

Supporting information for: Structure of Liquid Propionitrile at Interfaces. 1. Molecular Dynamics Simulations

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I. Orientations of CN Vectors at the Liquid-Vapor Interface

As was discussed in Section III.B.1 of the paper, the CN vector orientations at the liquid-vapor interface (LV) region have a slight dependence on the choice of molecular positions. We ascribe this dependence to the “overcounting” of molecules, which has been discussed in detail in our previous publication on the simulation of acetonitrile.¹ Here we show the orientation profile of the CN vector in the LV region as defined by the center of mass of propionitrile. This profile is plotted in Figure 1, and indeed shows that more propionitrile molecules tend to point their CN groups into the liquid phase than out of it, since the area above 90° is larger than that below 90° for the angular distribution in the LV region (blue curve).

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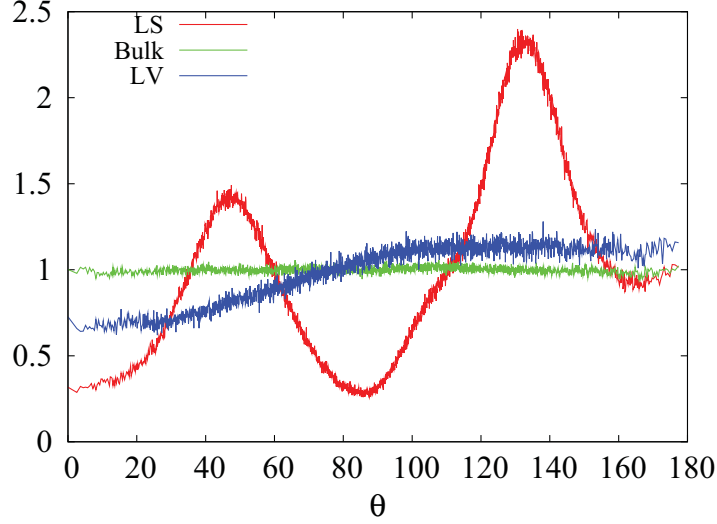


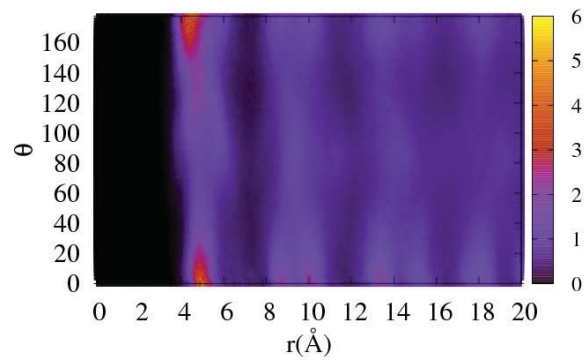
Figure 1: Angular distribution of θ in the first layer of the liquid-solid (LS) interface (red), the bulk (green) and the LV (blue) region, where θ is the angle between the CN vector and surface normal. Here each region is defined by the center of mass of propionitrile molecule: LS: $z_{cm} < 4.9$ Å; Bulk: $30 \text{ Å} < z_{cm} < 50 \text{ Å}$; LV: $56 \text{ Å} < z_{cm} < 63 \text{ Å}$.

II. Radial/Angular Correlation Function

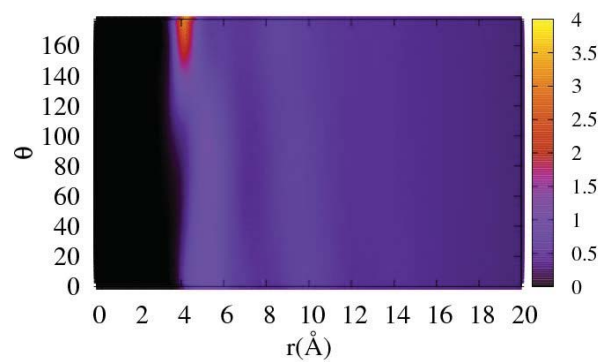
The radial/angular correlation function for CN vectors in a given region (liquid-solid, bulk or LV) is defined as¹

$$g(r, \theta) = \frac{1}{N_c} \sum_{i=1}^N \sum_{j=1}^N \langle \delta(r - r_{ij}) \delta(\theta - \theta_{ij}) \rangle, \quad (1)$$

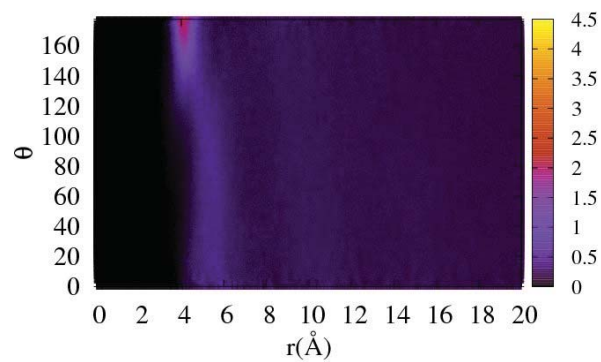
where N_c is the number of molecules contained in this region, r is the distance between center of mass of two molecules and θ is the angle between the CN vectors in between two propionitrile molecules. Contour plots of $g(r, \theta)$ in different regions are shown in Figure 2. Compared with the typical antiparallel structure in the bulk and LV region, the $g(r, \theta)$ of first LS layer shows both parallel correlation at $\theta = 0^\circ$, indicating angular correlation within the same sublayer, and antiparallel correlation at $\theta = 180^\circ$, indicating correlation between molecules in one sublayer with molecules in another sublayer. In the bulk there is only strong antiparallel correlation near $\theta = 180^\circ$, because such an arrangement minimizes the interactions between molecular dipoles. The antiparallel correlation is stronger in the LV region than in the bulk, as was seen previously for acetonitrile.¹



(A) LS



(B) Bulk



(C) LV

Figure 2: Contour plot of the radial/angular distribution function $g(r, \theta)$ in the LS, bulk and LV regions. r is the distance between the centers of mass of a pair of molecules and θ is the angle between their CN vectors.

References

- (1) Hu, Z. ; Weeks, J. D. *J. Phys. Chem. C* 2010, 114, 10202-10211.