Supporting Information for "Lattice Vibrations and Molecular Conformations in a Plastic Crystal: A Path to Solid-State Cooling Materials"

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FORCE FIELD DESCRIPTION AND PARAMETERS

To describe bulk NPG we use a force field of the CHARMM-type with potential energy function :

$$\begin{aligned} V_{\mathrm{NPG}}(\{\mathbf{r}_i\}) = & \sum_{\text{bonds}} k_b(b-b_0)^2 + \sum_{\text{angles}} k_\theta(\theta-\theta_0)^2 + \sum_{\text{dihedrals}} k_\chi\left[1+\cos(n\chi-\delta)\right] \\ & + \sum_{\text{impropers}} k_\phi(\phi-\phi_0)^2 + \sum_{\text{Urey-Bradley}} k_u(u-u_0)^2 \\ & + \sum_{\text{nonbonded}} \varepsilon_{ij}\left[\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{12} - \left(\frac{R_{\min,ij}}{r_{ij}}\right)^{6}\right] + \sum_{i<j} \frac{q_i q_j}{\varepsilon_r r_{ij}} \ , \end{aligned}$$

where k_b, k_θ, k_χ, k_ϕ and k_u are the bond, valence angle, dihedral angle, improper dihedral, and Urey-Bradley angle force constants, respectively. Accordingly, b, θ, χ, ϕ, and u are the bond length, bond angle, dihedral torsion angle, improper dihedral angle, and Urey–Bradley distance, respectively. Subindex “0” denotes equilibrium values. For the dihedral terms, n corresponds to multiplicity and δ to the phase, which dictates the location of the minima and maxima, respectively.

For the rest of terms, ε corresponds to the Lennard-Jones (LJ) well-depth, R_{min} to the interparticle distance at the LJ minimum interaction energy, q_i to the partial atomic charge and ε_r to the dielectric constant. The distance between atoms i and j is r_{ij}. The following tables show the values of all the force field parameters introduced above.

TABLE I. Lennard-Jones potential parameters where $\sigma = R_{min}/2^{1/6}$.

Label	**Description**	**σ (nm)**	**ε (kJ/mol)**
OR	Oxygen from a hydroxyl group	0.32	0.64
HOR	Hydrogen bonded to an oxygen	0.04	0.19
CR	Central or branched carbon	0.39	0.23
HCMM	Hydrogen bonded to methyl carbon	0.24	0.09

TABLE II. List of atoms with their assigned number, partial charge, q, and type.

#	**Atom**	**q (e)**	**Type**
1	O1	-0.68	OR
2	H1	0.40	HOR
3	O2	-0.68	OR
4	H2	0.40	HOR
5	C1	0.28	CR
6	H1A	0.00	HCMM
7	H1B	0.00	HCMM
8	C2	0.00	CR
9	C3	0.28	CR
10	H3A	0.00	HCMM
11	H3B	0.00	HCMM
12	C4	0.00	CR
13	H4A	0.00	HCMM
14	H4B	0.00	HCMM
15	H4C	0.00	HCMM
16	C5	0.00	CR
17	H5A	0.00	HCMM
18	H5B	0.00	HCMM
19	H5C	0.00	HCMM

TABLE III. $\{a_i\}$ correspond to the atoms indexes, as established in Table II. f_u is the function type. ϕ_0 and k_ϕ are the equilibrium improper dihedral and the improper dihedral constant, respectively.

a_i	a_j	a_k	a_l	f_u	ϕ_0 **(deg)**	k_ϕ **(kJ·mol^{-1}·rad^{-2})**	**Multiplicity**
1	5	8	9	9	0	-1.44	1
1	5	8	9	9	180	3.68	2
1	5	8	9	9	0	1.00	3
1	5	8	12	9	0	-1.44	1
1	5	8	12	9	180	3.68	2
1	5	8	12	9	0	1.00	3
1	5	8	16	9	0	-1.44	1
1	5	8	16	9	180	3.68	2
1	5	8	16	9	0	1.00	3
2	1	5	6	9	0	1.25	1
2	1	5	6	9	180	-0.58	2
2	1	5	6	9	0	0.72	3
2	1	5	7	9	0	1.25	1
2	1	5	7	9	180	-0.58	2
2	1	5	7	9	0	0.72	3
2	1	5	8	9	180	0.56	2
2	1	5	8	9	0	0.49	3
3	9	8	5	9	0	-1.44	1
3	9	8	5	9	180	3.68	2
3	9	8	5	9	0	1.00	3
3	9	8	12	9	0	-1.44	1
3	9	8	12	9	180	3.68	2
3	9	8	12	9	0	1.00	3
3	9	8	16	9	0	-1.44	1
3	9	8	16	9	180	3.68	2
3	9	8	16	9	0	1.00	3
4	3	9	8	9	180	0.56	2
4	3	9	8	9	0	0.49	3
4	3	9	10	9	0	1.25	1
4	3	9	10	9	180	-0.58	2
4	3	9	10	9	0	0.72	3
4	3	9	11	9	0	1.25	1
4	3	9	11	9	180	-0.58	2
4	3	9	11	9	0	0.72	3
5	8	9	10	9	0	1.34	1
5	8	9	10	9	180	-1.32	2
5	8	9	10	9	0	0.55	3
5	8	9	11	9	0	1.34	1

TABLE IV. $\{a_i\}$ correspond to the atoms indexes, as established in Table II. f_u is the function type. ϕ_0 and k_ϕ are the equilibrium improper dihedral and the improper dihedral constant, respectively (continuation of previous table).

a_i	a_j	a_k	a_l	f_u	ϕ_0 **(deg)**	k_ϕ **(kJ·mol^{-1}·rad^{-2})**	**Multiplicity**
5	8	9	11	9	180	-1.32	2
5	8	9	11	9	0	0.55	3
5	8	12	13	9	0	1.34	1
5	8	12	13	9	180	-1.32	2
5	8	12	13	9	0	0.55	3
5	8	12	14	9	0	1.34	1
5	8	12	14	9	180	-1.32	2
5	8	12	14	9	0	0.55	3
5	8	12	15	9	0	1.34	1
5	8	12	15	9	180	-1.32	2
5	8	12	15	9	0	0.55	3
5	8	16	17	9	0	1.34	1
5	8	16	17	9	180	-1.32	2
5	8	16	17	9	0	0.55	3
5	8	16	18	9	0	1.34	1
5	8	16	18	9	180	-1.32	2
5	8	16	18	9	0	0.55	3
5	8	16	19	9	0	1.34	1
5	8	16	19	9	180	-1.32	2
5	8	16	19	9	0	0.55	3
6	5	8	9	9	0	1.34	1
6	5	8	9	9	180	-1.32	2
6	5	8	9	9	0	0.55	3
6	5	8	12	9	0	1.34	1
6	5	8	12	9	180	-1.32	2
6	5	8	12	9	0	0.55	3
6	5	8	16	9	0	1.34	1
6	5	8	16	9	180	-1.32	2
6	5	8	16	9	0	0.55	3
7	5	8	9	9	0	1.34	1
7	5	8	9	9	180	-1.32	2

TABLE V. $\{a_i\}$ correspond to the atoms indexes, as established in Table II. f_u is the function type. θ_0 and k_θ are the equilibrium improper dihedral and the improper dihedral constant. u_0 and k_u are the Urey–Bradley equilibrium distance and the Urey–Bradley constant, respectively.

a_i	a_j	a_k	f_u	θ_0 **(deg)**	k_θ **(kJ·mol^{-1}·rad^{-2})**	u_0 **(deg)**	k_u **(kJ·mol^{-1}·rad^{-2})**
2	1	5	1	106.50	477.55	106.50	477.55
4	3	9	1	106.50	477.55	106.50	477.55
1	5	6	1	108.58	470.32	108.58	470.32
1	5	7	1	108.58	470.32	108.58	470.32
1	5	8	1	108.13	597.39	108.13	597.39
6	5	7	1	108.84	310.74	108.84	310.74
6	5	8	1	110.55	383.00	110.55	383.00
7	5	8	1	110.55	383.00	110.55	383.00
5	8	9	1	109.61	512.48	109.61	512.48
5	8	12	1	109.61	512.48	109.61	512.48
5	8	16	1	109.61	512.48	109.61	512.48
9	8	12	1	109.61	512.48	109.61	512.48
9	8	16	1	109.61	512.48	109.61	512.48
12	8	16	1	109.61	512.48	109.61	512.48
3	9	8	1	108.13	597.39	108.13	597.39
3	9	10	1	108.58	470.32	108.58	470.32
3	9	11	1	108.58	470.32	108.58	470.32
8	9	10	1	110.55	383.00	110.55	383.00
8	9	11	1	110.55	383.00	110.55	383.00
10	9	11	1	108.84	310.74	108.84	310.74
8	12	13	1	110.55	383.00	110.55	383.00
8	12	14	1	110.55	383.00	110.55	383.00
8	12	15	1	110.55	383.00	110.55	383.00
13	12	14	1	108.84	310.74	108.84	310.74
13	12	15	1	108.84	310.74	108.84	310.74
14	12	15	1	108.84	310.74	108.84	310.74
8	16	17	1	110.55	383.00	110.55	383.00
8	16	18	1	110.55	383.00	110.55	383.00
8	16	19	1	110.55	383.00	110.55	383.00
17	16	18	1	108.84	310.74	108.84	310.74
17	16	19	1	108.84	310.74	108.84	310.74
18	16	19	1	108.84	310.74	108.84	310.74

TABLE VI. $\{a_i\}$ correspond to the atoms indexes, as established in Table II. f_u is the function type; b_0 and k_b are the equilibrium bond length and the bond constant, respectively.

a_i	a_j	**fu**	b_0 **(nm)**	k_b **(kJ·mol^{-1}·nm^{-2})**
1	2	1	0.09720	469365.3
1	5	1	0.14180	303937.5
3	4	1	0.09720	469365.3
3	9	1	0.14180	303937.5
5	6	1	0.10930	287014.9
5	7	1	0.10930	287014.9
5	8	1	0.15080	256422.3
8	9	1	0.15080	256422.3
8	12	1	0.15080	256422.3
8	16	1	0.15080	256422.3
9	10	1	0.10930	287014.9
9	11	1	0.10930	287014.9
12	13	1	0.10930	287014.9
12	14	1	0.10930	287014.9
12	15	1	0.10930	287014.9
16	17	1	0.10930	287014.9
16	18	1	0.10930	287014.9
16	19	1	0.10930	287014.9