

Density Functional Approach for Modeling Polymer-CO₂ Interfaces

Over the past decade supercritical carbon dioxide (scCO₂) has emerged as one of the most significant solvents for polymer processing. During this period, manufacturing of polymer foams has remained the primary focus, since it is believed that scCO₂ has the potential to replace CFCs in the production of polymeric foams. In recent times, scCO₂ has also been used for polymer processing applications, such as bonding of polymer thin films, impregnation of proteins in the polymer matrix and fabrication of nanoparticle reinforced polymer composites, at smaller length scales (nano). The success of scCO₂ as a solvent is attributed to its four-fold advantage, viz., tunability to desired temperature and pressure, affinity to important organic molecules like PS and PMMA, low viscosity leading to enhanced mobility, and environmentally friendly nature. However, despite numerous advances on the experimental front, optimization of many processes involving polymer-scCO₂ binary mixture is still a challenge primarily because of the lack of theoretical models that can describe the binary system at the molecular level. This work is aimed at bridging the gap between theoretical and experimental knowledge through molecular-level analysis of the system using polymer density functional theory (PDFT). This theory offers semi-quantitative information at lower computational costs as compared to computer simulation. The basic idea of PDFT is to express the free energy as a functional of spatially varying density distribution, from which equilibrium density distribution and other thermodynamic information can be derived including solubility of CO₂ in polymer, interfacial tension, and glass transition characteristics (especially across the polymer-CO₂ interface).

As described in our previous report, model parameters of our PDFT have been determined to reproduce a relevant part of polymer-CO₂ phase diagram. In this report we will discuss some of our preliminary results for density profiles across the interface and the effects of the presence of CO₂ on these density profiles. It is believed that the information obtained from such results will help in optimizing the processing conditions and enhancing the quality of the products.

PDFT: Model Description

Our PDFT model describes a polymer molecule as a chain containing a fixed number of interaction sites n , with CO₂ molecules interspersed between the chains. For comparison with experimental results, a system that is open to CO₂ and has fixed number of polymer molecules is appropriate. The relevant free energy for such a system is Ω . Following the development by Christopher and Oxtoby, we write the free energy functional for the binary system as:

$$\begin{aligned} \beta\Omega[\rho_\alpha(\mathbf{r})] &= - \int d\mathbf{r} \exp(\beta u_0^{(0)}) + \sum_\alpha \mu_\alpha N_\alpha \\ &- \int \left(\prod_a^n d\mathbf{r}_a \exp(\beta u_a^{(0)}) \right) S\{\mathbf{r}_i\} + \beta F_{exc}[\rho_\alpha(\mathbf{r})] \\ &- \int d\mathbf{r} \rho_0(\mathbf{r}) \beta U_0(\mathbf{r}) - \sum_\alpha \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \beta U_\alpha(\mathbf{r}), \end{aligned} \quad (1)$$

where α is the site label and $\beta = 1/k_B T$ is the reciprocal temperature. The third term in the above equation represents the intramolecular interactions between the polymeric segments, with $S\{\mathbf{r}_i\}$ being the normalized intramolecular correlation function. The excess Helmholtz free energy F_{exc} represents the intermolecular interactions between polymeric sites and CO₂ molecules:

$$\begin{aligned} \beta F_{exc} &= \int d\mathbf{r} \Psi(\bar{\eta}(\mathbf{r})) \rho_s(\mathbf{r}) \\ &+ \frac{\beta}{2} \sum_{i,j=0}^n \iint d\mathbf{r} d\mathbf{r}' \phi_{i,j}^{att}(|\mathbf{r} - \mathbf{r}'|) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}'), \end{aligned} \quad (2)$$

where the first term on the right hand side accounts for the repulsive (hard sphere) contribution to the free energy, while the second term represents the perturbative contribution from attractive site-site interactions. The latter is modeled by the attractive part of the Lennard-Jones potential:

$$\phi_{i,j}^{att} = \begin{cases} 0 & x \leq \sigma \\ -4\pi\epsilon_{ij}x^{-6} & x > \sigma \end{cases} \quad (3)$$

the constants ϵ_{ij} and σ_{ij} (for $i,j=$ interaction sites of polymer and CO₂) are the energy and length parameters characterizing the pertinent binary system.

The equilibrium density profiles ρ_i for CO₂ molecule and polymer chain sites are obtained from the stationary condition of the free energy:

$$\left. \frac{\delta\Omega}{\delta\rho_i} \right|_{\tau, \nu, \mu} = 0 \quad (4)$$

Equations (1) and (4) lead to the following expressions for the density profiles of polymer sites ρ_α ($\alpha=1$ to n) and CO₂ molecule ρ_0 ,

$$\rho_\alpha = \frac{N \exp(\beta u_\alpha^{(0)}) \int \left(\prod_{a \neq \alpha}^n d\mathbf{r}_a \exp(\beta u_a^{(0)}) \right) S\{\mathbf{r}_i\}}{\int \left(\prod_a^n d\mathbf{r}_a \exp(\beta u_a^{(0)}) \right) S\{\mathbf{r}_i\}} \quad (5)$$

$$\rho_0 = \exp(\beta u_0^{(0)}) \quad (6)$$

Equations (5) and (6) constitute a set of $n+1$ coupled integral equations that have to be solved numerically. In our calculations we use $n=10$.

Results: Density Profiles

As mentioned earlier, numerical solutions for the coupled equations (5) and (6) give the spatially varying density distribution across the polymer-CO₂ interface. Details for solving multidimensional integrals involved in these equations have been described by Christopher and Oxtoby. The chemical potential of CO₂ was held constant at its bulk value at the phase coexistence, while the number of polymer molecules N was fixed. Calculations were performed at 10 Mpa and 323 K, as these conditions are in the range of the solubility data that we used for parameterization. These conditions also represent the supercritical region for CO₂, hence the results obtained relate well to the polymer-scCO₂ binary system.

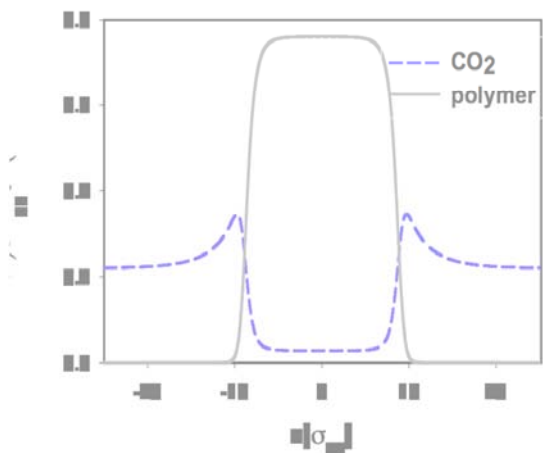


Figure 1a. Density profiles for CO₂ and polymer

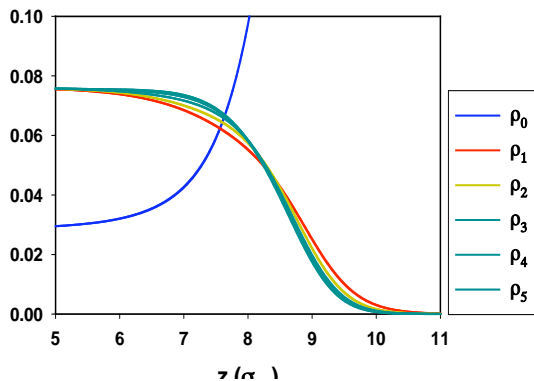


Figure 1b. Density profiles for CO₂ and individual segments

Figure 1 shows our results for equilibrium density profiles when a film of thickness 20σ is sliced out of a bulk polymer-CO₂ mixture and placed in a CO₂ gas phase. It shows a surface enhancement of CO₂ at the interface. Figure 1(b) shows the enlarged picture of the interface region with individual segment densities rather than the total polymer density. Due to symmetry, the density profiles for the first five segments are the same as that for the last five segments. It can be seen that the middle segments tend to be confined to the interior of the film,

while the end segments tend to be exposed to the gas phase.

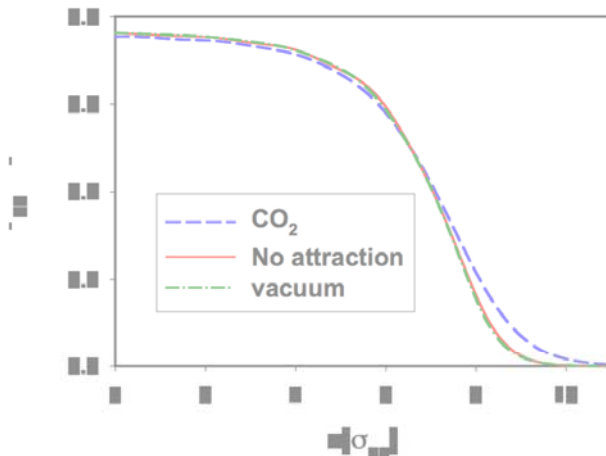


Figure 2. Effect of CO₂ on polymer density profile

For discerning the effect of CO₂ on the density profiles, we compare the polymer-CO₂ profiles with (i) pure polymer in vacuum, and (ii) a system containing a gas similar to CO₂ but whose attractive potential with the polymer has been set to zero. As shown in Figure 2, the polymer density profile for the polymer-nonattractive gas binary system and the pure polymer were similar. However, introduction of CO₂ tends to reduce the polymer density in the center of the film and allows the segments to spread out.

Conclusion

In this report we have briefly discussed the modeling of the polymer-CO₂ binary system using PDFT. Our density profiles show that the presence of CO₂ increases the salvation effect in polymers. In the future we will validate these PDFT results against experiments and simulation. For this purpose properties like surface tension, surface adsorption and the measure of the free volume profile across the film.

Publications

1. M. Talreja, I. Kusaka, D.L. Tomasko, "Structure of Polymer-CO₂ Interface: a Density Functional Study", (manuscript in preparation).