

## The effects of long-ranged and short-ranged forces in confined near-critical polymeric liquids

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**Abstract.** – The relative importance of long- and short-ranged forces on the thermal fluctuations at polymer interfaces was investigated with neutron reflection. Polyolefin blends were synthesised to create polymer pairs with a tuned interaction parameter, allowing the exploration of situations from near criticality to strongly immiscible cases in thin-film systems. We have observed for the polymer interfacial width, a transition from a region where long-ranged forces dominate, at higher degree of incompatibility, to a region approaching criticality where short-ranged truncation forces are more relevant.

The problem of the structure of the interface between two coexisting fluid phases has a long history, dating back to van der Waals [1], but there has been a recent burgeoning of theoretical work in this area, particularly in relation to the effects of confinement and reduced dimensionality on the fluid-phase behaviour [2]. The experimental effort has been a lot smaller than the theoretical one, largely because the study of the structure of interfaces between two coexisting fluids and the control of the strength of surface fields in confining geometries present difficult experimental problems. However, one subset of fluid mixtures has proved very fruitful for experiments — coexisting polymeric liquids, where the technique of neutron reflection has proved invaluable for probing the structure of interfaces with sub-nanometer resolution [3]. For confined thin polymer systems, the following questions are still open to debate: *How is*

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*the nature of the interface modified by interfacial fluctuations, and how is this modified by confinement effects in thin films?*

It is now clear that the equilibrium interface width in polymer systems is substantially broader than the mean-field prediction, and that the origin of this broadening is related to thermally excited capillary waves. Moreover, in confined systems the spectrum of excited capillary waves is modified, and this has a substantial effect on their contribution to the interfacial width in thin films. However, there is a controversy in the literature about the relative importance of long-ranged van der Waals forces [4–6] and short-ranged “truncation forces” [7, 8] in influencing the capillary wave spectrum. While the long-ranged dispersion forces lead to a logarithmic dependence of the interfacial width on the thickness, the short-ranged interactions involve a square-root dependence on the thickness. Recent computer simulations make clear that in principle both forces should be taken into account [9].

To probe this issue, we have performed systematic experiments to investigate the confinement effect on the interfacial width of polymer/polymer systems with a tuneable interaction parameter. In fact, in order to realise the full advantages of polymers as model systems for studying fluid interfaces and critical phenomena in confined geometries, it is necessary to be able to synthesise highly controlled polymers with well-defined interactions. A remarkable class of materials that is ideally fitted for this purpose are random copolymers of ethylene and ethyl-ethylene that are obtained by hydrogenating anionically polymerised polybutadiene with different chain microstructures [10, 11]. By varying the solvent in which the polymerisation takes place, random copolymers of microstructure  $(C_4H_8)_{1-x}(C_2H_3(C_2H_5))_x$  with a controlled copolymer ratio have been produced. Pairs of these copolymers have an unfavourable interaction, expressed as the Flory-Huggins interaction parameter  $\chi$ , that depends in a relatively simple way on the copolymers ratios of the components [7, 10]. Different conditions of miscibility were then probed by using a wide range of copolymer ratios that were varied from 0.5 to 0.86, while the molecular weight was about 150000 g/mol. The  $\chi$  parameter is calculated from the copolymer ratios  $x_1$  and  $x_2$  of the two components using the relation [10]  $\chi = (a_0 + a_1\bar{x} + a_2\bar{x}^2)(x_1 - x_2)^2$ . In the previous expression  $\bar{x}$  is the mean copolymer ratio and the coefficients  $a_0$ ,  $a_1$  and  $a_2$  are linear combinations of the homopolymers interaction parameter  $\chi_{A/B}$  and of the interactions between homopolymer and copolymer  $\chi_{A/A-B}$  and  $\chi_{B/A-B}$ . The values of these coefficients at 83 °C are, respectively, 0.062,  $-0.114$  and  $0.220$  [10]. The degree of immiscibility  $\chi N$ , where  $N$  is the degree of polymerisation of the polymers, was then varied from 4.1 to 31.

To investigate how long- and short-ranged forces interplay at the interface in confined systems approaching criticality, neutron reflectivity experiments were performed on bilayers formed by a film of 50%-deuterated (D) polyolefin and a layer of hydrogenated (H) polyolefin. For each polymer pair, a series of samples was prepared where the thickness of the bottom D layer was varied, while the thickness of the top H film was fixed at about 4000 Å. The bottom D polymer layer was spun cast onto silicon substrate from toluene solutions of different concentrations obtaining layers with thickness between 700 and 9000 Å. The polymer top H layer was spun onto a glass slide and the resulting film was floated in water and then deposited onto the D layer. The samples were annealed in a vacuum oven for 5 days at approximately 356 K, well above the glass transition of the polymers [10, 11].

Reflectivity profiles were measured on reflectometers at different facilities: on SURF/CRISP, Rutherford Appleton Laboratory (UK), on D17, Institut Max Von Lau-Paul Langevin (France), on V6, Hahn-Meitner Institut Berlin (Germany) and on AMOR, Paul Scherrer Institut (Switzerland). The resolution used varied between 3% and 6%.

Figure 1 shows, as an example, reflectivity curves obtained for a polymer pair with degree of immiscibility of  $\chi N = 5.9$  for two different thicknesses of the bottom layer: 785 Å and 4225 Å.

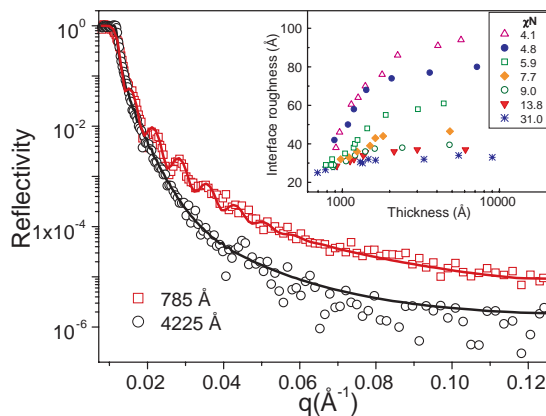


Fig. 1 – Neutron reflectivity, collected at SURF, of bilayers of polyolefins with  $\chi N = 5.9$ . The top hydrogenated layer (copolymer ratio 86%) was around 4000 Å for both samples while the bottom deuterated thin layer (copolymer ratio 70%) was 785 Å for the square symbols and 4225 Å for the circle symbols. Clearly, the fringes corresponding to the thickness of the bottom layer are visible for the thinner film. Fits are shown as lines in the plot (see text for details). In the insert, the interfacial roughness as a function of the bottom layer thickness for all systems measured is shown. Two different growth rates of the interface are observed for low and high values of immiscibility parameter, respectively, with the width increasing faster for lower values. All systems reach an equilibrium plateau. The legend in the figure shows the different values of  $\chi N$ . The error on the interfacial roughness for the profile shown in the figure is around 4 Å. This error increases for wider interfaces (see fig. 2).

The fringes related to the thickness of the bottom layer are clearly visible in the first profile, while the reflectivity falls off more rapidly as the thickness of the bottom layer is increased, indicating a wider interface in thicker layers. The solid lines represent fits obtained by a least-square fit to a three-layer model (Si/SiO<sub>2</sub>/D – polymer/H – polymer) with Gaussian roughness at the surface and at the polymer/polymer interface. The scattering length density,  $\rho$ , of the copolymer layers was also determined with neutron reflection on single layers and then fixed during the fitting procedure, while the thicknesses of the silicon oxide (SiO<sub>2</sub>) layer and of the copolymer films were also measured previously with spectroscopic ellipsometry. The surface roughness was fixed at about 8 Å (this value was obtained from the measure of the roughness of a single layer with neutron reflectivity and from AFM imaging of the surface of similar bilayer polymer samples). From the fits of the reflectivity profiles, the interface roughness as a function of the bottom layer thickness was obtained and is shown in the insert of fig. 1 for various  $\chi N$ . For all different  $\chi N$ , the roughness increases with the thickness up to a limit value, after which it is stable. By comparing systems with different degree of immiscibility, it can also be observed that as the layer thickness is increased, the interface roughness increases much faster for weakly immiscible polymer pairs, and the value of the limit thickness at which the interfacial width reaches equilibrium is higher. Moreover, as the degree of immiscibility is decreased and the interface becomes broader, the dependence on the thickness of the bottom layer is stronger. To understand the relative importance of short- and long-ranged forces in determining the width of the interface, a more quantitative analysis is needed. The width of the interface between immiscible polymers is well described by the self-consistent field theory with an additional broadening due to thermally excited capillary waves and the interfacial roughness  $\sigma_{INT}$  can be written as  $\sigma_{INT}^2 = \Delta_O^2 + \sigma_\zeta^2$ , where the

mean-squared roughness  $\Delta_O^2$  is related to the intrinsic width  $w_I$  by  $\Delta_O^2 = 2w_I^2/\pi$  and  $\sigma_\zeta^2$  is the mean-square dispersion obtained by integrating over the spectrum of capillary waves [4]. This integral is log-divergent, thus two cut-offs are introduced for the capillary excitations at large- and small- $q$  limits. The lower cut-off is related to the coherent length  $\lambda_{coh.}$  of the neutrons,  $q_{min} \sim 1/\lambda_{coh.}$ , and the upper cut-off is proportional to  $1/w_I$ . A detailed analysis by Semenov [12] of the discrete and continuous modes of fluctuations shows that the effective cut-off is  $q_{max} = 2\pi/(\pi w_I)$ . Long-ranged forces can affect the capillary wave's spectrum, and thus modify the contribution  $\sigma_\zeta$  to the interfacial width, and, as shown by [4] for a thin film between two semi-infinite media, this has the effect to introduce a dispersive capillary length  $a_{disp.} = \sqrt{\pi\gamma d^4/A}$ , where  $\gamma$  is the interfacial tension,  $A$  is the Hamaker constant that describes the interaction between the two semi-infinite media across the film of thickness  $d$ . For a neutron reflectivity experiments, assuming that the shortest capillary-wave wavelength is  $2\pi/(\pi w_I)$ ,  $\sigma_\zeta^2(d)$  can then be written as follows [1, 4]:

$$\sigma_\zeta^2 = \frac{k_B T}{4\pi\gamma} \ln \frac{(2\pi/\pi w_I)^2}{(2\pi/\lambda_{coh.})^2 + (2\pi/\lambda)^2}, \quad (1)$$

where  $k_B$  is the Boltzman constant,  $T$  is the temperature,  $\lambda$  is given by  $a_{disp.}$  and  $\lambda_{coh.}$  is of the order of microns. Thus, for very thin films,  $a_{disp.}$  will provide the lower wave vector cut-off, leading to the logarithmic dependence of the interface roughness on the film thickness  $d$ . For broader interfaces another effect needs to be taken into account. The short-ranged interactions between walls and the interface modify the interfacial profile. Interfacial fluctuations are then characterised by a large lateral correlation length,  $\xi$ , which increases exponentially with the film thickness  $d$ , and can act as a cut-off for the long-wavelength capillary waves. This is expressed by  $\xi \approx \xi_B e^{kd/2}$ , where  $\xi_B$  is the bulk correlation length and  $k^{-1}$  is a transverse decay length which should be of the order of the interfacial width [13, 14]. Using the same argument than above, a contribution due to the capillary waves can be calculated, considering that the lower cut-off of the capillary spectrum  $\lambda$  of eq. (1) is, in the first approximation, given by  $\xi$ . This means that for a thin layer, in the absence of long-range forces, the capillary-wave mean-square dispersion has an expression containing a term that is proportional to the thickness of the film  $d$  (as observed by [7]).

To determine the relative importance of long- and short-ranged forces, we fitted our data to equation  $\sigma_{INT}^2 = \Delta_O^2 + \sigma_\zeta^2$ , with  $\sigma_\zeta^2$  given by (1) considering  $\lambda$  equal to  $a_{disp}$  for the case of long-ranged forces and equal to  $\xi$  for the short-ranged forces. Fixing  $\lambda_{coh.}$  to  $20 \mu\text{m}$  as previously done [4], and using for the Hamaker constant the value  $2 \cdot 10^{-19} \text{ J}$  obtained from the fits and then fixed for all the systems (we are not sensitive to the exact value of the Hamaker constant [4]), for  $\chi N \geq 9$  the experimental data are in good agreement with the theoretical prediction of a logarithmic dependence on the film thickness. The best fit for  $\chi N = 31$ , shown in fig. 2 at the bottom, is achieved for  $\Delta_0 = 20 \pm 3 \text{ \AA}$  and  $\gamma = (0.93 \pm 0.25) \text{ mJ/m}^2$ . The predictions of the self-consistent field theory (SCFT) for  $\Delta_0$  and  $\gamma$  in the strong segregation limit are  $\Delta_0 = 18 \text{ \AA}$  and  $\gamma = 1.7 \text{ mJ/m}^2$ , respectively. For  $\chi N = 13.8$ , the best fit is obtained for  $\Delta_0 = 23 \pm 4 \text{ \AA}$  and  $\gamma = (0.77 \pm 0.28) \text{ mJ/m}^2$ , while the predicted values are  $\Delta_0 = 24 \text{ \AA}$  and  $\gamma = 1.3 \text{ mJ/m}^2$ , respectively. Thus, the comparisons of  $\Delta_0$  with the theory are good, while the interfacial tensions obtained are in general lower than the predicted values. Similar differences have been found also in numerical self-consistent field calculations and may be related to chain-end effects, as suggested by Werner *et al.* [15]. However the calculated reduction for the interfacial tension (8% for  $\chi N = 31$ , and 18% for  $\chi N = 13.8$ ) could only partially explain the different results. For lower degrees of immiscibility and in the region of transition, assuming  $\lambda = a_{disp}$  in eq. (1), it is not possible to fit the data. The

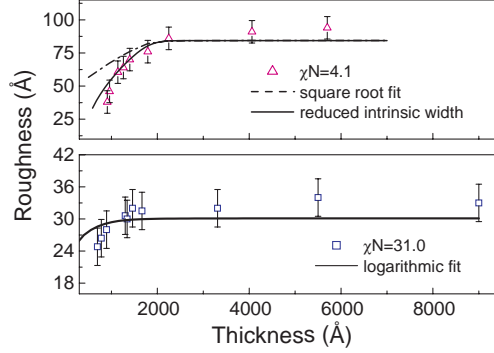


Fig. 2 – Interfacial roughness as a function of the bottom layer thickness for two systems with  $\chi N = 31$  (bottom figure) and  $\chi N = 4.1$  (top figure). The lines in the top figure are fits using eq. (1) where, in  $\sigma_\zeta^2(x)$ ,  $\gamma$  is equal to  $\xi$  without (dotted line) and with (solid line) the intrinsic width depending on the thickness. In the bottom figure the line is a fit to the experimental data using eq. (1) with  $\lambda$  equal to  $a_{disp.}$ . See text for details.

thickness dependence, in this case, has been suggested to be a combination of effects due to short- and long-ranged forces. However, assuming additivity between the two different interactions, as previously done in Monte Carlo simulations by Werner *et al.* [15], we cannot describe the experimental data in the transitional region. For  $\chi N = 4.1$ , eq. (1) with  $\lambda = \xi$  better approximates the experimental data for bottom layer thickness larger than  $\sim 1000$  Å, as shown in fig. 2 (top part).

The extrapolated values for  $\Delta_0$  and  $\gamma$  are  $\Delta_0 = (52 \pm 8)$  Å and  $\gamma = (0.09 \pm 0.04)$  mJ/m<sup>2</sup>, respectively, while for  $\xi_B$  and  $k^{-1}$  are  $\xi_B = (69 \pm 8)$  Å and  $k^{-1} = (150 \pm 12)$  Å, respectively (dotted line in the top part of fig. 2). The obtained value of  $\xi_B$  is in good agreement with the theoretical value of 77 Å estimated using the standard mean-field approximation [7, 16], and the obtained  $k^{-1}$  is also of the same order of the experimental width  $w$  —equal to  $(118 \pm 16)$  Å. For bottom layers thinner than  $\sim 200$  nm, the dependence of the interfacial roughness on the thickness becomes stronger, as clearly visible in the top part of fig. 2. For thin layers of the order of 5 times the interfacial width, short-range forces may affect not only the capillary-wave contribution to the interface but also the intrinsic interfacial width. This “squeezing” of the intrinsic interface has been predicted by Binder *et al.* in simulation [13]. Using the approach of Binder *et al.* [13] in the weak-segregation limit, the intrinsic interface should depend on the thickness as follows:

$$w_I(d) = \frac{w_I(\infty)}{\sqrt{1 + C \cdot \exp[-d/2\xi_B]}}, \quad (2)$$

where  $d$  is the film thickness,  $C$  is a constant related to the parameters characterising surfaces interactions and  $w_I(\infty)$  is the intrinsic width at larger value of thickness. Using this expression for the intrinsic width with the capillary-wave term as before, we have fitted the data and the following parameters have been obtained:  $\Delta_0 = 60 \pm 8$  Å,  $\gamma = (0.06 \pm 0.03)$  mJ/m<sup>2</sup>,  $\xi_B = (69 \pm 8)$  Å and  $k^{-1} = (150 \pm 12)$  Å and  $C = 50 \pm 20$ . Figure 2, top part, reports also this fit obtained (solid line) showing a good agreement also at lower thickness. These parameters are similar to the one reported before and the value of  $C$  is slightly higher but of the same order of the value 16 predicted theoretically in the weak-segregation limit [13]<sup>(1)</sup>.

<sup>(1)</sup>For higher values of  $\chi N$ , using the expression for the reduced intrinsic width given by eq. (2) added to the capillary-wave term, we do not improve significantly the fitting.

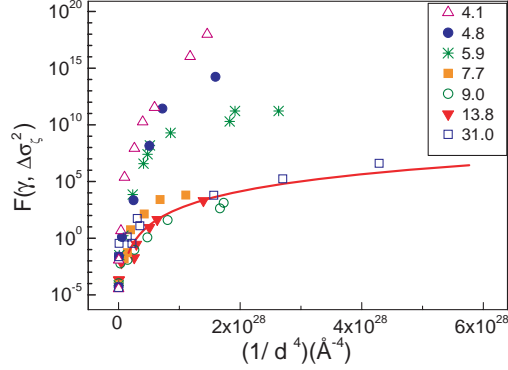


Fig. 3 – The figure shows the function  $F(\gamma, \Delta\sigma_\zeta^2)$ , defined in the text, as a function of the inverse of the fourth power on the bottom layer thickness  $d$ . The figure shows clearly that for  $\chi N$  higher than 7.7 the data collapse to a single function  $F(\gamma, \Delta\sigma_\zeta^2)$ , while deviations are seen for  $\chi N$  lower than 7.7. The legend in the figure shows the different values of  $\chi N$ .

This result may also suggest the need of an additional effect that cannot be explained by a simple Flory-Huggins or SCF theory for planar slab.

To investigate the validity of equation (1) in the long-ranged case, when  $\lambda$  is equal to  $a_{disp.}$ , in an independent way, a different analysis of the experimental data has also been performed. When the interface reaches the equilibrium value for thicker bottom layers, the thickness dependence of eq. (1) is not relevant and the term related to dispersion forces can be neglected. The interfacial roughness is then expressed more simply by

$$\sigma_\zeta^2 = \frac{k_B T}{4\pi\gamma} \ln \frac{(1/\Delta_0)^2}{(1/\lambda_{coh.})^2}. \quad (3)$$

The difference,  $\Delta\sigma_\zeta^2$ , between eqs. (1) and (3) is given by the following relation:

$$\Delta\sigma_\zeta^2 = \frac{k_B T}{4\pi\gamma} \ln \frac{(1/\lambda_{coh.})^2 + (A/4\pi\gamma d^4)}{(1/\lambda_{coh.})^2}. \quad (4)$$

By taking the exponential of both left- and right-hand sides, we arrive easily to an expression,

$$\gamma \left( e^{\Delta\sigma_\zeta^2 \gamma / A'} - 1 \right) = A'' \frac{1}{d^4}, \quad (5)$$

where  $A'$  and  $A''$  are two constant defined as  $A' = k_B T / 4\pi$  and  $A'' = (A\lambda_{coh.}^2) / 4\pi$ , where the right-hand side does not depend on the degree of miscibility. Thus, it is possible to define a function  $F(\gamma, \Delta\sigma_\zeta^2)$  equal to the left-hand side of (5), that for different condition of miscibility, will vary only with the thickness of the bottom layer  $d$ ,  $F(\gamma, \Delta\sigma_\zeta^2) \approx 1/d^4$ . In fig. 3 the function  $F(\gamma, \Delta\sigma_\zeta^2)$ , calculated from the experimental data, is plotted on a logarithmic scale as a function of  $1/d^4$ . For this calculation, the SCFT values for the interfacial tension  $\gamma$  were used.

From fig. 3, for  $\chi N$  higher than 7.7 the data collapse to the same values, as shown by the trend line (solid line), and the assumption of a logarithmic dependence on the thickness is verified: in this range therefore long-ranged forces are dominant in determining the width of the interface. As the degree of immiscibility is decreased and the interface becomes broader,

the dependence on the thickness of the bottom layer is stronger. This behaviour indicates that in this case short-ranged forces are more important in determining the interfacial profile. The observed behaviour in fig. 3 was also confirmed using different expressions for the interfacial tension needed in eq. (5): the interpolation formulae for the interfacial tension given by Tang and Freed [18] and the interfacial tensions extracted with the Werner *et al.* approximation [15]. Our results offer an explanation for the contrasting experimental results obtained in previous studies of interfacial widths between coexisting polymer phases. Kerle *et al.* [7,8] observed a square-root dependence on the thickness for a polymer pair rather close to the critical point, while Sferrazza *et al.* showed instead a logarithmic dependence on the thickness for the strongly immiscible polymer pair PS/PMMA [4–6].

To summarise, the thickness dependence of the interfacial width of polyolefin blends has been studied for different degrees of miscibility, to investigate the effect of confinement on interfacial fluctuations approaching criticality. The results show a gradual transition from a region where long-ranged dispersion forces are dominant in influencing the capillary-wave spectrum, for higher degrees of immiscibility, to a region where short-ranged forces become more important and the dependence of the interfacial width on films thickness is stronger.

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