518h Study of the Molecular Weight Dependence of Surface Tension of Low Molecular Weight Alkanes by Molecular Dynamics Simulation

Chunli Li and Phillip Choi

Surface tensions (γ) of a series of low molecular weight alkanes with chain lengths from 30 to 200 carbons at 150 ºC were calculated using molecular dynamics simulation. In particular, for each alkane, the internal energies of its bulk state (U_{3D}) and thin film state (U_{2D}) models consisted of the same number of molecules were calculated. And their difference (i.e., $U_{2D} - U_{3D}$) was then used along with the solvent accessible area (σ) of the thin film state model to determine the corresponding surface tension using the expression: $\gamma = (U_{2D} - U_{3D})/\sigma$. The approach is consistent with one of the macroscopic definitions of surface tension (i.e., $(\partial U/\partial \sigma)_{S,\,V,\,n}$) where S, V and n denote the entropy, volume and number of molecules of the system, respectively. Since simulations of the bulk and thin film states were carried out at a fixed temperature, the entropy change of each model system as a result of the change of its surface area was negligible. As a result, we feel justified to assume that S is constant. To keep volume constant, the bulk state was constructed in such a manner that its volume was set to be equal to the thin film state volume bounded by the solvent accessible areas. Doing so (i.e., adhering the above surface tension definition) would inevitably create a bulk state that tends to have a density value slightly lower than the corresponding experimental value, leading to higher U_{3D} and lower γ values. Since the computed surface tension depends significantly on the solvent accessible area used and such area depends on the size of the spherical probe used, various probe sizes were evaluated. And our results show that using a spherical probe of the size that was equal to the diameter of the largest free volume hole in the bulk material, so-called the critical probe size, led to serious underestimation of surface tension. It is worth noting that probes with the critical probe size are commonly used for the determination of the solvent accessible area for biological macromolecules. Nonetheless, when the diameter of the probe used was in the length scale that was comparable to the Kuhn length of polyethylene (~ 1 nm), good agreement was achieved. This finding seems reasonable as a probe with diameter larger than the Kuhn length of polyethylene (long chain alkane) would not sense the roughness of the alkane surfaces while too small a probe would yield additional surface area that may not be accessible to other molecules. Regardless of the probe size used, we were able to reproduce the experimentally observed molecular weight dependence of surface tension of these low molecular weight alkanes ($M_n^{-2/3}$). Analysis of various intra- and inter-molecular energy terms used in the calculation of the surface tension indicates that the observed molecular weight dependence originates from the stretching of the backbone carbon-carbon bonds.