

Density Functional approach for modeling  
Polymer-CO<sub>2</sub> Interfaces

Manish Talreja      Isamu Kusaka      David Tomasko

September 15, 2006

# Introduction

Over the past decade supercritical CO<sub>2</sub>(scCO<sub>2</sub>) has emerged as one of the most significant solvents for polymer processing. The success of scCO<sub>2</sub> as a solvent is attributed to its fourfold advantage viz. 'tunability' to desired temperature and pressure, affinity to organic molecules, low viscosity leading to enhanced mobility, and environment friendly nature. It is also believed that scCO<sub>2</sub> has the potential for replacing CFCs in the production of polymeric foams. Despite numerous advances on the experimental front, optimization of many processes involving scCO<sub>2</sub> is still a challenge. The primary reason for this is the lack of theoretical models that can describe the binary system on a fundamental basis. This work is aimed at bridging the gap between theoretical and experimental knowledge through molecular level analysis of the system using statistical mechanics.

Three techniques commonly used for describing polymers and their mixtures are self-consistent field theory (SCFT), polymer density functional theory (PDFT), and computer simulation. Among these, computer simulation is most accurate but becomes computationally very cumbersome for complex systems. SCFT is less demanding on this front but the results obtained are approximate at best. PDFT is an intermediate theory that offers semi-quantitative information about such systems. The basic idea behind this theory is to calculate the equilibrium free energy and density profiles of the system and subsequently use this information to establish various structure-property relationships. PDFT helps in calculation of various system properties like solubility of CO<sub>2</sub> in polymer and interfacial tension. Glass transition characteristics (especially at polymer-CO<sub>2</sub> interface) are among the most important properties of the binary system as they form the basis for deciding the processing conditions. An interesting feature of glass transition is that the T<sub>g</sub>(glass transition temperature) of a polymer thin film or polymer surface layer is not a fixed quantity, rather there exists a distribution of T<sub>g</sub> up to few nanometers from the periphery[1]. It is also observed that there occurs a

depression in  $T_g$  in the presence  $scCO_2$ . Due to size restrictions it is difficult to analyze these characteristics using experimental techniques. However, we believe that we can obtain substantial information in this regard from our theoretical model.

Before studying the interfacial properties, it is essential to have a good insight into phase diagram of the binary system. Phase diagram calculations are also required to parameterize the PDFT model such that it represents the pertinent polymer- $CO_2$  mixture. In this talk we will present the phase behavior of the polymer- $CO_2$  system, discuss the parameterization of our model, and briefly describe how we will obtain information about the structure property relationships.

## PDFT: Model Description

Our PDFT model describes a polymer chain as a random walk chain containing fixed number of sites ( $\mathbf{n}$ ) with  $CO_2$  molecules interspersed between the chains. PDFT is generally formulated in a system open to material transfer and hence we use grand canonical ensemble to represent the free energy as a functional of site densities. The relevant free energy of this ensemble is the grand potential( $\Omega$ ) which is minimized under the equilibrium condition to obtain the equilibrium density profiles for various sites. These are then used to extract all the useful information i.e. structure property relationships of the system. After rigorous statistical mechanics, we obtain the free energy functional for the binary system as

$$\begin{aligned} \Omega[\rho_a(\mathbf{r})] = & -\beta^{-1} \int d\mathbf{r} \exp(\beta \mathbf{u}_0^{(0)}) - \beta^{-1} \int \left( \prod_a^n d\mathbf{r}_a \exp(\beta \mathbf{u}_a^{(0)}) \right) \mathcal{S}\{\mathbf{r}_i\} + F_{exc}[\rho_a(\mathbf{r})] \\ & - \int d\mathbf{r} \rho_0(\mathbf{r}) \mathcal{U}_0(\mathbf{r}) - \sum_a \int d\mathbf{r} \rho_a(\mathbf{r}) \mathcal{U}_a(\mathbf{r}) \end{aligned} \quad (1)$$

where  $a$  is the site label and  $\beta = 1/k_B T$ ,  $T$  is the temperature and  $k_B$  is the Boltzmann constant. Second 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 canonical free energy term  $F_{exc}$ , represents the intermolecular interactions between polymeric sites and  $\text{CO}_2$  molecules.

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

the first term on the right hand side of the above equation accounts for the repulsive (hard sphere) contribution to the free energy, while the second term refers to the long-range attractive site-site interactions. The latter is modeled in accordance with 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  $\epsilon_{ij}$  and  $\sigma_{ij}$  (for  $i, j =$  interaction sites of polymer and  $\text{CO}_2$ ) account for energy and length parameters which characterize the pertinent system.

After obtaining the free energy functional, the next step is to calculate the density profiles for  $\text{CO}_2$  molecule and polymer chain sites by minimization under stationarity condition of free energy.

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

where  $\rho_i$  refers to polymer site and  $\text{CO}_2$  densities. Equations (1) and (4) lead to the following expressions for the density profiles of polymer sites  $\rho_\alpha$  ( $\alpha = 1$  to  $n$ ) and  $\text{CO}_2$  molecule  $\rho_0$ ,

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

$$\rho_0 = \exp(\beta \mathbf{u}_0^{(0)}) \quad (6)$$

Equations (5) and (6) represent a set of ' $n + 1$ ' coupled integral equations that have to be solved numerically.

## Phase diagram and model parameterization

Phase diagram studies of polymer-CO<sub>2</sub> binary mixtures have received considerable attention from many theorists over the years.[3, 4] Generally, a coarse grained approach is followed in which the quadrupole moment of CO<sub>2</sub> molecule is neglected and results from models of higher alkane-CO<sub>2</sub> mixtures are extended to draw inferences about polymer-CO<sub>2</sub> binary systems [4]. These phase diagrams provide guidelines for designing experiments for various applications that involve homogeneous phases like coating, fractionation and synthesis. Phase diagram calculations are also required for parameterization of models and thus relating the models to pertinent physical systems. The main input parameters to our model are contained in the sets  $\{\epsilon_{ij}\}$  and  $\{\sigma_{ij}\}$  where  $i, j = p$  for polymer and  $i, j = g$  for CO<sub>2</sub>(g). Among these,  $\{\epsilon_{gg}\}$  and  $\{\sigma_{gg}\}$  are determined from pure CO<sub>2</sub> critical properties. Since a polymer degrades way before it can reach the critical region, higher alkane critical properties or polymer PVT data are used for determining  $\{\epsilon_{pp}\}$  and  $\{\sigma_{pp}\}$ . For binary mixtures containing simple fluids, Lorentz-Berthelot mixing rules[5, 6] are used to obtain cross interaction parameters  $\{\epsilon_{pg}\}$  and  $\{\sigma_{pg}\}$ . For complex mixtures like in our case, these rules are modified as

$$\epsilon_{pg} = \gamma_{\epsilon} \sqrt{\epsilon_{gg} \epsilon_{pp}} \quad (7)$$

$$\sigma_{pg} = \gamma_{\sigma} (\sigma_{gg} + \sigma_{pp}) \quad (8)$$

Where  $\gamma_{\epsilon}$  and  $\gamma_{\sigma}$  are determined by fitting the model to cloud point and solubility data of CO<sub>2</sub> in polymers. Furthermore, the description of intra-site correlations also introduces a set of unknowns to our description of polymeric chain. For a freely jointed chain model, finite bond length would be the only unknown involved while for the case of harmonic spring representation, characteristic length and spring constant would be the two unknowns. These parameters can again be found by relating the model

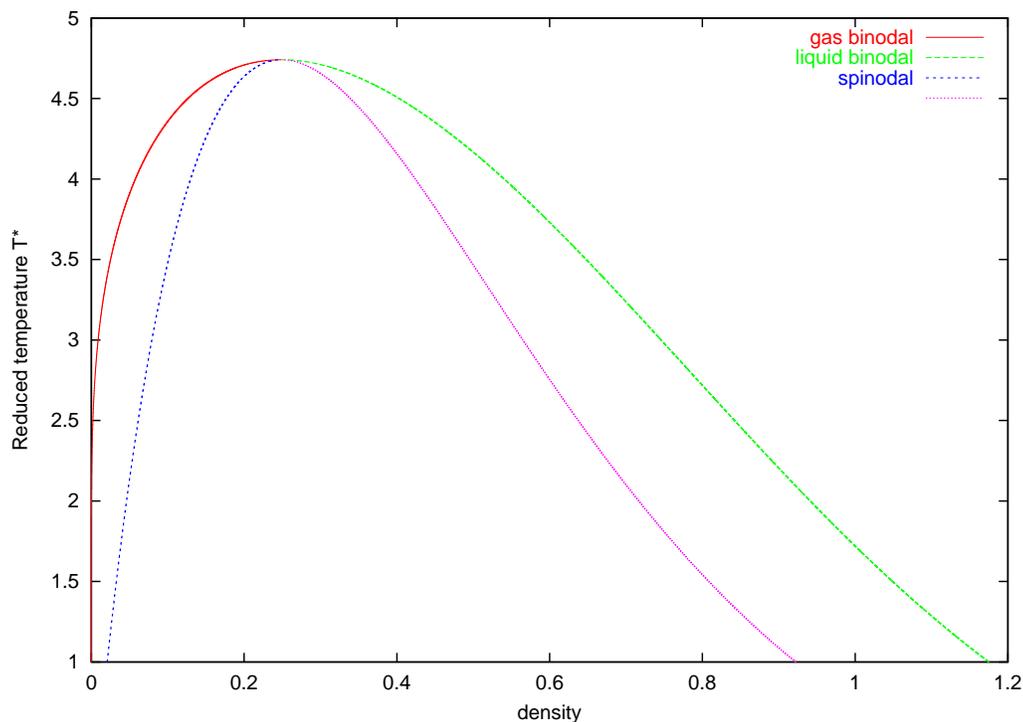


Figure 1: Gas-liquid equilibrium curve for  $\text{CO}_2$

to the experimental data. Pure component phase diagrams for  $\text{CO}_2$  and 10 segment chain molecules generated using our PDFT model have been depicted in figures 1 and 2.

## Conclusion

In this abstract we have briefly discussed the modeling of polymer- $\text{CO}_2$  binary system using PDFT. We have explained the basic structure of our model and described the important property structure relationships that can be generated from it. We have also shown from phase diagrams that our model is capable of representing correct physical

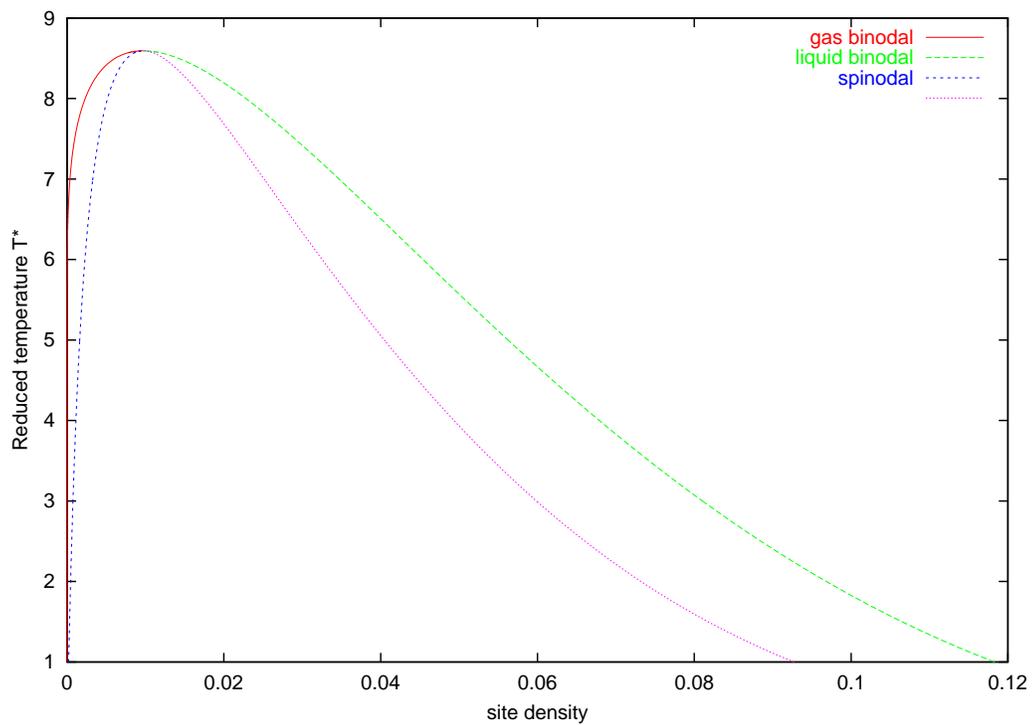


Figure 2: Gas-liquid equilibrium curve for 10 segment chain

behavior of molecules and discussed how we plan to parameterize the model such that it represents the pertinent binary system. In future, working with parameterized set of values, we will try to extract detailed information about equilibrium structure and properties of polymer-CO<sub>2</sub> interface.

## References

- [1] Ellison, C. J.; Torkelson, J. M.: Nature Materials Vol. 2, October 2003, **695**
- [2] Christopher, P. S.; Oxtoby, D.W.: J. Chem. Phys. Vol. 119, 2003, **10330**
- [3] Kirby, C. F.; McHugh M. A.: Chemical Reviews Vol. 99 No. 2, 1999, **565**
- [4] Virnau, P.; Muller, M.; MacDowell, L.G.; Binder, K.: Computer Physics Communications Vol. 147, 2002, **378**
- [5] Lorentz, H. A.: Ann. Phys. (Leipzig) Vol. 12, 1881, **127**
- [6] Berthelot, D. C.: C. R. Hebd. Seances Acad. Sci. Vol. 126, 1898, **1703**