge of point j ; \mathbf{G} is the supercell wave vector, $G \equiv |\mathbf{G}|$. The forces on

atom i due to ES potential are given by

$$\mathbf{F}_i = \mathbf{F}_i^{\text{real}} + \mathbf{F}_i^{\text{rec}} - \mathbf{F}_i^{\text{intra}}$$

where the individual components are the negative of the first derivative of ES contributions (*i.e.* Eqs. (12))

$$\mathbf{F}_i^{\text{real}} = \sum_{\substack{j=1 \\ j \neq i}} \sum_m \frac{Q_i Q_j}{r_{ij,m}^3} \left(\text{erfc}(\alpha r_{ij,m}) + \frac{2\alpha r_{ij,m}}{\sqrt{\pi}} \right) \mathbf{r}_{ij,m} \quad (13a)$$

$$\mathbf{F}_i^{\text{rec}} = \frac{4\pi Q_i}{V} \sum_{\mathbf{G} \neq 0} \mathbf{G} \frac{\exp(-G^2/4\alpha^2)}{G^2} \sum_{\substack{j=1 \\ j \neq i}} \sum_m Q_j \sin(\mathbf{G} \cdot \mathbf{r}_{ij,m}) \quad (13b)$$

$$\mathbf{F}_i^{\text{intra}} = \sum_{\substack{j \in \text{same mol.} \\ j \neq i}} Q_i Q_j \left(\frac{\text{erf}(\alpha r_{ij})}{r_{ij}} - \frac{2\alpha}{\sqrt{\pi}} \exp(-\alpha^2 r_{ij}^2) \right) \frac{\mathbf{r}_{ij}}{r_{ij}^2} \quad (13c)$$

The respective $\alpha\beta$ component of the second derivatives of ij atoms pair is, then, given by

$$\phi_{\alpha\beta}^{\text{ES}}(ij) = \phi_{\alpha\beta}^{\text{real}}(ij) + [\phi_{\alpha\beta}^{\text{rec}}(ij) - \phi_{\alpha\beta}^{\text{intra}}(ij)] \quad (14)$$

where

$$\begin{aligned} \phi_{\alpha\beta}^{\text{real}}(ij) &= \sum_m Q_i Q_j \left[\left(\frac{\text{erfc}(\alpha r_{ij,m})}{r_{ij,m}^3} + \frac{2\alpha \exp(-\alpha^2 r_{ij,m}^2)}{\sqrt{\pi} r_{ij,m}^2} \right) \delta_{\alpha\beta} - r_{ij,m,\alpha} r_{ij,m,\beta} \right. \\ &\quad \times \left. \left(\frac{6\alpha \exp(-\alpha^2 r_{ij,m}^2)}{\sqrt{\pi} r_{ij,m}^4} + \frac{4\alpha^3 \exp(-\alpha^2 r_{ij,m}^2)}{\sqrt{\pi} r_{ij,m}^2} + 3 \frac{\text{erfc}(\alpha r_{ij,m})}{r_{ij,m}^5} \right) \right] \quad (15a) \end{aligned}$$

$$\phi_{\alpha\beta}^{\text{rec}}(ij) = Q_i Q_j \frac{4\pi}{V} \sum_{\mathbf{G} \neq 0} G_\alpha G_\beta \cos(\mathbf{G} \cdot \mathbf{r}_{ij}) \frac{\exp(-G^2/4\alpha^2)}{G^2} \quad (15b)$$

$$\begin{aligned} \phi_{\alpha\beta}^{\text{intra}}(ij) &= Q_i Q_j \left[\left(\frac{\text{erf}(\alpha r_{ij})}{r_{ij}^3} - \frac{2\alpha \exp(-\alpha^2 r_{ij}^2)}{\sqrt{\pi} r_{ij}^2} \right) \delta_{\alpha\beta} + r_{ij,\alpha} r_{ij,\beta} \right. \\ &\quad \times \left. \left(\frac{6\alpha \exp(-\alpha^2 r_{ij}^2)}{\sqrt{\pi} r_{ij}^4} + \frac{4\alpha^3 \exp(-\alpha^2 r_{ij}^2)}{\sqrt{\pi} r_{ij}^2} - 3 \frac{\text{erf}(\alpha r_{ij})}{r_{ij}^5} \right) \right] \quad (15c) \end{aligned}$$

It is interesting to notice here that although there are no explicit intramolecular interac-

tions within rigid molecules, their respective force constants do not vanish when ES is used. This is because the reciprocal part of ES assumes infinite system of periodic images of the supercells. Therefore, all other images contribute with finite values to the intramolecular force constants.

References

- (S1) Venkataraman, G.; Sahni, V. C. *Rev. Mod. Phys.* **1970**, *42*, 409–470.
- (S2) Chaplot, S.; Sahni, V.; Rao, K. *Acta Crystallogr. Sect. A* **1981**, *37*, 374–377.
- (S3) Dasgupta, S.; Sengupta, S. *J. Phys. C: Solid State Phys.* **1987**, *20*, 1611–1617.
- (S4) Dove, M. T. *Introduction to Lattice Dynamics*; Cambridge University Press: New York, 2005.
- (S5) Maradudin, A. A.; Montroll, E. W.; Weiss, G. H.; Ipatova, I. P. *Theory of Lattice Dynamics in the Harmonic Approximation*, 2nd ed.; Solid State Physics; Academic Press: New York, 1971; Vol. Supplement 3.
- (S6) Born, M.; Huang, K. *Dynamical Theory of Crystal Lattices*; International series of monographs on physics; Clarendon Press, 1954.
- (S7) Ewald, P. P. *Annalen der Physik* **1921**, *369*, 253–287.
- (S8) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic: San Diego, 2002.