

# The Phase Diagram of Carbon Dioxide from Correlation Functions and a Many-body Potential

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## Supplementary Information

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## A. Computational Approach

### 1. Calculation of the Density of State (DoS) function

The density of state function,  $S(\nu)$ , is defined as the sum of the contribution from mass weighted atomic densities of all atoms in the system: [1, 2]

$$S(\nu) = (2/kT) \sum_{j=1}^N \sum_{k=1}^3 m_j S_j^k(\nu) \quad (\text{S-1})$$

where  $N$  is the total number of atoms in the system,  $m_j$  is the mass of atom  $j$ ,  $S_j^k(\nu)$  is the spectral density of atom  $j$  in  $k^{\text{th}}$  coordinate (In Cartesian coordinate,  $k = x, y, z$ ). By applying a Fourier transform to eqn S-1, we obtain the frequency-dependent spectrum:

$$S_j^k(\nu) = \lim_{\tau \rightarrow \infty} 1/(2\tau) \left| \int_{-\tau}^{\tau} v_j^k(t) \exp(-i2\pi\nu t) dt \right|^2 \quad (\text{S-2})$$

where  $v_j^k(t)$  is the velocity of atom  $j$  in  $k$  direction at time  $t$ .

The density of state function,  $S(\nu)$ , is calculated by combining eqns S-1 and S-2:

$$S(\nu) = (1/kT) \sum_{j=1}^N \sum_{k=1}^3 \lim_{\tau \rightarrow \infty} m_j/\tau \left| \int_{-\tau}^{\tau} v_j^k(t) \exp(-i2\pi\nu t) dt \right|^2 \quad (\text{S-3})$$

$$\begin{aligned} \int_0^{\infty} S(\nu) d\nu &= (1/2) \int_{-\infty}^{\infty} S(\nu) d\nu \\ &= (1/kT) \sum_{j=1}^N \sum_{k=1}^3 \overline{m_j v_j^k(t)^2} \\ &= (1/kT) \sum_{j=1}^N \sum_{k=1}^3 kT = 3N \end{aligned} \quad (\text{S-4})$$

where the integration of  $S(\nu)$  is equal to the total number degree of freedom of the system in eqn S-4.

The relationship between the density of state function,  $S(\nu)$ , the velocity correlation function,  $C(t)$ , and self-diffusion coefficient,  $D$  is given by eqns S-5 – S-7:

$$S(\nu) = (2/kT) \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} C(t) \exp(-i2\pi\nu t) dt \quad (\text{S-5})$$

$$D = (1/3) \int_{-\infty}^{\infty} C(t) dt = (1/6mN) \int_{-\infty}^{\infty} C(t) dt \quad (\text{S-6})$$

$$S(0) = (2/kT) \int_{-\infty}^{\infty} C(t) dt = 12mND / kT \quad (\text{S-7})$$

For a polyatomic molecule system, the DoS function is decomposed into translation, rotation, and vibration motions, which are assumed to be independent, so that we can write the total DoS as a sum of the individual DoS functions:

$$S(\nu) = S_{\text{trans}}(\nu) + S_{\text{rot}}(\nu) + S_{\text{vib}}(\nu) \quad (\text{S-8})$$

We calculate  $S_{\text{trans}}(\nu)$  and  $S_{\text{rot}}(\nu)$  by integrating over the respective functions:

$$S_{\text{trans}}(\nu) = (1/kT) \sum_{j=1}^M \sum_{k=1}^3 \lim_{\tau \rightarrow \infty} m_j/\tau \left| \int_{-\tau}^{\tau} v_j^k(t) \exp(-i2\pi\nu t) dt \right|^2 \quad (\text{S-9-a})$$

$$S_{\text{rot}}(\nu) = (1/kT) \sum_{j=1}^M \sum_{k=1}^3 \lim_{\tau \rightarrow \infty} I_j^k/\tau \left| \int_{-\tau}^{\tau} \omega_j^k(t) \exp(-i2\pi\nu t) dt \right|^2 \quad (\text{S-9-b})$$

where the  $M$  is total number of molecules in the system,  $m_j$  is the mass of molecule  $j$ .  $I_j^k$ ,  $v_j^k$  and  $\omega_j^k$  are the principle moments of inertia, the center of mass velocity and the angular velocity of molecule  $j$  in the  $k^{\text{th}}$  dimension, respectively. [2, 3]

## 2. Obtaining Thermodynamic Properties from the 2PT Method

The 2PT method approximate the total DoS into a linear combination of the DoSs of a solid and gas subsystem. This builds upon an early idea of Ree and Eyring[4] and early work by Wilson and co-workers[5]. The main idea is that the thermodynamics of each subsystem can be obtained straightforwardly using statistical thermodynamics and standard numerical techniques, with the only variable being the fraction of the liquid state that is “purely diffusive”, i.e. resides in the gas subsystem.

To start, we first consider the solid subsystem, and see that we can obtain the canonical partition function,  $Q$ , from the  $S(\nu)$ , assuming a Debye vibrating crystal: [1]

$$\ln Q = \int_0^{\infty} d\nu S(\nu) \ln q(\nu) \quad (\text{S-10})$$

where  $q = (\exp(-\beta h\nu/2) / (1 - \exp(-\beta h\nu/2)))$ ,  $\beta = 1/kT$  is the thermodynamic temperature, and  $h$  is Plank’s constant. The energy,  $E$ , entropy,  $S$ , Helmholtz free energy,  $A$ , constant volume heat capacity,  $C_v$  can then be obtained by numerical integration with the appropriate weighting functions: [2, 3]

$$E^S = E_o + T\beta^{-1} (\partial \ln Q / \partial T)_{N,V} = E_o + \beta^{-1} \int_0^{\infty} d\nu S(\nu) W_E(\nu) \quad (\text{S-11-a})$$

$$S^S = k \ln Q + \beta^{-1} (\partial \ln Q / \partial T)_{N,V} = k \int_0^{\infty} d\nu S(\nu) W_S(\nu) \quad (\text{S-11-b})$$

$$A^S = E_o - \beta^{-1} \ln Q = E_o + \beta^{-1} \int_0^{\infty} d\nu S(\nu) W_A(\nu) \quad (\text{S-11-c})$$

$$C_v^S = (\partial E / \partial T) \quad (\text{S-11-d})$$

$$W_E^S(\nu) = \beta h\nu/2 + \beta h\nu / (\exp(\beta h\nu) - 1) \quad (\text{S-12-a})$$

$$W_S^S(\nu) = \beta h\nu / (\exp(\beta h\nu) - 1) - \ln[1 - \exp(-\beta h\nu)] \quad (\text{S-12-b})$$

$$W_A^S(\nu) = \ln[(1 - \exp(\beta h\nu)) / (\exp(-\beta h\nu/2))] \quad (\text{S-12-c})$$

$$W_{C_v}^S(\nu) = [(\beta h\nu)^2 \exp(\beta h\nu)] / [\exp(-\beta h\nu) - 1]^2 \quad (\text{S-12-d})$$

For the gas subsystem, the DoS decays monotonically with frequency. Lin and co-workers found that for polyatomic molecules systems, the properties and weighting functions of gas portion can be decomposed into translation (trans), rotation (rot) and vibration (vib) motion, shown in eqn S-13.

$$S^g(\nu) = S_{\text{trans}}^g(\nu) + S_{\text{rot}}^g(\nu) + S_{\text{vib}}^g(\nu) \quad (\text{S-13})$$

where the superscript  $g$  means gas-like portion.

Besides, in 2PT model, it is assumed that all diffusive motion is included in gas-like portion, thus  $S(0) = S^g(0)$ , and all vibration motion is included in solid-like mode, indicating  $S_{\text{vib}}(\nu) = S_{\text{vib}}^S(\nu)$ . Based on these assumptions, the entropy of gas-like portion is further determined by  $S(0)$  and its fluidicity factor,  $f$ .

$$S_m^g(\nu) = S_m(0) / [1 + ((\pi\nu S_m(\nu)) / (6f_m M))^2] \quad (\text{S-14})$$

where the  $m$  means translation, rotation or vibration mode,  $S_m(0)$  is the zero point entropy on  $m$  mode and  $f_m$  is the fluidicity factor which is determined by eqns S-15 – S-16.

$$2\Delta_m^{-9/2}f_m^{15/2}-6\Delta_m^{-3}f_m^5-\Delta_m^{-3/2}f_m^{7/2}+6\Delta_m^{-3/2}f_m^{5/2}+2f_m^{-2}=0 \quad (\text{S-15})$$

$$\Delta_m = [(2S_m(0))/(9M)] [\pi kT/m]^{1/2} [N/V]^{1/3} [6/\pi]^{2/3} \quad (\text{S-16})$$

Thus, the total energy, entropy, free energy, and heat capacity relation can be derived as eqn S-17.

$$E_m = \beta^{-1} \left[ \int_0^\infty dv S_m^S(v) W_{m,E}^S(v) + \int_0^\infty dv S_m^g(v) W_{m,E}^g(v) \right] \quad (\text{S-17-a})$$

$$S_m = k \left[ \int_0^\infty dv S_m^S(v) W_{m,S}^S(v) + \int_0^\infty dv S_m^g(v) W_{m,S}^g(v) \right] \quad (\text{S-17-b})$$

$$A_m = \beta^{-1} \left[ \int_0^\infty dv S_m^S(v) W_{m,A}^S(v) + \int_0^\infty dv S_m^g(v) W_{m,A}^g(v) \right] \quad (\text{S-17-c})$$

$$C_{v,m} = k \left[ \int_0^\infty dv S_m^S(v) W_{m,Cv}^S(v) + \int_0^\infty dv S_m^g(v) W_{m,Cv}^g(v) \right] \quad (\text{S-17-d})$$

To obtain the weighting function of gas-like portion, the hard sphere particle assumption is applied, and the values are calculated by eqn S-18.

$$W_{rot,E}^g(v) = W_{trans,E}^g(v) = W_{trans,Cv}^g(v) = W_{rot,Cv}^g(v) = 0.5 \quad (\text{S-18-a})$$

$$W_{trans,S}^g(v) = (1/3) (S^{HS}/k) \quad (\text{S-18-b})$$

$$W_{rot,S}^g(v) = (1/3) (S^R/k) \quad (\text{S-18-c})$$

$$W_{rot,A}^g(v) = W_{rot,E}^g(v) - W_{rot,S}^g(v) \quad (\text{S-18-d})$$

where  $S^{HS}$  is the hard sphere entropy and  $S^R$  is the rotation entropy at ideal gas state, which are defined in eqn S-19.

$$S^{HS}/k = 5/2 + \ln \{ [(2\pi mkT) / h^2]^{3/2} [V / (f_{trans}N)] z(y) \} + y(3y-4)/(1-y)^2 \quad (\text{S-19-a})$$

$$S^R/k = 1 + \ln [ T / ( \sigma \theta_r ) ] \quad (\text{S-19-b})$$

with  $y = f_{trans}^{5/2} / \Delta_{rot}^{3/2}$ ,  $z(y)$  = the compressibility factor,  $\theta_r = h^2 / (8\pi I_r k)$  and  $\sigma$  = the symmetry number. The reference entropy,  $E_o$ , is obtained by eqn S-20. [3]

$$E_o = E^{MD} - \beta^{-1} 3N (1 - 0.5f_{trans} - 0.5f_{rot}) \quad (\text{S-20})$$

Based on the previous equations, properties of a system are determined by summing up the gas and solid contributions.

### 3. Obtaining partial atomic charges using Charge Equilibration (QEq)

Qeq theory is a method of predicting charge distributions that can respond to changes in a molecule's electrostatic environment. Before the equilibrium charge of a molecule can be determined, the charge-dependent energies of the individual atoms need to be determined, eqn S-21. [6]

$$E_A(Q) = E_{A0} + Q_A \left( \frac{\delta E}{\delta Q} \right)_{A0} + 1/2 Q_A^2 \left( \frac{\delta^2 E}{\delta Q^2} \right)_{A0} + \dots \quad (\text{S-21})$$

By removing all terms beyond the second order, the variables were written as derivatives with respect to Q:

$$\left( \frac{\delta E}{\delta Q} \right)_{A0} = 1/2 (IP + EA) = \chi_A^0 \quad (\text{S-22a})$$

$$\left(\frac{\delta^2 E}{\delta Q^2}\right)_{A0} = IP - EA = J_{AA}^0 \quad (\text{S-22b})$$

Where  $\chi_A^0$  is the electronegativity,  $J_{AA}^0$  is the Coulombic repulsion (also refers as the idempotential), IP is the ionization potential, and EA is the electron affinity.

$J_{AA}^0$  is approximately inversely proportional to the atomic radius ( $R_A^0$ ), as shown in eqn S-23.

$$J_{AA}^0 = \frac{14.4}{R_A^0} \quad (\text{S-23a})$$

$$R_A^0 = \frac{14.4}{J_{AA}^0} \quad (\text{S-23b})$$

where 14.4 is a conversion factor that allows  $J_{AA}^0$  to be in (eV) and  $R_A^0$  to be in (Å). [6]

The total electrostatic energy can be calculated with eqn S-24, where the  $\sum_{A < B} Q_A Q_B J_{AB}$  indicates as the interatomic electrostatic energy between atoms A and B.

$$E(Q_1 \dots Q_N) = \sum_A (E_{A0} + \chi_A^0 Q_A + 1/2 Q_A^2 J_{AA}^0) + \sum_{A < B} Q_A Q_B J_{AB} \quad (\text{S-24a})$$

Which can be rewritten as

$$E(Q_1 \dots Q_N) = \sum_A (E_{A0} + \chi_A^0 Q_A) + 1/2 \sum_{A,B} Q_A Q_B J_{AB} \quad (\text{S-24b})$$

The chemical potential can be found by taking the derivative of E with respect to Q

$$\chi_A(Q_1 \dots Q_N) = \frac{\delta E}{\delta Q_A} = \chi_A^0 + \sum_B J_{AB} Q_B \quad (\text{S-25a})$$

$$\chi_A(Q_1 \dots Q_N) = \chi_A^0 + J_{AA}^0 Q_A + \sum_{B \neq A} J_{AB} Q_B \quad (\text{S-25b})$$

where  $\chi_A(Q_1 \dots Q_N)$  is a function of the charges for all atoms. With the concepts that the equilibrium condition is met as all atomic chemical potentials are equal and the total charge is the sum of each atom-charge value, eqn S-26, the N Qeq equations are generated for the given molecule.

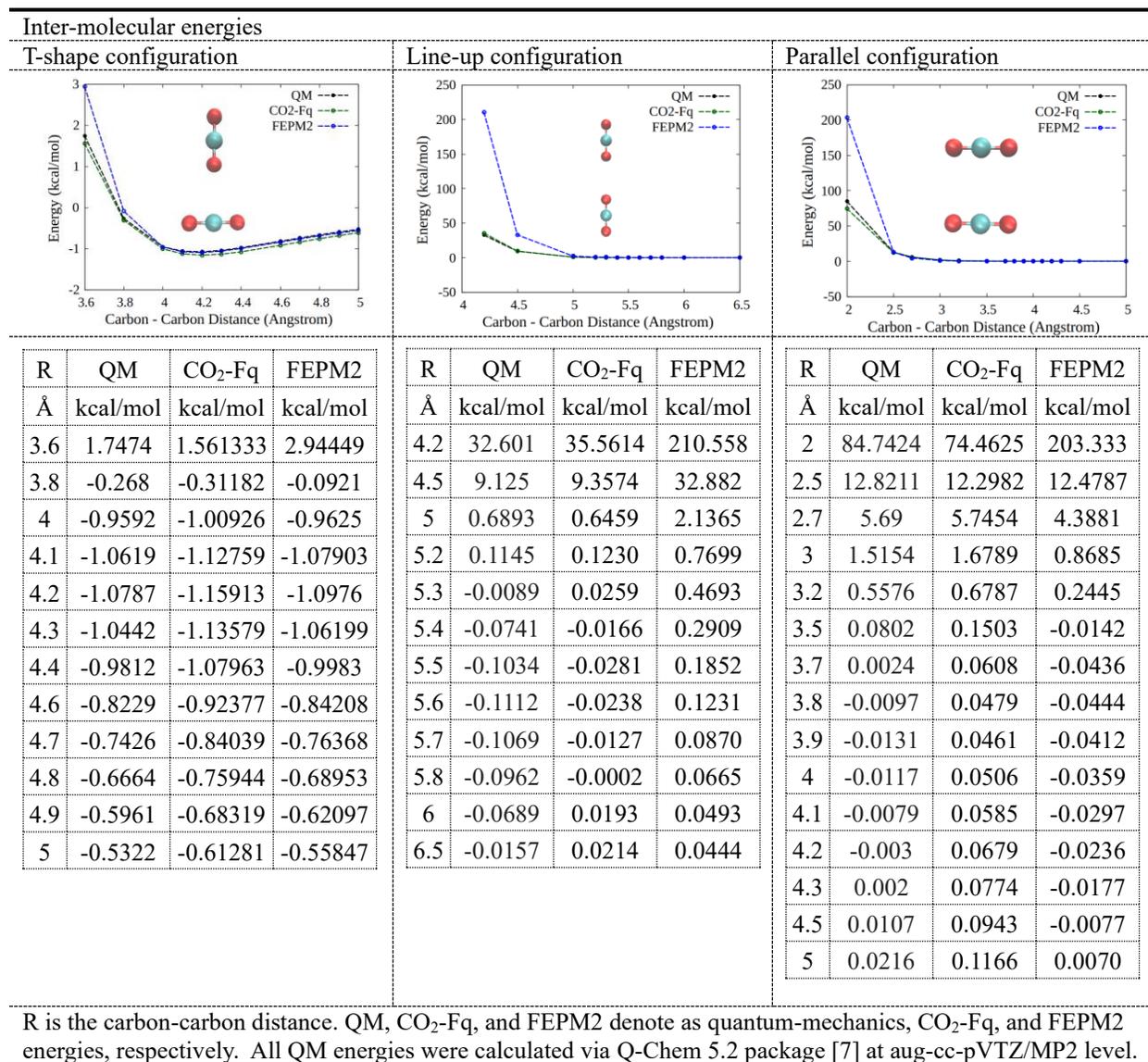
$$Q_{tot} = \sum_{i=1}^N Q_i \quad (\text{S-26})$$

## B. Tables

**Table S1** The intra-molecular energies of CO<sub>2</sub>

Intra-molecular energies			
C-O Bond stretching		O-C-O Angle bending	
C-O Bond	QM	CO <sub>2</sub> -Fq	FEPM2
Å	kcal/mol	kcal/mol	kcal/mol
1.109	4.8796	5.2077	2.0544
1.119	3.3385	3.6207	1.1556
1.129	2.1141	2.3451	0.5136
1.134	1.6145	1.8185	0.2889
1.139	1.1866	1.3632	0.1284
1.149	0.5370	0.6581	0
1.154	0.3108	0.4042	0.0321
1.159	0.1476	0.2136	0.1284
1.164	0.0453	0.0843	0.2889
1.169	0.0018	0.0145	0.5136
1.17	0	0.0075	0.5662
1.171	0.0005	0.0028	0.6215
1.172	0.0032	0.0004	0.6792
1.173	0.0081	0.0002	0.7396
1.174	0.0153	0.0023	0.8025
1.179	0.0839	0.0460	1.1556
1.184	0.2057	0.1439	1.5729
1.189	0.3791	0.2943	2.0544
1.194	0.6023	0.4955	2.6001
1.204	1.1917	1.0441	3.8841
1.209	1.5547	1.3884	4.6224
1.219	2.4099	2.2097	6.2916
1.229	3.4281	3.1981	8.2176
1.239	4.5984	4.3430	10.4004
1.249	5.9111	5.6338	12.84
O-C-O Angle	QM	CO <sub>2</sub> -Fq	FEPM2
Radian	kcal/mol	kcal/mol	kcal/mol
3.1416	0	0	0
3.1590	0.0168	0.0169	0.0450
3.1765	0.0670	0.0678	0.1801
3.1939	0.1509	0.1525	0.4052
3.2114	0.2683	0.2711	0.7204
3.2289	0.4195	0.4235	1.1256
3.2638	0.8233	0.8301	2.2061
3.2812	1.0764	1.0842	2.8814
3.3161	1.6854	1.6941	4.5022
3.4034	3.8201	3.8118	10.1300

QM, CO<sub>2</sub>-Fq, and FEPM2 denote as quantum-mechanics, CO<sub>2</sub>-Fq, and FEPM2 energies, respectively. All QM energies were calculated via Q-Chem 5.2 package [7] at aug-cc-pVTZ/MP2 level.

**Table S2** The inter-molecular binding energies of the CO<sub>2</sub> dimer**Table S3** CO<sub>2</sub> vibration frequencies from experiment and FEPM2/CO<sub>2</sub>-Fq MD simulations

	Experiments [3] [cm <sup>-1</sup> ]	FEPM2 (240K,100atm with liquid density) [cm <sup>-1</sup> ]	CO <sub>2</sub> -Fq (240K,100atm with liquid density) [cm <sup>-1</sup> ]
Symmetric stretching	1285.40 (Raman) 1388.15 (Raman)	1380	1278 1378
Asymmetric stretching	2349.16 (IR)	2661	2492
Angle bending	667.38 (IR)	1102	684

**Table S4** Equations and data used for thermodynamic properties calculation. Empirical thermodynamic data from References [8, 9]

	Equations / Data
Constant pressure heat capacity, $C_p$ [T in K; $C_p$ in J/mol/K]	$C_p^G = 27.437 + 0.042315 T - 1.955 \cdot 10^{-5} T^2 + 4 \cdot 10^{-9} T^3 - 2.99 \cdot 10^{-13} T^4$ $C_p^L = -338.956 + 5.28T - 0.0233T^2 + 3.6 \cdot 10^{-5} T^3$ $C_p^S = -1.63 + 0.542T - 0.00127T^2$
$\Delta H_{sub}$ at 195K, 1atm [kJ/mol]	25.2
$S^0$ at 298K, 1bar [J/mol/K]	213.785

**Table S5** Thermodynamic properties of CO<sub>2</sub> along the VLE curve using the FEPM2 and CO<sub>2</sub>-Fq models compared to experiments

	$T$	FEPM2				CO <sub>2</sub> -Fq				EXP[3, 9]	
		$\rho$	$S_{q\ 2PT}$	$E_{md\ 2PT}$	$E_{q\ 2PT}$	$\rho$	$S_{q\ 2PT}$	$E_{md\ 2PT}$	$E_{q\ 2PT}$	$S_{EXP}$	$E_{EXP}$
Saturated liquid	220	1.1663	113.74	17.25	17.25	1.1663	116.01	17.25	17.25	118.12	17.25
	230	1.1292	115.70	17.95	18.42	1.1292	118.25	18.27	17.86	121.59	18.06
	240	1.0896	120.40	19.60	19.51	1.0896	124.41	19.32	20.60	125.07	18.88
	250	1.0467	125.81	20.59	19.60	1.0467	126.37	20.27	19.81	128.64	19.74
	260	1.0000	128.19	21.71	21.12	1.0000	130.87	21.78	20.37	132.24	20.65
	270	0.9470	133.91	22.91	21.19	0.9470	132.53	22.42	21.50	135.94	21.61
	280	0.8850	136.71	24.36	23.20	0.8850	139.30	24.27	22.07	139.77	22.64
	290	0.8058	142.56	25.87	23.40	0.8058	145.01	25.82	23.47	143.95	23.81
	300	0.6803	151.21	28.29	25.85	0.6803	151.45	28.25	25.18	149.32	25.33
	302	0.6337	154.50	29.67	27.97	0.6337	152.20	28.03	26.20	--	--
Critical point	303.1 (FEPM2)	0.4459	155.30	29.53	27.03	0.4395	155.51	29.45	26.76	--	--
	302.5 (CO <sub>2</sub> -Fq)										
Saturated vapor	302	0.3082	159.00	30.78	28.59	--	--	--	--	--	--
	300	0.2703	162.20	30.95	28.25	--	--	--	--	164.68	29.28
	290	0.1724	168.07	31.40	29.02	--	--	--	--	169.61	30.19
	280	0.1220	170.03	31.65	29.57	--	--	--	--	172.73	30.59
	270	0.0885	172.78	31.42	28.79	--	--	--	--	175.20	30.78
	260	0.0645	174.80	31.34	29.14	--	--	--	--	177.44	30.86
	250	0.0467	179.26	30.79	29.82	--	--	--	--	179.51	30.87
	240	0.0333	182.10	30.47	29.46	--	--	--	--	181.67	30.82
	230	0.0234	182.60	30.05	29.86	--	--	--	--	183.35	30.74
	220	0.0160	184.86	29.57	29.90	--	--	--	--	186.71	30.62

$T$  is the temperature in K,  $\rho$  is the initial density in g/cm<sup>3</sup>,  $S_q$  is the entropy in J/mol/K,  $E_{md}$  is the internal classical energy in kJ/mol and  $E_q$  is the internal quantum energy in kJ/mol. The energy referent state is set as saturated liquid at 220K.

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