The QMFF-Cx forcefield for carbon validated to reproduce the mechanical and thermodynamics properties of Graphite

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Supplementary Materials

TABLES

Table S.I. Experimental structural and elastic properties of Graphite.

	300K[a]	300K-> 0K[b]	0K
Lattice Parameters (Å)[c]			
a	2.4612	0.0072	2.4684
c	6.7090	-0.0369	6.6721
Elastic Constants (GPa)			
C_{11}	1060±20	66±8	1126±22
C_{12}	180±20	20±2.5	200±20
C_{33}	36.5±1	4.2±0.5	40.7±1.1
C_{44}	4.5±0.5	0.01±0.001	4.51±0.5
C_{13}	15±5	23.8±40	39.5±40
Young's Moduli (GPa)			
E_1	1020±30		
E_3	36.5±1.0		
Poisson Ratios			
μ_{21}	0.16±0.06		
μ_{31}	0.34±0.08		
μ_{13}	0.012±0.003		

[a] See Donohue[15] and Blakslee et al.[17]
[b] See Bailey and Yates[16] and Gauster and Fritz[24]
[c] 298K was used instead of 300K

Table S.II. Charges (e^-) on the PD-X orientation of the DHC dimer at equilibrium, determined using three different charge schemes. The 6-311+G(2d,2p) basis set was used. These values are compared to that of the coronene dimer, reported in Ref[28]. We selected the ESP charges on the dimer when fitting to QMFF-Cx forcefield.

	Monomer			|ΔDimer[b]|		
Atom[a]	**Mulliken**	**ESP**	**CM4[c]**	**Mulliken**	**ESP**	**CM4**
C1	-0.0071	-0.0025	0.01	0.0035	0.0026	0.004
C2	-0.0500	0.0120	-0.01	0.0027	0.0030	0.004
C3	0.0281	-0.0048	-0.07	0.0031	5.0×10^{-5}	0.007
H			0.07			0.003

[a] C1 – 6 carbons of the innermost benzene ring, C2 – 6 sp^3 carbons not bound to H atoms, C3 – remaining 12 outermost carbons (bound to H atoms in the case of coronene)
[b] Average dimer charges of the PD-X configuration at the interaction minima (Δx = 1.45Å, Δz = 3.408Å)
[c] As reported in Ref.[28]
[d] Absolute value of change in dimer charge was reported

Table S.III. Comparison of binding energies (kcal/mol) with and without counterpoise corrections (cp) of DHC using various basis sets. Singlepoint calculations were performed at the equilibrium geometry obtained from 6-311G+(2d,2p) optimization. The calculated graphite cohesive energy is obtained by fitting the energies and forces of the PD-X structure to a LJ 12-6 potential. The convergence criteria were $5x10^{-5}$ Hartree for the energy and $5x10^{-6}$ rms for the density matrix.

	# basis funcs	PD-X		PD-Y		Eclipsed		[a] E_{coh}
		ΔE	ΔE_{cp}	ΔE	ΔE_{cp}	ΔE	ΔE_{cp}	
Pople								
6-31G(2,p)	720	-19.43	-13.94	-18.75	-13.39	-11.48	-6.79	-0.99
6-311G(2d,2p)	864	-20.04	-15.03	-19.18	-14.12	-12.12	-8.26	-1.07
6-311G(3df,3pd)	1680	-21.45	-16.93	-22.76	-18.00	-13.31	-9.28	-1.16
Pople + diffuse								
6-31+G(2,p)	912	-20.50	-15.28	-19.58	-14.81	-12.13	-7.12	-1.09
6-311+G(2d,2p)	1056	-22.10	-16.73	-21.29	-16.07	-15.06	-10.68	-1.20
6-311+G(3df,3pd)	1872	-23.81	-18.08	-22.20	-16.53	-16.78	-12.02	-1.35
Dunning								
cc-pvdz(-d)	432	-23.78	-19.82	-22.87	-19.20	-15.41	-12.91	-1.43
cc-pvdz	672	-21.85	-17.78	-20.92	-17.34	-14.34	-11.07	-1.28
cc-pvtz(-f)	1104	-20.73	-17.67	-20.03	-16.95	-12.81	-10.19	-1.27
cc-pvtz	1440	-20.39	-17.34	-19.48	-16.40	-12.10	-9.22	-1.17
cc-pvqz(-g)	2208	-18.07	-16.89	-17.88	-16.36	-10.70	-9.66	-1.11
Dunning + diffuse								
cc-pvdz(-d)+	624	-25.31	-19.01	-24.53	-18.30	-17.01	-10.82	-1.37
cc-pvdz+	1104	-22.49	-18.59	-21.81	-17.96	-15.12	-11.37	-1.34
cc-pvtz(-f)+	1536	-20.71	-17.90	-21.10	-18.07	-13.92	-11.20	-1.29
MIDIX	432	-30.77	-19.71	-29.84	-18.93	-20.25	-9.99	-1.42

[a] experimental cohesive energy of graphite is 1.19± 0.15 kcal/mol

Table S.IV. Mechanical properties at 0K for (hexagonal) Graphite using the QM-FF X6 potential with ζ = 16.1

C_{ij} Elastic Constant Matrix (Stiffness) GPa

$$\begin{pmatrix} 1126.29 & 195.79 & 0.113 & 0 & 0 & 0 \\ & 1126.32 & 0.113 & 0 & 0 & 0 \\ & & 39.80 & 0 & 0 & 0 \\ & & & 0.113 & 0 & 0 \\ & & & & 0.113 & 0 \\ & & & & & 453.24 \end{pmatrix}$$

S_{ij} Compliance Matrix GPa^{-1}

$$\begin{pmatrix} 9.16\times10^{-4} & -1.59\times10^{-4} & -2.00\times10^{-6} & 0 & 0 & 0 \\ & 9.16\times10^{-4} & -2.00\times10^{-6} & 0 & 0 & 0 \\ & & 2.51\times10^{-2} & 0 & 0 & 0 \\ & & & 8.83 & & \\ & & & & 8.82 & \\ & & & & & 2.15\times10^{-2} \end{pmatrix}$$

FIGURES

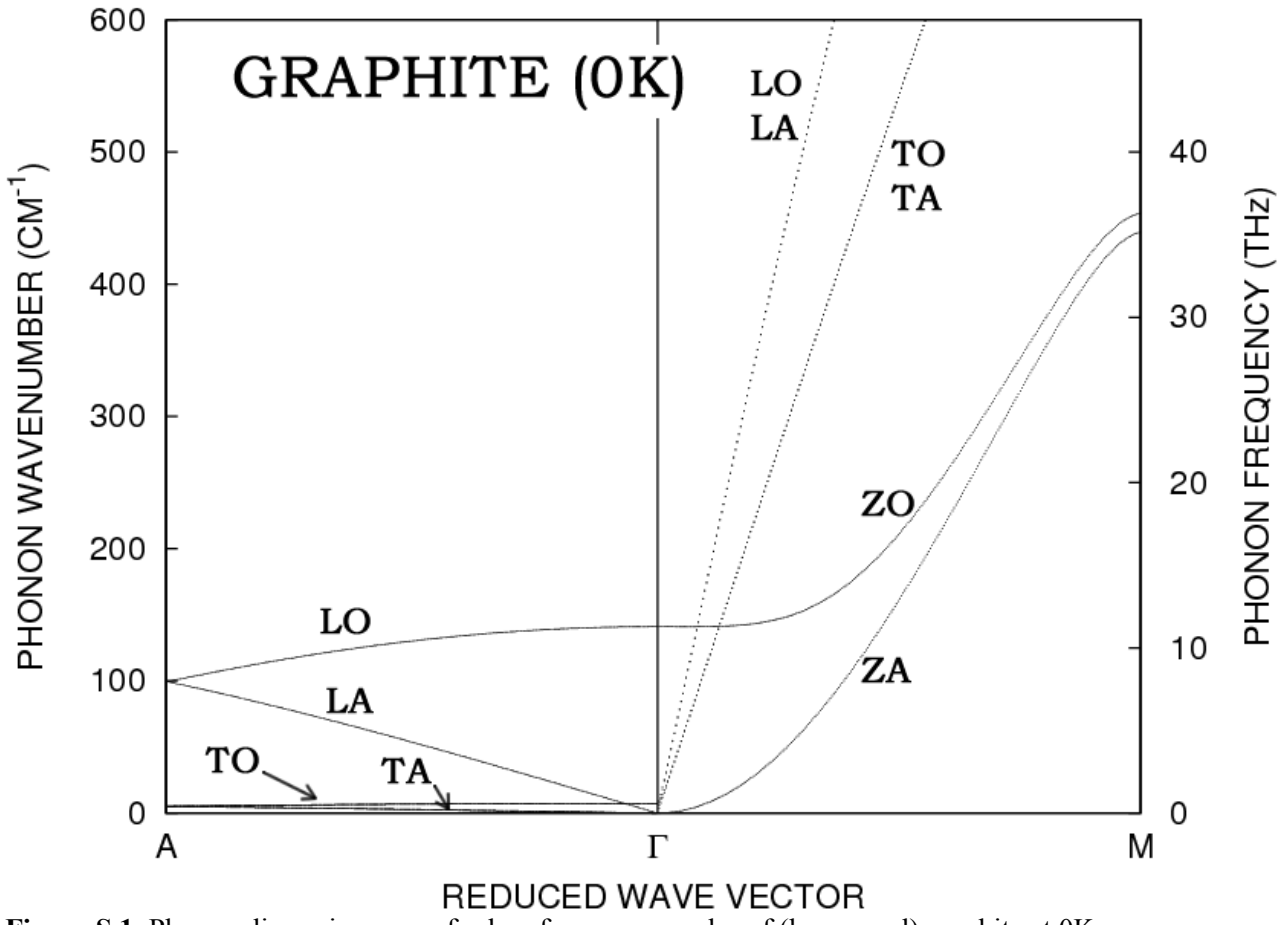


Figure S.1. Phonon dispersion curve for low frequency modes of (hexagonal) graphite at 0K

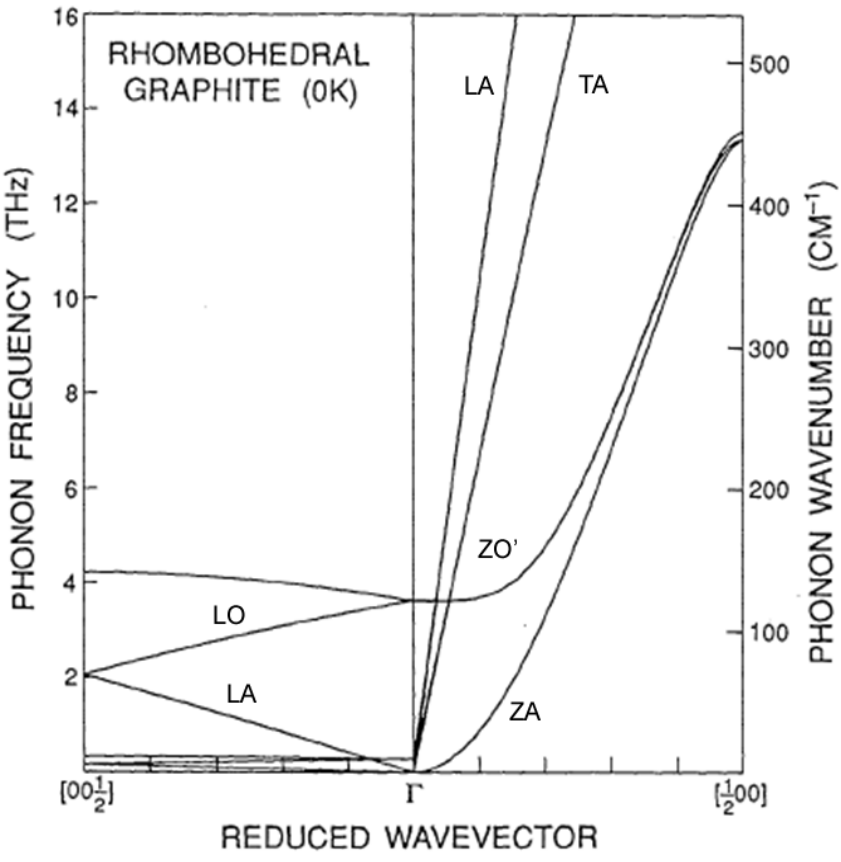
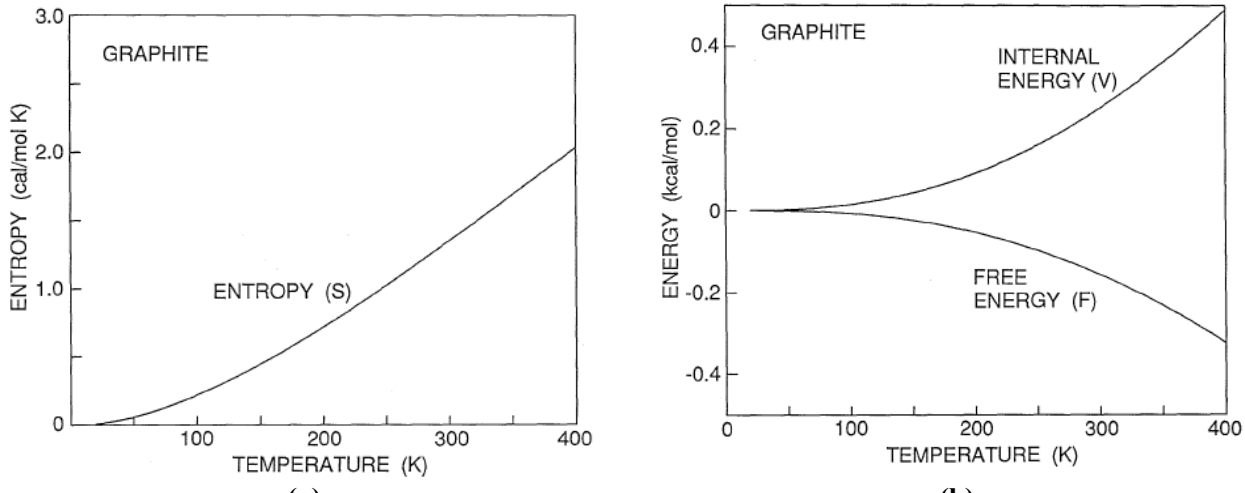


Figure S.2. Phonon dispersion curves for the low frequency modes of rhombohedral graphite at 0K (using the X6 potential)



(a) **(b)**

Figure S.3. (a) Vibrational entropy (S) of graphite (b) Vibrational internal energy (V) and free energy (F) of graphite