A biased Gibbs Ensemble Monte Carlo (GEMC) simulation technique for prediction of vapor liquid equilibria of all atom linear, branched and cyclic molecules with fixed bond length constraints

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Gibbs Ensemble Monte Carlo (GEMC) technique has been established as a powerful method to predict coexistence properties of pure and mixtures of fluids. Particle exchanges between the two phases are carried out to satisfy equality of chemical potential criterion at equilibrium. As with any open ensemble simulations, insertion of articulated molecules becomes prohibitively expensive for dense and confined fluids in GEMC. Configurational biased Monte Carlo (CBMC) techniques are routinely combined with GEMC to improve the insertion efficiency in such instances. In this poster we provide details of fragment sampling, also known as reservoir sampling and its implementation in GEMC as an alternative methodology for particle swap moves and also to alter conformation of molecules. Correct sampling of bond angle distribution with fixed bond length constraints of fragments is achieved with a novel Monte Carlo technique that is exceedingly simple and efficient. Results obtained for bond angle distributions for branch points containing three and four branches have been validated against those produced by a brute force Boltzmann rejection scheme at 298 and 1000 K. Extension of the algorithm for efficient sampling of cyclic molecules with constrained bond lengths such as an all atom model of benzene will also be discussed. Finally, vapor-liquid equilibria calculations for linear alkanes, branched united atom alkanes and all atom cyclic molecules will be presented.