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Polymers at Liquid/Vapor Interface

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Abstract

Polymers confined to the liquid/vapor interface are studied using molecular dynamics simulations. We show that for polymers which are weakly immiscible with the solvent, the density profile perpendicular to the liquid/vapor interface is strongly asymmetric. On the vapor side of the interface, the density distribution falls off as a Gaussian with a decay length on the order of the bead diameter, whereas on the liquid side, the density profile decays as a simple exponential. This result differs from that of a polymer absorbed from a good solvent with the density profile decaying as a power law. As the surface coverage increases, the average end-to-end distance and chain mobility systematically decreases toward that of the homopolymer melt.

Graphical Abstract

Confining polymers to thin films can have a strong effect on the conformation of the chain both perpendicular and parallel to the interface. For melts and semi-dilute solutions, polymers confined in strictly two-dimensions or in ultra-thin films are compact objects with fractal contours.^{1–4} However for confining thickness d such that $R_g \gg d \gg R_g/N^{1/2}$, where

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Notes

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Supporting Information. Additional snapshots of polymers at liquid/vapor interface and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

R_g is the radius of gyration and N is the degree of polymerization, the chain extension is largely unperturbed parallel to the interface but compressed normal to the interface.⁵⁻⁷ Examples of quasi-two dimensional systems include polymer confined between two closely spaced walls,^{3, 7-8} or polymers confined to a liquid/vapor (vacuum) interface.⁹⁻¹¹

Polymers at a liquid/vapor interface are particularly interesting as the degree of immiscibility for polymers in the vapor (vacuum) phase is typically much less than for the liquid. In a good solvent, if the surface tension of the polymer is lower than that of the solvent, near the liquid/vapor interface there exists a monomer-rich zone, independent of polymer molecular weight. Beyond this monomer-rich region, in a good solvent, the monomer density has a self-similar structure and decreases $\rho(z) \sim z^{-4/3}$.¹²⁻¹⁵ Poly(dimethylsiloxane) (PDMS) in toluene is an example of polymer in a good solvent. The density profile near the toluene/air interface has been studied experimentally by neutron reflectivity.¹⁰ In the opposite limit where the polymer and solvent are strongly immiscible, such as PDMS and water,^{9, 11} the polymer spreads on the surface and does not dissolve into the solvent. For solvents, which are intermediate between Θ and very poor, where the chains are weakly immiscible in the solvent and adsorption layer widens upon increasing the surface coverage, the functional form of the resulting density profiles perpendicular to the interface into the vapor and liquid phases have not been explored. This intermediate regime, illustrated in Figures 1 and S1, is the focus of the current study.

Here we present molecular dynamics simulations for polymers confined to the liquid/vapor interface under unsaturated adsorption conditions. Using the standard bead-spring model for the polymer, we vary the relative strength of the interaction to control the degree of miscibility between the polymer and liquid and the surface tension of the polymer and solvent. Focusing on the case where the polymer is weakly immiscible with the liquid (close to Θ conditions), we show that the polymer chains remain near the interface for low areal density while at high areal coverage, some loops and tails of the polymer chains at the interface enter the liquid. Unlike polymers adsorbed in good solution,¹³⁻¹⁴ we show in this case that the polymer density decay into the liquid is fit with a simple exponential decay $\rho_p(z) \sim \exp(-z/\lambda)$. We also explore the chain mobility as a function the area density of the polymer.

All the simulations were carried out using the bead-spring model.¹⁶ The polymer chains at the surface each contained $N_p=500$ beads, while the liquid was represented by oligomers chains containing $N_l=10$ beads each. All beads have a mass m and diameter σ and interact

via the Lennard-Jones (LJ) potential $U_{ij}(r)=4\epsilon_{ij} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$, where r is the distance between two beads. The interaction is cutoff at $r_c=2.5\sigma$. The interaction energy ϵ_{ll} between solvent (s) beads is set to $\epsilon_{ll}=\epsilon$, while the interaction ϵ_{pp} between polymer (p) beads is varied. Berthelot's mixing rule $\epsilon_{pl}=(\epsilon_{ll}*\epsilon_{pp})^{1/2}$ is used for the cross term. The characteristic unit of time is $\tau=\sigma(m/\epsilon)^{1/2}$. Beads along the chain are connected by an additional unbreakable finitely extensible nonlinear elastic (FENE) potential

$$U_{\text{FENE}}(r)=-\frac{1}{2}kR_0^2\ln\left[1-\left(\frac{r}{R_0}\right)^2\right], \text{ with } R_0=1.5\sigma \text{ and } k=30\epsilon/\sigma^2. \text{ A bond bending potential}^{17}$$

$U_B(\theta)=k_\theta(1+\cos\theta)$, where θ is the angle between two consecutive bonds and $k_\theta=0.75\epsilon$, is included. The simulation cell is a rectangular box of dimensions $L_x \times L_y \times L_z$ with $L_x=L_y$. The liquid/vapor interface is parallel to the x-y plane, in which periodic boundary conditions are imposed. In the z direction, the beads interact with a flat wall at $z=0$. The wall and beads interact with a LJ 9-3 potential $U_w(z)=4\epsilon_w \left[\frac{2}{15} \left(\frac{\sigma}{z}\right)^9 - \left(\frac{\sigma}{z}\right)^3 \right]$ where $\epsilon_w = 2\epsilon$ is the interaction strength between the wall and both the solvent and polymer monomers. The interaction with the wall is cutoff at $z_c = 2.5 \sigma$. The thickness of the film is large enough that the polymer chains at the liquid/vapor interface do not interact with the bounding wall at $z=0$. As no chains evaporate into the vapor, L_z is set so that the top of the simulation cell is $10-20 \sigma$ above the liquid/vapor interface. All simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) parallel MD code.¹⁸ The equations of motion were integrated using a velocity-Verlet algorithm with a time step $\delta t=0.01 \tau$. Temperature was maintained at $T=\epsilon/k_B$ for all simulations by coupling the system weakly to a Langevin heat bath¹⁹⁻²⁰ with a damping constant $\Gamma=0.01 \tau^{-1}$.

The liquid film consisting of 5,000 to 33,000 chains of length $N_f=10$ depending on the areal density of the polymer defined by $\rho_A = M_p \cdot N_p / (L_x \cdot L_y)$, where M_p is the number of polymer chains. For $\rho_A \sigma^2 = 3.1$, $M_p=10$ while for $\rho_A \sigma^2 = 3.86$, $M_p=40$. The polymer chains were randomly placed at the liquid/vapor interface and simulations were run for 1×10^6 to $2 \times 10^7 \tau$ depending on coverage. The liquid/vapor surface tension γ_{lv} of the polymer/liquid film was obtained by integrating the difference in the normal and transverse components of the pressure tensor across the interface.²¹⁻²³

For reference, we first simulated two homopolymer liquids of 5000 chains of length 10 and 500 chains of length 500 at $T=\epsilon/k_B$ to determine the surface tensions of each. For $N=10$, $\epsilon_{ij}=\epsilon$, $\gamma_{lv}=0.85 \epsilon/\sigma^2$, while for $N=500$, $\gamma_{lv}=1.0 \epsilon/\sigma^2$. Setting $\epsilon_{pp}=\epsilon_{ll}=\epsilon$ corresponds to the good solvent limit for a polymer chain of length $N_p=500$ in a liquid of chain length $N_f=10$. However, unlike PDMS in toluene, since the surface tension of the pure homopolymer is greater than that of the liquid, the longer chains did not remain at the liquid/vapor interface but quickly dissolved into the liquid. This is exactly what occurred when we placed the polymer chains at the interface with $\epsilon_{pp}=\epsilon_{ll}=\epsilon$.

To study the case of interest, namely polymer chains adsorbed at the liquid/vapor interface, we therefore had to reduce surface tension of the polymer compared that to our model liquid of short chains. To do so, we set $\epsilon_{pp} < \epsilon_{ll}$. A plot of the liquid/vapor surface tension for the neat $N_p=500$ homopolymer melt as a function of ϵ_{pp} is given in Figure S2. To model long polymer chains at the liquid/vapor we focused on two cases, $\epsilon_{pp}=0.8\epsilon$ and 0.85ϵ which corresponds to a polymer which is weakly immiscible in the liquid.²⁴ For larger values of ϵ_{pp} most of the chains dissolve into the liquid, while for smaller values of ϵ_{pp} the polymer chains spread uniformly at the liquid/vapor interface. If one wanted to model a good solvent with a thick adsorbed layer near the liquid/vapor interface using this bead-spring model, one would have to break Berthelot's rule and increase $\epsilon_{pl} > (\epsilon_{ll} \epsilon_{pp})^{1/2}$ while holding $\epsilon_{pp} < \epsilon_{ll}$ so that the surface tension of the polymer is lower than that of the liquid while keeping the solvent quality good.

For all coverages studied, the chains lie largely parallel to the interface as seen in Figures 1 and S1. As the surface coverage ρ_A increases, the average mean squared end-to-end distance $\langle R^2 \rangle$ and radius of gyration $\langle R_G^2 \rangle$ systematically decrease as shown in Figure 2a. For low coverages, $\langle R^2 \rangle$ is non-Gaussian and almost twice as large as in a homopolymer melt, $\langle R^2 \rangle = 1090 \sigma^2$ (Kuhn length $l_k = 2.2 \sigma$) with $\epsilon_{pp} = 0.8$. For the lowest coverage studied $\rho_A \sigma^2 = 0.4$, where the chains are two-dimensional, $\langle R^2 \rangle / \langle R_G^2 \rangle = 6.25$ as seen in Fig. 2a. As ρ_A increases, $\langle R^2 \rangle / \langle R_G^2 \rangle$ goes to 6 and the liquid/vapor surface tension γ_{lv} decreases as polymer chains cover more of the surfaces. As expected, as $\rho_A \sigma^2$ increases, $\langle R_z^2 \rangle$, the average end-to-end distance in the direction normal to the interface, increases as shown in the inset of Figure 2a. The distribution of end-to-end distances $P(R)$ in 3 dimensions and in the plane perpendicular to the interface R_1 for $\rho_A \sigma^2 = 0.4, 2.5$ and 5.0 are compared to 2 and 3 dimensional Gaussian distributions in Figure S3. As $\rho_A \sigma^2$ increases, the distributions become more Gaussian.

The liquid/vapor surface tension γ_{lv} as a function of ρ_A is shown in Figure 2b. The limiting values for a homopolymer melt of chain length $N_p = 500$ are $\gamma_{lv} = 0.58$ and $0.43e/\sigma^2$ for $\epsilon_{pp} = 0.85$ and $0.80e$, respectively as shown in Figure S2. Over this range of polymer coverage, the variation of the total monomer (solvent + polymer) density $\rho_T(z)$ in transverse direction, shown in Figure S4, is well described by an erf function $\text{erf}(\frac{z}{\sqrt{2}\Delta})$, where the interfacial width ranges from $\sim 0.8\sigma$ for the lowest values of ρ_A to 1.1σ for the largest values of ρ_A for the system sizes studied here. γ_{lv} decreases slightly with increasing ϵ_{pp} due to the increase in interfacial tension γ_{lv} .

The monomer density profiles of the liquid $\rho_l(z)$ and polymer $\rho_p(z)$ for varying polymer coverages and interaction strength are shown in Figure 3. Here, the densities are normalized by the bulk density for the liquid of chain length $N=10$, $\rho \sigma^3 = 0.85$. As clearly seen in Figure 3a, $\rho_p(z)$ is asymmetric with a much longer tail into the liquid than into the vapor. As $\rho_A \sigma^2$ increases both the fraction of the surface covered by polymer chains and the number of polymer chain segments extending into the liquid increases. This is consistent with the images shown in Figures 1 and S1 and show that we are in the unsaturated adsorption regime. Decreasing the polymer-polymer interaction $\epsilon_{pp} < 0.8e$, increases the segregation between the solvent and the polymer chains as fewer chain segments extend into the liquid.

The density profiles on the liquid and vapor side of the interface follow very different functional forms as shown in Figure 4. On the vapor side $\rho_p(z)$ measured from the local peak z_{peak} decays as a Gaussian with a decay length $\lambda_v \sim 1.5\sigma$ which is weakly dependent on ρ_A . On the liquid side, the density profile can be approximated by a simple exponential $\rho_p(z) = b_l \exp[-(z - z_{peak})/\lambda_l]$ as shown in Figure 4b. λ_l increases with increasing ρ_A as seen in the inset of Figure 4b for $\epsilon_{pp} = 0.8$ and $0.85e$ and decreases with decreasing ϵ_{pp} . In Figure S5, we show a ln-ln plot of $\rho_l(z)$ versus $(z_{peak} - z)$ which shows clearly that at least for this chain length, the power law decay, observed for polymer absorbed in a good solvent, is a poor fit in this case.

The mean squared displacement (MSD) of the inner 5 monomers of the polymer chain $g_1(t)$ is shown in Figure 5a for four values of $\rho_A \sigma^2$. As the motion is almost entirely in the plane

perpendicular to the interface, we show the two-dimensional diffusion constant

$D_{\parallel} = \langle r_{\parallel}^2 \rangle / 4t$ parallel to the interface in Figure 5b, where $\langle r_{\parallel}^2 \rangle$ is the displacement in the plane of the interface. $D_{\parallel}$ sharply decreases as ρ_A increases for low coverages but then decreases more slowly for high coverage. For comparison the three-dimensional diffusion constant for a polymer melt with chain length $N=500$, is about an order of magnitude lower for $\epsilon_{pp}=1.0$ than for $\rho_A \sigma^2=5.0$.²⁵ For the higher coverages, one can see the onset of the reptation $t^{1/4}$ regime in Figure 5a.

In conclusion, we have used molecular dynamics simulation to investigate the properties of polymer chains confined to a liquid/vapor interface. For the case of weakly immiscible polymers, we show that the density profile decays as a simple exponential into the liquid and as a Gaussian into the vapor. In contrast to adsorbed polymers in a good solvent,^{12–15} a power law is a poor fit of the polymer concentration decay into the liquid. These results suggest further study by x-ray or neutron scattering to explore the density profiles is warranted.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Snapshots of polymers at liquid/vapor interface for $\rho_A\sigma^2=1.1$ ($L_x=L_y=67.4\sigma$) (left) and $\rho_A\sigma^2=2.5$ ($L_x=L_y=44.7\sigma$) (right) viewed from top and side for $\epsilon_{pp}=0.8\epsilon$. Each of the 10 polymer chains is plotted with a different color. Liquid is not shown for clarity.

Figure 2.

a) Mean squared average end-to-end distance $\langle R^2 \rangle$ (black Squares) and radius of gyration $\langle R_G^2 \rangle / 6$ (red squares) for $\epsilon_{pp} = 0.8\epsilon$ versus the areal density of the polymer ρ_A . Inset shows mean square end-to-end distance $\langle R_z^2 \rangle$ in z direction, normal to interface. b) Liquid vapor surface tension γ_{lv} versus coverage for $\epsilon_{pp} = 0.8\epsilon$ (black squares) and 0.85ϵ (red circles).

Figure 3.

a) Monomer density profile $\rho_A(z)$ for liquid ($N_l=10$) (solid lines) and polymer $\rho_P(z)$ ($N_p=500$) (dashed lines) versus z for 3 values of $\rho_A\sigma^2$ for $\epsilon_{pp}=0.8e$. The position of the interface is shifted in z in (a) for clarity. b) $\rho_P(z)$ for $\rho_A\sigma^2=2.5$ for three values of polymer-polymer interaction ϵ_{pp} .

Figure 4.

Polymer concentration profile $\rho_p(z)$ for $\rho_A\sigma^2 = 0.40$ (blue), 1.1 (red), 2.0 (green) and 2.5 (black) on a) vapor side and b) liquid side for $\epsilon_{pp} = 0.8e$. Dashed lines are the best fit to

$\rho_p(z) = b_v \exp[-(z - z_{peak})^2 / \Delta_v^2]$ on vapor side and $\rho_p(z) = b_l \exp[-(z - z_{peak}) / \Delta_l]$ on liquid side. Inset: Δ_v/σ versus $\rho_A\sigma^2$ for $\epsilon_{pp} = 0.8e$ (dashed) and 0.85 (solid).

Figure 5.

a) Mean squared displacement of 5 inner monomer $g_1(t)$ for four values of ρ_A . b) Two-dimensional diffusion constant $D_{||}$ as a function of ρ_A .