Dynamics of water and ethanol intercalated in graphene oxide.

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Introduction

Water is the natural solvent as well as the major structure factor of living-beings which also influences many biological activities. Ethanol is also an important fluid in chemical, biological and industrial processes. The increasing population and chemical wastes from industries are making the availability of drinking water a global concern. On the other hand, ethanol is used for the production of fuels such as fuel graded ethanol, diesel-ethanol blends, etc. Ethanol as a commercial bio-fuel has promising environmental benefits [1]. It has been demonstrated that graphene oxide membranes are permeable by water, but not ethanol [2]. Thus, graphene oxide membranes were recently suggested for applications in separation of ethanol from water using a vapor permeation method.

The water and ethanol confined inside Graphene Oxide capillaries are restricted by the geometry of Graphene Oxide. Understanding microscopic diffusivity and viscosity mechanisms of water and ethanol in graphene oxide membranes is important for separations applications. We studied the anisotropy of water and ethanol diffusivity between the direction perpendicular to the plane an in-plane direction. We used quasi-elastic neutron scattering(QENS) to measure the diffusivity of ethanol and water.

Goals

Study the dynamics and viscoelastic behavior of water and ethanol intercalated Graphene Oxide at different temperatures to understand the separation process.

Methods

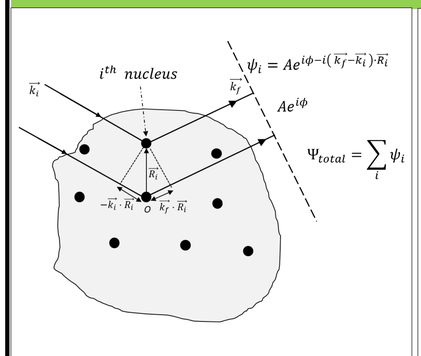

Figure 1.Schematic diagram of scattering event.

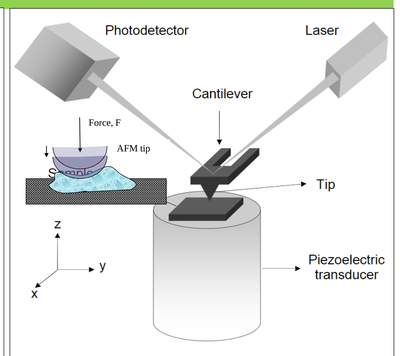

Figure 2. AFM schematic setup.

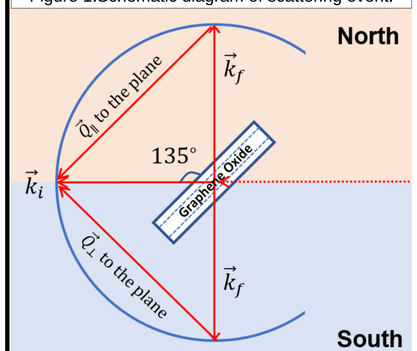

Figure 3. BASIS geometry that allows probing anisotropic diffusion in oriented samples.

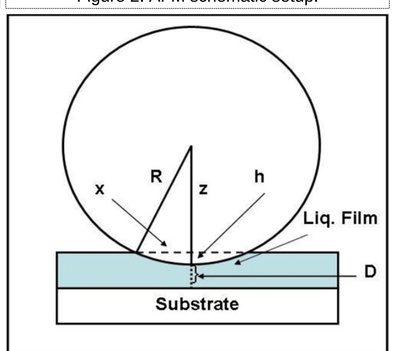

Figure 4. Contact geometry of flat surface and a spherical tip at very small separation D in the presence of a liquid film [3].

Double Scattering cross-sections

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{k_s}{k_i}\sum_i b_{inc}^2\, e^{-i\vec{Q}\cdot[\vec{R_i}(t)-\vec{R_i}(0)]}e^{-i\omega t} + \frac{k_s}{k_i}\sum_{i,j} b_{coh}^2\, e^{-i\vec{Q}\cdot[\vec{R_i}(t)-\vec{R_j}(0)]}e^{-i\omega t}$$

$$k_{ts} = k_L\left[\frac{A_0 cos\phi}{|A|} - 1\right]$$

$$\gamma = -\frac{k_L A_0 sin\phi}{|A|\omega}$$

$$F = \frac{6\pi\eta v R^2}{D}$$

Samples

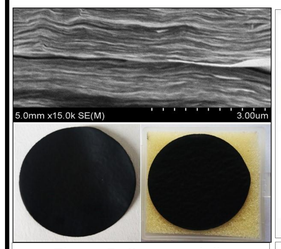

Figure 5. Commercially available GO membrane.

Figure 6. Commercially available GO powder.

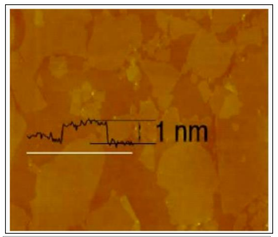

Figure 7. AFM image of High Surface Area GO

QENS Experiment and Data Analysis

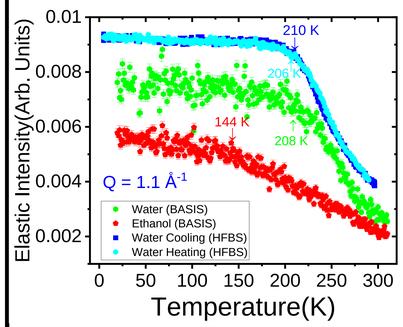

Figure 8. Elastic intensity of water and ethanol intercalated in GO.

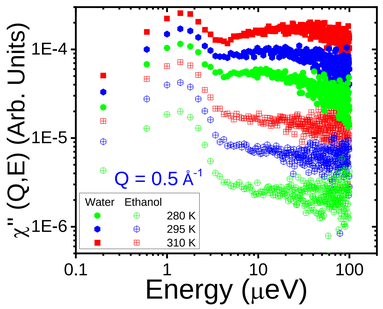

Figure 9. Dynamic susceptibility of water and ethanol confined in GO at different temperatures.

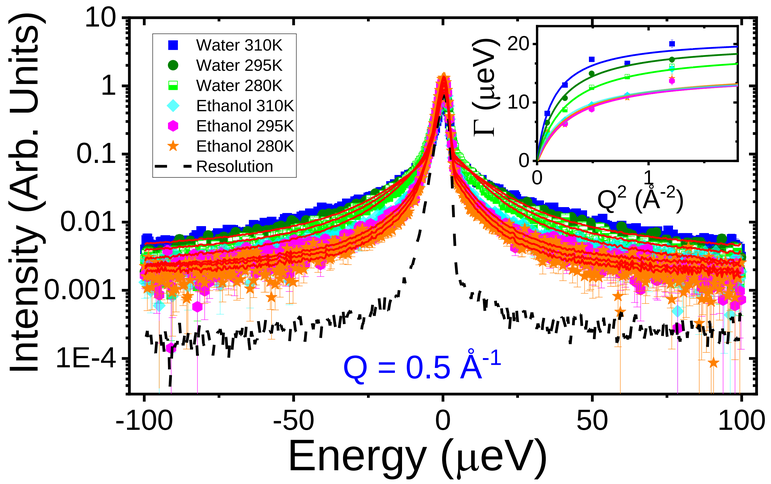

Figure 10. QENS spectra of water and ethanol intercalated GO at different temperatures. The symbols in the inset graph represent the dependence of Γ(Q) on Q^2 from which Diffusion coefficients are obtained.

QENS Experiment and Data Analysis…

- QENS measurements were performed at BASIS, Spallation Neutron Source, Oak Ridge, TN.
- Mantid[6] is used to reduce the data and DAVE [7] is used for analysis.
- Intensity I(Q,E) is fitted by using the following equation:

$$I(Q,E) = \left[A(Q)\delta(E) + \left(1 - A(Q)\right)S(Q,E) + B(Q,E)\right] \otimes R(Q,E)$$

- Broadening of the peaks compared to resolution reflects dynamics of water and ethanol molecules.

Model Equation:

$$S(Q,E) = \frac{1}{\pi}\frac{\Gamma(Q)}{\Gamma^2(Q) + E^2}$$

Γ(Q) = Half width at half maximum

$$\Gamma(Q) = \frac{DQ^2}{1 + DQ^2\tau_0}$$

Results

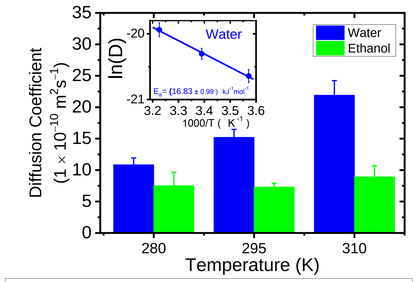

Figure 11. Diffusivities of water and ethanol in GO. The symbols in inset graph represents Arrehenius temperature dependence of diffusivity of water.

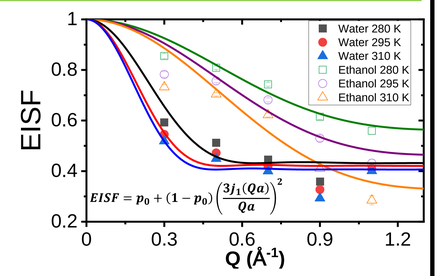

Figure 12. Elastic incoherent structure factor(EISF) for water and ethanol obtained from data measured at BASIS at different temperatures.

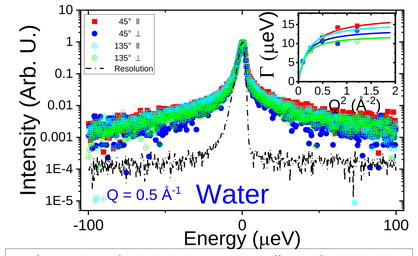

Figure 13. The QENS spectra collected at 310 K with Q's in parallel and perpendicular orientations as shown in figure 3 for water confined in GO .

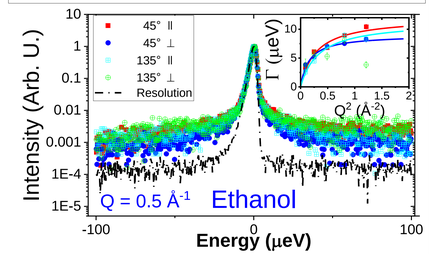

Figure 14. The QENS spectra collected at 310 K with Q's in parallel and perpendicular orientations as shown in figure 3 for ethanol confined in GO .

Conclusions

- Absence of phase transition in elastic scan:- **both water and ethanol are confined.**
- The diffusion of water is greater than ethanol.
- There is only single type of measurable dynamics of confined water and ethanol in GO within the instrument resolution.
- The diffusivity of water confined in GO shows Arrehenius temperature dependence.
- The obtained activation energy of confined water is close to the bulk water.
- There were no differences in QENS spectra's for parallel and perpendicular components:- **almost isotropic diffusion** of water and ethanol in GO.

Acknowledgement

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References

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