Supplementary Information (SI) for Physical Chemistry Chemical Physics.

# Supporting Information:
# Compressed asymmetric polymer brushes exhibit a symmetric interpenetration zone

Leonid I. Klushin,[†,‡] Ivan V. Lukiev,[¶,‡] Ivan V. Mikhailov,[*,‡] Oleg V. Borisov,[§]
and Aleksander M. Skvortsov[‖,‡]

*†Department of Physics, American University of Beirut, P.O. Box 11-0236, Beirut 1107 2020, Lebanon*

*‡Department of NRC "Kurchatov Institute" - PINP-IMC, Saint Petersburg, Russia*

*¶Center for Chemical Engineering, ITMO University, 197101 St. Petersburg, Russia*

*§Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR 5254 CNRS UPPA, Pau, France*

*‖Chemical-Pharmaceutical University, Professora Popova 14, 197022 St. Petersburg, Russia*

E-mail: i.v.mikhailov-imc.ras@yandex.ru

# 1. Pressure in a semi-dilute polymer/solvent system connected to a solvent reservoir

We consider a semi-dilute polymer solution where the amount of the polymer within a variable volume is fixed while the solvent can move in and out of a reservoir characterized by some value of the solvent chemical potential which is eventually controlled by the pressure in the reservoir. According to naive expectations, the full pressure of the polymer solution must be the sum of two contributions: the osmotic pressure of the polymer and the pressure of the solvent imposed by the reservoir. This hypothesis is tested below within a consistent mean-field framework.

A common way to quantify the osmotic pressure of the polymer is based on the Flory-Huggins expression for the free energy density (normalized by $k_BT$ where $T$ is the temperature and $k_B$ is the Boltzmann constant):

$$A_{FH}(\varphi_p) = \chi_{FH}\varphi_p(1-\varphi_p) + (1-\varphi_p)\ln(1-\varphi_p) \tag{1}$$

where $\varphi_p$ is the polymer volume fraction, $\chi_{FH} = \frac{q}{2k_BT}(2\epsilon_{ps} - \epsilon_{pp} - \epsilon_{ss})$, $q$ is the coordination number of the underlying lattice, and $\epsilon_{ps}, \epsilon_{pp}, \epsilon_{ss}$ are the energies of the polymer-solvent, polymer-polymer and solvent-solvent pairwise contacts, respectively. This gives the osmotic pressure as

$$\Pi(\varphi_p) = \varphi_p \frac{\partial A_{FH}(\varphi_p)}{\partial \varphi_p} - A_{FH}(\varphi_p) = -\varphi_p - \ln(1-\varphi_p) - \chi_{FH}\varphi_p^2 \tag{2}$$

However, within this approach the solvent pressure cannot be properly defined since the polymer/solvent mixture is described as densely packed and the solvent itself is perfectly incompressible.

To rectify this deficiency, we treat the solvent reservoir as a lattice fluid, i.e. a mixture of solvent molecules and voids with the mean-field free energy density

$$A_R(\varphi) = -\chi\varphi^2 + (1-\varphi)\ln(1-\varphi) + \varphi\ln\varphi \tag{3}$$

Here $\chi = \frac{q}{2k_BT}(2\epsilon_{sv} - \epsilon_{ss} - \epsilon_{vv}) = -\frac{q\epsilon_{ss}}{2k_BT}$ since pairing with a void doesn't carry energy. The empty space was taken as the reference state to facilitate the connection to the triple mixture introduced below. The chemical potential of the solvent and the pressure in the reservoir as functions of the solvent volume fraction $\varphi$ are:

$$\mu_R(\varphi) = \frac{\partial A_R(\varphi)}{\partial\varphi} = -2\chi\varphi + \ln\varphi - \ln(1-\varphi) \tag{4}$$

$$P_R(\varphi) = \varphi\frac{\partial A_R(\varphi)}{\partial\varphi} - A_R(\varphi) = -\ln(1-\varphi) - \chi\varphi^2 \tag{5}$$

defining the function $\mu_R(P_R)$ parametrically. Explicit expressions are obtained in the case $\chi \gg 1$ (approximately, neglecting terms of order $e^{-\chi}$):

$$\mu_R = -\chi + P_R \tag{6}$$

and in the case of $\chi = 0$ (exact):

$$\mu_R = \ln(e^{P_R} - 1) \tag{7}$$

The first case corresponds to a properly condensed weakly compressible liquid, while the second case is the entropy-dominated version of a supercritical fluid.

The semi-dilute polymer solution within the same approach is described as a triple mixture (polymer/solvent/voids) with the mean-field free energy density:

$$A_3(\varphi_s, \varphi_p) = -\chi(\varphi_s + \varphi_p)^2 + (1-\varphi_s-\varphi_p)\ln(1-\varphi_s-\varphi_p) + \varphi_s\ln\varphi_s \tag{8}$$

where $\varphi_s$, $\varphi_p$, and $(1-\varphi_s-\varphi_p)$ are the volume fractions of solvent, polymer and voids, correspondingly.

Throughout the paper we assume the athermal solvent conditions $\epsilon_{ss} = \epsilon_{sp} = \epsilon_{pp}$, so that the Flory-Huggins parameter $\chi_{FH}$, with the corresponding simplification for the polymer osmotic pressure. As before, the empty space is taken as the reference state. The chemical potential of the solvent and the total pressure in the triple mixture are given by:

$$\mu_s(\varphi_p, \varphi_s) = -2\chi(\varphi_p + \varphi_s) + \ln \varphi_s - \ln(1 - \varphi_p - \varphi_s) \tag{9}$$

$$P_3(\varphi_p, \varphi_s) = \varphi_p \frac{\partial A_3}{\partial \varphi_p} + \varphi_s \frac{\partial A_3}{\partial \varphi_s} - A_3 = -\ln(1 - \varphi_p - \varphi_s) - \varphi_p - \chi(\varphi_p + \varphi_s)^2 \tag{10}$$

Imposing the chemical potential of the reservoir, $\mu_s(\varphi_p, \varphi_s) = \mu_R(P_R)$, defines the solvent volume fraction as a function of the polymer volume fraction and the reservoir pressure, $\varphi_s(\varphi_p, P_R)$. Finally, the pressure in the triple mixture, $P_3(\varphi_p, P_R)$, under the conditions that the total number of monomer units forming the polymer chains is fixed, while the solvent molecules are exchanged with the reservoir, is obtained by substituting $\varphi_s(\varphi_p, P_R)$ into Eq. (10). Our goal is to compare the result to the naïve additivity expectations. In the case when the solvent is a simple entropy-dominated supercritical fluid with $\chi = 0$, Eqs. (7), (9) give

$$\varphi_s = (1 - e^{-P_R})(1 - \varphi_p) \tag{11}$$

$$\ln(1 - \varphi_s - \varphi_p) = \ln(1 - \varphi_p) - P_R \tag{12}$$

leading to exact additivity for arbitrary reservoir pressures and polymer volume fractions,

$$P_3(\varphi_p, P_R) = \Pi(\varphi_p) + P_R \tag{13}$$

If the solvent is a dense weakly compressible liquid with $\chi \gg 1$, approximate pressure additivity also follows analytically from Eqs. (6), (9), (10) combined with the observation that the volume fraction of voids, $(1 - \varphi_s - \varphi_p)$, is a decreasing function of the polymer concentration, and is hence bounded from above by $e^{-\chi}$. This estimate follows from the fact that $e^{-\chi}$ is the volume fraction of voids in the liquid phase of the solvent coexisting with its saturated vapor at zero polymer concentration, as follows from the standard analysis of the lattice gas model with the free energy density (3).[1]

Analytical predictions for the pressure additivity are perfectly supported by numerical calculations shown in Figure S1 for $\chi = 0$ (panel a) and for $\chi = 5$ (panel b).

Deviations from additivity are observed for supercritical solvents with $\chi = 0.3$ and $\chi = -0.3$ as illustrated in Figure S2. Note that the same $\chi$ parameter characterizes the interaction between monomer units in the polymer chain. At low reservoir pressures, $P_R \ll 1$, the solvent is actually a low density gas, and the semidilute polymer solution contains a significant volume fraction of voids leading to an effective change in the Flory-Huggins parameter. Hence, in the case of weak attraction between monomer units, $\chi = 0.3$, the gauge pressure falls below the osmotic pressure in the densely packed polymer/solvent mixture with $\chi_{FH} = 0$ as shown in panel (a). Conversely, in the case of additional repulsion between solvent molecules (and between monomer units), $\chi - 0.3$, the gauge pressure is higher than $\Pi(\varphi_p | \chi_{FH} = 0)$, see panel (b). This situation is not to be expected under real experimental conditions but may occur in grand canonical ensemble simulations. Note that at large reservoir pressures, $P_R \gtrsim 1$, the volume fraction of voids is small and pressure additivity is fully restored. On the other hand, approximate additivity is always guaranteed at high polymer volume fractions.

## 2. SCF model parameters

We study the effect of asymmetry on the interpenetration of two planar interacting polymer brushes under athermal solvent conditions ($\chi_{FH} = 0$).

Two types of asymmetric brush pairs were considered systematically:

1) both brushes have fixed and equal values of the grafting density $\sigma_1 = \sigma_2 = 0.1$; the polymerization indices of the grafted chains were different and varied as follows: $N_1 = 40$, 60, 80, and 100; $N_2 = 200 - N_1$;

2) the brushes have fixed and equal values of the chain polymerization index $N_1 = N_2 = 100$ and variable grafting density values: $\sigma_1$ was taken as 0.03, 0.05, 0.07, and 0.1; $\sigma_2 = 0.2 - \sigma_1$; A few other parameter values for asymmetric pairs were taken to further verify the predictions of the scaling theory.

In some cases, other parameters were considered.

## 3. Symmetrical brushes

Analytical theory in the second virial approximation predicts the value of the midplane density in the Helmholtz $D$ ensemble:

$$\varphi(D) = \frac{N\sigma}{H_0}\left[\frac{2H_0}{D} - \left(\frac{D}{2H_0}\right)^2\right] \tag{14}$$

Equation of state corresponding to the expression of the Flory-Huggins free energy density under athermal solvent conditions $\chi_{FH} = 0$:

$$\Pi(\varphi) = -\varphi - \ln(1 - \varphi) \tag{15}$$

Analytical theory Ansatz for the partial brush density profiles and the resultant overlap function:

$$\varphi_{1,2}(z) = \frac{\varphi_m}{2}\left[1 \mp \tanh\frac{z - D/2}{\delta}\right], \tag{16}$$

$$\varphi_1(z)\varphi_2(z) = \frac{\varphi_m^2}{4}\left[\cosh^{-2}\left(\frac{z - D/2}{\delta}\right)\right] \tag{17}$$

The prediction of the scaling theory for the penetration length $\delta$ in symmetric brush pairs; $B$ is a numerical prefactor:

$$\delta = B\ D^{-1/3}N^{2/3} \tag{18}$$

# 4. Figures

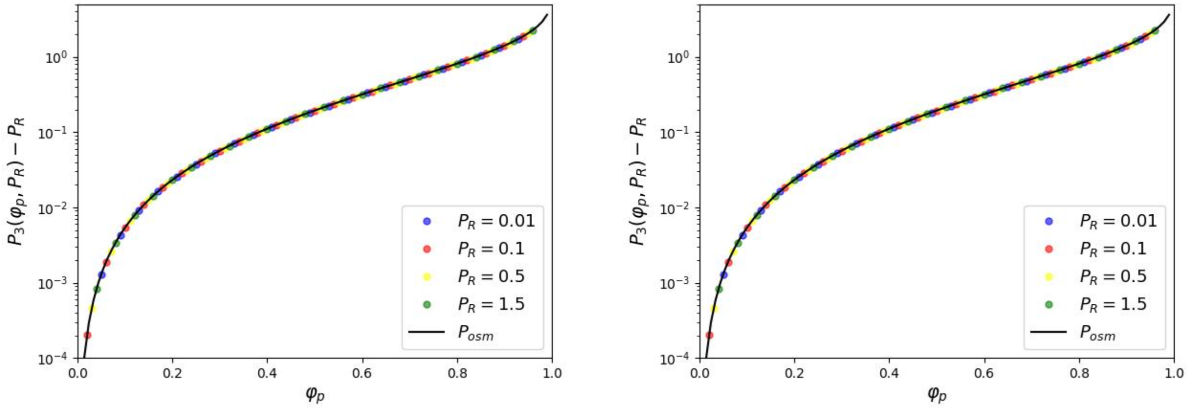

Figure S1: Comparison of the gauge pressure in the semi-dilute polymer solution (triple mixture), $P_3(\varphi_p, P_R) - P_R$, with the polymer osmotic pressure, $\Pi(\varphi_p|\chi_{FH} = 0)$, as functions of the volume fraction of the polymer, $\varphi_p$ : (a) simple supercritical solvent with $\chi = 0$; (b) condensed weakly compressible solvent with $\chi = 5$.

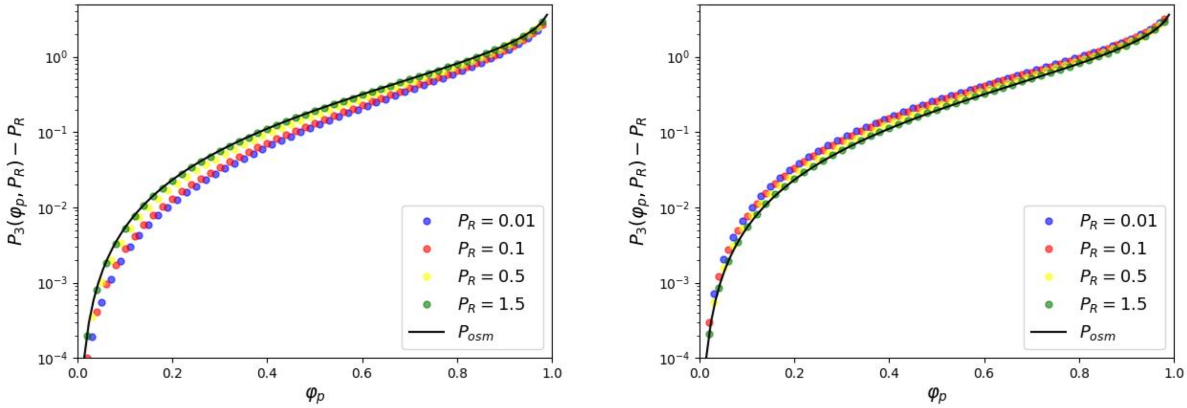

Figure S2: Comparison of the gauge pressure in the semi-dilute polymer solution (triple mixture), $P_3(\varphi_p, P_R) - P_R$, with the polymer osmotic pressure, $\Pi(\varphi_p|\chi_{FH} = 0)$, as functions of the volume fraction of the polymer, $\varphi_p$ : (a) weakly self-attractive supercritical solvent with $\chi = 0.3$ ; (b) supercritical solvent with extra repulsion, $\chi = -0.3$ (Legend the same as in Fig.S1).

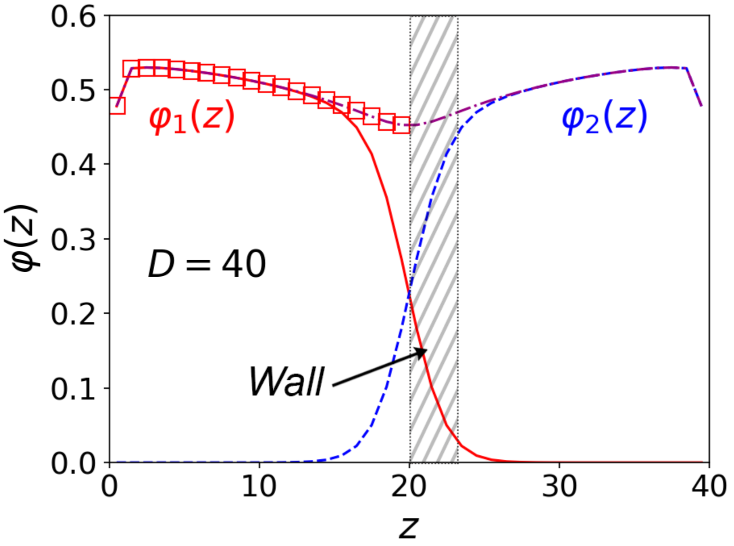

Figure S3: Numerical SCF density profiles of brushes compressed by a wall (red symbols) and by an opposing brush (red solid line for left brush and blue dashed line for right brush). Purple dash-dotted line corresponds to the total density $\varphi_1(z) + \varphi_2(z)$.

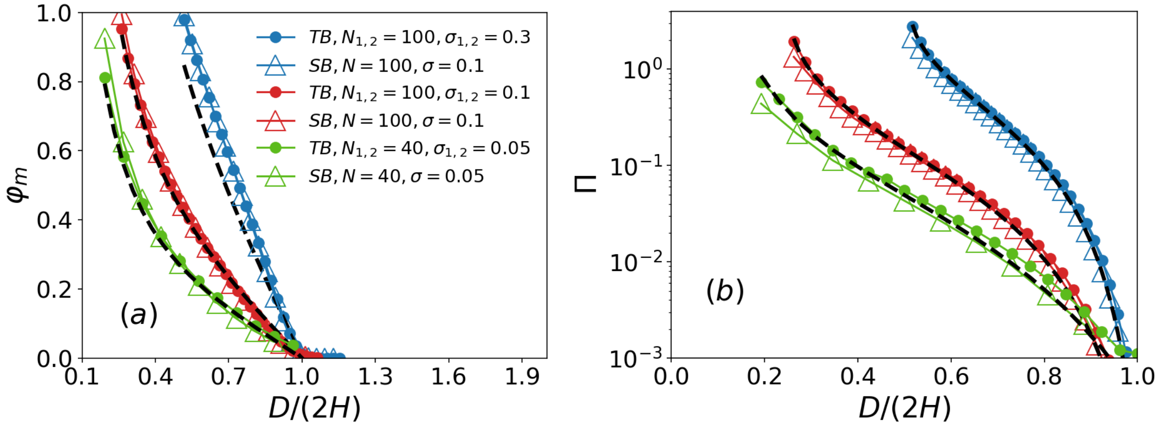

Figure S4: Comparison of SCF data for the brush-wall and brush-brush compression(colored symbols) with analytical theory predictions (black dashed lines): (a) the midplane density as a function of the reduced interplanar separation: data points for a single brush (SB) compressed by a wall and for two opposing brushes (TB) identified in the legend; analytical theory curve represents Eq ( 14); (b) Osmotic (disjoining) pressure vs. the reduced separation; theoretical curves calculated according to the equation of state (15) at the midplane.

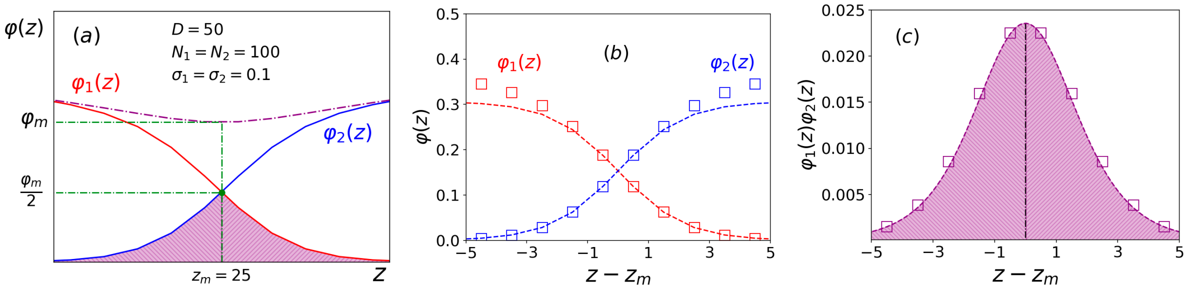

Figure S5: Partial brush density profiles $\varphi_1(z)$ and $\varphi_2(z)$ for the symmetrical case. Left panel illustrates $\varphi_m(z)$ and $z_m$ parameters; purple dash-dotted curve gives the total density $\varphi_1(z) + \varphi_2(z)$; shaded area under solid curves represents twice the value of the $\Sigma$ parameter. Central panel: comparison of the SCF partial brush density profiles (solid curves) compared to the Ansatz of Eq (16) (symbols and dashed curves). Right panel: overlap function $\varphi_1(z)\varphi_2(z)$ obtained by SCF calculations (unfilled symbols) in comparison to Eq (17) (dashed line); the shaded area under the dashed line is the overlap integral $\Gamma$.

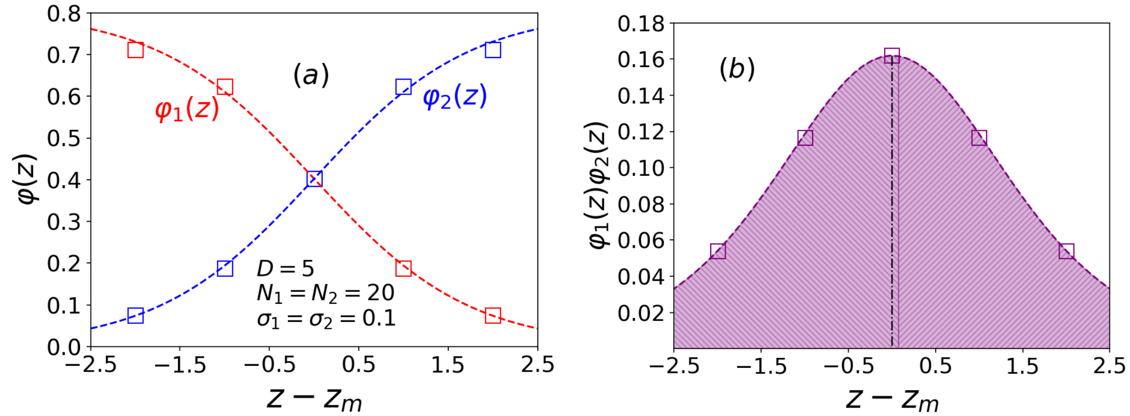

Figure S6: Short brushes in the strong interpenetration limit. The same as in panels (b) and (c) of Figure S5 for short brushes under strong compression. Note that interpenetration zone extends to the opposing grafting surfaces. The Ansatz of Eqs. (16,17) is still valid. The shaded area under the dashed curve is the overlap integral $\Gamma$.

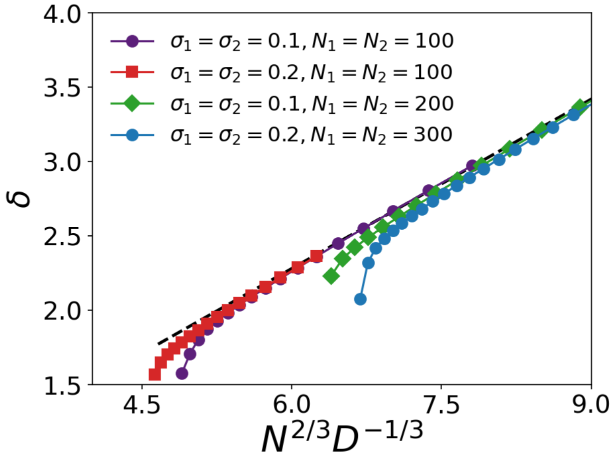

Figure S7: Scaling of the penetration length $\delta$ for the symmetric case in the Helmholtz $D$-ensemble: scaling prediction (black dashed line) compared to the numerical SCF results (symbols). The fitting prefactor in eq 18 is taken as $B = 0.38$; $\delta = \frac{1}{2}(\delta_{left} + \delta_{right})$. Parameters of brushes are indicated in the legend.

# References

(1) Jones, R. *Soft Condensed Matter*; Oxford Master Series in Physics. Oxford: Oxford University Press, 2002; p 208.