FLOW OF FLUIDS IN VARIOUS NANOGEOMETRIES

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Summary and Conclusions

This thesis deals with the study of self-diffusion coefficient of fluid confined in various nanogeometries. The self-diffusion of fluid confined inside rectangular and cylindrical nanotube by using a dynamical model which is based on microscopic considerations has been studied. The theoretical model is based on the consideration that the confinement affects the movement at atomic level. The model predicts that the diffusion parallel to walls of channel is different from that of diffusion perpendicular to the walls. Near the walls the dynamics of fluid has been found to slow down to an extent that below a certain value of ratio of width to the diameter of particle, the molecules behave as if these belong to solid. The results are contrasted with the result obtained from the model based on similar considerations for a fluid confined only in one direction. It is found that tendency of freezing near the wall increases due to confinement from second direction. Empirical relation which governs the behaviour of diffusion coefficient as function of distance from the confining walls has also been proposed. The effect of confinement is more pronounced for denser fluids than for dilute fluid. The results of cylindrical nanotube have been contrasted with that of fluid confined in rectangular nanotube and it is observed that for different geometries having same cross-section area the effect of confinement is almost same. Further, expressions for second and fourth sum rules of velocity auto correlation function have been obtained for fluid confined in a rectangular nanotube. The sum rules obtained are

anisotropic and are function of density profiles. These sum rules coupled with the direct effect of confinement on motion of fluid particles have been used to study the self diffusion coefficient. To vary the density of fluid in a nanotube, we consider model density profiles. The perpendicular diffusion coefficient is found to be more strongly dependent on the width of the tube than the parallel diffusion. The perpendicular diffusion of fluid does not follow properties of the diffusion coefficient observed in bulk fluid. The local diffusion is found to increase with the increase in density. Our results for average diffusion across the nanotube are consistent with the results obtained by molecular dynamic simulations for diffusion coefficients for argon-fluid confined inside krypton walls. Also, the dynamics of fluid contained in a nano-cube has been studied by proposing theoretical model which is based on the microscopic consideration. The confinement affecting the movement at atomic level has been used to study the self-diffusion through Green Kubo relation. It is found that close to the walls, the dynamics of fluid slows down to an extent that it affects the flow of fluid even in the middle of the nanocube. Results are contrasted with the results obtained from similar considerations for fluid confined in rectangular nanotube. It is found that tendency of freezing near the wall is more in case of nanocube than in the rectangular nanotube. An empirical relation has also been proposed to explain the behaviour of wall mediated self-diffusion as a function of distance in either direction. Finally, the dynamics of fluid confined in a nano-channels having structured walls has been studied through velocity autocorrelation function (VACF) and memory function approach. The strong interaction between fluid molecules and with confining wall influences the static and dynamic properties of confined fluid. The VACF is used to determine the self diffusivity of the confined fluid. The memory function formalism has been applied to a fluid confined in a nano-channel from z-direction. The three analytic closure models for the memory function have been considered for taking most of the features of VACF of bulk fluids in consideration. The Mori's constant are used as input into the models has been obtained by evaluating frequency sum rules of VACF. Once VACF is obtained through memory function, the self diffusivity of the confined fluid can be evaluated. The interaction between fluid-fluid molecules and fluid-wall molecules have been considered and for the solid wall interactions are modelled using Lennard Jones (LJ) 12-6 potential.