

2-phase thermodynamic (2PT) model for efficient entropy calculation in liquid state

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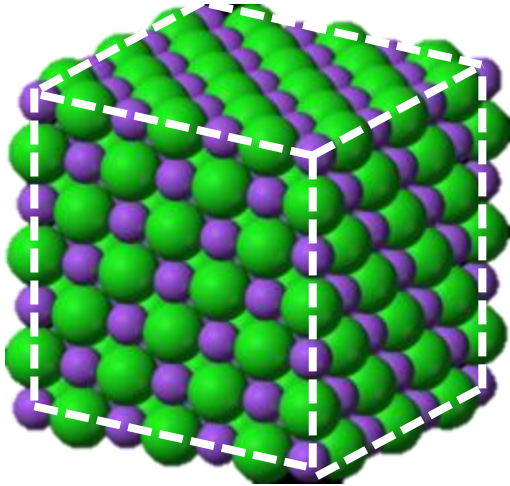
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With Shiang-Tai Lin (NTU), Bill Goddard (Caltech) and Hemant Kumar, Chandan Dasgupta and Ajay Sood (IISc)

Funding DST, India

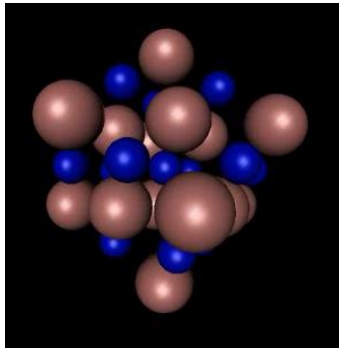
Thermodynamics of Crystal

- Atoms vibrating around its equilibrium position

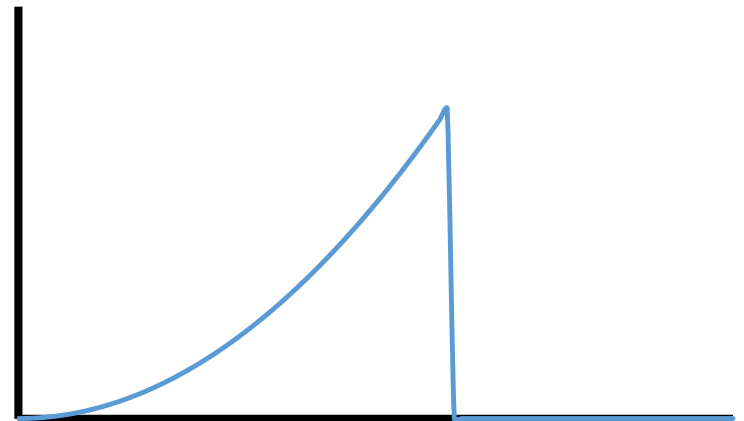


Debye model

$$S(\nu) = \frac{4\pi V \nu^2}{u^3}$$



$S(\nu)$



ν

Harmonic Approximation (Quantum) : 1PT method

Berens et al JCP,79 2375 (83)

For crystals: each mode is a harmonic oscillator

Partition function of a harmonic oscillator

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu \quad q_{HO}^Q(\nu) = \sum_n \exp(-\beta\varepsilon_n) = \frac{\exp(-\beta h\nu/2)}{1 - \exp(-\beta h\nu/2)}$$

The partition function of the system is the sum from all the oscillators

$$\ln Q = \int_0^\infty d\nu S(\nu) \ln q_{HO}(\nu)$$

Thermodynamic properties

$$E = V_0 + T\beta^{-1} \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = V_0 + \beta^{-1} \int_0^\infty d\nu S(\nu) W_E(\nu)$$

Ref. energy

$$S = k \ln Q + \beta^{-1} \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = k_B \int_0^\infty d\nu S(\nu) W_S(\nu)$$

$$A = V_0 - \beta^{-1} \ln Q = V_0 + \beta^{-1} \int_0^\infty d\nu S(\nu) W_A(\nu)$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{N,V} = k_B \int_0^\infty d\nu S(\nu) W_{C_v}(\nu)$$

Weighting functions

$$W_E^Q(\nu) = \frac{\beta h\nu}{2} + \frac{\beta h\nu}{\exp(\beta h\nu) - 1}$$

Zero point energy

$$W_S^Q(\nu) = \frac{\beta h\nu}{\exp(\beta h\nu) - 1} - \ln[1 - \exp(-\beta h\nu)]$$

$$W_A^Q(\nu) = \ln \frac{1 - \exp(\beta h\nu)}{\exp(-\beta h\nu/2)}$$

$$W_{C_v}^Q(\nu) = \frac{(\beta h\nu)^2 \exp(\beta h\nu)}{[1 - \exp(-\beta h\nu)]^2}$$

Harmonic Approximation (Classical) : 1PT method

For crystals: each mode is a harmonic oscillator

Berens et al JCP,79 2375 (83)

Partition function of a harmonic oscillator

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu \quad q_{HO}^C(\nu) = \sum_n \exp(-\beta\varepsilon_n) = 1/\beta h\nu$$

The partition function of the system is the sum from all the oscillators

$$\ln Q = \int_0^\infty d\nu S(\nu) \ln q_{HO}(\nu)$$

Thermodynamic properties

Weighting functions

$$E = V_0 + T\beta^{-1} \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = V_0 + \beta^{-1} \int_0^\infty d\nu S(\nu) W_E(\nu)$$

← Ref. energy

$$W_E^C(\nu) = 1$$

$$S = k \ln Q + \beta^{-1} \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = k_B \int_0^\infty d\nu S(\nu) W_S(\nu)$$

$$W_S^C(\nu) = 1 - \ln \beta h\nu$$

$$A = V_0 - \beta^{-1} \ln Q = V_0 + \beta^{-1} \int_0^\infty d\nu S(\nu) W_A(\nu)$$

$$W_A^C(\nu) = \ln \beta h\nu$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{N,V} = k_B \int_0^\infty d\nu S(\nu) W_{C_v}(\nu)$$

$$W_{C_v}^C(\nu) = 1$$

The Normal Modes from VAC

- The $S(\nu)$ calculated from the Fourier transform of VAC

$$S(\nu) = \frac{2}{kT} \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} \sum_{j=1}^N \langle v_j(0) \cdot v_j(t) \rangle e^{-i2\pi\nu t} dt$$

- Integration of $S(\nu)$ gives the total degrees of freedom

$$\int_0^{\infty} S(\nu) d\nu = 3N$$

N : total number of atoms

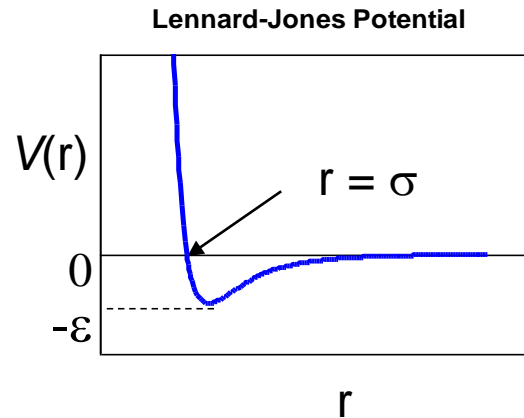
- Zero frequency $S(0)$ gives diffusivity

$$D = \frac{kT}{12mN} S(0)$$

Testing with the LJ System

- Intermolecular potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$



- Phase diagram

- critical point

$$T_c^* = 1.316 \pm 0.006$$

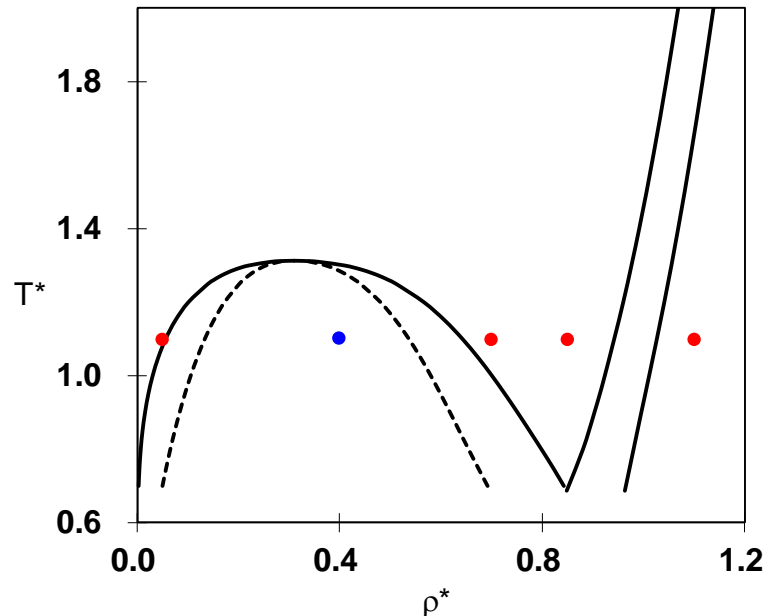
$$\rho_c^* = 0.304 \pm 0.006$$

- triple point

$$T_{tp}^* \approx 0.69$$

$$(T^* = kT/\epsilon \quad \rho^* = \rho\sigma^3)$$

T - ρ diagram for Lennard Jones Fluid



● stable

● unstable

The Density of States

Lin, S. T.; Blanco, M.; Goddard, W. A.. *J. Chem. Phys.* 2003, 119, 11792.

Example: Lennard-Jones particles

$T^*=1.1$
 $\rho^*=0.05$ gas
 $\rho^*=0.40$ instable system
 $\rho^*=0.70$ metastable liquid
 $\rho^*=0.85$ liquid
 $\rho^*=1.10$ crystal

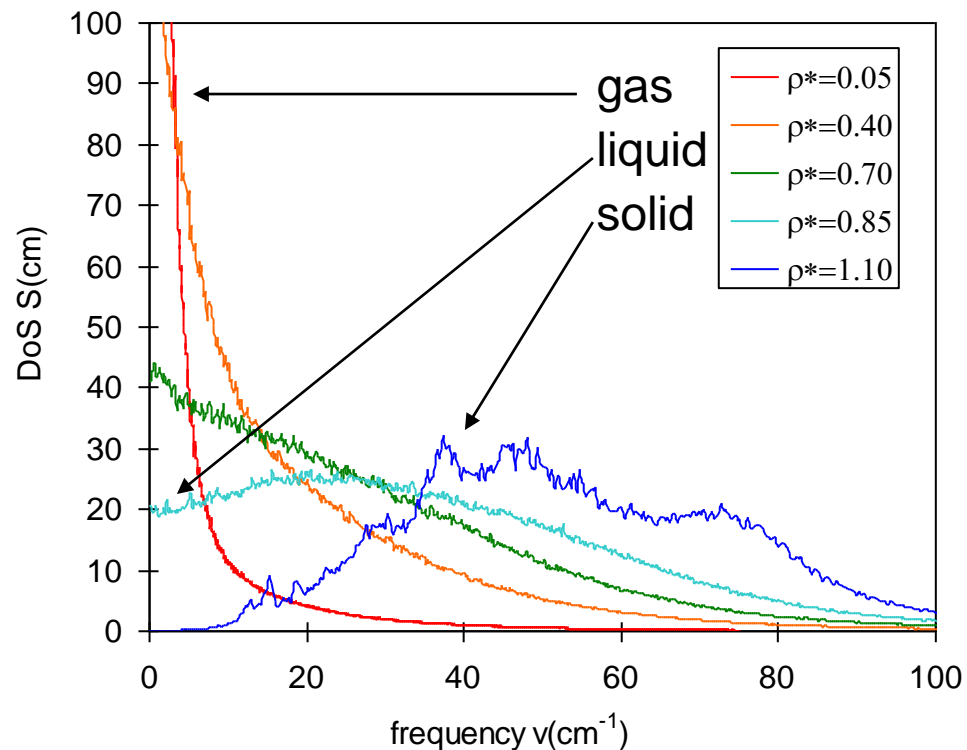
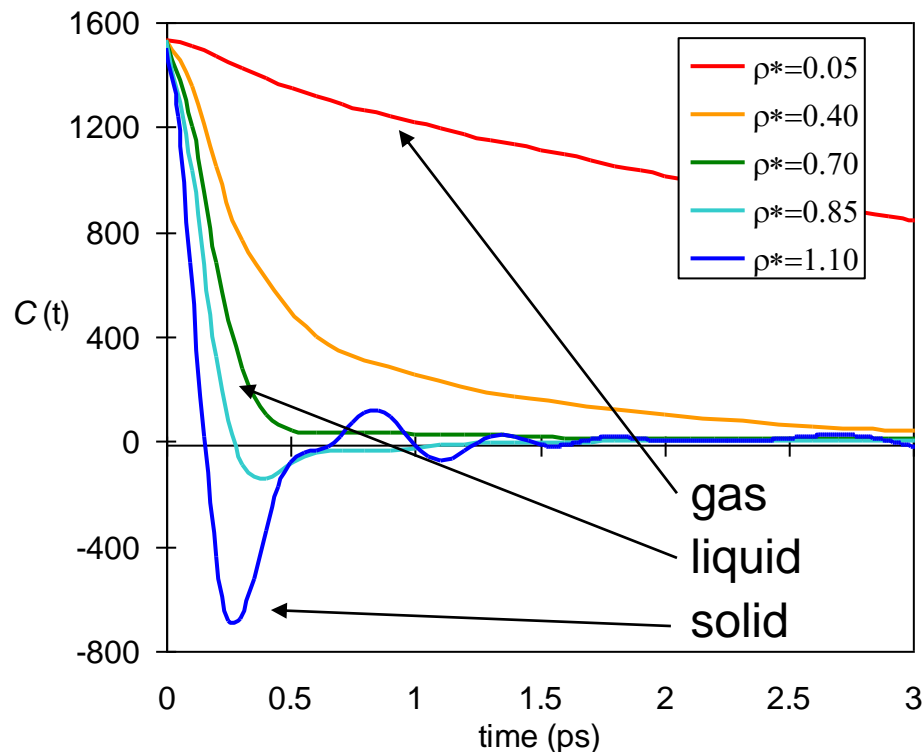
Velocity Autocorrelation

$$C(t) = \langle v(0) \cdot v(t) \rangle$$

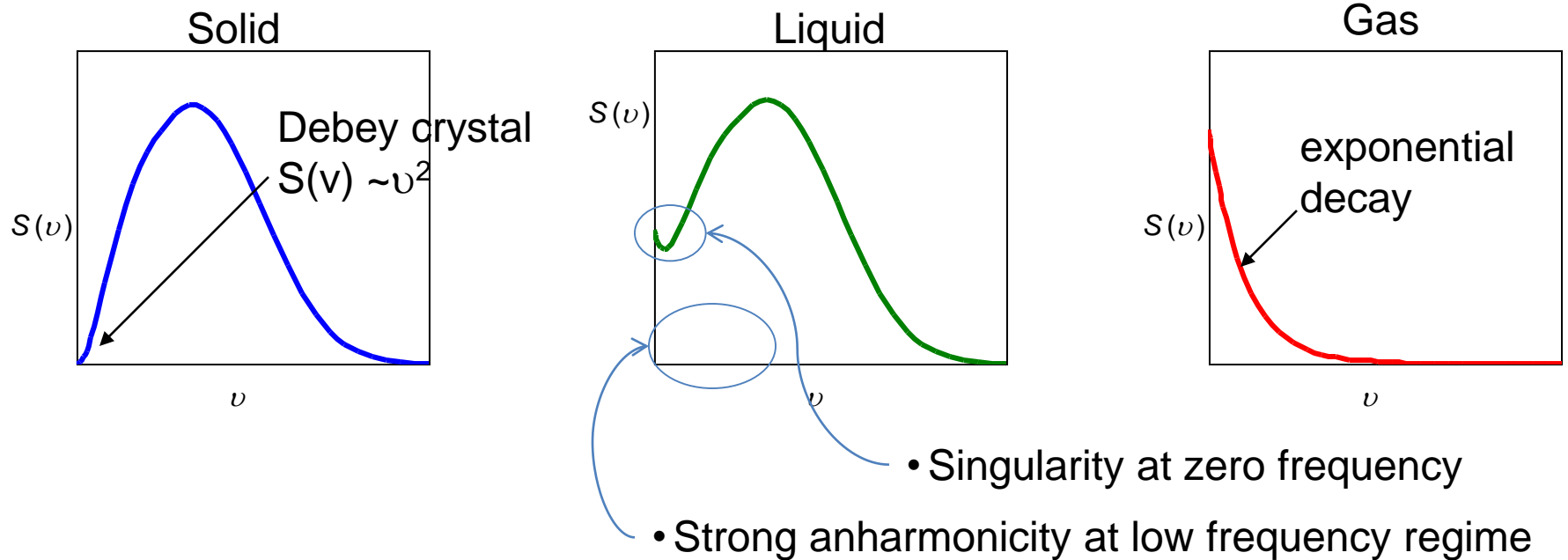
Fourier Transform

$$S(\nu) = \frac{2}{kT} \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} C(t) e^{-i2\pi\nu t} dt$$

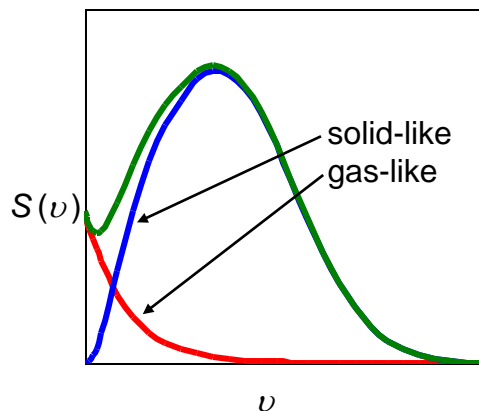
Density of States



The Density of States Distribution $S(\nu)$



The **2PT** idea: Liquid \equiv Solid+Gas



- Decompose liquid $S(\nu)$ to a gas and a solid contribution
- $S(0)$ attributed to gas phase diffusion
- Gas component contains anharmonic effects
- Solid component contains quantum effects
- Two-Phase Thermodynamics Model (2PT)

Lin, S. T.; Blanco, M.; Goddard, W. A.. *J. Chem. Phys.* 2003, 119, 11792.

- The basic idea
- The DoS
- Thermodynamic properties

$$S(\nu) = S^{gas}(\nu) + S^{solid}(\nu)$$

$$P = \int_0^{\infty} d\nu S^s(\nu) W_P^{HO}(\nu) + \int_0^{\infty} d\nu S^g(\nu) W_P^g(\nu)$$

- The gas component
- VAC for hard sphere gas
- DoS for hard sphere gas

$$c^{HS}(t) = \frac{3kT}{m} \exp(-\alpha t)$$

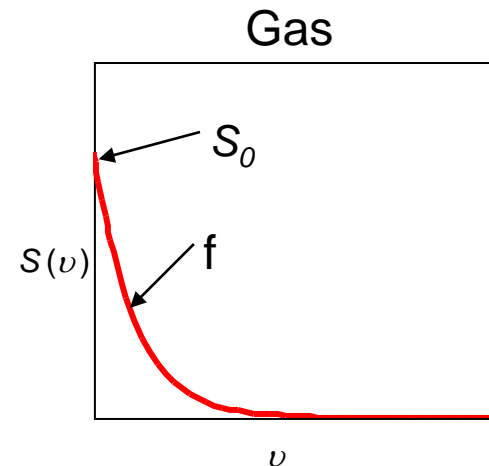
$\alpha(T, \rho^{HS}, \sigma^{HS})$: friction coefficient

- Two unknowns (α and N^{gas}) or (s_0 and f)

$$S^{HS}(\nu) = \frac{12N^{gas}\alpha}{\alpha^2 + 4\pi^2\nu^2} = \frac{s_0}{1 + \left[\frac{\pi s_0 \nu}{6fN} \right]^2}$$

$$N^{gas} = fN$$

$$s_0 = S^{HS}(0) = \frac{12N^{gas}}{\alpha}$$



Determining s_0 and f from MD Simulation

- s_0 (DoS of the gas component at $v=0$)
 - completely remove $S(0)$ of the fluid
 - f (gas component fraction)
 - $T \rightarrow \infty$ or $\rho \rightarrow 0$: $f \rightarrow 1$ (all gas)
 - $\rho \rightarrow \infty$: $f \rightarrow 0$ (all solid)
- $s_0 = S(0)$, $S^{solid}(0) = 0$

- one unknown σ^{HS}

$$f = \frac{D(T, \rho)}{D_0^{HS}(T, \rho; \sigma^{HS})}$$

$$D(T, \rho) = \frac{kTS(0)}{12mN}$$

$$D_0^{HS}(T, \rho; \sigma^{HS}) = \frac{3}{8} \frac{1}{\rho \sigma^{HS^2}} \left(\frac{kT}{\pi m} \right)^{1/2} \quad (\text{Chapman - Enskog})$$

- σ^{HS} (hard sphere radius for describing the gas molecules)
 - gas component diffusivity should agree with statistical mechanical predictions at the same T and ρ
 - gas component diffusivity from MD simulation

$$D^{HS}(T, f\rho) = \frac{kTs_0}{12mfN}$$

- HS diffusivity from the Enskog theory

$$D^{HS}(T, f\rho) = D_0^{HS}(T, f\rho; \sigma^{HS}) \frac{4fy}{z(fy) - 1}$$

$$y = \frac{\pi}{6} \rho \sigma^{HS^3}$$

$$z(y) = \frac{1 + y + y^2 - y^3}{(1 - y)^3}$$

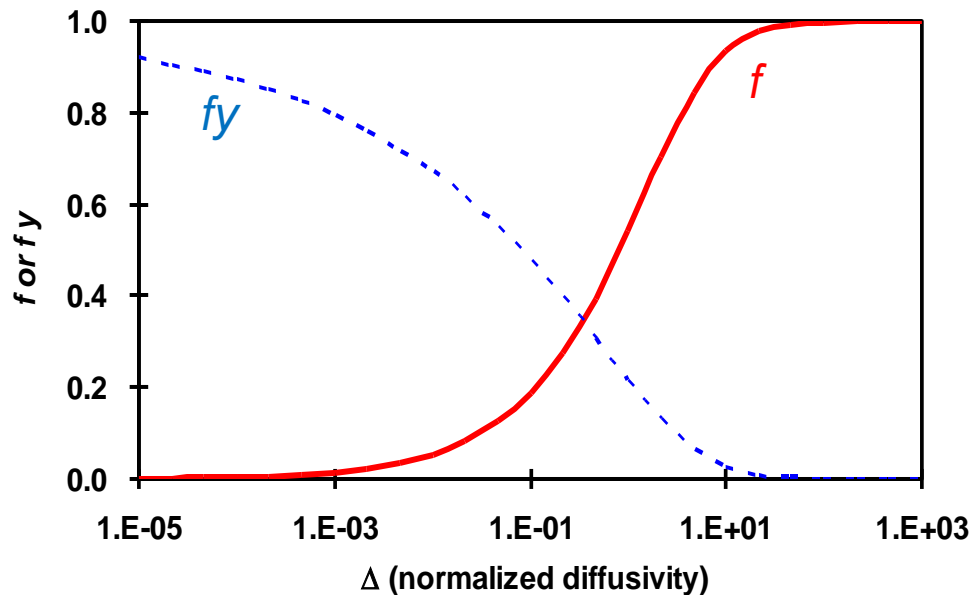
At Last...

- A universal equation for f

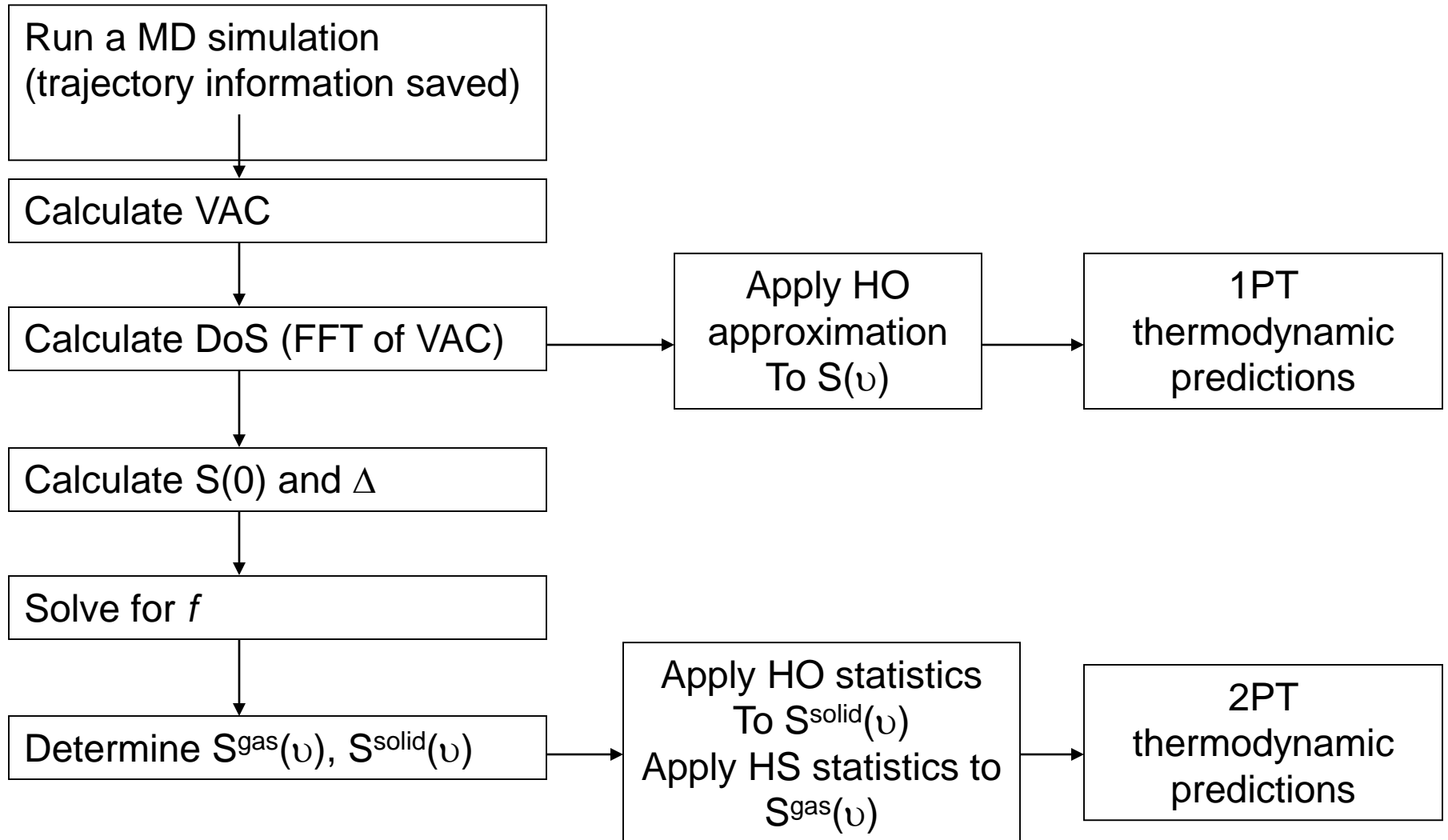
$$2\Delta^{-9/2} f^{15/2} - 6\Delta^{-3} f^5 - \Delta^{-3/2} y^{7/2} + 6\Delta^{-3/2} f^{5/2} + 2f - 2 = 0$$

$$\text{normalized diffusivity } y: \Delta(T, \rho, m, s_0) = \frac{2s_0}{9N} \left(\frac{\pi kT}{m}\right)^{1/2} \rho^{1/3} \left(\frac{6}{\pi}\right)^{2/3}$$

- Graphical representation

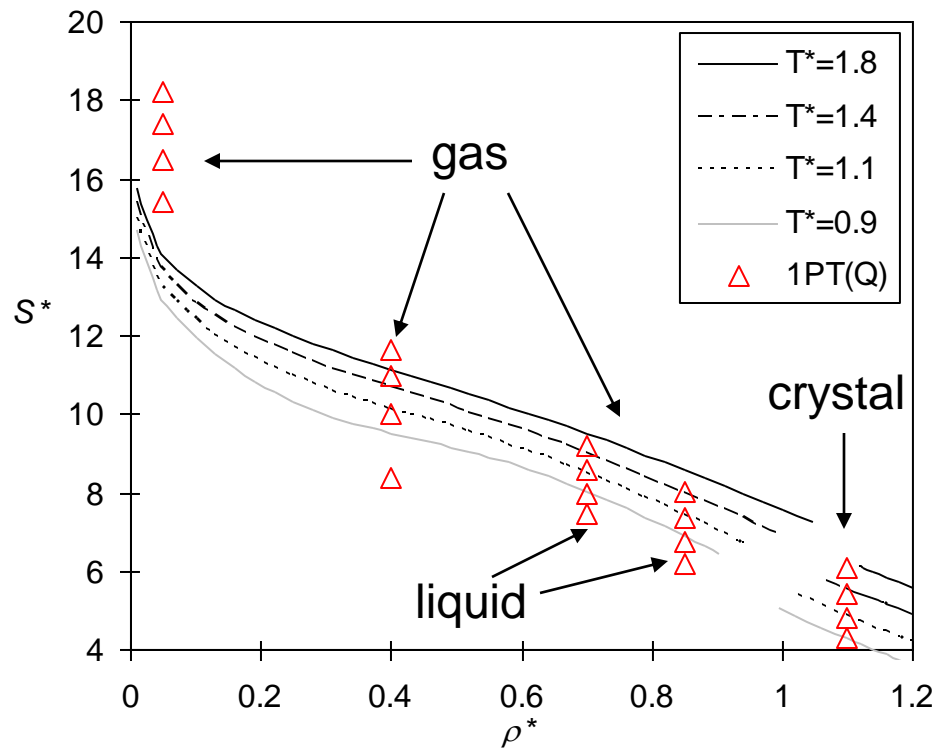


Comparison of the 1PT and 2PT methods

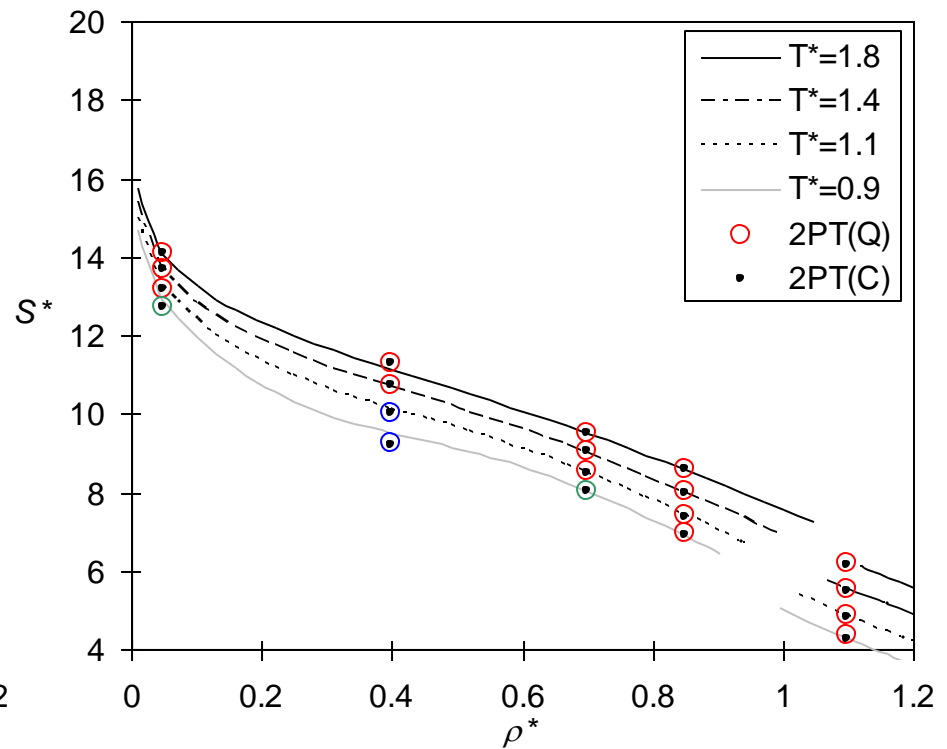


Entropy

1PT



2PT model

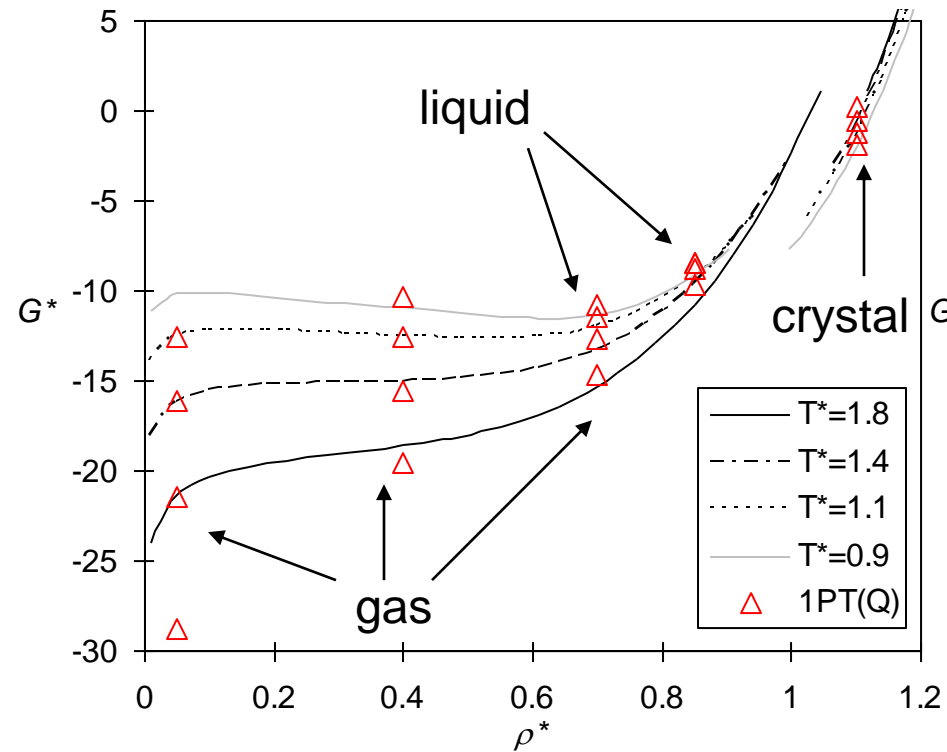


- Overestimate entropy for low density gases
- Underestimate entropy for liquids
- Accurate for crystals

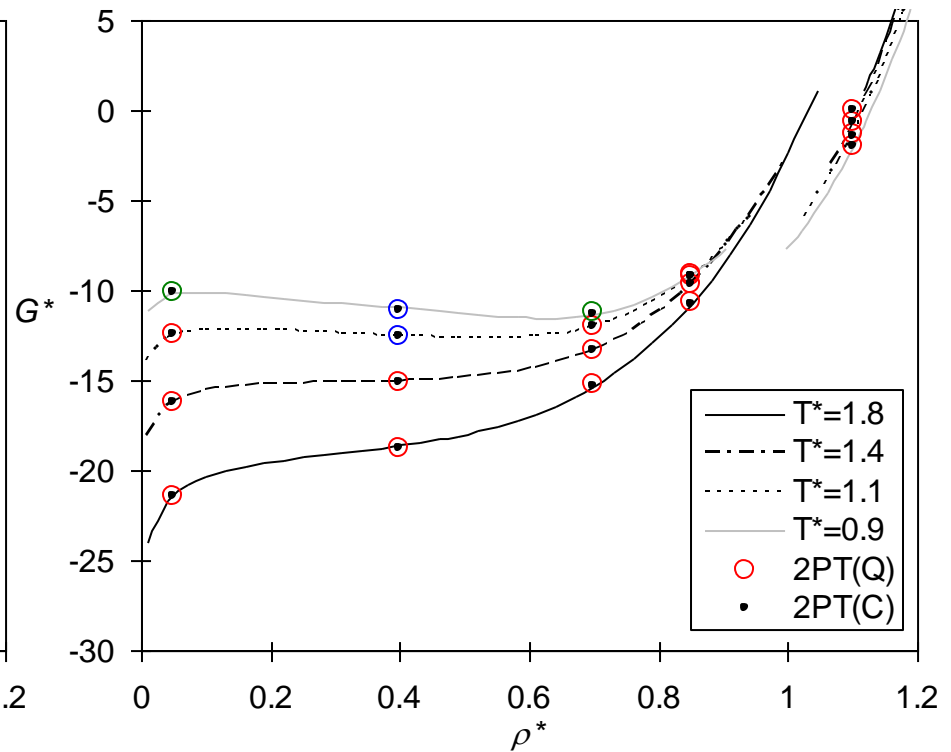
- Accurate for gas, liquid, and crystal
- Accurate in metastable regime
- Quantum Effects most important for crystals ($\sim 1.5\%$)

Gibbs Free Energy

1PT



2PT model

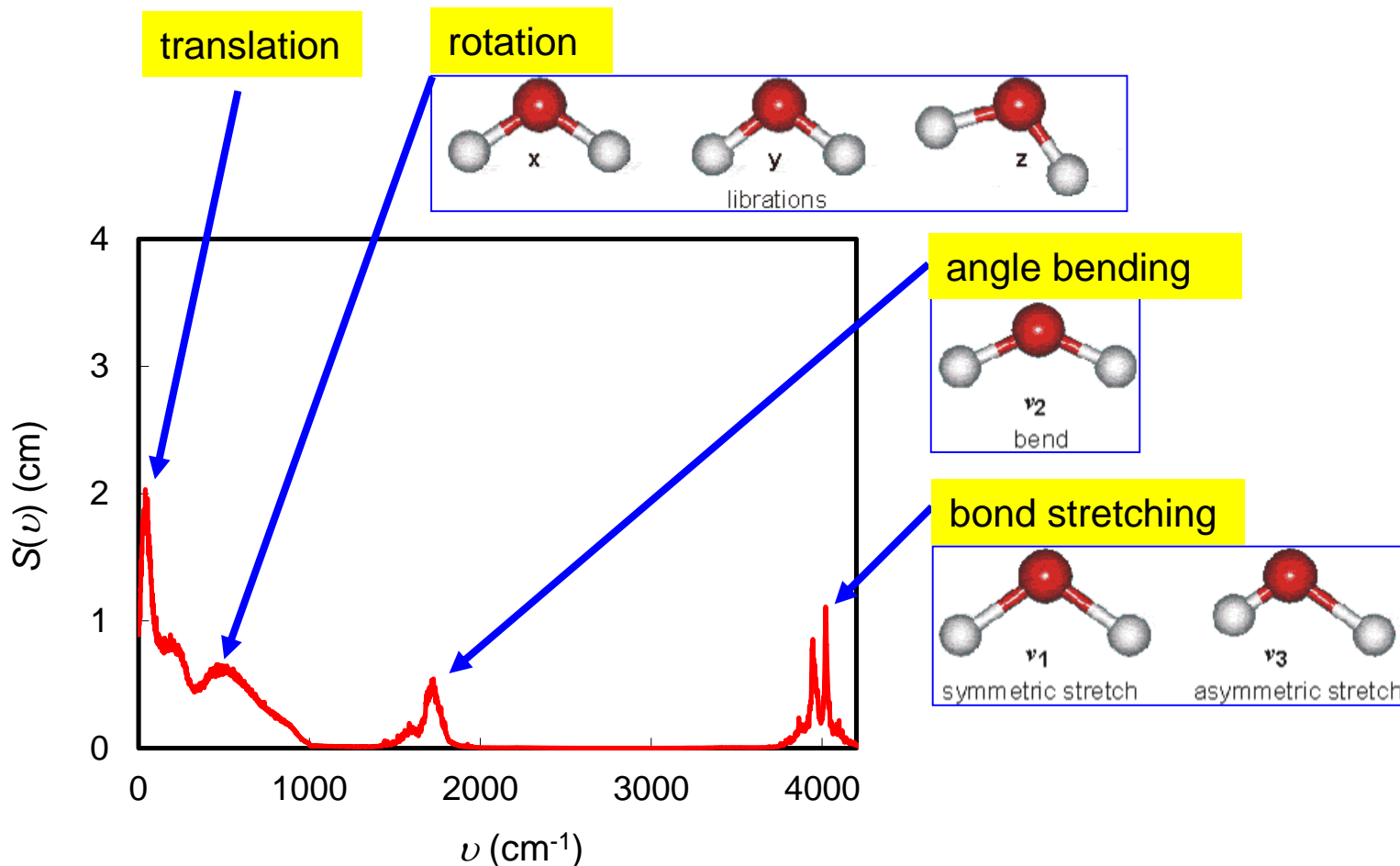


- Underestimate free energy for low density gases
- overestimate entropy for liquids
- Accurate for crystals

- Accurate for gas, liquid, and crystal
- Accurate in metastable regime

Density of States (Normal Modes) of Water

- The DoS of liquid water



2PT for Molecular Systems

- Decomposition of DoS to translation, rotation, and intramolecular vibrations

$$S(\nu) = S_{tran}(\nu) + S_{rot}(\nu) + S_{vib}(\nu)$$

- Applying 2PT to trans and rot components

$$S_{tran}(\nu) = S_{tran}^{gas}(\nu) + S_{tran}^{solid}(\nu)$$

$$S_{rot}(\nu) = S_{rot}^{gas}(\nu) + S_{rot}^{solid}(\nu)$$

- Applying proper quantum statistics to the corresponding components

The DoS of Liquid Water

$$S(\nu) = S_{trn}(\nu) + S_{rot}(\nu) + S_{vib}(\nu)$$

The rotational density of state is determined from the angular velocity

$$S_{rot}(\nu) = \beta \sum_{l=1}^M \sum_{k=1}^3 \lim_{\tau \rightarrow \infty} \frac{I_l^k}{\tau} \left| \int_{-\tau}^{\tau} \omega_l^k(t) e^{-i2\pi\nu t} dt \right|^2$$

The atomic velocity was decomposed into translation, rotation, and vibration components at every step

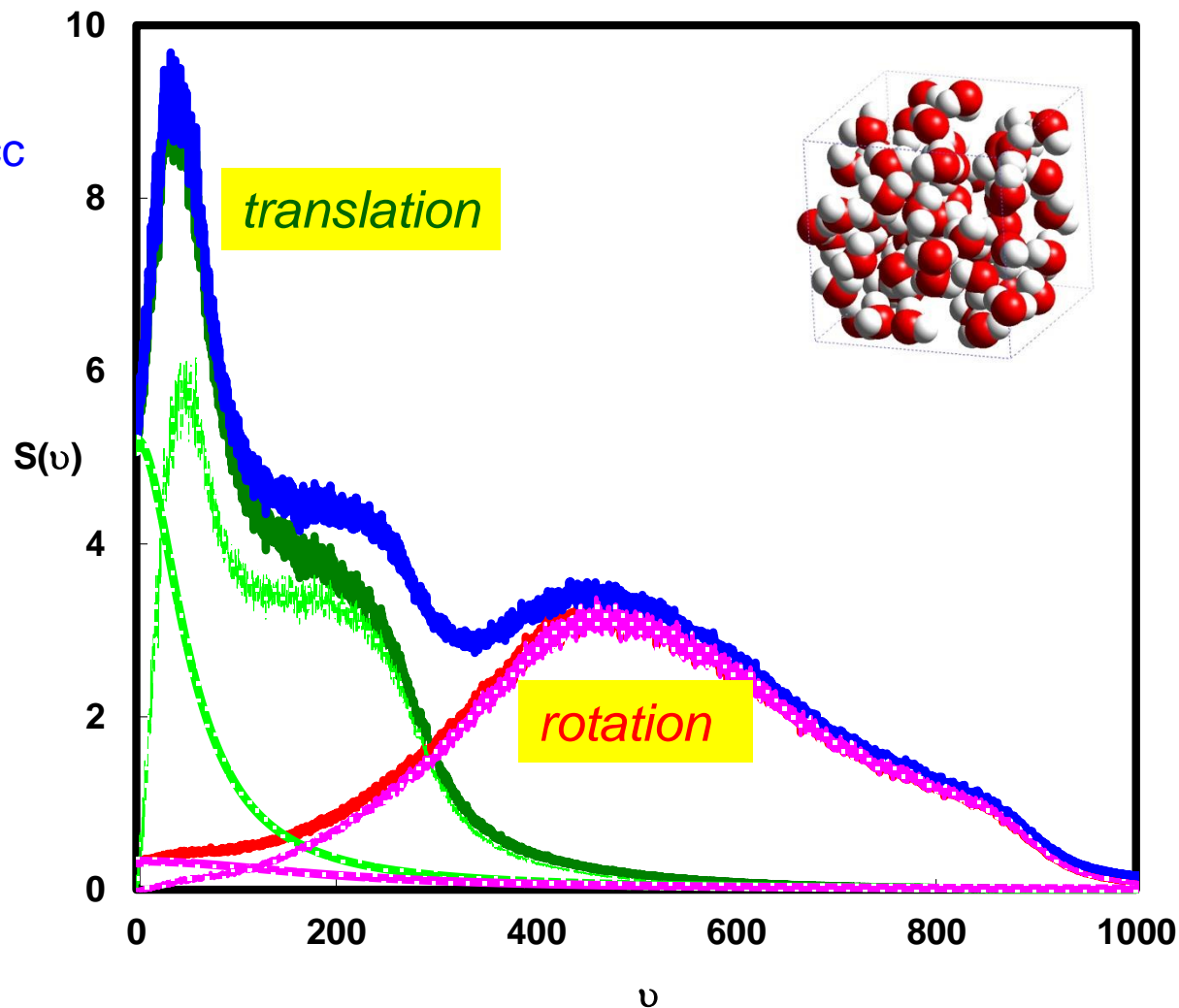
$$\mathbf{v}_j^k(t) = \mathbf{v}_{j,trn}^k(t) + \mathbf{v}_{j,rot}^k(t) + \mathbf{v}_{j,vib}^k(t)$$

The angular velocity is determined from angular momentum and moment of inertia tensor

$$\vec{L} = \sum m_j (\vec{r}_j \times \vec{v}_j) = \underline{\underline{I}} \vec{\omega}$$

The DoS of Liquid Water

SPC water at
25°C and 1 g/cc

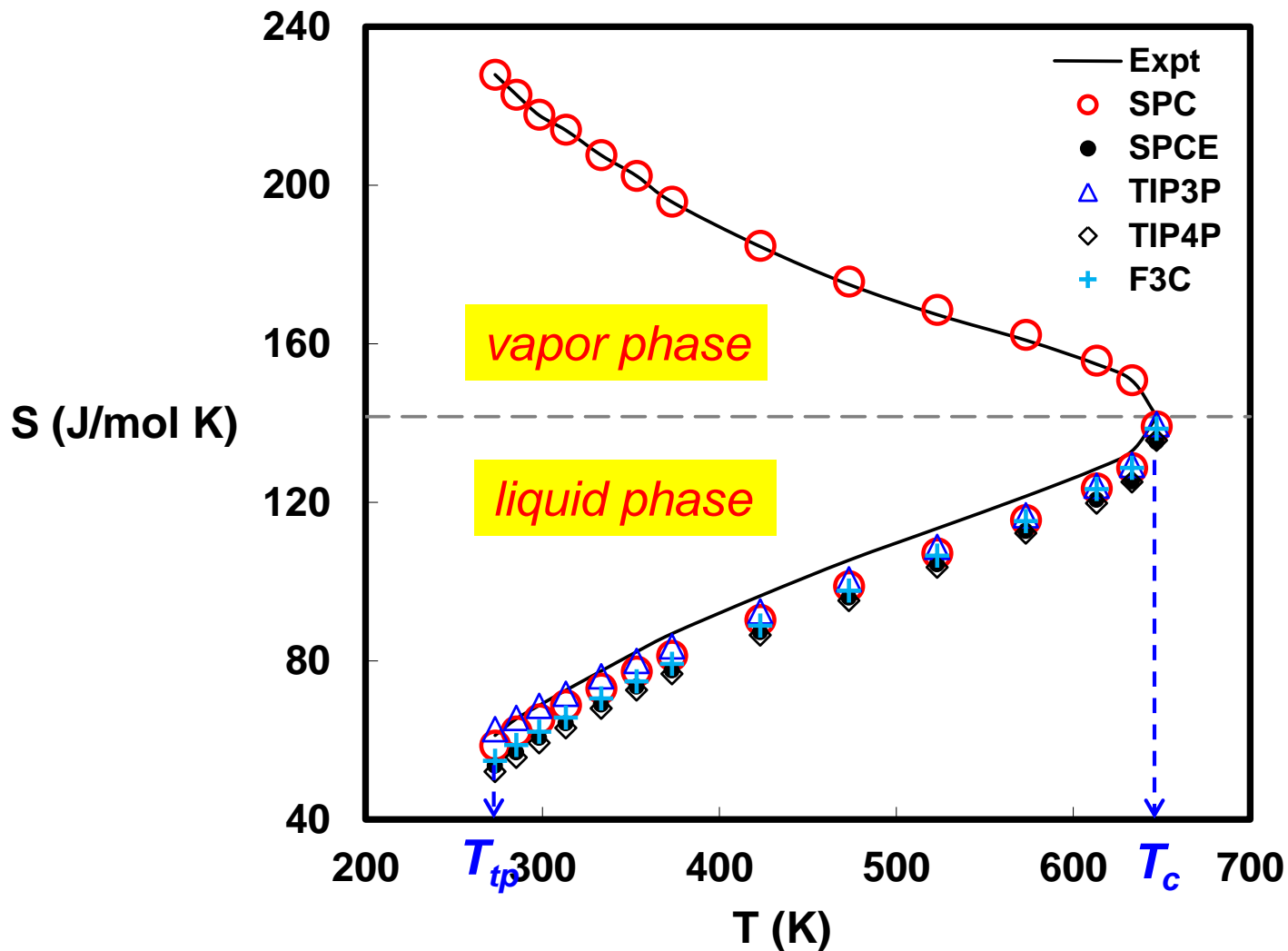


$$f_{\text{trn}} = 0.29$$
$$f_{\text{rot}} = 0.07$$

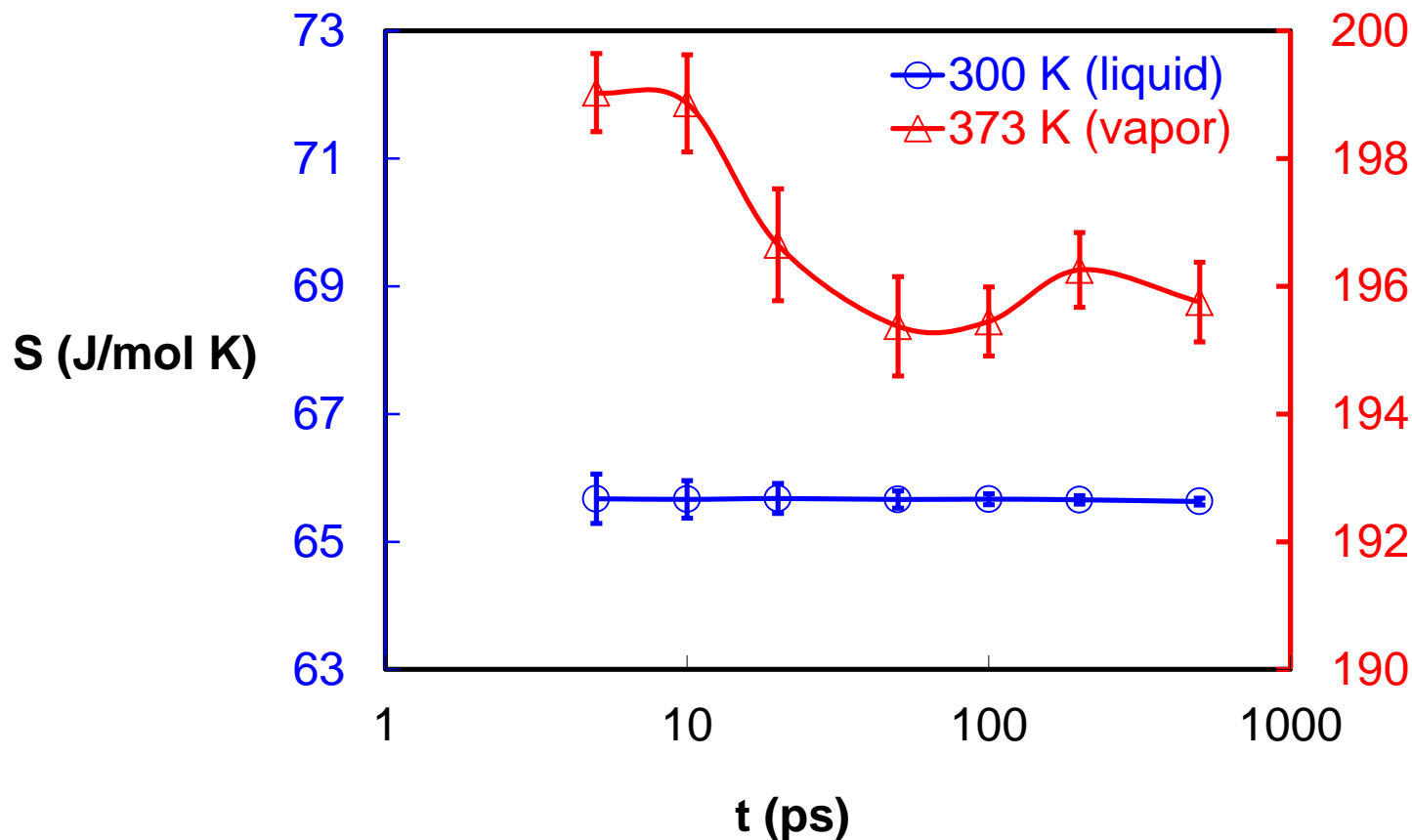
2PT Entropy for Liquid Water at STP

water models					
	F3C	SPC	SPC/E	TIP3P	TIP4P-Ew
$S_{\text{trn}}(2\text{PT})$	50.59±0.25	53.05±0.14	49.87±0.14	55.59±0.15	49.79±0.07
$S_{\text{rot}}(2\text{PT})$	11.54±0.06	12.03±0.03	10.41±0.04	12.90±0.04	9.53±0.07
$S_{\text{vib}}(2\text{PT})$	0.04±0.00	-	-	-	-
$S(2\text{PT})$	62.18±0.30	65.09±0.13	60.28±0.16	68.49±0.14	59.32±0.12
$S(\text{FD})$	-	65.10±3.35	64.48±3.35	70.86±3.35	-
$S(\text{FEP})$	-	68.20	63.36	72.58	63.62
$S(\text{expt})^e$			69.95±0.03		

2PT Entropy of Water along VLE

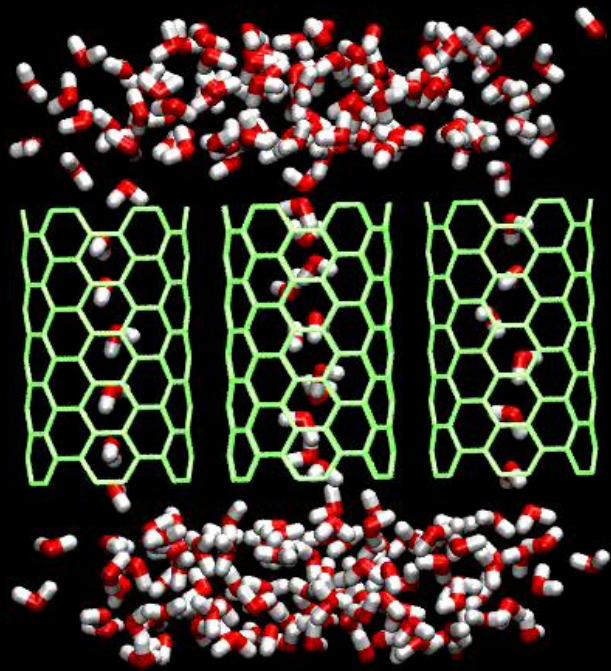


Convergence and Efficiency



- Liquid phase entropy converges within **10 ps**
- Vapor phase entropy converges within **50 ps**

Water flow inside single nanotube and bundle



Free Energy of Confined Water

CNT	E(Kcal/mol)	TS _{trn} (Kcal/mol)	TS _{rot} (Kcal/mol)	E-TS
(5,5)	-8.26	2.97	2.16	-13.39(0.04)
(6,6)	-8.89	3.84	1.67	-14.40(0.04)
(7,7)	-8.67	4.04	1.42	-14.13(0.01)
(8,8)	-9.38	3.67	1.12	-14.17(0.01)
BULK	-9.45	4.02	0.93	-14.40(0.005)

Loss in energy is compensated by the gain in rotational entropy.

Kumar et. al. JCP, 134, 124105 (2011)

Kumar et.al. Molecular Simulation, 41, 504-511 (2015),

Summary

- Determines absolute value of entropy from single MD trajectory. Entropy converges with 20 ps trajectory
- Includes quantum corrections
- Allows calculation of entropy of each individual molecule in the system
- Gain in rotational entropy allow water entry inside hydrophobic pore of the tube
- Both entropy and energy of transfer decrease with increasing temperature, keeping the free energy of transfer nearly constant..