Local Viscosity of Supercooled Glycerol Near T_g Probed by Rotational Diffusion of Ensenbles and Single Dye Molecules

Soft Matter Optical Spectroscopy
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Contents

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Glycerol

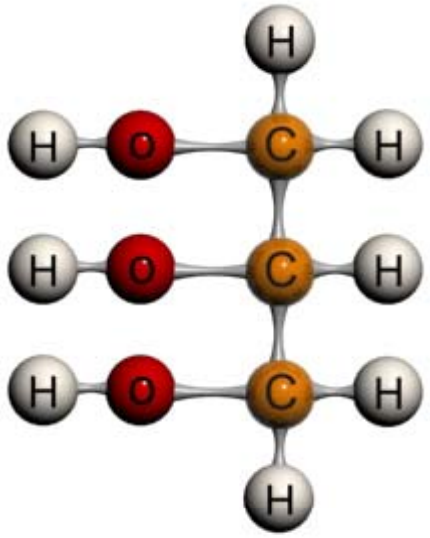
Archetypal Molecular Glass

High viscosity (1000 times higher than water at R.T.)

From intermolecular hydrogen bonds

T_g = 190K

Newtonian Liquid



Procedures

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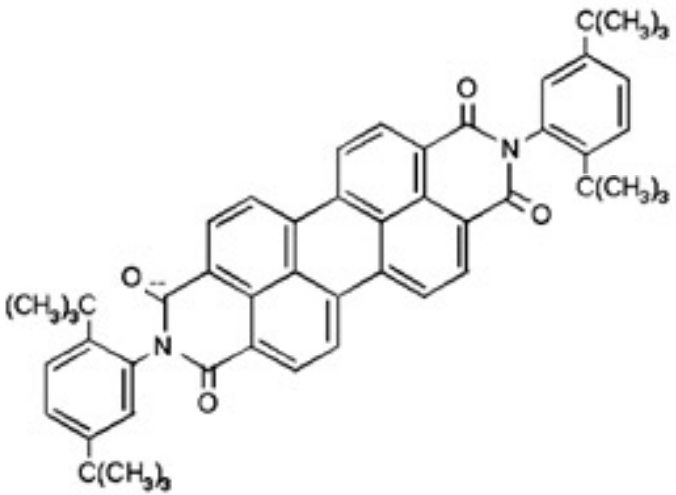
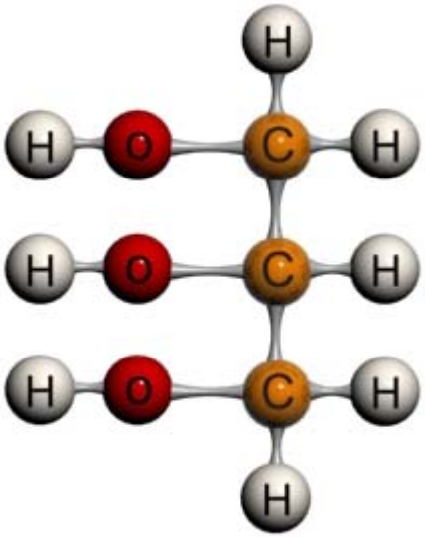


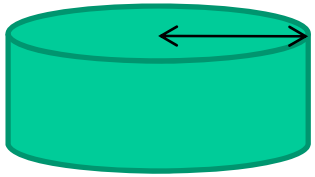
N,N'-Bis(2,5-di-tert-butylphenyl)
-3,4,9,10-perylenedicarboximide



Ensemble 10^{-7}M

Single Molecule 10^{-9}M

Spin-coating
at 6000rpm



20mm

0.5-2μm

Water < 0.1%

Procedures

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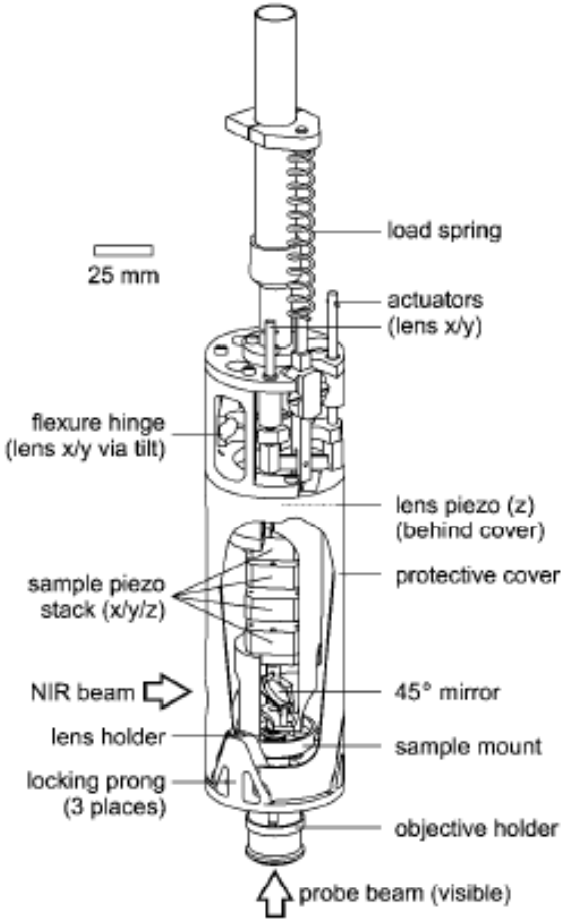
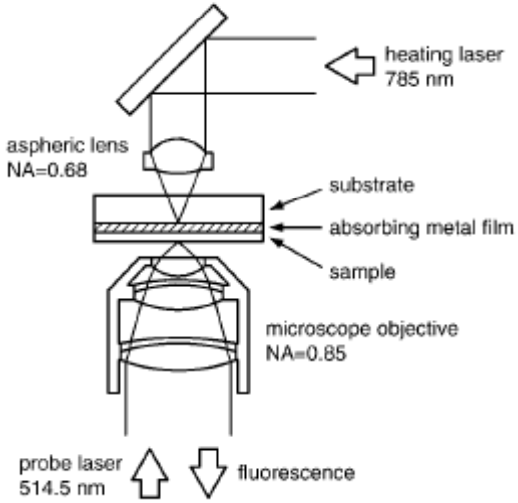
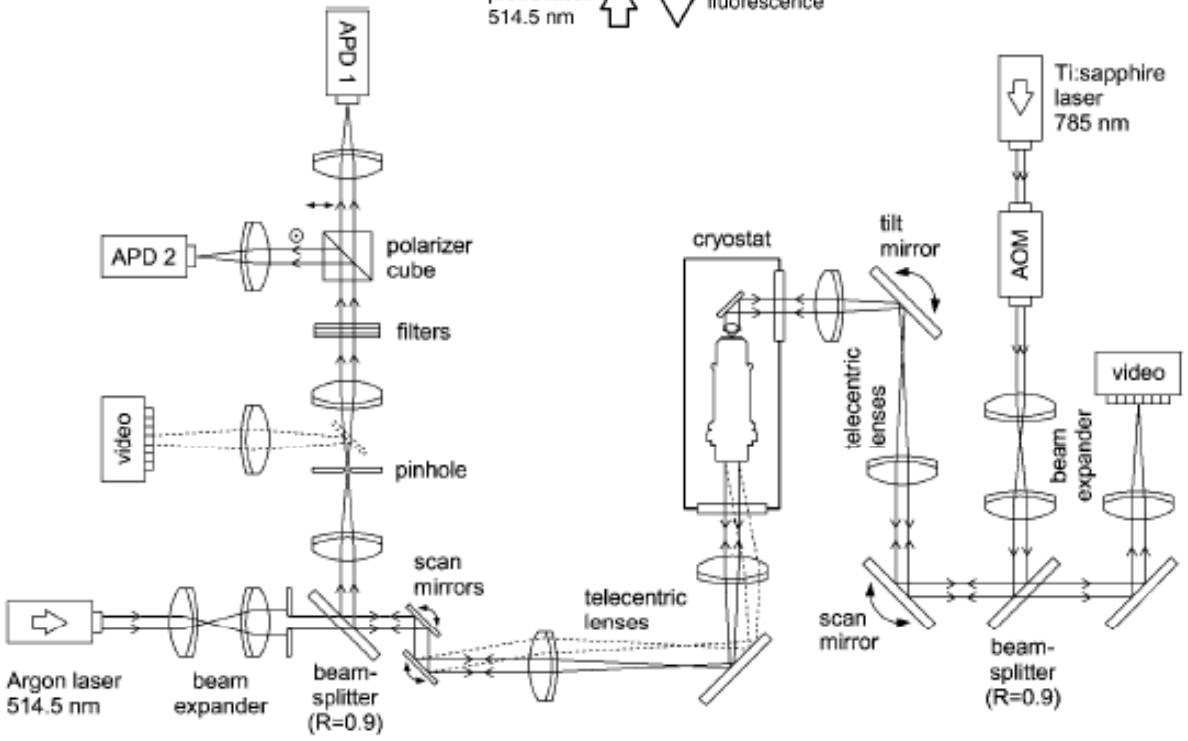
Biophysical Journal 90, 2958 (2006)







Viscosity

Debye–Stoke–Einstein relation

$$< t_R >= \frac{V\eta}{k_B T}$$

Vogel–Fulcher–Tammann–Hesse law

$$\eta = \eta_0 10^{B/(T-T_0)}$$

Fluorescence Anisotropy

$$r = \frac{F_{parallel} - F_{ortho}}{F_{parallel} + 2F_{ortho}}$$

$$C_r'(t) = \frac{< r(t'+t)r(t') >}{< r(t') >^2} - 1 \approx \frac{< c_{SM} >}{N} \exp(-\frac{t}{< t_R >})$$

Linear Dichroism

$$A = \frac{F_{parallel} - F_{ortho}}{F_{parallel} + F_{ortho}}$$

$$C_A^{'}(t) = \frac{< (A(t'+t)+1)(A(t')+1) >}{< (A(t')+1) >^2} - 1 \approx \frac{1}{2}\exp(-\frac{t}{< t_R >})$$

Results – Ensemble

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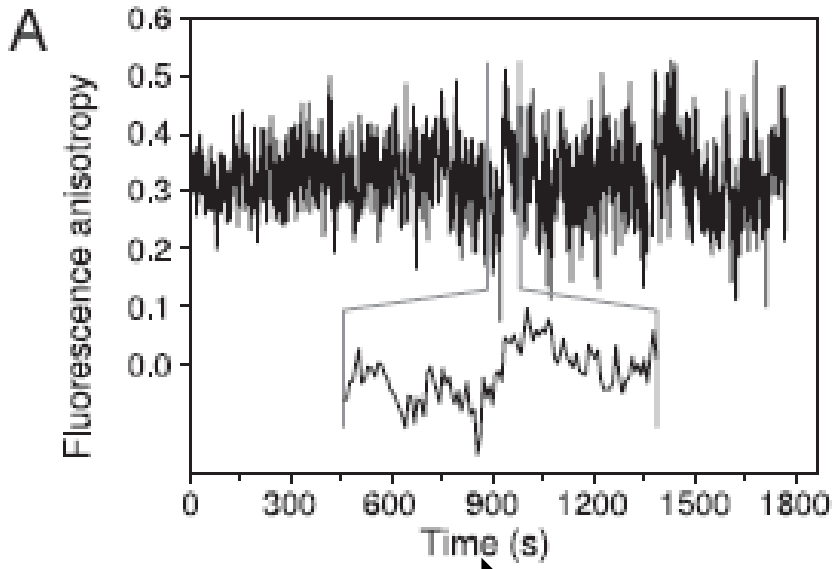

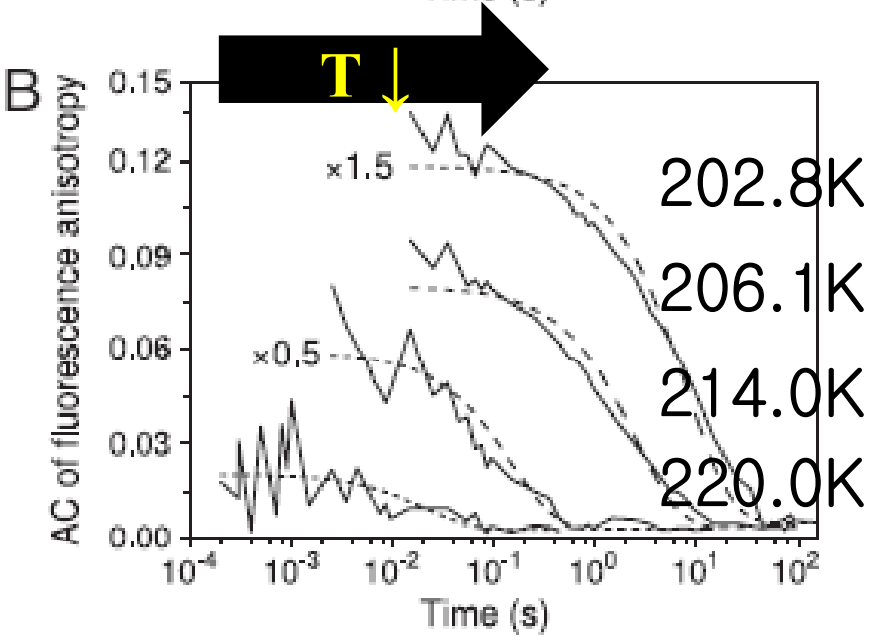

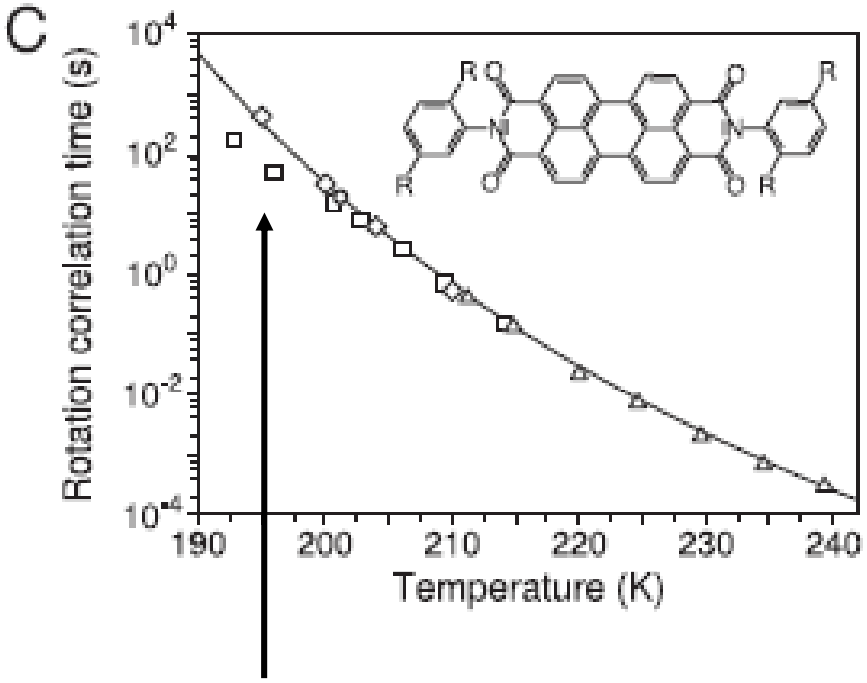

From photobleaching

Gregor I, Patra D, Enderlein J (2005)
ChemPhysChem 6:164–170.

Results – Single Molecule

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Anti-correlation (at 204.4K)

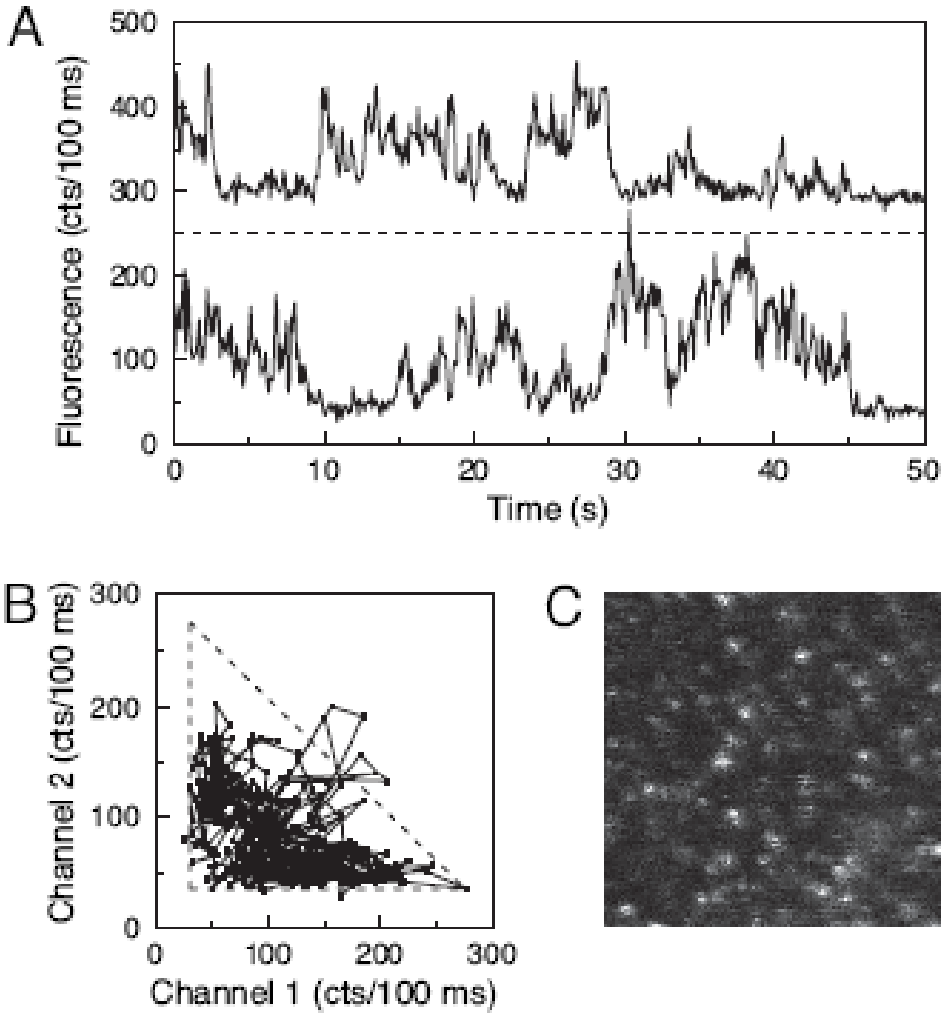

Fig. 2. Orientational diffusion of single molecules. (*A*) Polarized single-molecule fluorescence traces at $T = 204.4$ K revealing in-plane rotational diffusion. The traces show anticorrelated fluctuations. The total intensity fluctuates because of out-of-plane tumbling. (*B*) A correlation plot of the traces in *A* confirms the anticorrelation. A majority of points are included in a triangle bounded by the line with slope −1 and the offsets caused by the background counts in the two channels (dashed lines). (*C*) Example of a 20-×-20-μm fluorescence image showing single-molecule spots. The gray scale corresponds to the sum of the two detection channels, ranging from 30 counts (black) to 210 counts (white) for a integration time of 10 ms per pixel and an excitation intensity of 4.5 kW/cm^2.

Results – Single Molecule

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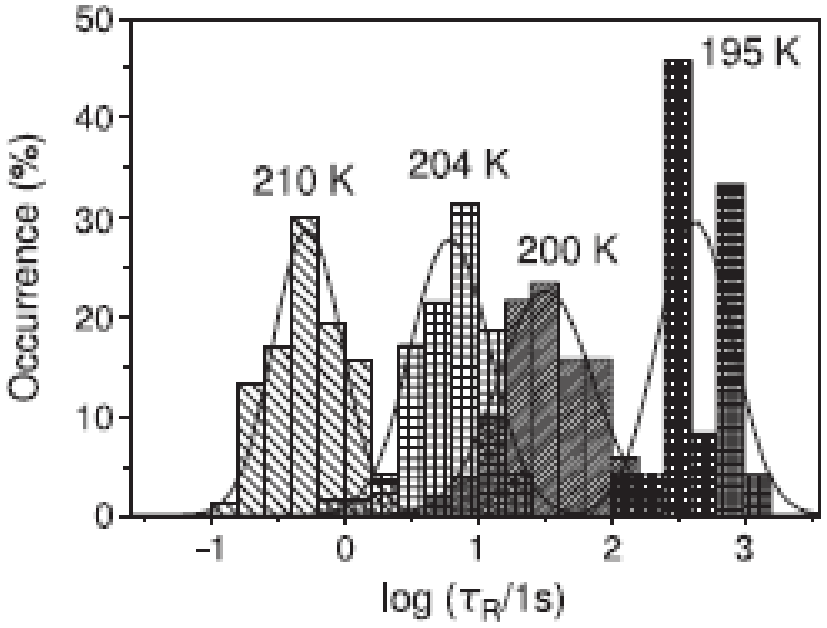

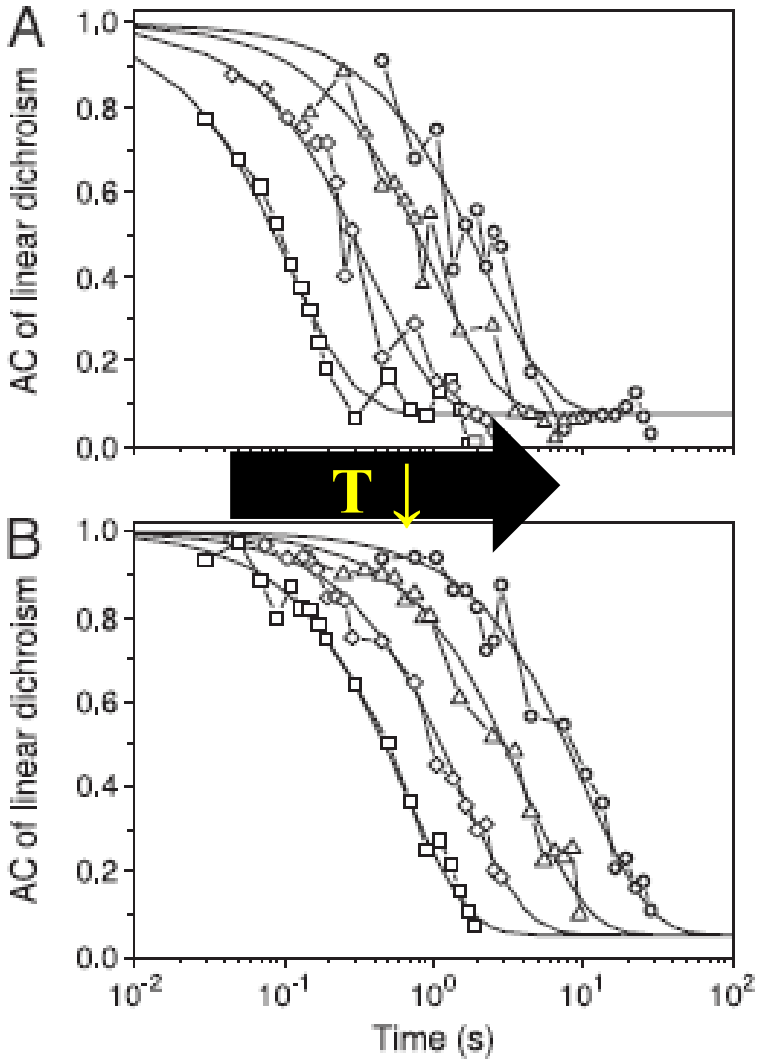

Results – Single Molecule

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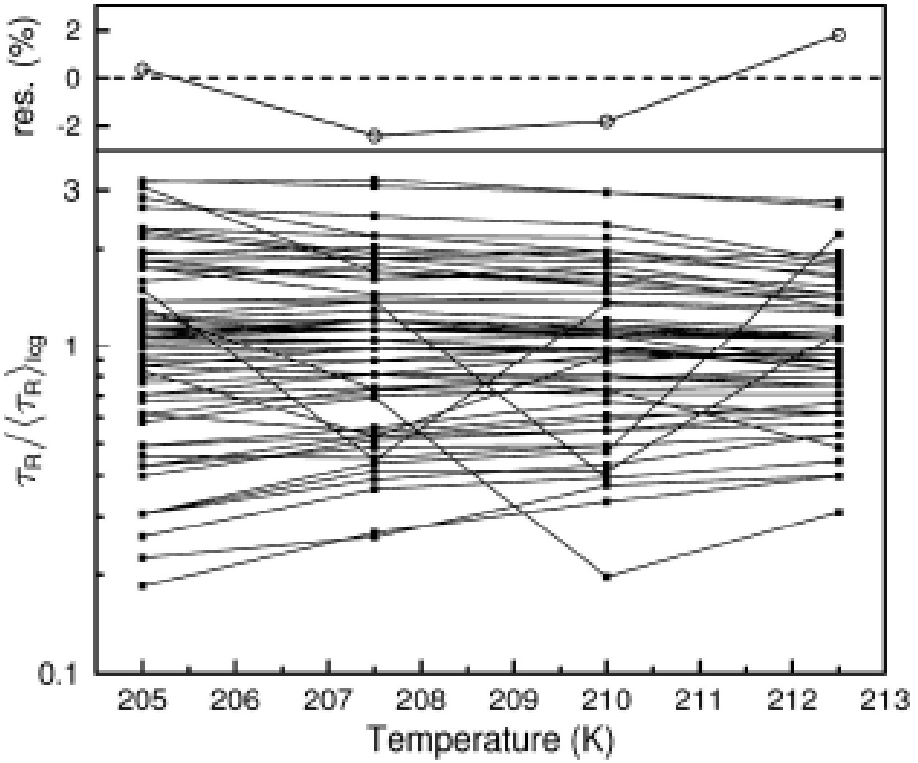

Discussion

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(1) Finding the broad distribution of the tumbling rates of individual molecules

(2) Environment changes are scarce, nearly absent – slow/fast tumblers remain very long time

Discussion

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Are Slow/fast tumbles glycerol-PDI solid?

No!

1) glycerol-PDI solid only affect to offset of fig.5
2) Size of PDI is constant
   (hydrodynamic volume)