

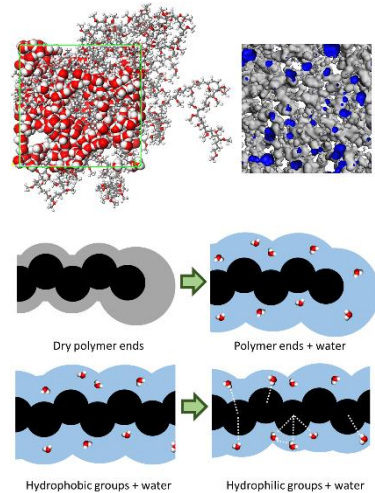
Free volume in polymer-water mixture.

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Free volume theory is one of the most successful concepts in polymer physics which says that a molecule or its constituents would move if they have enough space to do so. The first mathematical formulation came from Batchinski and McLeod who concluded the product of viscosity and the free volume quantity should be constant. Later on, Vogel, Fulcher and Tammann showed viscosities over wide temperature range obey super-Arrhenius relation. Doolittle managed to replace temperature in VFT equation with the free volume defined with respect to molecular hard-core volume that he fixed constant. Later, Williams, Landel and Ferry linked their equation with Doolittle's free volume theory by exploiting similarities in the both equations while they fixed amount of the free volume at T_g to $f_g = 1/C_1$. At the same time, they postulated the occupied volume should expand because of contributions originating from molecular vibrations. Simha and Boyer redefined the reference hard-core free volume thus increasing the free volume fraction at T_g towards more significant values. The universal value of the f_g was doubted as obtained from average of available polymers that time. The picture of the universal value was rejected by the recent LCL model by White and Lipson. As for multicomponent polymers, based on earlier picture, Fox suggested different polymers in a mixture would act like impurities to each other thus affecting T_g equally. Recent multicomponent problems that involve polymers in confinements, biological watery systems or nanocomposites pose challenges to the standing free volume theory. The free volume arguments are still used to interpret the behaviour of these novel systems based on the free volume-mobility relationship embedded deep in the free volume theory. But, the equations used for modelling the measurements still incorporate assumptions such as the iso-free-volume at T_g , linear expansion of the constituents' free volume that is not plausible in anomalous region of water, or intrinsic T_g 's of all components of the system that wouldn't stand in nanocomposites or confinements. Therefore, along with using free volume arguments, the free volume in the structures gets often measured by independent methods. Aside of molecular spectroscopies, that interfere with the measured free volume, there are only two possible direct methods for the free volume measurements. One is experimental method called positronium annihilation lifetime spectroscopy (PALS) that relates free volume in the structure with measured annihilation rate of positrons. But, the PALS probes only some of the cavities and provides their averaged cavity size. The fractional free volume from PALS is obtained as a combination of the iso-free-volume state f_g and measured expansion behaviour of the cavity sizes. The second method for direct measurements of the cavity free volume comes with molecular simulations and geometrical analyses of the intermolecular volumes. In this contribution, the free volume calculations are reported in "wet" poly-(vinyl methylether) with confined water ($c_w < 30\%$). The study consists of developing computational tools to analyse the free volume, comparisons with PALS measurements and some of the free volume theories. The simulations show that some of the free volume theories predict correct amounts of the free volume, mobility-free volume relationship stands, but despite larger free volume in *wet* PVME



the cavities are smaller compared to the *dry* system, and we don't see increased free volume around wet polymer ends.

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