# HFBS Experiments Talk

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HFBS TUTORIAL
FEB. 5, 2008

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Movies are imbedded and will play if you make the document a trusted document.

# General Outline

- Quantum Rotation in Methyl Iodide.
  - Demonstration of methyl rotational tunneling in methyl iodide.
  - Shows how to distinguish the between libration motion, tunneling, and jump diffusion.
- Polymers and HFBS.
  - Demonstration of the usefulness of HFBS for looking at the dynamics of poly (vinyl methyl ether).
  - Shows how to interpret a fixed window scan and corresponding quasi-elastic spectra.

# Quantum Rotations in Methyl Iodide

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# Quantum Phenomena

*…weird things happen at small length scales…*

- Wave/particle behavior of matter: $\Psi(x,t)$
- Quantized/discrete energy levels for confined particles
- Observable motion that is classically forbidden

# Classically *Forbidden* Phenomena

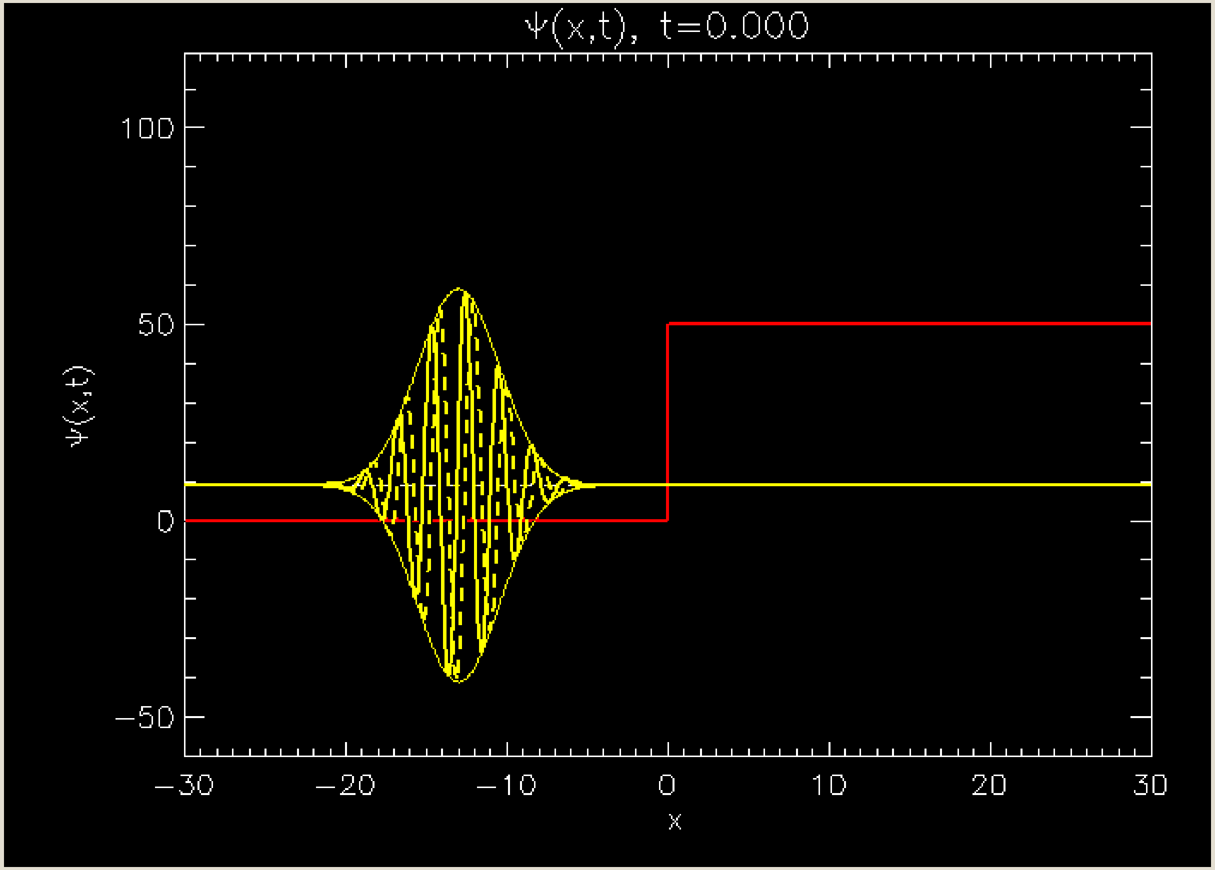

Caption: Train *Tunneling* through a house.

- Prob ~ $1/10^{(10^{39})}$

- Stars in universe: $10^{21}$
- Size of universe (m): $10^{27}$
- Water molecules in ocean: $5\times10^{46}$
- Hydrogen atoms in universe: $10^{79}$
- Probability of a monkey typing Hamlet with random keystrokes: $1/10^{(10^{5})}$

# Quantum Phenomena

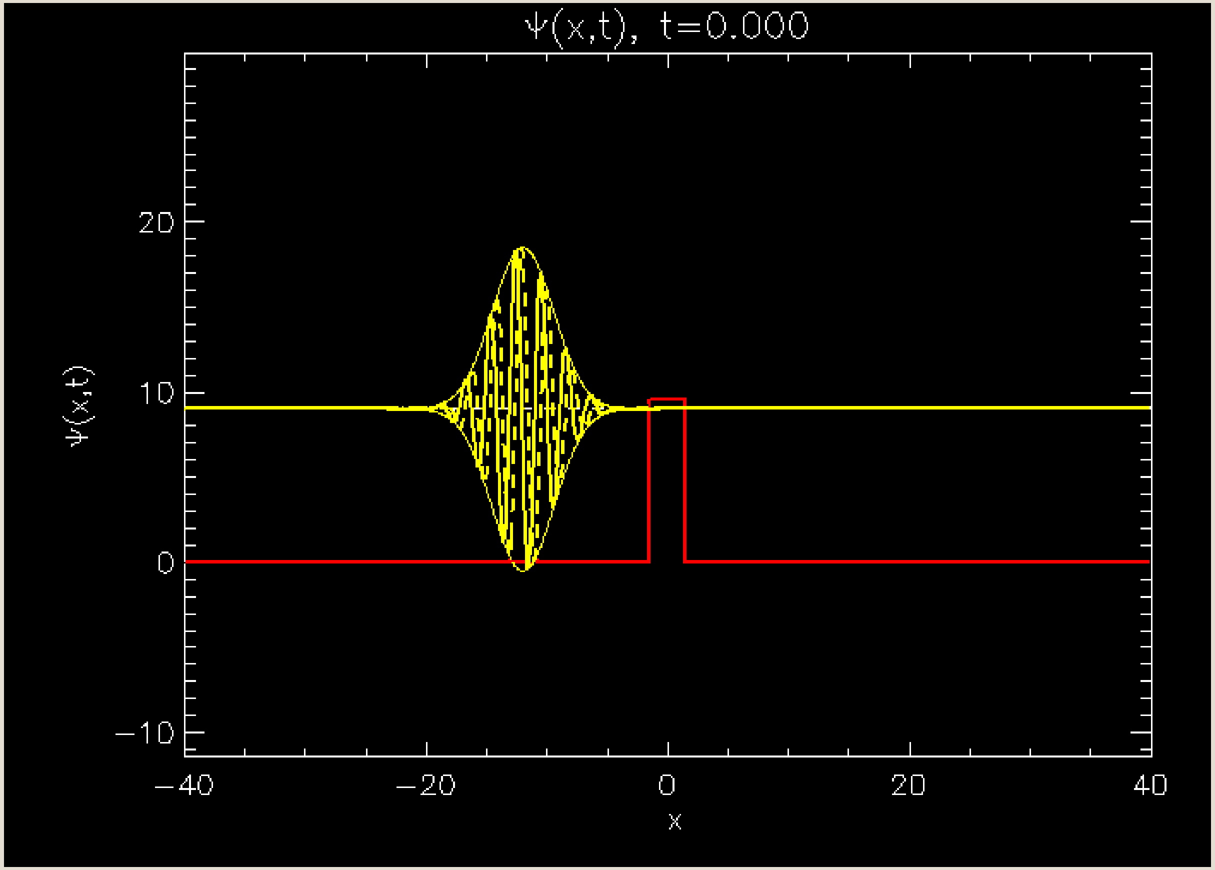
*…weird things happen at small length scales…*




- Wavepacket reflecting from a step barrier

# Quantum Phenomena

*…weird things happen at small length scales…*




- Wavepacket tunneling through barrier

# What are quantum rotations?

- Molecules in molecular solids can undergo reorientational motion.

- $H_2$ is a dumbell rotor and its quantum rotations are nearly “free” (i.e. no barrier hinders its motion)

$$E_\ell = BJ(J+1), \quad J = 0,1,2,\ldots$$

$$B = \frac{\hbar^2}{2I}$$

- Hindered rotors can perform torsional oscillations and even rotational tunneling through the barrier!

# Why study quantum rotations?

- Rotational dynamics as studied with neutrons reflect the molecular environment, i.e. the *energy landscape*
- Neutron tunneling spectroscopy provides extremely detailed information on the shape and magnitude of the potential energy of the molecular groups.
- Rotational tunneling measurements can be used to quantify interatomic interactions.
- Good test of first-principles/DFT calculations

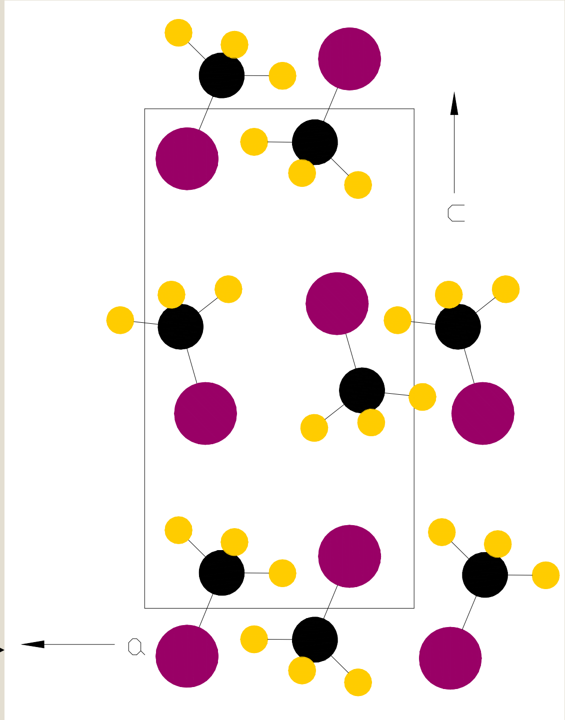
# Bulk $CH_3I$

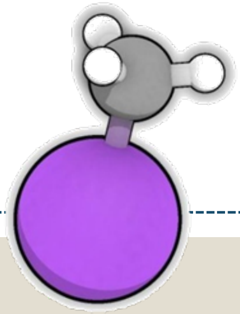
## A Canonical Rotational System

- Properties
  - MP: -66.5$^{o}$C
  - MW: 141.94 g/mol
  - Dipole moment: $\mu$ = 1.62 debye

Projection onto the a-c plane

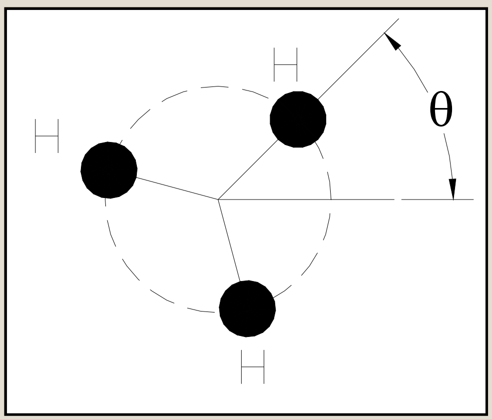
(Prager et.al.,J.Chem.Phys. **86**, 2563 (1987))





# The Methyl Group: $CH_3$

- We want to study the dynamics about the main molecular axis




$I[CH_3] = 5.3\times10^{-47}\ \mathrm{kg\cdot m^2}$

$$B = \frac{\hbar^2}{2I} = 0.65\ \mathrm{meV}$$

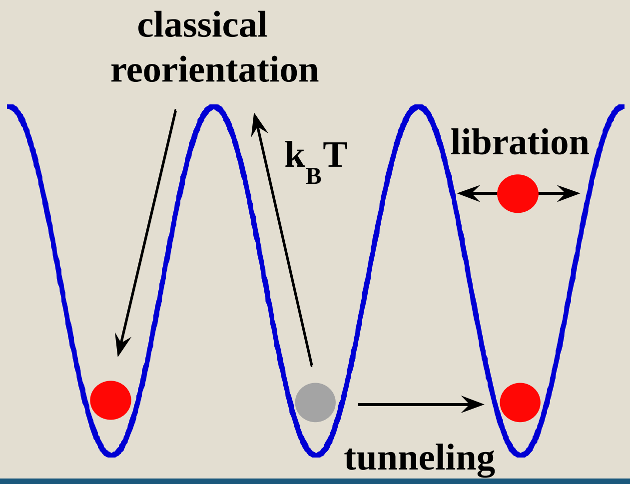
Free rotor energy levels: $E_j = BJ(J+1), \quad j = 0,1,2,\ldots$

| Useful conversions |
|---|
| 1 meV ↔ 4 ps |
| 1 μeV ↔ 4 ns |

# Bulk $CH_3I$ Dynamics

- Interaction potential of methyl group (1) van der Waals term, (2) short-range steric repulsion, and (3) additional multipole terms

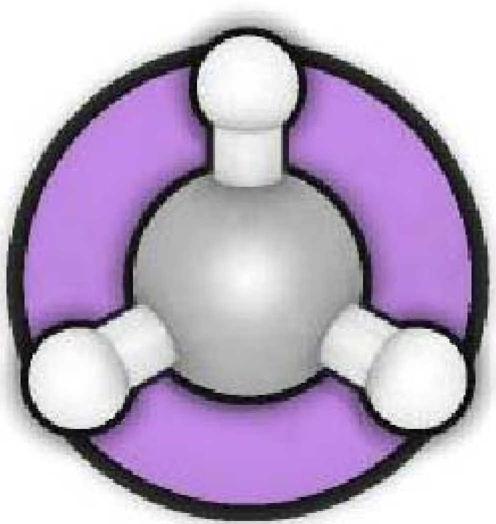
- Simplified model based on symmetry alone:




$$V(\theta) = \frac{V_3}{2}(1 - \cos 3\theta)$$

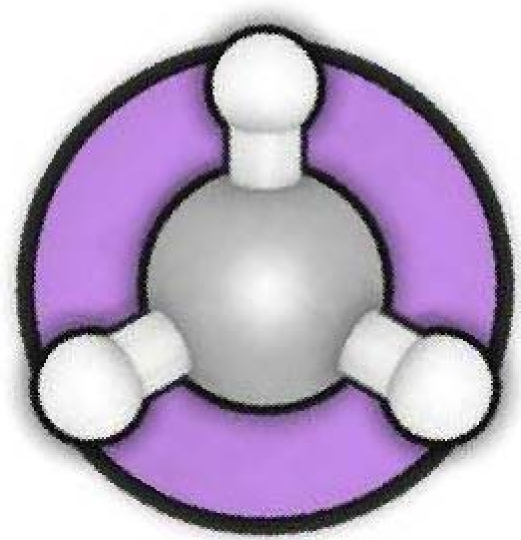
# Pictorial description of motions.

- Pictures looking down the C-I axis showing the motions of the hydrogen.



Libration

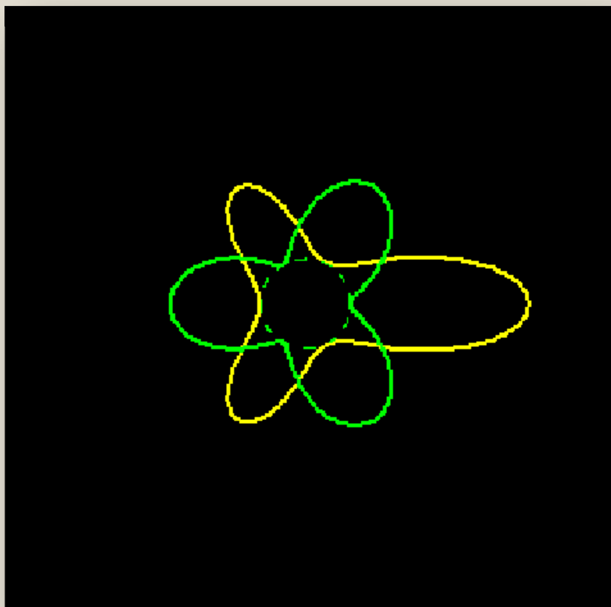
Tunneling



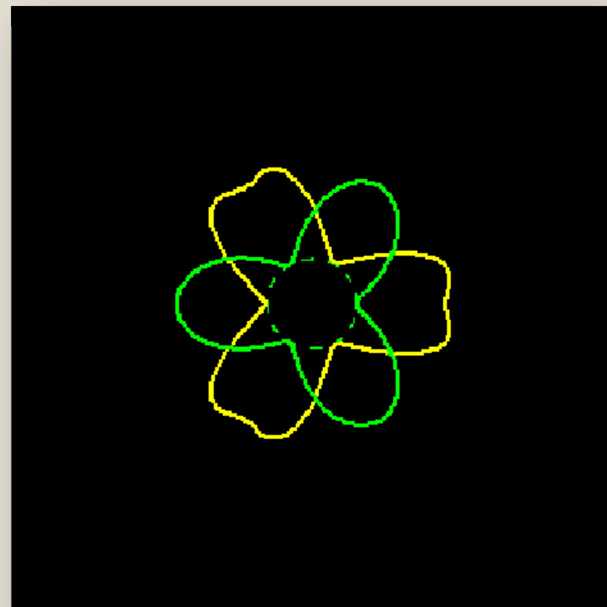
Jump Diffusion

# Quantum Rotational Dynamics

Tunneling



Torsional oscillations



# Using Inelastic Neutron Scattering to See Quantum Rotational Tunneling

Neutron scattering law for methyl tunneling

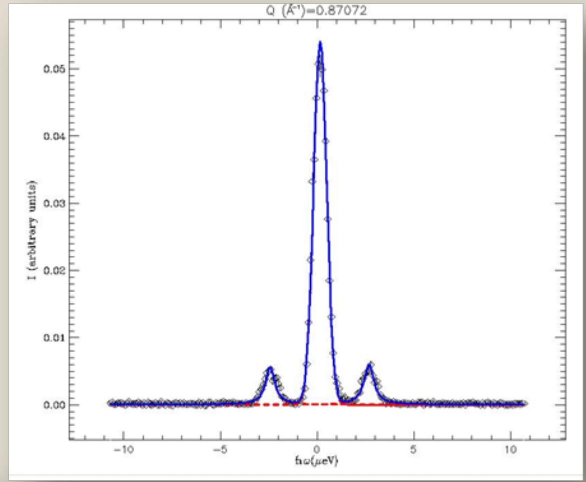
$$S(Q,\omega)=A_0(Q)\delta(\omega)+(1-A_0(Q))\frac{1}{2}[\delta(\omega-\omega_t)+\delta(\omega+\omega_t)]$$

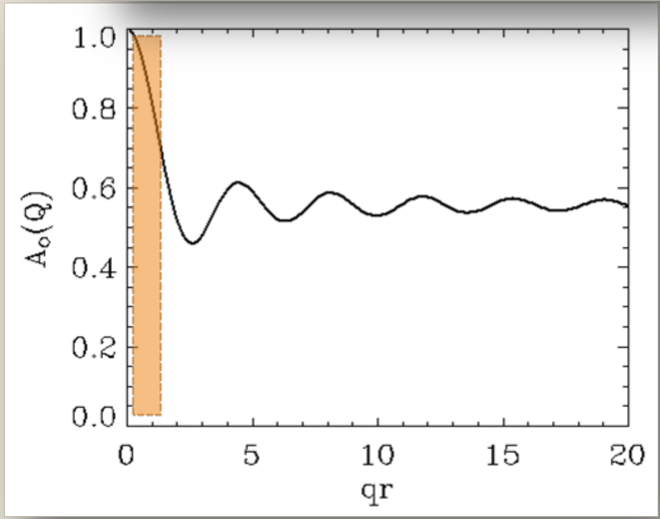
$$A_0(Q)=\frac{5+4j_0\left(Qr\sqrt{3}\right)}{9}$$

r: radius of methyl group

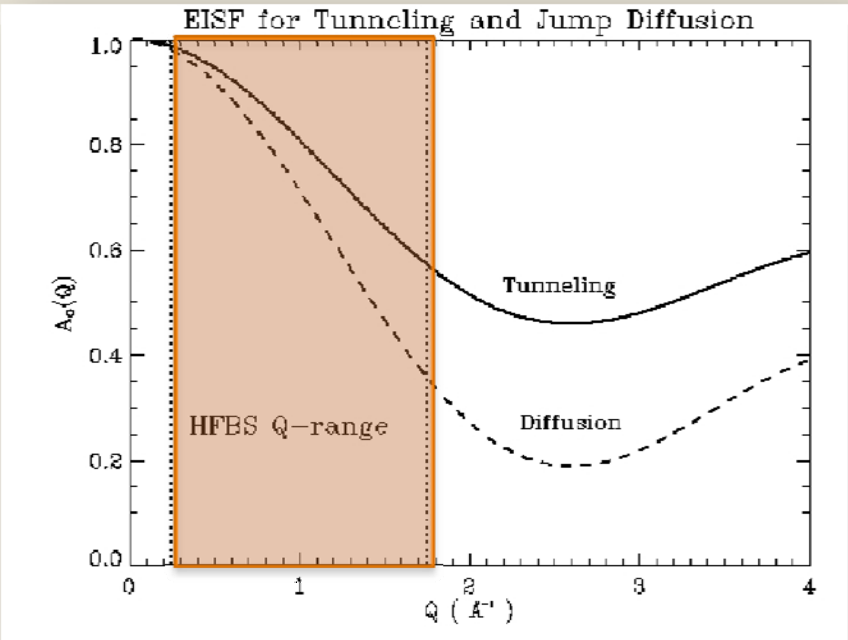
$\omega_t$: tunneling energy

$A_o$: elastic incoherent structure factor (EISF)



# EISF for Tunneling and Jump Diffusion




- Fit of previous equation to the data gives the model of the dynamics.

$$A_0(Q) = \frac{5 + 4 j_0\left(Qr\sqrt{3}\right)}{9}$$

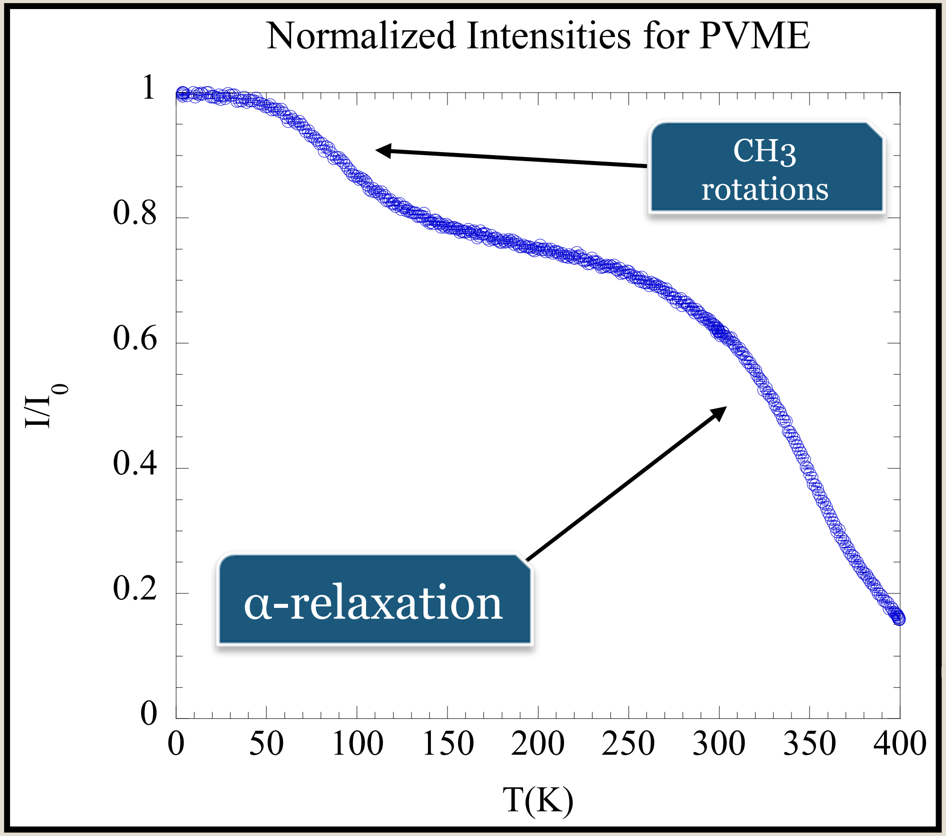
- This gives us the value for the radius of the methyl rotation.

# Polymers

## POLY(VINYL METHYL ETHER)
## (PVME)

# Poly(vinyl methyl ether)

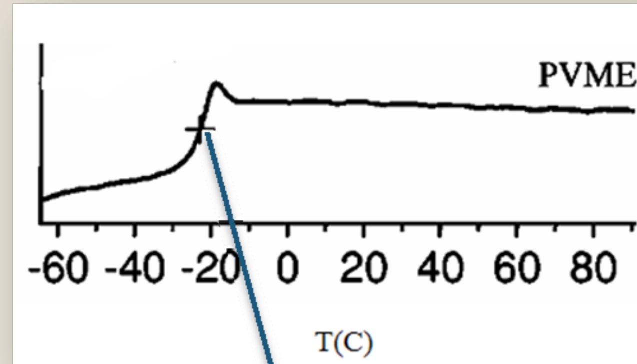
*Fixed Window Scan*



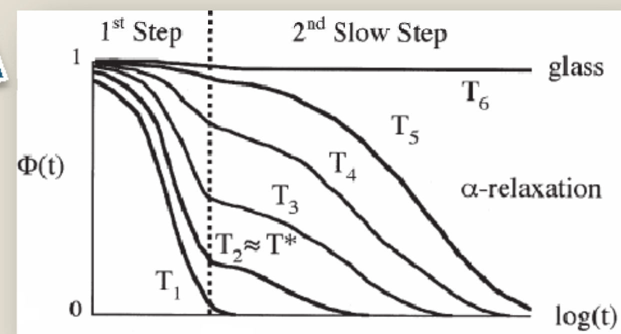

*Observation of fast and slow motions in a single scan!*

$-[CH-CH_2-]_n$
$O-CH_3$

*DSC*

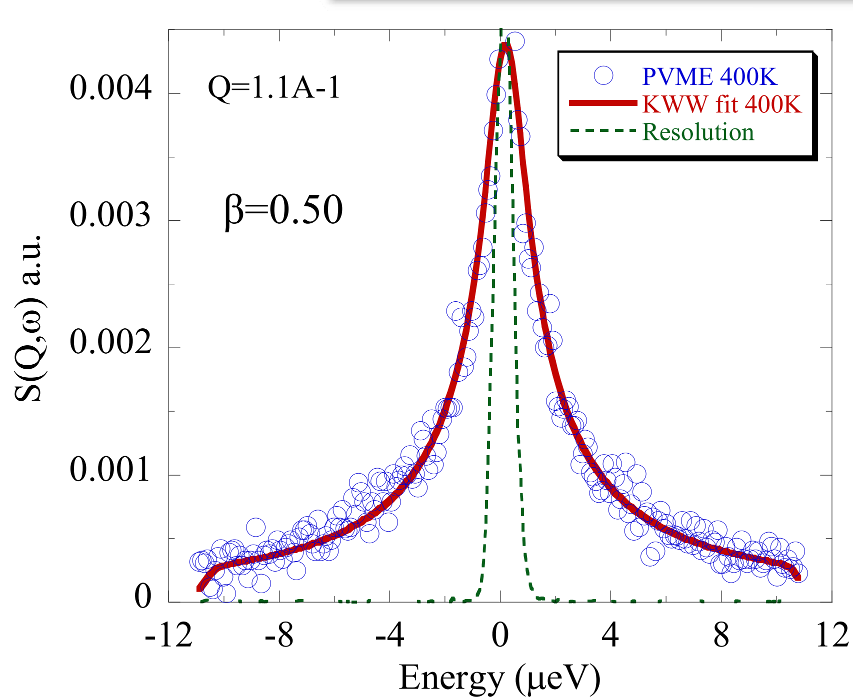


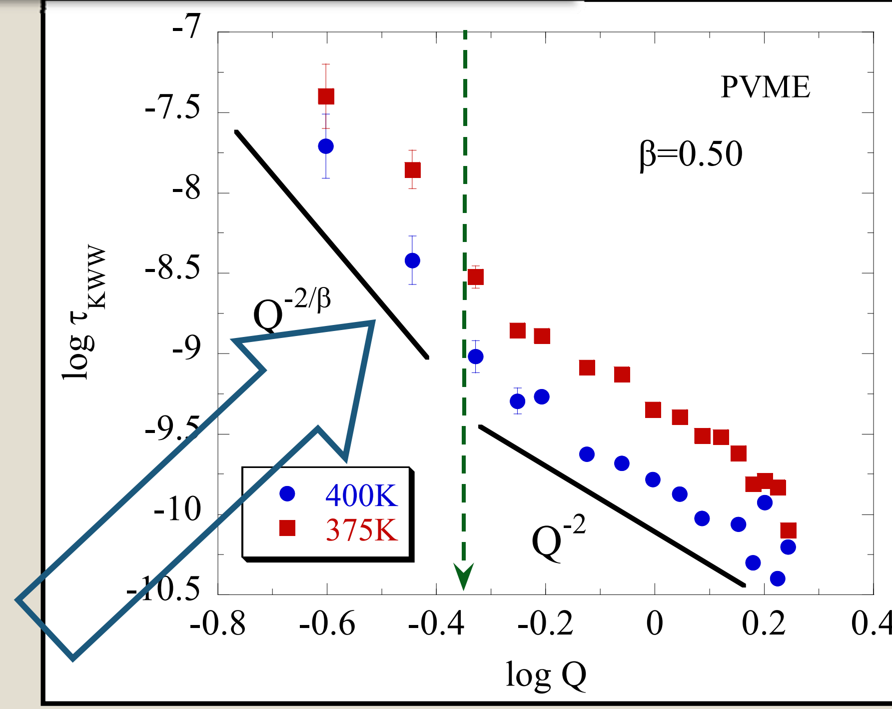

$T_g$=250 K




*MCT correlation function*

# Q dependence of characteristic time scales




$$S(Q,t) = A(Q,T)\ \exp\left[-\left(\frac{t}{\tau_{self}}\right)^{\beta}\right] \quad \textit{KWW}$$

*β is the KWW shape parameter which is usually temperature independent in polymers.*

$$\tau_{self}(Q,T) = a_0(T)Q^{-2/\beta}$$

*$a_0(T)$ is the temperature dependent pre-factor*

PVME shows a crossover from $Q^{-2/\beta}$ to $Q^{-2}$ in $\tau$!

# *Implications of $Q^{-2/\beta}$ power law*

Van-Hove correlation function

$G_s(r,t)$

*Gaussian case*

$$G_s^{Gauss}(r,t) = \left[\frac{\alpha(t)}{\pi}\right]^{3/2} \exp\left[-\alpha(t) r^2\right]$$

*Intermediate scattering function:*

$$S_{self}^{Gauss}(Q,t) = \exp\left[-\frac{Q^2 < r^2(t) >}{6}\right]$$

$$< r^2(t) > \approx t$$

$$S_{self}(Q,t) = A(Q,T) \exp\left[-\left(\frac{t}{\tau_{self}(Q,T)}\right)^{\beta}\right]$$

*where pre-factor A(Q,T)*

$$A(Q,T) = \exp\left(-\frac{Q^2 < u^2 >}{3}\right)$$

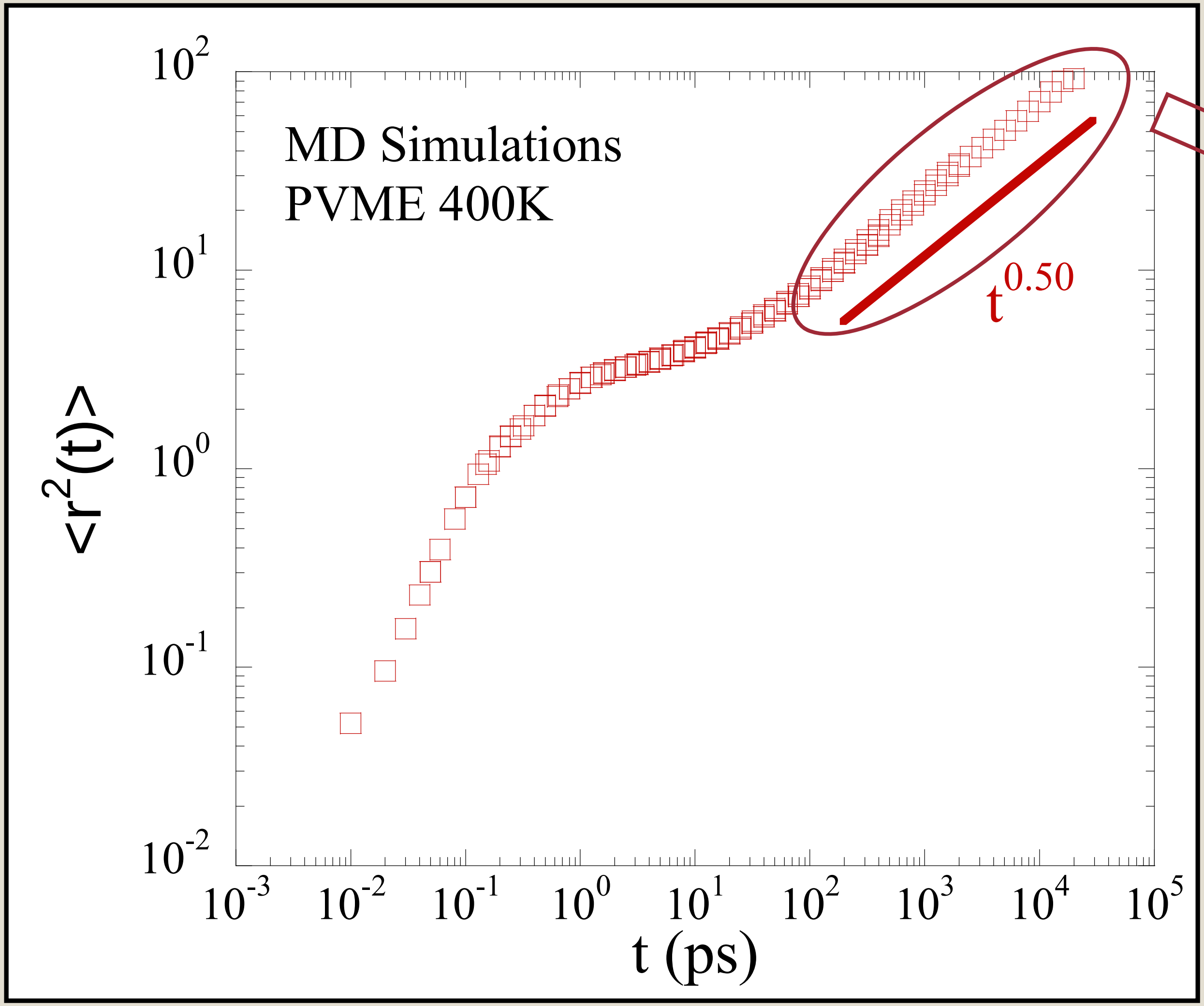
*Power law for characteristic times τ(Q,T):*

$$\tau_{self}(Q,T) = a_0(T) Q^{-2/\beta}$$

$$S_{self}(Q,t) = \exp\left(-\frac{\left\{2 < u^2 > +6\left[\frac{t}{a_0(t)}\right]^{\beta}\right\}}{6} Q^2\right)$$

$$< r^2(t) > = 2 < u^2 > +6\left[\frac{t}{a_0(T)}\right]^{\beta}$$

# MD Simulations for PVME

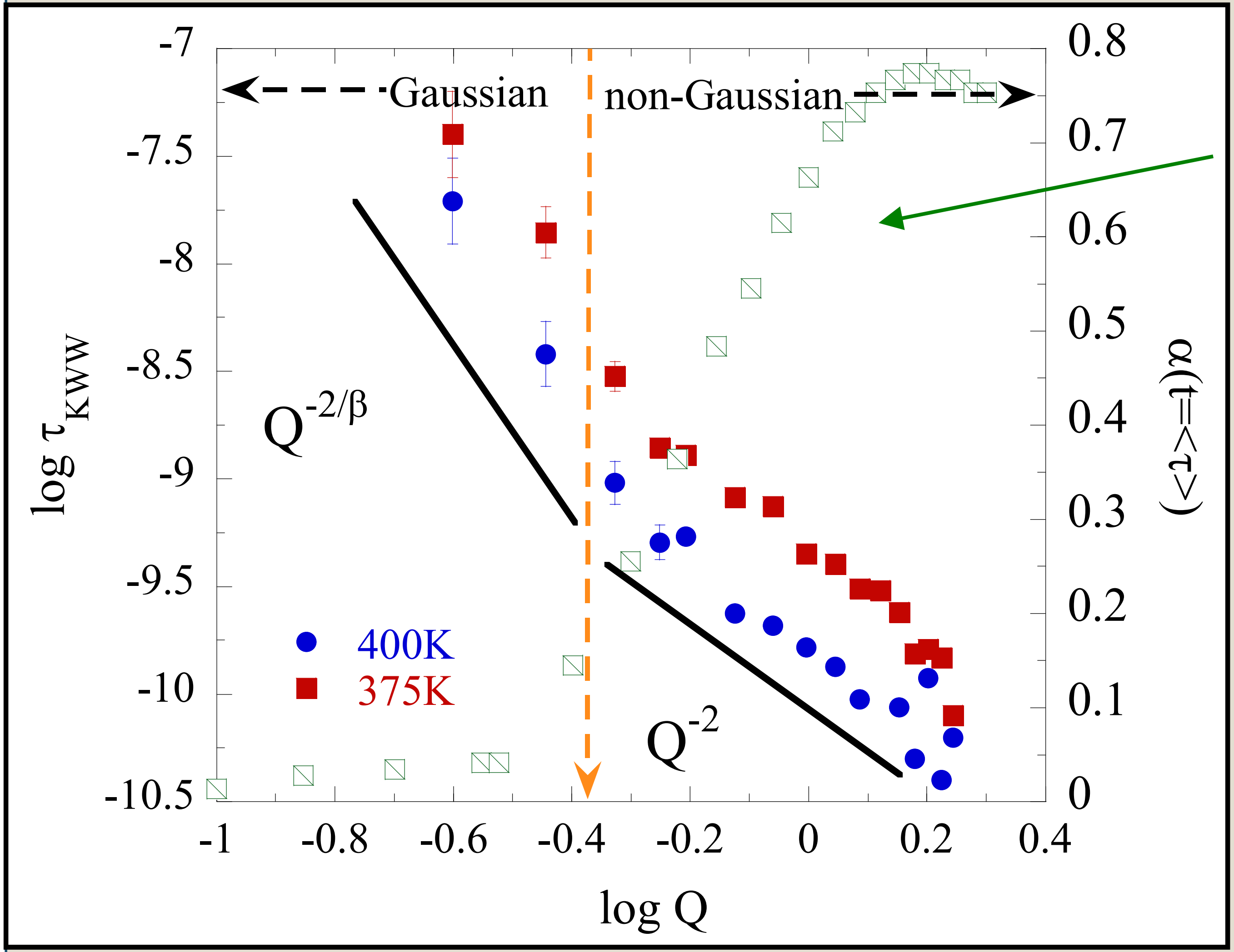



sub-diffusive like increase in MSD:

$$< r^2(t) > \approx t^{\beta}$$

After ps ballistic regime, a sub-diffusive regime is observed

# A crossover from Gaussian to non-Gaussian regime




non-Gaussian parameter

$$\alpha_2(t) = \frac{3}{5}\frac{\langle r^4(t)\rangle}{\langle r^2(t)\rangle^2} - 1$$

low $\alpha_2(t)$ in Gaussian Regime

Q

high $\alpha_2(t)$ in non-Gaussian Regime

# A general picture of dynamics in polymers